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# Petroleum Refinery Enforcement Manual

by

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# DISCLAIMER

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# ACKNOWLEDGMENTS

This report was prepared under the direction of Mr. Thomas C. Ponder, Jr., and Ms. Nancy A. Kilbourn. Authors include Ms. Jean Carruthers, Mr. Jack McClure, Mr. Dilip Mehta, and Ms. Roberta Pollard-Cavalli. The Task Manager for the U.S. Environmental Protection Agency was Mr. Robert L. King.

# ABSTRACT

Petroleum refining involves a wide variety of processes which are used to convert crude oil into many different, marketable products. The environmental regulations which govern the refining industry cover a multitude of sources and pollutants. Like the industry itself, these regulations are in a dynamic state of change. The complexity of refining processes and the regulations applicable to refineries created a need for a refinery enforcement manual. The manual has been developed to assist enforcement personnel in understanding the refining industry, as well as to aid them in making inspections and determining compliance with emission regulations. The manual includes detailed process descriptions; a glossary of refinery terms; a discussion of current regulations applicable to refineries; a discussion of enforcement procedures, including checklists which can be used during inspections; a list of all the refineries in the United States; discussions on refining theories; and a bibliography.

# SECTION 1

# INTRODUCTION

## 1.1 BACKGROUND

Numerous earlier EPA publications give suggestions regarding methods of inspection of petroleum refineries. With the advent of revised State Implementation Plans (SIP's) in early 1979, emphasis on control of hydrocarbons from refineries has increased greatly. The SIP revisions include provisions for control of hydrocarbons from vacuum producing systems, wastewater treatment systems, process turnarounds, and fugitive emissions. In the long term, additional guidelines will be promulgated that will affect controls for process heaters and boilers and for handling of waste sludge. Consequently, the inspector is faced with a large number of separate regulations covering control of a multitude of sources and pollutants. Compounding this problem is the dynamic state of change of the various regulations.

The changing status of regulations applicable to refineries and the complexity of refining processes create a need for a refinery enforcement manual. This manual has been developed to meet that need and is prepared in such a way that information on changes in regulations or technology can be easily incorporated. It presents ample background information on the petroleum refining industry to aid enforcement personnel in inspections. The primary purpose of this manual is to assist enforcement personnel in making inspections and determining compliance with emission regulations.

## 1.2 GUIDE TO THE MANUAL

This manual is presented as a loose-leaf style notebook to allow easy updating (Section 1.3). The notebook style also makes possible the simple addition or deletion of material as appropriate for an individual inspector.

The manual contains six sections. This introduction, the first section, explains how to use and update the manual, and discusses the inspector's legal right of entry.

Section 2 is an overview of the refining industry, describing the various process units contained in a refinery. Review of this section acquaints the inspector with the basic operation of the process units.

Section 3 summarizes the applicable regulations that the inspector will be enforcing.

Section 4 presents detailed process descriptions, monitoring and inspection procedures, and related descriptive material concerning many of the common refinery processes. The inspector can gain an understanding of the entire refining operation by studying these process descriptions.

Section 5 describes the three levels of inspection and the process units inspected at each level. The first-level inspection requires approximately 2 hours; the second level, approximately 2 days; and, the third level, approximately 2 weeks. The specific units to be inspected at each level are listed in this section. The inspector is to be well acquainted with the information in Section 4, concerning the units to be inspected, before performing the inspection.

Section 6 tabulates checklist data from previous inspections for each process unit, so that the inspector can monitor the changing compliance status at a refinery.

The appendixes provide additional information for the inspector including assumptions of the basic refining theory described in this manual, instructions on monitoring equipment leaks, and use of the organic vapor analyzer. A glossary and a bibliography are presented after the appendices. Primary references are given at the end of each section or subsection.

## 1.3 HOW TO UPDATE THIS MANUAL

This manual is designed to be revised or updated as new data become available. The page numbering system allows for easy insertion of new pages or the updating of existing pages. The system has four parts and is printed across the bottom of each page as below:

Title Section Title
Issue Date Page Number

An actual example of the page numbering system is as follows:

Petroleum Refinery Enforcement Manual Alkylation
3/80 4.6-1

Pages are numbered consecutively within each major section (or appendix), except Section 4. Pages in Section 4 are numbered within each subsection: for example, 4.0-1, 4.6-1. New and revised pages will be added as necessary. Examples of updating the manual follow.

### New Page

When a new page containing additional data is sent to the user, it will be numbered as follows:

Petroleum Refinery Enforcement Manual Alkylation
1/81 4.6-1.1

This page is to be inserted between pages 4.6-1 and 4.6-2.

### Revised page

If page 4.6-1 is revised, it will be reissued with the same page number and the issue date of the revision:

Petroleum Refinery Enforcement Manual Alkylation
1/81-R1 4.6-1

This page is to be inserted in place of the superseded page 4.6-1 that was issued 3/80.

## 1.4 LEGAL RIGHTS

### Credentials

The inspector is authorized to conduct official inspections under the provisions of Section 114 of the Clean Air Act, as amended, 42 U.S.C. 74 14(a)(1) and (2). With respect to the inspector's authority, Section 114(a)(2) states as follows:

> The Administrator or his authorized representative upon presentation of his credentials -
>
> (A) shall have a right of entry to, upon, or through any premises in which an emission source is located or in which any records required to be maintained (under paragraph (1) of this section) are located, and
>
> (B) may at reasonable times have access to copy any records, inspect any monitoring equipment or method [required under paragraph (1)], and sample any emissions which the owner or operator of such source is required to sample [under paragraph (1)] (parentheses added).

### Denial of Entry

If the inspector is refused entry to a facility, the events leading to the denial should be documented in writing. These records are valuable for future enforcement proceedings. Visible emission measurements or estimates should be obtained after leaving the facility premises and included with the written record of events. When refused entry to a plant, the inspector may obtain a search warrant if necessary. Guideline S-12 provides a model affidavit in support of an application for a warrant.[1]

### Waivers

Most refineries maintain a sign-in sheet intended for plant records and containing spaces for the name and affiliation of the signers. There is no reason that the inspector should not sign this log sheet upon request. Under no circumstances, however, should an inspector sign a release from liability (waiver) upon entering a facility under authority of Section 114. Such a signature could waive the right to collect damages for injury while on company property. If asked to sign a waiver, the inspector should mark through the language of the waiver before signing the sheet, or write "no waiver" next to the signature.

## Secrecy and Confidentiality

An inspector should never sign a pledge or statement of secrecy regarding information obtained during the inspection, unless an earlier agreement provides for disclosure under conditions that satisfy 40 CFR Part 2 (41 FR 36902 et seq.), September 1, 1976. The EPA is required under Section 114 to make inspection information available to the public, except that trade secrets are not to be disclosed.

A refiner's claim of confidentiality in refusing the release of emission data to an inspector is unjustified. Confidentiality applies only to the release of proprietary data to the public; it does not apply to information obtained by an inspector performing duties under Section 114 of the Clean Air Act. Therefore, if refinery personnel claim that emission data are confidential, the inspector should explain that confidentiality applies only to release of proprietary information to the public. A copy of Section 114(s) should be shown to plant personnel and the provisions explained, if necessary.

In the event that plant officials continue to refuse to provide emission information, the inspector should record the names of these individuals. The enforcement agency can then send them a letter requesting the information, accompanied by a detailed discussion of the confidentiality provision of the Clean Air Act.

## Reference

1. U.S. Environmental Protection Agency. Office of Enforcement. EPA Visible Emissions Inspection Procedures. Stationary Source Inspection Series. February 1979.

2. John Quarles' memo of November 8, 1972, which was included as an appendix to EPA Guideline S-12, specifically instructs EPA employees to refuse to sign a release (waiver) upon entering a source under the authority of Section 114. These instructions also apply to EPA contractors in pursuit of their authorized duties if the contractor has been designated an "authorized representative" of EPA. (OGC must authorize these contractors by letter.)

3. Under no conditions should a visitor's release for liability be signed by an inspector while on the plant premises. To do so could waive the right to obtain damages for injury as explained in Mr. Quarles' memo. State and local agency inspectors should also be aware of the risk of signing a release for liabilty.

# SECTION 2

# PETROLEUM REFINING - OVERVIEW

## 2.1 INTRODUCTION

### 2.1.1 Petroleum

Petroleum, usually called crude oil, is a complex mixture of hydrocarbons, with small amounts of other substances, that occurs as an oily liquid in many places in the upper strata of the earth. Many crude oils, such as those from Arabia and Iraq, have a strong odor of hydrogen sulfide and sulfur compounds; others, such as those from Nigeria and Indonesia, contain very little sulfur and do not have any unpleasant odor. The color of crude oil ranges from clear to black.

Crude oil in the ground is associated with hydrocarbon gases, of which substantial quantities are dissolved in the oil under pressure. Methane and ethane constitute by far the greatest proportion of the gases associated with crude oil.

It has been estimated that crude oil contains over 3000 different chemical compounds, and the chemical composition varies with the source. Hydrocarbons are the predominant components; the remainder consists chiefly of organic compounds containing oxygen, nitrogen, sulfur, and traces of inorganic compounds containing iron, nickel, vanadium, and arsenic.

The molecular weight of the hydrocarbons in crude oil varies widely because they contain different numbers of carbon atoms per molecule. The chemical structure of these hydrocarbons also differs greatly. The types of hydrocarbons present in crude oil are paraffins (alkanes), naphthenes (cycloparaffins), and aromatics.

Crude oil is separated by distillation into fractions designated as (1) light ends; (2) straight-run gasolines, with boiling points that range up to about 204°C (400°F); (3) middle distillates, boiling at about 185° to 343°C (365° to 650°F), from which are obtained kerosene, heating oils, and fuels for diesel, jet, rocket, and gas turbine engines; (4) wide-cut gas oil, boiling at 343° to 538°C (650° to 1000°F), from which are obtained waxes, lubricating oils, and feedstock for catalytic cracking operations that produce gasoline; and (5) residual oil, from which asphalt, coke, and tar may be obtained.

### 2.1.2 Petroleum Refining

The refining sector of the petroleum industry converts crude oils, various semifinished petroleum fractions, and hydrocarbon gases into useful products. These products are refined by various physical, thermal, catalytic, and chemical processes, into the wide range of products mentioned earlier. Refinery products generally are not pure chemical compunds but are mixtures of chemical compounds. Table 2-1 characterizes many of these products. In each case the boiling range, rather than a single boiling point, is due to the fractions being a mixture of chemical compounds.

Because refining processes are complex and are specific to each refinery, intermediate storage may be needed for certain fractions that will be returned to various units for further processing. Since each refinery is designed, engineered, and constructed to handle specific crude oils and to produce specific refined or semirefined products, there is no "typical" refinery. Additionally, the processing parameters change with the type of crude oil to be refined. For example, an increase in the refining of Alaska's North Slope crude has led to expanded use of catalytic reformers and fluid-bed catalytic cracking units.

Even though there is no typical refinery, most U.S. refineries are designed to maximize the production of light distillates, i.e., gasoline. The following operations (Figure 2-1) are basic:

TABLE 2-1. CHARACTERIZATION OF FRACTIONS OBTAINED FROM CRUDE OIL

| Fraction | Carbon atoms | Molecular weight | API gravity | Boiling range, °F[a] |
|---|---|---|---|---|
| Gas | 1 to 4 | 16 to 58 |  | -259 to 31 |
| Gasoline | 5 to 12 | 72 to 170 | 58 to 62 | 31 to 400 |
| Jet fuel | 10 to 16 | 156 to 226 | 40 to 46 | 356 to 525 |
| Gas oil | 15 to 22 | 212 to 294 | 34 to 38 | 500 to 700 |
| Lube oil | 19 to 35 | 268 to 492 | 24 to 30 | 640 to 875 |
| Residuum | 36 to 90 | 492 to 1262 | 8 to 18 | 875+ |

[a] °F = 5/9 (°C) + 32

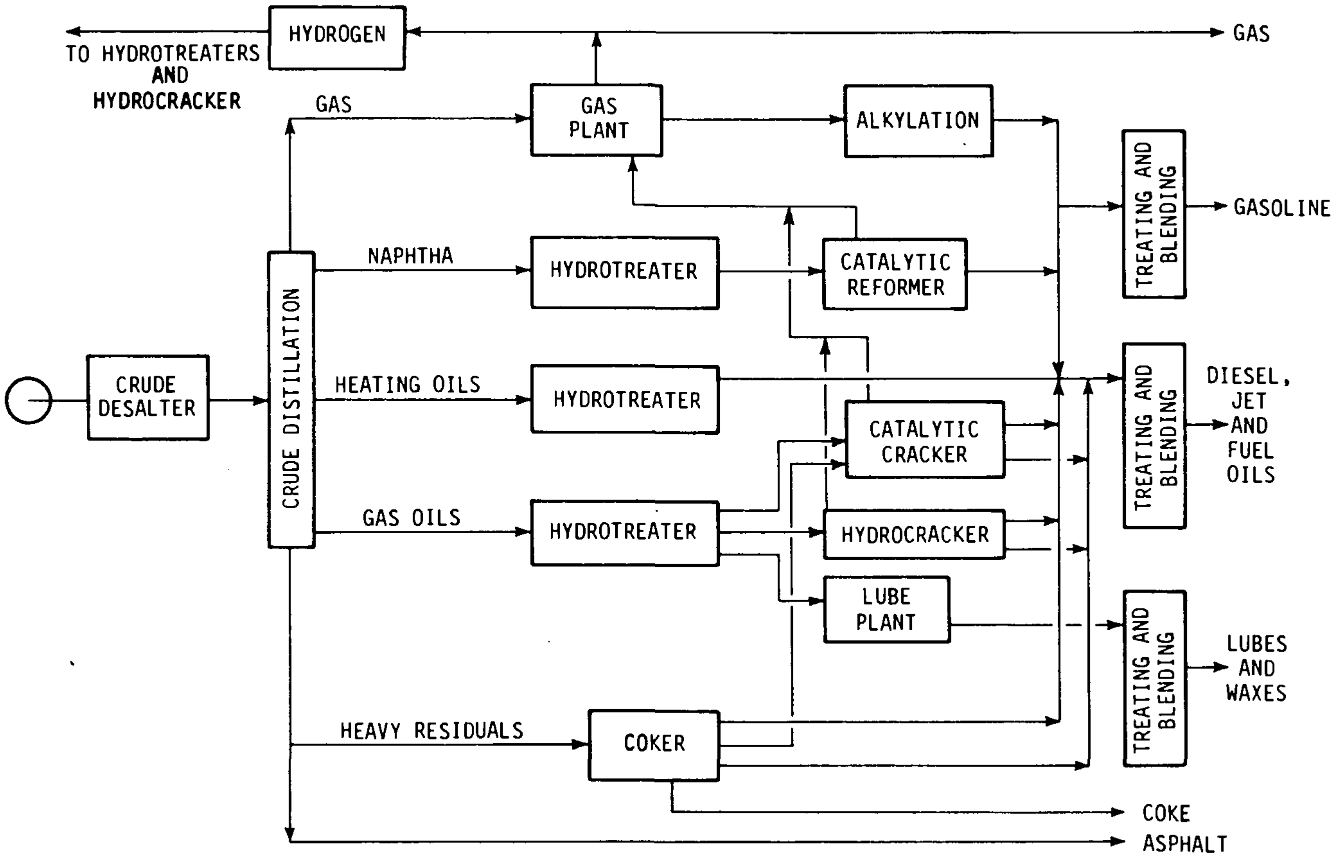


Figure 2-1. Typical processing steps in a petroleum refinery.

(1) separation processes, separating the crude oils to isolate the desired products (e.g., distillation); (2) decomposition processes, breaking large hydrocarbon chains into smaller ones by cracking (e.g., catalytic cracking, coking); (3) formation processes, building the products by chemical reaction (e.g., reforming, alkylation, isomerization); (4) treating processes, removing impurities or compounds that are detrimental to operation of the refinery; (5) recovery operations (e.g., sulfur recovery, fuel gas recovery); (6) storage; and (7) auxiliary facilities. Figure 2-1 shows the interrelationships of these processes, which are described in the following subsections.

## 2.2 SEPARATION PROCESSES

### 2.2.1 Desalting

Crude oil is a mixture of hydrocarbon compounds contaminated by water, salt, and sand. Although most of the water and sand settle out and separate during storage, the crude is saturated with water, dissolved salts, and minerals. Crude oil desalting is a combination separation/reaction operation, in which an impressed electrical current field and/or chemical additives are used to coalesce the salt particles, which are then washed away with water.

Electrical desalting, the most common technique, involves the addition of water to crude under pressure and at 71° to 149°C (160° to 300°F). This mixture is emulsified and introduced into a high-potential electrostatic field, which causes the impurities to associate with the water phase and at the same time causes the water phase to agglomerate so that it can be removed. The desalted crude proceeds to the distillation units.

Chemical desalting of crude is accomplished by adding water to the heated [93° to 149°C (200° to 300°F)] and pressurized oil. The pressure must be high enough to prevent vaporization of the water. The mixture is emulsified, and the salt enters the water phase. Chemical additives may be used to break the emulsion and allow the water phase to settle. The water containing the salt is discharged from the system.

### 2.2.2 Crude Distillation

The first major separation operation in refining is crude oil distillation. In distillation towers (columns) various constant-boiling-range fractions are separated, the lowest boiling fraction leaving the top of the tower and the highest boiling fraction leaving the bottom. Products may be withdrawn as sidestreams at appropriate points on the tower. The sidestreams are further processed in small towers called strippers, in which steam is used to free the sidestream (cut) from its more volatile components so that the boiling point of the product can be adjusted to a specified value. There are three major types of distillation systems: single-stage, two-stage, and two-stage with a vacuum tower.

Single-Stage Distillation--

The crude feed is preheated by outgoing streams before entering a direct-fired, furnace-type heater, from which it goes to a distillation column for separation into gas, gasoline, naphtha, kerosene, gas oil, fuel oil, and residuum. These sidestreams are steam-stripped and then routed to storage. Topping plants use single-stage distillation, usually separating the crude into five or six sidestreams. Very little additional treating is performed at these plants. The number and type of fractions that result from distillation depend on the crude base and on operating conditions.

Two-Stage Distillation--

Two-stage distillation provides more cuts than the single-stage system. The process includes a primary tower (preflash tower), which operates at above atmospheric pressure, and a secondary tower (atmospheric tower), which operates at atmospheric pressure. These units, together with a stabilizer (stabilizing tower), are used to separate the crude into light ends, depropanized light gasoline, light kerosene, naphtha, kerosene, light diesel, heavy diesel, and residuum.

The preflash overhead is fed to the stabilizer for removal of the lighter hydrocarbons (usually dissolved gaseous hydrocarbons such as propane). In the stabilizer, the light hydrocarbons are removed overhead, and the stabilized product is removed at the bottom.

The preflash bottoms feed the atmospheric tower, where again side cuts are taken and steam stripped to remove the light ends.

### Two-Stage Distillation with Vacuum Tower--

This system incorporates the two-stage arrangement and adds to it a vacuum tower. The bottoms from the atmospheric tower feed the vacuum distillation tower, which operates at below atmospheric pressure. Operation under a vacuum allows the reduction of operating temperatures and thus prevents coking in the heater tubes or on trays and thermal degradation, which may occur in high-temperature operations.

The petroleum refinery uses vacuum distillation to produce light and heavy gas oils, heavy fuel oil, vacuum gas oil, lubricating oil fractions, and vacuum bottoms. A refinery that produces lubricating oils may use two separate vacuum towers, one especially designed to recover lube oil fractions and the other designed for fuel oil fractions.

Although steam is not usually injected into the vacuum unit, in some wet vacuum units steam is added to the distillation column operating under a vacuum. The dry vacuum process has the advantage of using smaller towers and smaller condensing equipment for a given throughput and also is more economical and energy efficient than the wet process.

A vacuum is usually created by steam jet ejectors discharging to surface condensers (shell and tube), which limits air pollution. Alternatively, direct contact condensers are used, in which case, water, steam, and hydrocarbon vapors are mixed. This type of condenser can generate air pollutants; however, the noncondensables from these units usually are vented to the refinery flare system as a means of controlling hydrocarbon emissions.

Appendix C provides more details of the principles of fractionation. Literature references and definition of terms are given in the Bibliography and Glossary at the end of this manual.

### 2.2.3 Deasphalting

Deasphalting separates asphalts or resins from more viscous fractions. Refineries and chemical plants commonly accomplish such separation by liquid-liquid extraction. In this operation, a mixture is separated into two components by means of a selective solvent, the separation being due to differences in solubility. For ease of separation, the solvent must yield a two-phase mixture with appreciable difference in densities of the two phases.

In deasphalting, residuum from the vacuum tower and liquid propane are heated to a controlled temperature and mixed at a controlled ratio as feed to the deasphalting tower. The two phases that result are separated, and propane is removed from the deasphalted oil phase by a two-stage evaporation process and steam stripping. The asphalt phase is heated and steam stripped for removal of residual propane. The propane is then condensed and recycled. Overhead from both strippers is water washed, compressed, and condensed before being recycled as propane extractant.

## 2.3 DECOMPOSITION PROCESSES

### 2.3.1 Catalytic Cracking

Catalytic cracking is a relatively inexpensive method of breaking down heavier distillate fractions into lighter gasoline material and thus increasing the overall gasoline yield from crude oil. The variety of catalysts and system designs provide a wide range of operating flexibility for the catalytic cracking process.

Two well-known catalytic processes are in use today--the fluid catalytic cracker (FCC) and the Thermofor catalytic cracker (TCC). The FCC uses a powdered catalyst and the TCC or Houdriflow, no longer generally manufactured, uses a bead catalyst.

In the FCC, finely powdered catalyst is lifted into the reaction zone by the incoming oil, which vaporizes immediately upon contact with the hot catalyst. When the reaction is complete, the product and catalyst are lifted into a regeneration zone by air. In the reaction and regeneration zones, the catalyst powder is held in a suspended state by the passage of gases through it, and a small amount of catalyst is moved from the reactor to the regenerator and vice versa. Oil tends to saturate the enormous volume of pulverized catalyst in the reactor, and hence the catalyst must be steam stripped before it enters the regenerator.

The TCC is a moving-bed system with catalyst in the form of beads or pellets. The catalyst is lifted by air, or in old plants by bucket elevators, to a high position so that it can flow downward by the force of gravity. It moves through the oil zone, causing reaction, and then through a regeneration zone.

In both the FCC and TCC processes the catalyst must be regenerated. Coke that forms on the catalyst particles during the reaction must be continuously removed to maintain catalyst activity. In the regenerator, a controlled stream of air is added to burn off the coke. The resulting combustion gases flow through a series of cyclones for removal of the entrained catalyst. The regenerator gases (often rich in carbon monoxide, CO) may be burned as fuel in a CO boiler to generate refinery steam and eliminate CO emissions.

Reactor products are condensed and stabilized in a large distillation tower, where several streams are taken off. The lightest streams are sent to a gas recovery unit, and the heaviest streams are recycled to the catalytic cracker. The recycle ratio and the ratio of catalyst to oil depend on the type of feedstock and the desired product.

More detailed explanations of the fluid unit are given in Section 4.2 and Appendix B.

### 2.3.2 Hydrocracking

Hydrocracking units perform both cracking and hydrogenation. Products from hydrocracking are essentially saturated materials with high concentrations of isoparaffins and naphthenes.

The hydrocracker functions in a manner similar to the catalytic cracker but operates over a wider range of feedstock boiling points. Because of their great flexibility, hydrocracking processes may be operated to produce high-quality motor gasoline, petrochemical naphtha, jet fuel, and diesel oils. With the new catalysts available, a single hydrocracking unit can be used to convert feedstocks as heavy as vacuum gas oils into either naphtha or high yields of middle distillates, simply by regulation of the fractionation cut points and reactor temperatures. Hydrocracking is also used to desulfurize high-sulfur crude oils while upgrading the heavier fractions into lighter fuel oils. The inherent flexibility of the process will allow a gradual increase in yield of motor gasoline to meet current market demand.

The fixed-bed hydrocracking catalysts maintain high activity in the presence of nitrogen and sulfur compounds. Various process configurations and catalyst systems can be combined to yield the optimum product spectrum for a particular feedstock.

The feedstock undergoes heat exchange with the second reactor product, combined with preheated recycle and makeup hydrogen, and introduced into the first reactor. The first reactor product is combined with preheated recycle and additional liquid recycle and introduced into the second reactor. The product is exchanged with feedstock, condensed, and separated to recover recycle hydrogen. A second flash stage removes gases, and the liquid product enters the fractionator, from which various product streams are taken for blending or further processing. The bottom product is recycled to the second reactor. Because this process consumes hydrogen (200 to 350 volumes of hydrogen per volume of feedstock), refineries often operate a hydrogen production facility onsite.

In the United States, about one-third of the hydrocracking capacity is on the West Coast, where it is used to upgrade heavy fuels to motor gasoline and jet fuel. Another one-third is on the Gulf Coast, where it is used to alternate production of motor gasoline and light distillates according to market demands.

### 2.3.3 Coking

Coking is a severe form of thermal cracking; it is an ultimate-yield destructive distillation process that produces gas, distillate, and coke from residuals that may resist cracking by other methods. Although coke was earlier considered a low-value byproduct, it is now used in electrode manufacture when sulfur and metals contents are low enough. Coke with intermediate-range sulfur content may be used as fuel for steam generator boilers.

There are two principal coking processes, delayed and fluid. Delayed coking is the more widely used, and very few fluid coking units are in service.

In the delayed coking process, the feedstock goes directly to the fractionator. The lighter material is vaporized and leaves the fractionator overhead. It is cooled and separated, and the vapor phase is sent to the refinery fuel gas system. Various sidestreams from the fractionator include naphtha and light and heavy gas oils, which may be further processed. The bottoms from the fractionator are pumped through a furnace to the coking drums. Overhead from the coking drums flows back to the fractionator and is recycled.

Coke forms on the coking drum walls and eventually fills the drum. After a purging with steam, the drum is isolated and opened; coke is broken free by high-pressure water jets. At least two coking drums are provided so that one may be mechanically or hydraulically decoked while the other is filling. These drums are usually sized so that they can be decoked and returned to service during one work shift. The coke particles are washed out with water and separated from the water on vibrating screens.

In the fluid coking process, the feedstock enters the reactor, where it is mixed with a fluidized bed of preheated recycled coke particles. The hydrocarbons in the liquid feed crack and vaporize, while the nonvolatile material is deposited on the suspended coke particles. The coke particles thus grow larger, sink to the bottom of the reactor, and flow to the burner. In the burner, the particles are fluidized with air, partially burned, and recycled to the reactor. A portion of the coke produced in the reactor is withdrawn as product. The overhead vapor can be desulfurized to yield fuel gas suitable for process heaters or steam/power generation.

### 2.3.4 Visbreaking

Viscosity breaking, or "visbreaking," is a milder form of thermal cracking than coking; it is used to reduce the viscosity of some residual fractions so that they may be blended into fuel oils. It is applied when the demand for middle distillates exceeds that for motor gasoline.

The atmospheric or vacuum-reduced crude is preheated by heat exchange with visbroken fuel oil and fed to a furnace. Mild cracking in furnace tubes produces a mixture of residual oil, naphtha, and gas. The reaction products are quenched with a recycle stream and sent to a fractionator, in which the visbreaker bottoms accumulate in the lower portion. A simple pump system in the tower allows fractionation of the flashed vapors into gas, gasoline, and light and heavy gas oils. The gas oil sidestream normally flows through a steam-stripping tower for separation of the motor gasoline fraction.

## 2.4 FORMATION PROCESSES

### 2.4.1 Catalytic Reforming

Catalytic reforming is used to alter the structure of saturated straight-chain paraffins, which have very low octane numbers, to yield a different kind of molecule with much higher octane characteristics. The process converts straight-carbon-chain naphtha to a ring or branch-structured gasoline. Catalytic reforming is also called platforming (when a platinum catalyst is used), ultraforming, or magnaforming.

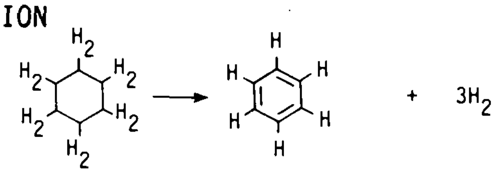
Catalytic reforming is a high-temperature, low-pressure, fixed-bed process using a bimetallic catalyst. The most important property of the catalyst is that which causes ring formation and permits ring preservation in molecules that have just undergone partial dehydrogenation (aromatization). As would be expected with a substance as complex as crude oil, the process reactions are numerous and complex. (A basic organic chemistry text will explain these reactions in detail.) Table 2-2 presents the major types of reactions that occur in catalytic reforming units. Naphthene dehydrogenation, naphthene dehydroisomerization, and paraffin isomerization are the predominant reactions. The other reactions may become significant at high temperatures, high pressures, and low-space velocities. Avoidance of hydrocracking is particularly important since it can lead to excessive coke deposition, which deactivates the catalyst.

Compared with the feed, the final product contains a high percentage of aromatic compounds and a small quantity of aliphatic hydrocarbons. Some of the aromatics (benzene, toluene, and xylenes) may be isolated to become petrochemical feedstock, but the major portion becomes motor gasoline blending stock.

Catalytic reforming units are regenerative or nonregenerative. Regenerative reformers are the most common since they operate at the low pressures that produce larger yields of high-octane gasoline and also produce more hydrogen.

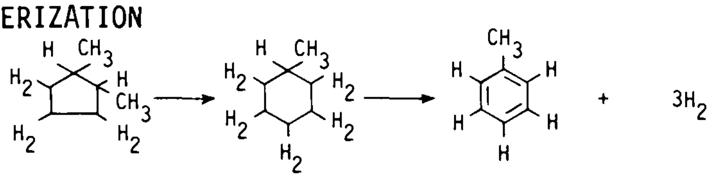
## TABLE 2-2. MAJOR REACTIONS OCCURRING IN CATALYTIC REFORMING[1]

### NAPHTHENE DEHYDROGENATION



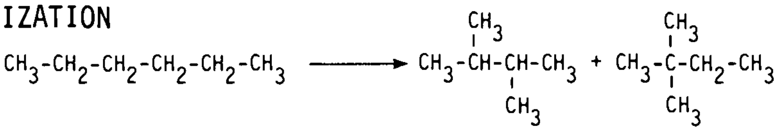
CYCLOHEXANE BENZENE

### NAPHTHENE DEHYDROISOMERIZATION



1,2-DIMETHYLCYCLOPENTANE METHYLCYCLOHEXANE TOLUENE

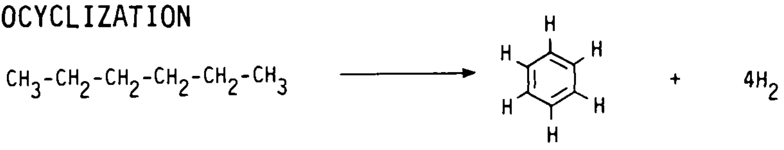
### PARAFFIN ISOMERIZATION



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}\overset{CH_3}{CH}\text{-}\underset{CH_3}{CH}\text{-}CH_3 + CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}CH_2\text{-}CH_3$$

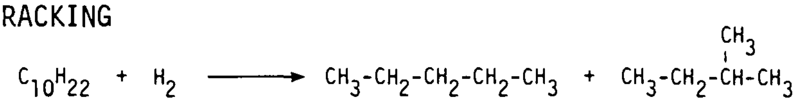
n-HEXANE 2,3-DIMETHYLBUTANE NEOHEXANE (2,2-DIMETHYLBUTANE)

### PARAFFIN DEHYDROCYCLIZATION



n-HEXANE BENZENE

### PARAFFIN HYDROCRACKING



$$C_{10}H_{22} + H_2 \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + CH_3\text{-}CH_2\text{-}\overset{CH_3}{CH}\text{-}CH_3$$

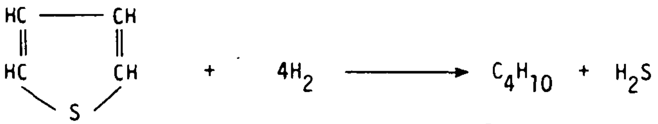
n-DECANE PENTANE ISOPENTANE

### OLEFIN HYDROGENATION

$$C_5H_{10} + H_2 \longrightarrow C_5H_{12}$$

PENTENE PENTANE

### HYDRODESULFURIZATION



THIOPHENE BUTANE

Before entering the reforming unit, the naphtha feed is hydrotreated to remove elements that may poison the reforming catalyst. The hydrotreated naphtha is mixed with hydrogen from the reformate stabilizer, exchanged with product streams, and heated in a furnace. This feed mixture then passes through several reactors. The charge is heated before entering each reactor to compensate for the endothermic reactions that occur. The final reactor effluent is cooled, and the gases are separated from the liquid products. The gases may be recycled, sent to the hydrogen recovery system, or sent to the plant fuel system.

The liquid products are sent to a stabilizer (tower). The noncondensable overhead from the stabilizer goes to the fuel gas system, and the condensable liquids are treated for recovery of light ends. Bottoms from the stabilizer are the reformate product, which is usually sent to gasoline blending.

So that a reactor may be regenerated, most reforming units contain a spare ("swing") reactor, which is periodically placed in service during the regeneration cycle. During regeneration, the coke deposited on the catalyst is burned off by a carefully controlled stream of inert gases and a limited amount of air.

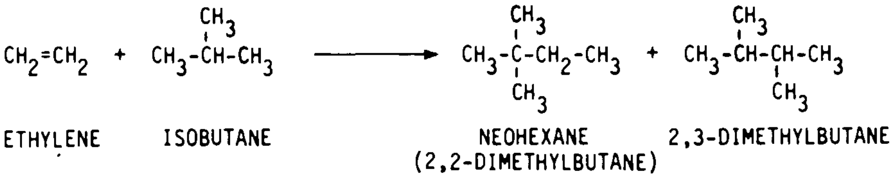
The nonregenerative systems do not have a spare reactor; instead, the unit is shut down when the catalyst is deactivated, and the catalyst is replaced. In other respects operation of these units is similar to that of regenerative reformers.

### 2.4.2 Alkylation

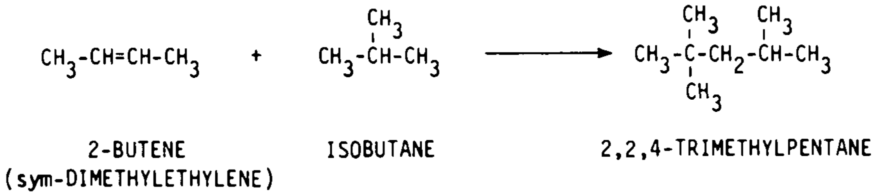
The alkylation process for production of high-octane gasoline resulted from the discovery that isoparaffin hydrocarbons unite with olefins in the presence of a catalyst. The process may involve isobutane and olefins, which produce high-octane dimers or trimers. Table 2-3 summarizes some of the alkylation reactions.

Sulfuric acids or hydrofluoric acid is used to catalyze the alkylation reaction. The reactants are combined with rapid and violent mixing into refrigerated liquid acid. The resultant vapors are separated from the acid mixture, caustic washed, water

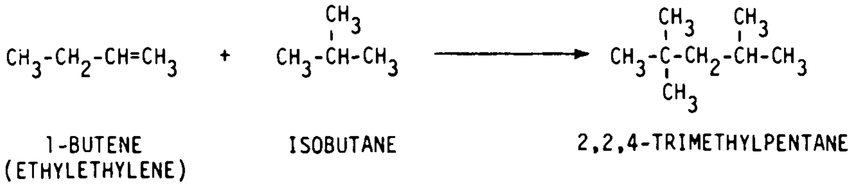
## TABLE 2-3. SUMMARY OF REACTIONS OCCURRING IN ALKYLATION



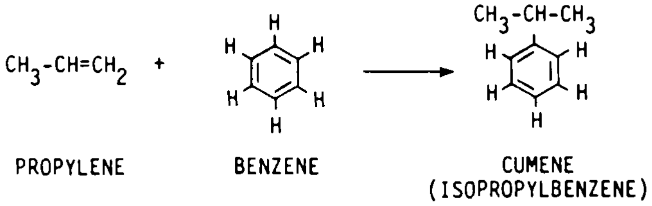
$CH_2{=}CH_2 + CH_3\text{-}CH(CH_3)\text{-}CH_3 \rightarrow CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH_3 + CH_3\text{-}CH(CH_3)\text{-}CH(CH_3)\text{-}CH_3$

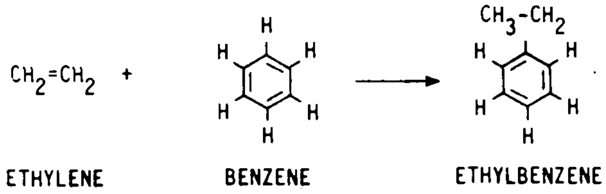


$CH_3\text{-}CH{=}CH\text{-}CH_3 + CH_3\text{-}CH(CH_3)\text{-}CH_3 \rightarrow CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$



$CH_3\text{-}CH_2\text{-}CH{=}CH_3 + CH_3\text{-}CH(CH_3)\text{-}CH_3 \rightarrow CH_3\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$





washed, and stabilized in a fractionation tower (debutanizer). The tower bottoms are taken as alkylate, and the overhead vapors are condensed and recycled. The tower also yields a normal butane fraction.

### 2.4.3 Isomerization

As in catalytic reforming, the isomerization processes rearrange the molecular structure of the feedstock while reducing losses that normally occur in cracking or condensation reactions. In the isomerization reactions nothing is added to or taken away from the material. Formation of branched-chain compounds from straight-chain compounds increases the octane number. The main types of isomerization are butane, pentane, hexane, and xylene isomerization.

Butane isomerization is closely linked with alkylation when alkylate is required and isobutane is in short supply. Isobutane is produced to provide feedstock for the alkylation unit. Building alkylation and isomerization units together permits sharing of common distillation equipment. Isomerization of butanes is increasing as a means of supplying petrochemical feedstock. Isomerization of pentane and hexane yields products more suited for motor gasoline blending stocks because they have desirable antiknock properties. If a refinery is extracting paraxylene from the catalytic reformate, the remaining orthoxylene and metaxylene may be fed to an isomerization unit to produce paraxylene. (Details of this type of isomerization are given in Reference 2).

The butane isomerization process converts normal butane into isobutane over a catalyst in the presence of hydrogen. A mixed butane feedstock is fed into the deisobutanizer tower (distillation tower) from which isobutane product is taken overhead. The bottoms undergo heat exchange with the reactor product after recycle, and makeup hydrogen is added. The mixture is heated to the reaction temperature in a furnace. Vaporized butanes enter the fixed-bed catalytic reactor, undergo heat exchange with the reactor feed, and are condensed; the reactor effluent flows to the separator for recovery of recycle hydrogen. Separator liquid is sent to the stabilizer, where overheads are condensed and noncondensables flow to the refinery gas system. Stabilizer bottoms go to the deisobutanizer, where the overhead is the product isobutane.

### 2.4.4 Polymerization

Polymerization is the combining of monomers. In a refinery operation, propylene (olefin; monomer) would be polymerized to yield dimer (2-propylenes), trimer (3-propylenes), tetramer (4-propylenes) and perhaps higher order polymers.

This process is used very rarely in refineries today. It was first introduced to provide a motor gasoline blending stock when octane levels were very low. The octane gain from blending of polymer (poly) gasoline was soon replaced by blending of alkylate from alkylation units. Polymers are valuable in some applications, however, such as additives for motor oil.

A refinery stream of propylene and butylenes is mixed with recycle propane and water, subjected to heat exchange with reactor product, preheated, and introduced into the top of a multiple-fixed-bed reactor. Solid phosphoric acid deposited on an inert carrier is the catalyst. Water is injected between the several fixed beds for temperature control. The reactor product is cooled by heat exchange with feed and sent to the depropanizer (distillation tower). The overhead product is recycled to the reactor feed. Bottom material is debutanized in a distillation tower, from which butane goes overhead and polymer gasoline is taken as bottoms.

## 2.5 TREATING PROCESSES

The objective of all petroleum refinery treatment of intermediate fractions or products is to remove or render inactive compounds that would otherwise reduce the quality of these fractions or products. Treating is particularly important for removing sulfur, nitrogen, and metal compounds from feed for a catalytic cracker or catalytic reformer. If these compounds were not removed, they would attack the catalyst. Therefore, this treatment both improves performance and lengthens catalyst life.

Refinery treating processes can be classified as catalytic or chemical. Several processes can be applied, depending upon the content of undesirable compounds and the required severity of the treatment. The vent or waste gas streams from the treating processes usually contain the hydrogenated form of the undesirable compound. These streams can be sent to the sulfur recovery process or the refinery fuel system.

### 2.5.1 Catalytic Treating

Hydrotreating is the most widely used process for all types of petroleum products. With the appropriate catalyst and operating conditions, hydrotreating can desulfurize, eliminate other impurities such as nitrogen and oxygen, decolorize and stabilize, and correct odor problems and many other product deficiencies.

Hydrodesulfurization processes convert the sulfur in sulfur compounds into more easily removed hydrogen sulfide ($H_2S$) by use of rugged catalysts and hydrogen. The processes also convert some nitrogen compounds into ammonia.

Other hydrogenation or hydrotreating processes (not intended primarily to attack sulfur) saturate olefinic materials, which are undesirable in many refinery products. For example, certain cracked gasoline stocks contain hydrocarbons that tend to polymerize (form gums) upon exposure to air. These can be stabilized by a mild catalytic hydrotreating process.

### 2.5.2 Chemical Processes

Chemical treating processes scrub fractions with inorganic acids such as sulfuric acid ($H_2SO_4$) and bases such as sodium hydroxide (NaOH) to remove undesirable acids and sulfur compounds. Certain chemical treating processes use proprietary chemicals to remove specific impurities and improve the quality and/or performance of petroleum products.

Acid gas removal processes bring feed streams into contact with a selective solvent or absorbent. These materials absorb the acid gases (normally hydrogen sulfide); they are regenerated by stripping and then recycled. The stripped acid gases are disposed of either in the sulfur recovery unit or by incineration. The sulfur recovery process (Claus unit) is preferred because it minimizes emissions.

Many processes are commercially available to perform all types of treating operations. The Bibliography gives literature references in the categories of acid gas removal, chemical sweetening, hydrotreating, and hydrodesulfurization processes.

## 2.6 RECOVERY OPERATIONS

### 2.6.1 Sulfur Recovery

Sulfur compounds in petroleum fractions are converted into $H_2S$ by treating processes. This $H_2S$ is collected and sent to the sulfur recovery plant (Claus unit).

In the Claus unit, $H_2S$ is burned with air to form elemental sulfur. The overall chemical reaction is:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$

The reaction is normally conducted in stages in which part of the $H_2S$ is oxidized with air to form $SO_2$, as follows:

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$$

This $SO_2$ is combined with the remaining $H_2S$ over a fixed-bed catalyst to complete the reaction:

$$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

A number of catalytic stages can be used to increase the sulfur recovery and reduce $SO_2$ emissions.

Final exhaust gases may contain sulfur carbonyls, carbon disulfide ($CS_2$), $H_2S$, and some elemental sulfur. These are normally incinerated at high temperature in a tail gas unit, and the exhaust gas contains only small quantities of $SO_2$.

### 2.6.2 Fuel Gas Recovery

The fuel gas plant incorporates a system of operations for recovering useful hydrocarbon vapor mixtures from the crude oil distillation unit and other refinery processes. While adding value to the overall refinery process, the recovery process also prevents hydrocarbon losses and emissions. A well-operated gas recovery system is essential to the overall economics of petroleum refining.

Vapors (noncondensable gases) from the crude distillation towers, the reformers, and the catalytic cracking units are collected and sent to the gas processing unit for light-ends recovery. The gases are compressed, condensed, and distilled (separated) into various mixtures having constant vapor pressure. These mixtures may be used as refinery fuel (burned in fired heaters and boilers), sold as liquefied petroluem gases, used as feedstock for hydrogen production, used as alkylation feedstock, or sold as petrochemical feedstock.

## 2.7 STORAGE

All refineries use tanks and vessels for storage of feedstocks (crude oil, pressurized liquid hydrocarbons, etc.) and of intermediate products awaiting further processing and/or blending. A certain amount of lower volume storage within the processing area is referred to as "rundown tankage." Tankage is also provided for finished products awaiting shipment and for use in loading and unloading operations.

## 2.8 AUXILIARY FACILITIES

A refinery requires many auxiliary facilities, which can include those for steam generation, production of electrical power, wastewater treatment, and hydrogen production, as well as cooling towers and blowdown systems (including flares and liquid incineration).

Many large refineries now generate some of their own electrical power. Steam leaving turbines goes into refinery steam systems at various pressure levels.

Wastewater treatment systems can range from a simple API separator to very elaborate biological treatment systems. All water streams are treated to meet environmental standards as well as to recover various products.

Process water is recirculated and cooled to the specified temperatures in cooling towers. Air coolers are being used with increasing frequency to reduce requirements for cooling water.

Because product treating processes require hydrogen, the hydrogen production facilities are often considered as auxiliary or utility systems.

Blowdown systems receive releases of liquid and gaseous streams from emergency vents and safety valves. These systems entail collection, separation, and disposition by a flare or incinerator.

## 2.9 CHARACTERIZATION OF THE PETROLEUM REFINING INDUSTRY

### 2.9.1 Statistical Summary of the Industry

A tabulation of the refineries in the United States (current as of January 1979) is given in Appendix A. The tables in this appendix indicate refinery capacity; location, including the number of the U.S. EPA Air Quality Control Region (AQCR); and the attainment status for photochemical oxidants of the area in which each refinery is located. The tables are arranged by state according to EPA region. The appendix includes a table for each region, summarizing the total number of refineries and their combined capacity in each state in the region.

Table 2-4 lists the total number of refineries, the number of refineries in photochemical oxidant nonattainment areas, and

TABLE 2-4. SUMMARY OF OPERATING REFINERIES IN THE UNITED STATES[a]

| EPA Region | Number of refineries | Total capacities, bbl/day | Refineries in attainment areas[b] | Refineries in nonattainment areas |
|---|---|---|---|---|
| I | 1 | 13,400 | 0 | 1 |
| II | 11 | 1,790,820 | 4 | 7 |
| III | 16 | 1,028,660 | 3 | 13 |
| IV | 21 | 699,800 | 14 | 7 |
| V | 40 | 2,841,398 | 10 | 30 |
| VI | 108 | 7,541,560 | 54 | 54 |
| VII | 13 | 571,339 | 11 | 2 |
| VIII | 34 | 642,898 | 25 | 9 |
| IX | 46 | 2,537,420 | 5 | 41 |
| X | 12 | 477,500 | 7 | 5 |
| Total | 302 | 18,144,795 | 133 | 169 |

[a] As of January 1979

[b] Attainment of standards for photochemical oxidants.

the combined refining capacities for each EPA region and for the country as a whole.

There are 302 refineries operating in the United States, 169 of which are located in nonattainment areas for photochemical oxidants. The total national refining capacity is estimated at 18,144,795 barrels per day (BPD). Approximately half of the refineries in Region VI are in oxidant nonattainment areas. Region IX ranks second in number of refineries, most of which are in California and all of which are in oxidant nonattainment areas. The other regions in decreasing order of number of refineries in oxidant nonattainment areas are Regions V, III, VIII, IV, II, X, VII, and I.

The Standard Industrial Classification (SIC) code 2911, "Petroleum Refineries," is the criterion for inclusion in this tabulation.

### 2.9.2 Trends In The Industry

During collection of information for this manual some trends, or potential trends, related to corporate structure in the refining industry were noted.

One trend is the diversification in ownership of refineries, which is done for various reasons. As an example, operators of a relatively complex refinery may wish to increase the capacity for crude distillation by installing a new atmospheric distillation column. To avoid being subject to a Prevention of Significant Deterioration (PSD) review, the refinery officials may form a new company to build the unit, because small refineries are exempt from some PSD conditions. The new company buys property on or near the site of the larger original refinery and constructs the new atmospheric distillation unit and perhaps accessory storage tanks. This constitutes a new refinery, which will sell most or all of its products to the neighboring, larger refinery. In essence this increases the capacity of the larger refinery, but the small refinery is exempt from certain regulations. Personnel of the larger refinery may actually operate units and equipment of the newly created, smaller refinery.

Financial advantages other than those involved in circumventing regulations also encourage diversification of ownership. Such advantages relate primarily to income tax, depreciation of equipment, and financing. As an example, a company may need a new, expensive item of equipment but prefer not to increase its liabilities because doing so will lower the bond rating. The owners then form a second company, which purchases the needed equipment and leases it to the original company. Thus, the bond rating is not affected.

Another form of diversification is the formation within a large petroleum corporation of a specialized company whose business is the treatment and disposal of refinery and petrochemical wastes. A similar potential trend is the hiring of outside companies to undertake wastewater disposal or wastewater treatment. This trend is significant in enforcement of requirements for reasonably available control technology (RACT) for wastewater separators. Even though the refineries that engage wastewater treatment companies remove their oily water from the refinery premises, the volatile organic compounds (VOC) in the water still must be controlled. Some refineries have partially divorced themselves from responsibility for some emissions by using disposal companies. Such practices of diversification in ownership are followed in several regions of the United States.

Another trend is the addition of distillation columns to bulk storage terminals. This results in a change in classification from petroleum storage to petroleum refining. All of these trends are significant, because EPA personnel must keep abreast of and maintain files on these new, small refineries in order to enforce regulations. Changes in classification of facilities that have been diversified must be identified and recorded.

Trends in the total number and average size of refineries in the United States are noted in Table 2-5. The total throughput of crude oil has increased yearly since 1965 and average capacity

TABLE 2-5. OPERATING REFINERIES AND CRUDE OIL THROUGHPUT[3]

| Year | Number of operating refineries | Crude oil throughput, barrels per stream day | Average capacity, barrels per stream day |
|---|---|---|---|
| 1965 | 265 | 10,721,550 | 40,459 |
| 1966 | 261 | 10,952,495 | 41,964 |
| 1967 | 269 | 11,657,975 | 43,338 |
| 1968 | 263 | 12,079,201 | 45,929 |
| 1969 | 262 | 12,651,375 | 48,288 |
| 1970 | 253 | 13,284,985 | 52,510 |
| 1971 | 247 | 13,709,442 | 55,504 |
| 1972 | 247 | 13,991,580 | 56,646 |
| 1973 | 247 | 14,876,650 | 60,229 |
| 1974 | 259 | 15,463,650 | 59,705 |
| 1975 | 256 | 15,687,321 | 61,289 |
| 1976 | 266 | 16,912,596 | 63,581 |
| 1977 | 285 | 17,618,955 | 61,821 |
| 1978 | 289 | 17,169,909 | 59,411 |

increased from 1965 through 1973. The total number of refineries, however, decreased during the same period. This decrease apparently was caused by the inability of independent refiners to compete with the expanding major oil companies. ("Major" and "independent" are arbitrary designations for the 20 or so largest and all smaller petroleum refining companies, respectively.) The entitlements program of the U.S. Department of Energy (DOE) (instituted in 1973 by the Federal Energy Administration) was established to help reverse this trend.

The entitlements program has resulted in a tendency toward construction of smaller refineries. The purpose of the program is to protect independent, small refiners by ensuring that large refiners having access to cheaper, domestic crude do not gain an advantage over small refiners not having the same access. Refiners processing less than 10,000 barrels per day of crude oil are the most heavily subsidized group in the entitlements program. The effect of this program can be seen by the sharp increase in the number of new, small refiners coming onstream in 1974 and after.[4]

The average capacity per refinery did not rise as sharply from the end of 1973 through 1977 as it had during other 4-year time periods, an indication that the recent trend is toward building refineries of low capacity. The addition of many small refineries does not account for all of the increases in total crude throughput since 1974. Expansion of existing refineries has continued, and not all oil companies are diversifying and establishing new, smaller companies for each expansion. Nonetheless, the declining rate of increases in average capacities and the increasing number of refineries demonstrate an industrywide tendency to construct small refineries.

## 2.10 REFERENCES

1. Petrochemical Handbook Issue. Petroleum Refiner, 38(11), November 1960.

2. 1977 Petrochemical Handbook Issue. Hydrocarbon Processing, 56(11):237-239, November 1977.

3. R. F. Boland, et al. Screening Study for Miscellaneous Sources of Hydrocarbon Emissions in Petroleum Refineries. EPA-450/3-76-041, December 1976.

4. Prescott, J. H. Small Is In, Big Is Out in Oil-Refining World. Chemical Engineering, October 10, 1977, pp. 80-84.

# SECTION 3

# REGULATIONS

## 3.1 INTRODUCTION

This section of the manual discusses some of the regulations that the inspector will enforce. The inspector should obtain a copy of all applicable regulations and become familiar with them before any enforcement inspection.

## 3.2 BACKGROUND

The Clean Air Act of 1970 is based on a two-component air resource management strategy. The first component consists of the national ambient air quality standards (NAAQS), which were established for a number of pollutants and were to be implemented over the whole Nation. The standards were set on two levels: primary standards established the maximum allowable concentrations of pollutants in the atmosphere to protect public health; secondary standards set the safety margin concentration level. The concentration levels were established to protect the public "from any known or anticipated adverse effects."

The second component of the Clean Air Act set emission standards. These standards were established so that emissions throughout the United States would be reduced enough to meet at least the primary NAAQS by 1975. The emission standards were set nationally by EPA and locally by each state for new sources, and were set by each state for existing sources.

Congress began preparing new legislation in 1975 when the primary NAAQS had not been met and evidently would not be met by 1977, when the 2-year extension elapsed. The new legislation, the Clean Air Act Amendments of 1977 (CAAA), was based on the two-component system of the original act; however, it placed new emphasis on the regulation concerning new or expanding plants. The CAAA substantially changed the criteria for obtaining permits for new or expanding plants. In setting these standards, known as the New Source Performance Standards (NSPS), the Act required EPA to impose strict standards without forcing massive shutdowns in existing facilities.

## 3.3 NEW SOURCE PERFORMANCE STANDARDS

NSPS applicable to refineries are contained in subparts J and K of "Standards of Performance For New Stationary Sources." Subpart J includes standards for fluid catalytic cracking (FCC) catalyst regenerators, fuel gas combustion devices, and Claus sulfur recovery plants. The Claus process is the most widely used method for extraction of sulfur from acid gases (see Section 4.16 for a detailed description). Subpart K includes standards for storage facilities for volatile organic compounds (VOC).

Any FCC catalyst regenerator that was built or modified after June 11, 1973, is subject to NSPS. The specific emissions standards are as follows:

Particulates: 1.0 kg/1000 kg of coke burnoff
Opacity: 30 percent
Carbon monoxide: 0.050 percent by volume

Particulate emissions may exceed this level if the gases pass through a waste heat boiler or incinerator. The incremental increase cannot, however, exceed 43.0 g/MJ (0.10 lb/million Btu) of heat input that is attributable to any auxiliary fuel burned. The 30 percent opacity limitation may be exceeded for one 6-minute period in any 1 hour.

Any fuel gas combustion device (heater) that is built or modified after June 11, 1973, must burn fuel with a hydrogen sulfide ($H_2S$) content less than 230 mg/dscm (0.10 gr/dscf). The $H_2S$ content of fuel gas may exceed this level if the gases from the combustion are treated to reduce sulfur dioxide ($SO_2$) emissions.

Any Claus sulfur recovery unit that is built or modified after October 4, 1976, is subject to emission levels based on the control methods used. If emissions are controlled by an oxidation or a reduction control system followed by incineration, the unit may not emit more than 0.025 percent by volume of $SO_2$ at zero percent oxygen (dry basis). If emissions are controlled by a reduction control system not followed by incineration, the unit may not emit more than 0.030 percent by volume of reduced sulfur compounds and 0.0010 percent by volume of $H_2S$ calculated as $SO_2$ at zero percent oxygen (dry basis).

Subpart K of NSPS applies only to storage vessels having capacities greater than 151,416 liters (40,000 gallons or 952 barrels) and containing volatile organic compounds. If tank capacity is between 151,416 and 245,000 liters (40,000 to 65,000 gallons or 952 to 1548 barrels), the standard is enforceable for tanks built or modified after March 8, 1974. If tank capacity is greater than 245,000 liters (65,000 gallons), the standard is enforceable for tanks built or modified after June 11, 1973.

The standard for storage vessels is in two parts. If the true vapor pressure of the stored material is greater than 10.5 kPa (kilo Pascals) (1.5 psia) but less than or equal to 77 kPa (11.1 psia), the vessel must be equipped with a floating roof, a vapor recovery system, or their equivalents. If the true vapor pressure of the stored material exceeds 77 kPa (11.1 psia), the tank must be equipped with a vapor recovery system.

NSPS include some special provisions for Claus plants. The standards do not apply to plants with a capacity of 20 long tons per day or less and associated with a small petroleum refinery. [A small petroleum refinery is defined as one with a crude oil processing capacity of 7.9 million liters (50,000 barrels) or less per stream day and that is owned or controlled by a refinery with a total combined crude oil processing capacity of 21.8

million liters (137,500 barrels) or less per stream day.] Also, the Claus plant need not be physically located within the boundaries of a petroleum refinery to be an affected facility, provided it processes gases produced within a petroleum refinery.

## 3.4 PREVENTION OF SIGNIFICANT AIR QUALITY DETERIORATION

On December 5, 1974, EPA published regulations under the 1970 version of the Clean Air Act for the prevention of significant air quality deterioration (PSD). These regulations established a program for protecting areas having air quality cleaner than the national ambient air quality standards (NAAQS).

Under EPA's regulatory program, clean areas could be designated under any of three classes. Specified numerical increments of air pollution were permitted under each class up to a level considered to be significant for that area. Class I increments permitted only minor air quality deterioration; Class II increments, moderate deterioration; Class III increments, deterioration up to the secondary NAAQS.

EPA initially designated all clean areas as Class II. States, Indian governing bodies, and Federal land managers were given authority to redesignate their lands under specified procedures. The area classification system was administered and enforced through a preconstruction permit program for 19 specified types of stationary air pollution sources. This preconstruction review, in addition to limiting future air quality deterioration, required any source subject to the requirements to apply best available control technology (BACT) (see Section 3.4.3 for definition of BACT).

On August 7, 1977, the Clean Air Act Amendments of 1977 became law. The 1977 amendments changed the 1970 act and EPA's regulations in many respects, particularly with regard to PSD. In addition to mandating certain immediately effective changes to the PSD regulations, the amended Clean Air Act contained comprehensive new PSD requirements. These regulations, which are more stringent, are contained in 40 CFR 52.21, SUPPLEMENT 1 (Federal Register, Vol. 43, No. 118, Monday, June 19, 1978, Part V).

The sources that are subject to PSD regulations include the following:

> Any stationary source listed in Table 3-1 that emits, or has the potential to emit, 91 Mg/yr (100 tons/yr) of any air pollutant regulated under the Clean Air Act. (See Section 3.4.3 for emissions definitions.)
>
> Any source that emits, or has the potential to emit, 227 Mg/yr (250 tons/yr) or more of any air pollutant regulated under the Clean Air Act.

The two types of PSD reviews are TIER I and TIER II. TIER I is an abbreviated review, intended for smaller sources of air pollutants that have a proportionately smaller impact on air quality. TIER II is a more intensive review, intended for larger and more significant sources of air pollutants.

### 3.4.1 TIER I Review

> The applicant must demonstrate that the requirements for all applicable State Implementation Plans (SIP), NSPS, and National Emissions Standards for Hazardous Air Pollutants (NESHAPS) have been met. This demonstration may be accomplished by presenting an enforceable SIP permit.
>
> Allowable emissions (see Section 3.4.3) from the source must be less than 45 Mg/yr, 454 kg/day, or 45 kg/h (50 tons/yr 1000 lb/day, or 100 lb/h).
>
> The source must not have an impact on a Class I area or an area where the applicable increment is known to be violated. If there is doubt about this requirement, the applicant should contact the EPA regional office.
>
> The data sheets in Appendix I list source information required to determine if PSD regulations apply and to conduct TIER I reviews.

### 3.4.2 TIER II Review

If allowable emissions from a source are equal to or greater than 45 Mg/yr (50 ton/yr), 454 kg/day (1000 lb/day), or 45 kg/h (100 lb/h), the source is given a TIER II review. This review

## TABLE 3-1. SOURCES SUBJECT TO PSD REVIEW

| |
|---|
| Fossil-fuel-fired steam electric plants of more than 264 million MJ/h (250 million Btu/h) heat input |
| Kraft pulp mills |
| Portland cement plants |
| Primary zinc smelters |
| Iron and steel mill plants |
| Primary aluminum ore reduction plants |
| Primary copper smelters |
| Municipal incinerators capable of charging more than 227 metric tons (250 tons) of refuse per day |
| Sintering plants |
| Chemical process plants |
| Fossil-fuel-fired boilers (or combinations thereof) totaling more than 264 million MJ/h (250 million Btu/h) heat input. |
| Hydrofluoric acid plants |
| Sulfur acid plants |
| Petroleum refineries |
| Lime plants |
| Phosphate rock processing plants |
| Coke oven batteries |
| Sulfur recovery plants |
| Carbon black plants (furnace process) |
| Primary lead smelters |
| Fuel conversion plants |
| Secondary metal production plants |
| Petroleum storage and transfer units with a total storage capacity exceeding 48 million liters (300,000 barrels or 12.6 million gallons) |
| Charcoal production plants |
| Taconite ore processing plants |
| Glass fiber processing plants |
| Nitric acid plants |

has two parts: a control technology review and an air quality review.

Control Technology Review--

In the first phase of a Tier II review, the applicant must demonstrate that he is applying best available control technology. To accomplish this, the applicant must prepare a BACT presentation for each applicable pollutant. This includes the data requirements for precipitators, baghouses, and $SO_2$ scrubbers.

If, after BACT is applied, allowable emissions are equal to or greater than 45 Mg/yr (50 ton/yr), 454 kg/day (1000 lb/day), or 45 kg/h (100 lb/h), an Air Quality Impact Analysis must be made.

Air Quality Review--

The applicant must demonstrate that the allowable emission increases from the proposed source or modification will not cause a violation of either of the following:

Any national ambient air quality standard in any air quality control region.

Any applicable maximum allowable increase over the baseline concentration in any area (see Section 3.4.3).

To meet these requirements, the applicant must submit an analysis of the impact of the proposed source on the NAAQS and the PSD increment. The analysis must be supported with the data needed to estimate air quality impact, including data on meteorology, topography, source emissions, and air quality.

As part of the analysis, the applicant must describe the air quality impacts and the nature and extent of any or all general, commercial, residential, industrial, and other growth in the impact area since the baseline date of August 7, 1977.

Preliminary screening techniques can be used to determine whether full-scale modeling is necessary. For screening purposes, conservative estimates of emission characteristics and ambient impacts are modeled using relatively straightforward formulas. If screening procedures indicate that ambient concentrations would exceed one-half of the remaining ambient increment or ceiling allowance, more refined techniques are used.

Any permit application submitted after August 7, 1978, must include an analysis of air quality monitoring data for any pollutant emitted by the source or modification for which an NAAQS exists, except nonmethane hydrocarbons. The monitoring data may be required for a period of up to 1 year.

Air quality data are used to determine whether emissions from the proposed source or modification would cause a violation of the NAAQS. Existing data are used to the maximum extent practicable, and preconstruction monitoring is required only as necessary. In general, monitoring data are not to be used to determine how much of the available increment has been consumed.

The applicant is required to include an analysis of the impairment to visibility, soils, and vegetation that would occur as a result of the source or modification and the general commercial, residential, industrial, and other growth associated with the source or modification.

The data sheets in Appendix I list source information required for a TIER II review.

### 3.4.3 Definitions

The following definitions are found in the regulations on prevention of significant deterioration (40 CFR 51.24, July 1, 1979).

> Allowable emissions means the emission rate calculated using the maximum rated capacity of the source (unless the source is subject to enforceable permit conditions that limit the operating rate or hours of operation, or both) and the most stringent of the following: (i) Applicable standards as set forth in 40 CFR, Part 60 and Part 61; or (ii) The applicable state implementation plan emission limitation; or (iii) The emission rate specified as a permit condition [Section 5.24 (b) (17)].
>
> Baseline concentration means that ambient concentration level reflecting actual air quality as of August 7, 1977, minus any contribution from major stationary sources and

major modifications on which construction commenced on or after January 6, 1975. The baseline concentration shall include contributions from: (i) The actual emissions of other sources in existence on August 7, 1977, except that contributions from facilities within such existing sources for which a plan revision proposing less restrictive requirements was submitted on or before August 7, 1977, and was pending action by the Administrator on that date shall be determined from the allowable emissions of such facilities under the plant as revised; and (ii) The allowable emissions of major stationary sources and major modifications which commenced construction before January 6, 1975, but were not in operation by August 7, 1977. [Section 51.24 (b) (11)]

Best available control technology means an emission limitation (including a visible emission standard) based on the maximum degree of reduction for each pollutant subject to regulation under the act which would be emitted from any proposed major stationary source or major modification which the Administrator, on a case-by-case basis, taking into account energy, environmental, and economic impacts and other costs, determines is achievable for such source or modification through application of production processes or available methods, systems, and techniques for control of such pollutant. In no event shall application of best available control technology result in emissions of any pollutant which would exceed the emissions allowed by any applicable standard under 40 CFR, Part 60 and Part 61. If the Administrator determines that technological or economic limitations on the application of measurement methodology to a particular class of sources would make the imposition of an emission standard infeasible, a design, equipment, work practice or operational standard, or combination thereof, may be prescribed instead to require the application of best available control technology. Such standard shall, to the degree possible, set forth the emission reduction achievable by implementation of such design, equipment, work practice or operation, and shall provide for compliance by means which achieve equivalent results. [Section 51.24 (b) (10)]

Potential to emit means the capability, at maximum capacity, to emit a pollutant in the absence of air pollution control equipment. Air pollution control equipment includes control equipment which is not, aside from air pollution control laws and regulations, vital to production of the normal product of the source or to its normal operation. Annual potential shall be based on the maximum annual rated capacity of the source, unless the source is subject to enforceable permit conditions which limit the annual hours of operation. Enforceable permit conditions on the type or amount of materials combusted or processed may be used in determining the potential emission rate of a source.

### 3.4.4 Proposed Changes to PSD Regulations

EPA has proposed to change the PSD regulations in response to a court decision (Alabama Power Company vs. Costle, June 18, 1979) that overturned those regulations in major respects. The thrust of the proposed changes includes major changes in the definitions of baseline concentration and potential emissions and the elimination of the TIER system of PSD review.

Within the definition of baseline concentration, the baseline date is proposed to be changed from August 7, 1977, to the date of the first completed application after August 7, 1977, for every part of an Air Quality Control Region designated as unclassifiable or as an attainment area. Within the definition of potential emissions, potential to emit is proposed to be changed from "in the absence of air pollution control equipment" to "in the presence of air pollution control equipment." Annual potential is proposed now to ignore any permit conditions that limit the annual hours of operation and consider each source as operating 8760 hours per year. These changes in definitions substantially change the implications of the original regulations.

The proposed regulations would exempt on a pollutant-specific basis major modifications from all permit requirements and new major sources on a pollutant-specific basis from all requirements when emissions of the particular pollutant are below a specified "de minimis" or significant emission rate. Table 3-2 (Table 1 in the proposed changes and so referred to in this report) lists the "de minimis" emission rates.

Table 1 would have two principal uses. First, it would be used to show that the net increase associated with a modification would be "de minimis" for all pollutants for which the source is major. A showing for all regulated pollutants for which the source is major would be required of modifications at major stationary sources in PSD areas. A successful showing would exempt a modification from PSD requirements. Such a source would,

## TABLE 3-2. GUIDELINES FOR SIGNIFICANT EMISSION RATES (TABLE 1 IN PROPOSED CHANGES)

| Pollutant | Emission rate, tons/yr |
|---|---|
| Carbon monoxide | 100 |
| Nitrogen dioxide | 10 |
| Total suspended particulates | 10 |
| Sulfur dioxide | 10 |
| Ozone | 10 |
| Lead | 1 |
| Mercury | 2 |
| Beryllium | 0.004 |
| Asbestos | 1 |
| Fluorides | 0.02 |
| Sulfuric acid mist | 1 |
| Vinyl chloride | 1 |
| Total reduced sulfur: | |
| Hydrogen sulfide | 1 |
| Methyl mercaptan | 1 |
| Dimethyl sulfide | 1 |
| Dimethyl disulfide | 1 |
| Reduced sulfur compounds: | |
| Hydrogen sulfide | 1 |
| Carbon disulfide | 10 |
| Carbonyl sulfide | 10 |

however, be required to provide notice to the Administrator and, therein, make the "de minimis" demonstration. The proposed regulations incorporate the "de minimis" concept by requiring that major modifications have a significant net increase in potential emissions.

Even if a modification cannot be shown to be minor, Table 1 can be used to limit the pollutants for which BACT must be applied or an air quality analysis done. If a modification to a source is subject to review because it results in a significant net increase in potential emissions of a pollutant for which the source is major, or if a new source is subject to review because it will have the potential to emit a regulated pollutant in major amounts, the source may still avoid BACT or an air quality analysis for other pollutants it emits if it emits such pollutants in "de minimis" amounts. Table 1 identifies the emission cutoffs that would trigger the need for control technology and ambient review for those other pollutants. Thus, when a major stationary source or modification is subject to PSD review because of potential emissions of one or more pollutants, the review would apply to only those other pollutants that the source would have the potential to emit in amounts above those proposed in Table 1.

Table 3-3 (Table 2 in the proposed changes and so referred to in this report) is proposed as an additional mechanism to limit the air quality review for pollutants that the source would have the potential to emit in significant amounts but that have an insignificant ambient impact. Table 2 does not apply to pollutants that a new major source would emit in excess of the applicable threshold of 90/227 Mg, nor does it apply to major construction that would be located in a nonattainment area or would adversely impact a Class 1 area.

## 3.5 REASONABLY AVAILABLE CONTROL TECHNOLOGY

In October and December 1977 and in June 1978, EPA promulgated control technique guidelines (CTG) for process unit turnarounds, storage tanks, vacuum-producing systems, wastewater

## TABLE 3-3. GUIDELINES FOR SIGNIFICANT AMBIENT AIR QUALITY IMPACTS (TABLE 2 IN PROPOSED CHANGES)

| Pollutant | Air quality impact |
|---|---|
| Carbon monoxide | 500 μg/m$^3$, 8-hour avg. |
| Nitrogen dioxide | 1 μg/m$^3$, annual |
| Total suspended particulates | 5 μg/m$^3$, 24-hour |
| Sulfur dioxide | 5 μg/m$^3$, 24-hour |
| Lead | 0.03 μg/m$^3$, 3-month |
| Mercury | 0.1 μg/m$^3$, 24-hour |
| Beryllium | 0.005 μg/m$^3$, 24-hour |
| Asbestos | 1 μg/m$^3$, 1-hour |
| Fluorides | 0.01 μg/m$^3$, 24-hour |
| Sulfuric acid mist | 1 μg/m$^3$, 24-hour |
| Vinyl chloride | 1 μg/m$^3$, maximum value |
| Total reduced sulfur: | |
| Hydrogen sulfide | 1 μg/m$^3$, 1-hour |
| Methyl mercaptan | 0.5 μg/m$^3$, 1-hour |
| Dimethyl sulfide | 0.5 μg/m$^3$, 1-hour |
| Dimethyl disulfide | 2 μg/m$^3$, 1-hour |
| Reduced sulfur compounds: | |
| Hydrogen sulfide | 1 μg/m$^3$, 1-hour |
| Carbon disulfide | 200 μg/m$^3$, 1-hour |
| Carbonyl sulfide | 200 μg/m$^3$, 1-hour |

separators, and fugitive emissions. Annual nationwide emissions of volatile organic compounds (VOC) from these sources are estimated to be 1.46 million Mg (1.6 million tons), which represents approximately 6.7 percent of the total VOC emitted from stationary sources. The overview of reasonably available control technology (RACT) requirements for petroleum refineries is based on a literal interpretation of the CTG and a discussion between PEDCo personnel and a representative of EPA's Office of Air Quality Planning and Standards (OAQPS).

### 3.5.1 Process Unit Turnarounds

Refinery units are periodically shut down and emptied for internal inspection and maintenance. The procedure of shutting down a unit, repairing or inspecting it, and restarting it is termed "unit turnaround." The CTG do not set specific practices to be followed during turnarounds but do recommend depressurizing process units to 137.9 kPa (5 psig) before atmospheric venting.

In a typical process unit turnaround, liquid contents are pumped from the vessel to some available storage facility. The vessel is then depressurized; flushed with water, steam, or nitrogen; and ventilated. The major potential for VOC emissions occurs when the vessel is depressurized by venting the hydrocarbon vapors to the atmosphere. Incineration of vapors in a flare or as fuel gas (until the pressure in the vessel is as close as practicable to atmospheric pressure) greatly reduces VOC emissions to the atmosphere and complies with RACT requirements. The pressure at which the vapors are vented to the atmosphere depends on the pressure of the disposal system. Many refineries, however, should be able to depressurize process units to 137.9 kPa (5 psig) before atmospheric venting (as recommended in the CTG) without significant process changes. At some refineries the safety relief valves and blowdown systems may require modification.

### 3.5.2 Storage Tanks

Storage tanks for petroleum liquids are a significant source of VOC emissions. Combined emissions from fixed-roof and external and internal floating-roof storage tanks are about 830,000 Mg/yr (915,000 ton/yr). It is estimated that 67.5 percent of these emissions [560,000 Mg (617,000 tons)] are from fixed-roof storage tanks containing petroleum liquids with true vapor pressures above 10.5 kPa (1.5 psia). Estimated emissions from external floating-roof tanks during 1978 were 65,000 Mg (71,650 tons).

The VOC emissions from fixed-roof tanks can be controlled by one of the following methods:

Retrofitting with internal floating roofs
Retrofitting with external floating roofs
Retrofitting with vapor recovery systems

Tanks with capacities less than 151,416 liters (40,000 gallons or 952 barrels) are specifically exempt from the preceding requirements.

RACT for external floating-roof tanks is as follows:

A welded, external floating-roof tank with a primary metallic shoe or liquid-mounted seal must be retrofitted with a rim-mounted secondary seal if the true vapor pressure of the stored material exceeds 27.6 kPa (4 psia).

A welded or riveted external floating-roof tank equipped with a vapor-mounted seal must be retrofitted with a rim-mounted secondary seal if the true vapor pressure of the stored liquid exceeds 10.5 kPa (1.5 psia).

A riveted, external floating-roof tank equipped with a primary metallic shoe or liquid-mounted seal must be retrofitted with a rim-mounted secondary seal if the true vapor pressure of the stored liquid exceeds 10.5 kPa (1.5 psia).

The following external floating-roof tanks are specifically exempt from the preceding requirement:

External floating-roof tanks having capacities less than 1,600,000 liters (420,000 gallons or 10,000 barrels) and used to store produced crude oil and condensate prior to custody transfer

A metallic-type shoe seal in a welded tank that has a tank wall

External floating-roof tanks storing waxy, heavy-pour crudes.

### 3.5.3 Vacuum-Producing Systems

The vacuum-producing systems associated with vacuum distillation and other refinery processes are potential sources of atmospheric emissions of VOC. Three types of vacuum-producing systems may be used:

Steam ejectors with contact (barometric) condensers
Steam ejectors with surface (shell and tube) condensers
Mechanical vacuum pumps

A petroleum refinery is not allowed to discharge more than 1.36 kg (3 lb) of noncondensable VOC into the atmosphere in any 1 hour from any vacuum-producing system unless the total VOC discharge has been reduced by at least 90 percent. If the uncontrolled discharge is greater than 1.36 kg/h (3 lb/h), it should be vented to an incinerator, flare, or refinery fuel gas system. If a refinery uses contact condensers, hot wells associated with these condensers must be covered.

### 3.5.4 Wastewater Separators

Contaminated wastewater originates from several sources in petroleum refineries, including (but not limited to) leaks, spills, pump and compressor seal cooling and flushing, sampling, equipment cleaning, and rainwater runoff. Contaminated wastewater is collected in the process drain system and directed to the refinery wastewater treatment as required. Refinery drains and wastewater treatment facilities are a source of emissions resulting from evaporation of VOC contained in wastewater. When a petroleum refinery is recovering at least 760 liters (201 gallons or 4.8 barrels) or more of VOC per day from a wastewater separator and the VOC have a Reid vapor pressure of 3.5 kPa (0.5 psia) or greater, the separator must be equipped with one of the following vapor loss control devices:

Solid cover
Floating pontoon or double-deck cover
Vapor recovery system

### 3.5.5 Fugitive Emissions

Equipment leaks in petroleum refineries are a significant source of VOC emissions. Nationwide VOC emissions from equipment leaks in petroleum refineries are presently estimated to be 170,000 Mg/yr (187,393 tons/yr), or about 1 percent of the total VOC emissions from stationary sources. Equipment considered includes pump seals, compressor seals, and seal oil degassing vents; pipeline valves, flanges, and other connections; pressure relief devices; process drains; and open-ended pipes.

When a VOC concentration of over 10,000 ppm is found in proximity to a potential leak source, the source is leaking from 1 to 10 kg/day (2.2 to 22 lb/day) depending on the source. If the leak is not located or repaired for a year, annual emissions from this single source can be from 0.4 to 3.7 Mg (0.44 to 4.1 tons) of VOC.

The VOC emissions from equipment leaks are controlled in two phases: first, the leaks must be located (monitoring), and then the leak must be repaired (maintenance).

Monitoring includes annual, quarterly, and weekly inspections. The refinery operator determines the VOC concentration near each potential leak source with a portable VOC detection instrument. If the VOC concentration at the source exceeds 10,000 ppm, the leak should be repaired within 15 days. The monitoring intervals are as follows:

Monitor with a portable VOC detection device annually:

Pump seals
Pipeline valves in liquid service
Process drains

Monitor with a portable VOC detection device quarterly:

Compressor seals
Pipeline valves in gas service
Pressure relief valves in gas service

Monitor visually weekly:

Pump seals

No individual monitoring necessary:

Pipeline flanges
Pressure relief in liquid service

Whenever a liquid leak from a pump seal is observed during the visual inspection and whenever a relief valve vents to the atmosphere, the operator must immediately monitor the VOC concentration of that component. If a leak is detected, it should be repaired within 15 days.

Some of the components having VOC concentrations in excess of 10,000 ppm will not be able to be repaired within 15 days. The refinery operator should report quarterly leaks that cannot be repaired within the time frame and make arrangements for the equipment to be repaired during the next scheduled turnaround. If the operator is unable to bring a component into compliance, he should apply for a variance.

## 3.6 STATE IMPLEMENTATION PLANS

The CAAA of 1977 required each state in which there is a nonattainment area to adopt and submit a revised state implementation plan (SIP). Official designation of attainment areas for the NAAQS has been made but is subject to change as more air quality monitoring data are developed. Although the original date for completion of the SIP's was 1980, the standards for some pollutants and, hence, some nonattainment areas have been changed; the date has been extended accordingly for states preparing new SIP's. The ozone plan portion of the SIP submittals relating to stationary sources of volatile organic compounds must contain regulations reflecting the application of RACT.

Although the SIP's will differ, most will include emission standards for particulates, carbon monoxide, sulfur dioxide, nitrogen oxides, and volatile organic compounds from petroleum refineries. As an example, the Kansas SIP is presented on the following pages in outline form.

## KANSAS
(effective January 1, 1971)

I. Particulates

A. Regulation 28-19-20. This regulation addresses particulate emissions limitations for any processing machine, equipment, device, or other articles excluding indirect heating equipment and incinerators. (In a refinery this would include FCC units, coking units, sulfur plants and fugitives.)

| Process weight rate, lb/h | tons/h | Rate of emission, lb/h | Process weight rate, lb/h | tons/h | Rate of emission, lb/h |
|---|---|---|---|---|---|
| 100 | 0.05 | 0.551 | 16,000 | 8.00 | 16.5 |
| 200 | 0.10 | 0.877 | 18,000 | 9.00 | 17.9 |
| 400 | 0.20 | 1.40 | 20,000 | 10.00 | 19.2 |
| 600 | 0.30 | 1.83 | 30,000 | 15.00 | 25.2 |
| 800 | 0.40 | 2.22 | 40,000 | 20.00 | 30.5 |
| 1,000 | 0.50 | 2.58 | 50,000 | 25.00 | 35.4 |
| 1,500 | 0.75 | 3.38 | 60,000 | 30.00 | 40.0 |
| 2,000 | 1.00 | 4.10 | 70,000 | 35.00 | 41.3 |
| 2,500 | 1.25 | 4.76 | 80,000 | 40.00 | 42.5 |
| 3,000 | 1.50 | 5.38 | 90,000 | 45.00 | 43.6 |
| 3,500 | 1.75 | 5.96 | 100,000 | 50.00 | 44.6 |
| 4,000 | 2.00 | 6.52 | 120,000 | 60.00 | 46.3 |
| 5,000 | 2.50 | 7.58 | 140,000 | 70.00 | 47.8 |
| 6,000 | 3.00 | 8.56 | 160,000 | 80.00 | 49.0 |
| 7,000 | 3.50 | 9.49 | 200,000 | 100.00 | 51.2 |
| 8,000 | 4.00 | 10.4 | 1,000,000 | 500.00 | 69.0 |
| 9,000 | 4.50 | 11.2 | 2,000,000 | 1,000.00 | 77.6 |
| 10,000 | 5.00 | 12.0 | 6,000,000 | 3,000.00 | 92.7 |
| 12,000 | 6.00 | 13.6 | | | |

To calculate the rate of emissions:

1. Change lb/h to tons/h by dividing by 2000
2. Insert into one of the following equations:

    a. If process weight < 30 tons/h → $E = (4.1)(P^{0.67})$
    b. If process weight > 30 tons/h → $E = (55)(P^{0.11}) - 40$

    where $E$ = rate of emissions in lb/h, and
    $P$ = process weight in tons/h

3. Example calculation:

Let process weight rate = 250,000 lb/h

250,000/2000 = 125 tons/h = P

Since P > 30 tons/h

$E = (55)(P^{0.11}) - 40$

$E = (55)(125^{0.11}) - 40$

$E = (55)\ (1.7) - 40$

$E = 93.5 - 40$

$E = 53.5$ lb/h

B. Regulation 28-19-31. This regulation addresses particulate emissions limitation for any indirect heating equipment. (For a petroleum refinery, this includes process heaters, boilers, and direct-fired compressors).

| Total input, $10^6$ Btu/h | Allowable lb/h $10^6$ Btu* | Total input, $10^6$ Btu/h | Allowable lb/h $10^6$Btu* |
|---|---|---|---|
| 10 or less | 0.60 | 1,000 | 0.21 |
| 50 | 0.41 | 2,000 | 0.17 |
| 100 | 0.35 | 5,000 | 0.14 |
| 500 | 0.24 | 7,500 | 0.13 |
| 700 | 0.22 | 10,000 or more | 0.12 |

*The allowable emission rate for equipment having intermediate heat input between 10 x $10^6$ Btu and 10,000 x $10^6$ Btu may be determined by the formula:

$$A = \frac{1.026}{I^{.233}}$$

where A = the allowable emission rate in lb/h/$10^6$ Btu
I = the total heat input in $10^6$ Btu/h

Example calculation:

Let I = 17.2 x $10^6$ Btu/h

$$A = \frac{1.026}{I^{.233}}$$

$$A = \frac{1.026}{17.2^{.233}}$$

$$A = \frac{1.026}{1.94}$$

$$A = 0.53$$

II. Opacity

Regulation 28-19-31B. This regulation addresses the opacity of stack gases and fugitive emissions.

A. Existing equipment: 40 percent opacity allowed

B. New equipment: 20 percent opacity allowed

III. Regulation 28-19-31C

This regulation addresses sulfur dioxide emissions and is applicable to heaters, boilers, and compressors. The emissions limit is 1.5 pounds of sulfur per million Btu of heat input per hour. Indirect heating equipment having a heat input of less than 250 million Btu per hour is exempt.

IV. Regulation 28-19-31D

This regulation addresses nitrogen oxide emissions and is applicable to heaters, boilers, and compressors. The emissions limit is 0.30 pounds of nitrogen oxides per million Btu of heat input per hour. Indirect heating equipment having a heat input of less than 250 million Btu per hour is exempt.

V. Regulation 28-19-23

This regulation addresses hydrocarbon emissions and is applicable to storage tanks, ethylene plants, and vapor blowdown systems.

A. Any storage tank of 40,000-gallon capacity or greater storing material which has a vapor pressure greater than 3.0 psia must be equipped with one of the following vapor loss control devices:

   1. A double deck type floating roof or internal floating cover; not allowed for materials with vapor pressure greater than 13.0 psia

   2. A vapor recovery system

   3. Other equipment as may be approved by the Kansas State Department of Health.

B. No person shall emit ethylene unless the waste gas is burned at 1300°F for 0.3 seconds or more in a direct flame afterburner.

C. No person shall emit any gas stream excluding methane of more than 50 lb/day from a vapor blowdown system unless the gases are burned by smokeless flares.

D. Installations and equipment existing on January 1, 1972, shall be exempt from the provisions of this regulation.

VI. Regulation 28-19-24

This regulation addresses carbon monoxide emissions and is applicable to FCC catalyst regenerators and coking units. No person shall emit CO from any catalyst regeneration of a petroleum cracking system, petroleum fluid coker, or other petroleum process unless the gas stream is burned at 1300°F for 0.3 seconds or more in a direct-flame afterburner.

# PROCESS
# OPERATIONS

# SECTION 4.0

# PROCESS OPERATIONS

An integrated refinery is made up of many interconnected processes. By recognizing and understanding the individual processes, the inspector can gain an understanding of the entire refinery operation. This section presents process descriptions, monitoring and inspection procedures, and related descriptive material for a large number of common refining processes. The processes are not categorized or grouped by type or quantity of emissions; rather, they are presented as independent sections. To prepare for an inspection at a relatively simple refinery, the inspector may need to consult only six or eight sections. The enforcement procedures are discussed in Section 5. Specific emissions from valves, pumps, compressor seals, and other refinery equipment components are discussed in Appendix H.

To gain further understanding of the refinery being inspected, the inspector should first stop in the control room for each process unit. In the main control room for the fluid catalytic cracking unit, for example, the recorders of concern to the inspector are the temperature, pressure, and space velocity gauges. The inspector should also ask to see the control room logbook or, in larger refineries, a computer printout of the operational parameters.

When recording any data from the logbook in the control room, ask for conversion factors. Pressure is usually read in pounds per square inch gauge (psig), but a factor of 10 may need to be applied. Temperature is recorded in degrees Fahrenheit. The metric system has not reached refineries. It is particularly important that a conversion factor be known for flow rates.

Before starting an inspection, the inspector should consult this section of the manual to insure he has an understanding of the operation of the unit, the types and sources of emissions, and the information to be obtained. Section 5 delineates the various levels of inspection to be performed.

Each refinery process is described in terms of the following subsections:

### 4.n.1 Process Description

This subsection presents a description of the process, taken from the literature. The description gives the inspector a complete view of the process. A conceptual diagram illustrating the process flow accompanies each description. Table 4.0-1 shows the symbols that are used in the diagrams.

### 4.n.2 Emission Sources

A discussion of the types and sources of emissions is presented. Data from EPA publication AP-42 are not repeated, but the reader is directed to the pollutants of concern and their sources, including vents and leaks in seals, packing, and flanges.[1]

A major reference study providing information on emission sources is the 1978 survey conducted by the California Air Resources Board.[2] This survey estimated the extent of leakage from various refinery equipment.

### 4.n.3 Emission Controls

This description of the control methods used to reduce emissions, including add-on devices and process modifications, helps the inspector in his discussions with plant personnel.

### 4.n.4 Instrumentation

Refinery processes are enclosed, high-volume operations. A great deal of instrumentation is used to monitor flows, emissions, operating conditions, and control systems. The inspector should understand the pertinent readings from these instruments.

TABLE 4.0-1. SYMBOLS USED IN PROCESS FLOW DIAGRAMS

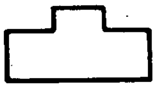
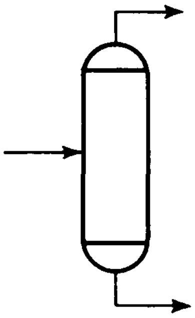
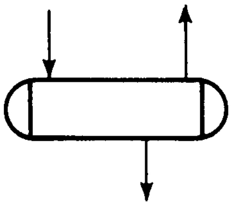
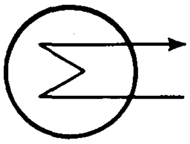
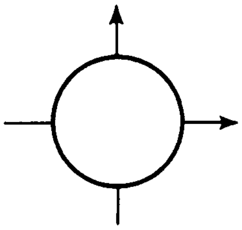
| SYMBOL | DESCRIPTION |
|---|---|
|  or  | Direct-fired heater; also referred to as furnace, pipe still, or heater. |
|  | Fractionating tower; also referred to as fractionator, distillation column, stabilizer, or stripper. |
|  | Separator or settler. |
|  | Accumulator. |
|  or  | Heat exchanger. |

TABLE 4.0-1 (continued)

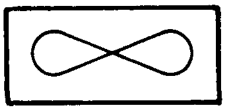
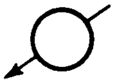
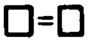
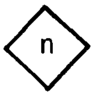
| SYMBOL | DESCRIPTION |
|---|---|
|  | Air-cooled heat exchanger. |
|  or  | Condenser. |
|  | Pump. |
|  or  | Compressor. |
|  | Steam ejector. |

TABLE 4.0-1 (continued)

| SYMBOL | DESCRIPTION |
|---|---|
|  | Valve. |
|  | Emission point, with point source number (n) indicated inside the diagram. |

This subsection describes flow rates, operating temperature, operating pressure, and other parameters related to emissions. The parameters stated in the text are based on engineering judgment.

## 4.n.5 Startup/Shutdown/Malfunctions

This subsection describes the frequency of startup/shutdown operations and their effect on emissions. Emissions at these times, and during malfunctions or upsets, are frequently vented to the plant blowdown system. Increases in emissions can, however, still occur.

## 4.n.6 References

The references are intended to document the information presented in the subsection. References for this subsection are listed below.

1. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. 2d ed. AP-42. 1979.

2. State of California. Air Resources Board. Emissions From Leaking Valves, Flanges, Pumps and Compressor Seals and Other Equipment at Oil Refineries. Report No. LE-78-001. April 1978.

## 4.1 DISTILLATION[1-9]

Distillation refers to the complete operation required to separate materials having different boiling points. This operation includes heating, vaporization, fractionation, condensation, and cooling. The most important distillation unit in the refinery is that which separates incoming crude oil into various boiling point fractions. This section discusses the distillation process that occurs under both atmospheric and vacuum conditions. Higher efficiencies and lower costs are achieved when the crude oil separation is accomplished in these two steps: the total crude is fractionated in a tower at essentially atmospheric pressure, the high-boiling bottoms fraction (residual) from the atmospheric still is then fed to a second fractionator operated at vacuum conditions. The main separation technique used in distillation is fractionation, which is discussed in detail in Appendix C. The inspector should refer to the literature references in the Bibliography for additional information.

### 4.1.1 Process Description

#### Atmospheric Distillation

Before the incoming crude enters the atmospheric distillation unit it is usually treated to remove salt, which would corrode the equipment (Section 4.9). A typical atmospheric distillation unit is illustrated in Figure 4.1-1. The crude is preheated by exchange with outgoing streams to about 290°C (550°F), whereupon it enters the crude heater. In the heater the temperature of the crude is raised to about 400°C (750°F), which partially vaporizes it. The crude then flows to a distillation column (crude tower), which serves as the atmospheric fractionator. This tower normally contains 30 to 50 fractionation trays and three or more liquid sidestream draws. The crude is separated into several cuts, including gas containing light hydrocarbons (butanes, propane, and lighter hydrocarbons), light naphtha with a boiling range of 40° to 120°C (100° to 250°F), heavy

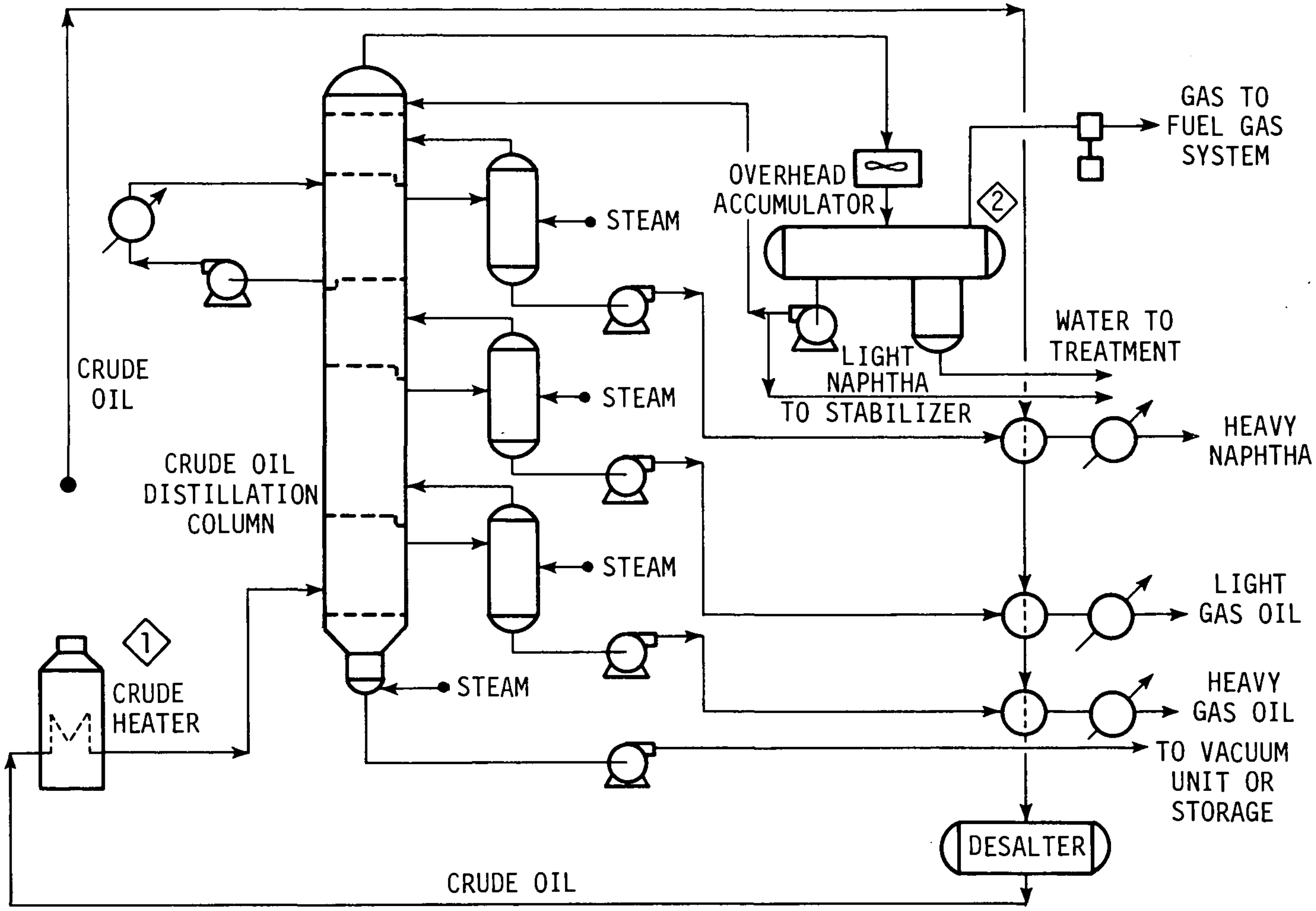


Figure 4.1-1. Typical crude oil distillation unit.

naphtha with a boiling range of 90° to 175°C (200° to 350°F), light gas oil with a boiling range of 160° to 260°C (325° to 500°F), heavy gas oil with a boiling range of 230° to 340°C (450° to 650°F), and residuum.

As shown in Figure 4.1-1, the gas and the pentane and lighter fractions come off the top of the crude tower and flow to the overhead condenser and accumulator. In the accumulator, two phases are present: a gas phase containing light hydrocarbons (butanes and propane) and a liquid phase containing water and the pentane and lighter crude fractions. The gas from the accumulator, which is usually compressed, flows to the refinery fuel gas system. The water collected in the accumulator was either present in the crude or entered the tower from the stripping steam (see below). This water is sent to the wastewater treatment facility. The pentane and lighter fractions contain light gasoline and some propane and butane. Some of this fraction is returned to the top of the crude tower as reflux, and the rest is sent to a stabilizer (fractionator) where the propane and butane are removed.

As discussed in Section 2.2.2, the crude tower usually produces three or more sidestreams that are stripped of their light ends by steam. This step is necessary because the liquid sidestreams withdrawn from the column contain low-boiling components that lower the flash point; the lighter products pass through the heavier products and are in equilibrium with them on every tray. These light ends are stripped from each sidestream in a separate, small stripping tower containing 4 to 10 trays. Steam is introduced under the bottom tray and the steam and stripped light ends are returned to the crude tower above the corresponding side draw tray. This procedure also reduces the vapor pressure of the sidestreams. Each sidestream (shown in Figure 4.1-1 as heavy naphtha, light gas oil, and heavy gas oil) is stream stripped, subjected to heat exchange with crude oil, cooled, and pumped to storage.

The hot residual is steam stripped in the base of the crude tower, whereupon it usually flows to the vacuum distillation unit (vacuum tower). Alternatives to vacuum distillation may be used (e.g., residual oil supercritical extraction or ROSE, residuum extraction, coking, or Residfining), but most refineries follow atmospheric distillation with vacuum distillation.

## Vacuum Distillation

The vacuum distillation unit is used to separate the heavier portion of the crude into fractions. A typical vacuum distillation unit is shown in Figure 4.1-2. If this operation were performed at atmospheric pressure, the temperatures necessary to vaporize the atmospheric bottoms would cause thermal cracking and resultant discoloration of product; coke formation would also cause fouling in the equipment. In the vacuum unit, hot residual bottoms from the crude tower flow to a vacuum heater, which heats the oil to 400°C (750°F). The residual then flows to the vacuum tower, where distillation occurs under the combination of high temperature (390° to 450°C; 730° to 850°F) and low pressure (3.3 to 5.3 kPa; 25 to 40 mm Hg absolute).

Vaporization is improved when the effective pressure is lowered even further to 1.3 kPa (10 mm Hg) or less by the addition of steam at the furnace inlet and the bottom of the vacuum tower. Addition at the furnace inlet increases the furnace tube velocity and minimizes coke formation in the furnace, as well as decreasing the partial pressure of the hydrocarbons in the vacuum tower.

At least one gas oil stream is taken off from the side of the vacuum tower. The sidestream is subjected to heat exchange with the feed, cooled, and pumped to storage. The vacuum residual from the bottom of the tower is either cooled and sent to storage or sent to the coking unit for further processing.

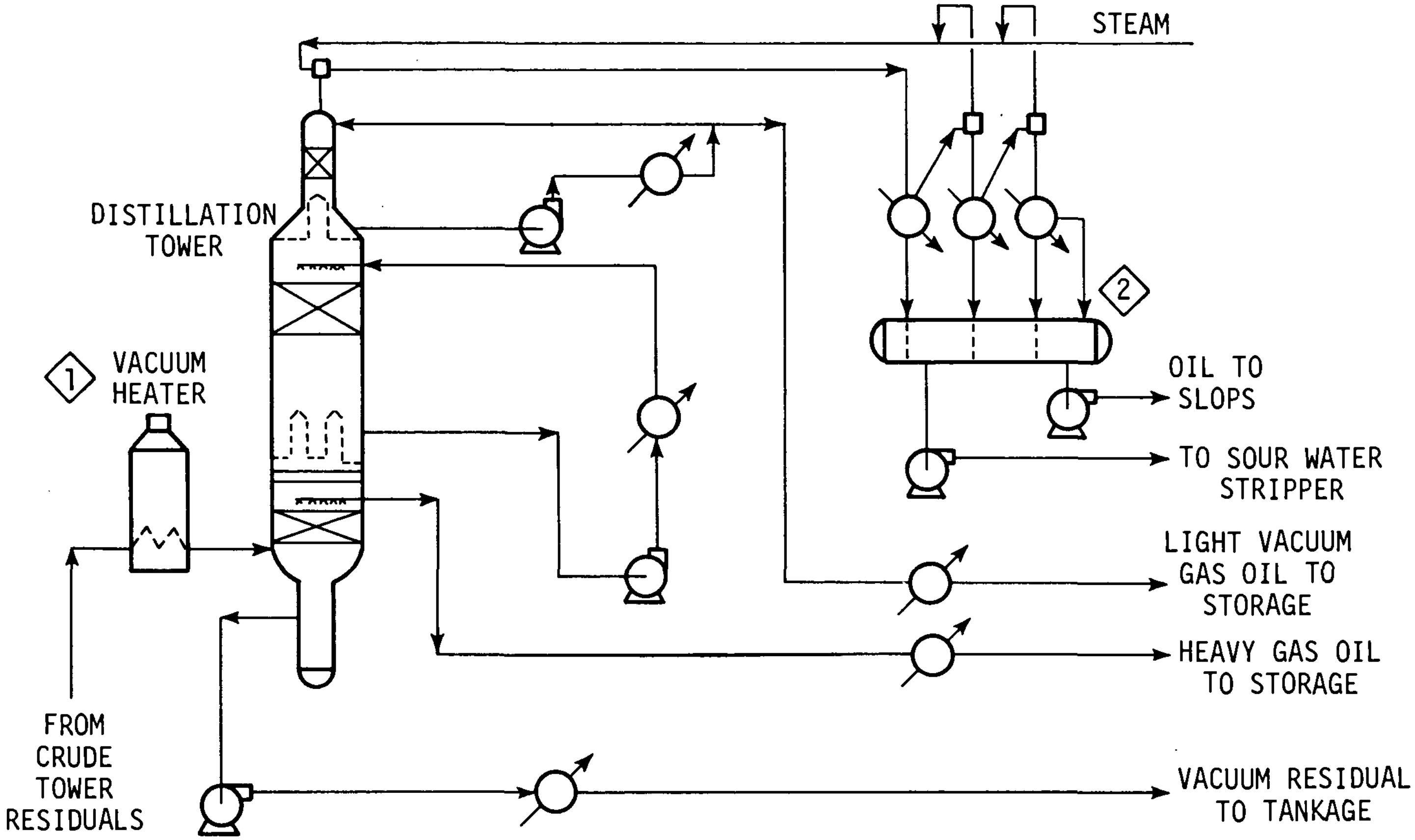


Figure 4.1-2. Vacuum distillation unit.

The desired operating pressure is maintained by the use of steam ejectors (Figure 4.1-2) and barometric or surface condensers. The size and number of ejectors and condensers are determined by the vacuum needed and quantity of vapors handled. For a tower operating at 3.3 kPa (25 mm Hg absolute), three ejector stages are usually required. The first stage condenses the steam and compresses the noncondensable overhead gases. The overhead gas and steam are cooled in an intercondenser. A steam nozzle discharges a jet of high-velocity steam across a suction chamber that is connected to the tower. The exiting steam and any entrained vapors are condensed by direct water quench in a barometric condenser or a surface (shell and tube) condenser. The second stage removes the noncondensable gases from the condenser. The steam and noncondensable gas are cooled in the second intercondenser. The third stage removes the noncondensable gases from the second intercondenser. The gas and steam are cooled in an aftercondenser. The noncondensed gas is vented to a heater, the refinery fuel gas system, or the atmosphere. The condensers may be barometric (contact) or surface (shell and tube). The condensed gas and steam flow to an accumulator, where the phases are separated. The hydrocarbon liquid is sent to a slop oil tank. The water phase is sent to a sour water stripper for purification.

Where contact condensers are used, the steam and overhead gas are mixed with the cooling water. These hydrocarbon vapors may be emitted to the atmosphere, posing an air pollution problem.

### 4.1.2 Emission Sources

The heaters in the crude distillation unit (Figure 4.1-1, point 1) and the vacuum unit (Figure 4.1-2, point 1) are potential sources of sulfur dioxide and particulate emissions.

The overhead accumulator vent in both the crude distillation unit (Figure 4.1-1, point 2) and the vacuum unit (Figure 4.1-2, point 2) are potential sources of hydrogen sulfide and hydrocarbon emissions.

In vacuum units using barometric condensers, the oily condensate produces evaporative emissions of hydrocarbons from the hot well (sump) to which it is discharged.

The study by the California Air Resources Board found that the distillation units contributed 1.2 percent of all the fugitive emissions from the refinery. Of the devices tested in distillation units, 22 percent of the pump seals leaked and 1.2 percent of the valves leaked. Fractionation units in general, however, were found to contribute 5.4 percent of the total refinery fugitive emissions. Of the devices tested in fractionation units, leakage occurred in 32 percent of the pump seals, 50 percent of the compressor seals, 12 percent of the valve outlets, 12 percent of the threaded fittings, and 11 percent of the valves.

### 4.1.3 Emission Controls

The gas or oils fired by process heaters are fairly clean fuels. Particulates can generally be controlled by proper operating practices and adjustments of the air-to-fuel ratio.

The fuel gas stream from the overhead accumulator vent contains hydrogen sulfide, which is removed in the amine unit and eventually converted into elemental sulfur in the sulfur plant.

The wastewater from the overhead accumulator on the atmospheric distillation unit contains hydrocarbons and may emit volatile organic compounds if it flows in open ditches. The use of closed piping prevents the emissions.

The noncondensable emissions from steam ejectors are controlled by venting into blowdown systems or fuel gas systems and incineration in furnaces, waste heat boilers, or incinerators. Vapor recovery units return condensable hydrocarbon vapors to process streams. Incineration is accomplished by catalytic or direct flame combustion. These controls reduce the hydrocarbon emissions from this source to negligible amounts.

Emissions of vapors from the hot wells associated with barometric condensers can be controlled by covers and incineration. Emissions of oily condensate can be eliminated by mechanical vacuum pumps or surface condensers that discharge to a closed drainage system.

Noncondensables and oily condensate and their emissions can be minimized by installing a lean-oil absorption unit between the vacuum tower and the first-stage vacuum jet. The rich oil effluent is used as charge stock and is not regenerated.

Steam ejectors with surface condensers form a closed system and need no further controls.

### 4.1.4 Instrumentation

Process control in a petroleum refinery is automatic. Most refineries use trend analyzing instruments to monitor changes in process parameters. Three parameters are monitored for the towers in a distillation unit: feed rate, feed temperature, and overhead temperature.

A rise in the feed temperature is detected and the heat input reduced before an upset can occur. Automatic control of the heaters can, in this case, result in emissions caused by an improper air-to-fuel ratio. When the feed rate is increased, so is the demand on the heater; greater fuel usage then results in higher sulfur or particulate emissions. When the overhead temperature increases, cracking is occurring in the tower and more vapors are exiting overhead. As the vapors increase in quantity, the accumulator may be unable to separate the phases, allowing the vapor to become trapped in the liquid. The vapor would then enter the wastewater and be emitted as volatile organic compounds at the treatment facility. A high feed temperature can also create this problem.

### 4.1.5 Startup/Shutdown/Malfunctions

Startups and shutdowns are potentially troublesome and hazardous. Plant operators are usually especially alert and cautious during these periods.

The major steps in unit startup are as follows:

Preliminary preparations
Elimination of air
Tightness testing
Disposal of purge material
Elimination of water
Operation of the unit on stream

Hydrocarbon gas can be used to remove the purge gas (steam or nitrogen) from the unit. Presumably, this gas is removed from the column by normal operating methods. If the gas is vented, that procedure could be a source of emissions. Refluxing with liquid products can be used in startup and shutdown procedures to facilitate transition into regular operation with a minimum of process upsets.

The major steps in unit shutdown are as follows:

Furnace drying
Oil wash
Vapor purging
Steam purging
Water washing

These steps overlap in the shutdown operation. Oil wash begins as the sidestream draws are closed off and before the feed is removed; coil outlet temperatures are also cut at this time. The feed is then removed by continuous overhead reflux to the tower. The oil is pumped from all levels of the tower as it accumulates. The system is then steamed and water washed.

The furnace-drying period is about 4 hours. Steam is introduced into the furnace and exhausted into the closed tower. All steam is then removed from the furnace, isolated from the tower, and allowed to cool.

The oil vapors are purged through the vapor recovery system until the final stage, when unit safety valves are bypassed and the vapor is steamed directly to the unit flare. At this time all auxiliary equipment is steaming out to rundown tankage.

The steam-cooling period begins after the oil washing is complete and about 2 hours before furnace drying is to begin; the operation takes about 10 hours. A high volume of live steam is introduced into the tower bottom and sidestreams. It is initially removed through the flare systems; after the vapor-purging period, the system is opened to the atmosphere.

The water washing begins at the conclusion of the steam-cooling period. Water is introduced into the top of the tower at a gradually increasing flow rate. When the washing is complete, the unit is cooled, depressurized, purged, and prepared for workers to enter.

### 4.1.6 References

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5. Holland, C. D., and P. T. Eubank. Solve More Distillation Problems. Part 2. Hydrocarbon Processing, 53(11): 176, 1974.

6. Kern, R. Layout Arrangements for Distillation Columns. Chemical Engineering, August 15, 1977. pp. 153-160.

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9. Yaws, C. L., et al. Estimate Multicomponent Recovery. Hydrocarbon Processing, February 1979. pp. 99-100.

## 4.2 CATALYTIC CRACKING[1,2]

Catalytic cracking is one of the decomposition processes briefly discussed in Section 2. In the reactor of a catalytic cracking unit, gas oil (heavy distillate) carbon chains are broken down in the presence of heat and a catalyst. The reaction products are hydrocarbons of lighter weight and a lower boiling temperature. The catalytic cracking unit is used to upgrade the heavy distillates to lighter, more useful distillates such as gasoline, kerosene, and heating fuels.

### 4.2.1 Process Description

The catalyst in a catalytic cracking process is handled by one of four methods: fluidized bed, moving bed, fixed bed, and once-through operation. Fluidized-bed processes are predominant but some moving-bed units are still in operation. Moving-bed processes include Thermofor catalytic cracking (TCC) using bucket elevators or air-lift processes, and the Houdriflow air-lift process. Fixed-bed and once-through catalytic crackers are not in general use today.

#### Fluidized-Bed Catalytic Cracking Unit

Several proprietary fluidized-bed catalytic cracking processes are available from engineering construction companies and oil refining research and development groups. The process may be called Flexicracking, fluid catalytic cracking (FCC), Orthoflow, or UltraCat Cracking; the difference between them is subtle. The following description (and subsequent sections) refers to a FCC unit, but the principles of operation apply to any of the fluid processes mentioned above.

As product needs change, different catalysts--low alumina, high alumina, kaolin, clay, and zeolite--have been used in FCC processes. These and molecular sieves are currently being used.

Figures 4.2-1 through 4.2-3 illustrate various aspects of the FCC unit. Figure 4.2-1 shows the reactor/regenerator portion of the process and the flue gas control devices. Figure 4.2-2

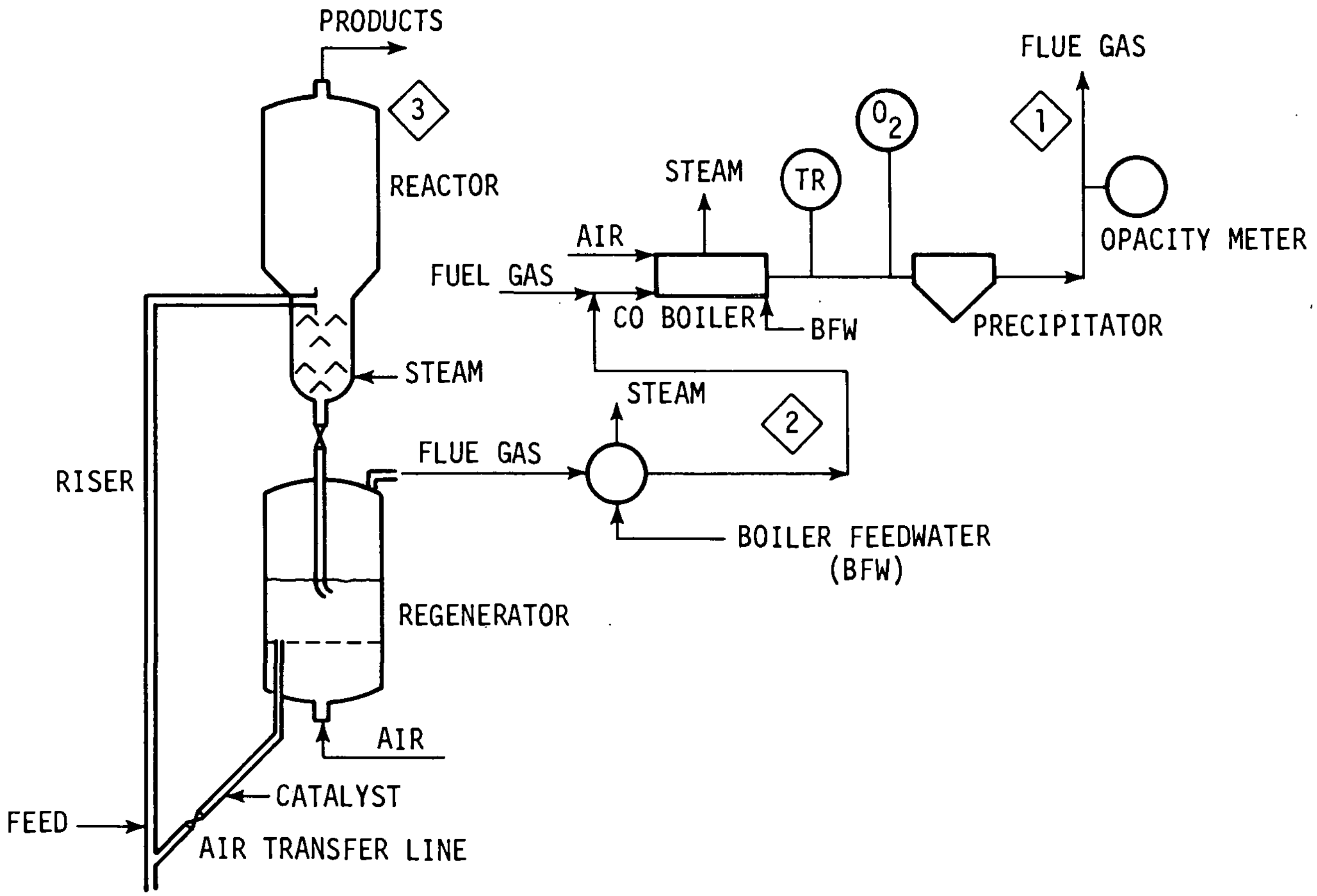

Figure 4.2-1. Reactor/regenerator portion of a fluid catalytic cracking unit.

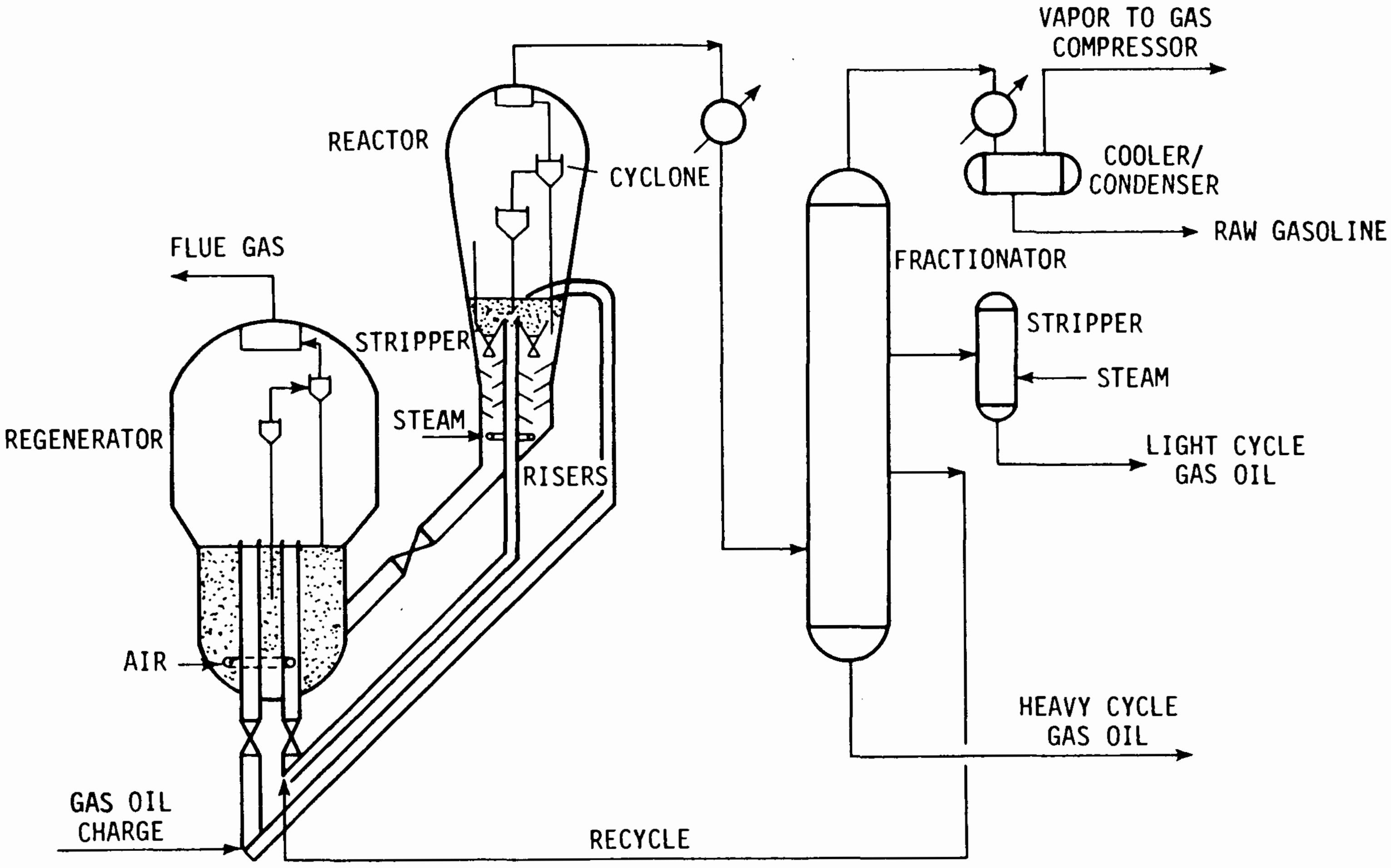

Figure 4.2-2. Fractionator portion of a fluid catalytic cracking unit with two risers.

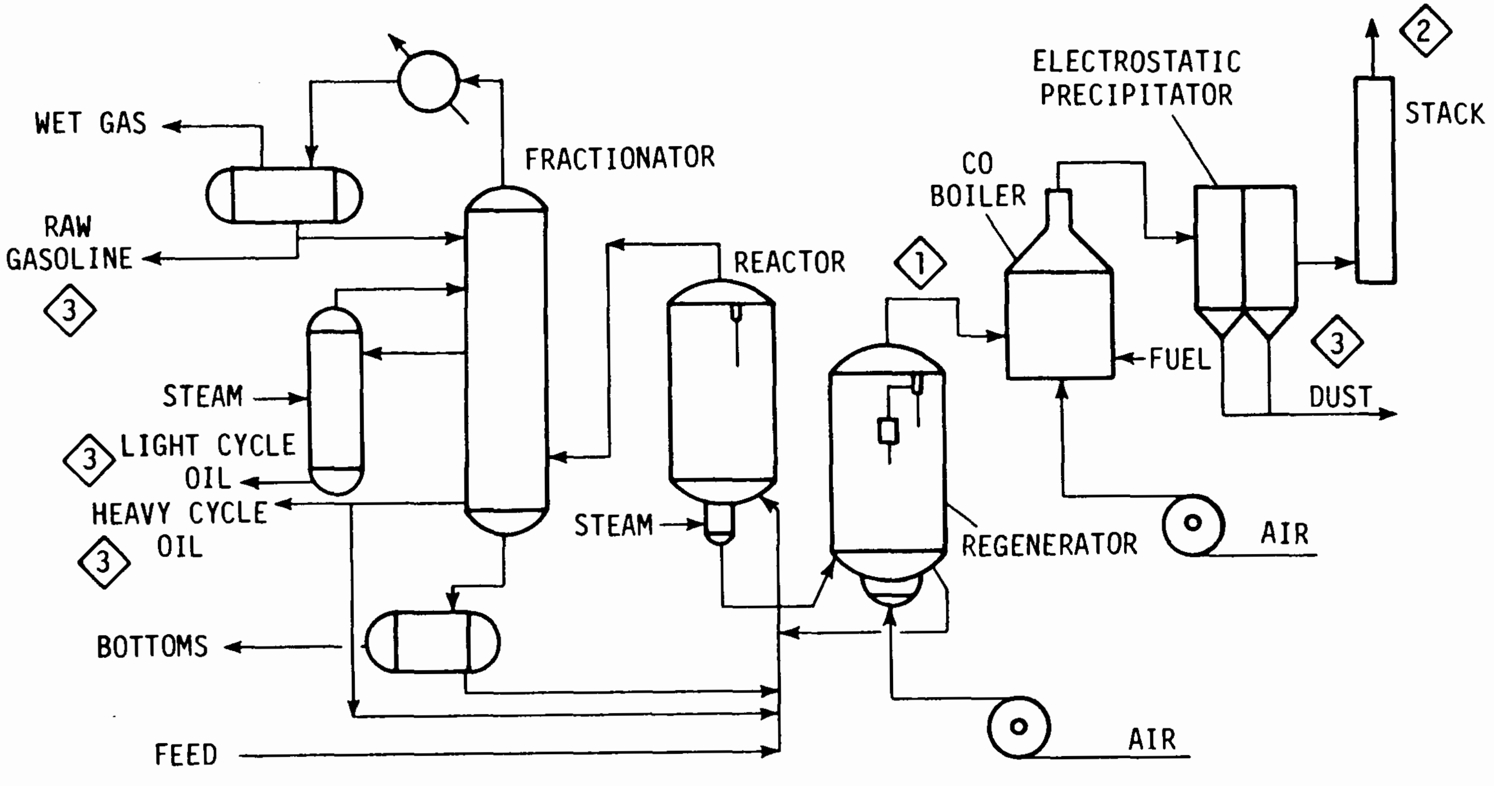

Figure 4.2-3. Overview of fluid catalytic cracking unit.

shows the fractionator portion of an FCC unit having two risers. Figure 4.2-3 is an overview of the FCC process that also shows the points of emission.

The liquid gas oil feed in an FCC unit is preheated by exchange with the outgoing product. The feed then comes into contact with hot catalyst in a vertical tube leading to the reactor vessel (Figure 4.2-1). The gas oil vaporizes at this point of initial contact. A second vertical tube may be present to carry the recycle feed stream (Figure 4.2-2). These tubes are referred to as the riser sections because the gas oil vapors rise and carry the catalyst with them. The rising catalyst behaves as a fluid, giving the process its name.

The gas oil vapors undergo cracking reactions in the risers and some reaction products are deposited on the catalyst. The mixture of catalyst and products flows from the risers to the reaction vessel. As the mixture enters, steam is injected to strip the products from the catalyst. The products rise as vapors through the reactor vessel and are discharged through cyclones, where fine catalyst particles are removed (Figure 4.2-2). The vapors are then passed through a condenser and routed to a fractionator (also known as a distillation or stabilization column) for separation. The noncondensables or light gases flow from the top of the fractionator to the gas recovery system. Other cuts from the fractionator may include alkylation unit feed, light cycle oil, heavy cycle oil, and slurry oil. Gasoline is recovered from the cooler-condenser. The heavier liquid products separated in the fractionator may be recycled to the FCC reactor or further processed in another unit (such as the coker or asphalt plant).

As with any catalytic process, the catalyst in an FCC unit loses activity (effectiveness in changing the rate of a specific reaction) with use. After steam stripping, coke (carbon) and some metals remain deposited on the catalyst. The results of these deposits are pore shrinkage and a loss of available catalytic surface area. The used (spent) catalyst is thus routed from the reactor to a regenerator where the catalyst is partially restored by burning the coke off in a controlled combustion reaction. The air injected into the vessel for the combustion reaction also serves to fluidize the catalyst.

Combustion gases from the regenerator are cleaned and passed through cyclones for recovery of catalyst. The regenerated catalyst flows down a transfer line for reuse (Figure 4.2-1).

## Moving-Bed Catalytic Cracking Unit

Moving-bed catalytic cracking units use heat and pellet catalysts to crack the heavy distillate oils and form more useful products. Unlike the powdered catalyst sometimes used in fluidized-bed units, beads or pellets are easy to handle and do not cause plugging. Synthetic silica-alumina compositions, including acid-treated bentonite clay, fuller's earth, aluminum hydrosilicates, and bauxite, are often used as catalyst. Natural catalysts are softer, have lower activity and selectivity, and higher losses due to attrition than synthetic catalysts. Therefore natural catalysts are less desirable than synthetic catalysts.

As in an FCC unit, carbon is the main material deposited on the catalyst in a TCC or Houdriflow unit. The carbon deposits are burned off the catalyst under controlled temperature and air rates in a regeneration kiln.

A moving-bed catalytic cracking unit consists of a combination reactor-kiln vessel, a catalyst lift, a catalyst elutriator, a catalyst fines separator, and an air heater that is used only for startup (See Figure 4.2-4). A hot catalyst storage vessel usually acts as a support for the catalyst lift and the catalyst elutriator. A fresh catalyst storage vessel is located just above the cracking reactor.

Charge stocks are fed into the moving-bed cracking unit near the top of the reactor vessel through a specially designed nozzle. The charge stocks may enter as liquid, vapor, or a mixture of liquid and vapor. The physical state of the charge stock depends on the design requirements of the cracking unit and the

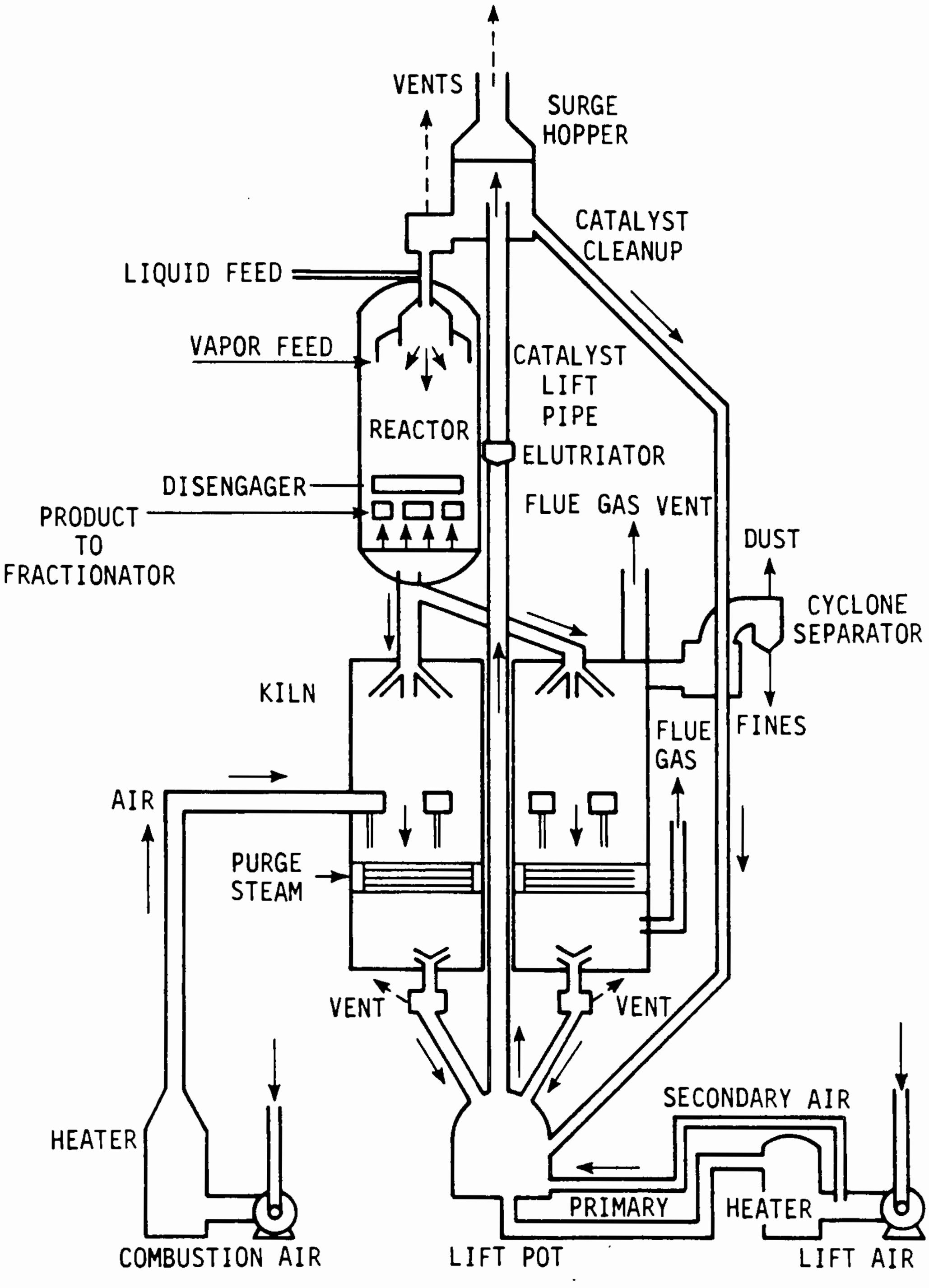

Figure 4.2-4. Moving-bed (airlift) catalytic cracking unit.

composition of the heavy distillate feed streams. The entry nozzle directs the flow of the charge stock so that it is uniformly distributed on the hot catalyst, which is being continuously fed into the reactor from the top of the vessel (Figure 4.2-4). Partial cracking occurs when the charge stock comes into contact with the catalyst, along with almost immediate vaporization of liquid feed. The cracked and uncracked vapors remain mixed as they flow down through the solid bed of catalyst, which itself is moving downward through the reactor and into the kiln. Before reaching the bottom of the reactor, the catalyst and vapors are separated in a disengager. The vapors are collected in a chamber outside the reactor shell and sent to a fractionator.

The catalyst that flows from the disengager has residual oils remaining on it, which are vaporized and purged by the injection of steam at low pressure. The steam and purged hydrocarbon vapors are collected and routed to a fractionator.

After leaving the purge zone, the catalyst continues its downward flow through a group of pipes and into the kiln. Steam is injected with the catalyst into the pipes to reduce the pressure to about atmospheric at the entry to the kiln. In the top zone of the kiln, the downward moving catalyst is met with a countercurrent flow of air from the air inlet channels (Figure 4.2-4). The resulting combustion reactions burn some of the coke deposits from the catalyst. More coke deposits are removed in the cooling zone and the bottom zone of the kiln. The excess heat produced in the combustion reactions is removed by heat exchange with internal cooling coils. About 70 percent of the gases exit through the flue gas vent at the top of the kiln. This flue gas is channeled through a fume burner for removal of remaining hydrocarbons. The other 30 percent is entrained in catalyst, from which it is separated at the bottom of the kiln. The catalyst is then sent to a catalyst cooler and on to the lift pot. The flue gas is vented to the atmosphere or to a control device.

Flue gas and steam are used to lift the regenerated catalyst from the lift pot up through the lift pipe to the surge hopper above the reactor. A lift disengager is located at the top of the lift pipe to separate the catalyst from the lift gas (Figure 4.2-5). The catalyst is transferred through a line to the top of the reactor. Gravity pulls the catalyst down through the reactor, and the cycle continues.

The fresh catalyst storage hopper is located between the surge hopper and the reactor.

### 4.2.2 Emission Sources

The major source of emissions from both fluidized-bed units and moving-bed units is the regenerator flue gas stream. Carbon monoxide (CO), at an uncontrolled emission rate of approximately 10.8 $kg/m^3$ of fresh feed, is a major contaminant in the stream. This stream is generally routed to a CO boiler, whereupon the stack from the boiler becomes the emission point (Figures 4.2-1, 4.2-3, and 4.2-5, point 1). It must be noted that CO is not a major pollution source from some new fluid catalytic crackers that use improved catalyst and high-temperature regeneration. In these cases, the catalyst is regenerated at a high temperature--over 732°C (1350°F)--and the carbon monoxide is burned in the regenerator instead of being emitted to the atmosphere.

Particulates are another major pollutant from catalytic crackers. Those particulates not collected in control devices (e.g., cyclones, electrostatic precipitators) are emitted to the atmosphere from the CO boiler stack or the regenerator. The uncontrolled particulate emission rate is usually much higher for fluidized-bed units than for moving-bed units.

The sulfur compounds in the feed to catalytic crackers cause sulfur oxide emissions. When the catalyst becomes coated with carbon it is regenerated to restore its activity. The carbon coating contains sulfur compounds and metals. During regeneration, combustion converts the carbon to gaseous form and the

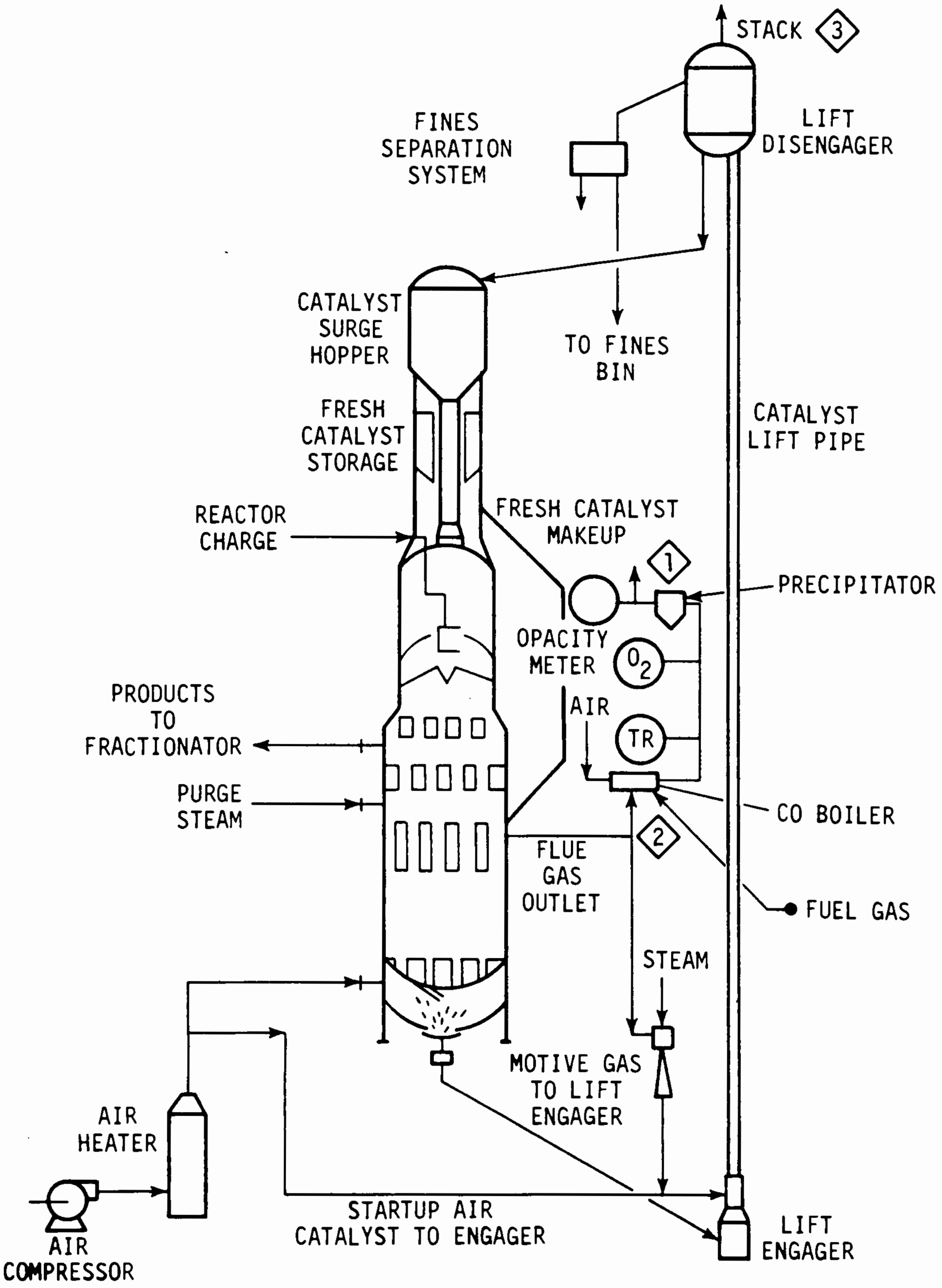

Figure 4.2-5. Points of emission from moving-bed catalytic cracking unit.

sulfur compounds to sulfur oxide. The sulfur and metals are emitted to the atmosphere.

Amoco has developed a new catalyst for fluid catalytic crackers that lessens the sulfur oxide emission rate from the regenerator. The catalyst retains the sulfur until it is returned to the reactor, where it is reacted with hydrogen to form hydrogen sulfide ($H_2S$). The $H_2S$ leaves the reactor with the cracked product and is later converted to sulfur in the Claus plant.

Other emissions from the CO boiler stack are any uncombusted aldehydes, ammonia, hydrocarbons, and contaminants in the regenerator flue gas that were not combusted in the CO boiler. These contaminants are oxides of nitrogen, sulfur dioxide, and sulfur trioxide. In the absence of a CO boiler and high temperature regeneration, all of these flue gas contaminants are emitted to the atmosphere. The stack would be at point 2 on Figures 4.2-2, 4.2-3, and 4.2-5. The composition of contaminants depends on the feed and operating conditions of the unit.

If an external cyclone or an electrostatic precipitator is used in either a fluidized-bed unit or a moving-bed unit, catalyst fines can result in significant particulate emissions as the fines are transferred from the bases of the cyclones and the ESP hoppers (Figure 4.2-3, point 3).

Hydrocarbons may also be emitted from leaking valves, flanges, and pump and compressor seals on fluidized-bed or moving-bed units.

Moving-bed units may emit particulates from the disengaging drum of the catalyst transfer system (Figure 4.2-5, point 3). Fluidized-bed units continuously lose particulates to the atmosphere from the reactor product vent (Figure 4.2-1, point 3).

## 4.2.3 Emission Controls

### Cyclones

The regenerator off-gas (flue gas) contains a substantial amount of particulates in the form of catalyst fines. A multicyclone (also known as a swirl-vane dry classifier) is often used as the primary particulate removal device. It can remove particulates having a diameter of 40 microns or greater. The flue gases are forced tangentially into a cylindrical vessel, where strong centrifugal force separates out the large particles. The gases spiral upward and out of the first cyclone, and may enter a second cyclone for finer separation. These cyclones are usually internal (located inside the regenerator housing); they are important as catalyst recovery equipment. In some refineries, external cyclones (located outside of the regenerator housing) are also used after the CO boiler for additional particulate control. The base of an external cyclone, which is usually tapered for collection of the catalyst fines, is periodically opened for removal of the fines into disposal hoppers. Internal cyclone efficiency is improved with an external separation device.

### Carbon Monoxide Boiler

Regenerator flue gas from the internal cyclone system (Figure 4.2-1, point 2) also contains a significant amount of CO and other contaminants. The CO is generally burned in a CO boiler to prevent its escape to the atmosphere. This control unit operates the same way as an ordinary process unit boiler. Some additional fuel gas and air must be provided for combustion, as indicated on Figure 4.2-1. Other contaminants in the regenerator flue gas (aldehydes, ammonia, and hydrocarbons) can also be controlled by combustion in a CO boiler. The boiler is beneficial to the refiner because it controls emissions of CO and other contaminants and converts energy, that would otherwise be lost, to steam.

### Electrostatic Precipitator

The flue gas from the CO boiler contains particulates formed in the boiler during combustion, as well as fine (less than 40 microns) residual catalyst particulates. In fluidized-bed units, an electrostatic precipitator generally follows the CO boiler, although a third-stage cyclone or water scrubber may be used instead. In a moving-bed unit, an ESP and an additional particulate control device may be used if the emission level is severe enough to warrant control.

In the ESP, very fine particulates are charged by high-voltage, direct current coronas. Large, plate-like electrodes are used for collection of the charged particles. They are periodically removed from the electrodes by rapping or washing. An internal cyclone and ESP system achieve about 99 percent efficiency.

### High-Temperature Regeneration

High-temperature regeneration is an alternative to the CO boiler as a control technique for CO emissions from fluidized-bed units. New catalysts and regenerator designs accelerate the conversion of CO to $CO_2$, thereby reducing CO emissions. The heat liberated in the conversion is used in the regenerator to increase the efficiency of the catalytic cracker. The higher temperature in the catalyst bed gives the process its name, high-temperature regeneration. The increase in temperature over a conventional regeneration system is about 78°C (140°F). Cyclone temperatures have a small increase of about 17°C (30°F). The flue gas from a high-temperature regenerator contains about 0.4 percent CO by weight, as compared with an uncontrolled CO content of about 9.3 percent from a standard regenerator system.

### Catalyst Attrition Control Techniques

In a TCC unit, particulate emissions are controlled by preventing the attrition of catalyst. Factors important in minimizing catalyst attrition include design, maintenance and operation of the unit, and characteristics of the catalyst itself. The following procedures will minimize particulate emissions:

> Among components of the lift system, the feed pot, tapered lift pipe, and disengagement system in the separator should be designed for minimum catalyst attrition. When flow rates are greater than design, problems with these components will increase particulate emissions.
>
> Good maintenance is an essential control technique. High attrition rates can be caused by such malfunctions as misaligned or worn lift pipe components, partially blocked catalyst passages, or worn disengaging system components.
>
> Variations in the lift air rate, which are caused by ambient temperature changes, must be corrected promptly.
>
> The elutriator should be operated to prevent an increase in emissions from the accumulation of fines in the catalyst inventory.
>
> Proper use of the shaveoff system will reduce fines in the lift air.
>
> Catalyst treatment techniques minimize attrition and reduce erosion of critical system components whose failure could cause abnormal attrition.

## 4.2.4 Instrumentation

### Fluidized-Bed Catalytic Cracking Unit

The inspector in the control room (board room) for the fluidized-bed unit monitors temperature, pressure, and space velocity gauges. The temperature of the catalyst (as it comes in contact with the feed) ranges from 520°C to 550°C (960° to 1020°F). The reactor temperature ranges from 450°C to 550°C (850° to 1020°F). The temperature of the flue gas from the regenerator is between 540° and 650°C (1000° and 1200°F). A heat exchanger is applied at this point to produce steam from boiler feedwater. The gauge pressure of the reactor vessel, risers, and regenerator varies depending on the configuration of the unit. A fluidized-bed reactor typically operates at low positive pressure, such as 170 to 450 kPa (10 to 50 psig). Space velocity varies with a number of operating parameters; therefore, the range must be obtained from the unit operator.

The inspector must know the appropriate conversion factors before he records data from the instruments in the board room. Instruments may have been altered to protect trade secrets or to add convenience to data recording. Pressure is usually read in pounds per square inch gauge, but a factor of 10 may need to applied to convert the gauge reading to the actual pressure. Temperature is recorded in degrees Fahrenheit. Refiners have not adopted the metric system. It is particularly important that a conversion factor be known for flow rates.

A temperature reading well above the normal reactor temperature means that cracking is occurring. As a result, large quantities of coke (carbon) are being deposited on the catalyst. The inspector may see more particulates coming out of the CO boiler and the ESP or scrubber. Opacity could reach levels that do not comply with air pollution regulations if the control equipment is not designed to handle this larger particulate load.

A low temperature usually means that the desired reaction is not complete. The refiner will be worried about the quality of his product, but the pollution control equipment will not be affected.

Instead of feed rate, a recorder reports the space velocity of feed in the riser of a fluid catalytic cracking unit. Space velocity is defined as the ratio of the volume of inlet material (at standard conditions and per unit of time) to the volume of the retention space. Knowing the volume of retention space gives the inspector the feed rate to the unit. A high or low feed rate may result in excessive coking of the catalyst unless the operating temperature or pressure is adjusted. Excessive coking may produce a noncompliant opacity level because of particulate emissions. The inspector should ask for the feed rate to the unit when entering the control room.

Several readings are important for observing the status of ESP's. The control room reports the primary and secondary current and the primary voltage. The primary voltage should be compared with the design value. A number less than design may mean the system is overloaded and could short out soon. A low (around zero) primary current value usually means that the system has shorted out, probably because of a broken discharge wire. Constant fluctuation in the secondary current reading means a short is in progress. The hopper heaters should be on. The hopper level should not be full.

The opacity recorder for the CO boiler stack is also usually located in the control room; the opacity monitor is located in the CO boiler stack. The instrument may be an optical transmissometer or an optical density meter that converts its readings to opacity. Readings from the meter are usually in percentage of opacity. Sometimes they are in percentage of transmittance, which can be converted to percentage of opacity by subtracting from 100.

Figure 4.2-1 also shows regulators labeled "TR" and "$O_2$," which refer to temperature recorders and oxygen analyzers. The temperature of the gas entering the ESP must be regulated for proper operation. A high temperature can melt electrodes or cause heat damage to the sensitive ESP equipment. The oxygen analyzer is a control device that monitors the extent of combustion in the CO boiler. A low percentage of oxygen indicates that some CO could be leaving the stack. A high percentage of oxygen indicates no emission problems.

## Moving-Bed Catalytic Cracking Unit

The operating conditions of a moving-bed catalytic cracking unit are about the same as those of a fluidized-bed unit. The reactor temperature ranges from 475° to 550°C (890° to 1022°F), with a pressure of 170 to 310 kPa (10 to 30 psig). Regenerator temperature ranges from 675° to 760°C (1250° to 1400°F) with a pressure of 205 to 345 kPa (15 to 35 psig). These temperatures and pressures should be noted by the inspector. The feed rate and catalyst temperature should also be noted.

Conversion factors should be obtained when recording data from instruments in the board room. The instruments are often set to read an altered version of the true value.

The preceding discussion of instrumentation for fluidized-bed units describes the problems indicated by extreme temperature, pressure, or flow rate readings. That discussion applies to moving-bed units as well. The information about CO boilers and control device also applies to the moving-bed units.

### 4.2.5 Startup/Shutdown/Malfunctions

An FCC or moving-bed unit emits excessive particulates during startup because of the loading of catalyst into the system. The CO boiler that is generally associated with catalytic crackers does not operate efficiently until the proper conditions are achieved. As a result, CO emission rates are high during startup. Emission rates of the other regenerator flue gas contaminants are also high.

Startup is defined as the time required for line out (return to normal) and attainment of compliance with pollution regulations. The typical startup time for an FCC or moving-bed unit is 1 to 7 days. In addition to problems during startup of the cracker the pollution control equipment may also malfunction. For example, startup of an ESP can be delayed up to 3 days if power failure occurs or a discharge wire breaks. Malfunctions and repair times of pollution control equipment are listed in Table 4.2-1.

### 4.2.6 References

1. Refining Process Handbook. Hydrocarbon Processing, September 1978. pp. 109.

Table 4.2-1. TYPICAL TIMES FOR REPAIR OF UNIT MALFUNCTIONS

| Malfunction | Action by company | Repair time |
|---|---|---|
| Hot tube in CO boiler | Bypass boiler; may emit directly to the atmosphere | 2 days |
| Electrical outage | Bypass ESPs | Several hours to days. |
| Electrical short in ESP | Bypass portion of ESP | Several days to months. |
| Excessive reaction temperature | Reduce heat input | Several hours |

2. Nelson, W. L. Petroleum Refinery Engineering. McGraw-Hill Book Company, New York, 1958. pp. 801-808.

# VISCOSITY BREAKING

## 4.3 VISCOSITY BREAKING

Viscosity breaking (or "visbreaking") and coking are the two principal thermal cracking methods used in petroleum refining today. Visbreaking uses milder conditions than either delayed or fluid coking to cause the thermal decomposition of large hydrocarbon molecules. Therefore, less cracking takes place during visbreaking than during coking.

The visbreaking process is primarily used to convert atmospheric distillation bottoms and vacuum distillation bottoms into middle distillates and a stable, heavy fuel oil with a more favorable pour point and lower viscosity than the feed material. If visbreaking were not used, middle distillates would have to be added as blending (cutting) stock to lower the viscosity and pour points. Visbreaking is thus a method for conserving valuable middle distillates.

### 4.3.1 Process Description

The visbreaking process is a once-through operation. The residue (bottoms) is preheated and fed into a tube-still (visbreaker) furnace, where the hydrocarbons in the residue are partially cracked (See Figure 4.3-1). At the same time, coke is formed through polymerization, condensation, dehydrogenation, and dealkylation reactions. The temperature and residence time of the process stream in the furnace are controlled. The operating temperature of a cracking furnace, which is higher than that of other refinery furnaces, is influenced by the type of feed. The tubes in the heater box are heated by radiant heat from burners located near the floor. Coke may be deposited on the hot tube surfaces, especially in liquid phase operations; the surfaces must be cleaned regularly to maintain efficient heat transfer. A convection section at the top of the furnace recovers heat from the combustion gases. This recovered heat is used to generate steam, heat other process streams, or preheat air.

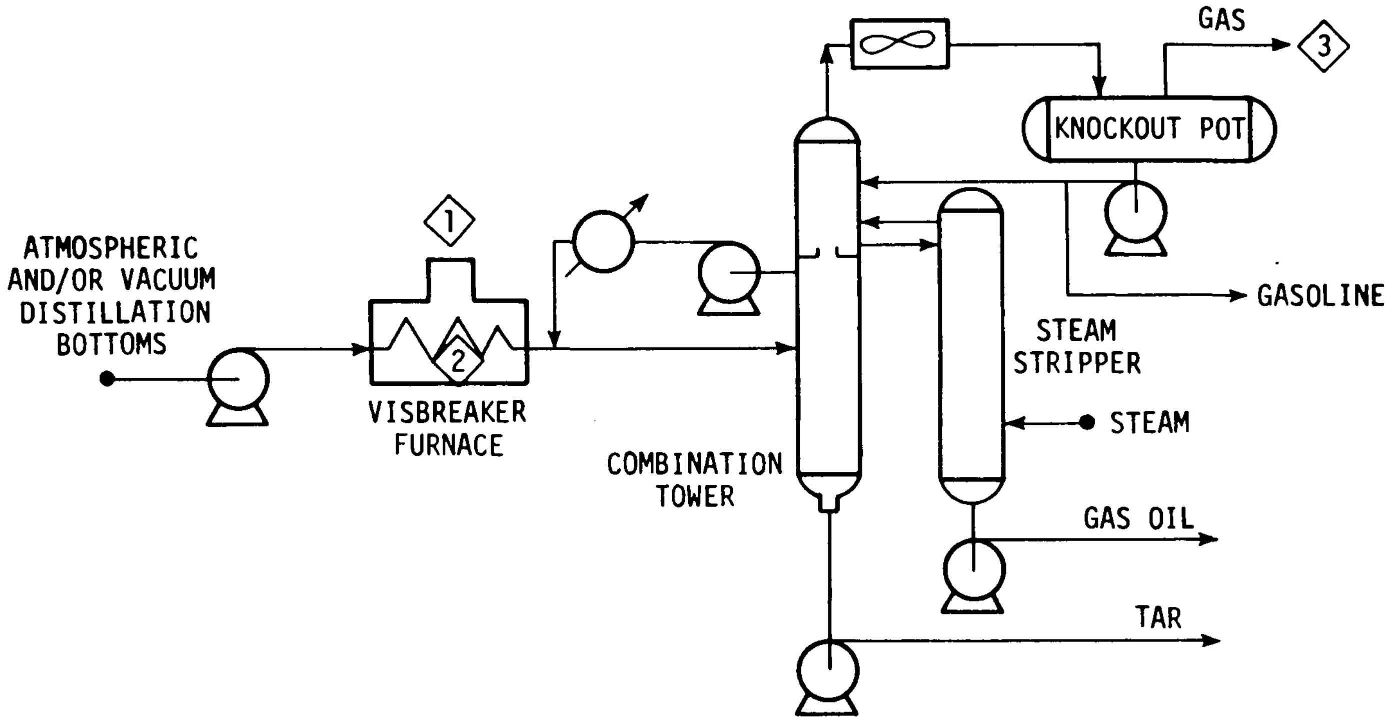

Figure 4.3-1. Visbreaking process.

One constraint on visbreaker operation is the formation of coke deposits because of the high temperature. Another constraint is the stability of the visbreaking product. The stability of the colloidal residue solution is maintained at low percentages of conversion of heavy hydrocarbons to lighter molecules. As conversion continues the solution becomes unstable, and asphaltenes and coke are deposited on storage equipment and other equipment that comes in contact with the residue. At the conversion limit, deposits form on the visbreaking unit itself.

These two constraints are in conflict, because the production of stable residue requires short reaction times at high temperatures. Heat transfer must occur at a high rate, which causes a high rate of coke formation on the heater tubes and a decrease in the heat transfer rate. The severity of visbreaking operation is thus limited either by excess coking or by fuel stability, depending on the feedstock and the design of the unit. When installing a visbreaking unit, a refiner must choose the constraint that is more advantageous for that refinery.

The effluent from the visbreaker furnace may be rapidly cooled (quenched) with a recycle stream of gas oil, or it may proceed to a soaker drum (See Figure 4.3-2). The soaker drum, which is optional, provides an additional chamber for longer residence time and further conversion. It is separate from the furnace, and allows the furnace to operate at slightly lower temperatures than other visbreaking units by providing additional residence time for conversion. Effluent from the soaking drum is quenched.

After quenching, the visbroken mixture must be separated. The stream enters the lower end of a combination tower, where it is flashed (Figure 4.3-1). The visbroken bottoms ("tar") accumulate at the base of the tower, and the flashed vapors are fractionated in the upper section of the tower. These vapors can be fractionated into light ends, gasoline, light gas oil, and heavy gas oil. An alternative design in the fractionating tower separates only light ends and gasoline from the visbreaker bottoms.

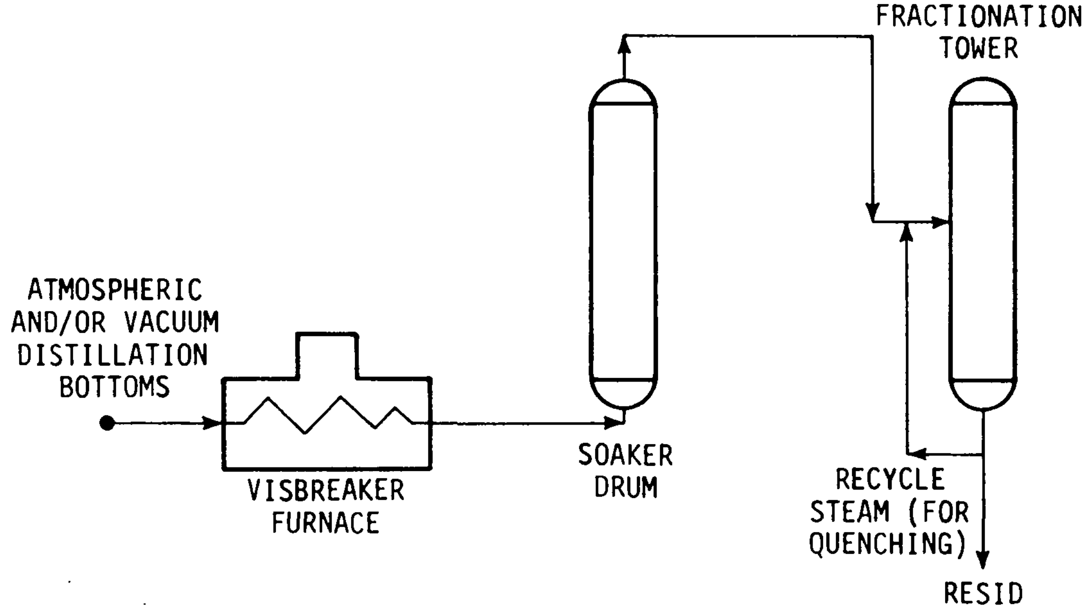

Figure 4.3-2. Visbreaking unit with soaker drum.

This design results in less viscous bottoms, which require a minimum of blending stock to meet viscosity specifications. In a third design, the light ends are flashed off and the remaining mixture routed to a fractionating tower that is operated at a vacuum.

After separation by fractionation, the heavy gas oil fraction is stripped of light ends. The gas oil may then be blended with visbreaker bottoms to meet necessary viscosity, sulfur, and pour-point specifications, or it may be used as feed for the catalytic cracker. The light ends are collected from the fractionator and steam stripper (stabilizer) accumulators and are fed either to a gas recovery plant or to the refinery fuel gas system. Visbreaker bottoms that do not contain or have not been blended with gas oil may be used as feed for the coking unit. The use of visbroken material depends on the demand for various products.

### 4.3.2 Emission Sources

The visbreaker furnace stack is the major source of emissions in a visbreaking unit (Figure 4.3-1, point 1). Particulates, $SO_2$, and $NO_x$ are contained in the furnace exhaust. The amount of each pollutant emitted depends on the type of fuel (fuel oil, natural gas, or refinery fuel gas). For example, gaseous fuels are usually not as significant a source of particulates as fuel oil.

The furnace itself can be a source of emissions during a maintenance shutdown (Figure 4.3-1, point 2). Furnace tubes are generally cleaned with steam-air mixtures. Coke deposits (which contain sulfur and nitrogen) emit particulates, CO, $SO_2$, and $NO_x$ if burned in the furnace.

The light ends collected from the fractionation and stabilization stages of visbreaking may contain some $H_2S$, which is created by a desulfurization side reaction of the thermal cracking process. Therefore, the gas stream from the accumulators is a potential source of $H_2S$ emissions (Figure 4.3-1, point 3).

Fugitive leaks from valves, flanges, pump seals, and compressor seals are sources of hydrocarbon emissions.

### 4.3.3 Emission Controls

Particulates, $SO_2$, and $NO_x$ are not usually emitted from visbreaking units in large enough quantities to warrant the use of control equipment. When coke is deposited on the tube stills, it can be removed mechanically rather than burned. This method avoids the excess air pollution of burning, but it creates an additional solid waste that must be disposed.

The gas stream from the accumulators may be sent to an acid gas treating plant to minimize $H_2S$ emissions. Sour steam condensate may have to be sent to a sour water stripper. Fugitive leaks can be controlled by proper maintenance.

### 4.3.4 Instrumentation

The inspector should note the temperature and pressure of the visbreaker furnace. The usual operating temperature is in the range of 460° to 475°C (860° to 890°F), with pressure normally ranging from 1685 to 1825 kPa (230 to 250 psig); however, this pressure can be as low as 445 kPa (50 psig). The feed rate varies with the size of the unit.

The fractionation tower associated with the unit is run either at pressure greater than 3550 kPa (500 psig) or under vacuum conditions in order to separate the heavy material. The pressure depends on the design of the fractionating system. Level controls in the distillation tower indicate the amount of material on tower plates, and the temperatures along the tower are continuously monitored. The inspector may note the temperatures at various levels to determine whether the fractionator is operating properly (as described in Section 4.1).

Typical stream stripper operating parameters are a temperature of 302°C (575°F) at 2170 kPa (300 psig), using 3.95 kg (8.7 lb) of steam per barrel of feed. The feed rate of gas oil into the stripper varies with the charge to the visbreaking unit.

### 4.3.5 Startup/Shutdown/Malfunctions

The startup period is similar to that of a distillation unit. The startup of the visbreaker furnace should not pose any major problems; however, some hydrocarbons may be emitted. If particulate control equipment or a scrubber is to be used on the unit, emission problems may develop while the control equipment is being brought on line.

Emissions can be significant during unit shutdown (see Subsection 4.3.3). The shutdown procedure for a visbreaking unit would be typical of that for a process unit turnaround. Emission of volatile organics to the atmosphere can be minimized by venting gases from the unit to a flare or fuel gas system for as long as possible. The preferred procedure is to purge the system to the flare with an inert gas before opening vessels to the atmosphere.

Visbreaking units run for an average of 500 days between scheduled maintenance shutdowns. The downtime for a maintenance turnaround averages 2 weeks; for emergency shutdowns (malfunctions), the average downtime per run is 9 days.[1] This average is usually the total for several malfunctions, each with a downtime of a few days. Malfunctions are the same as those for heaters and distillation units.

### 4.3.6 Reference

1. Nelson, W. L., Guide to Refinery Operating Costs. The Petroleum Publishing Company, Tulsa, Oklahoma, 1976. p. 88.

## 4.4 HYDROCRACKING[1,2]

Of the various cracking methods available to refiners today, hydrocracking is the most versatile. Families of catalysts have been developed for specific uses, and processing designs allow for efficient catalyst usage. This process, which combines hydrogenation and catalytic cracking, can be used to upgrade a wide range of feedstocks into lighter, more valuable products. Because hydrogenation is involved, a hydrocracking unit also improves the quality of the material that it processes by desulfurizing and denitrifying it.

Hydrocrackers are used in refineries along the Gulf Coast to produce motor fuels and light oil distillates. One-third of the nation's hydrocracking capacity is located in California, although less than one-seventh of the total refinery production is conducted there. Hydrocrackers are prevalent in California because the State's strict sulfur regulations sharply reduce the marketability of high-sulfur No. 6 fuel oil. The hydrocrackers are used to convert heavy fuel oils into lighter fuels of lower sulfur content, such as motor or jet fuel.

The feed materials for hydrocrackers range from naphtha to deasphalted vacuum residues. Depending on the feed, products range from liquified petroleum gas to lubricating oils. Hydrocracking is especially useful in allowing the production of gasoline or jet fuel to be maximized as needed. Often a refiner will supplement the cracking ability of a fluidized catalytic cracker by adding a hydrocracker unit, to which effluent from the fluid catalytic cracking unit may be used as feed.

Several variations of the hydrocracking process with different catalyst systems are used today, depending on the type and compositions of the charge materials and the desired products. H-G hydrocracking, a Gulf and Air Products process, converts light and heavy gas oils into lower boiling derivatives. Flexicracking, an Exxon process, uses feed material such as vacuum gas oils, catalytic cycle oil, deasphalted oil, and paraffinic raffinates to produce gasoline, naphtha, jet fuels, and midbarrel products. BP Trading Ltd. has a hydrocracking process that converts full-range wax distillates (350° to 550°C; 660° to 1020°F) into gasoline, diesel oils, and chemical feedstocks. Badiche Anilin und Soda-Fabrik AG and Institute Francais du Pétrole processes use heavy sour feedstocks composed of naphthas, middle distillates, virgin gas oil, and deasphalted vacuum residues as charge material. Products from these processes include liquefied petroleum gas (LPG), naphthas for petrochemicals, gasoline, jet fuel, and diesel oil. Chevron's isocracking, Standard Oil's ultracracking, and Union Oil's unicracking are other hydrocracking techniques used in the refining industry.

### 4.4.1 Process Description

The typical hydrocracking process is carried out in one or two stages, depending upon the concentrations of nitrogen and sulfur in the feedstock. Feedstocks having high nitrogen and/or sulfur content are processed in two reactor stages, as are those with high concentrations of unsaturates or aromatics. Conversely, feedstocks with low concentrations of sulfur and nitrogen and high concentrations of saturates are generally hydrocracked in a one-stage unit.

#### Two-Stage Hydrocracking

In a two-stage hydrocracking process (Figure 4.4-1) the first reactor has a hydrogen-rich atmosphere and acts as a hydrodesulfurizer (or hydrotreater, see Section 4.9). It is run at high temperature and pressure. The catalyst bed is fixed, and therefore occasional shutdowns are required for catalyst regeneration. In this reactor, an exothermic reaction causes unsaturates to become saturated and nitrogen and sulfur from the feed to be converted into ammonia ($NH_3$) and hydrogen sulfide ($H_2S$). Partial cracking also occurs in the first reactor.

The catalyst used in hydrocrackers must provide sites for hydrogenation and cracking reactions. The various catalysts currently available differ in degree of acidity, hydrogenation

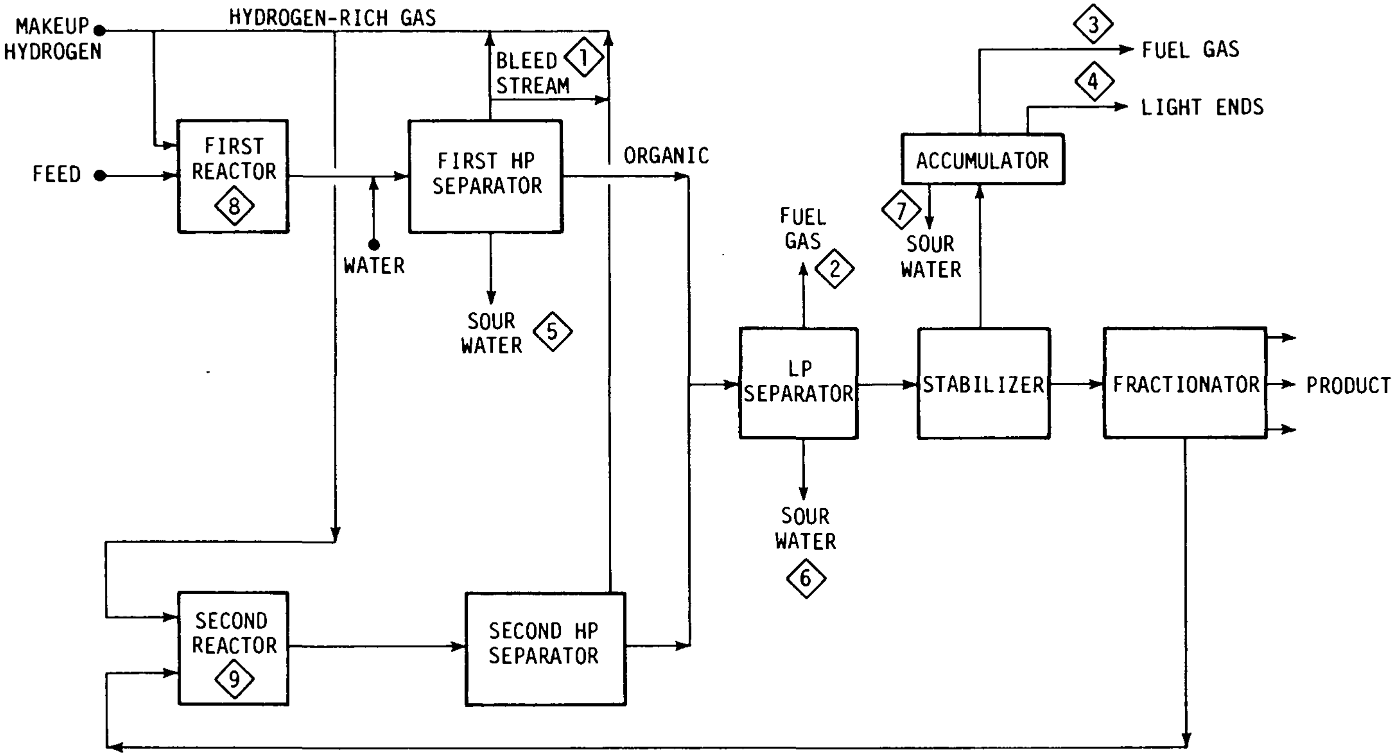

Figure 4.4-1. Two-stage hydrocracking unit.

activity, surface area, and porosity. The type of feed and the products desired dictate the type of catalyst selected.

In many two-stage hydrocrackers, particularly in older units, $NH_3$ and $H_2S$ must be separated from the effluent of the first-stage reactor. If the $NH_3$ and $H_2S$ are not separated from the organic phase, these impurities may poison the catalyst in the second-stage reactor. Newer hydrocrackers use ammonia-resistant catalyst and the separation step is omitted. Instead, $NH_3$ and $H_2S$ impurities are removed during the fractionation process that follows the second-stage reactor.

Where a separation is required between the reactors, effluent from the first-stage reactor is cooled by heat exchange with reactor feed. Water is then added to the product stream so that most of the ammonia is extracted from the organic phase. Then the mixture is sent to a high-pressure separator, which yields a hydrogen-rich gas containing significant amounts of $H_2S$, a hydrocarbon liquid phase containing some $H_2S$ and very little $NH_3$, and a water phase containing most of the $NH_3$ impurities and a small amount of $H_2S$.

The hydrogen-rich gas stream is recycled to the reactors. Makeup hydrogen is fed to the first reactor to replace the hydrogen consumed in the reaction. The hydrocarbon liquid phase contains a mixture of the desired products and unreacted feed; therefore, it is sent to a fractionating tower. The water phase is sent to a sour water stripper or wastewater treatment.

In the fractionating section, the hydrocarbon liquids from the first-stage high-pressure separator are added to the hydrocarbon liquids from a high-pressure separator associated with the second reactor. Together, these liquids are fed to a low-pressure separator. The lower pressure causes more fuel gas to be flashed out of the liquid. The remaining liquid flows to a stabilizer, where more $H_2S$ and light ends are stripped out and taken overhead. The effluent from the stabilizer then flows to the fractionating tower, in which the desired products are separated. The fractionator bottoms are the unreacted feed, which is sent to the second reactor.

In the second reactor, cracking of the organics is completed to extinction by continuously recycling any converted effluent. Makeup hydrogen is also continually fed to the second reactor. The operating conditions of the second reactor are less severe than those of the first reactor.

## One-Stage Hydrocracking

One-stage hydrocracking units crack and hydrogenate the distillate charge in one reactor (see Figure 4.4-2). The charge generally contains less sulfur and nitrogen than the charge to a two-stage hydrocracker, but the catalyst is more sulfur-resistant than catalyst used in the second stage of a two-stage hydrocracker. The reactor generally is the fixed-bed type, with a regenerable catalyst.

Hydrogen is introduced to the feed stream and the mixture is preheated, then fed into the reactor, which is run at high temperatures and pressures. The hydrogen-rich atmosphere allows hydrogenation to take place along with the cracking reactions. The reactions are highly exothermic and should cause the reactor temperature to increase dramatically. Operating temperature can be maintained, however, by injecting cold recycle gas that has been scrubbed for removal of $H_2S$, or cold, fresh hydrogen between the catalyst beds.

The reactor effluent contains a gas phase and a liquid phase. The gas phase is rich in hydrogen and contains $H_2S$; this stream is routed to a sour gas scrubber and then to a recycle gas compressor. The liquid phase contains hydrocarbons and is recovered as the product mixture. This mixture is routed to a fractionator, where it is separated into the desired fractions. Gasoline and middle distillates are the usual products from a one-stage hydrocracker.

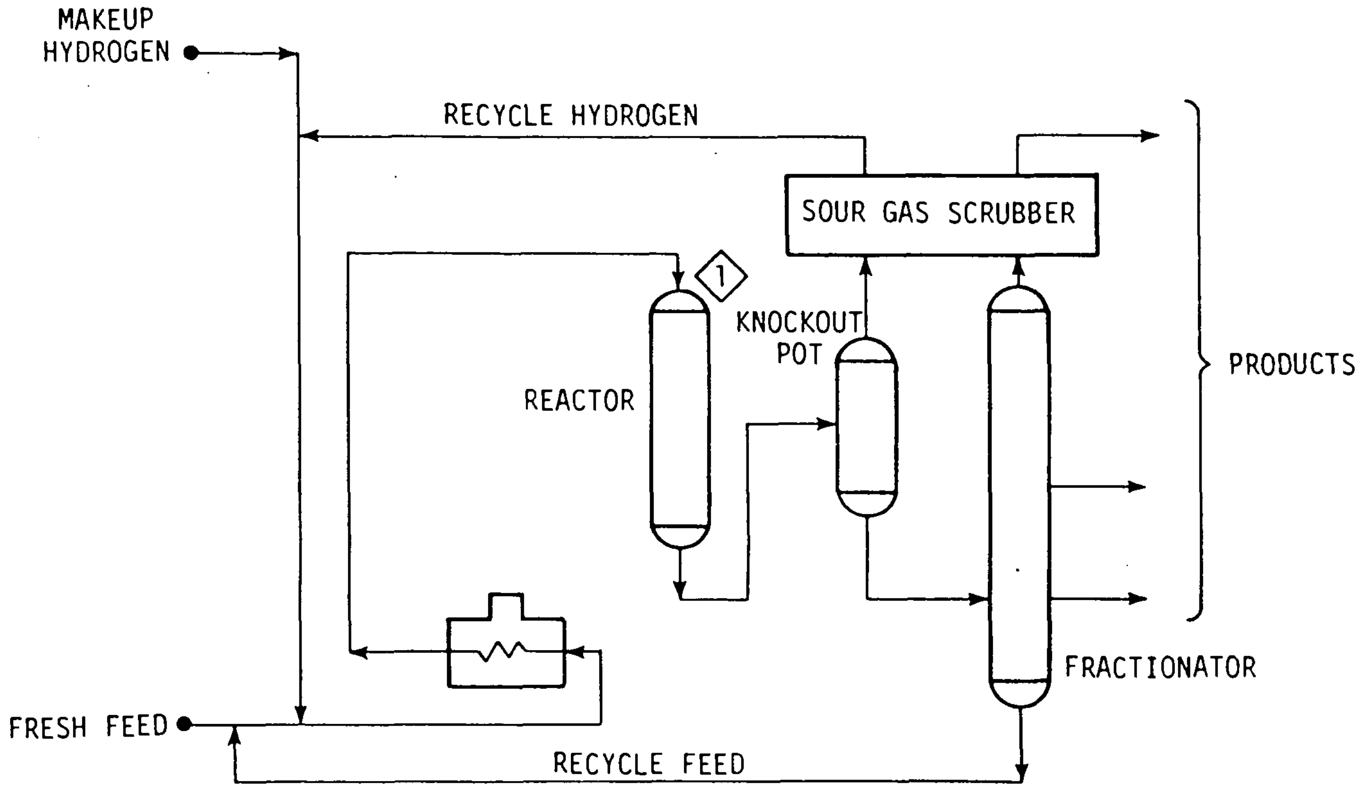

Figure 4.4-2. One-stage hydrocracking unit.

### 4.4.2 Emission Sources

Because the material fed into a two-stage hydrocracking unit generally contains significant amounts of sulfur and/or nitrogen impurities, there is a potential for emission of sulfur and nitrogen compounds. For example, the bleed gas from the hydrogen-rich gas in the first reaction stage of a two-stage unit may contain 0.5 to 1.5 percent by volume of $H_2S$ (Figure 4.4-1, point 1). Light ends and fuel gas produced in the unit also contain some $H_2S$, and these streams must be treated for $H_2S$ removal (Figure 4.4-1, points 2, 3, and 4).

Sour water is a byproduct of the high- and low-pressure separators and the stabilizer accumulator in a two-stage reactor. This sour water, a potential source of $H_2S$ and $NH_3$ emissions (Figure 4.4-1, points 5, 6 and 7), must be treated for removal of these impurities.

Catalyst regeneration is a significant source of carbon monoxide emissions in both one- and two-stage hydrocracking units. The coke that accumulates on the catalyst must be burned off, a process that generates carbon monoxide. (Figure 4.4-1, points 8 and 9; Figure 4.4-2, point 1).

Regeneration may also cause particulate emissions. Use of steam in the catalyst regeneration process results in some contaminated, condensed steam, which becomes another sour water waste stream and thus a potential source of $NH_3$ and $H_2S$ emissions.

Because feedstocks to a one-stage hydrocracking unit are low in sulfur and nitrogen content, the concentrations of $H_2S$ and $NH_3$ in waste streams are low, and these streams are not considered significant sources of emissions.

Common to all units are hydrocarbon emissions from leaks in valves, flanges, threaded fittings, pump seals, and compressor seals. The 1978 study by the California Air Resources Board showed leakage in 2.5 percent of the 2344 sources of fugitive emissions inspected at hydrocracking units. In the survey of entire refineries, the highest percentage of leaking equipment in a single unit was 11.0 percent at the isomerization unit. The lowest percentage of leaks was 1.1 percent at the coking unit.

### 4.4.3 Emission Controls

Sour gas (acid gas) streams (overhead from separators, fuel gas, and light ends) must be treated for the removal of $H_2S$ to prevent $H_2S$ emissions. The $H_2S$ is removed by absorption into an alkaline solution under fairly high pressure.

The solution is then regenerated by heating at low pressure. Among several available sour gas treatment processes, the primary difference is in the alkaline absorbants. Commonly used absorbing media include an aqueous monoethanolamine (MEA) solution, a diethanolamine (DEA) solution, and a potassium carbonate solution (Section 4.14).

Sour water streams from the high- and low-pressure separators and the stabilizer accumulator must be stripped of $H_2S$ and $NH_3$ (Section 4.21.1). Carbon monoxide emissions can be controlled by incineration in a CO boiler (Subsection 4.2.3), but this is generally not needed for a hydrocracking unit because CO emissions occur only during catalyst regeneration.

Hydrocarbon emissions from equipment leaks can be controlled by proper maintenance.

### 4.4.4 Instrumentation

Pressure and temperature are key parameters in this operation. In two-stage hydrocracking, pressures of about 20,684 kPa (3000 psia) and a temperature of 371°C (700°F) must be maintained during the hydrocracking reaction step or first stage. The second-stage (or fractionator bottom hydrocracking reaction) is controlled at 10,342 kPa (1500 psia) and 316°C (600°F). Each reactor is equipped with a temperature and flow recorder and controller. Because the reactions are exothermic, cold hydrogen is injected to control the reactor's temperature. High-pressure water separators that remove sulfur and nitrogen from the hydrocarbons are equipped with level controllers and flow controllers and recorders. Temperature control is unnecessary during the water/oil separation.

Several controls are needed in the distillation phase of hydrocracking. Level and pressure controllers are used for the first fuel gas separation step. The stabilizer section is monitored for temperature, flow, and level. The overheads from the stabilizer go into an accumulator, where the fuel gas exit is pressure-controlled and the light ends are controlled by level. The bottoms from the stabilizer to the fractionator are controlled by level, as are the strippers and accumulator. The fractionator reboiler is controlled by flow and the overhead return by temperature.

### 4.4.5 Startup/Shutdown/Malfunctions

The startup of a hydrocracking unit involves stabilizing the reactors and the fractionator temperatures and pressures. The major sources of emissions during startup are the catalyst bed (particulates) and leaks (hydrocarbons). The $H_2S$ and $NH_3$ generated in the hydrocracking unit may be accidentally emitted to the atmosphere during the startup period if the systems for treatment of sour gas and sour water are inadequate. The length of the startup period is variable.

Periodic shutdowns of the hydrocracker are necessary for catalyst regeneration as well as for routine maintenance and emergencies. As mentioned, carbon monoxide emissions and the sour water waste stream are significant potential problems during catalyst regeneration. When the catalyst is replaced every 2 years or so, particulate emissions may occur if the catalyst is spilled. During process unit turnarounds, all vapors should be routed to the flare or the refinery fuel gas system to prevent emission of hydrocarbons, $NH_3$, $H_2S$, or other gases.

The malfunctions in a hydrocracking unit are similar to those that may occur in catalytic crackers, hydrotreaters, or fractionators (distillation units). These include electrical problems, insufficient separation in the fractionator, water in the unit, leaks resulting in pressure drop, and other mechanical problems. The frequency of malfunctions is not predictable.

### 4.4.6 References

1. Billon, A., et al. More Ways To Use Hydrocracking. Hydrocarbon Processing, May 1978. pp. 122-127.

2. McGrath, H. G., and M. E. Charles. Origin and Refining of Petroleum. American Chemical Society, 1971, pp. 113-129.

## 4.5 CATALYTIC REFORMING[1,2,3]

The need to increase the antiknock properties of naphtha as a blending stock for motor fuels is the greatest single reason for installing catalytic reforming. Catalytic reforming was discovered during the search for ways to improve thermal reforming, one of the first reforming processes. Researchers sought to eliminate the destruction of paraffins inherent in thermal reforming and to create a method for synthesizing aromatics. The catalytic reforming method, in which noble metals were originally used for catalysts, emerged as a more selective process, promoting desired reactions and minimizing unwanted ones.

### 4.5.1 Process Description

Catalytic reforming processes involve a complicated series of catalytic reactions that change the chemical structure of the hydrocarbons. The hydrocarbon reforming process can be described in terms of the following four principal reactions: (1) dehydrogenation of naphthenes to aromatics to near completion with very little ring rupture; (2) isomerization of paraffins to more highly branched forms; (3) dehydrocyclization of paraffins to aromatics; and (4) hydrocracking of paraffins to lower molecular weights, but with a minimum production of light hydrocarbon gases. The predominant reaction is the dehydrogenation of naphthenes to form aromatics. Some of these aromatics are isolated to become petrochemical feedstocks, but most become motor fuel blending stocks of high antiknock quality. Table 2-2 shows each of these reactions.

The reactions occur over a noble metal catalyst such as platinum on alumina or platinum-rhenium. Catalysts that promote reforming reactions can often cause the side reaction of hydrocracking to produce unwanted lighter products. Higher reactor pressures would suppress hydrocracking, but would also suppress reforming and thus would yield a product of lower antiknock quality. Until about 10 years ago the most popular reforming catalyst was platinum on alumina. This has since been replaced by bimetallic catalysts containing platinum plus other metal promoters such as rhenium. The improved activity and selectivity of these newer catalysts permit operations at lower pressures and greater severities (i.e., higher temperatures, higher catalyst-to-oil ratios, and lower space velocity) without shortening the regeneration cycle. Where greater severity is not needed, the newer catalyst gives greater throughput from existing units, accounting in part for the increase in total capacity during the early 1970's.

Use of the reforming catalysts developed most recently permits still lower pressures, in the range of 2515 to 3550 kPa (350 to 500 psig) and greater severities. The greater severity increases the formation of carbon on the catalyst (coke laydown), which deactivates the catalyst and necessitates more frequent catalyst regeneration.

The reforming reactions are carried out in a controlled atmosphere of pressurized hydrogen to inhibit undesirable side reactions such as the production of olefins; this atmosphere reduces susceptibility to oxidation and enhances stability in storage. The hydrogen also minimizes coke laydown.

Most feedstocks for reforming are hydrotreated first to remove arsenic, sulfur, and nitrogen compounds, which would poison the reforming catalyst. The cost of the hydrotreating step is justified by the extended life of the reforming catalyst.

Various types of catalytic reforming systems in use in the United States include Platforming, Ultraforming, Powerforming, Magnaforming, Houdriforming, and catforming.

## Platforming

Platforming, the original catalytic reforming system, is the most widely used. The Platforming unit consists of five major sections: (1) reactors containing the particulate catalyst in fixed beds, (2) heaters that bring hydrotreated naphtha charge and recycle gas to reaction temperature and provide the heat of reaction, (3) a product cooling system and a liquid/gas separator, (4) a hydrogen gas recycle system, and, (5) a fractionator to separate light hydrocarbons dissolved in the separator liquid.

Platforming units have at least three adiabatic reactor vessels, each containing particulate catalyst in a fixed bed, operating in series. Figure 4.5-1 shows the process flow for a Platforming unit. Because the reaction between the combined feed and the catalyst is so highly endothermic, it is necessary to heat the feed before it enters each reactor. After the reaction process, the effluent from the last reactor is cooled and sent to the receiver, where it is separated into a gas and a liquid stream. Most of the gas, which is largely hydrogen, is compressed and recycled into the reactors, where it provides the protective pressurized hydrogen atmosphere. The remainder of the gas comprises a net hydrogen product stream; it is withdrawn from the system by the pressure control on the reaction system. The liquid stream from the receiver, which contains dissolved light hydrocarbons, is routed to the fractionator, in which a stabilized reformate is produced for blending into finished gasoline pools.

The most variation in design of a Platforming unit is in catalyst regeneration. In Platforming systems that operate at relatively high pressures and with high ratios of recycle gas to naphtha feed, the catalyst degenerates slowly; this allows for an uninterrupted process run, which ranges from few months to more than a year. The length of the run is determined by the deterioration of the catalyst. Either the reactor inlet temperature requirement exceeds the capacity of the heater or catalyst selectivity diminishes to the point that it is economical to shut down the unit and regenerate the catalyst.

The catalyst is either regenerated at the refinery or is shipped offsite and replaced with new catalyst. The in-place regeneration procedure burns the carbon deposits from the catalyst by using the recycle compressor to circulate an air/combustion gas products mixture through the reactor at a controlled

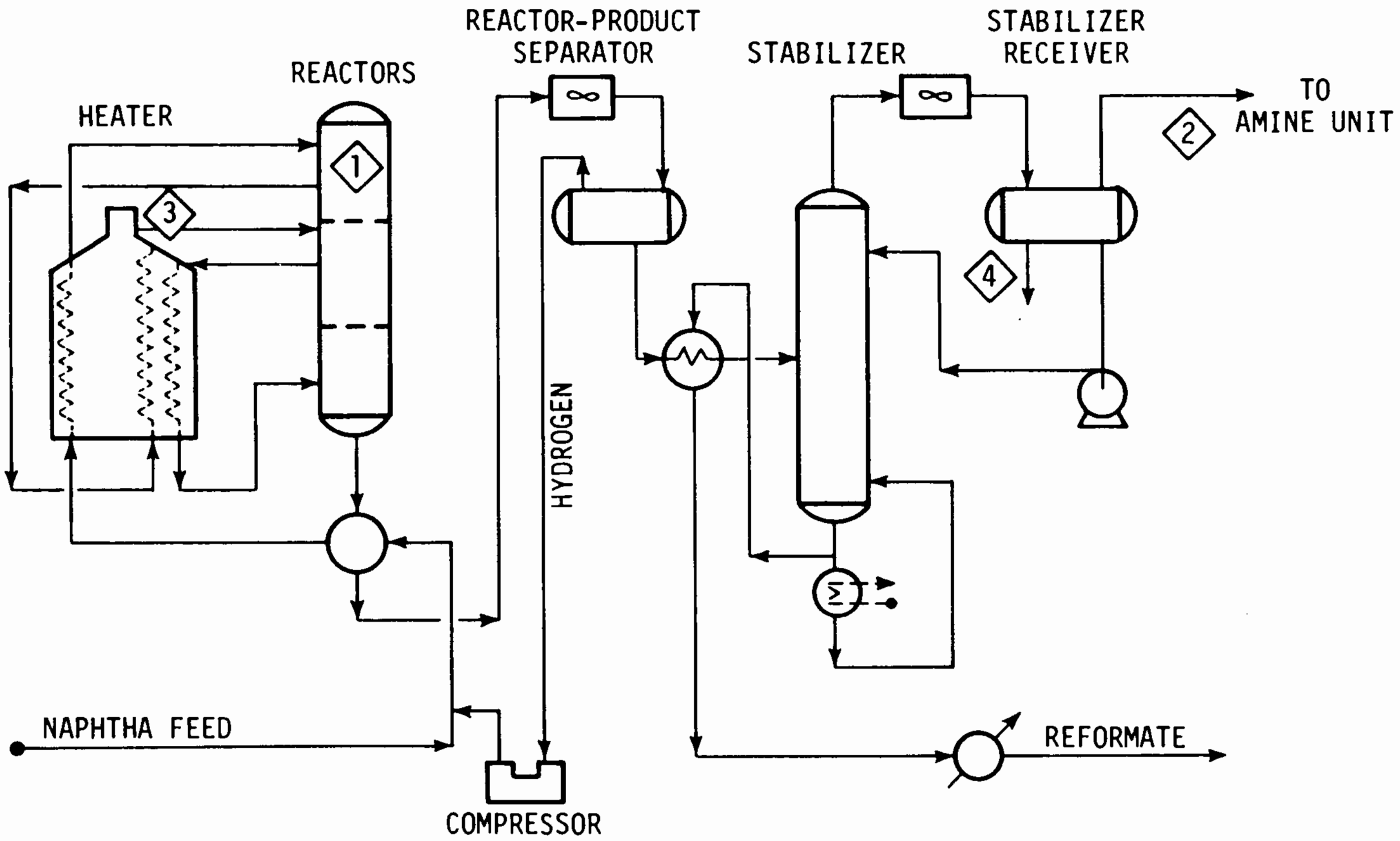

Figure 4.5-1. Process flow diagram of Platforming unit.

burning temperature. This process returns catalytic capacity to the level it held before regeneration. To eliminate much of the downtime necessary to complete in-place regeneration, some Platforming systems completely replace the spent catalyst.

A second type of regeneration operates at lower pressure and low ratios of recycle gas to naphtha feed. The catalyst of these Platforming units deteriorates rapidly, and the catalyst must be changed often. To avoid long periods of downtime, such units are equipped with an extra reactor, so that each reactor can be isolated at least once a day for regeneration. Without shutdown of the system, the "swing-reactor" system provides reformate yields of a given octane number, but the cost of installation and operation are considerably higher.

Processes other than Platforming have stressed the regenerability of the catalyst. The platinum catalysts are difficult to regenerate, but development work has provided techniques that restore a substantial portion of the reforming characteristics of the catalyst. Advantage is taken of the ability to regenerate the catalyst by operating at lower pressures and thus increasing liquid product yields. The trend in the design of semiregenerative processes is to operate in the range of 2515 kPa (350 psig).

## Ultraforming and Powerforming

The Ultraforming and Powerforming processes are cyclic regenerative processes operating for relatively short on-stream periods. The catalyst is rugged, and a regeneration-rejuvenation technique effectively restores the catalyst's reforming characteristics. As a result, these processes take full advantage of the high yields at low pressures and operate at about 1480 kPa (200 psig) with low recycle gas rates. Capital investment for the cyclic units is high, but they reform naphthas effectively to high octane levels. These processes are very similar to Platforming; therefore, no process description is included.

### Magnaforming

The Magnaforming concept supplements the improvements in catalysts with processing conditions that optimize catalyst use and performance. The Magnaforming process decreases the amount of recycle gas to the first reforming reactor and increases the recycle gas to the last reactor. Figure 4.5-2 shows the process flow in Magnaforming. In the primary reforming reactor, the dehydrogenation of naphthenes is rapid and highly endothermic. A large temperature drop occurs, with the result that the system approaches the thermodynamic equilibrium of the naphthene-aromatic-hydrogen system. This slows down the dehydrogenation reaction relative to the hydrocracking reaction. By decreasing hydrogen to the first reactor this effect is minimized, and gas production caused by hydrocracking is decreased.

Magnaforming differs from the other reforming process by use of a four-reactor rather than three-reactor system, with inlet temperatures ascending from the first to the last reactor. The mole ratio of recycle gas to feed might be 2.5 to 3 in the first reactor and 9 to 10 in the last reactor. Liquid yields higher by at least 1 to 2 percent and increases in hydrogen production have been obtained with both platinum and platinum-rhenium catalysts. This higher yield reportedly justifies a 6.5 percent increase in investment for the Magnaforming design over conventional three-reactor systems.

Process flows for IFP (Institute Francais du Petrole) reforming, Houdriforming, Powerforming, Rheniforming, and Ultraforming are described in the September 1978 "Hydrocarbon Processing."[2] These processes have either semiregeneration or cyclic catalytic regeneration. Basically, they are similar in operation to Platforming or Magnaforming but a different bimetallic catalyst gives different yields.

## 4.5.2 Emission Sources

The catalytic reforming process unit is a closed system. The only continuous emissions are those from process heaters

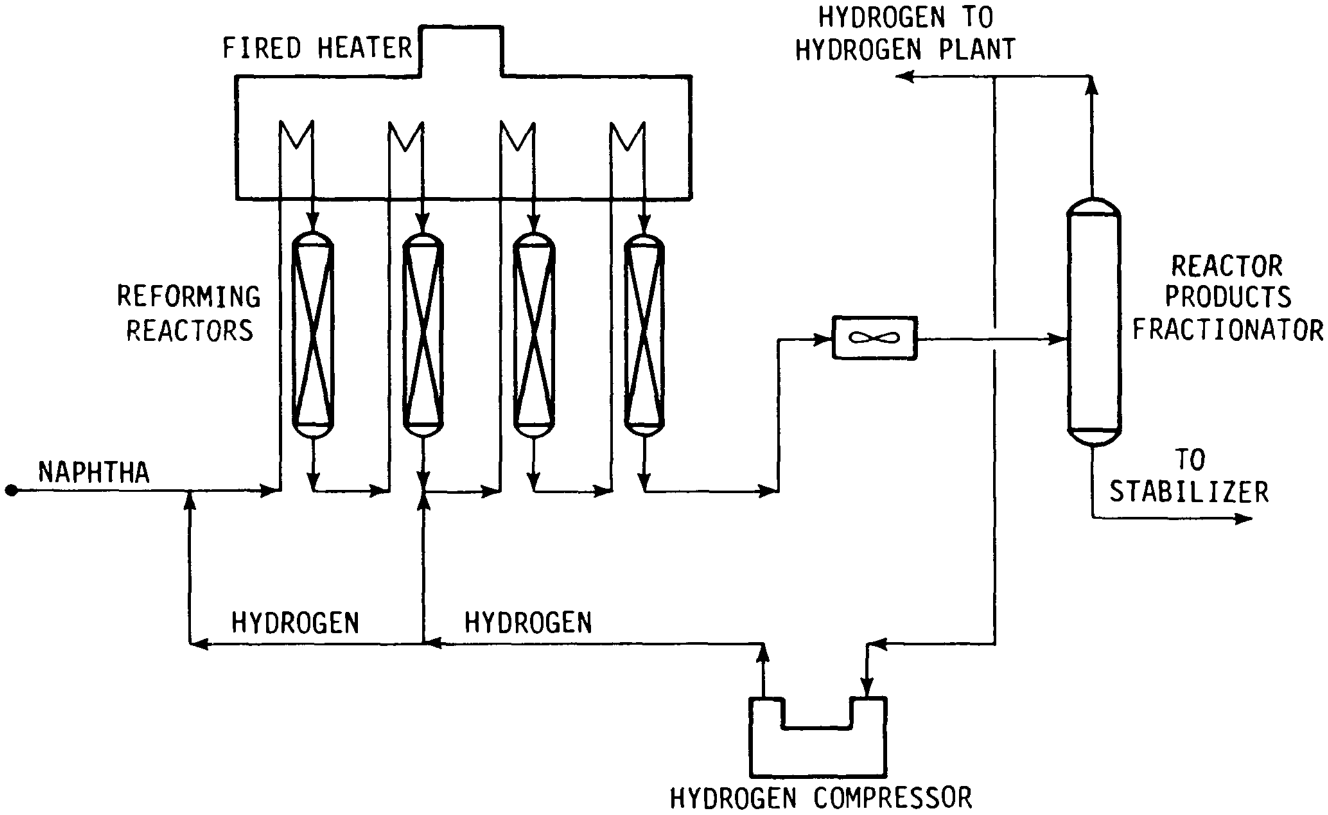

Figure 4.5-2. Process flow diagram of Magnaforming unit.

(Figure 4.5-1, point 3), the hydrogen sulfide in the fuel gas stream (Figure 4.5-1, point 2), a small volume of wastewater containing a low concentration of oil that is produced by the reformer overhead accumulator (Figure 4.5-1, point 4), and possible equipment leaks.

Unlike fluid catalytic cracking catalysts, which are regenerated continuously, reforming catalysts are regenerated periodically. Figure 4.5-1, point 1, shows the emission point of these gases during regeneration. A steam and air mixture is introduced to the catalyst bed, causing combustion of the coke deposits. The combustion may produce carbon monoxide (CO) and unoxidized hydrocarbons. AP-42 estimates the emissions from this source at 0.240 to 2.4 grams/liter (0.002 to 0.02 lb/bbl);[3] this quantity is considered negligible. These emissions could become significant, however, if the unit required frequent regeneration.

The study by the California Air Resources Board found that reformers contributed 1.5 percent of the total refinery fugitive emissions. Among the devices tested, leakage was found in 12 percent of the threaded fittings, 2.8 percent of the valves, 2.1 percent of the valve outlets, and 3.6 percent of the pump seals.

### 4.5.3 Emission Controls

Emissions from process heaters can be reduced by desulfurization of the fuel. Generally, particulates can be controlled by proper operating practices and adjustment of the air-to-fuel ratio.

The fuel gas stream goes to the amine unit for hydrogen sulfide ($H_2S$), which is eventually handled in the sulfur plant. Therefore, $H_2S$ is not an emission problem at the reforming unit.

The wastewater from the overhead accumulator (stabilizer receiver) is collected and sent to the refinery's wastewater treatment facility. Generally the concentration of oil is low and does not pose a volatile organic emission problem.

The principal control measure for hydrocarbons in catalyst regeneration flue gas is incineration in a heater firebox or smoke plume burner. These devices reduce hydrocarbon emissions to negligible quantities. Use of a control device on these regenerator offgases is not widespread, however, because this emission source is not considered significant. Incineration of organics containing sulfur may produce $SO_x$ emissions. Incineration also can produce CO and $NO_x$ emissions.

The fugitive emission sources can best be controlled by instituting a good maintenance program.

### 4.5.4 Instrumentation

The inspector should monitor stack opacity to determine whether process heaters are a source of particulate emissions. The type of fuel and its sulfur should be noted for indications of sulfur emissions.

Since frequent regeneration can cause emissions of carbon monoxide and volatile organics, the inspector's attention will be focused on changes in process parameters that lead to regeneration. Frequency of regeneration is determined by the severity of the operations, type of feed, and availability of hydrogen.

With the platinum reforming catalyst at a pressure of 2515 kPa (350 psig), regeneration is usually infrequent because the catalyst ages slowly. At 1480 kPa (200 psig), however, the catalyst ages rapidly and frequent regeneration is needed. The platinum-rhenium catalysts age less rapidly than platinum; it is possible to regenerate infrequently by operating at a lower pressure and thus to realize higher liquid product yields and higher hydrogen production.

It is important for the inspector to realize that pressure is the controlling variable that determines whether the dehydrogenation or hydrocracking reaction predominates. Hydrocracking is promoted by high pressure, and dehydrogenation by low pressure. Generally speaking, an increase in liquid product yield at a given octane number is accompanied by an increase in hydrogen production to satisfy the carbon-hydrogen balance of the system.

Therefore, the operating pressure of the unit varies with reforming feed, reforming catalyst, and the ratio of hydrogen to hydrocarbon. Table 4.5-1 summarizes the octane numbers associated with high and low severity operations. A low pressure may lead to rapid catalyst aging and necessitate more frequent regeneration, which causes emissions of hydrocarbons and carbon monoxide.

The reformers generally operate at temperatures between 430° and 480°C (800° and 900°F). The operating temperatures may fall outside this range when relatively heavier or lighter feedstocks are processed.

Hydrogen pressure is an important control variable, since it inhibits undesirable side reactions and delays coking of the catalyst. The pressure of the unit is monitored.

The relative yield of butanes and gas is monitored as an indication of the catalyst activity. If yields fall, regeneration may be required, with the resultant emissions of hydrocarbons and carbon monoxide.

### 4.5.5 Startup/Shutdown/Malfunctions

Since the stream processed in this unit must be practically free of sulfur, startup and shutdown should not cause significant sulfur emissions. The most frequent shutdown is for regeneration. Although we have indicated that emissions of hydrocarbons and carbon monoxide from regeneration are negligible, this becomes an important emission source when regeneration is frequent. The frequency at which the catalyst is regenerated is determined by the severity of the operation, quality of hydrogen, and type of feed. Therefore, the frequency and duration of downtime for regeneration cannot be estimated. Regenerating the catalyst may generate a small amount of particulates.

On the average, the reforming unit is shut down for general inspection once during every year of operation, but time between shutdowns ranges from 8 to 25 months. The downtime for a scheduled shutdown averages 15 days.

## TABLE 4.5-1. NAPHTHA YIELDS UNDER VARYING CONDITIONS[1]

| Type of operation | Research octane number, clear | | | | | |
|---|---|---|---|---|---|---|
| | 85 | 90 | 95 | 100 | 103 | 105 |
| Low severity operation: | | | | | | |
| Reformer pressure, kPa | ← 1135 to 3550 → | | | | | |
| Reformer pressure, psig | ← 150 to 500 → | | | | | |
| Weight space velocity, hourly | ← 2.8 → | | | | | |
| Volume percent $C_5$+ | 86.5 | 83.0 | 75.0 | 55.0 | | |
| High severity operation: | | | | | | |
| Pressure, kPa | | | | 2515 | 2515 | 2515 |
| Pressure, psig | | | | 350 | 350 | 350 |
| Weight hourly space velocity | | | | 1.5 | 1.0 | 0.8 |
| Volume percent $C_5$+ | 86.5 | 83.8 | 80.0 | 74.5 | 71.1 | 67.6 |

The shutdown procedures follow a sequence of venting pressure to the refinery flare system. Flow of feed is stopped, heat is removed, and the unit is flushed with inert gas, then with air. In the startup sequence, air is displaced by inert gas, heating is started, process flow is started, and the unit is pressurized when at temperature.

Reforming malfunctions include a decline in hydrogen purity due to production of light ends in the reactors; loss of hydrogen pressure due to compressor failure; loss of hydrogen due to a malfunction at the hydrogen plant; problems in the reformer heater such as blown tubes, hot spots, inability to control temperatures in the heaters, or flame-out; loss of reformer feedstock due to a failure at the crude unit or hydrogen desulfurization unit; loss of reformer feedstock due to pump failure on the reforming unit; and loss of cooling water to the unit. The frequency of malfunctions varies with the type of crude being processed, severity of the operation, maintenance practices, and reliability of upstream processes. Each of the malfunctions described requires a different period of downtime. Emergency downtimes average 10 days.

### 4.5.6 References

1. Schwarzenbek, E. F. Catalytic Reforming. In H. G. McGrath and M. E. Charles, eds., Origin and Refining of Petroleum. American Chemical Society, Washington, D.C., 1971. p. 102.

2. Refining Handbook. Hydrocarbon Processing, 57(9): 159-166, September 1978.

3. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. 2nd ed. AP-42, 1979.

## 4.6 ALKYLATION[1,2]

In alkylation, branched hydrocarbons are synthesized by the addition of an alkane or aromatic hydrocarbon to an alkene (olefin) in the presence of an acid catalyst. The product, alkylate, is desirable as an antiknock additive in motor and aviation fuel.

### 4.6.1 Process Description

There are four types of alkylation units: hydrofluoric (HF) acid, sulfuric acid, aluminum chloride, and thermal, the first two being the most common. Because aluminum chloride and thermal alkylation are not commonly used in petroleum refineries, these processes are not discussed in this manual. Details on the aluminum chloride alkylation process are given in Reference 1, and on the thermal alkylation process, in Reference 2. A discussion of the hydrofluoric acid and sulfuric acid alkylation units follows.

#### Hydrofluoric Acid Alkylation

In a hydrofluoric acid alkylation process, an isoparaffin is combined with an olefin or olefin mixture to form a highly branched, high-octane gasoline component. Isobutane may be alkylated with propylene, butylenes, amylenes, or even higher boiling olefins. The particular olefin used as a reactant determines the octane number of the alkylate produced. Butylenes or a mixture of butylenes and propylene are the most common olefin charge stocks. A simplified block diagram, Figure 4.6-1, depicts the complex flow of this process. This is a conceptual diagram that represents the activities occurring in the process; the size of the blocks does not indicate the relative importance of the process steps. Figure 4.6-2 is a typical process flow diagram.

The mixture of olefins and isobutane is introduced into a vessel that serves as both a reactor and settler (see Figure 4.6-2). At the same time, hydrofluoric acid is fed into the reactor/settler vessel. The hydrogen ion from the acid initiates a reaction with the hydrocarbon mixture, leading to the

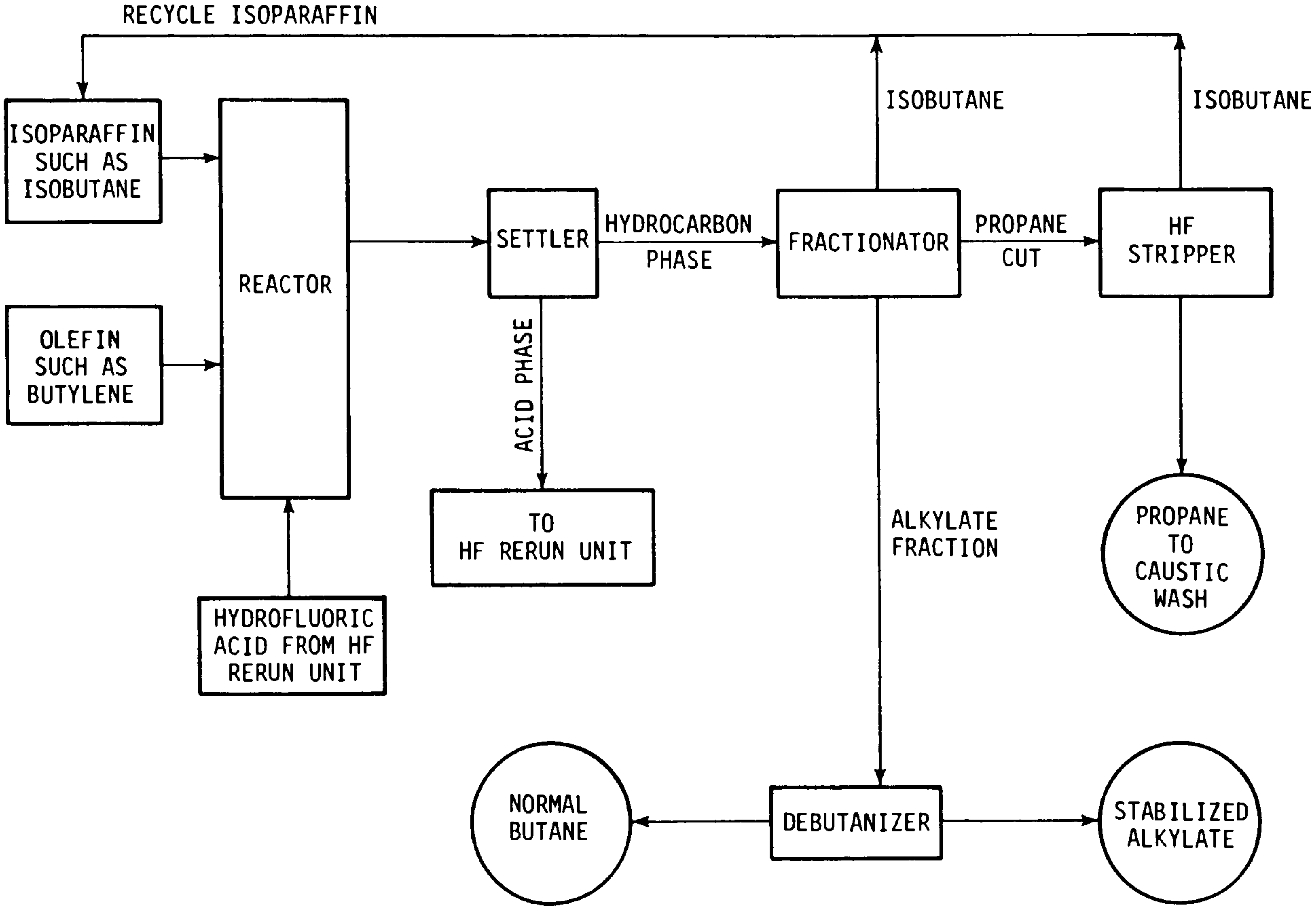

Figure 4.6-1. Block flow diagram of hydrofluoric acid alkylation.

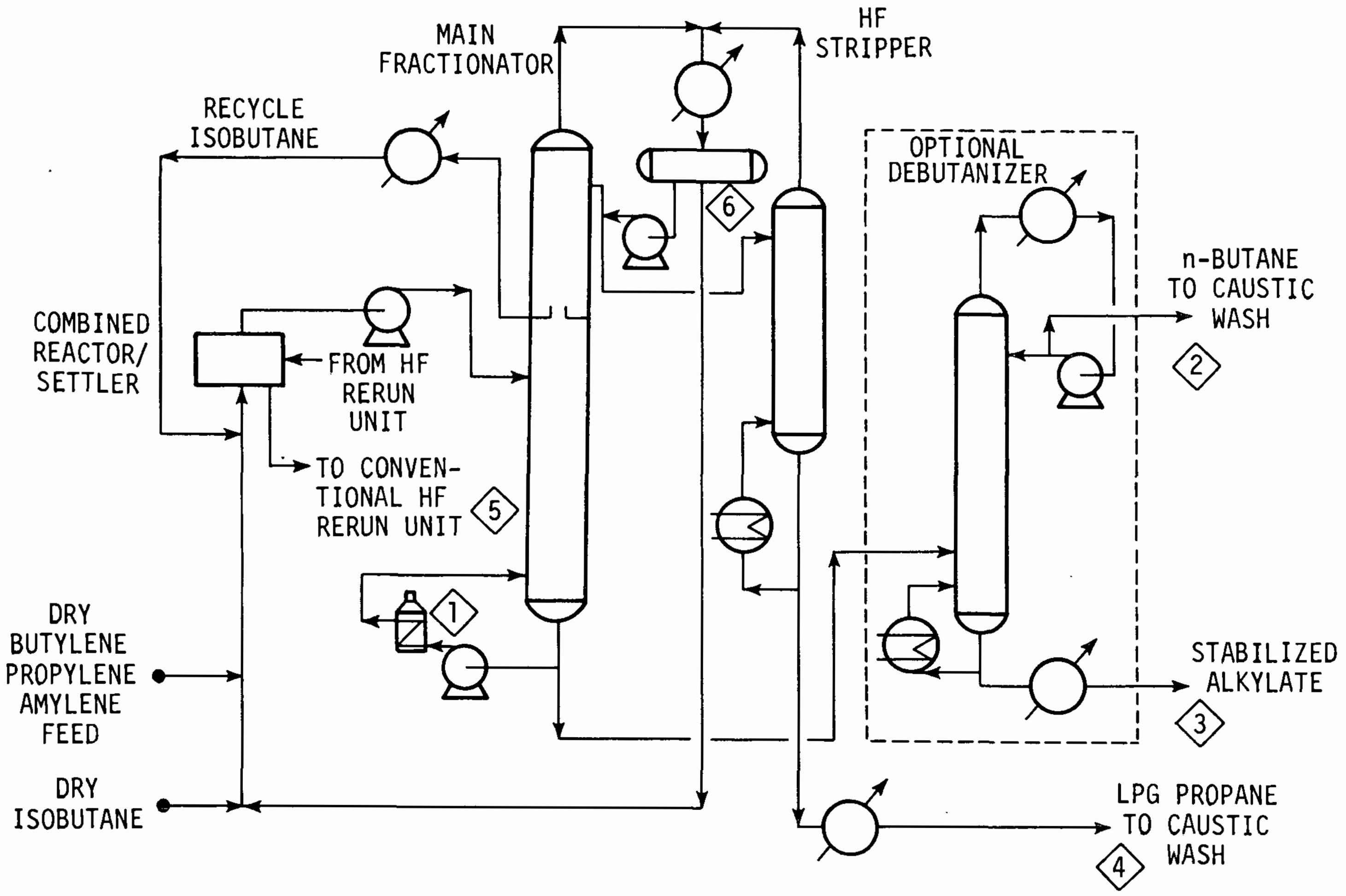

Figure 4.6-2. Process flow diagram of hydrofluoric acid alkylation.

formation of alkylate. Settling results in a hydrocarbon phase and an acid phase.

The hydrocarbon phase consists of propane (small quantities inevitably enter the reactor with the isobutane and olefin), alkylate product, recycle isobutane, and some hydrofluoric acid. The acid phase consists of hydrofluoric acid saturated with hydrocarbons. So that acid may continue to catalyze the alkylation reaction, this saturated acid must be regenerated or fresh acid must be supplied. An acid rerun tower may be used for purification of the HF stream. In regeneration of the acid, tar is produced as a byproduct.

The hydrocarbon phase flows to the main fractionator for separation into isobutane that is recycled to the reactor, a propane cut that continues to the HF stripper, and an alkylate fraction.

In the HF stripper, dissolved hydrofluoric acid and isobutane are removed from the propane cut. The resulting propane then goes to caustic treating for final removal of traces of HF. The isobutane is recycled to the reactor. The amount of HF in the HF stripper is regulated by recycling.

The alkylate fraction may be routed to a debutanizer, or the vapor side stream from the main fractionator that contains alkylates may be steam stripped to remove butane (Figure 4.6-2). The stabilized alkylate contains traces of hydrofluoric acid and organically combined fluorides, which must be removed before the alkylate is used in gasoline blending.

## Sulfuric Acid Alkylation

Isobutane and the olefin butene (also called butylene) are used primarily as feedstocks in the sulfuric acid alkylation process. Strength of the sulfuric acid catalyst is approximately 94 to 98 percent. Because the acid becomes saturated with hydrocarbons and thus loses strength, the acid must be regenerated to catalyze the alkylation reaction further. Spent acid from the process is generally exchanged for fresh acid from a supplier and shipped offsite for regeneration.

Two common means of sulfuric acid alkylation are by effluent refrigeration and cascade autorefrigeration. A discussion of each process follows.

### Sulfuric Acid Alkylation With Effluent Refrigeration

The simplified block flow diagram, Figure 4.6-3, gives a conceptual idea of this complex process. Figure 4.6-4 illustrates the process flow.

In the effluent refrigeration system, the olefin and isoparaffin (isobutane) streams are mixed before entering the horizontal reactor. In the reactor, contact of the hydrocarbon mixture with concentrated sulfuric acid is achieved by circulation of the liquid contents at high velocities for 5 to 40 minutes to induce mixing. The resulting reactions are exothermic. The reaction forms an emulsion of 35 to 50 percent hydrocarbons and 50 to 65 percent sulfuric acid, which is sent to the settler for separation. Since some of the acid becomes saturated with hydrocarbons, fresh acid is needed to maintain enough acid strength to initiate the alkylation reaction. The separated hydrocarbons undergo pressure reduction, which causes vaporization and cooling of the hydrocarbons. The cooled hydrocarbons (consisting mainly of isobutane) flow through the reactor cooling elements and act as a refrigerant. Since the reaction is exothermic, this cooling is necessary.

The mixture of liquids and vapors from the cooling elements flow to the vapor-liquid separator (Figure 4.6-4). The liquid mixture is treated in the treating section, while the vapors are compressed and condensed. The condensate flows to an accumulator and then to the depropanizer. The propane overhead is sent to the refinery fuel gas system and the depropanizer bottoms undergo pressure reduction, then are sent to a flash drum. In the flash drum, the bottoms and some liquid from the accumulator are partially vaporized.

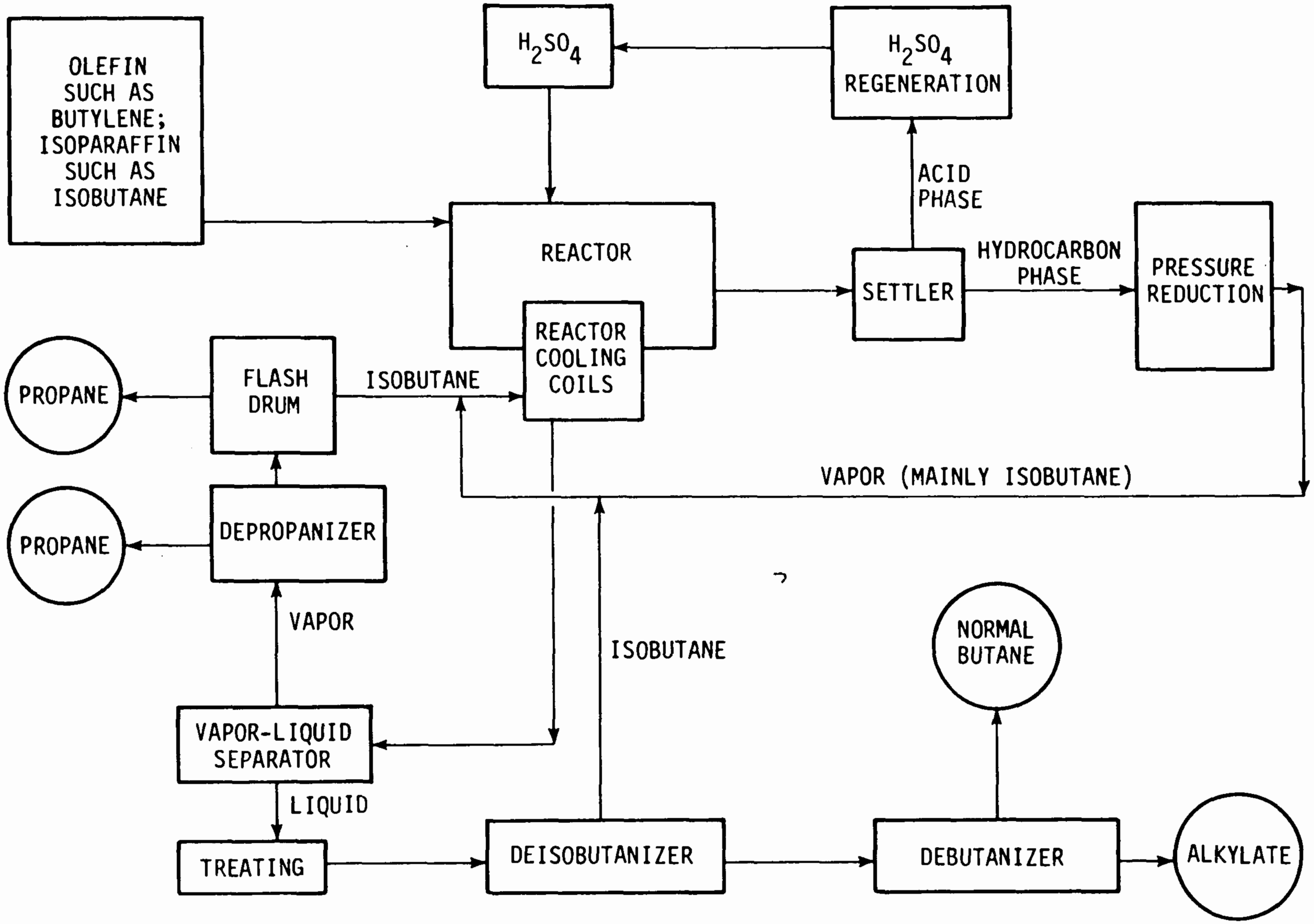

Figure 4.6-3. Block flow diagram of sulfuric acid alkylation with effluent refrigeration.

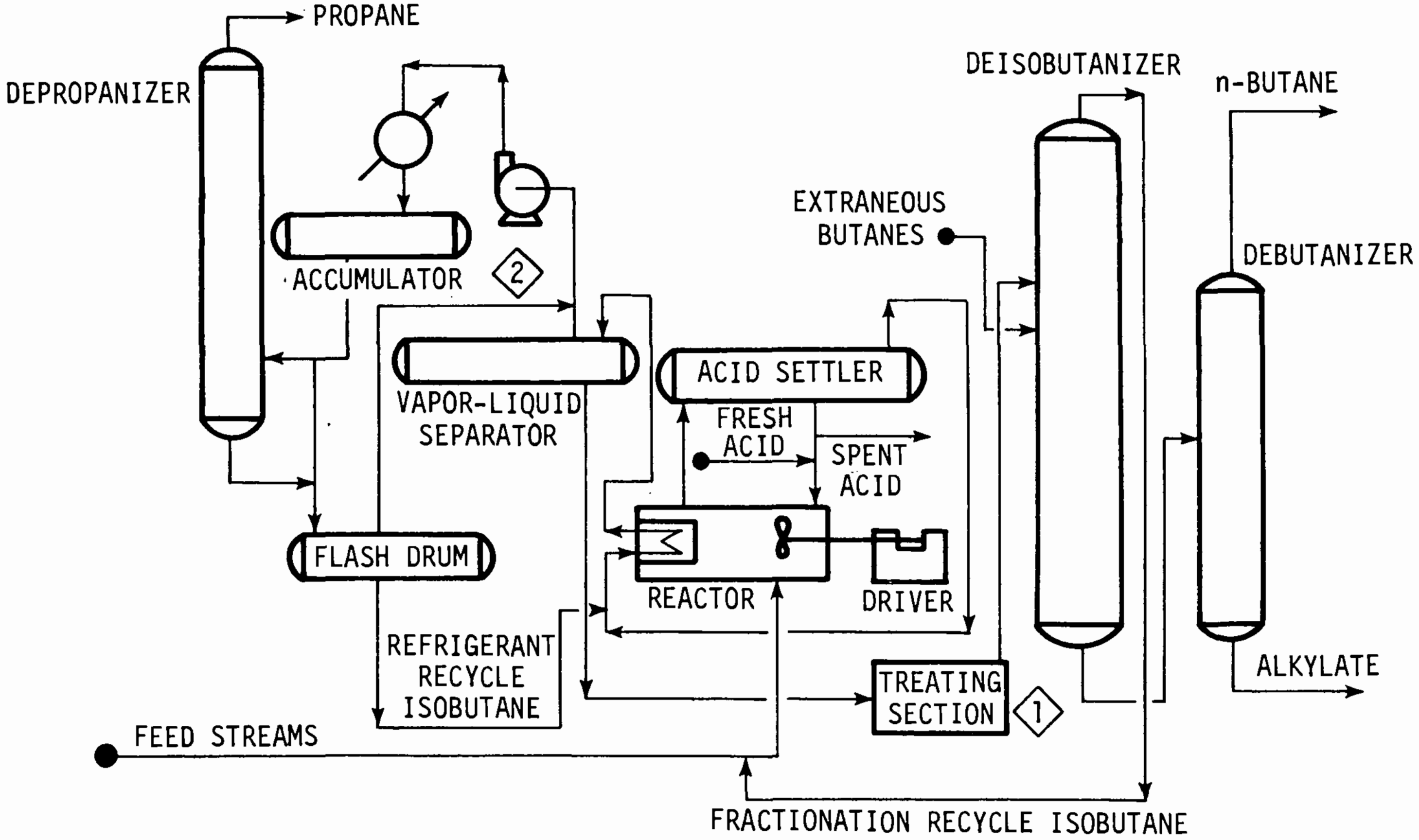

Figure 4.6-4. Process flow diagram of sulfuric acid alkylation with effluent refrigeration.

The liquid from the vapor-liquid separator is cold [approximately -8°C (18°F)]. This stream undergoes heat exchange with the fresh feed before proceeding to a treating section. Treatment consists of a caustic wash followed by a water wash. After treatment, the liquid stream is routed to the deisobutanizer. The resulting isobutane is recycled as reactor feed. The alkylate product is in the deisobutanizer bottoms, which are handled in various ways depending on the end usage of the alkylate. Generally, some normal butane is removed if the alkylate is to be used in aviation or motor fuels. Additional fractionation is needed for alkylate used in aviation gasoline, in which an exact end point is required.

### Sulfuric Acid Alkylation With Cascade Autorefrigeration

Cascade autorefrigeration is similar to effluent refrigertion except that a multicompartment reactor/settler vessel is used rather than a single compartment reactor with separate settling vessel. There are usually two to eight reactor compartments (zones) in a multicomponent reactor/settler. The number of zones depends on the capacity of the reactor. Figure 4.6-5 is a simplified block diagram showing this process.

In cascade refrigeration the olefin feed is cooled in a flash drum (illustrated in Figure 4.6-6 as a combination flash drum and heat exchanger) and undergoes indirect heat exchange. Recycle isobutane is also cycled through the flash drum/heat exchanger. The olefin is fed in parallel to each reactor zone. Isobutane and sulfuric acid are introduced into the reactor before the first reactor zone. The resulting mixture of these two liquids flows in series, or cascades, through the reactor zones and reacts exothermally with the olefin. The light hydrocarbons evaporate directly from the hydrocarbon-sulfuric acid reaction mixture and thus cause cooling by evaporation. Because this process cools the reaction without the use of cooling elements, it is called autorefrigeration. The liquids from the last

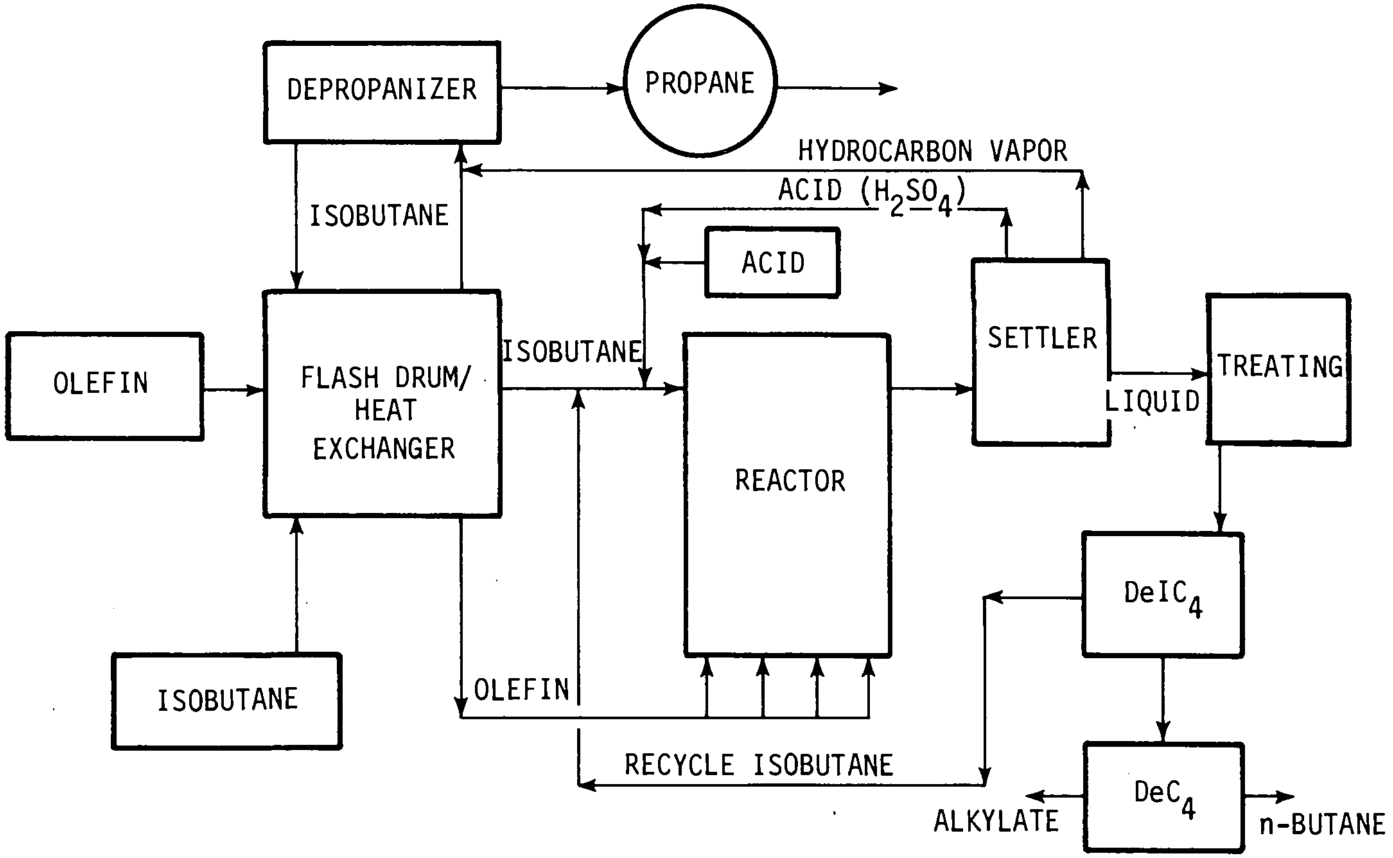

Figure 4.6-5. Block flow diagram of sulfuric acid alkylation with cascade autorefrigeration.

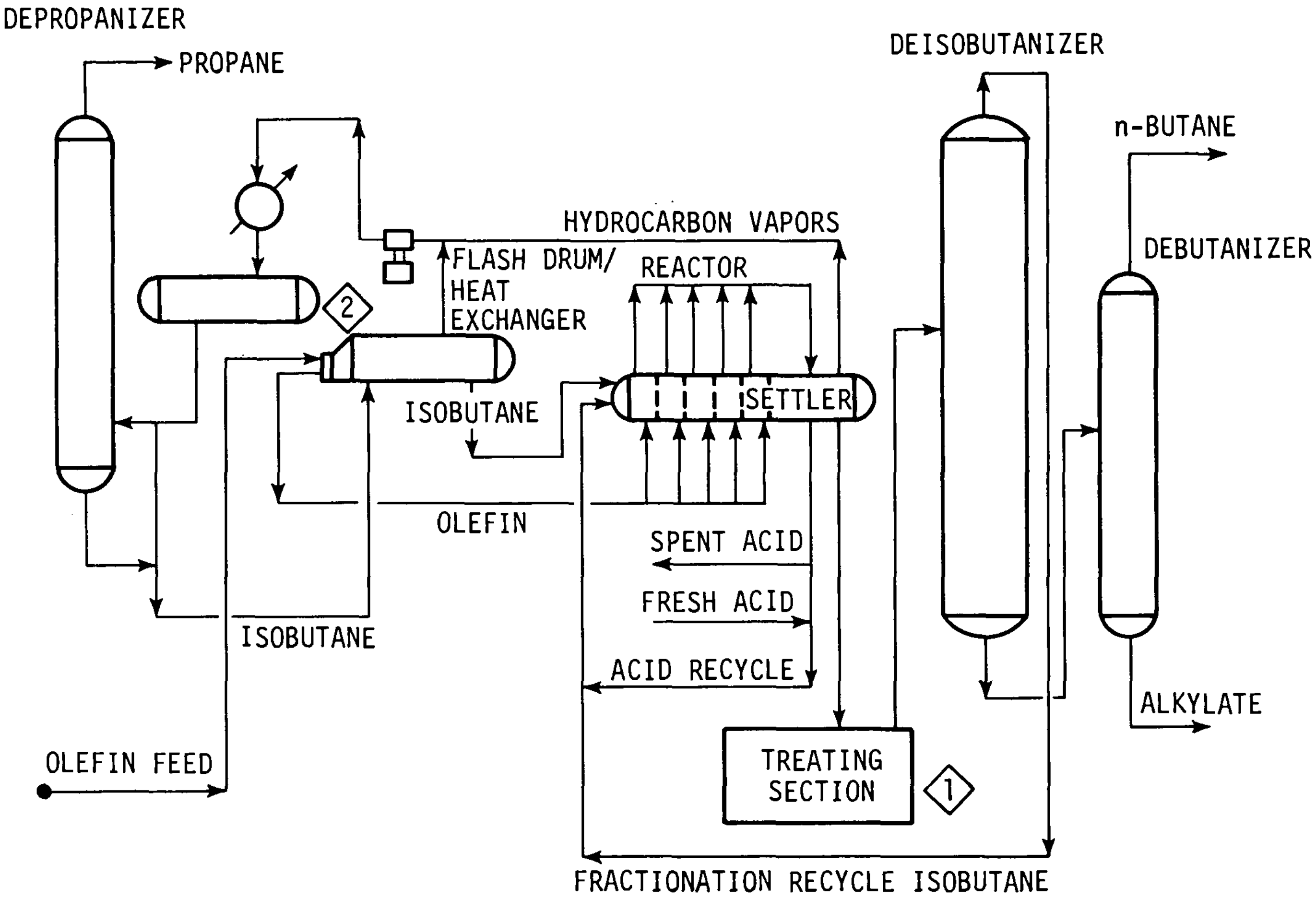

Figure 4.6-6. Process flow diagram of sulfuric acid alkylation with cascade autorefrigeration.

reactor zone flow into the settler section of the reactor/settler vessel, where the acid separates from the hydrocarbon.

After the acid is separated from the hydrocarbon, the acid is recycled. Spent acid is removed and fresh acid supplied as necessary. Some of the acid is contaminated by hydrocarbons. Additional acid is needed to maintain enough acid strength to initiate the alkylation reaction. The liquid hydrocarbon phase contains the alkylate. This phase undergoes treating, deisobutanizing (shown as $DeIC_4$ in Figure 4.6-5), debutanizing (shown as $DeC_4$), and other finishing steps of the effluent refrigeration process.

The hydrocarbon vapor phase (rich in isobutane and propane) is sent from the settler to a compressor. Vapors from the flash drum/heat exchanger also enter the compressor. Following compression is condensation. The condensate enters an accumulator. The resulting vapors are routed to a depropanizer, while the liquids are added to depropanizer bottoms. These liquids undergo pressure reduction for cooling before they enter the flash drum. The isobutane from the flash drum is recycled to the reactor.

### 4.6.2 Emission Sources

The alkylation units are potential sources of particulates, fluorides, sulfur oxides, and volatile organic compounds.

Potential emission points of particulates include emissions from fired heaters (Figure 4.6-2, point 1).

Potential emissions of fluorides shown in Figure 4.6-2 include the following:

1. Hydrofluoric acid and organically combined fluorides that appear in the following streams: n-butane (point 2), stabilized alkylate (point 3), and propane (point 4).
2. A waste stream from the HF acid regenerator (point 5); this stream is either incinerated or treated with an alkaline solution to recover the fluoride as a solid waste, which is placed in a landfill.

3. Some HF units may incorporate a process vent from the main fractionator accumulator (point 6) for releasing noncondensable ethane from the system. Generally, however, the alkylation processes are closed systems with no process vents to the atmosphere because of possible discharges containing HF. The system includes vents from pumps, exchangers, and all equipment in acid service, all of which discharge to an alkaline scrubber, where HF is removed before the stream is exhausted to the atmosphere or a blowdown system. Scrubbing is done with spent caustic, lime slurry, or potassium hydroxide. The recovered fluoride is placed in a landfill.

Potential sulfur emissions from alkylation units are as follows:

1. Sulfur oxides from process heaters (Figure 4.6-2, point 1).
2. Liquid wastes associated with water and caustic scrubbing of feed and product streams (Figure 4.6-4 point 1; Figure 4.6-6, point 1). These wastes are generally processed in the refinery's neutralization and wastewater treatment facilites.
3. Small quantities of liquid containing sulfuric acid, from the depropanizer accumulator (Figure 4.6-4, point 2; Figure 4.6-6, point 2).

In both the hydrofluoric acid and sulfuric acid alkylation units, leaks are a major source of emissions of hydrocarbons, organic fluorides, and organic sulfides. The highly corrosive acid makes these units susceptible to leaks.

### 4.6.3 Emission Controls

Alkylation units are not equipped with common air pollution control equipment as used in the fluid catalytic cracking unit. This section therefore describes the operating practices used to control emissions.

The sulfur oxide emissions from process heaters can be reduced by desulfurization of the fuel. Generally, particulates can be controlled by proper operating practices and by adjustment of the air-to-fuel ratio.

In the hydrofluoric alkylation unit, potential emissions of hydrofluoric acid and organically combined fluorides are controlled by the following procedures.

Butanes and alkylate leaving the unit are passed over walnut-sized potassium hydroxide (KOH) pellets to remove any traces of acid. These streams are also protected by bubblers, which require only visual checking. Bottoms from the HF stripper are also passed over walnut-sized KOH pellets to prevent any entrainment of HF with the propane.

A hot bauxite treatment is commonly used to reduce combined fluoride to less than 10 ppm in the propane stream.

A neutralization pit handles area runoff, condensate, and liquid wastes. Lime is added to remove the acid by formation of insoluble calcium fluoride. The recovered fluoride goes to a landfill.

The relief gas system can use a knockout drum and liquid KOH scrubber. A small flow of dry sweep gas is passed through the scrubbers continuously to maintain constant operation.

Dispersal of caustic vapors or hydrocarbon vapors to the atmosphere can be controlled by using a vapor recovery system to confine the vapors and vent them to a flare. The HF process usually has an alkaline scrubber that removes HF prior to flaring. Walnut-sized potassium hydroxide pellets are usually used for scrubbing. The potassium fluoride is treated with lime. The resulting calcium fluoride goes to landfill.

In the sulfuric acid alkylation process, the liquid wastes associated with water and caustic scrubbing of the feed and product streams can be controlled by processing in the refinery's neutralization and wastewater treatment facilities.

The spent sulfuric acid, which may be shipped offsite for regeneration, is saturated with volatile hydrocarbons. The hydrocarbon vapors can be controlled by flaring or incineration.

A study by the California Air Resources Board revealed that an alkylation unit contributes 8.4 percent of the total refinery fugitive emissions; emissions from this unit occur by leakage from valves, flanges, threaded fittings, valve outlets, pump seals, and compressor seals. The pump seals in the alkylation unit leak the most (33 percent of all seals). Leaks were found at 30 percent of the threaded fittings, 18 percent of the valves, and 0.4 percent of the flanges; no leaks were found at valve outlets or compressor seals. All leakage can be limited by proper maintenance.

Because prompt maintenance is the only feasible control for fugitive emissions, prompt detection of emissions is critical. Detection of HF leaks is important because of the physiological hazard as well as the potential for damage to equipment. Studs exposed to acid may suffer stress corrosion cracking or embrittlement in a short period of time. Flanged connections at points where HF can be present are usually painted with a special indicating paint, which turns from brillant orange to yellow when it comes in contact with acid. This change in color is often the first indication of a leaking joint.

Lines carrying HF may be jacketed to contain any possible leakage. A water spray or alkali dump system is usually provided for use in the event that a mechanical failure releases acid.

A differential conductivity cell records continuously the amount of electrolyte in the secondary water from the unit before it is discharged. The secondary water used in HF regeneration is also checked because large volumes of acid could escape to the system if a leak developed. Caustic is injected to the secondary water when HF is detected.

### 4.6.4 Instrumentation

Neither the hydrofluoric acid or the sulfuric acid alkylation unit is operated under severe conditions. Tables 4.6-1 and 4.6-2 list the operating ranges of the hydrofluoric acid and sulfuric acid alkylation processes. The inspector should note the exact values of these operating parameters, because values outside of target ranges may result in excess emissions.

TABLE 4.6-1. RANGES OF OPERATING CONDITIONS FOR HYDROFLUORIC ACID ALKYLATION[a]

| Process parameter | Operating range |
|---|---|
| Pressure, kPa | 790 to 1135 |
| Pressure, psig | 100 to 150 |
| Temperature, °C | 15 to 52 |
| Temperature, °F | 60 to 125 |
| Ratio of isobutane/olefin in feed | 3 to 12 |
| Olefin contact time, min | 8 to 20 |
| Catalyst acidity, wt % | 80 to 95 |
| Acid in emulsion, vol % | 25 to 80 |

[a] Reference 2, p. 134.

TABLE 4.6-2. RANGES OF OPERATING CONDITIONS FOR SULFURIC ACID ALKYLATION[a]

| Process parameter | Operating range |
|---|---|
| Pressure, kPa | 445 to 790 |
| Pressure, psig | 50 to 100 |
| Temperature, °C | 2 to 15 |
| Temperature, °F | 35 to 60 |
| Ratio of isobutane/olefin in feed | 3 to 12 |
| Olefin space velocity, volume of olefin per hour per volume of acid | 0.1 to 0.6 |
| Olefin contact time, min | 20 to 30 |
| Catalyst acidity, wt % | 88 to 95 |
| Acid in emulsion, vol % | 40 to 60 |

[a] Reference 2, p. 134.

The sulfuric acid units usually operate at temperatures between 2° and 15°C (35° and 60°F). For processing of butylenes, the range is 2° to 13°C (35° to 55°F). For processing of olefin feed mixtures containing high percentages of propylene, the preferred range is 10° to 15°C (50° to 60°F). Therefore, the inspector should note both the temperature and the type of feed.

Temperatures above the upper limit can cause cracking of the feed and lighter products, and concentration of acid in the lighter products. The caustic scrubbers could become overloaded with resulting excess emissions of organics and fluorides.

Usual operating range of the HF unit is 15° to 50°C (60° to 125°F). The unit operating temperature is usually set by the temperature of the available cooling water. Higher octane alkylate can be produced at temperatures around 15°C (60°F).

Inadequate temperature control leads to reduction of alkylate yields and octane numbers, and to an increase in acid consumption. With increasing acid consumption, the scrubbers or caustic treaters may become overloaded, as may the acid recovery unit; these overloads would cause emissions.

Pressure has no significant effect on alkylation reactions as long as it is high enough to maintain a liquid phase, which is needed for the reaction to occur. Short contact time or high space velocity can adversely affect alkylate yield and quality.

Prompt detection and remedy of leakage from valves, flanges, threaded fittings, pump seals, and compressor seals are essential for control of fugitive emissions.

### 4.6.5 Startup/Shutdown/Malfunctions

During startup of an alkylation unit (which requires a minimum of 1.5 days), leaks in equipment would lead to emissions. The quantities of hydrocarbons and acid vapors emitted depend on the processing equipment used at the unit. Because of the variability in process equipment and in operating conditions, it is impossible to specify a time frame for identifying and repairing such leaks.

Malfunctions requiring the emergency shutdown of one or more components can cause emissions of hydrocarbons (and sometimes acid) unless the refinery vents vapors to a flare or fuel gas system.

Leakage is a common problem with alkylation units and can necessitate shutdown of the unit. Generally, streams can be rerouted while leaks are being repaired. Repair usually requires 1 day or less.

On most alkylation units steam reboilers are used rather than heaters to heat the fractionating towers. The use of direct-fired furnaces for deisobutanizer column reboilers can provide thermal defluorination of the alkylate product. The only type of malfunction associated with steam reboilers is tube blockage, which is rare. Malfunctions in the fractionators are the same as those in other fractionators.

When malfunctions do occur, emergency downtime for the entire alkylation unit averages about 10 days. This figure may represent several shutdowns, which may occur before the unit can resume normal operation. On an average, shutdown for general unit inspection occurs once every year of operation, within a range of 9 to 16 months between shutdowns. The downtime for a scheduled shutdown is generally about 15 days.

### 4.6.6 References

1. Dickenson, R. L. and W. S. Reveal. Ethylene Alkylate: Commercial Production by the Shell Process. American Petroleum Proceedings, 1971.

2. Lafferty, Jr., W. L. and R. W. Stokeld. Alkylation and Isomerization. In H. G. McGrath and M. E. Charles, eds., Origin and Refining of Petroleum, American Chemical Society, 1971.

## 4.7 ISOMERIZATION

The isomerization process is similar to catalytic reforming in that both rearrange the molecular form of a feedstock while reducing the losses that normally occur in cracking or condensation reactions. An isomerization reaction is illustrated in Table 2-2. This process is used to upgrade normal paraffins (straight-chain hydrocarbons) to isoparaffins (branched-chain hydrocarbons).

### 4.7.1 Process Description

The isomerization process is usually applied to butane or to mixtures of pentane and hexane. When butane is the feedstock, the isobutane product is normally used as feed to an alkylation unit. Pentane/hexane feeds, from crude distillation of catalytic reforming, are processed to improve their octane ratings, and the product is blended to gasoline. Pentane, having a research octane rating of about 62, can be converted into isopentane having a research octane rating of 92.

Isomerization catalysts were developed along two paths: (1) Friedel-Crafts halide systems and (2) dual-site heterogeneous catalysts, which originated with the commercial introduction of platinum-aluminas for catalytic reforming in the 1940's. The Friedel-Crafts systems (aluminum chloride-hydrocarbon complexes) were used exclusively during the early stages of World War II, when the first commercial processes were introduced to manufacture isobutane as a feedstock for alkylate for aircraft. This practice is now obsolete, chiefly because the extreme reactivity of the catalyst initiated a number of side reactions that led to destruction of the reactants and products.

The new method uses noble metal catalysts on a solid catalyst support. The feed is mixed with hydrogen to suppress unwanted reactions.

The main types of isomerization use butane, pentane, hexane, or xylene as feedstocks. Because butane and mixtures of pentane and hexane are the most common, this section focuses on isomerization units that use these feedstocks. The xylene isomerization unit is not common in refineries, and is not described here. Details of the xylene unit are given in Hydrocarbon Processing, November 1977, pp. 237-239.

### Butane Isomerization

The butane isomerization process (also called Butamer) converts normal butane into isobutane in the presence of a platinum-containing catalyst and hydrogen. The hydrogen suppresses the polymerization of trace amounts of olefins formed during the isomerization reaction. Figure 4.7-1 illustrates the butane isomerization process.

A mixed butane feedstock enters the deisobutanizer tower, where the isobutane product is taken overhead. A sidestream of normal butane from the deisobutanizer is mixed with hydrogen recycle, raised to reaction temperatures of 150° to 200°C (300° to 400°F) and made to flow over the fixed-bed catalyst. A high-activity, selective catalyst promotes the desired conversion of normal butane to isobutane at low temperatures, so that equilibrium conditions are favored. Table 4.7-1 summarizes the operating conditions. The reactor effluent is cooled and then routed to a high-pressure separator for recovery of the hydrogen. Gas from the separator and a small amount of makeup hydrogen are recycled to the reactor by means of a compressor. Separator liquid is sent to the stabilizer for removal of coproduct light gas (hydrogen, ethane, and propane) overhead. This gas flows to the refinery fuel gas system. The stabilizer bottoms are returned to the deisobutanizer, where isobutane from the fresh feed and that produced in the isomerization reactor are recovered overhead. The normal butane is recycled until it is converted to isobutane.

A small amount (parts per million) of organic chloride is added to the feed to help maintain catalyst activity by replacing the hydrogen chloride lost in the stabilizer overhead.

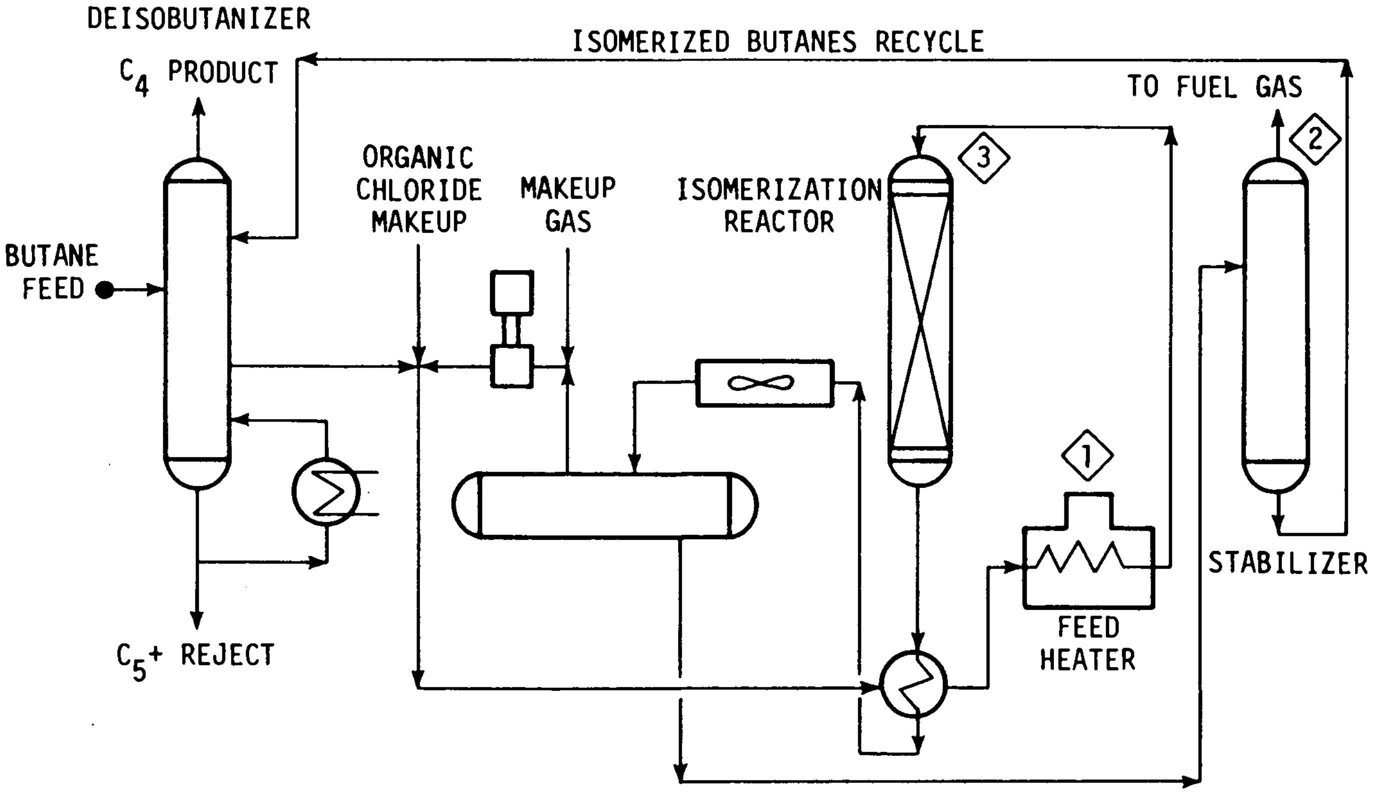

Figure 4.7-1. Butane isomerization process.

## TABLE 4.7-1. OPERATING CONDITIONS FOR BUTANE ISOMERIZATION

| Process parameter | Operating range |
|---|---|
| Reactor pressure, kPa | 1400 to 2860 |
| Reactor pressure, psig | 200 to 400 |
| Reactor temperature, °C | 150 to 200 |
| Reactor temperature, °F | 300 to 400 |
| Liquid hourly space velocity[a] | 3 to 5 |
| Mole/ratio of hydrogen to oil in feed | 0.1 to 0.5:1 |

[a] Dimensionless number

The platinum-containing catalyst is activated and regenerated "in situ" (in place). Because of the hydroscopic nature of the isomerization catalyst system, a regenerable catalyst offers the refiner ease in reactor loading and operating flexibility.

### Pentane and/or Hexane Isomerization

Pentane, hexane, or a mixture of the two from straight-run catalytic reforming or solvent extraction is processed in an isomerization unit to increase the octane rating of pentane and/or hexane fractions. The isomerization reaction takes place in a hydrogen atmosphere to minimize polymerization. Figure 4.7-2 illustrates the pentane/hexane isomerization process.

Before being processed in the isomerization unit, the feed is treated in a conventional hydrodesulfurization unit to remove sulfur, which would poison the isomerization catalyst. The desulfurized feed is mixed with hydrogen, heated, and passed over the platinum-containing catalyst in a lead reactor, in which the aromatics and olefins are saturated. Isomerization of normal paraffins to isoparaffins also occurs in the lead reactor. The reactor effluent is cooled before entering the tail reactor, in which further isomerization takes place at more favorable, low-temperature conditions. When pentane is the feed, only one reactor is used. Tail reactor effluent is cooled and sent to a high-pressure separator. Gas from this separator, together with a small amount of makeup hydrogen, is recycled to the reactors. Separator liquid flows to a stabilizer, and the stabilizer off-gas goes to the refinery fuel gas system. The stabilizer bottoms give a final product suitable for blending directly into motor gasoline. A small amount of organic chloride is added to the feedstock to help maintain catalyst activity by replacing the hydrogen chloride lost in the stabilizer overheads.

The catalyst is highly active and selective so as to provide high product yield, depending on feedstock. Long cycle times of

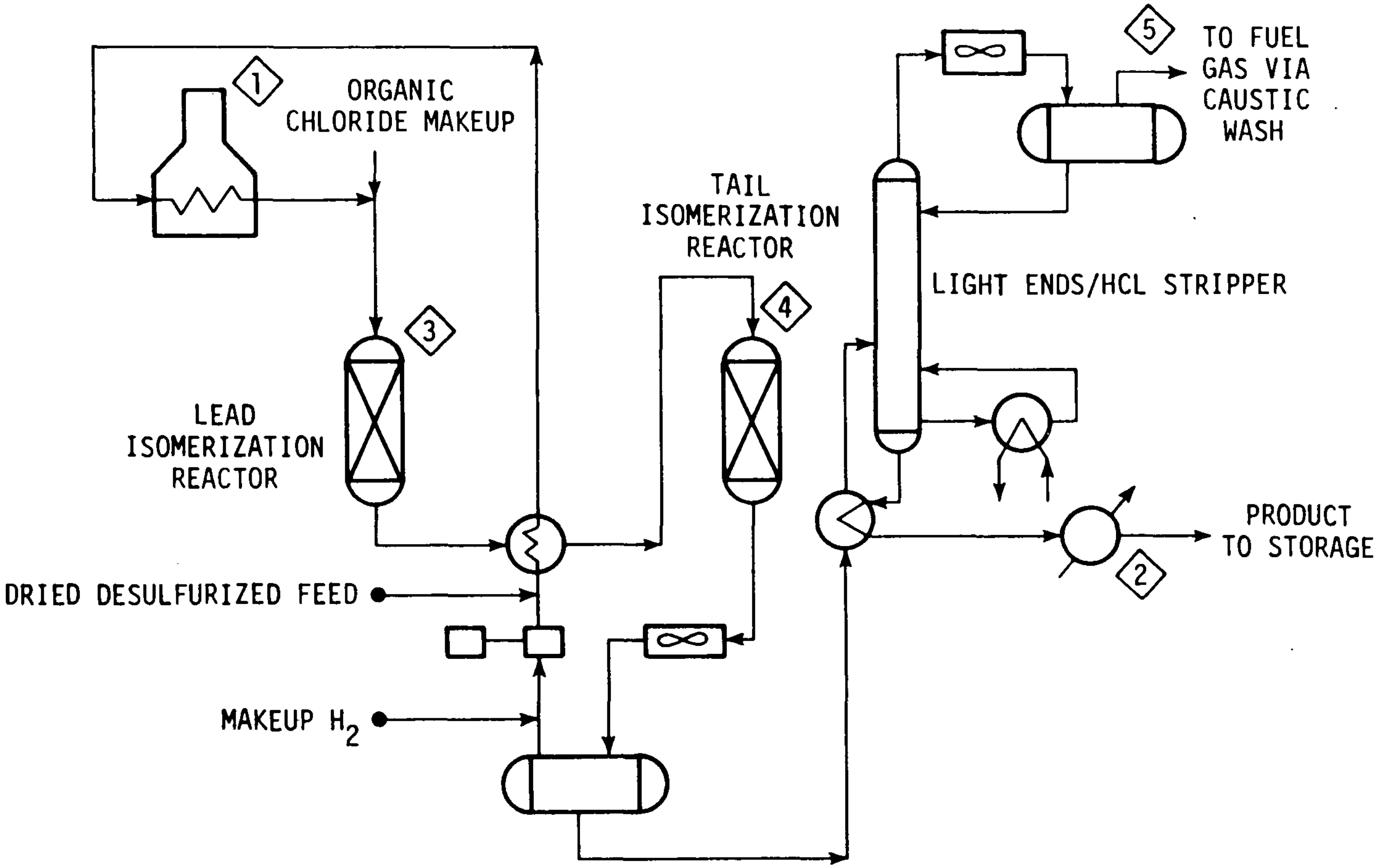

Figure 4.7-2. Pentane/hexane isomerization process flow.

up to 2 years have been observed, but should accidental deactivation occur, the catalyst can be easily regenerated and reactivated to full activity.

The reactor pressure ranges from 2170 to 7000 kPa (300 to 1000 psig), with operation usually around 300 psig. The lead reactor temperature ranges from 150° to 260°C (300° to 500°F), and the tail reactor temperature ranges from 120° to 205°C (250° to 400°F).[1] The lower temperature is more favorable for isoparaffin yields.

### 4.7.2 Emission Sources

Isomerization is a closed process. Because the feed must be nearly sulfur-free to protect the catalyst, the gas streams are not contaminated with hydrogen sulfide.

Combustion gases from the fired heaters (Figure 4.7-1, point 1, and Figure 4.7-2, point 1) are a source of particulate and sulfur oxide emissions.

Isomerization also can emit hydrogen chloride. Organic chloride added to the feed to increase catalyst activity eventually shows up in the vapor stream as hydrogen chloride. Most of the hydrogen chloride is recycled to the process, but some of it is eliminated with the stabilizer overhead. (Figure 4.7-1, point 2, and Figure 4.7-2, point 2). This gas should be treated to remove the hydrogen chloride before the gas is burned as fuel.

Unlike the catalysts of fluid catalytic cracking, which are regenerated continuously, isomerization catalysts are regenerated only periodically. Figure 4.7-1, point 3, and Figure 4.7-2, points 3 and 4, show the emission points during regeneration. The isomerization catalyst is very stable and can be expected to last at least 2 years before regeneration. During regeneration, the introduction of a steam and air mixture to the catalyst bed caused combustion of the coke deposits. This combustion may produce carbon monoxide (CO) and unoxidized hydrocarbons. Some refiners replace the spent catalyst by returning it to the catalyst manufacturer rather than regenerating. Thus, the catalyst is not an emission source at these refineries.

The California Air Resources Board found that isomerization units contribute 11 percent of the total fugitive emissions at a refinery. Among the devices tested, 14 percent of the valves leaked and none of the flanges leaked.

### 4.7.3 Emission Controls

Emissions from process heaters can be reduced by desulfurization of the fuel. Generally, particulates can be controlled by proper operating practices and adjustment of the air-to-fuel ratio.

The fuel gas stream goes to caustic treating for hydrogen chloride removal. The caustic solution neutralizes the hydrogen chloride. The resulting calcium chloride is then disposed of by landfilling.

The principal control measure for hydrocarbons in catalyst regeneration flue gas is incineration in a heater firebox, or use of a smoke plume burner. These devices reduce hydrocarbon emissions to negligible quantities. Since these emissions are infrequent and insignificant in volume, control devices are not commonly applied to regeneration offgases. Many refiners return the spent catalyst to the manufacturer and replace it with fresh catalyst, thereby reducing hydrocarbon emissions from regeneration.

Fugitive emissions can best be controlled by adherence to a good maintenance program.

### 4.7.4 Instrumentation

The type of feed and flowrate are monitored. As discussed earlier, the type of feed results in different process flow schemes. The feed rate should be compared with design values. A flowrate lower than the design value may indicate that the reactor will soon be regenerated.

Reactor temperatures are very important. Temperatures outside the design range may indicate that hydrocracking is occurring. Deposition of coke on the catalyst necessitates regeneration, which causes emissions. As discussed earlier, low temperatures lead to poor yields of product.

The inspector should monitor the organic chloride makeup rate. A high rate may indicate a high concentration of hydrogen chloride in the stabilizer overhead or deactivation of the catalyst. With high concentrations of hydrogen chloride in the stabilizer overhead, the caustic wash unit should be checked to determine whether it is designed to reduce these higher concentrations to acceptable concentrations. When the catalyst is deactivated, it must be regenerated or replaced.

### 4.7.5 Startup/Shutdown/Malfunctions

Since the stream processed in the isomerization unit must be nearly free of sulfur, startups and shutdowns should not cause significant sulfur emissions. Subsection 4.7.2 discusses the negligible quantity of carbon monoxide and hydrocarbon emissions from regeneration. The frequency at which the catalyst is regenerated is determined by the quality of the feed and type of feed. Therefore, estimates of downtime for regeneration are not available.

On the average, this unit is shut down for general inspection once each year of operation. Average downtime for a scheduled shutdown is 10 days.

The shutdown procedure follows a sequence of venting to the refinery flare, stopping the feed flow, removing heat, and flushing with inert gas, followed by flushing with air. In startup, air is displaced with inert gas, which is then heated and the process flow starts. The unit is pressurized when at temperature.

Malfunctions on an isomerization unit include a loss of hydrogen due to a compressor failure or to a malfunction at the hydrogen plant; loss of isomerization feed due to a malfunction upstream (i.e., hydrogen desulfurization unit, crude unit); and loss of temperature control. The frequency of malfunctions varies with the type of feed, quality of the feed, refinery maintenance practices, and reliability of upstream processes. Generally, emergency downtime for this unit averages 5 days.

### 4.7.6 Reference

1. Refining Process Handbook. Hydrocarbon Processing, 57(9): 170-172, September 1978.

## 4.8 POLYMERIZATION[1-5]

Like alkylation, polymerization is a formation process used to produce a high-octane gasoline from refinery gases. In polymerization, however, only the olefinic gases in the feed react, linking together to form olefinic liquid. Any paraffinic gases in the feed pass through the process unchanged. Unlike the alkylation unit, which requires an olefin and isoparaffin for feed, the polymerization unit requires two olefins. An example of a polymerization reaction is two molecules of isobutylene ($C_4H_8$, an olefin) combining to form one molecule of a branched-chain octylene ($C_8H_{16}$). With the rising importance of olefins as petrochemical feedstock, polymerization is being phased out as a refining process. It is discussed here because some units are still used by refiners.

### 4.8.1 Process Description

Polymerization is a continuous, catalytic conversion of olefin gases to liquid condensation products. The feed usually consists of propylene and/or butylene from cracking operations, which is processed to form polymer gasoline for motor gasoline blending. The feed is usually caustic washed and water washed to remove sulfur and nitrogen compounds.

The treated, olefin-rich feed stream is brought into contact with a catalyst consisting of a solid support impregnated with solid phosphoric acid or liquid phosphoric acid.

#### Polymerization with Solid Phosphoric Acid

The olefin-rich feed enters the top of a fixed catalyst bed. Pellets impregnated with the phosphoric acid catalyst are packed in the fixed reactor, which operates at temperatures between 175° and 225°C (350° and 435°F) and pressures of 2860 and 8375 kPa (400 to 1200 psig), depending on the feedstock and desired octane rating of the product. The exothermic reaction temperature is controlled in a chamber reactor using depropanizer overhead as recycle to the feed and as the quench stream between catalyst chambers. Figure 4.8-1 illustates the process flow of a polymerization unit with a solid phosphoric acid catalyst in a chamber reactor. Addition of the depropanizer overheads to the feed reduces the olefin concentration, with the result that less heat is produced in the polymerization reaction.

The reactor effluent flows to the depropanizer, where propane and lighter gases are removed overhead. The depropanizer bottoms flow to the debutanizer, where butane is removed overhead and the product, polymer gasoline, is removed as bottoms.

### Polymerization with Liquid Phosphoric Acid Catalyst

The olefin feed is caustic washed for removal of hydrogen sulfide and mercaptans, then water washed for removal of nitrogen compounds. Figure 4.8-2 illustrates the flow of this process. The liquid phosphoric acid catalyst is brought into intimate contact with the hydrocarbon feed in the reactor, which operates at temperatures of 150° to 205°C (300° to 400°F) and pressures of 1135 to 2860 kPa (150 to 400 psig). The hydrocarbon polymer and acid from the reactor are separated in a settler vessel, and the acid is returned to the reactor after cooling. The hydrocarbon from the settler is caustic scrubbed to protect the product recovery equipment from acid carryover. In normal operation, all of the acid is removed from the hydrocarbon stream in the settler, and consumption of caustic is negligible. The hydrocarbon stream then flows to the stabilizer, from which liquid petroleum gas is recovered overhead and the product, polymer gasoline, is recovered as bottoms.

## 4.8.2 Emission Sources

The polymerization unit is a potential source of sulfur, phosphoric acid, and volatile organic emissions.

The main source of sulfur emissions is the caustic washing section of the process, which removes mercaptans and hydrogen sulfide from the feed (Figure 4.8-1, point 1; Figure 4.8-2,

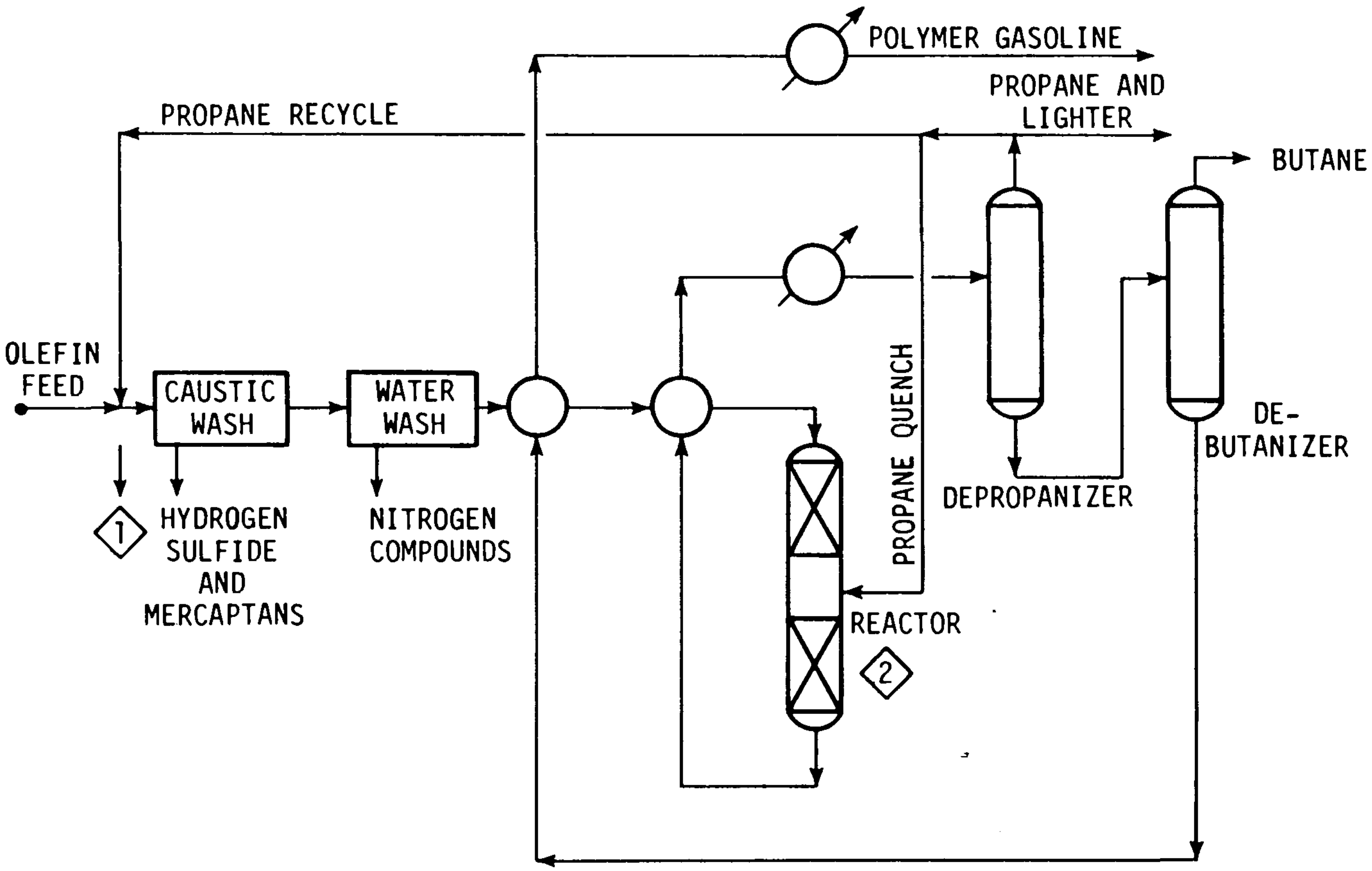

Figure 4.8-1. Process flow of polymerization with solid phosphoric acid catalyst.

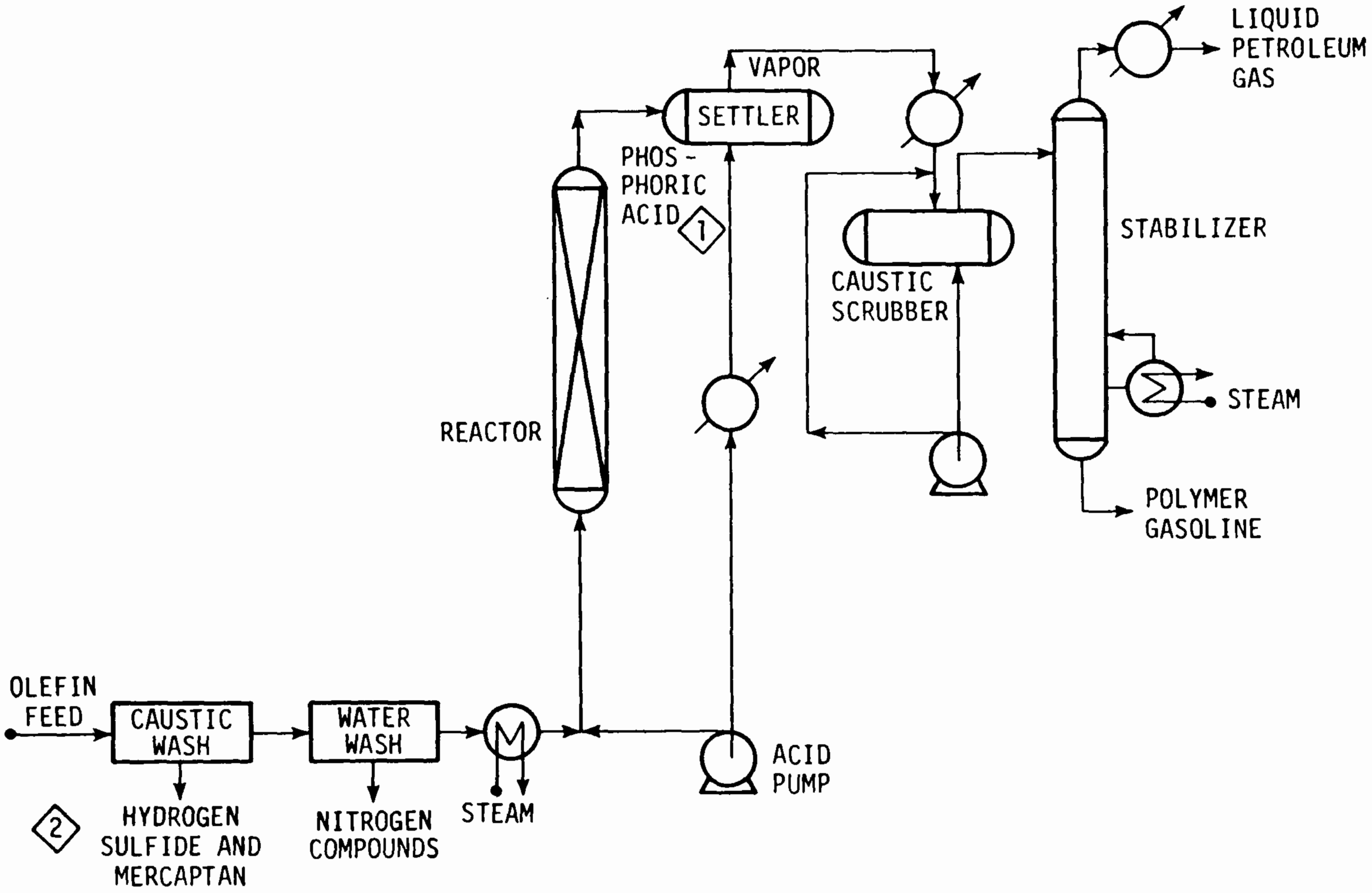

Figure 4.8-2. Process flow of polymerization with liquid phosphoric acid catalyst.

point 1). Sulfur emissions occur when the sulfur content of the feed exceeds the design value for the caustic washing section.

In the solid phosphoric acid process, the only waste stream is the spent catalyst (Figure 4.8-1, point 2). This spent catalyst contains volatile organics and phosphoric acid. The catalyst must be replaced periodically, and it is usually more economical to dispose of it than to regenerate it. Disposal of the catalyst causes a minimal amount of emissions.

In the liquid phosphoric acid process, the acid may carryover from the settler to the liquid petroleum gas and polymer gasoline. The caustic scrubber neutralizes these potential acid-saturated organic emissions.

The process is a closed system with no vents to the atmosphere. Some fugitive emissions may occur. The California Air Resources Board did not include this unit in its study, and the sources of these fugitive emissions have not been identified.

### 4.8.3 Emission Controls

Because this process is essentially a closed system with no vents to the atmosphere, it is not equipped with typical pollution control devices such as a CO boiler.

The sulfur emissions are essentially eliminated by caustic washing. The resulting calcium sulfate can be disposed of in a landfill.

Emissions of hydrocarbon and acid from catalyst disposal can be reduced by minimizing the number of turnarounds on the unit and by use of a flare. The catalyst must be regenerated if it comes in contact with nitrogen; therefore, the water washing must satisfactorily remove the nitrogen compounds.

Only orthophosphoric acid ($H_3PO_4$) is a catalyst; metaphosphoric acid ($HPO_3$) is inactive. Water is added to the feed to form orthophosphoric acid. Too much water will turn the solid catalyst to mud and render it corrosive. Temperature control is also important because high temperatures cause cracking, which leads to coke deposits on the catalyst, rendering it inactive.

High temperatures also dry the catalyst and reduce its activity. When the catalyst is regenerated, volatile organic emissions should be flared. A discussion of the regeneration procedure follows in Subsection 4.8.5.

The liquid catalyst can be replaced continuously without interrupting plant operation.

The liquid acid carryover is effectively controlled by the caustic scrubber, in which the lime neutralizes any acid.

### 4.8.4 Instrumentation

Temperatures of solid catalyst reactors range from 175° to 225°C (350° to 435°F), and of liquid catalyst reactors, from 150° to 205°C (300° to 400°F). Temperature depends on the type of feed and desired octane rating of the product. As discussed earlier, high temperatures cause cracking and deposition of coke on the catalysts, and thereby necessitate regeneration. Regeneration or replacement of the catalyst generates emissions of acid-saturated hydrocarbons. The temperature is monitored, as are feed type and product octane rating. Since these parameters are interrelated, the inspector may note that time between turnarounds depends on one of them.

### 4.8.5 Startup/Shutdown/Malfunctions

The liquid acid process can be started up rapidly, typically in 1 to 2 hours, because a liquid catalyst circulates through heat exchangers and thus facilitates rapid but controllable heating, with no need for propane recycle.

The reactor using a solid acid catalyst takes 8 to 16 hours for startup. Most of the time is for heating the catalyst bed and establishing propane for recycling.

Shutdown of the liquid catalyst process takes about 4 hours; shutdown of the solid catalyst process takes 6 to 8 hours to cool the reactor and unload the catalyst. Regenerating the solid catalyst bed takes 10 to 16 hours. Regeneration is achieved by passing air at 340°C (650°F) into the reactor at such a rate that the temperature does not exceed 510°C (950°F) (hot spots cause volatilization of the acid). The catalyst is hydrated by maintaining an atmosphere of steam at 260°C (500°F). When air is passed over the catalyst during regeneration, the volatile organics leave the system and should be flared.

Common malfunctions include loss of feed due to an upset at an upstream unit, pump failures, reactor feed distribution problems, and temperature control problems. The frequency of the malfunctions varies with the type of feed, operating conditions used to produce the needed octane of the polymer gasoline, refinery maintenance practices, and reliability of upstream processes. Because each malfunction involves a different downtime, emergency downtime for this unit cannot be reliably estimated.

### 4.8.6 References

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2. Chemical Technology: An Encyclopedic Treatment Vol. IV. Petroleum and Organic Chemicals Barnes and Noble Books, New York, 1972. p. 54.

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# TREATING

## 4.9 CRUDE AND PRODUCT TREATING[1,2]

Most refineries include some form of crude desalting as the first step. Inorganic salts, which can cause corrosion, plugging of exchangers, and coking of furnaces, are removed from crude oils by electrical and chemical desalting processes. These processes also remove arsenic and other trace metals that can poison the catalysts in later processes.

Many commercial treating processes are available to remove undesirable impurities, such as acids and sulfur compounds, and to improve color, odor, and stability of refinery petroleum products. The principal treating processes are chemical sweetening, lube treating, and hydrotreating. Hydrotreating is discussed in Section 4.10.

### 4.9.1 Process Description

Crude desalting and the two treating processes of chemical sweetening and lube treating are described in this section.

### Crude Desalting

Electrostatic and chemical desalting processes remove inorganic salts and trace metals from crude oils. The electrostatic desalting process, which is more widely used, is discussed here in greater detail.

In electrical desalting, water and demulsifier chemicals are added to dissolve impurities from the crude oil. The crude, water, and chemical mixture is then exchanged with products to raise its temperature. The heat lowers the surface temperature of the oil causing the water to agglomerate. The mixture then flows through a mixing valve resulting in an emulsion. The emulsion is then introduced to a treating vessel, where an electrostatic field causes the water droplets to agglomerate and settle to the lower portion of the vessel. A small quantity of a demulsifying chemical is sometimes added to treat crude or slop oils that have abnormally high concentrations of suspended solids. The treated crude flows to the atmospheric distillation

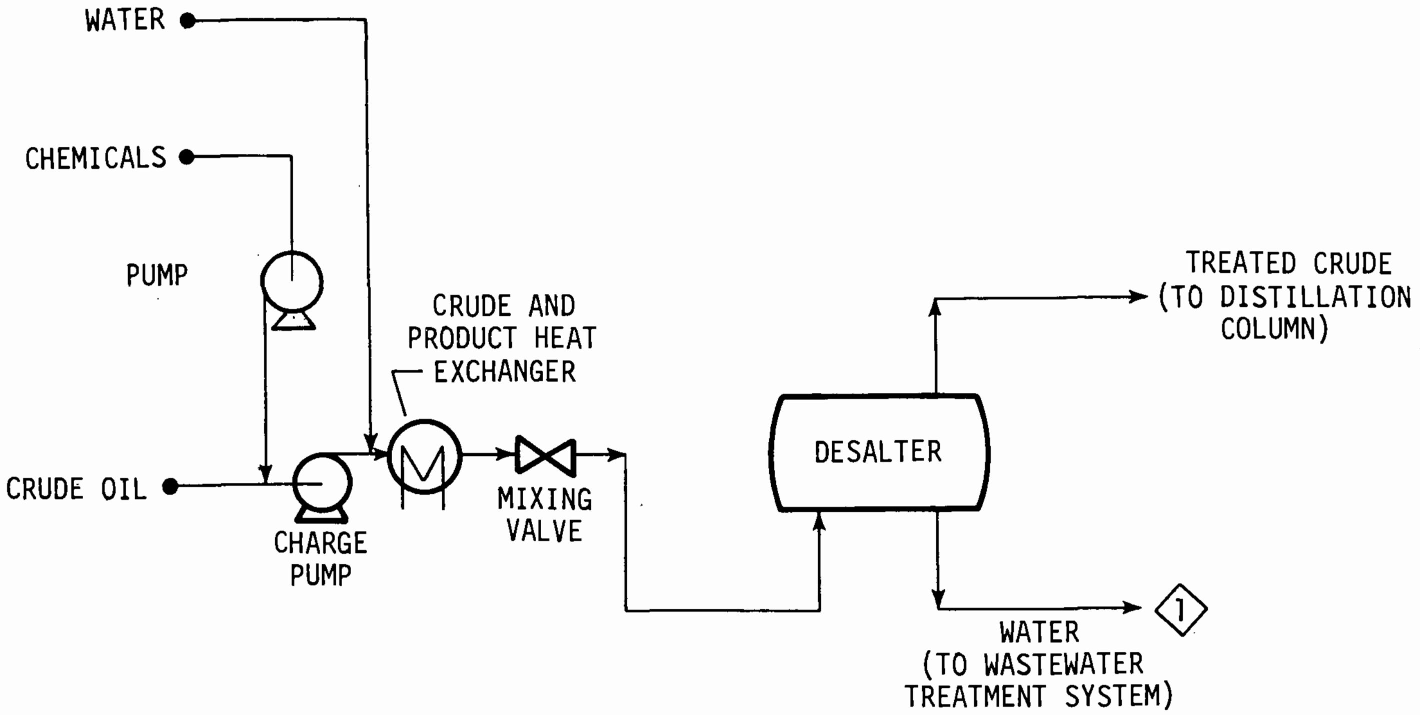

Figure 4.9-1. Flow diagram of desalting process.

column. The water containing salt, flows to the wastewater treatment facility. Figure 4.9-1 illustrates this matter.

In chemical desalting, inorganic salts are separated from oil by water washing in the presence of chemicals. The chemicals that are used depend on the type of salts and the nature of the crude oil.

The chemicals are added to the crude oil upstream from the charge pump so that they are mixed thoroughly with the oil. Fresh water is added to dissolve the salts not already in solution. The crude oil and fresh water are passed through a mixing valve to form an emulsion and assure good contact. In some cases, water is added upstream from the charge pump so that the emulsion is formed by the pump impellers. The emulsion of water in oil is then heated before it enters the settler to a temperature that ranges from 65° to 180°C (150° to 350°F), depending on the type of crude being processed. The surface tension of the oil is lowered by heat, thus allowing water particles to coagulate. Similarly, the reduced viscosity of the oil offers less resistance to separation of the salt solution.

The settler, which may be equipped with baffles to reduce flow turbulence and channeling, has a settling time of from 20 to 60 minutes. The treated crude oil flows from the top of the settler for further processing in a distillation column. The salts are withdrawn as a solution in water and discharged to the wastewater treatment system.

A two- or three-stage electrostatic or chemical desalting process may be used to reduce the salt content of crude oil before it enters the crude distillation tower. The increased investment cost for multiple stages is offset by reduction in corrosion, plugging, and catalyst poisoning in downstream equipment.

## Chemical Sweetening

Chemical sweetening improves the color and odor of petroleum products by eliminating mercaptans (R-SH; SH is a thiol group attached to an organic alkyl radical such as $CH_3$ or $C_2H_5$), $H_2S$, and dissolved free sulfur. The three most common chemical sweetening processes are solvent extraction, Bender sweetening, and oxidation sweetening.

The original solvent extraction process for sulfur reduction was simple caustic washing. Most of the patented processes are modifications of caustic washing to make thiols more soluble in the caustic solution. Some of the solvent extraction processes, primarily used for gasoline treating, are briefly described below.

> Solutizer process
>
> In this process, the sour gasoline is contacted countercurrently in the extraction column with a "solutizer" solution--a 25 percent caustic solution containing a small amount of solutizing agent such as potassium isobutyl rate. The solutizing agent makes thiols more soluble in caustic solution and enables complete removal of thiols from gasoline.
>
> Unisol process
>
> The Unisol or caustic methanol process uses methanol at the center of the packed treating column and caustic soda throughout the entire length of the column. Sour gasoline is passed through this column to extract $H_2S$ and mercaptans. Small amounts of methanol are lost with the gasoline. The methanol must be distilled after it (and mercaptans) has been steam stripped from the caustic.
>
> Caustic washing
>
> In this process, sour gasoline is contacted with sodium, calcium, or magnesium hydroxides for removal of $H_2S$ and mercaptans. Caustic solutions ranging from 5 to 15 percent are used.

Bender sweetening is used to treat such distillate streams as light naphtha, gasoline, kerosene, and No. 2 fuel oil. It is especially effective for the treatment of jet fuel. Sweetening is accomplished by converting mercaptans to disulfides in the presence of a fixed-bed catalyst. Figure 4.9-2 is a flow diagram of a typical Bender sweetening process.

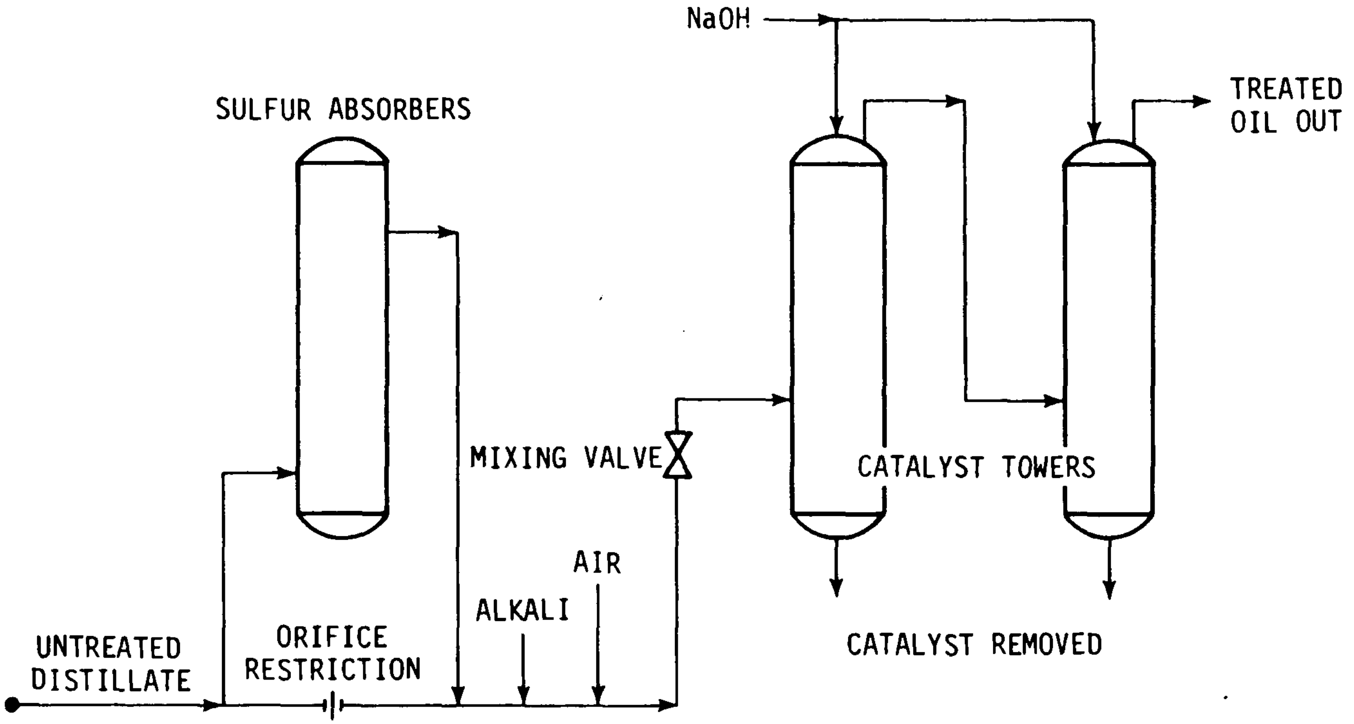

Figure 4.9-2. Flow diagram of Bender sweetening process.

The untreated distillate is passed through the sulfur absorber to remove $H_2S$ from the feedstock by caustic treatment. Sulfur, small amounts of caustic solution, and air are added to the distillate. This mixture is then passed over a bed of solid catalyst in two catalyst towers. The caustic soda solution enters the top of each tower. A small amount of caustic solution is added to the distillate to maintain the effluent in a slightly alkaline state.

Oxidation sweetening converts the sulfur in thiol to disulfide. The most common oxidation sweetening process is the Merox process, which is discussed in detail in the following paragraphs. Other processes are doctor treating (sodium plumbite the oxidizing agent); lead sulfide sweetening (lead sulfide acts as a catalyst and thus may be cycled as an oxidizing agent); and copper sweetening (cupric chloride used as the oxidizing agent). These three processes are not very common; but can be used to convert sulfur in thiol to disulfide. Complete removal of sulfur, however, is important to increase the effectiveness of tetraethyl-lead (gasoline additive to improve octane number) and to reduce corrosion by $SO_2$ or $SO_3$ in the exhaust pipes of cars.

The highly successful Merox process can be used either as a sweetening process (converting thiols to disulfides, which remain in the product) or as a solvent extraction process that reduces the amount of sulfur. Both operations can be conducted on a single feed material. Figure 4.9-3 is a flow diagram of a typical Merox process.

The sour gasoline is contacted with the caustic solution containing the Merox catalyst to extract the mercaptans. The extracted gasoline is then sweetened by reacting with air in the presence of Merox-containing caustic solution. The extracted product passes through a settler, where the Merox solution and the sweetened gasoline are separated. The sweetened gasoline is sent to storage and the Merox solution is recycled to the Merox sweetener mixer.

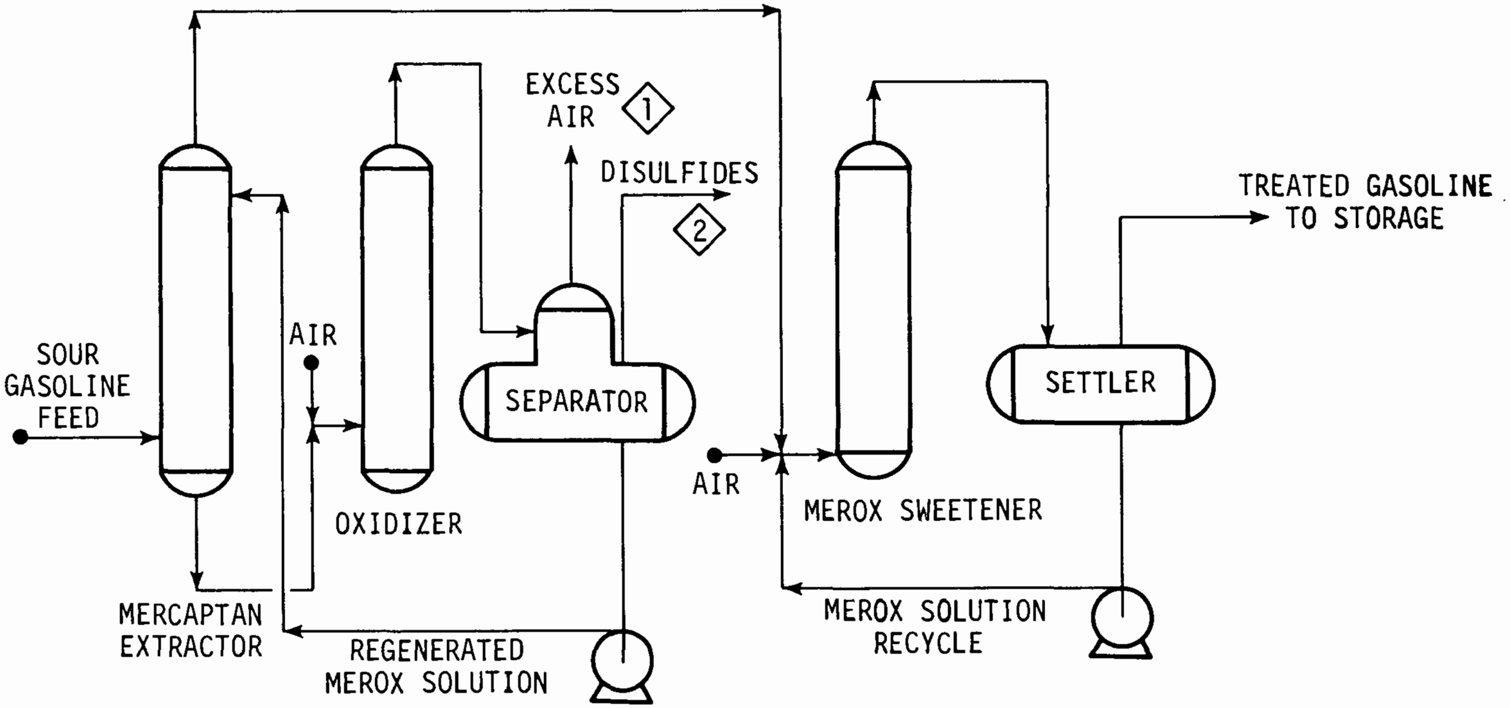

Figure 4.9-3. Flow diagram of Merox process.

The Merox solution used in the extraction is mixed with air and regenerated in the oxidizer. In the separator, the disulfides (which are insoluble in the caustic) are separated as an oil-disulfides layer, and the excess air is vented to the atmosphere. The regenerated Merox solution is returned to the extractor.

A major advantage of the Merox process is the reduction of operating costs by eliminating the large amount of steam needed for caustic regeneration in the older sweetening processes. In the Merox process, caustic regeneration consists only of introducing air and then settling. The heating and stripping operations used in most cyclic extraction processes are not needed.

Sweetening alone is adequate for feedstocks having moderate or low thiol content, as with catalytic cracked gasoline. Both Merox sweetening and extraction, however, are used for feedstocks having high thiol content; light straight naphthas are an example.

## Lube Treating

Solvent refining processes are used to improve the viscosity index and the paraffin content of lubricating oil stocks. Many solvents--such as furfural, phenol, cresylic acid/propane (DUO-SOL), liquid $SO_2$, methyl isobutyl ketone (MIBK), and propylene/acetone--have been used in lube treating processes. In each case, oil and solvent are first contacted counter-currently in a packed column or in a series of tanks, and the refined oil and extract layers are then separated. The recovery of solvent from the oil and extract layers is a major part of the solvent recovery process, and it differs according to the boiling point of the solvent used.

The common lube treating processes are phenol extraction and furfural refining.

Phenol extraction improves the viscosity index and color of lubricating oils. It also reduces the tendency of the oils to form carbon and sludge. Figure 4.9-4 is a flow diagram of a phenol extraction process.

The heated feedstock (distillates or residual feedstock) flows through a phenol absorber tower to recover the small amount of phenol from extract and raffinate streams. The feed is pumped from the absorber to the centrifugal extractor. The raffinate stream is heated to about 290°C (550°F) and is flashed in the raffinate furnace. Phenol vapor from this section is condensed and stored. The raffinate oil flows down in a bottom section of a raffinate tower in which it is steam stripped to remove solvent. The treated oil is withdrawn from the bottom and stored. Steam and solvent vapors flow from the stripping section to vacuum equipment.

The extract stream from the centrifugal extractor is heated and flows to a drying tower, in which all the water is removed as a phenol-water azeotrope. This vapor is condensed and enters the phenol-water drum. Dry extract solution is pumped from the bottom of the extract flash tower. Most of the phenol is vaporized in the extract furnace. The remaining extract solution flows from the extract flash tower to a extract stripper, in which the last traces of solvent are removed for storage.

Furfural refining is used to extract undesirable components from petroleum lubricating oil stocks in order to produce high-quality oils. Furfural has a high solvent power for components that are relatively unstable to oxygen, and for such undesirable materials as resins and sulfur compounds. Figure 4.9-5 is a flow diagram of a typical furfural extraction process.

The untreated oil and furfural solvent are contacted in a continuous countercurrent extractor. Furfural enters the extraction tower at the top, and the oil enters at some intermediate point in the tower. The refined oil mixture rises to the top and the extract oil settles to the bottom. The temperature of the furfural depends largely upon the miscibility of the furfural and the oil being refined. A substantial temperature gradient is maintained between the 120°C (250°F) at the top of the tower and

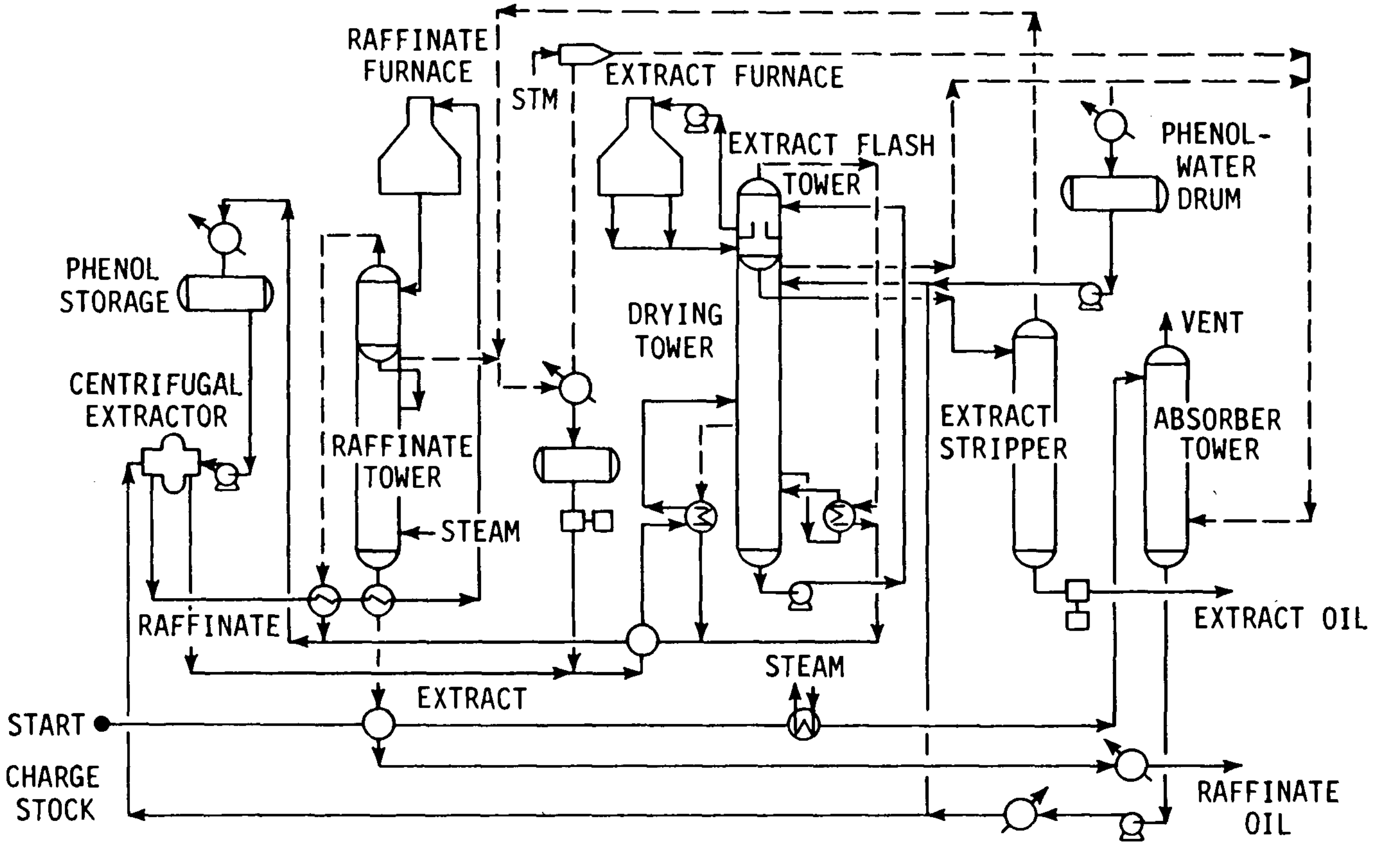

Figure 4.9-4. Flow diagram of phenol extraction process.

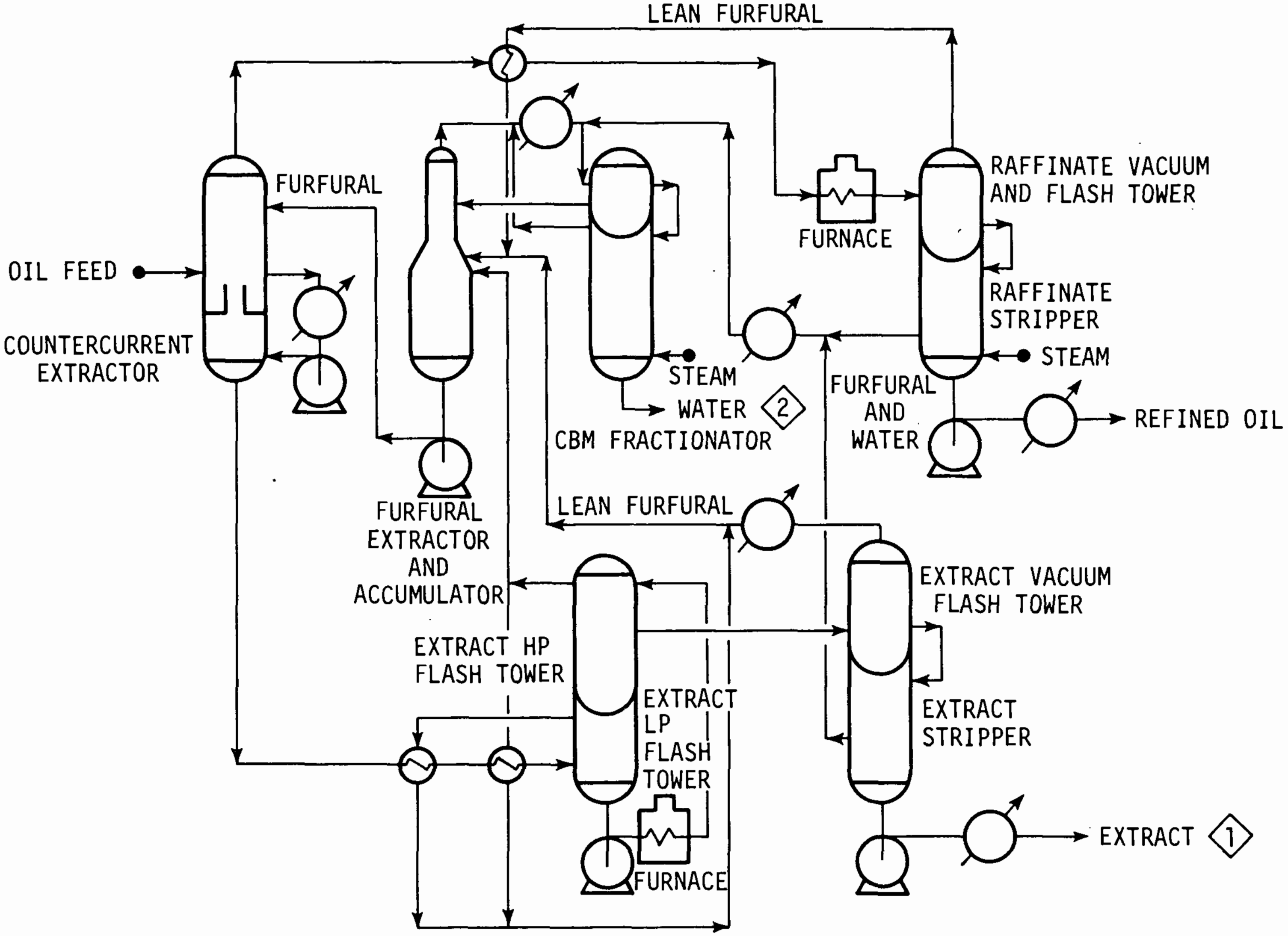

Figure 4.9-5. Flow diagram of furfural refining process.

the 60°C (140°F) at the bottom of the tower by indirect, external water coolers. Extraction generally is accomplished by passing the furfural in dispersed phase downward over Raschig ring nests through the prevailing oil phase. Other types of extraction equipment (towers containing rotating discs or stationary baffles; centrifugal extractors) are also used.

Both the refined oil and the extract are heated in furnaces, fractionated, and finally stripped for the removal of furfural. Most of the furfural, nearly pure, is distilled from the extract solution; the rest is associated with large amounts of water from the stripping stream. When the steam-furfural mixture is condensed, two immiscible solutions are formed, one rich in furfural and the other rich in water. The wet furfural from all sources is collected, condensed, and delivered to the accumulator. The furfural-rich solution from the accumulator is distilled for removal of water, and the pure furfural is pumped back to the countercurrent extractor to complete the process loop. Similarly, the water-rich solution is fractionated for the recovery of furfural in the form of a constant boiling mixture (CBM), which is returned to the accumulator.

The operating conditions and the yields of raffinate (refined oil) depend upon the nature of the charge stock and the degree of refining desired.

### 4.9.2 Emission Sources

Information about emissions will be given only for the major processes of electrostatic desalting, the Merox process, and furfural refining.

In electrostatic desalting, the major emission source is a water effluent stream (Figure 4.9-1, point 1) containing dissolved chemicals mainly composed of chlorides, sulfates, and bicarbonates. Small amounts of oil and sulfides are also found.

In the Merox process, the two emission sources are the excess air stream leaving the separator (Figure 4.9-3, point 1), which may contain disulfides, and the oil-disulfide product stream leaving the separator (Figure 4.9-3, point 2), which can be a source of $SO_2$ emission if the oil-disulfide product is incinerated.

In furfural refining, the extract stream (Figure 4.9-5, point 1) is relatively rich in naphthenic, aromatic, and unsaturated hydrocarbons; it also contains large amounts of sulfur. If extracts are burned in process heaters or boilers, a large volume of $SO_2$ will be emitted. The water effluent stream (Figure 4.9-5, point 2) leaving the CBM extractor can contain oil and furfural solution.

Atmospheric emissions are negligible, because the actual vapor pressure of the hydrocarbons in the lube oil process is very low.

### 4.9.3 Emission Controls

The water effluent stream leaving the electrostatic desalting unit is collected and sent to wastewater treatment. Impurities such as oil are removed by the primary treatment facility (API separator), and dissolved chemicals are removed by the secondary treatment facility (settling chambers and clarifiers).

The excess air stream from the Merox process, which may contain disulfide, is sent to an incinerator. The oil-disulfide product stream can also be burned in process heaters or incinerator. If there is a large volume of oil-disulfide product, however, the $SO_2$ emissions from the incinerator may require control.

The extract stream from furfural refining is usually cracked; it makes an excellent feed material for hydrocracking. If a refinery does not have a cracking plant, the extract portion of the oil can be burned in process heaters or boilers. It may also be used for certain services that are not too exacting, such as the lubrication of slow-moving, heavy machine parts.

### 4.9.4 Instrumentation

In electrostatic desalting, the temperature of the process stream entering the settler varies from 65° to 180°C (150° to 350°F) depending on the type of the crude. The temperature of this process stream must be controlled, because heat reduces the viscosity of the oil, giving less resistance to separation of salt solution. The surface tension of the oil is also lowered by heat, allowing water particles to coagulate.

In the Merox process, the flows of sour gasoline feed and of the regenerated Merox solution entering the mercaptan extractor are recorded and controlled. The flow of recycled Merox solution entering the Merox sweetener is also recorded and controlled.

In furfural refining, the temperature of oil feed entering the extractor is maintained at approximately 90°C (200°F) by heating it in the charge oil heater. The temperature of regenerated furfural solution entering the extractor is maintained at 105°C (225°F) by the furfural cooler. The furfural countercurrent extraction is carried out at atmospheric pressure.

The flows of charge oil and regenerated furfural solution are recorded and controlled.

### 4.9.5 Startup/Shutdown/Malfunctions

Shutdowns of the desalter unit are infrequent, because little maintenance is required. The unit can usually be bypassed and drained during a malfunction.

Shutdowns of the Merox unit are also infrequent. The catalyst is regenerated once every 2 to 3 years. During a malfunction, the sour gasoline is stored until the unit is back in operation.

### 4.9.6 References

1. Nelson, W. L. Petroleum Refinery Engineering. McGraw-Hill Book Company, New York, 1958. pp. 347-366.

2. Refining Process Handbook. Hydrocarbon Processing. September 1978. pp. 178, 188, 191, 196, and 212.

## 4.10 HYDROTREATING

Hydrotreating (or hydrodesulfurization) is an extremely versatile process that can be applied to straight-run products, cracked products, feedstocks to catalytic reforming and catalytic cracking, and lubricating oils. It has two purposes: the treatment of petroleum fractions to remove such impurities as sulfur, nitrogen, and metal compounds, thus preventing downstream corrosion and catalyst poisoning; and the treatment of products to improve color and odor. Hydrotreating is the most common process for pretreating catalyst reformer and catalyst cracker feedstocks to remove sulfur and nitrogen, which can poison the catalyst. This pretreatment prolongs catalyst life and the time between regeneration cycles in the reformer and the cracker. Hydrotreating is also used to sweeten and improve the color and stability of kerosene, jet fuels, and lubricating oils.

The wide range of hydrotreating processes that are available reflects these many applications. Among the processes are Autofining, Go-fining, Gulfining, Hydrofining, lube oil hydrotreating, Ultrafining, and Unionfining. Gulfining and Hydrofining processes are discussed in detail in the following section.

### 4.10.1 Process Description

#### Gulfining

Gulfining is a desulfurization process, licensed by Gulf Research and Development Company, that is capable of handling straight distillate or cracked stocks. Kerosene, light gas oils, light catalytic cycle oils, and stocks with similar boiling ranges are normally desulfurized on units designed for general light gas oil processing. Stocks with higher boiling ranges (heavy gas oils, full-range vacuum gas oils) require more severe conditions.

A simplified flow diagram of the Gulfining process is shown in Figure 4.10-1. The gas oil feed is mixed with makeup and

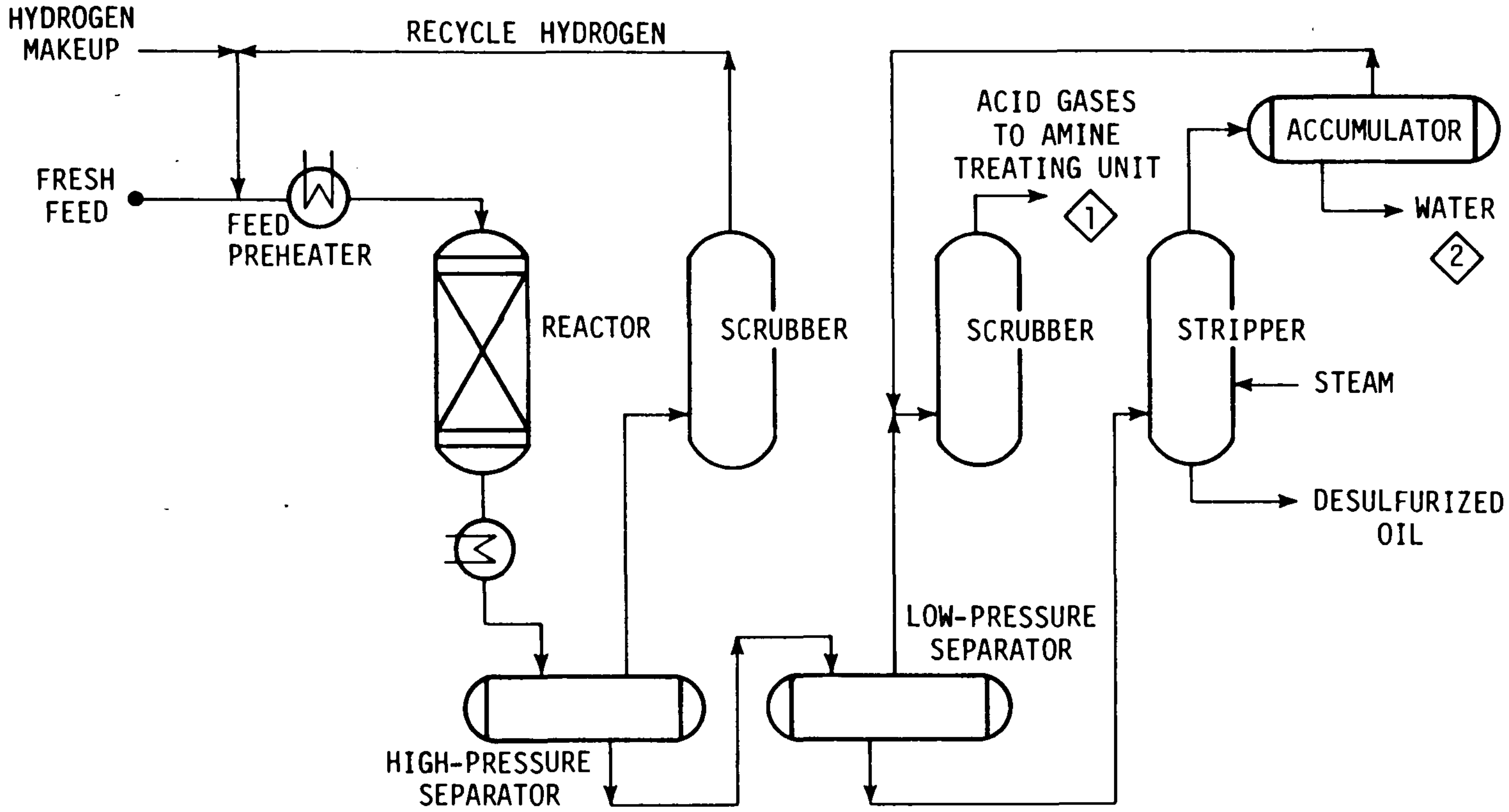

Figure 4.10-1. Flow diagram of Gulfining unit.

recycled hydrogen, and is heated before flowing into the fixed-bed reactor containing proprietary catalyst. Sulfur and nitrogen compounds are converted in this reactor to hydrogen sulfide ($H_2S$) and ammonia ($NH_3$). The reaction product is cooled and sent to a high-pressure separator (flash drum), where the hydrogen-rich stream is flashed from the reactor product and recycled. Oil from the bottom of the high-pressure separator is fed to the low-pressure separator (flash drum), where $H_2S$, $NH_3$, and light ends are recovered. The oil product from the low-pressure separator is fed to the steam stripper tower and stabilized by removal of light ends.

## Hydrofining

Hydrofining is a desulfurization process licensed by Exxon Research and Engineering Company. The catalytic cracker or coker naphthas can be partially hydrotreated to form stable desulfurized fuel, or they can be completely hydrotreated to remove sulfur, nitrogen, and saturate olefins to yield reformer feedstock or petrochemical-grade naphtha.

A simplified flow diagram of Hydrofining is shown in Figure 4.10-2. The gaseous-phase naphthas are mixed with hydrogen-rich gas and preheated to reaction temperature before entering the fixed-bed reactor. In the reactor, naphthas are contacted in the presence of hydrogen with a metallic oxide catalyst. The sulfur and nitrogen compounds break down to form $H_2S$ and $NH_3$. Some cracking of naphthas into lighter fractions will occur as a side reaction.

The hot effluent leaving the reactor is cooled before entering the high-pressure separator, where hydrogen is removed and recycled to the feed stream. The liquid from the separator is preheated before it enters the stripper. In the stripper, steam is injected to remove the acid gases from the product.

The overhead stream, which consists of acid gases and steam, flows to a condenser and accumulator; the steam is returned to

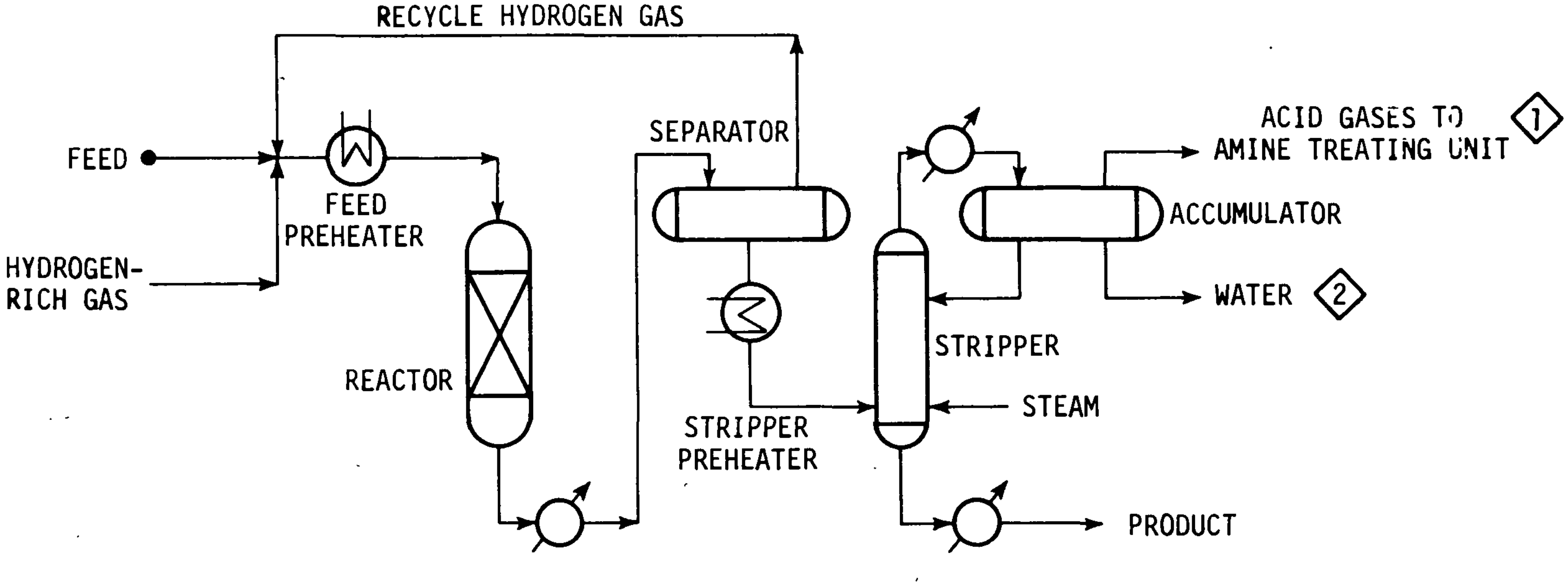

Figure 4.10-2. Flow diagram of Hydrofining unit.

the stripper column as a reflux. The acid gas stream leaving the overhead accumulator then proceeds to the amine treating unit.

The operating conditions of the Gulfining and Hydrofining units can vary widely depending on the feed composition. The reactor temperature varies between 290° and 425°C (550° and 800°F) and the reactor pressure varies between 1480 and 10,440 kPa (200 and 1500 psig). The higher temperatures and pressures are used during severe operations, such as the treating of high-boiling, highly contaminated, or unsaturated stocks. Hydrocracking occurs under these conditions, and hydrogen saturates the cracked material. The oxides of cobalt, molybdenum, tungsten, or nickel can be used as catalyst.

### 4.10.2 Emission Sources

The Gulfining and Hydrofining units have two possible emission sources. The gas stream leaving the overhead of the accumulator (Figure 4.10-1, point 1; Figure 4.10-2, point 1) contains such impurities as $H_2S$ and $NH_3$. Water leaving the accumulator (Figure 4.10-1, point 2; Figure 4.10-2, point 2) also contains $H_2S$ and $NH_3$. During regeneration of the catalyst, a steam-air mixture is used to burn carbon off the catalyst. This procedure releases large quantities of carbon monoxide for a short period. The catalyst is regenerated about twice a year. The high operating pressure also creates a potential for hydrocarbon leaks from these units.

### 4.10.3 Emission Controls

The gas stream leaving the overhead accumulator of the Gulfining and the Hydrofining processes is sent to an amine treating unit to remove $H_2S$ and $NH_3$. The treated gas, which contains light ends and hydrogen, then proceeds to the refinery fuel gas system. Water leaving the accumulator is treated in a sour water stripper to remove $H_2S$ and $NH_3$.

### 4.10.4 Instrumentation

The principal variables in the Gulfining and Hydrofining processes are reaction temperature and hydrogen partial pressure. In general, sulfur removal increases as temperature and hydrogen partial pressure are increased.

The temperature of feed entering the reactor is regulated between 290° and 425°C (550° and 800°F). The desulfurization level increases with higher temperature. Coking reactions become much more prevalent, however, when operating temperatures approach 415°C (780°F). Coke is deposited on the catalyst, reducing catalyst activity and necessitating regeneration, which results in emissions.

The temperature of feed also depends on the type of catalyst used. High-activity catalysts are available to increase desulfurization capabilities and to decrease feed temperature, thus reducing fuel consumption. The reduced fuel consumption causes fewer particulate and sulfur dioxide emissions from heaters.

Hydrogen partial pressure affects desulfurization levels in relation to the boiling range of the feed. For a given feed, there exists a point above which increased hydrogen partial pressure has little effect on desulfurization. Below this point, however, desulfurization drops off rapidly as hydrogen pressure is reduced. For each feedstock, the optimum reactor pressure is selected from the range of 1480 to 10,440 kPa (200 to 1500 psig), based on the duty required (percent desulfurization) and related operating variables.

### 4.10.5 Startup/Shutdown/Malfunctions

The Gulfining and Hydrofining units are shut down about twice a year to regenerate the catalyst.

During a malfunction, feed to the Gulfining and Hydrofining units is usually stored until the units are back in operation. Otherwise, the sulfur and nitrogen in the untreated catalytic reformer and catalytic cracker feedstocks would poison the catalyst.

## 4.10.6 References

1. Metzger, K. J., et al. Gulfining: A Flexible Distillate Desulfurization Process API Proceedings, 1971. pp. 72-82.

2. Nelson, W. L. Petroleum Refining Engineering. McGraw-Hill Book Company, New York, 1958. pp. 332-335.

3. Refining Process Handbook. Hydrocarbon Processing, September 1978. pp. 139.

## 4.11 WAX AND GREASE PRODUCTION

Petroleum waxes boil in the temperature range of lubricating oils and cannot be separated by distillation. Because waxes crystallize at low temperatures, they are undesirable in motor oils and must be removed. Waxes are classified according to physical form. Paraffin waxes have large crystals and are obtained from light lubricating oils. Microcrystalline waxes have small crystals and are obtained from residual oil and tank bottoms.

Most greases are formed by adding thickeners to lubricating oils. Common thickeners are calcium, sodium, aluminum, barium, lithium, and lead soaps. Calcium, barium, and aluminum soaps produce greases resistant to water; barium and lead soaps produce greases that are used in heavy duty service.[1]

### 4.11.1 Process Description

#### Solvent Dewaxing

In the solvent dewaxing process, the mixture of oil to be dewaxed and solvent is chilled. Wax separates out and can then be removed by filtration. Modern processes use special solvents, such as methyl ethyl ketone (MEK) in mixture with benzene and/or toluene, trichloroethylene, ethylene dichloride and benzene (Bari-Sol), propane, and urea. The MEK process, which is the most widely used, is discussed in detail in the following section.

Each of the components in the mixture of MEK, benzene, and toluene has a specific function. The MEK causes the wax to solidify in a crystalline and easily filterable form; the benzene and toluene increase the capacity of the solvent for dissolving oil. A typical MEK dewaxing process is shown in Figure 4.111.

The mixture of waxy oil feed and solvent is chilled to crystallize the wax. The chilling is accomplished in two stages in heat exchangers: first, by exchange with cold products; second, by the use of a refrigerant such as ammonia ($NH_3$). The

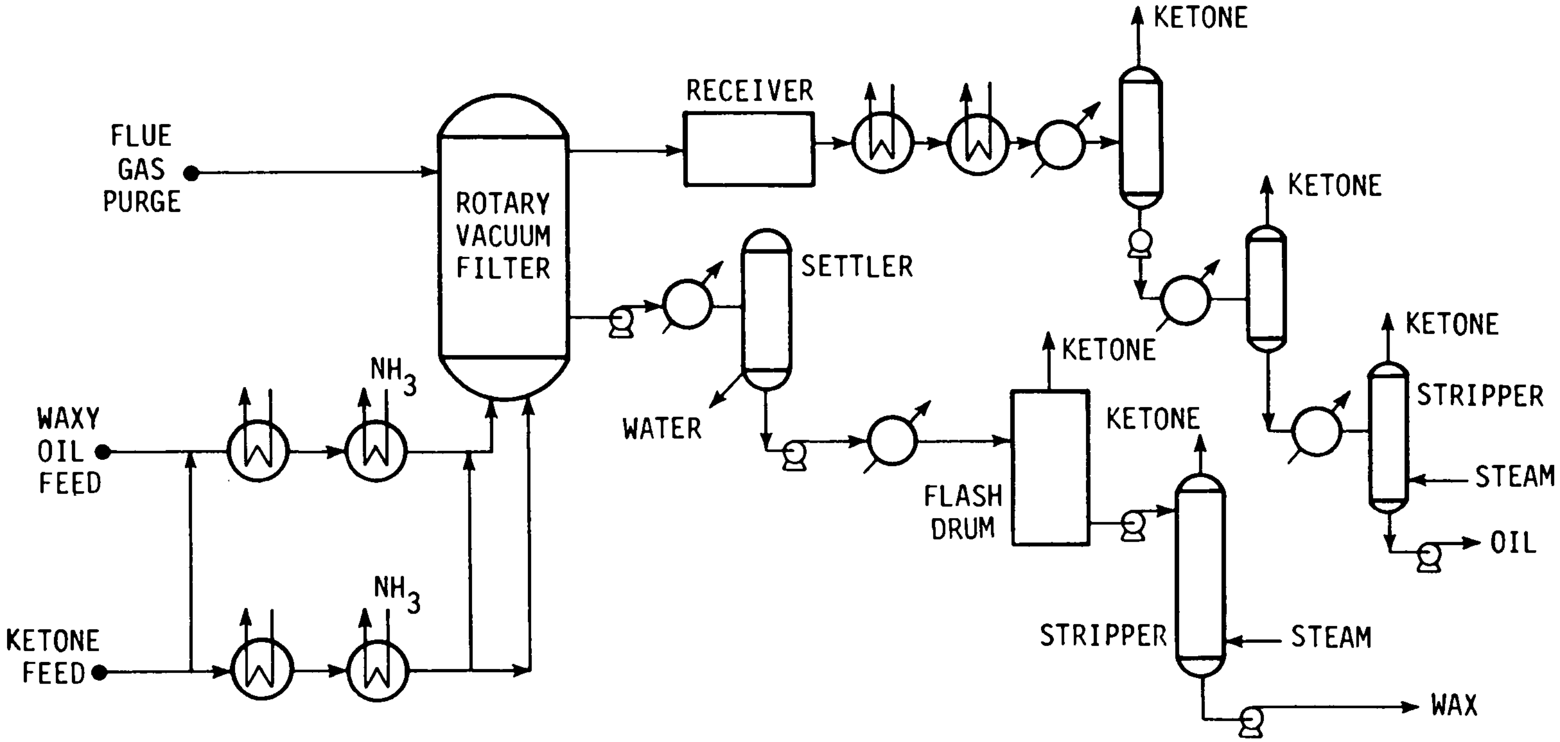

Figure 4.11-1. Typical dewaxing process using methyl ethyl ketone solvent.

chilled feed is then filtered continuously on rotary vacuum filters to separate the crystallized wax from the oil-solvent solution. A blowback of flue gas to the filters aids in drying and removing the wax cake. While the cake is still on the filter, it is washed with solvent to remove the retained oil. The wax cake, which contains water and also some solvent, is melted and charged to a settler where the wax and water are separated. The melted wax is sent to a flash drum and steam stripper to recover the solvent, which is recycled.

The oil-solvent solution is collected in a receiver and heated in exchangers. It is then pumped to a two-stage flash drum and steam stripper for recovery of solvent for recycle.

The dewaxing temperature is equal to a few degrees below the desired pour point. Low pressure exists throughout the process. The solvent/oil ratio ranges between 1:1 and 4:1.[2]

## Grease Manufacturing

A typical grease manufacturing process is shown in Figure 4.112. The first step is the charging of oil feed to the contactor. Soap slurry is then added, and saponification is conducted in the contactor as the temperature increases to a preset maximum of 65° to 73°C (149° to 163°F). The saponification reaction takes 30 to 45 minutes. Excess water is removed through a vacuum line, if necessary. The rest of the oil is then charged to the contactor to complete the manufacture of the grease. After completion, final portions of finishing oil are added to lower the temperature of the grease and thereby increase its viscosity to a given specification.

Heavier greases are normally finished in the scraper kettle because of their high viscosity at lower finishing temperatures. The finished grease from either the contactor or the scraper kettle is packaged directly or further processed in a grease mill or polisher, depending on the specification of the final product.[3]

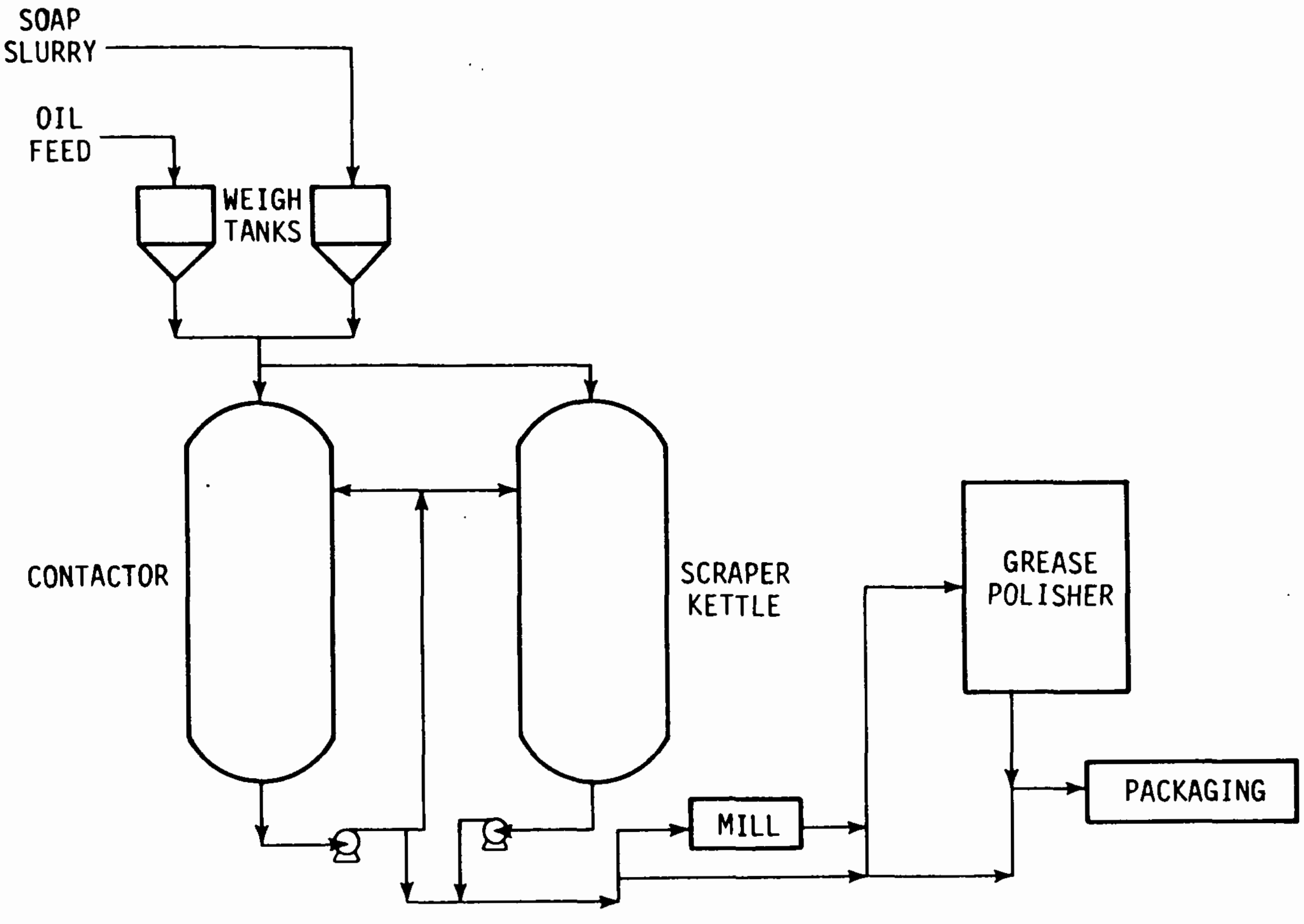

Figure 4.11-2. Typical grease manufacturing process.

### 4.11.2 Emission Sources

Dewaxing processes use special solvents, such as benzene, toluene, MEK, ethylene dichloride, trichloroethylene, and propane. These solvents are recovered and reused in the process. Their volatility, however, can cause some solvent loss through leaks in fittings, valves, and pumps. Small amounts of solvent may also be entrained in products and process residues.

No major emission sources are present in grease manufacturing. Fugitive emissions through leaks in fittings, valves, and pumps are negligible because the actual vapor pressure of the hydrocarbons in the lubricating oils is very low.

### 4.11.3 Emission Controls

Solvent recovery is a closed system that requires no special control measures. Fugitive emissions through leaks in fittings, valves, and pumps can be controlled by good engineering and manufacturing practices. No emission controls are used for the small amount of solvent that may be entrained in products and process residues.

### 4.11.4 Instrumentation

The ratio of solvent to oil feed, which is very important for proper control of a dewaxing unit, ranges from 1:1 to 4:1 depending on the nature and viscosity of the oil feed. The ratio is maintained by a ratio flow controller. The temperature of a dewaxing process is regulated to a few degrees below the desired pour point of the dewaxed oil.

In grease manufacturing, accurate measurements are made of the oil feed and soap slurry charged to the contactor. Time cycles of 30 to 45 minutes are required for saponification. The manufacture of calcium grease typically takes 11/2 to 2 hours; the manufacture of soda-based grease takes 2 to 3 hours.

### 4.11.5 Startup/Shutdown/Malfunctions

Because startup, shutdown, and malfunctions do not generate significant emissions, the inspector need not concentrate on monitoring emissions during those periods.

### 4.11.6 References

1. Nelson, W. L. Petroleum Refinery Engineering. McGraw-Hill Book Company, New York, 1958. pp. 66-69.
2. Kirk-Othmer Encyclopedia of Chemical Technology. Vol 15, John Wiley & Sons, New York, 1968. pp. 92110.
3. Refinery Process Handbook. Hydrocarbon Processing, September 1978. pp. 224.

## 4.12 ASPHALT PRODUCTION[1]

The residue from vacuum distillation may be referred to as asphalt, residuum, or flux. This bottom product is a mixture of resins, asphaltenes, and oils. Resins are highly cross-linked polymers. When heated, these polymers form additional cross-linkages and thus become more rigid. Asphaltenes are high-molecular-weight agglomerates that are insoluble in alkanes from propane to heptane. Asphaltene molecules contain about five aromatic rings arranged in a stack, plus nitrogen, oxygen, sulfur, and some free radical sites. Oils are less complex aromatic compounds. In addition, trace metals such as vanadium and nickel that are present in crude oil tend to become concentrated in asphalt and other heavy oils. Asphalt may also be obtained from solvent deasphalting processes.

The asphalt used in road paving is usually the bottoms from vacuum or atmospheric distillation; they need no further processing.

The asphalt used in shingles and composition roofing must be harder than that used in paving. Air blowing is used to lower the penetration and to raise the softening point of the asphalt. The improved properties of airblown asphalt--increased hardness, higher melting point, and greater resistance to weathering--result from the oxidation reactions which occur during the blowing process. When a very high melting point and extreme hardness are desired, a catalyst (such as ferric chloride or phosphorus pentoxide) is added to the asphalt before it is blown.

### 4.12.1 Process Description

Figure 4.12-1 is a diagram of an asphalt air-blowing process. The feed from the vacuum distillation unit may be stored or pumped directly to the asphalt plant. Asphalt coming directly from the distillation tower is heated and may require cooling before it enters the airblowing reactor vessel. Asphalt that has been in storage must be heated before it enters the reactor.

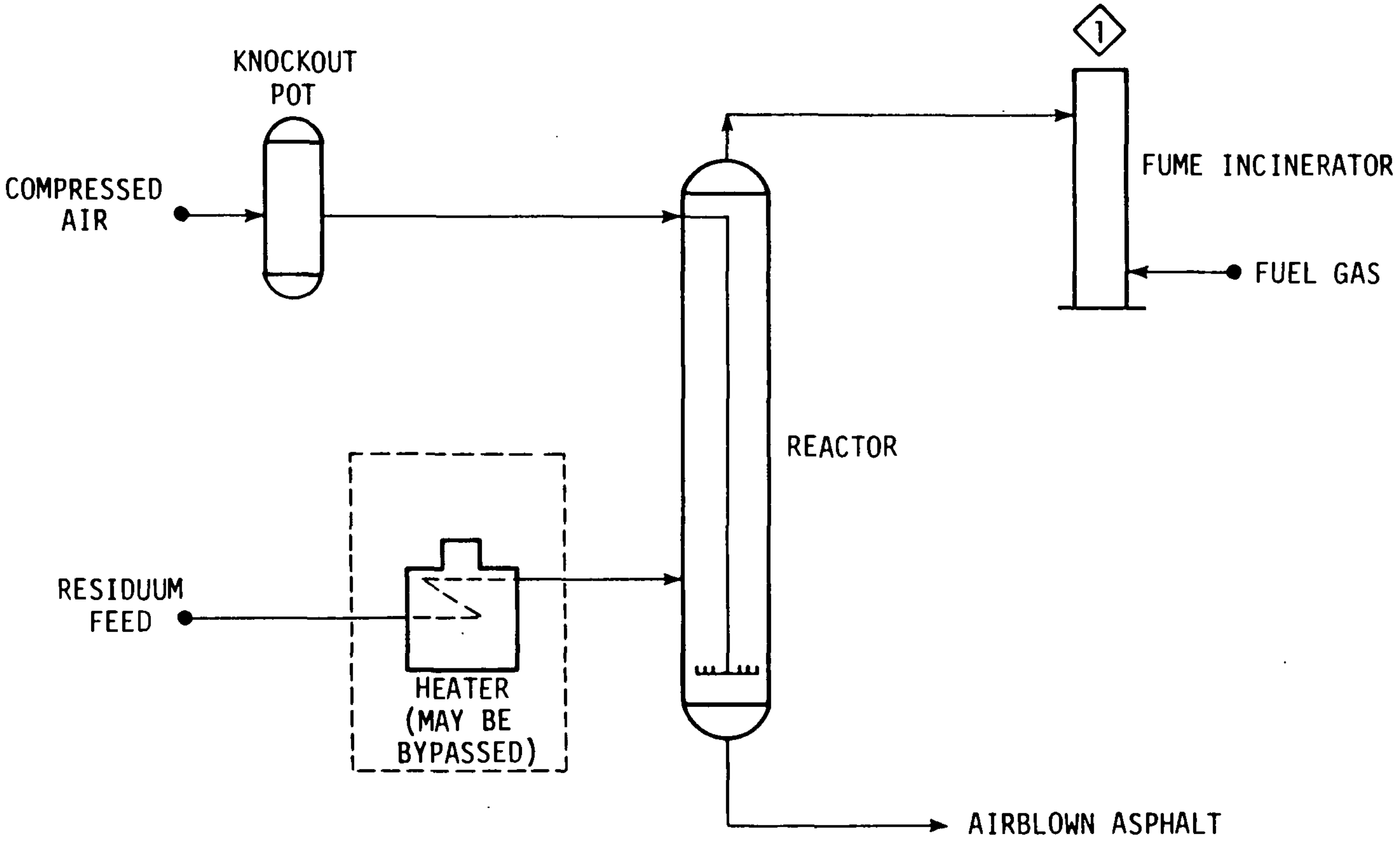

Figure 4.12-1. Block flow diagram of asphalt air-blowing unit.

When the feed has reached the proper temperature, it enters and partially fills the vertical reactor.

Asphalt blowing is a batch process. After the reactor is sufficiently filled, compressed air that has been passed through a knockout pot is injected into the asphalt through a sparger at the base of the reactor. The knockout pot removes water or other liquids from the compressed air. The oxygen in the air reacts with the asphalt, resulting in oxidation, polymerization, and increased cross-linkage of the asphalt molecules. Blowing may continue for 1 to 24 hours. Because the reactions are exothermic, the blowing process supplies its own heat. Temperature is regulated by the airflow rate and by water cooling. The product (airblown asphalt) is removed from the bottom of the reactor, cooled, and loaded for shipping or sent to storage. A fume incinerator is associated with the process to burn the hydrocarbon gases generated in the reactor.

### 4.12.2 Emission Sources

The gaseous stream from the reactor contains hydrocarbon vapor and an aerosol of oil droplets. This stream used to be a major source of emissions at refineries. Fume incinerators now burn these hydrocarbons, but the incinerator itself is a potential source of hydrocarbon, sulfur oxide, and nitrogen oxide emissions (Figure 4.12-1, point 1).

Hydrocarbon leaks from process unit equipment are minimal at an asphalt plant because the feed and product have extremely low volatility. The study on equipment leaks by the California Air Resources Board does not report leaks from asphalt plants. Leaks due to corrosion of rupture disks on the reactor and storage tanks are possible sources of emissions.

### 4.12.3 Emission Controls

Proper operation of the fume (vent gas) incinerator should minimize atmospheric emissions from the asphalt plant. Proper maintenance of all equipment is important for this purpose.

### 4.12.4 Instrumentation

The air-blowing reactor is generally maintained at a temperature of 205° to 315°C (400° to 600°F). The reactor temperature and the rate of airflow into the reactor are continuously monitored and should be noted by the inspector.

In a batch operation, the flow rate of asphalt into the reactor is not significant in itself; however, the flow rate multiplied by the time required to "load" (partially fill) the reactor is equal to the operating capacity of the reactor. The flow rate and the temperature of the asphalt entering the reactor should be noted. The fume incinerator temperature should also be noted. If the incinerator stack is monitored with an opacity meter, the inspector should record that reading.

### 4.12.5 Startup/Shutdown/Malfunctions

Because asphalt air-blowing is a batch process, startups and shutdowns are routine. No significant emissions occur during these periods.

Construction products like asphalt are in seasonal demand; it is common for refineries to shut down their asphalt plants during the off-season. A turnaround for routine maintenance of a process unit should pose no emission problems if vapors are properly disposed.

Malfunction of the incinerator is the greatest potential emission problem in an asphalt plant. This and other malfunctions are infrequent, however, and can be corrected in a short period of time.

### 4.12.6 Reference

1. Refining Process Handbook. Hydrocarbon Processing, September 1978. pp. 220.

## 4.13 COKING[1-4]

Coking is a thermal cracking process, conducted under stringent conditions, which converts low-value residual fuel oil to higher value gas oil plus a byproduct of petroleum coke. Coke with low sulfur and metal contents has recently become a valuable raw material in the manufacture of electrodes and aerospace components. Power plants also use low-sulfur coke for fuel because of its heating value of 32,600 to 37,200 kJ/kg (14,000 to 16,000 Btu/lb.)

### 4.13.1 Process Description

Typical feeds to the coking process include reduced crudes, vacuum distillation residues, tars, and catalytic cycle oil. Products include gas, naphtha, gasoline, heavy and light gas oil, as well as coke. There are two types of coking processes, delayed and fluid; delayed coking is the more widely used. An additional coke processing step is coke calcining. Descriptions of these processes follow.

### Delayed Coking Process

In the delayed coking process, the feed enters the coker tower (fractionator), where gas oil, gasoline, and lighter fractions are flashed off and recovered. Figure 4.13-1 is a typical flow diagram of a delayed coking process. The fractionator bottoms are combined with a recycle stream and are heated to a reaction temperature of 480° to 580°C (900° to 1080°F) in the coker heater. Heater velocities are controlled by steam injection. Mild cracking and some vaporization occur in the heater. The vapor-liquid mixture from the heater then enters the coke drum, where the primary coking reaction takes place. The coke drum provides the proper residence time, pressure, and temperature for coking. In the coke drum, the vapor portion of the feed undergoes further cracking as it passes through the drum, and the liquid portion undergoes successive cracking and polymerization until it is converted to vapor and coke.

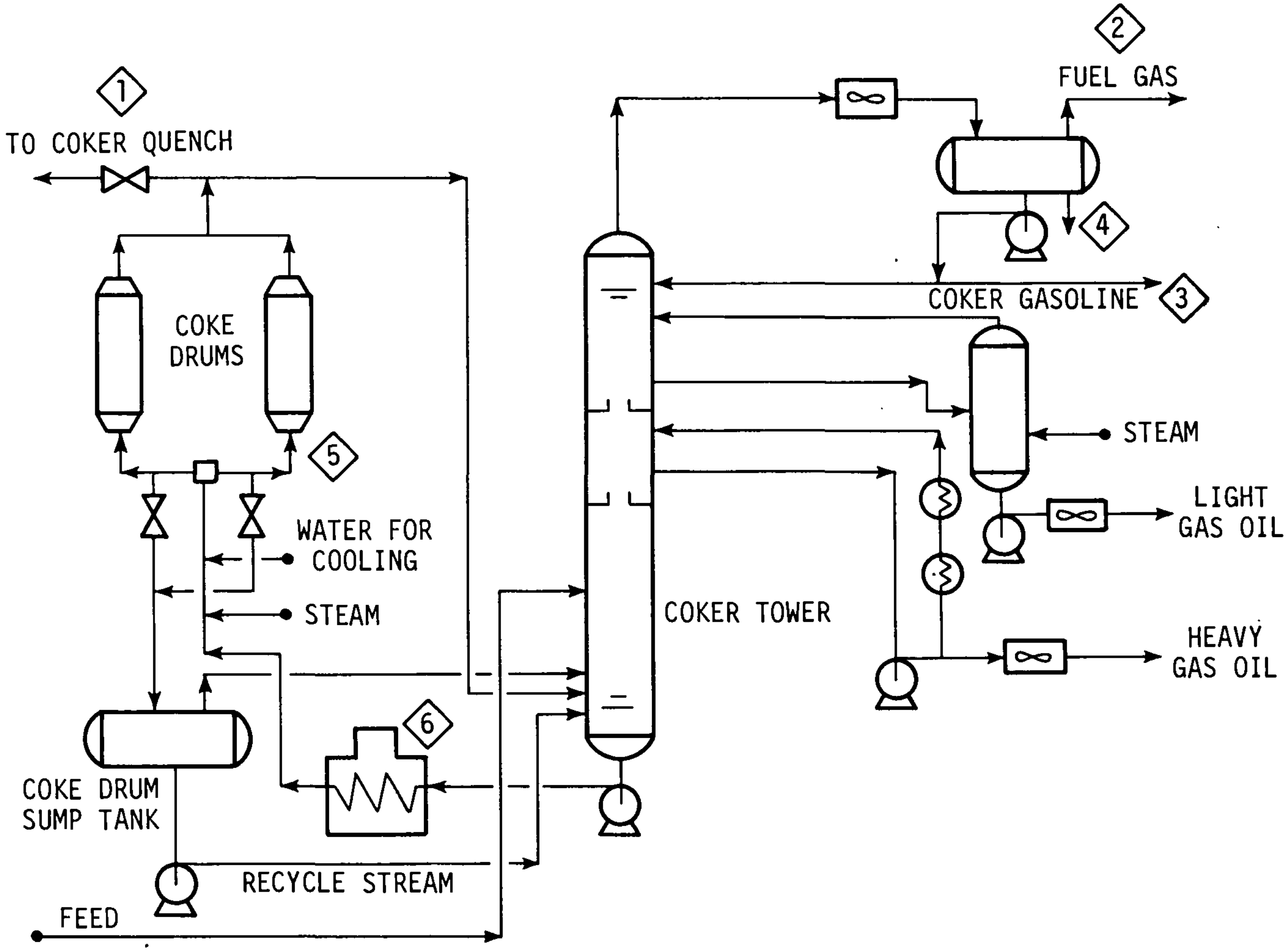

Figure 4.13-1. Flow diagram of delayed coking unit.

Overhead vapors from the coke drum enter the coker tower and are separated into gas, naphtha, and light and heavy gas oils, which are withdrawn as products; a recycle portion flows to the bottom of the tower, where it is combined with fresh feed for another pass through the heater. The solid coke remains in the coking drum. A coking unit has at least two coking drums. One or more are in operation while the others are down for removal of coke.

In removal of coke from the drum, steam is first injected into the drum to remove the hydrocarbon vapors, which are cooled to form a steam-hydrocarbon mixture that is separated into three parts:

1. Water with coke particles that is added to the coke removal stream.
2. Hydrocarbon liquid that is added to the slop oil system.
3. Noncondensables that either go to the flare system or to a heater to be used as fuel. This stream is primarily fuel gas and usually contains some sulfur compounds.

After the drum is filled with cooling water and then drained, the coke is cut out (broken free of the drum) by use of a high-pressure (13,890 kPa; 2000 psig) water jet. The coke particles are separated from the water by the use of screens. Fine particles remaining in the water are removed in a thickener, and the water is recycled to the coke cutting process.

## Fluid Coking Process

In the fluid coking process, the coking reaction is carried out on a fluidized bed of hot coke particles. In the fluidized bed, gas is circulated upward at a controlled velocity through a bed of fairly uniform particles. The bed looks and behaves as if it were liquid, in that it flows like a liquid and can be pumped. An essential characteristic is a narrow range of particle sizes.

Large particles sink and could clog the gas vents. Fine particles blown out of the bed are potential particulate emissions. A fluidized bed reactor allows for very rapid and efficient heat transfer.

Figure 4.13-2 is a flow diagram of a typical fluid coking unit. The fresh feed, usually vacuum residuum, is dispersed into the fluidized coke bed reactor, operating typically between 525° and 590°C (975° and 1100°F). A portion of the feedstock is thermally converted to vapors including gasoline-boiling-range fractions, which leave the reactor as overhead vapors. The remainder of the charge stock is converted to coke, which is deposited on the fluidized coke particles already in the reaction zone. Heat balance is maintained by circulating coke between the reactor and the burner, where a portion of the coke is burned with blower air to supply preheat and heat of reaction. A portion of the coke is withdrawn as a product through an elutriator by countercurrent stripping, from which fines are returned to the burner.

The gas and distillate products leave the reactor through cyclones and enter a tower located above the reactor. In this tower, called a scrubber because it removes any carryover of fine particles, the vapors are partially condensed. The high-boiling distillate is recycled to the reactor and coked. The remaining vapors are fractionated into naphtha and light and heavy gas oil products.

## Coke Calcining

To increase the value of coke more petroleum refiners are considering coke calcining. Coke is calcined to convert "green coke" to the more valuable "needle coké" and to reduce the sulfur content. A process flow diagram is shown in Figure 4.13-3. The green coke produced from a coking unit arrives by belt conveyor to one of two raw coke feeding bins. Two belt weigh-feeders lead to the slightly inclined, cylindrical, rotary kiln calciner. The calcination reaction is carried out between 1315° and 1480°C

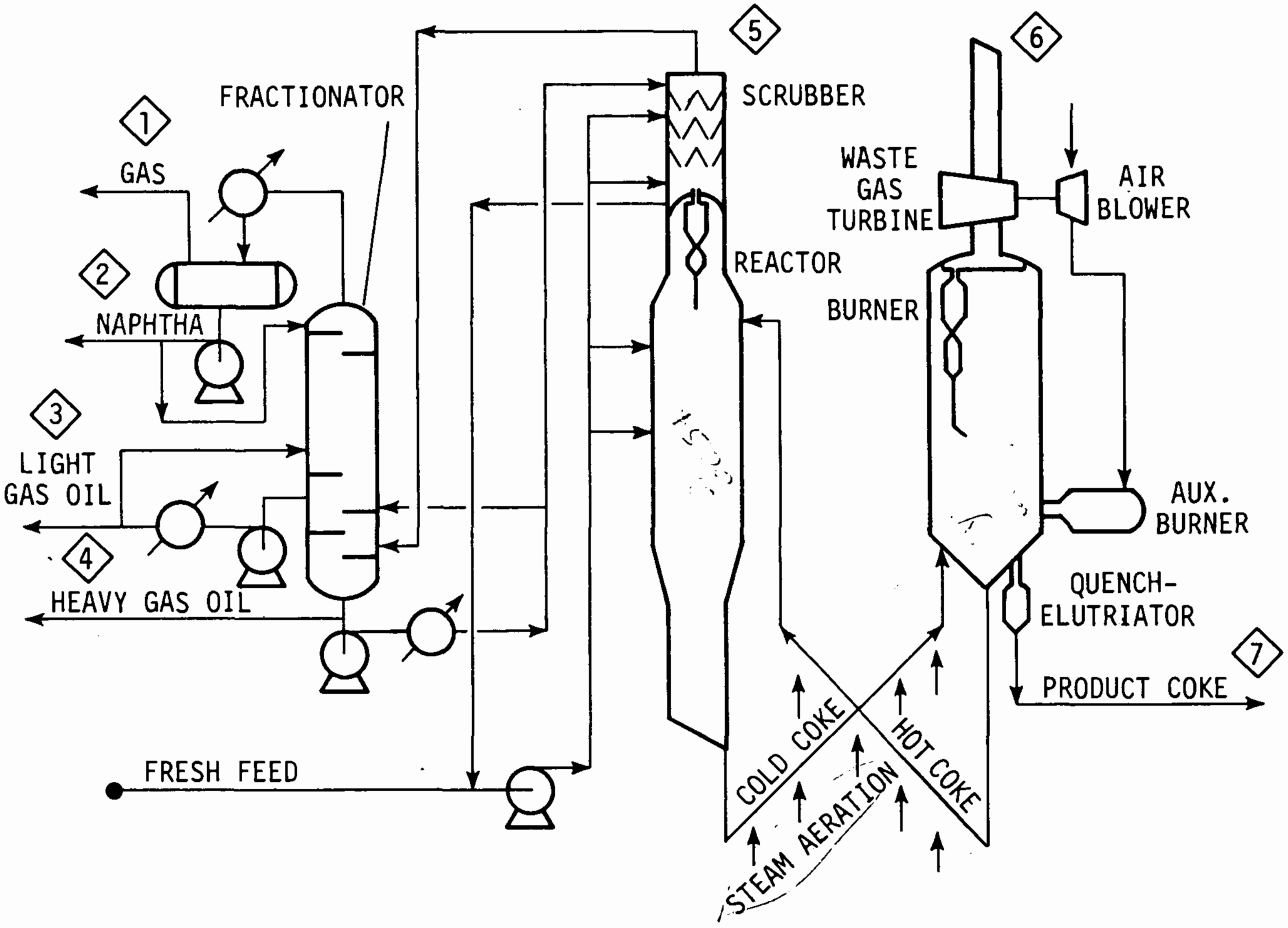

Figure 4.13-2. Flow diagram of fluid coking unit.

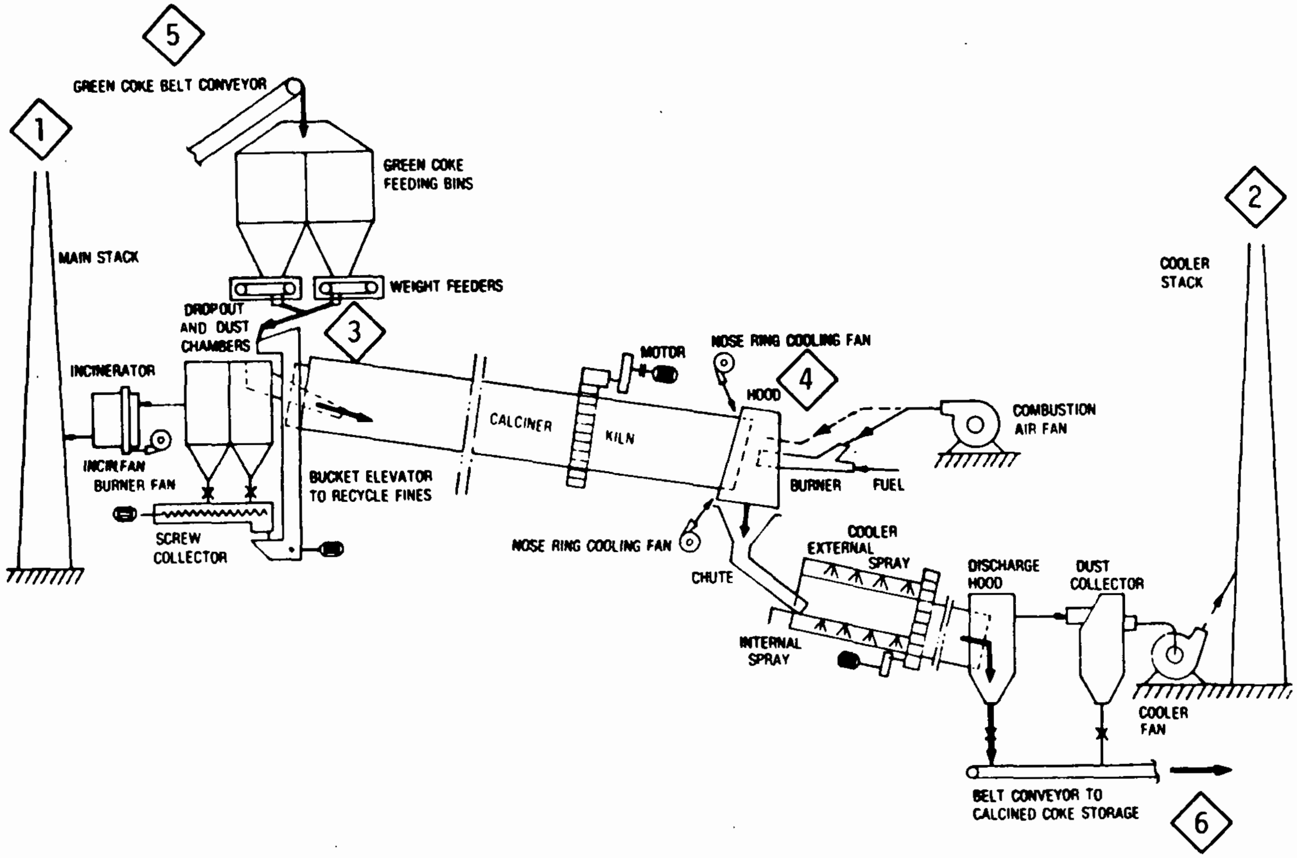

Figure 4.13-3. Flow diagram of coke calcination process.[2]

(2400° and 2700°F). The kiln is refractory-lined and has specific internal structures to control coke movement and residence time. The coke travels countercurrently to the combustion gases coming from a burner fixed to the firing hood at the opposite end of the kiln. The calcined coke leaving the kiln goes through a transfer chute to a water spray cooler. The coke is then discharged through the cooler discharge hood and conveyed by belt to the calcined coke storage.

Gases coming from the cooler discharge end hood and conveyors are routed through a dust collecting chamber and then to the cooler stack by a fan. The combustion gases from the upper end of the kiln are treated in a dust chamber and a dropout chamber to recover coke particles. The recovered coke is recycled to the kiln by means of a collecting screw and an elevator. The partially cleaned flue gas passes through an incinerator, where the last coke particles are burned before the gas leaves the main stack.

### 4.13.2 Emission Sources

The feedstocks in coking operations are richer in sulfur than is the crude oil being processed. Consequently, streams from coking units are potential sources of hydrogen sulfide ($H_2S$) and organic sulfur compounds. Finely divided coke is present in the unit and some of it is further reduced in size by partial combustion and friction. Because coke has a high ash content, it is a potential source of particulate emissions both as unburned material and as fly ash.

#### A. Delayed Coking Reactors

Potential points of sulfide emissions, all shown in Figure 4.13-1, include:

1. Steam from the steamout operation (point 1)
2. Accumulator fuel gas (point 2)
3. Coker gasoline (point 3)
4. Water drawn from the overhead accumulator (point 4)

5. Water used in coke cutting (point 5)

6. The fired heater (point 6)

Potential points of particulate emissions include:

1. The fired heater (point 6)

2. Coking units. (These units, which are usually covered with coke dust, must be cleaned and washed often to prevent fugitive coke-dust emissions.)

B. Fluid Coking Reactors

Potential points of sulfide emissions, shown in Figure 4.13-2, include:

1. Accumulator fuel gas (point 1)

2. Naphtha (point 2)

3. Light gas oil (point 3)

4. Heavy gas oil (point 4)

5. Reactor scrubber (point 5)

6. Burner or CO boiler (point 6)

Potential sources of particulates, shown in Figure 4.13-2, include:

1. Reactor scrubbers (point 5)

2. Burner or CO boiler (point 6)

3. Product coke recovery (point 7)

C. Coke Calcination

Potential sources of sulfides, shown in Figure 4.13-3, include:

1. Gases from stacks (points 1 and 2)

2. Gases from the kiln (points 3 and 4)

Potential sources of particulates, shown in Figure 4.13-3, include:

1. Conveyor belts (points 5 and 6)
2. Stacks and the kiln (points 1, 2, 3, and 4)

### 4.13.3 Emission Controls

In the delayed coke process, large quantities of steam and hydrocarbons may be released to the atmosphere when the coke drum is opened. More steam may be produced by vaporization of the cutting water and by release of pockets of trapped steam/hydrocarbon vapors from cutting operations. These hydrocarbon emissions can be minimized by venting the quenching stream to a vapor recovery or blowdown system. Flaring of organics containing sulfur in a blowdown system may produce $SO_x$ emissions. When the drum has cooled to 100°C (212°F), the steam purge can be replaced by a water flood. Allowing further cooling to approximately ambient temperature will minimize vaporization and escape of steam and hydrocarbons when the drum is opened.

In the fluid coking process, the gas from the burner (Figure 4.13-2, point 6) contains carbon monoxide and sulfur-bearing hydrocarbons. Since this waste gas has value as a fuel, a CO boiler can be used to generate steam for use on the unit and to control the emissions.

In coke calcining, multicyclones and a CO incinerator are the most common emission controls.

### 4.13.4 Instrumentation

Temperatures are measured in the coking reactors, the coke drums, the distillation column, and the coking towers. Process steam temperatures and/or pressures are also measured. Rates of feed to and discharges from the process are measured and controlled.

A gas flow rate above the recommended operating range would lead to particulate emissions that could overwhelm control measures. Temperature fluctuations may affect coke conversion and yields as well as the amount of material being recycled. The resultant emissions would be significant only if they increased to a point that the control measures were not designed to handle.

### 4.13.5 Startup/Shutdown/Malfunctions

Scheduled shutdowns for maintenance are requisite in the delayed coking process. Of particular concern are the coking drums, which are subject to rapid heating and cooling cycles that make them susceptible to cracking, warping of the shell, and lining failure. Welded areas are particularly vulnerable. Thermal stress is the primary cause of failure, rather than corrosion from the sulfur content of the feed. A drum failure can cause uncontrolled and significant releases of particulates and sulfur compounds.

When the coke drums are overfilled by charging at rates higher than the design rate, coke foam could go overhead to the fractionator and necessitate a shutdown. During a shutdown, hydrocarbon and sulfur compounds are emitted to the atmosphere. The coke drum is cooled and decoked. The fractionator is also shut down, cooled, and restarted.

Successful operation of fluid coking units depends on continuous circulation of coke between the reactor and burner. The aeration taps on the transfer lines between the reactor and the burner must operate properly. Loss of coke in the reactor shuts down the unit. It is important also that the feed be properly injected into the reactor. When the charge rate is too high, fluidization is poor and the reactor must be shut down. A unit shutdown can cause emissions of particulates, hydrocarbon, and carbon monoxide. A time frame relative to these malfunctions is not available. Their frequency depends on the type of feed and on general operating practices. The startup and shutdown times depend on the severity of the malfunction. Generally, emergency downtime for this unit averages 11 days between turnarounds. These downdays represent several shutdowns of varying lengths. There are minimum downtimes. About 1 day is needed for shutdown of the unit, and 1.5 to 2 days for startup; thus the minimum downtime is 2.5 to 3 days.

The other shutdown and startup operations would follow the usual sequence of heating or cooling, venting to the refinery flare, and flushing with inert gas and air. The 24 to 48 hour cycle for coking drums is part of the process rather than a startup/shutdown cycle.

The coking units are shut down on the average of once every 8 months for general inspection and maintenance (turnaround). This may vary within a range of 3 to 14 months. The downtime for a scheduled shutdown averages 16 days.

### 4.13.6 References

1. Russ, R. J. Coke Quality and How To Make It. Hydrocarbon Processing, September 1971. pp. 132-136.
2. Reis, T. To Coke, Desulfurize and Calcine. Hydrocarbon Processing, April 1975. pp. 144-150.
3. Refining Report. Here Is What's New In Delayed Coking. The Oil and Gas Journal, April 6, 1970. pp. 92-96.
4. Refining Process Handbook. Hydrocarbon Processing, September 1978. p. 103.

AMINE
TREATER

## 4.14 AMINE TREATER[1]

The amine treater removes the acidic impurities, mainly hydrogen sulfide ($H_2S$) and carbon dioxide ($CO_2$), from refinery gas streams. In some refineries, the amine treater is part of the sulfur plant rather than a separate unit. The amine treater is also known as a gas sweetening unit, an acid gas treating unit, or an amine scrubber.

### 4.14.1 Process Description

The amine treater is a single absorption/regeneration cycle circulating an aqueous amine solution. The most frequently used amines are monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), and diisopropanolamine (DIPA). The main advantage of DGA is its ability to remove carbonyl sulfide (COS) and mercaptans, thus eliminating the need for downstream liquid treating units. The DGA is more expensive, however, than most of the commonly used amines. Figure 4.14-1 is a flow diagram of a typical amine treater.

The feed gas stream containing the impurities (such as $H_2S$ and $CO_2$) is contacted countercurrently with an amine solution that enters at the top of the packed or tray tower (absorber). The feed gas stream enters at the bottom of the tower. The treated gas stream leaving the absorber may either be further processed in lightend recovery processes or may be charged as a raw material to other refinery or petrochemical processes.

The rich amine solution from the bottom of the absorber is flashed at a reduced pressure to remove the entrained gases, including part of the acid gas, and then heated in a rich/lean amine exchanger. The heated, rich amine stream then flows to the stripper tower where the amine is regenerated. In the stripper, absorption reactions are reversed, with heat supplied by stripping steam that is generated in the reboiler. The acid gases are separated from the amine solution by steam. The overhead stream, consisting of acid gases and steam, flows to a condenser and accumulator; the steam is separated from the acid gas and

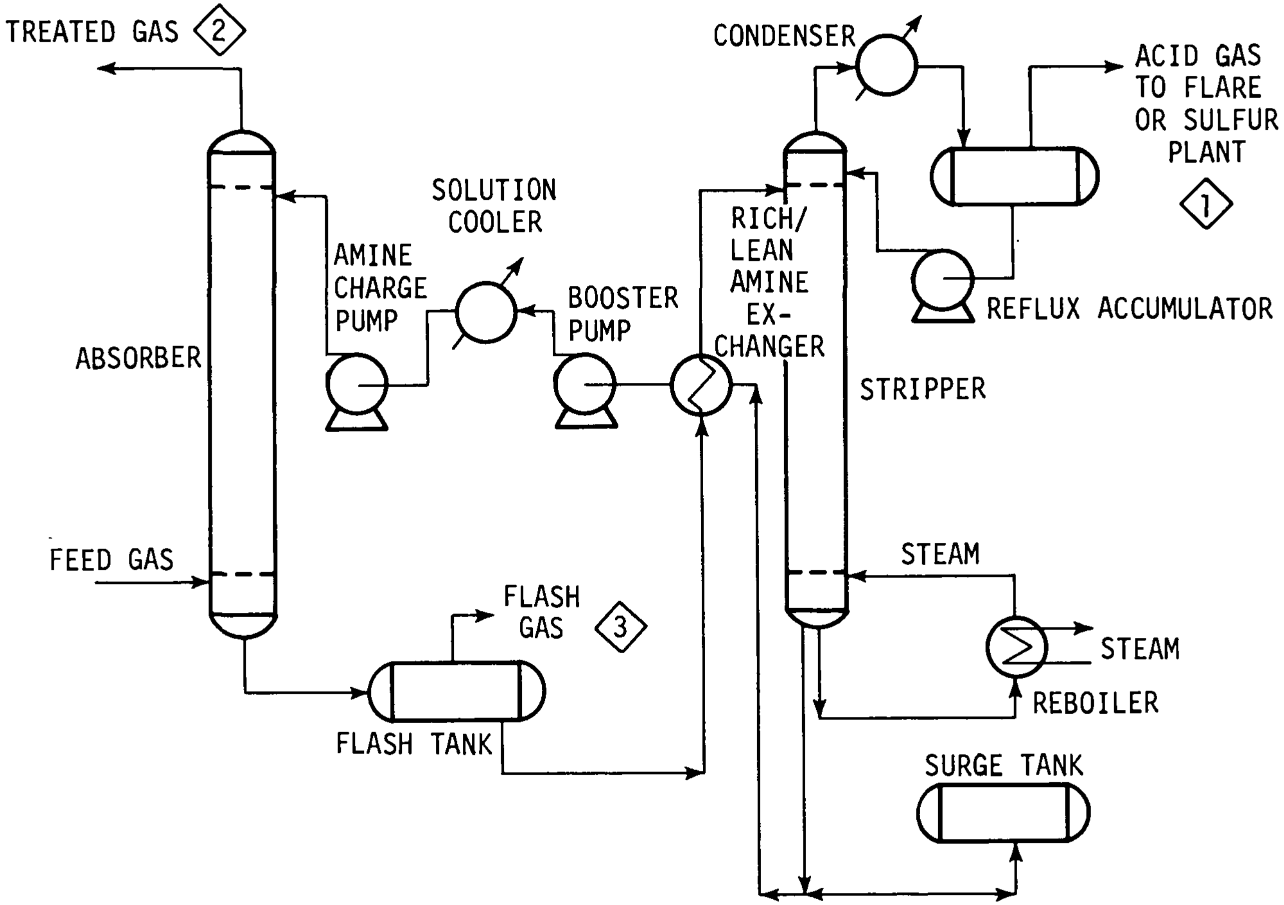

Figure 4.14-1. Flow diagram of a typical amine treater.

returned to the stripper column as a reflux. Condensation of steam from the acid gas in the accumulator leaves a concentrated acid gas.

The lean amine solution from the bottom of the reboiler is exchanged with the rich amine solution and pumped back to the absorber to complete the process loop.

The operating conditions for an absorber can vary widely. The absorber pressure ranges from slightly above atmospheric to 6995 kPa (1000 psig). The temperature of the amine entering the absorber ranges from 40° to 60°C (100° to 140°F). The stripper operates at near atmospheric pressure and a bottom temperature of approximately 115°C (240°F). The amine circulation rate depends on the feed rate and the partial pressure of the acidic components.

### 4.14.2 Emission Sources

There are three emission sources in the amine treater. The major emission source is the acid gas stream (Figure 4.14-1, point 1). The treated gas stream may contain $H_2S$ (Figure 4.141, point 2). The flash gas stream also contains $H_2S$ and $CO_2$ (Figure 4.141, point 3).

Additional components emitted to the atmosphere from the stack include nitrogen, sulfur dioxide ($SO_2$), water, and oxygen.

### 4.14.3 Emission Controls

The acid gases from the reflux accumulator are burned in a flare, heater, or other incinerating device. In cases of high sulfur concentrations, the acid gases may be processed for sulfur recovery. The treated gas is either processed in a liquefied petroleum gas plant or sent to a refinery fuel gas system. The flash gas stream is sent to a flare.

### 4.14.4 Instrumentation

The sulfur content of the treated gas stream is monitored frequently--or perhaps continuously--to determine whether the amine unit is operating properly. When the $H_2S$ content of the treated gas exceeds the allowable limit, fresh amine is added to the lean amine solution to remove excess $H_2S$ from the feed gas.

When the acid gas is disposed of by combustion in a flare, heater, or incinerator, the $H_2S$ content of the acid gas stream should be monitored continuously. When the acid gas is processed for sulfur recovery, the $H_2S$ content of the acid gas stream is usually not monitored.

Control of the amine circulation rate in the absorber is essential for proper operation of the treater. The circulation rate of the amine solution is determined by the acid gas content of the feed gas, concentration of the amine solution, and the type of amine to be used.

The ratio of feed gas to amine is maintained by the amine flow controller.

The solution cooler maintains the temperature of the lean amine stream entering the absorber at 40° to 60°C (100° to 140°F). The reboiler maintains the stripper temperature at approximately 115°C (240°F).

### 4.14.5 Startup/Shutdown/Malfunctions

The amine treater needs little maintenance work when compared with a catalytic reforming unit; shutdown of the unit is thus less frequent. In large refineries, the amine treater is usually part of a sulfur plant and is shut down with that plant once every 2 to 3 years.

The concentration of amine is continuously maintained at a required level by adding fresh amine into the system, and shutdown is not required to change the amine solution.

When hydrocarbons are carried over with the amine solution in the stripper, the unit is shut down to drain the hydrocarbons from the stripper. During the malfunction of the amine treater, the refinery gas stream is bypassed to a flare, reboiler, or other incinerating device, thus emitting large volumes of $SO_2$.

### 4.14.6 Reference

1. GPA Explores $H_2S$ Removal Methods. The Oil and Gas Journal, July 17, 1978. pp. 6673.

## 4.15 GAS PROCESSING[1,2]

The gas processing section of a refinery is identified by the following names: vapor recovery unit (VRU), light-ends unit (L ends), or simply, gas plant. The purpose of the gas plant is to recover valuable products from the refinery fuel gas produced at most refinery units.

The vapor recovery products include methane used as feedstocks for petrochemical plants, butanes for gasoline blending, and liquefied petroleum gas (LPG). The LPG is propane or butane, or mixtures of both. The product that is recovered depends on market conditions. Generally, LPG is recovered. The remainder of this section is primarily directed at discussing the LPG recovery process.

### 4.15.1 Process Description

Figure 4.15-1 is a flow diagram of a typical vapor recovery unit. The feed stream consists of refinery gas from the following units or conversion processes: crude distillation, catalytic reforming, catalytic cracking, steam cracking, thermal cracking, coking, visbreaking, polymerization, and alkylation. After processing in the gas plant, the LPG yields from these processes usually vary within a relatively wide range, as shown in Table 4.15-1.

TABLE 4.15-1. LIQUEFIED PETROLEUM GAS YIELDS FROM CONVERSION PROCESSES

| Process | LPG yield, percentage by weight |
|---|---|
| Catalytic reforming | 5 to 10 |
| Catalytic cracking | 15 to 20 |
| Steam cracking | 23 to 30 |
| Polymerization/alkylation | 10 to 15 |
| Thermal cracking | 10 to 20 |
| Coking/visbreaking | 5 to 10 |

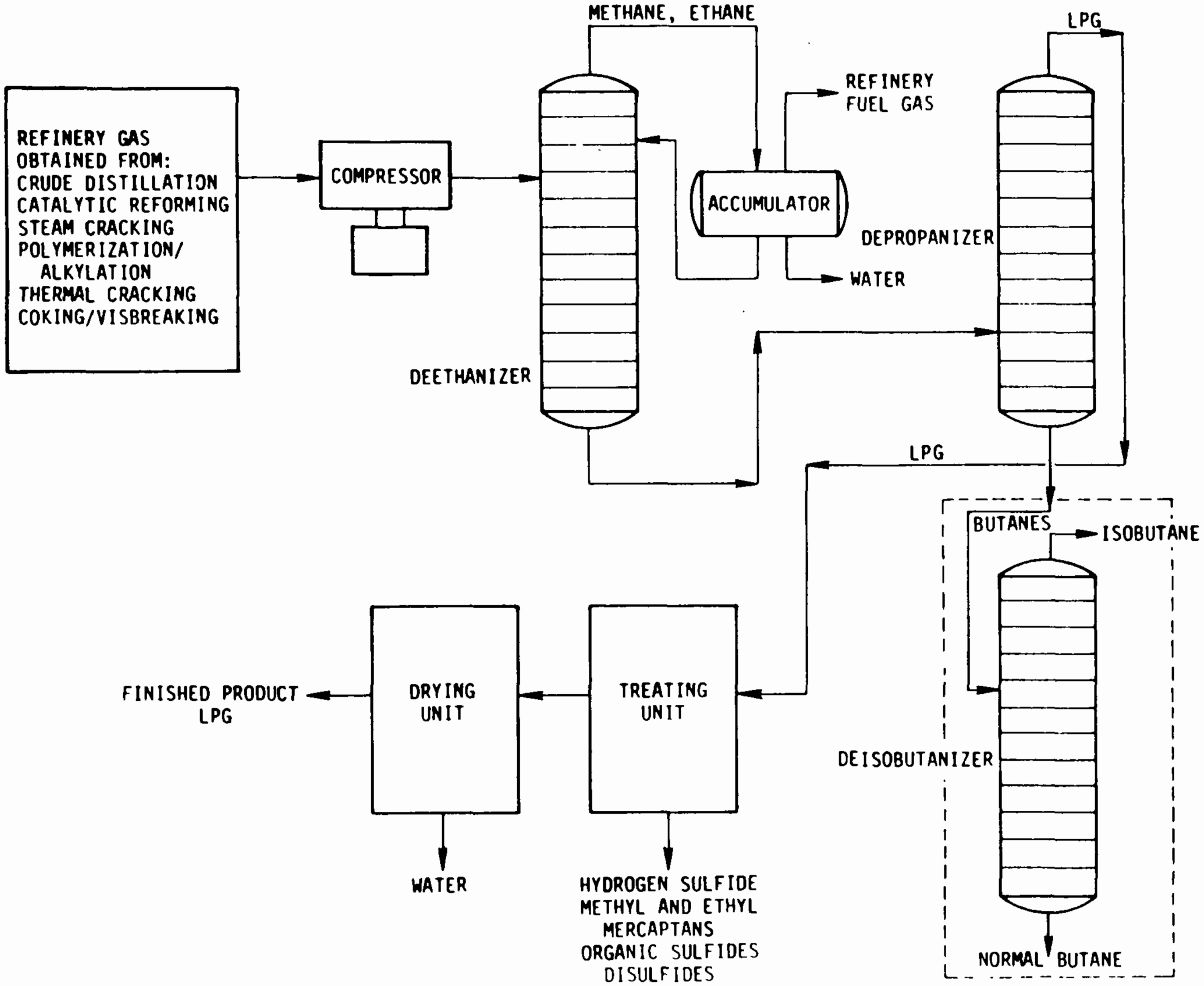

Figure 4.15-1. Flow diagram of vapor recovery unit.

The conversion processes that create the feed stream to the vapor recovery unit are summarized below. For a more detailed description, refer to Sections 2.3 and 2.4.

Catalytic reforming reacts virgin naphtha from the crude oil fractionating tower. The aromatics ($C_6/C_7$) that are produced are used for gasoline blend stocks or chemical intermediates; LPG is a possible byproduct. Sulfur must be removed from the naphtha stream before reforming to avoid contaminating the reforming catalyst. The sulfur is removed by converting it to hydrogen sulfide over a molybdate catalyst.

Catalytic cracking units, referred to as cat crackers, use a feedstock of heavy gas oil to produce gasoline and unsaturated gases. High temperature and silica-aluminum catalyst are needed for the cracker reaction. The unsaturated gases are intermediates that undergo further chemical reaction. An "integrated" refinery has both crackers and reformers to reduce production of middle distillates. The fuel gas from this operation is sent by pipeline to the gas plant.

Noncatalytic cracking processes that yield the LPG byproduct include steam and thermal cracking, visbreaking, delayed coking, and fluid coking.

The recovered refinery gas feed stream is highly compressed before being sent to a deethanizer (distillation column). Overhead products--methanes and ethanes--pass through an accumulator, which removes the water and produces refinery fuel gas. The fuel gas stream contains methane, ethanes, and propanes. This stream may be further processed to remove the methane, a valuable petrochemical feedstock. The bottoms are further distilled in a depropanizer, which separates the liquefied petroleum gas and the butanes. The butanes are then sent either to gasoline blending or to a deisobutanizer for separation into isobutane and normal butane, which is piped to the gasoline blending unit; the overhead contains isobutane, which is alkylation feedstock.

The overhead stream from the depropanizer contains the liquefied petroleum gas, which is treated by removing the sulfur to make the gas noncorrosive and nontoxic. Hydrogen sulfide, mercaptans, and elemental sulfur are removed by washing with caustic soda, the Girbotal or Merox extraction processes.

In the caustic soda method, sodium or potassium hydroxide react with hydrogen sulfide and mercaptans. The reaction products are removed from the LPG. The reaction is comparable to an extraction reaction. Caustic solutions range in concentration from 5 to 20 percent. The Girbotal process utilizes a packed tower in countercurrent flow to extract sulfur compounds. Monoethanolamine (MEA) or diethanolamine (DEA) are the extracting agents. The Merox unit (developed by the Universal Oil Company) converts mercaptans to disulfides by reacting them in air and alkali in the presence of a chelated iron catalyst.

Sulfides can also be removed from the LPG by molecular sieve adsorption. Synthetic metal aluminosilicates are made into molecular sieve adsorption pellets. The sieve adsorbs molecules having critical diameters of 10 angstoms. Molecular sieve adsorption is advantageous because the sieves also dry the LPG.

After the treating process, the LPG is sent to the drying unit and percolated through an adsorption tower packed with calcium chloride, alumina, silica gel, or molecular sieves. Calcium chloride is the least expensive drying method, although it does present a disposal problem. The LPG is passed through two towers connected in series. When calcium chloride is used in the towers, heavy brine forms in the first tower. When the brine concentration reaches 25 percent calcium chloride the first tower is drained and recharged with brine and the LPG flows are reversed; the first tower thus becomes the second tower. The brine is usually drained once in every 8-hour shift.

The finished LPG product is graded according to the Reid vapor pressure and to the temperature at which 90 percent of the LPG is evaporated. Grading requirements (from the Natural Gasoline Association of America) are listed in Table 4.15-2.

TABLE 4.15-2. GRADING REQUIREMENTS FOR LIQUEFIED PETROLEUM GAS

| | |
|---|---|
| Reid vapor pressure | 68.9 to 234.4 kPa (10 to 34 psia) |
| Percentage evaporated at 60°C (140°F) | 25 to 85 |
| Percentage evaporated at 135°C (275°F) | Not less than 90 |
| End point | Not higher than 190.5°C (375°F) |
| Corrosion | Noncorrosive |
| Doctor test | Negative; sweet |
| Color | Not less than plus 25 |

## 4.15.2 Emission Sources

Major emissions associated with LPG recovery and production are discussed in detail in the sections dealing with distillation (4.1), catalytic cracking (4.2), hydrocracking (4.4), and reforming (4.5). Emissions of fugitive volatile organic compounds (VOC) are sometimes a problem around the processing equipment because LPG is a vapor at ambient temperature and atmospheric pressure. Hydrogen sulfide and sulfur dioxide emissions are also possible pollutants. These are discussed in the sulfur recovery section of the manual (4.16).

## 4.15.3 Emission Controls

Most of the emissions from the crude distillation cracking, sulfur removal or sweetening process, and the reforming LPG stream are fugitive VOCs. These emissions can be controlled by using an active inspection and maintenance (I&M) program for pipe fittings, valves, and pumps. The I&M program would use a VOC analyzer, appropriate record keeping, and a maintenance program to stop leaks.

### 4.15.4 Instrumentation

Temperature and pressure are the two significant control parameters that determine product yield. The temperature and corresponding pressure must be kept low to reduce losses, because LPG is a gas at ambient temperature.

The instrumentation must be checked regularly for correct calibration and operation so that VOC emissions are kept at a minimum. The sections on catalytic cracking (4.2) and hydrocracking (4.4) discuss instrumentation equipment that is also applicable to LPG manufacturing.

### 4.15.5 Startup/Shutdown/Malfunctions

As discussed previously, LPG is a byproduct stream produced during gasoline cracking; it is also separated from crude oil during distillation. Startup, shutdown, and malfunctions of LPG processing are dependent on the method of gasoline cracking and crude distillation. Refer to the information in the sections on distillation (4.1.5), catalytic cracking (4.2.5), visbreaking (4.3.5), hydrocracking (4.4.5), and catalytic reforming (4.5.5).

### 4.15.6 References

1. Williams, A. F., and W. L. Lom. Liquefied Petroleum Gases: A Guide to Properties, Applications and Usage of Propane and Butane. John Wiley & Sons, New York, 1977. p. 397.

2. Sittig, M. Petroleum Refining Industry: Energy Saving and Environmental Control. Noyes Data Corporation, Park Ridge, New Jersey, 1978. p. 110.

SULFUR
PLANT

## 4.16 SULFUR PLANT

The Claus process is the most widely used method of recovering sulfur from acid gases. The degree of sulfur recovery obtainable by a Claus plant is dependent on the number of catalytic reactors and on the concentration of hydrogen sulfide ($H_2S$) in the feed. Claus units are generally constructed with two, three, or four catalytic reactors. The best available control technology (BACT) requires three catalytic reactors. In a refinery Claus unit, the $H_2S$ concentration in the acid gas is generally above 70 percent. Table 4.16-1 shows typical recovery percentages for various concentrations of $H_2S$ in the acid gas feed at plants with two, three, and four reactors.[1]

### 4.16.1 Process Description

The acid gas stream, which may originate from an amine treating unit, sour water stripper, or other gas sweetening processes, is fed to the Claus unit for recovery of sulfur. The classic Claus process consists of two basic steps. First, a portion of the $H_2S$ is converted to sulfur dioxide ($SO_2$) by combustion. Second, the remaining $H_2S$ reacts with the newly formed $SO_2$ to produce elemental sulfur. The following equations illustrate these reactions.

$$H_2S + 1.5O_2 \rightarrow SO_2 + H_2O \quad \text{(thermal combustion)} \qquad \text{(Eq. 1)}$$

$$2H_2S + SO_2 \rightarrow \frac{3}{n} S_n + 2H_2O \quad \text{(thermal and catalytic)} \qquad \text{(Eq. 2)}$$

The symbol $S_n$ represents elemental sulfur in the vapor form, such as $S_2$, $S_4$, $S_6$, and $S_8$.

The ideal ratio of $H_2S$ to $SO_2$ after the combustion oxidation reaction is 2.0, as illustrated in Equation 2. The sulfur produced by this reaction is in the vapor form and is recovered by cooling the gas to condense the sulfur.

In addition to these reactions, some sulfur is produced directly by dissociation of $H_2S$, as shown below:

$$H_2S \rightarrow H_2 + 0.5S_2 \qquad \text{(Eq. 3)}$$

## TABLE 4.16-1. TYPICAL CLAUS PLANT SULFUR RECOVERY AT VARIOUS FEED COMPOSITIONS[1]

| $H_2S$ in sulfur plant feed (dry basis), % | Calculated recovery, % | | |
|---|---|---|---|
| | Two reactors | Three reactors | Four reactors |
| 20 | 92.7 | 93.8 | 95.0 |
| 30 | 93.1 | 94.4 | 95.7 |
| 40 | 93.5 | 94.8 | 96.1 |
| 50 | 93.9 | 95.3 | 96.5 |
| 60 | 94.4 | 95.7 | 96.7 |
| 70 | 94.7 | 96.1 | 96.8 |
| 80 | 95.0 | 96.4 | 97.0 |
| 90 | 95.3 | 96.6 | 97.1 |

This is a minor reaction, however, and does not contribute appreciably to the overall sulfur recovery.

The typical Claus process employing both noncatalytic (thermal) and catalytic reactions is shown in Figure 4.16-1.

Some recent sulfur plant designs involve two separate, individually fired combustion chambers in a thermal reactor. All of the ammonia-bearing acid gas stream is burned completely in one combustion chamber with a slight excess of air to create an oxidizing atmosphere. The oxidizing environment and the reactor temperature favor combustion of ammonia ($NH_3$) to nitrogen ($N_2$). Oxidation of ammonia prevents formation of ammonium-sulfur salts which the plug the catalyst bed in the reactors. The "clean" or non-ammonia-bearing acid gas stream is fed to the second combustion chamber, where a small portion of it is burned to generate the balance of the $SO_2$ required to produce elemental sulfur. The effluents from the two combustion chambers enter the reaction furnace, where their mixture allows formation of sulfur (Equation 2). The first combustion chamber is larger than the second and provides longer retention time.

Generally about 50 to 60 percent of the feed sulfur is recovered in the sulfur condenser following the noncatalytic or thermal reaction. Additional combined sulfur is converted to elemental sulfur by the reactions of Equation 2 in the catalytic reactors downstream of the thermal reactor. After each reactor stage the gases are passed through a condenser, which converts the vaporous sulfur to molten sulfur.

Following the oxidation (combustion) reaction in the thermal reactor, the hot gases, at a temperature of 1260° to 1370°C (2300° to 2500°F), are fed to a waste heat boiler, where steam is generated as the gases are cooled to about 300°C (600°F). The pressure of steam generation in the boiler ranges between 350 and 4100 kPa (50 and 600 psig).

Gases from the waste heat boiler are fed to the first sulfur condenser, where the elemental sulfur from the thermal reactor is

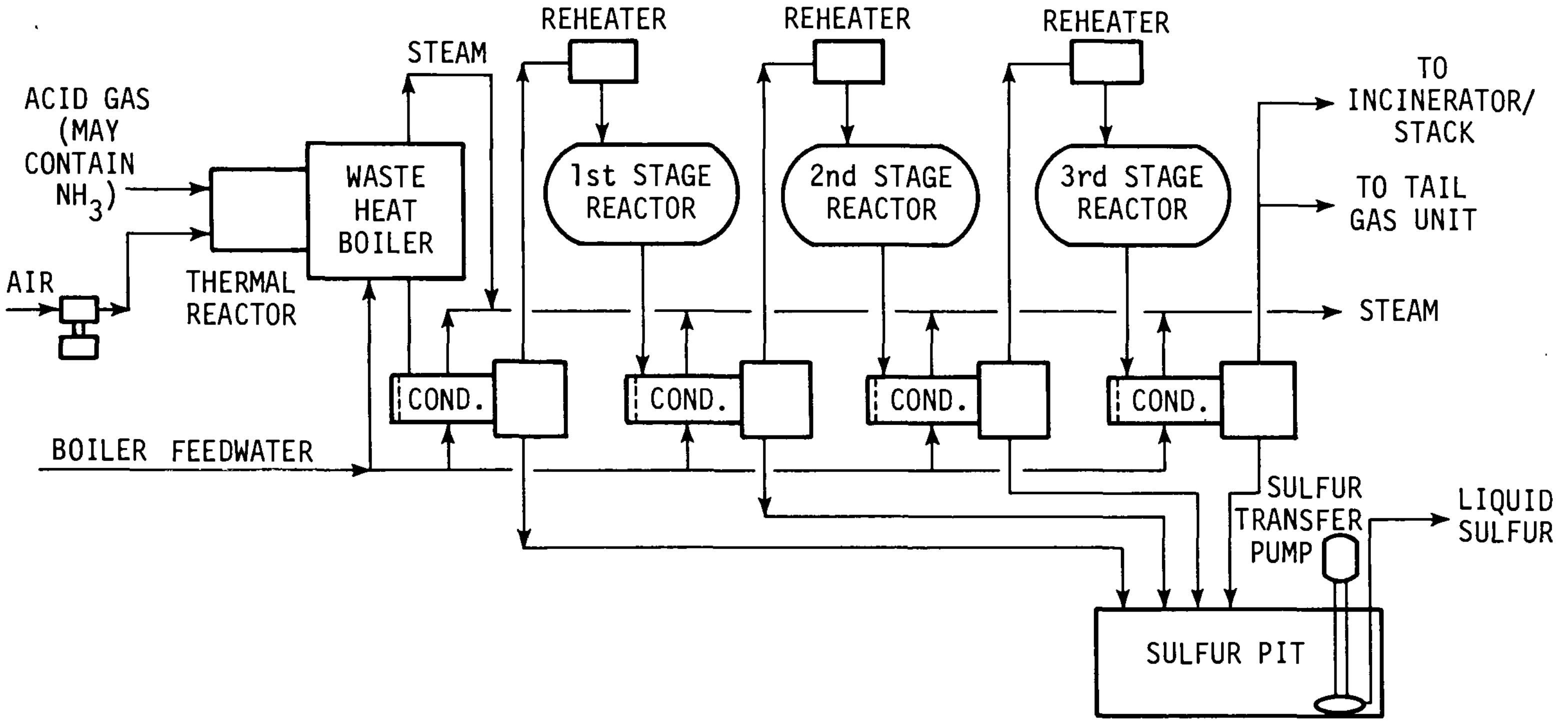

Figure 4.16-1. Typical Claus sulfur recovery process.

condensed. Steam is generated in the sulfur condenser at pressures ranging between 140 and 690 kPa (20 and 100 psig).

The noncondensed gases leave the first sulfur condenser and are heated from 320° to 340°C (600° to 650°F) before they enter the first catalytic reactor. The gases must be heated above the sulfur dew point to prevent condensation of sulfur on the catalyst and to yield the optimum sulfur recovery in the reactor. A fixed-bed catalytic reactor with an activated alumina ($Al_2O_3$) catalyst is used to improve the overall sulfur recovery.

Following the first catalytic reactor, the sulfur-laden gases are fed to the second sulfur condenser for recovery of the additional molten sulfur. The noncondensed gases are again reheated from 200° to 230°C (400° to 440°F) before they enter the second catalytic reactor.

Following the second catalytic reactor, the sulfur-laden gases are fed to the third sulfur condenser for recovery of the additional molten sulfur. The noncondensed gases leave the second catalytic condenser and are reheated from 190° to 200°C (370° to 400°F) before they enter the third catalytic reactor.

Following the final catalytic reactor and sulfur condensation step, the remaining gases are fed to an incinerator. In the incinerator all sulfur compounds in the Claus unit tail gas are converted to $SO_2$ by combustion before being discharged from a stack to the atmosphere.

## 4.16.2 Emission Sources

Acid gases in a refinery usually contain measurable quantities of one or more impurities, including hydrocarbons, carbon dioxide, water, and possibly ammonia, which come from sour water strippers. These impurities can reduce the efficiency of the Claus process. In the combustion zone, these impurities sometimes produce materials that undergo side reactions.

The major pollutant from a Claus unit is the $SO_2$ that results from incineration of the tail gases. The Claus unit tail gas contains $H_2S$, $SO_2$, and elemental sulfur.

The concentration of $SO_2$ in the stack gases depends on the degree of sulfur recovery by the Claus unit, incineration temperature, catalyst activity, and amount of excess air used in the combustion. The concentration of $SO_2$ can range between 3,000 ppm and 20,000 ppm, but normally is 5,000 ppm.[2,3]

Sulfur fires in the catalytic reactors are possible when the reactor temperature exceeds 200°C (400°F), and when a fire occurs a large volume of $SO_2$ is emitted to the atmosphere from the stack.

Additional emissions from the stack after incineration are generally considered to be innocuous. These include $N_2$, $CO_2$, $H_2O$, and $O_2$.

### 4.16.3 Emission Controls

Numerous Claus plant tail gas desulfurization systems are in commercial operation in the United States and worldwide. Four of the processes have demonstrated their ability to meet $SO_2$ compliance levels. They are the Beavon process, the Shell Claus off-gas treating (SCOT) process, the Wellman-Lord process, and the Institut Francais du Petrole (IFP) process. These are discussed in detail in the following sections.

#### Beavon Process

The Beavon process was developed jointly by the Ralph M. Parsons Company and the Union Oil Company of California* and is licensed by the Union Oil Company. A schematic diagram of the process is shown in Figure 4.16-2. The Claus plant tail gas is heated to reaction temperature by mixing with the hot combustion products formed in the reducing gas (CO, $H_2$) generator. The combined gas stream is then passed through a cobalt-molybdenum catalyst bed, where all sulfur compounds are converted to $H_2S$ by

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*Ralph M. Parsons Co., Pasadena, California, 91124;
Union Oil Company of California, Brea, California, 92621.

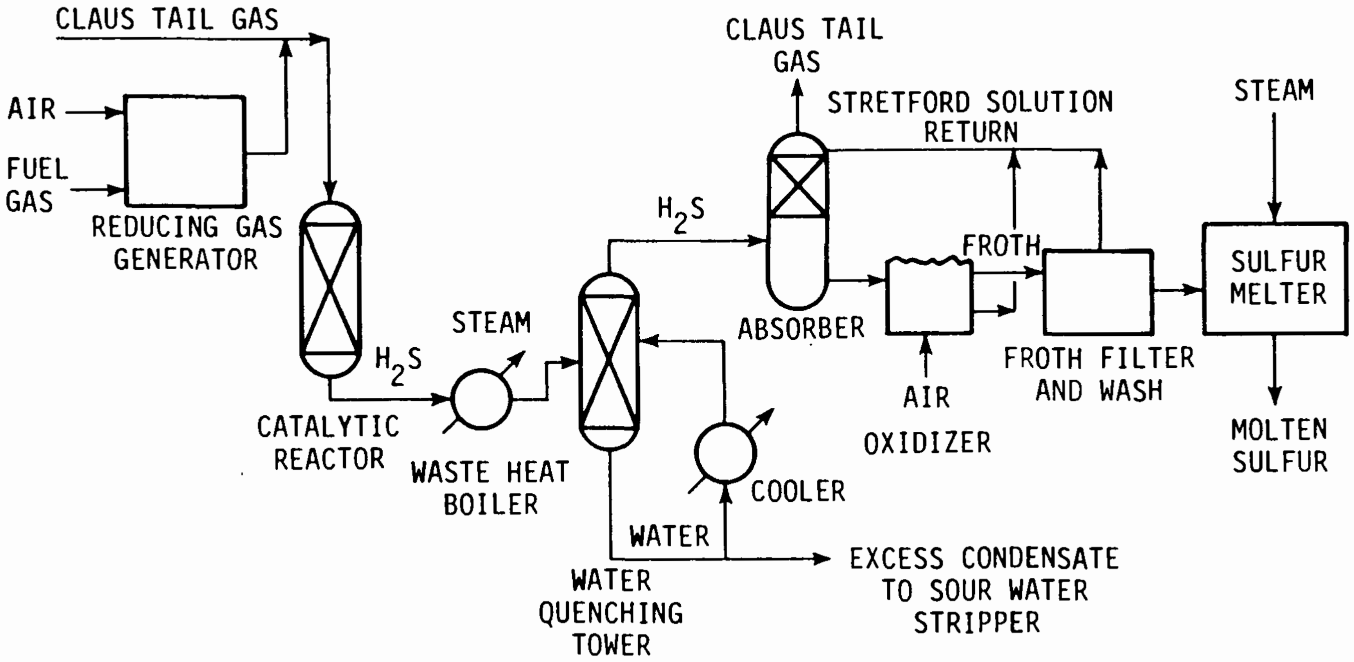

Figure 4.16-2. Flow diagram of the Beavon process.

hydrogenation and hydrolysis according to the following reactions:

$$S + H_2 \rightarrow H_2S$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

$$CS_2 + 2H_2O \rightleftarrows 2H_2S + CO_2$$

$$COS + H_2O \rightleftarrows H_2S + CO_2$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

After exiting the catalytic reactor, the gas stream is cooled in a waste heat boiler and/or quench tower and then fed to a Stretford absorber. The $H_2S$ is absorbed in an aqueous solution of sodium carbonate ($Na_2CO_3$), sodium metavanadate ($NaVO_3$), and anthraquinone 2,7-disulfonic acid (ADA). The $H_2S$ is initially absorbed in the alkaline solution in the following reaction:

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3$$

Sodium bisulfide (NaHS) and sodium bicarbonate ($NaHCO_3$) further react with $NaVO_3$ to precipitate sulfur.

$$NaHS + NaHCO_3 + 2NaVO_3 \rightarrow S + Na_2V_2O_5 + Na_2CO_3 + H_2O$$

The reduced vanadium is subsequently oxidized back to the pentavalent state by blowing with air in the presence of the ADA, which works as an oxidation catalyst:

$$Na_2V_2O_5 + 1/2\ O_2 \rightarrow 2NaVO_3$$

In the same operation, the finely divided sulfur appears as a froth, which is skimmed off, filtered, and washed. The product sulfur is then separated from the washwater and melted. The Stretford solution is recirculated to the absorber from the oxidizer and the sulfur filter.

The treated tail gas exits the system from the absorber overhead. It is odorless and contains only a trace of $H_2S$ and small amounts of carbonyl sulfide (COS) and carbon disulfide ($CS_2$), which are not converted in the catalytic reactor. The concentration of all sulfur compounds combined is less than 100 ppm. Incineration of the off-gas is not required.

## SCOT Process

The SCOT process was developed by Shell International Research Mij. B.V., The Netherlands, and is licensed in the United States by Shell Development Company.* Figure 4.16-3 is a flow diagram of this process. The sulfur compounds in the Claus plant tail gas are converted to hydrogen sulfide as in the Beavon process; i.e., the Claus off-gas is heated along with the addition of reducing gas ($H_2$, CO) and passed through a reactor containing a cobalt-molybdenum catalyst. The gas is cooled by use of a waste heat boiler for steam generation and a water quenching tower. Excess condensate from the quench is routed to a sour water stripper.

Gas from the quench tower is contacted countercurrently in an absorption column with a di-isopropanolamine (DIPA) solution, which absorbs all but trace amounts of the $H_2S$ plus about 30 percent of the $CO_2$. The sulfide-rich DIPA is sent to a conventional stripper, where the $H_2S$ is removed from the solution. The overhead gas, mostly $H_2S$, is recycled to the Claus unit inlet. The lean amine solution is returned to the absorber. The absorber outlet gas, containing some unabsorbed $H_2S$ and residual organic sulfides, is sent to the original Claus tail gas incinerator before discharge to the atmosphere. Typical concentrations of $SO_2$ range from 200 to 500 ppm.

## Wellman-Lord Process

This process, developed by Davy-Powergas, Inc., is illustrated in Figure 4.16-4. The Claus tail gas stream is incinerated, and the gas is then cooled in a waste heat boiler and

*Shell Development Company, Houston, Texas.

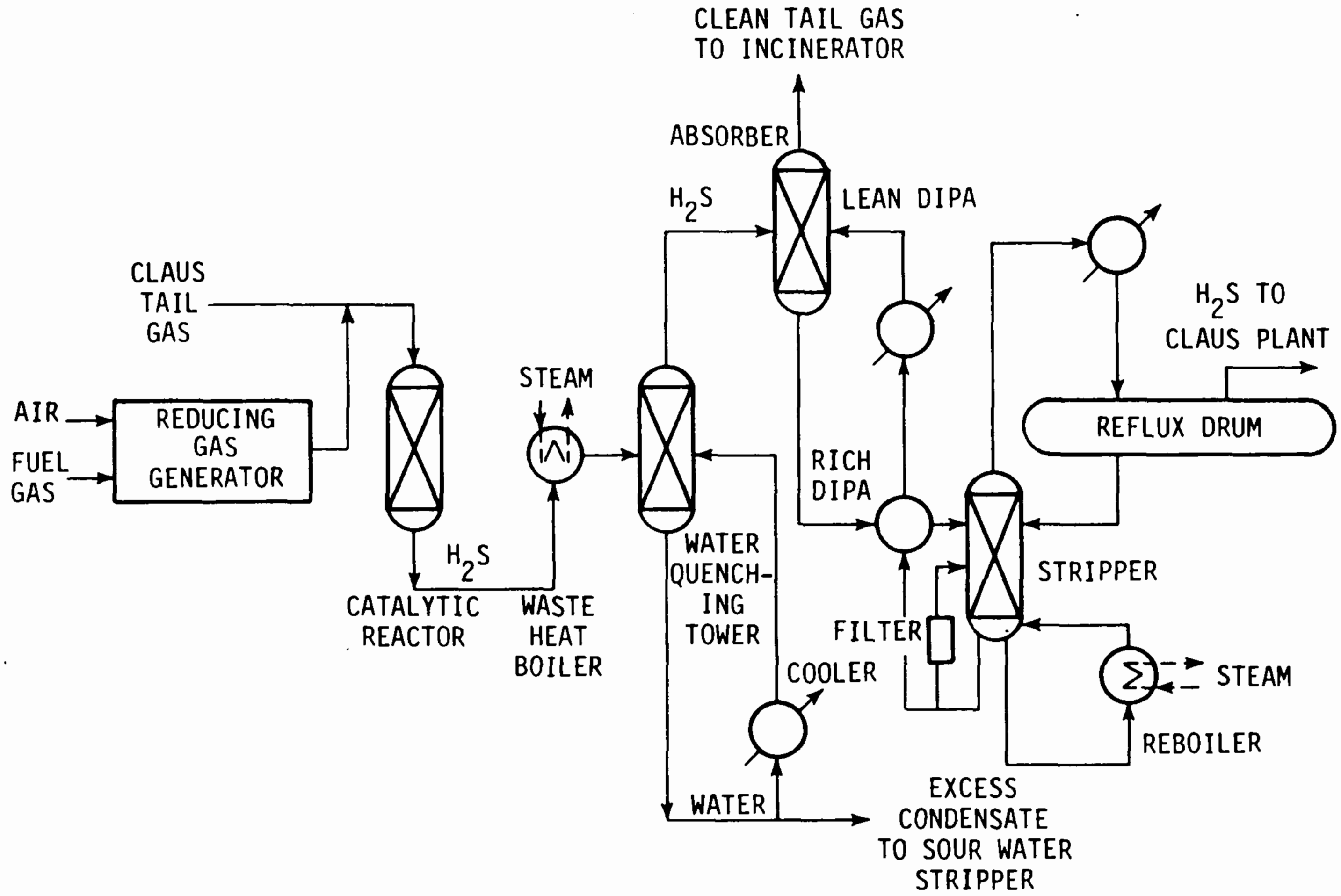

Figure 4.16-3. Flow diagram of SCOT process.

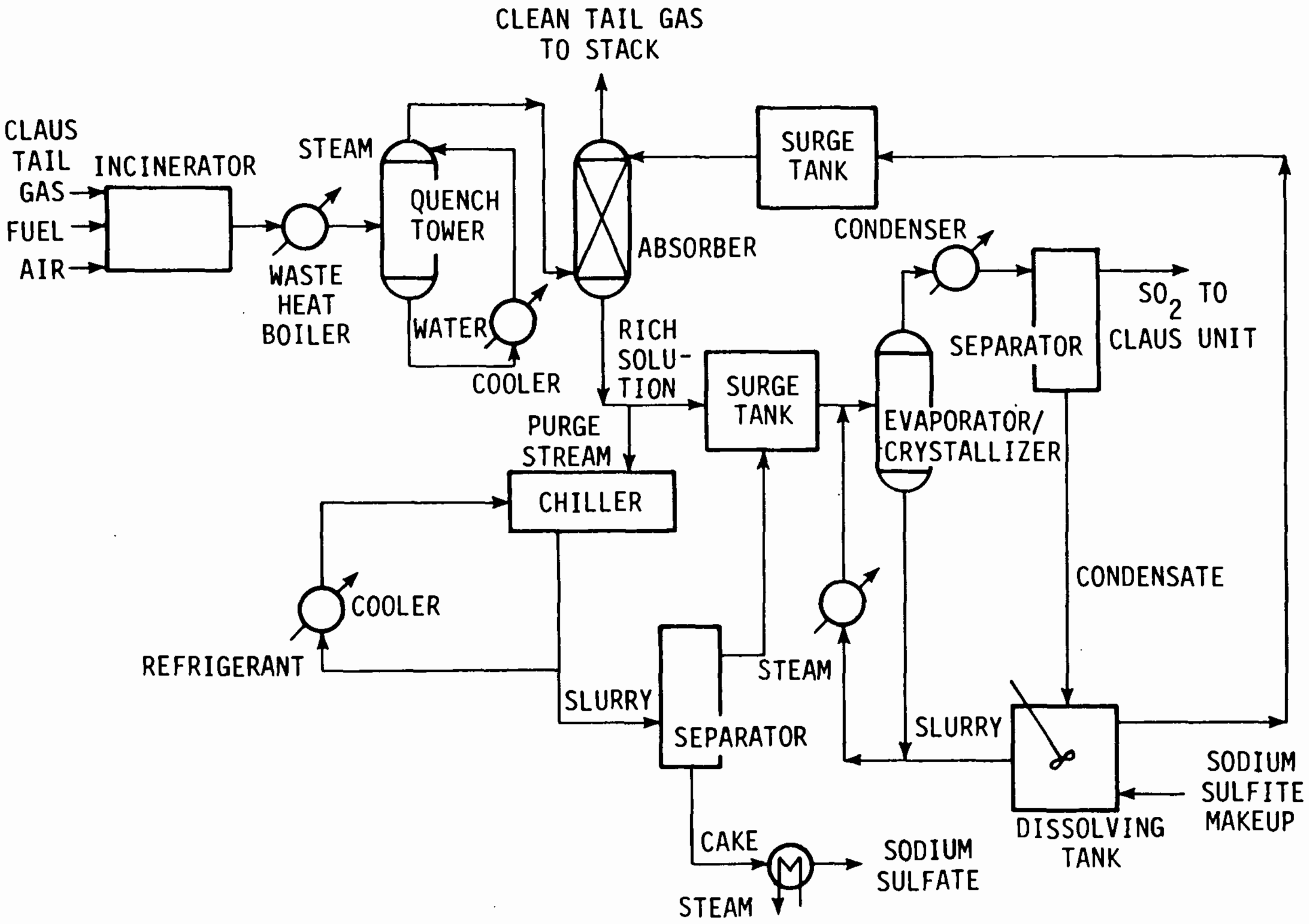

Figure 4.16-4. Wellman-Lord $SO_2$ recovery process flow diagram.

direct-quench tower before entering the absorber. In the absorber, the gas stream is scrubbed with a lean $Na_2SO_3$ solution to form sodium bisulfite ($NaHSO_3$) and sodium pyrosulfite ($Na_2S_2O_5$) by the following reactions:

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$$

$$2NaHSO_3 \rightarrow Na_2S_2O_5 + H_2O$$

The rich bisulfite solution is fed to an evaporator/crystallizer regeneration system. Heat supplied to the evaporator causes the decomposition of the bisulfite and pyrosulfite:

$$2NaHSO_3 \rightarrow Na_2SO_3 + SO_2 + H_2O$$

$$Na_2S_2O_5 \rightarrow SO_2 + Na_2SO_3$$

The $SO_2$ and water vapor pass overhead from the evaporator to a primary condenser, where 80 to 90 percent of the water is removed. The condensate is stripped with steam to remove dissolved $SO_2$. Stripper overhead and condenser overhead vapors are mixed and sent to a secondary condenser. Condensate is returned to the stripper, and the vapor stream is recycled to the Claus plant. The recycle is 90 to 95 percent $SO_2$.

The main problem with the Wellman-Lord process is the formation of nonregenerable sulfate and thiosulfate by the following side reactions:

$$Na_2SO_3 + 1/2\ O_2 \rightarrow Na_2SO_4$$

$$SO_2 + 3Na_2SO_3 \rightarrow 2Na_2SO_4 + Na_2S_2O_3$$

$$Na_2S_2O_3 \rightarrow S + Na_2SO_3$$

$$2Na_2SO_3 + SO_3 \rightarrow Na_2SO_4 + Na_2S_2O_5$$

Because of the sulfate and thiosulfate formation, a portion of the solution must be purged from the system, necessitating replacement of chemicals and disposal of wastes. Chemical requirements have been minimized by a system that selectively removes the sulfate by crystallization. The concentrated purge stream can then be dried for sale or disposal. Davy-Powergas is currently developing processes that chemically reduce the sulfate back to sodium sulfite.

## IFP-1500 Process

The IFP process, developed by the Institut Francais du Petrole, is shown schematically in Figure 4.16-5. This process converts mixed hydrogen sulfide/sulfur dioxide streams to sulfur and water by a liquid-phase Claus reaction using a proprietary catalyst. The process is used primarily to clean Claus unit tail gas. The technology is an extension of the Claus reduction process but is carried out in the liquid phase.

The tail gas, at Claus unit exit pressure, is injected into the bottom of a packed tower, which provides the necessary surface area for gas-liquid contact. A low-vapor-pressure polyethylene glycol solvent containing a proprietary carboxylic acid salt catalyst in solution circulates countercurrently to the gas.

The catalyst forms a complex with $H_2S$ and $SO_2$, which in turn reacts with more of the gases to regenerate the catalyst and form elemental sulfur. The reaction is exothermic, and the heat released is removed by injecting and vaporizing steam condensate. Temperature is maintained at about 120° to 130°C (250° to 270°F), high enough to keep the sulfur molten but not to cause much loss of sulfur or glycol overhead. The sulfur accumulates in the bottom of the tower and is drawn off continuously through a seal leg. Overheads are incinerated.

The vendor claims that the IFP-1500 process is insensitive to changes in gas flow rates. It has been shown to operate on flows as low as 30 percent of design rate without adverse effect. Another stated advantage is maintenance-free operation for about 24 continuous months. After this period, a shutdown is needed to wash away spent catalyst deposited on the packing material. A water wash is all that is required. Outlet $SO_2$ concentration is 1000 to 2000 ppm.

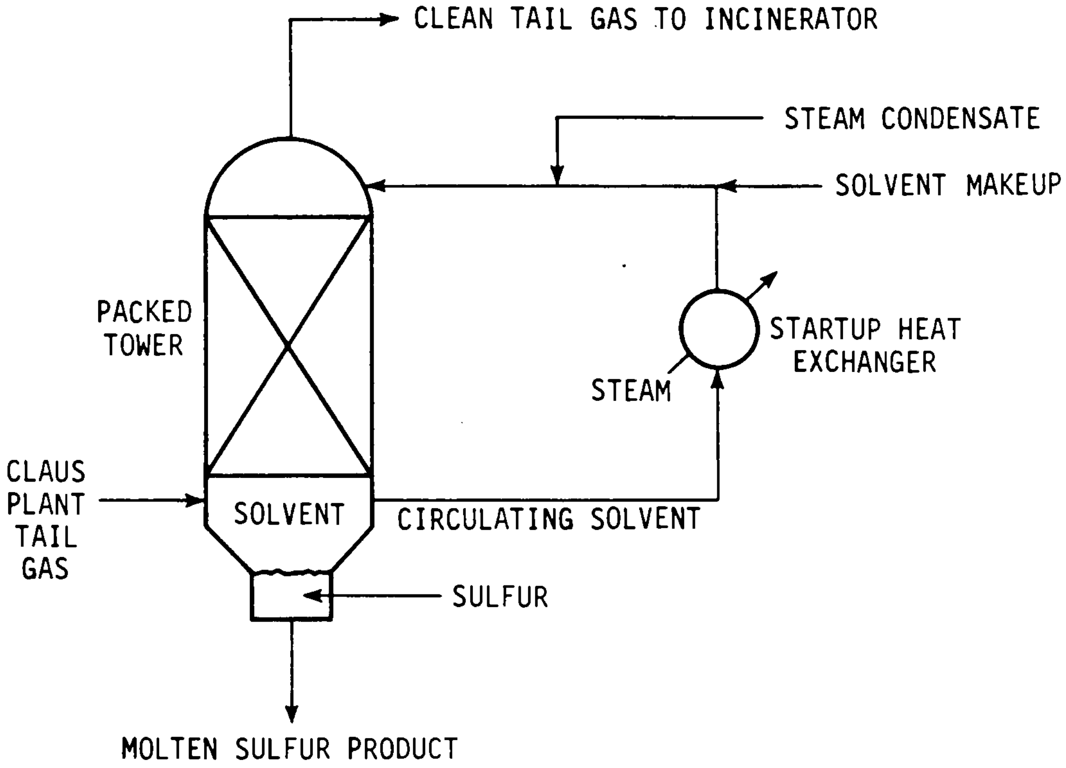

Figure 4.16-5. IFP-1500 Claus tail-gas treatment.

## 4.16.4 Instrumentation

1) Ratio of Hydrogen Sulfide to Sulfur Dioxide

The $H_2S/SO_2$ ratio is very important for the proper control of a Claus unit. Since $H_2S$ concentration in acid gas feed varies significantly, the $H_2S/SO_2$ ratio must be monitored. The $H_2S/SO_2$ ratio is controlled by a ratio controller that maintains a proper ratio of acid gas to air in the reactor. A correct $H_2S/SO_2$ ratio indicates whether the stoichiometry of the Claus reaction is correct throughout the sulfur plant.

2) Temperature Control[4]

The temperature of the noncondensed gases entering the catalyst converters must be maintained above the sulfur dew point to prevent sulfur condensation on the catalyst and to faciliate optimum sulfur recovery in the reactor. An optimum temperature for the converter must be established, although the optimum temperature changes with catalyst aging. An approximation of the desired reaction rate is maintained by increasing the temperature to compensate for the drop in catalyst activity.

The temperature at the incinerator stack must be high enough to ensure complete combustion of sulfur compounds to $SO_2$. The usual incinerator temperature is about 1200°C (2200°F) but would increase to 1400°C (2600°F) when the acid gas feed is bypassed directly to the incinerator, thus increasing the $SO_2$ emission at the stack. Hence, incinerator temperature is a good indicator of the amount of acid gas bypassed. The stack gas temperature is measured with a standard Type K (nickel, chromium-nickel, aluminum) thermocouple.

Emission of $SO_2$ is continuously monitored at the stack. Stack monitoring is useful in plant optimization studies since trends in $SO_2$ emission indicate when operational changes are successful. The analyzer is located at the base of the stack for easy access during troubleshooting.

## 4.16.5 Startup/Shutdown/Malfunctions[5]

Startup and shutdown of a Claus sulfur unit require considerable attention by the operator, since operation during these critical phases can greatly affect the overall plant efficiency. Once the Claus unit is onstream, however, little monitoring is needed except in unusual circumstances.

Most of the Claus units installed today have refractory-lined external combustion chambers. The most difficult startup problems are associated with the external combustion chamber. Carefully controlled curing of the refractory is necessary to prevent spalling. If the refractory is heated too rapidly, water in the refractory will vaporize rapidly, causing damage to the refractory. Gradual heating of the refractory is especially important during the initial startup. During the refractory curing, it is imperative that the curing temperature be held constant because temperature oscillations often lead to improper curing and subsequent failure of refractories.

Before either the pilot or the main burner is ignited, the waste heat boiler must be filled with water to prevent damage to the tubes.

The most important part of the Claus sulfur plant operations is the procedure to be followed for planned shutdowns. Stoichiometric combustion of fuel gas is used to purge the sulfur compounds and also to cool the unit. Fuel gas is added to the burner, and when the fuel gas flame is established, the acid gas is shut off.

Airflow to the unit is increased to oxidize the fuel gas stoichiometrically. Incomplete combustion of fuel gas because of less than stoichiometric air can cause carbon formation that can seriously foul the unit. Generally, the carbon is deposited on the catalytic reactor and can sometimes block the flow through reactors. Deposition of carbon on boiler and sulfur condenser tubes can cause production of off-color sulfur. Thus, it is important that adequate air is available and the fuel gas is fully oxidized. Natural gas is recommended for shutdown procedures because the variable composition of fuel gas makes proper oxidation difficult.

Control of the combustion temperature when stoichiometric combustion conditions exist is also important. The stoichiometric combustion temperature ranges between 1650° and 2040°C (3000° and 3700°F), depending upon the fuel gas composition. This range is too high for the refractory in the external combustion chamber. Inert gases such as nitrogen are used to reduce the temperature of the stoichiometric products of combustion and to maintain reasonable chamber temperatures. Excess air cannot be used at this stage because sulfur ignites spontaneously in the presence of oxygen at temperatures above 204°F (400°F). Reactor temperatures usually exceed this level at the time of shutdown. Therefore, excess oxygen of only 2 percent is used to ensure proper combustion of the fuel gas and prevent spontaneous ignition of sulfur in the reactor. Regular analysis of the combustion products is required to maintain this close control because sulfur fires can occur even with the small amount of excess oxygen used for proper combustion. If a sulfur fire is detected, the air should be promptly shut off. Inert gas such as nitrogen should continue being fed to the unit. The nitrogen will extinguish the sulfur fire and continue to purge the unit of free sulfur.

It is imperative that the sulfur be purged from the unit prior to cooling because sulfur will solidify at temperatures below 121°C (250°F). The presence of solidified sulfur can necessitate replacement of the catalyst and manual cleaning of the boiler and sulfur condenser tubes.

Emergency shutdowns often cause serious problems in a Claus unit if the proper precautions are not taken. If the burner cannot be relit soon after an emergency shutdown, such as one caused by a low level of water in the boiler, inert gas should be fed to purge the reactor of sulfur. Otherwise the sulfur could solidify and cause considerable damage to the plant.

Most of the problems in the operation of a tail gas unit stem from Claus unit upsets and fluctuations. In the Beavon/Stretford process, tail gas flow rates higher than the design rates can cause solvent overloading. Mechanical problems have also been encountered with the froth filter, which may be eliminated on future units. Excess $SO_2$ causes contamination of the amine solution in a SCOT unit and corrosion of the quench water pump and pipes. This problem can be prevented by monitoring the pH of the quench water and by ensuring an excess of hydrogen in the reactor by use of the reducing gas injection system. Emissions of $SO_2$ and $H_2S$ caused by fluctuating tail gas flow rates can be reduced or averted by proper flow controls on the Claus unit.

### 4.16.6 References

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3. Communication between Ford, Bacon, and Davis, Dallas, Texas, and U.S. Environmental Protection Agency, Raleigh, North Carolina. September 9, 1971.

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5. Parnell, D. C. Claus Sulfur Recovery Unit Startups. Chemical Engineering Progress, August 1969. pp. 8892.

SULFURIC
ACID

## 4.17 SULFURIC ACID PLANT[1-4]

Crude oils contain elemental sulfur, hydrogen sulfide, and other sulfur compounds. The sulfur must be removed because it can contaminate catalysts during intermediate cracking and can generate corrosive gases and sulfur dioxide emissions during fuel oil, kerosene, and gasoline combustion.

One way to handle the sulfur produced as an oil refinery byproduct is to build a sulfuric acid plant. Fifty-five percent of the sulfuric acid produced is used in the refinery for the alkylation unit. The production of sulfuric acid is not limited, however, to the oil industry. Sulfuric acid is a necessary part of the organic chemical, inorganic pigment, metal, fertilizer, and detergent industries.

The standard contact process is used to manufacture about 90 percent of the sulfuric acid in the United States. Variations in this conventional process are the acid recirculation process, the Simonson-Mantius vacuum process, and the Chemico drum concentration process. At the refinery, sulfuric acid is made from recovered elemental sulfur, hydrogen sulfide from the amine stripper, and spent acid from the alkylation units. Sulfuric acid is also produced from sulfur obtained from the Claus unit tail gas described in Section 4.16.

### 4.17.1 Process Description

#### Standard Contact Process

Hydrogen sulfide or elemental sulfur is the raw material for sulfuric acid production at refineries. Three basic reactions of acid production are illustrated below:

$$\underset{\text{Sulfur}}{S} + \underset{\text{Oxygen}}{O_2} \rightarrow \underset{\text{Sulfur dioxide}}{SO_2}$$

$$\underset{\substack{\text{Sulfur}\\\text{dioxide}}}{2SO_2} + \underset{\text{Oxygen}}{O_2} \rightarrow \underset{\text{Sulfur trioxide}}{2SO_3}$$

| | | | | |
|---|---|---|---|---|
| $SO_3$ | + | $H_2O$ | → | $H_2SO_4$ |
| Sulfur trioxide | | Water | | Sulfuric acid |

In these reactions, the sulfur or hydrogen sulfide is first burned to sulfur dioxide. The sulfur dioxide is then catalytically converted to sulfur trioxide, which is absorbed by a sulfuric acid solution.

Figure 4.17-1 is a flow diagram of an elemental sulfur burning plant for sulfuric acid production. Dry air scrubbed with 95 percent $H_2SO_4$ is used in burning elemental sulfur to sulfur dioxide. A catalytic converter, using a vanadium pentoxide catalyst, transforms the $SO_2$ to $SO_3$. The heat (energy) from this exothermic reaction is usually directed to steam production. The converter heater systems are of two types: internal heat exchanger, with cooling tubes embedded in the catalyst; or external coolers installed between the converters.

The sulfur trioxide is cooled and transferred to an absorption tower where it is absorbed by a solution of 99 percent $H_2SO_4$. In some cases an oleum solution of uncombined $SO_3$ in $H_2SO_4$ is produced. This excess $SO_3$ is sent to another column for further absorption. The oleum tower gases are recycled to the first absorption column to remove any residual $SO_3$.

Spent acid regeneration in the contact process is becoming more attractive as a solution to unwanted byproducts. High-quality $H_2SO_4$ can be produced by thermal decomposition of $H_2SO_4$ at high temperatures to $SO_2$, and then conversion of the $SO_2$ to concentrated $H_2SO_4$ or oleum. The reactions in this spent acid process are shown below:

| | | | | |
|---|---|---|---|---|
| $H_2SO_4$ | → | $H_2O$ | + | $SO_3$ |
| Sulfuric acid | | Water | | Sulfur trioxide |

| | | | | |
|---|---|---|---|---|
| $SO_3$ | → | $SO_2$ | + | $1/2\ O_2$ |
| Sulfur trioxide | | Sulfur dioxide | | Oxygen |

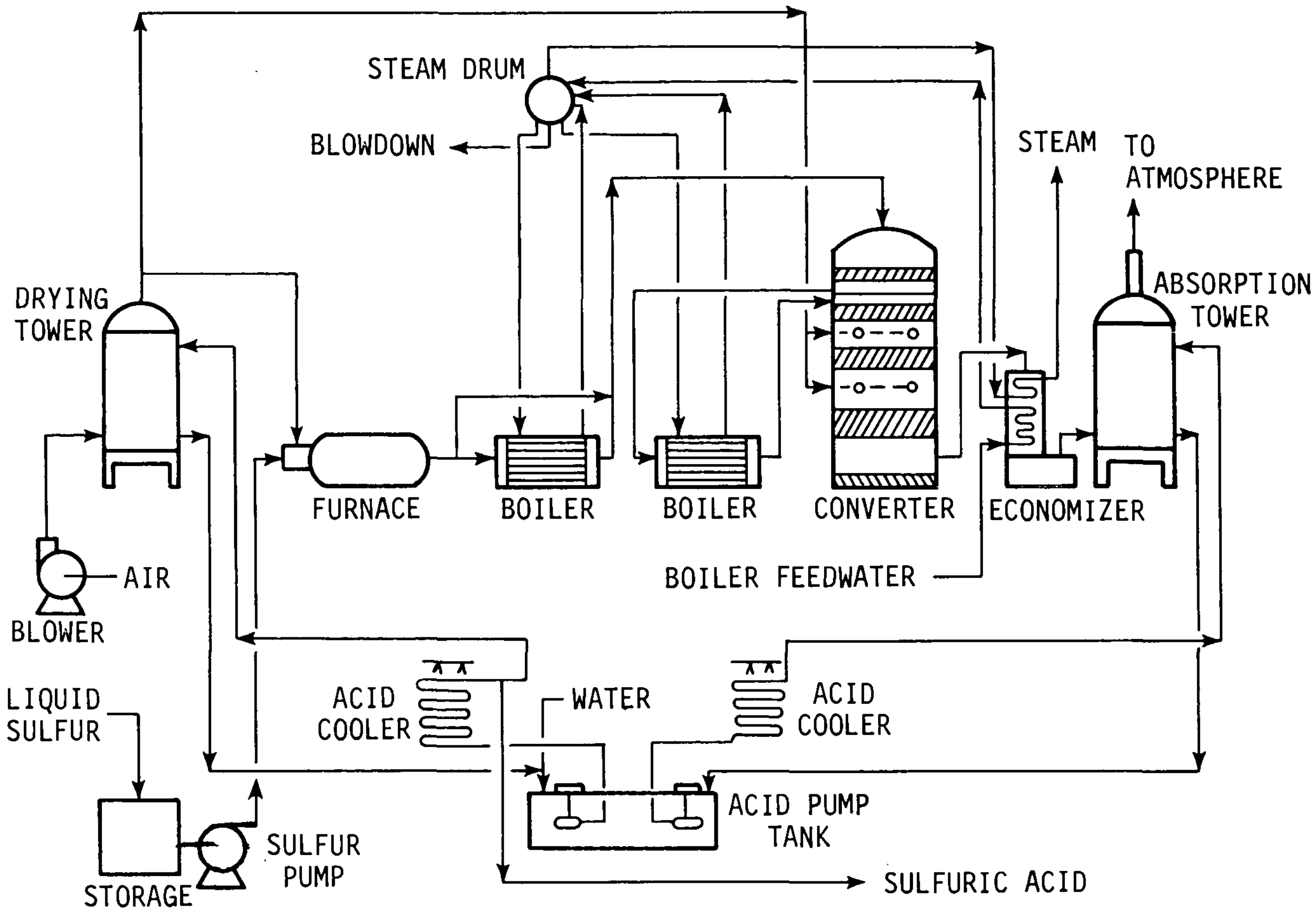

Figure 4.17-1. Flow diagram of contact-process sulfuric acid plant burning elemental sulfur.

$$\begin{array}{ccccccc} H_2SO_4 & \rightarrow & H_2O & + & SO_2 & + & 1/2\ O_2 \\ \text{Sulfuric acid} & & \text{Water} & & \text{Sulfur dioxide} & & \text{Oxygen} \end{array}$$

The first reaction step is conducted at temperatures above 500°C (932°F). The second step requires even higher temperatures. The efficiency of the whole process ranges between 60 and 70 percent.

Figure 4.17-2 is a flow diagram of an acid regeneration plant. This acid decomposition unit is combined with a heat recovery system for high-pressure steam production.

A rotary atomizer feeds spent acid into a vertical decomposition furnace. The lower part of the decomposition furnace is held at 100°C (212°F) for maximum efficiency. The decomposition gases leaving the gas heat exchangers are cleaned in a venturi scrubber and cooled to 90°C (194°F). The $SO_2$ gases are further cooled in the countercurrent cooling tower with a water section containing 1 percent $H_2SO_4$. The gases pass through the electrostatic precipitators for mist elimination.

The gas stream is then dried and discharged into a sulfur trioxide converter. The gas from the converter flows to a tower where a solution of 93 to 98 percent $H_2SO_4$ absorbs the $SO_3$.

Another design for the heat recovery system of a regeneration sulfuric acid plant includes a waste heat boiler. In this design, the decomposition furnace has three combustion chambers using heavy fuel oil and air preheated to a temperature of about 300°C (570°F).

### The Simonson-Mantius Vacuum Concentration Process

In the Simonson-Mantius variation of the contact process, steam heating vaporizes the water from the vacuum-maintained acid. This method is more economical than the standard process if low-pressure waste steam is available and if the operating range is dilute. The vacuum method allows lower operating temperatures to be used.

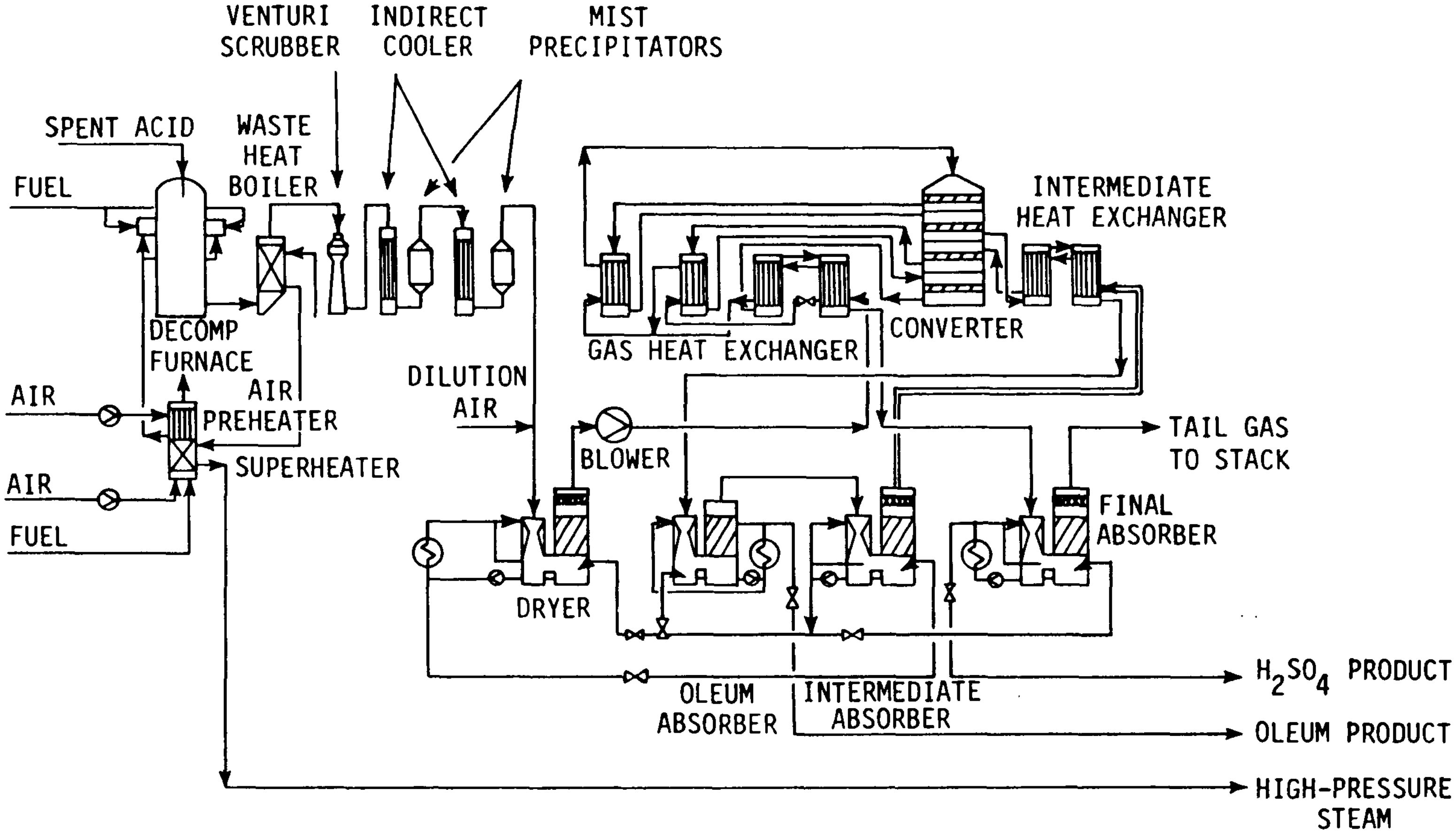

Figure 4.17-2. Flow diagram of acid regeneration plant.[2]

Figure 4.17-3 is a simplified flow diagram of a vacuum concentration process. The 30 percent feed acid is sent to the first concentrator unit, which is held at 66°C (150°F) and 13.5 kPa (4 in. Hg). Steam heating is used to increase the concentration of acid to 50 percent. In the same manner, the acid is further concentrated in two additional units to 93 percent. Each concentrator unit is held at a lower pressure and a higher temperature than the preceding one. The acid is then pumped through an acid cooler to a product storage tank held at 43°C (110°F).

### The Chemico Drum Concentration Process

The Chemico drum concentration process is similar to the Simonson-Mantius process with the exception of the concentrator unit. Figure 4.17-4 is a flow diagram of this process. The water is removed from the acid in the concentrator drum, which is operated at atmospheric pressure. The acid, sent through a furnace fired with fuel gas, is directly in contact with the fuel gas before it reaches the three stages of the concentrator drum. One advantage of using the drum process is the cleaning of gases in the venturi scrubber after leaving the drums. The concentrated acid is then cooled and stored. This process produces acid at a concentration of 93 percent.

### Contact Process With Single Absorption and Acid Recirculation

The Chemetics International process for a sulfuric acid plant is a single absorption process using pressure to improve catalysis and to recycle a substantial amount of $SO_2$ via a simple acid circulating system. This process, which is shown in Figure 4.17-5, increases efficiency, lowers emissions, reduces equipment size, and saves power. In the first step the inlet air is filtered, dried by contact with sulfuric acid, and compressed to between 505 and 1520 kPa (5 and 15 atm). The dry air passes through a furnace where molten sulfur is burned to form a hot $SO_2$ gas and cooled in a waste heat boiler. The $SO_2$ gas is then

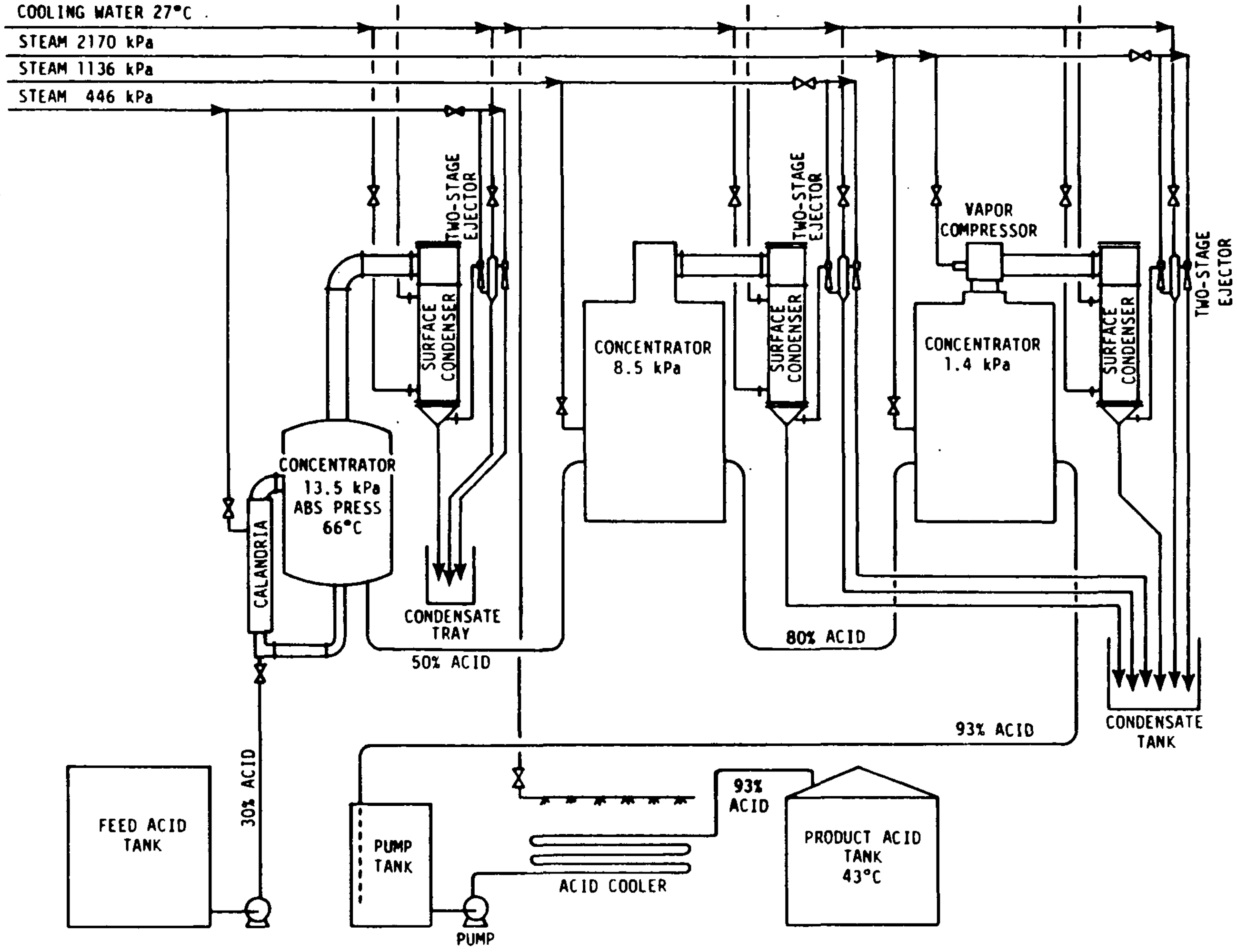

Figure 4.17-3. Flow diagram of vacuum concentration process.[3]

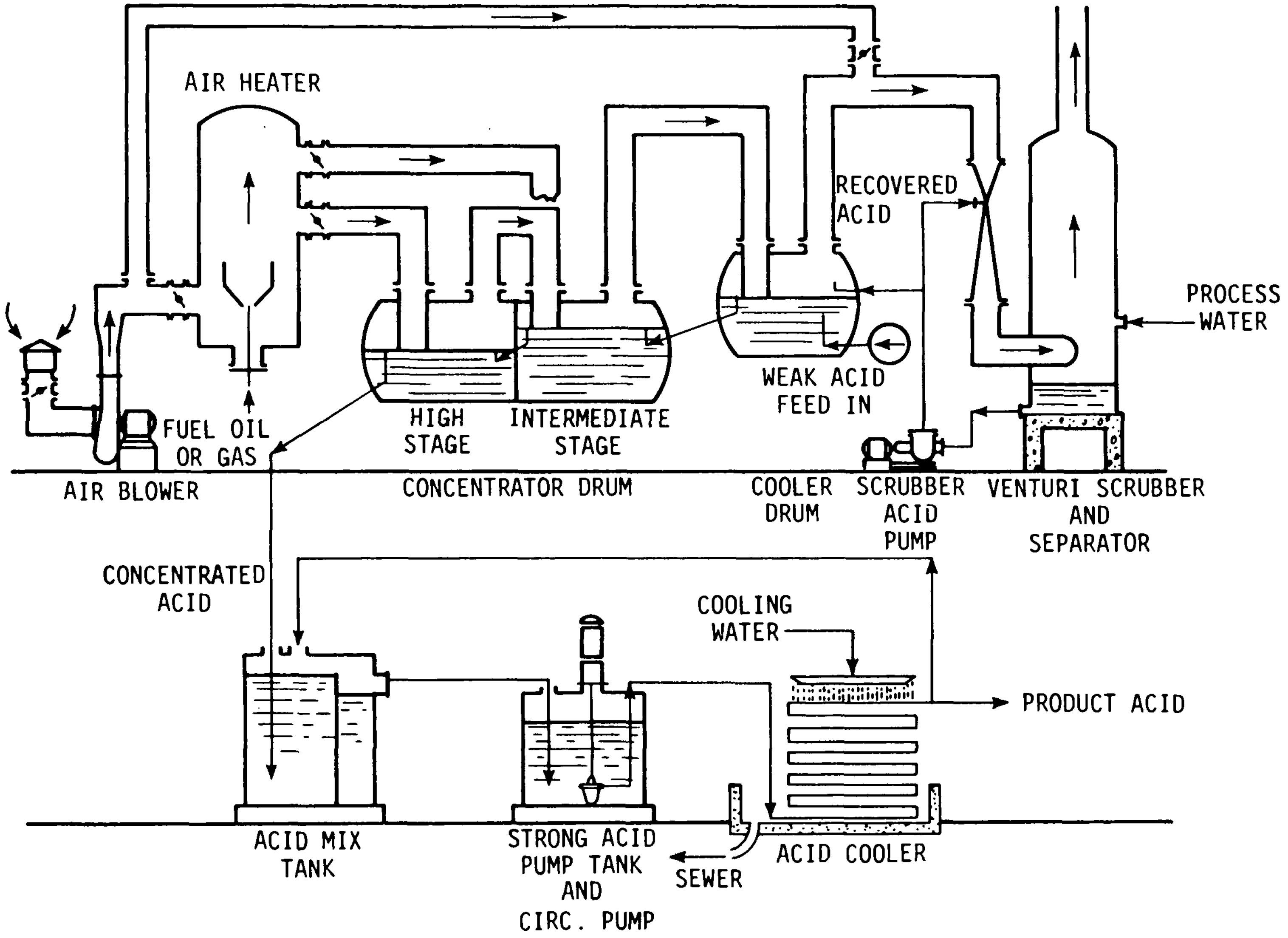

Figure 4.17-4. Flow diagram of Chemico drum concentration process.[3]

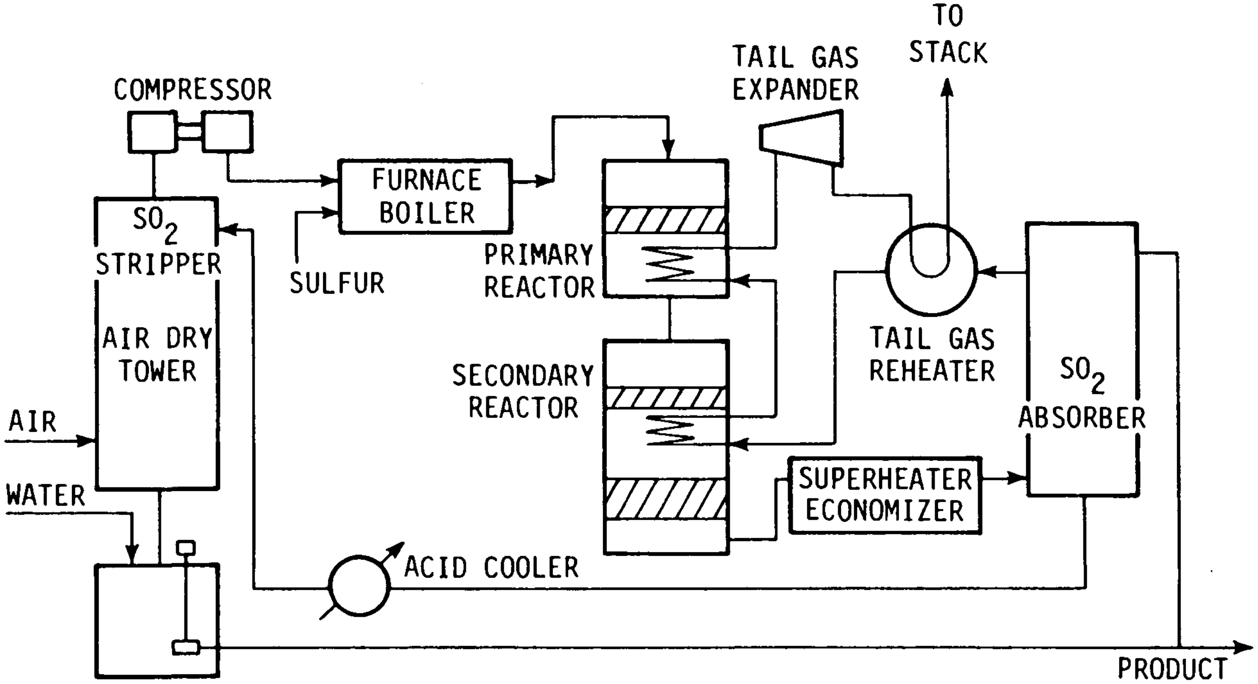

Figure 4.17-5. Flow diagram of acid recirculation process.[4]

converted to $SO_3$, cooled, and absorbed in the acid. The exhaust gas is reheated using process heat and passed to an expansion turbine. The $SO_2$-free acid is sent to the top of the absorber. In the absorber, it produces a warm, $SO_2$-rich acid stream, which passes through the coolers to the drying tower. The $SO_2$ is transferred to the inlet air while it is simultaneously being dried. The $SO_2$-free acid is then recirculated to the absorber.

### 4.17.2 Emission Sources

Sulfur oxides, mainly dioxide, and acid mist are the primary emissions of the acid plant. Sulfur dioxide emissions are proportional to the conversion efficiency of $SO_2$ to $SO_3$. Conversion efficiency depends on the number of stages in the catalytic reactor, the quantity of catalyst, reactor temperature and pressure, and reactant concentrations. Single absorption plants usually have efficiencies of 95 to 98 percent.

Most of the sulfur dioxide is emitted in the exit gases from the absorber. There are some fugitive $SO_2$ emissions, however, from tank vents while loading, and from process equipment leaks. In a well-operated plant, there are minor fugitive emissions.

Acid mist is produced when sulfur trioxide combines with water vapor below the sulfur trioxide dew point. Absorber exit gases are the primary emitters of acid mist. The feedstock and strength of the acid product determine the amount of acid mist emitted. Clean elemental sulfur feedstock produces little acid mist; spent acid and hydrogen sulfide, however, oxidize the water vapor and the water combines with the sulfur trioxide to produce acid mist.

The concentration of acid mist emissions is directly proportional to the concentration of the acid product. For instance, oleum plants produce more acid mist with higher stability and finer particle size than do 99 percent sulfuric acid plants.

### 4.17.3 Emission Controls

Sulfur dioxide emissions can be reduced by dual absorption or by the sodium sulfite-bisulfite process. These acid mist control methods produce no unwanted byproducts. When a dual absorber is used for sulfuric acid production, the efficiency of the conversion from $SO_2$ to $SO_3$ increases from about 96 (for a single absorption process) to 99.7 percent or higher. The two absorbers are run in series, and the increased operating efficiency reduces $SO_2$ emissions.

In the sodium sulfite-bisulfite process, scrubbing is used to remove $SO_2$ from the exit gases by a solution of sodium sulfite. The $SO_2$ is separated from the sulfite, and the sulfite is recycled to the plant. Sulfite-bisulfite absorption can remove 99.8 percent or more of the $SO_2$ in the exit gases.

Acid mist emissions are reduced by an electrostatic precipitation (ESP) or fiber mist eliminator. The ESP has been shown to be 99 percent efficient with good operating and maintenance practices.

The fiber mist eliminator is usually of the vertical tube, vertical panel, or horizontal dual-pod type. Only small quantities of acid mist are removed by the absorber. Glass or fluorocarbon fibers are used to collect the acid mist from the exit gas stream. The removal efficiency of these units usually exceeds 99.9 percent. This excellent control is achieved with minimal maintenance because fiber beds do not have moving parts.

Certain problems, however, are associated with the mist eliminator: entrainment of large particles; a persistent, visible plume; reduced capacity because of pluggage. Entrainment is corrected by monitoring gas flow rates and conducting a physical inspection of the unit, including the liquid seals. When a visible plume is spotted, a sample is taken to determine whether the plume is caused by unabsorbed $SO_3$. If it is, changes are made in the operation of the absorbing tower.

Pluggage is caused by a buildup of iron sulfate or sublimed sulfur on the mist eliminator. The buildup of iron sulfate results from water in the system; the sublimed sulfur results from improper operation of the sulfur burner. Correction involves water washing the sulfate deposits and washing the sublimed sulfur with a 0.5 percent sodium sulfide solution after the elements are neutralized with soda ash. Preventive measures include keeping records of pressure drop, flow rate, operating tower information, mist eliminator drain rate, and acid strength.

Mist formation can be regulated by keeping as little water in the sulfur trioxide gas stream as possible. The water content can be minimized by lowering the organic content of the sulfur, thoroughly drying the process air stream, and increasing absorbing tower acid strengths.

Mist eliminator problems are detected by inserting a clean, wooden stick into a suspect gas stream. If problems are present, the stick will show a certain number of black spots for a given period of exposure. The stick tests should be carried out where the gas velocity is in excess of 304.8 m/min (1000 ft/min).

Sampling is a more precise technique than the stick test, but it is time consuming and does not distinguish between liquid acid mist and sulfur trioxide vapor.

### 4.17.4 Instrumentation

Temperature, pressure, flow rate, and raw material influence the efficiency of the acid production process. Temperature and pressure are controlled and monitored closely. The temperature varies (depending on the process) around 400°C (750°F). Spent acid undergoes thermal decomposition, however, at about 1000°C (1830°F). Heat must be removed from the process because the $SO_3$ formation is exothermic and the equilibrium constant becomes less favorable as the temperature rises. Increasing the pressure forces the system to react to sulfur trioxide, because 1.5 moles of reactants form 1 mole of product, which requires less volume. Increasing the oxygen content increases reaction efficiency.

Concentrations of oxygen and sulfur dioxide, which are the reactants, must be monitored.

### 4.17.5 Startup/Shutdown/Malfunctions

During acid plant startup, an energy (heat) source initiates the conversion of sulfur dioxide to sulfur trioxide. When the reaction has begun, the energy source is removed and the process produces its own heat energy (plus excess energy for steam production). Temperature is critical during startup, and should be closely monitored.

Acid plant shutdown does not cause problems. Shutdown is effected simply by shutting off the feedstock and oxygen supply.

Malfunctions might occur as a result of the corrosive nature of the acid product. Nickel chromium alloys and polytetrafluoroethylene (PTFE) coating have reduced malfunctions.

### 4.17.6 References

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3. Smith, G. M., and E. Mantius. The Concentration of Sulfuric Acid. Chemical Engineering Progress, September 1978. pp. 79-80.

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# BLENDING

## 4.18 PRODUCT BLENDING[1]

Petroleum refineries increase operating flexibility and profits by blending intermediate crude oil derivatives into a variety of finished goods. Blending minimizes costs by combining low-cost intermediates with higher cost materials to produce incremental products at maximum profit.

Computers aid in formulating and metering the in-line blending of gasoline and other high-volume product operations. Data about intermediate material inventories, costs, and physical properties are stored in the computer. Operational research techniques (linear programming) select the components that will produce the required volume of a specified blended product at the lowest possible cost.

### 4.18.1 Process Description

A pipeline, receiving tank, and metering pumps and valves are usually the only equipment necessary for intermediate blending. In-line and tank mixers may also be used. Stream analyzers are sometimes used to test the boiling point, specific gravity, Reid Vapor Pressure (RVP), and octane of the blended product to ensure that it is within specifications.

Blends are usually based on a few parameters. For instance, gasoline is blended to obtain a specific RVP by using components with boiling ranges within the product specification and adjusting for octane values. A typical gasoline might consist of light-straight-run (LSR) stock, reformate, alkylate, and FCC gasoline blended with n-butane to arrive at the prescribed RVP and octane level. Motor oil blends depend heavily on viscosity.

### 4.18.2 Emission Sources

Fugitive volatile organic compounds (VOC) are the most common emissions from a product blending operation. Leaky unions, fittings, pumps, and valves are the primary sources. Tank loading emissions can be significant, especially where a fixed-roof blend tank is filled with gasoline at a pressure of 69 kPa (10 psia). Lubricating oils emit low levels of VOC; fuel oil emits slightly higher levels because it has a higher vapor pressure.

### 4.18.3 Emission Controls

Pipefittings should be checked and replaced or tightened whenever necessary to eliminate VOC emissions. Tanks built after 1971 and having vapor pressure between 10 and 76 kPa (1.5 and 11 psia) must be equipped with floating roofs to minimize emissions. In some instances, emissions from tanks are controlled by vapor recovery systems.

Valve and pump seals should be checked regularly and tightened or replaced if leaking. Sampling ports and piping and instrument lines should be checked and repaired as necessary.

### 4.18.4 Instrumentation

Volume measurement and control are the most important functions in a blending operation. Volumes must be measured accurately to control the blend and ultimate quality of a product. Instrumentation is complicated if a computer is used to control flow rates and volumes. Continuous sampling devices and testing equipment are usually associated with the metering pumps and valves. Parameters monitored include boiling point, vapor pressure, octane number, and viscosity.

### 4.18.5 Startup/Shutdown/Malfunctions

Startup and shutdown of a blending operation create no particular problems. The pipes, valves, and pumps are relatively standard and do not present unfamiliar problems to the refining industry.

Pumps, valves, and fittings should be carefully inspected for VOC leaks during startup of a blending operation. Pump and valve packing should be tightened or changed if a leak is detected. Fittings should be tightened or replaced as necessary.

If blend tanks are to be empty for any extended period, they should be cleaned to minimize VOC emissions.

### 4.18.6 Reference

1. Nelson, W. L. Petroleum Refining Engineering. McGraw-Hill Book Company, New York, 1958. pp. 141-146.

## 4.19 CRUDE AND PRODUCT STORAGE[1]

### 4.19.1 Vessel Description

A refinery includes facilities for storage of large volumes of crude oil, intermediates, and finished products. Storage vessels provide a surge capacity and reservoir for refinery operations. Vessels in a refinery include fixed-roof tanks, pressure tanks, floating-roof tanks, and conservation tanks. These are constructed in a variety of shapes, most commonly as cylinders, spheres, or spheroids. Steel plate is the usual material of construction, and sections of the shell are welded together. Capacities range from a few thousand liters (gallons) up to 79 million liters (500,000 barrels).

A New Source Performance Standard (NSPS) has been promulgated in 40 CFR Part 60 Subpart K, Standards of Performance for Storage Vessels for Petroleum Liquids. This regulation specifies the type of storage required for three volatility categories: low, intermediate, and high. Table 4.19-1 defines volatility categories in terms of vapor pressure and lists the types of tanks acceptable for storage of liquids in each category. The vapor pressures of various hydrocarbons and petrochemicals are listed in Table 4.19-2. The inspector may refer to this table or to Appendix E to determine the type of storage vessel required for various refinery products.

The fixed-roof tank is the minimum accepted standard for storage of low volatility liquids. A cylindrical steel tank shell is topped by a fixed conical roof having a minimum slope of 6.25 cm/m (3/4 in./ft). The tanks are generally equipped with a pressure/vacuum (p/v) vent designed to accommodate minor changes in vapor volume. Fixed-roof tanks are used to store low-vapor-pressure materials such as crude oil, middle to heavy distillates, and asphalts. Figure 4.19-1 illustrates a fixed-roof storage tank.

TABLE 4.19-1. ACCEPTABLE STORAGE TANKS FOR PETROLEUM LIQUIDS OF LOW, INTERMEDIATE, AND HIGH VOLATILITY

| Volatility of stored liquid | Vapor pressure range | | Storage tank[a] |
|---|---|---|---|
| | kPa | psia | |
| Low | <10 | <1.5 | Fixed-roof tank |
| Intermediate | 10 to 79 | 1.5 to 11.2 | Floating-roof tank<br>Covered floating-roof tank<br>Variable-vapor-space tank (lifter roof and flexible diaphragm) with vapor controls for loading losses |
| High | >77 | >11.2 | Pressure tanks sealed or vented to recovery systems:<br>Low pressure, 119 to 205 kPa (17.2 to 29.7 psia)<br>Intermediate pressure, 205 to 308 kPa (29.1 to 44.7 psia)<br>High pressure, >308 kPa (44.7 psia) |

[a] Meeting minimum acceptable standard under NSPS.

## TABLE 4.19-2. PHYSICAL PROPERTIES OF HYDROCARBONS

| | Vapor molecular weight at 60°F | Product density lb/gal at 60°F | Vapor pressure in psia at: | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 40°F | 50°F | 60°F | 70°F | 80°F | 90°F | 100°F |
| Fuels | | | | | | | | | |
| Gasoline RVP 13 | 62 | 5.6 | 4.7 | 5.7 | 6.9 | 8.3 | 9.9 | 11.7 | 13.8 |
| Gasoline RVP 10 | 66 | 5.6 | 3.4 | 4.2 | 5.2 | 6.2 | 7.4 | 8.8 | 10.5 |
| Gasoline RVP 7 | 68 | 5.6 | 2.3 | 2.9 | 3.5 | 4.3 | 5.2 | 6.2 | 7.4 |
| Crude oil RVP 5 | 50 | 7.1 | 1.8 | 2.3 | 2.8 | 3.4 | 4.0 | 4.8 | 5.7 |
| Jet naphtha (JP-4) | 80 | 6.4 | 0.8 | 1.0 | 1.3 | 1.6 | 1.9 | 2.4 | 2.7 |
| Jet kerosene | 130 | 7.0 | 0.0041 | 0.0060 | 0.0085 | 0.011 | 0.015 | 0.021 | 0.029 |
| Distillate fuel No. 2 | 130 | 7.1 | 0.0031 | 0.0045 | 0.0074 | 0.0090 | 0.012 | 0.016 | 0.022 |
| Residual oil No. 6 | 190 | 7.9 | 0.00002 | 0.00003 | 0.00004 | 0.00006 | 0.00009 | 0.00013 | 0.00019 |

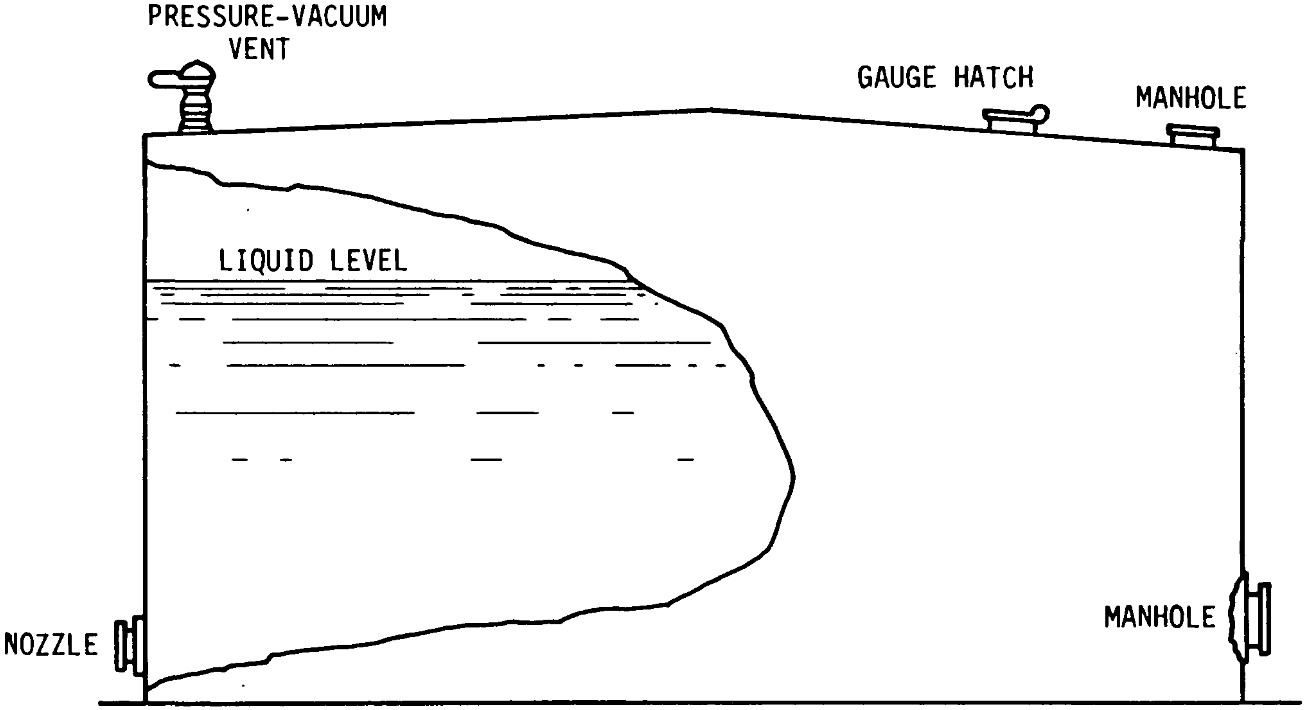

Figure 4.19-1. Fixed-roof storage tank.

Floating-roof tanks are used for storing volatile material with vapor pressures in the lower explosive range, such as gasoline and the liquid intermediates (alkylate, poly-gasoline, reformate, catalytic cracker gasoline, etc.) used in the blending of gasoline. A floating-roof tank reduces evaporative losses in storage by minimizing vapor spaces. The tank consists of a welded or riveted cylindrical steel wall equipped with a deck or roof, which is free to float on the surface of the stored liquid. The roof rises and falls with the level of stored liquid. So that the liquid surface remains completely covered, the roof is equipped with a sliding seal that fits against the tank wall. Sliding seals are also provided at support columns and at all other points where tank appurtenances pass through the floating roof. Antirotational guides maintain the alignment of the roof.

The most commonly used floating-roof tank is the conventional open tank. Because the open-tank roof deck is exposed to the weather, provisions must be made for rainwater drainage, snow removal, and protection of the sliding seal against dirt. Floating-roof decks are of three general types: pontoon, pan, and double deck.

The pontoon roof, shown in Figure 4.19-2, is a pan-type floating roof with pontoons arranged to provide floating stability under heavy loads of water and snow.

The pan roof, shown in Figure 4.19-3, is a flat metal plate with a vertical rim and stiffening braces to maintain rigidity. The single metal-plate roof in contact with the liquid readily conducts solar heat, with the result that vaporization losses are higher than those from other floating-roof decks. The roof is equipped with automatic vents for pressure and vacuum release.

As shown in Figure 4.19-4, the doubledeck roof consists of a hollow double deck covering the entire surface of the tank. The double deck adds rigidity, and the dead air space between the upper and lower decks provides effective insulation from solar heat.

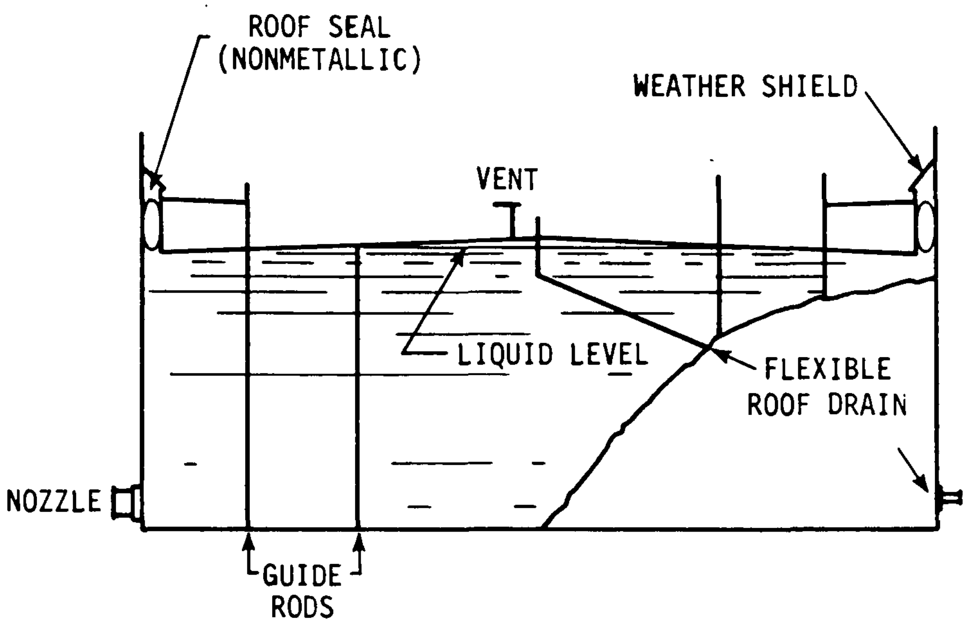

Figure 4.19-2. Single-deck pontoon-floating-roof storage tank with nonmetallic seals.

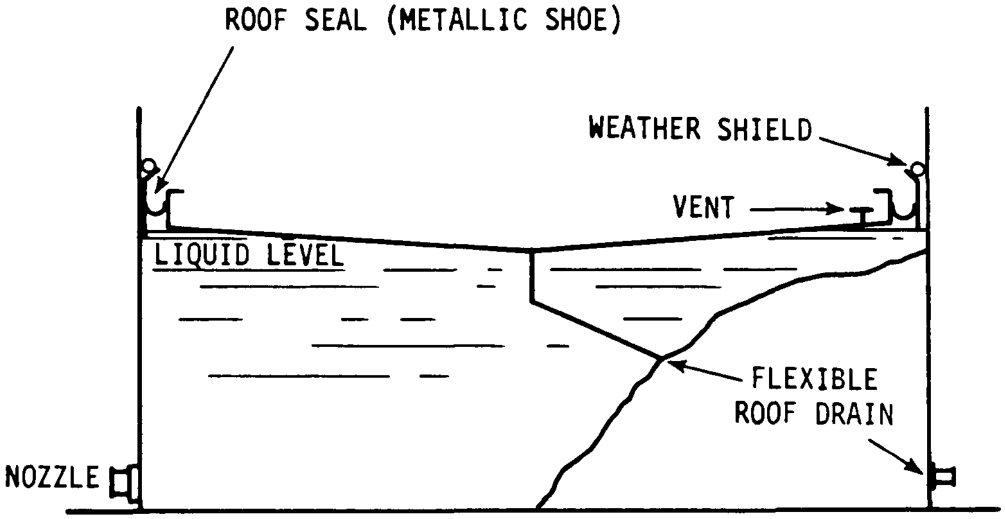

Figure 4.19-3. Pan-type floating-roof storage tank with metallic seals.

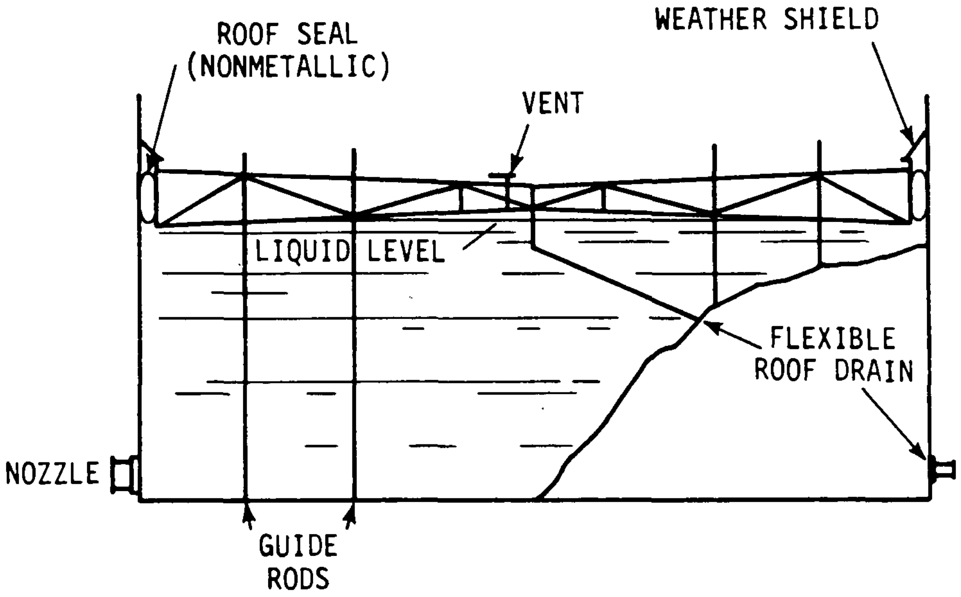

Figure 4.19-4. Double-deck floating-roof storage tank with nonmetallic seals.

The covered floating-roof tank is essentially a fixed-roof tank with a floating deck inside the tank (Figure 4.19-5). The American Petroleum Institute (API) has designated the term "covered floating roof" to describe a fixed-roof tank with an internal steel pan-type floating roof. They have designated the term "internal floating cover" to describe internal covers constructed of materials other than steel. Floating roofs and covers can be installed inside existing fixed-roof tanks. The fixed roof protects the floating roof from the weather, and no provision is needed for rain drainage, snow removal, or seal protection. Antirotational guides must be provided to maintain roof alignment, and the space between the fixed and floating roofs must be vented to prevent the formation of a flammable mixture.

Variable-vapor-space tanks have not been built for several years. Tank manufacturers report, however, that new orders for variable-vapor-space tanks have been received. These tanks are equipped with expandable vapor reservoirs to accommodate fluctuations in vapor volume attributable to changes in temperature and barometric pressure. A variable-vapor-space device is normally connected to the vapor space of one or more fixed-roof tanks. The two most common types of variable-vapor-space tanks are lifter-roof tanks and flexible-diaphragm tanks. Storage vessels classified as conservation tanks include lifter-roof tanks and tanks with internal, flexible diaphragms or internal, floating blankets. These tanks are used in storage of volatile fuel.

In a lifter-roof tank design, a telescoping roof fits loosely around the outside of the main tank wall. The space between the roof and the wall is closed by either a wet seal, which consists of a trough filled with liquid, or a dry seal, which consists of a flexible coated fabric in place of the trough (Figure 4.19-6).

In a flexible-diaphragm tank, a flexible membrane provides the expandable volume. Such a tank may be a separate gas-holder

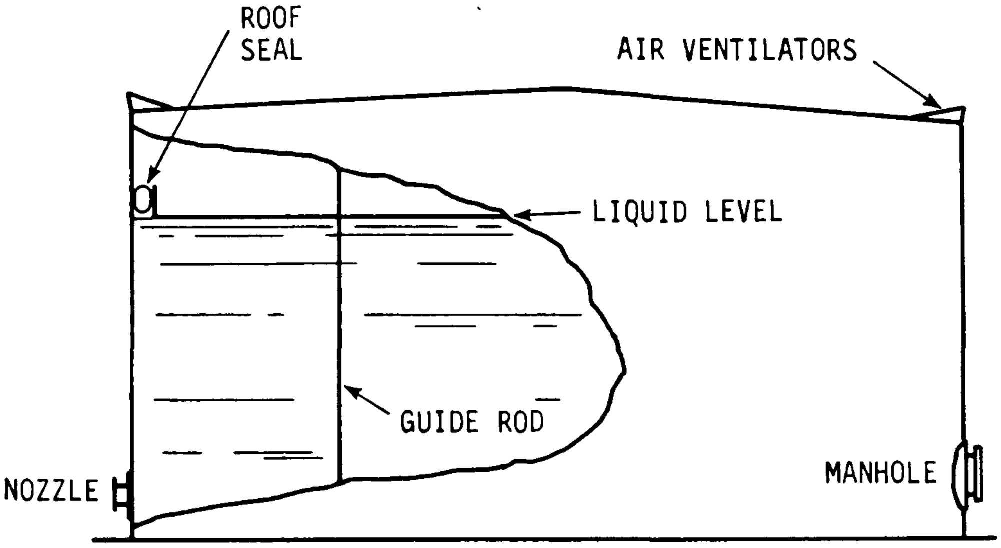

Figure 4.19-5. Covered floating-roof storage tank.

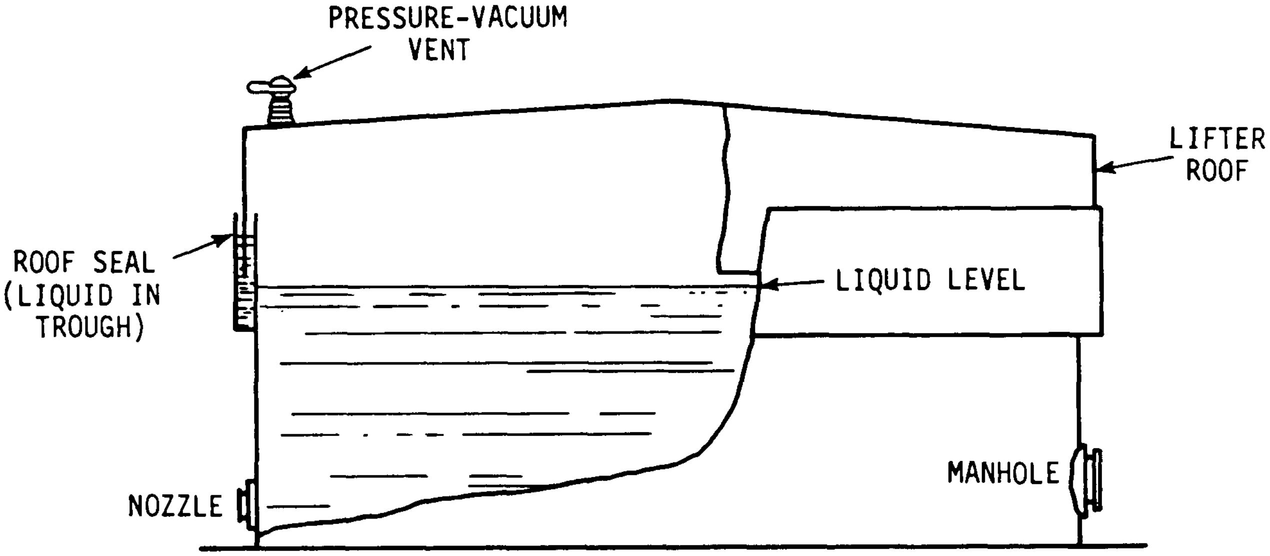

Figure 4.19-6. Lifter-roof storage tank with wet seal.

unit or an integral unit mounted atop a fixed-roof tank (Figure 4.19-7).

Pressure tanks are designed to withstand relatively large pressure variations without loss of stored materials. They are constructed in many sizes and shapes, depending on the operating pressure range. Noded spheroid tanks are accepted for operating pressures up to 200 kPa (29 psia). Spheroids have been operated at pressures up to 310 kPa (45 psia). High-pressure tanks, either cylindrical, spherical, or blimp shaped, have been operated at pressures up to 1827 kPa (265 psia). Pressure tanks are used to store such high-vapor-pressure materials as butane and propane.

### 4.19.2 Emission Sources

Storage facilities represent the largest single potential source of hydrocarbon emissions from refineries. Emissions of hydrocarbon vapors result from the volatility of the stored materials. The API has developed empirical formulas, based on field testing, that correlate tank evaporative losses with the following parameters:

True vapor pressure of the liquid stored
Temperature changes in the tank
Height of the vapor space
Tank diameter
Schedule of tank filling and emptying
Mechanical condition of tank and p/v valve seals
Tank design and type of exterior paint

These evaporative emissions are classified as breathing losses, working losses, and standing losses (floating-roof tanks only).

Breathing losses are hydrocarbon emissions resulting from changes in temperature and barometric pressure. The vapor space in a tank contains air mixed with the vapor of the stored liquid. Pressure relief valves and vacuum vents on top of the storage vessels prevent pressure increase above the safe operating range or operation under a vacuum. As the temperature rises during the day, liquid vaporizes and mixes with the air and vapor in the vapor space. As the pressure increases and exceeds the set value

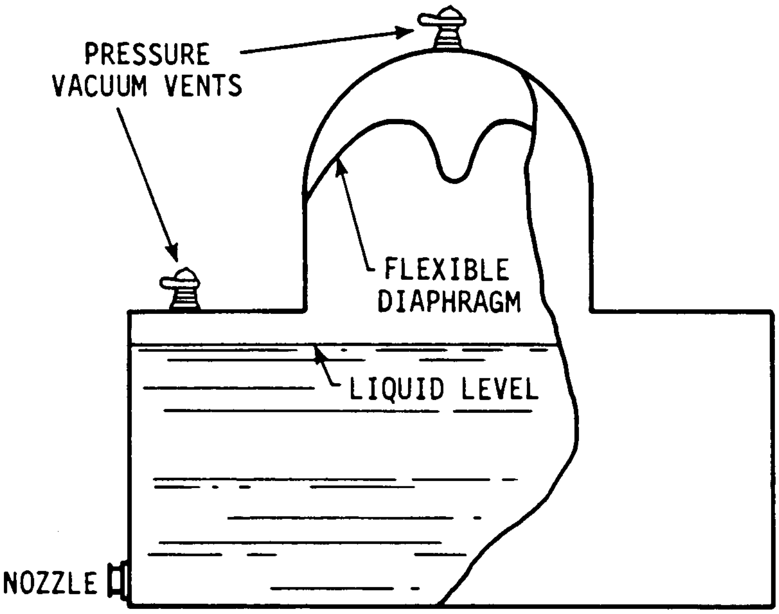

Figure 4.19-7. Flexible-diaphragm storage tank.

on the relief valve, the valve opens and vents the airvapor mixture to the atmosphere. As the temperature drops, as at night, the vapor space cools and contracts. Fresh air is drawn in through the vacuum vents. Since this dilution upsets the saturation equilibrium, more volatile hydrocarbons evaporate to restore the equilibrium. This release of hydrocarbon vapors with the diurnal changes in atmospheric temperature is referred to as the tank's "breathing" cycle.

Working losses are associated with the filling and emptying of a storage vessel. As a storage vessel is filled, the vapor space is compressed, the pressure inside the tank increases, and the pressure relief valve vents the air-hydrocarbon mixture to the atmosphere. Conversely, as the tank is emptied, the vapor space expands, creating a vacuum, and air rushes in through the vacuum vents. Evaporation of volatile hydrocarbons restores the saturation equilibrium.

Standing losses are associated only with a floating-roof tank. These emissions result from the capillary flow of liquid between the outer side of the sealing ring and the inner side of the tank wall and subsequent evaporation. In addition to standing losses, other emissions from floating-roof tanks include withdrawal losses, losses from vents of a vapor recovery system, and filling losses from a variable-vapor-space tank.

Withdrawal losses result from evaporation of stored liquid that wets the tank wall as the roof descends during emptying operations. These losses are small in comparison with other types of losses.

Losses from a vapor recovery unit vent occur when intermediate-volatility liquids are stored in a fixed-roof tank with a vapor recovery system. (Subsection 4.19.3 fully discusses the operation of a vapor recovery system.) The vapor recovery system recovers the organic portion of tankage vapors and vents the air portion back to the atmosphere. Because of inefficiencies in the vapor recovery system, small quantities of volatile organics are also vented with the air to the atmosphere. In many systems, however, the vapor stream is collected and burned with heavy ends directly in a furnace. Such systems do not vent organic vapors to the atmosphere.

Filling losses from a variable-vapor-space tank occur when vapor is displaced by the liquid during filling operations. Because the variable-vapor-space tank has expandable vapor storage capacity, this loss is not as large as the filling loss associated with fixed-roof tanks. Loss of vapor occurs only when the vapor storage capacity of the tank is exceeded.

A pressure tank is generally a sealed, no-loss system. Losses through relief vent openings can occur, however, when the pressure inside the tank exceeds the design pressure. This happens only when the tank is filled improperly or when abnormal vapor expansion occurs. Losses can also occur during the filling of low-pressure tanks that are not equipped with means for disposing of excess displaced vapors. These losses do not occur regularly, and the losses from pressure tanks storing volatile liquids are not significant under normal operating conditions.

Storage of crude oil also generates liquid waste stream. The residence time in the storage tank allows the settling out of water containing dissolved salts. This is withdrawn from the bottom of the vessel and sent to the wastewater facilities in the refinery.

### 4.19.3 Emission Controls

Hydrocarbon emissions from fixed-roof, floating-roof, and high-pressure storage tanks are controlled in several ways. Breathing and working losses from fixed-roof storage tanks can be controlled by the use of conservation vents. A conservation vent is a pressure/vacuum relief valve that vents only when a set pressure differential is exceeded. NSPS and RACT do not require that emission control methods be applied to fixed-roof storage of low-volatility liquids [less than 10.5 kPa (1.52 psia)]; therefore this discussion of emission control methods focuses on the control techniques applied to storage of intermediate-volatility liquids.

Intermediate-volatility liquids can be stored in floating-roof tanks, internal floating-roof tanks, variable-vapor-space tanks with vapor recovery, or fixed-roof tanks with vapor recovery. Although simple fixed-roof tanks have been used for storing intermediate-volatility liquid in the past, NSPS and RACT do not allow this practice.

In new construction for storage of intermediate-volatility liquids, emissions can be controlled by selecting a form of tankage with emission losses lower than those from fixed-cone-roof tanks. Tanks with lower loss rates include floating-roof tanks, internal floating covers, and variable-vapor-space tanks equipped with vapor recovery systems.

A second approach to controlling losses from fixed-roof storage of intermediate-volatility liquids involves retrofit control technology, such as internal floating roofs and vapor recovery systems. Internal floating roofs (Section 4.19.1, Figure 4.19-5) can generally be installed inside existing fixed-roof tanks of welded construction. Tanks of bolted construction are difficult to retrofit.

Vapor recovery systems can also be installed on existing fixed-cone-roof tanks. Figure 4.19-8 is a flow diagram of a simplified vapor recovery system; the systems for tank farms, terminals, etc., are more complex. Vapors generated in the fixed-roof tank are displaced through a piping system to a storage tank called a vapor saver. The vapor saver evens out surge flows and saves a reserve of vapors to return to the storage tank during in-breathing modes. In-breathing of saturated vapors instead of air prevents the evaporation of additional volatile organics. Several storage tanks can be connected by manifold to a single vapor saver and vapor recovery system. Vapor recovery systems usually are not as cost-effective as internal floating roofs, particularly for tanks with high filling rates.

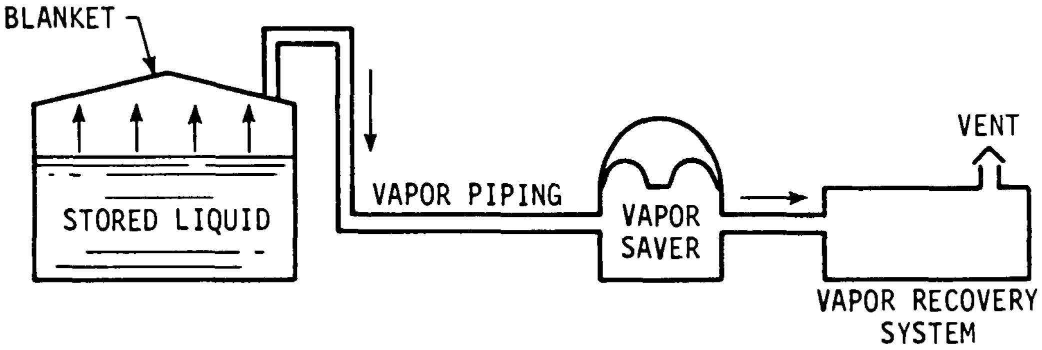

Figure 4.19-8. Simplified vapor recovery system.

Figure 4.19-9 illustrates a vapor recovery unit in more detail. The recovered vapors are compressed, then flow to the refinery fuel gas system or directly to a heater box. During compression, the heavy ends are separated as liquids, which are discharged to the heaters. A refinery has the option of recovering the hydrocarbon vapors, provided that tanks storing the same products are manifolded to one vapor recovery system. Figure 4.19-10 illustrates this option. After the recovered vapors are compressed, the hydrocarbon gas is cooled. The resulting liquids flow back to the storage tanks. The cooled vapors are introduced into an absorption column, where the product (such as gasoline) absorbs the hydrocarbons present in the vapor feed. The air removed from the vapor feed is vented to the atmosphere through a back pressure control valve. The product flows to a two-stage flash separator, where dissolved air is removed from the product. The product is returned to storage. The dissolved air removed in the flash separator contains hydrocarbons and is piped to a flare or fuel gas system.

Another means of emission control is use of pressure tankage. Low-pressure tanks operating between 117 and 200 kPa (17 and 29 psia) have been used for storage of motor gasolines, pentanes, and natural gasolines having vapor pressures up to 200 kPa. With proper design, these low-pressure tanks can prevent breathing losses from intermediate-volatility liquids. Working losses occur during filling when the pressure of the vapor space exceeds the pressure vent setting and vapors are expelled. These losses, which depend on the pump-in rate, may be reduced by increasing the vent setting; however, the higher cost of a high-pressure tank to accommodate the higher setting may prohibit this option. Vapor recovery systems may be needed to control working losses.

High-pressure tanks represent the highest level of emission control for storage of volatile liquids. There should be no need for controls on high-pressure tankage. Any losses from high-pressure tankage indicate that the tankage is misapplied or is

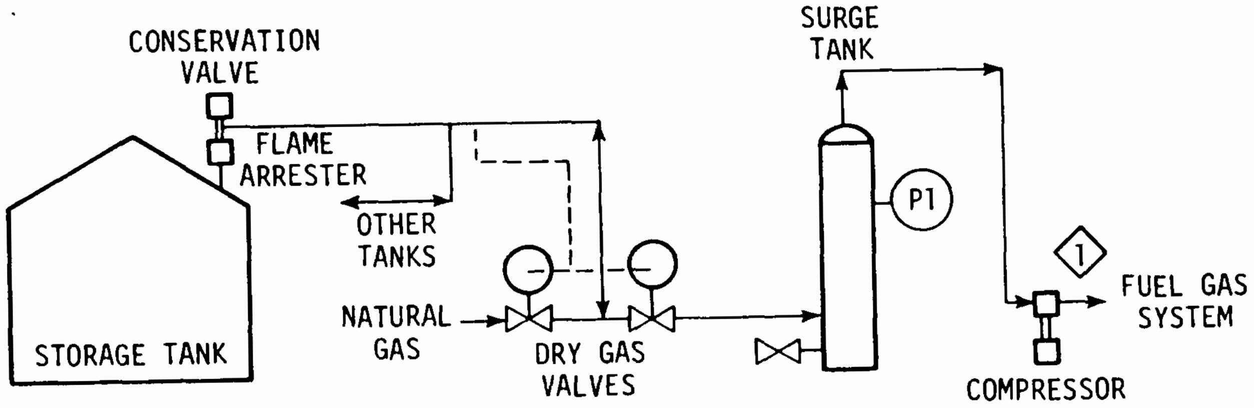

Figure 4.19-9. Flow diagram of vapor recovery system.

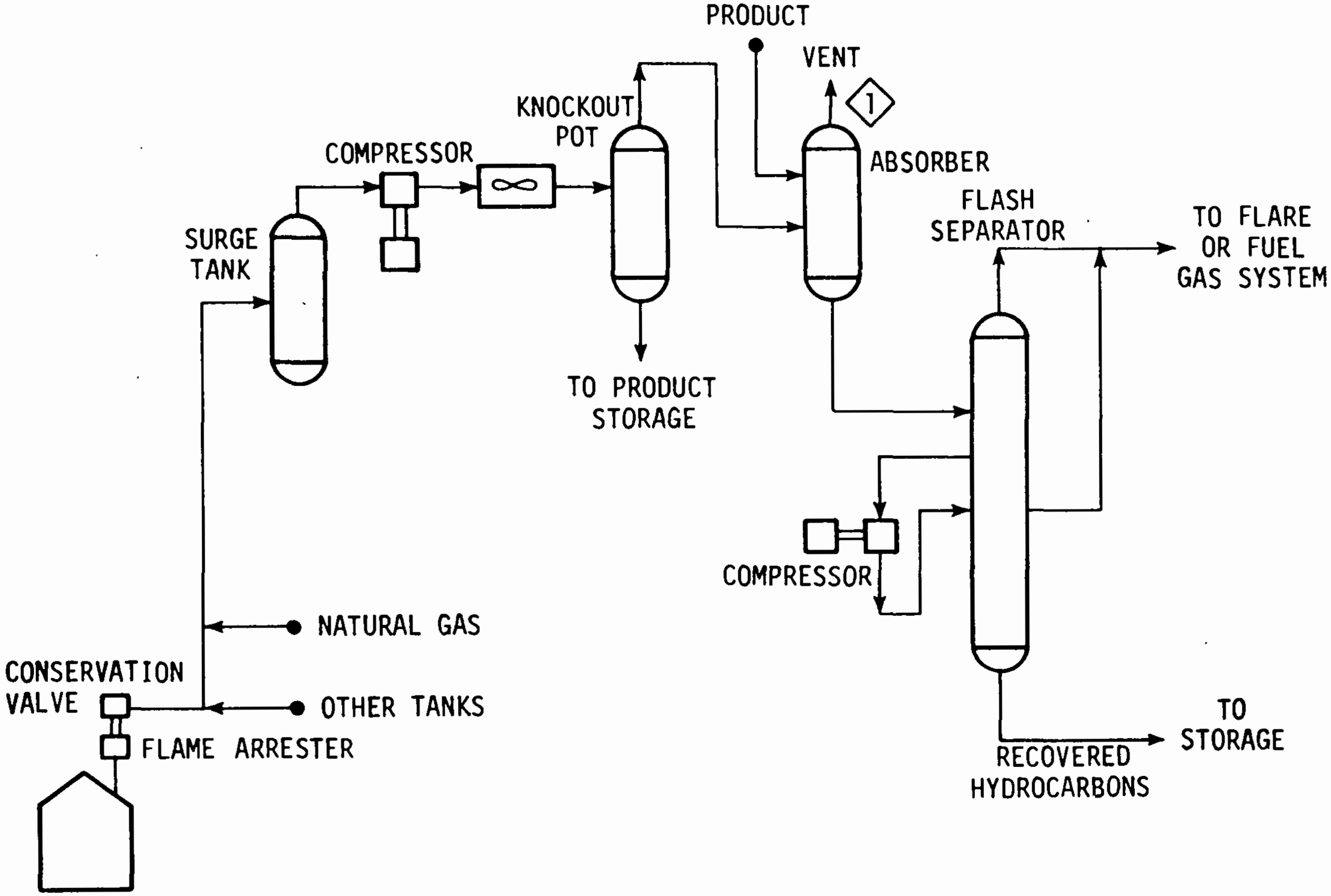

Figure 4.19-10. Vapor recovery system with absorption.

not in working order. Good housekeeping and routine maintenance are the primary controls available for these losses.

Hydrocarbon emissions can be further reduced by selection of paint for the tank shell and roof; that is, the protective coating applied to the outside of the shell and roof influences the vapor space and liquid temperatures. White or silver paint greatly reduces the amount of heat absorbed. A cool roof and shell also allows dissipation of heat retained in the stored material. The condition of the paint also influences its effectiveness in reducing emissions.

### 4.19.4 Instrumentation

Common measurements on storage tanks are liquid level, temperature, and operating pressure. Where vapor recovery systems are used, additional pressure readings are needed from the manifold system and surge tank. Petroleum fractions and products are stored below their normal boiling range, and tanks other than pressurized vessels are operated at low positive pressures.

### 4.19.5 Startup/Shutdown/Malfunctions

Tank farm operations are normally smooth with very few upsets. Filling and emptying rates are observed carefully because of the potential hazard from fire or explosion. In addition, filling rates are matched to the capacity of the vapor recovery system to avoid excessive hydrocarbon emissions.

Periodic plant maintenance includes storage tank cleaning, during which large amounts of hydrocarbons are released to the atmosphere. The material in the tank is withdrawn while nitrogen is introduced as an inert blanket to prevent explosive mixtures. The nitrogen-hydrocarbon vapor mixture is then vented to the atmosphere. The tank is usually cleaned chemically. Cleaning operations can take from a few days to two weeks, depending upon the accumulation of deposits in the tank. After the cleaning operations, the tank is again filled with nitrogen and the petroleum material is introduced. The nitrogen and evaporated hydrocarbon mixture is again vented to the atmosphere. Periodically, the seals are checked for cracking and are replaced as required.

### 4.19.6 References

1. Nelson, W. L. Petroleum Refinery Engineering. McGrawHill Book Company, New York, 1958. pp. 271274.

2. U.S. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. 3d ed. Supplement 8. AP42, 1978, p. 4.37.

## 4.20 PROCESS HEATERS AND BOILERS[1,2]

Process heaters are used extensively in refinery operation to heat and thermally crack fluids. When a process requires a temperature above 204°C (400°F) or when hot streams are not available for heat exchange, the refiner relies on process heaters to supply the specific quantity of heat needed for the process. These heaters are also called process furnaces, direct-fired heaters, tube stills, or pipe stills.

A specific type of fired heater is the boiler whose function is to produce steam. The steam is used in the refinery as a heating medium, as a process fluid (hydrogen production and steam stripping), or even to generate electricity.

A CO boiler is a specific type of boiler that is fueled with waste gas.

### 4.20.1 Process Description

#### Process Heaters

Process heaters consist of two main sections: a radiant section and a convection section.

In the radiant section, heat is transferred from the combustion of fuel to the tubes containing the process fluid. In addition to this heat, the refractory walls become red hot at 540° to 1090°C (1000° to 2000°F) and emit heat, which is absorbed by the tubes and transferred to the process streams within the tubes.

In the convection section, heat is exchanged between the hot combustion gases and the convection tubes containing the process fluid. Often additional tubes are added in this section of the heater for superheating steam. The recovery of heat in this section improves heater efficiency and reduces the temperature of the flue gas exiting the stack.

Fuel is delivered to the furnace through the burners. The function of the burner is to mix the fuel and air; maintain a flame of proper shape, size, and stability; and ensure complete combustion. The burners are normally mounted near the bottom of the heater but can also be side or end mounted. The heaters fire a wide variety of fuels, both gaseous and liquid. Natural gas or refinery gas is delivered to the burner at 120 to 240 kPa (3 to 20 psig). The fuel gas is mixed with air, and the mixture is injected into the fire box (radiant section) of the furnace. Air is drafted or forced through air registers into the fire box, where combustion occurs. When heavy fuel oil (No. 6) is used for firing the furnace, the oil must be atomized either by mechanical means or by use of steam. In a steam-atomized burner, the steam and oil are fed simultaneously into an oil gun at about 790 kPa (100 psig). Steam and oil then form an emulsion-like mixture in the oil gun, mix with air, and are injected into a fire box.

The flue gas leaves the furnace through the stack. The stacks are designed to induce a draft (low-level vacuum) in the fire box, so that the flue gases are discharged to the atmosphere.

The size of a fired heater is defined in terms of its design heat absorption capability or duty. The range is from 10.6 to 527.5 GJ/h (10 million to 500 million Btu/h).

There are many variations in the layout, design, and detailed construction of fired heaters. A consequence of this flexibility is that most fired heaters are custom-engineered for a particular application.

Fired heaters can be classified into general service categories as follows:

Column reboilers--This is considered one of the least critical of heater applications, since differentials between the inlet and outlet temperatures across the heater are relatively small. Depending on the particular application, the outlet temperatures of reboiler fluids range from 205° to 290°C (400° to 550°F).

Fractionating-column feed heaters--These are the workhorses of many process operations. The charge stock is sent to the process heater before it enters distillation equipment. A typical example of this service is a feed heater for an atmospheric distillation column. Crude oil entering the heater as a liquid at 230°C (450°F) might exit near 370°C (700°F) with about 60 percent of the charge stock vaporized. A typical small heater is shown in Figure 4.20-1.

Reactor-feed preheaters--Process heaters in this application raise the charge stock temperature to the level needed to maintain a chemical reaction in reactor vessels. The following examples illustrate the diversity of applications of reactor-feed preheaters:

> Single-phase/multicomponent heating, such as the heating of mixtures of vaporized hydrocarbons and recycle gas prior to catalytic reforming. In this service the charge stock enters the process heater at about 430°C (800°F) and exits at approximately 540°C (1000°F).
>
> Mixed-phase/multicomponent heating, such as the heating of mixtures of liquid hydrocarbons and recycle hydrogen gas for reaction in a hydrocracker. Fluid enters at approximately 370°C (700°F) and exits at approximately 455°C (850°F).

Heaters of heat-transfer media--A process heater in this service is generally used to raise the temperature of a recirculating heat-transfer medium, such as heating oil, Dowtherm, or water. Fluids flowing through the heater in these systems almost always remain in liquid phase from inlet to outlet.

Fired reactors--In heaters of this category a chemical reaction occurs within the tube coil. As a class, these units represent the heater industry's most sophisticated technology. The following two applications typify the majority of fired reactor installations.

> Hydrocarbon reformer heaters - The tubes of the combustion chamber function individually as vertical reaction vessels filled with nickel-bearing catalyst. In reformers, the fluid outlet temperatures range from 790° to 900°C (1450°F to 1650°F).

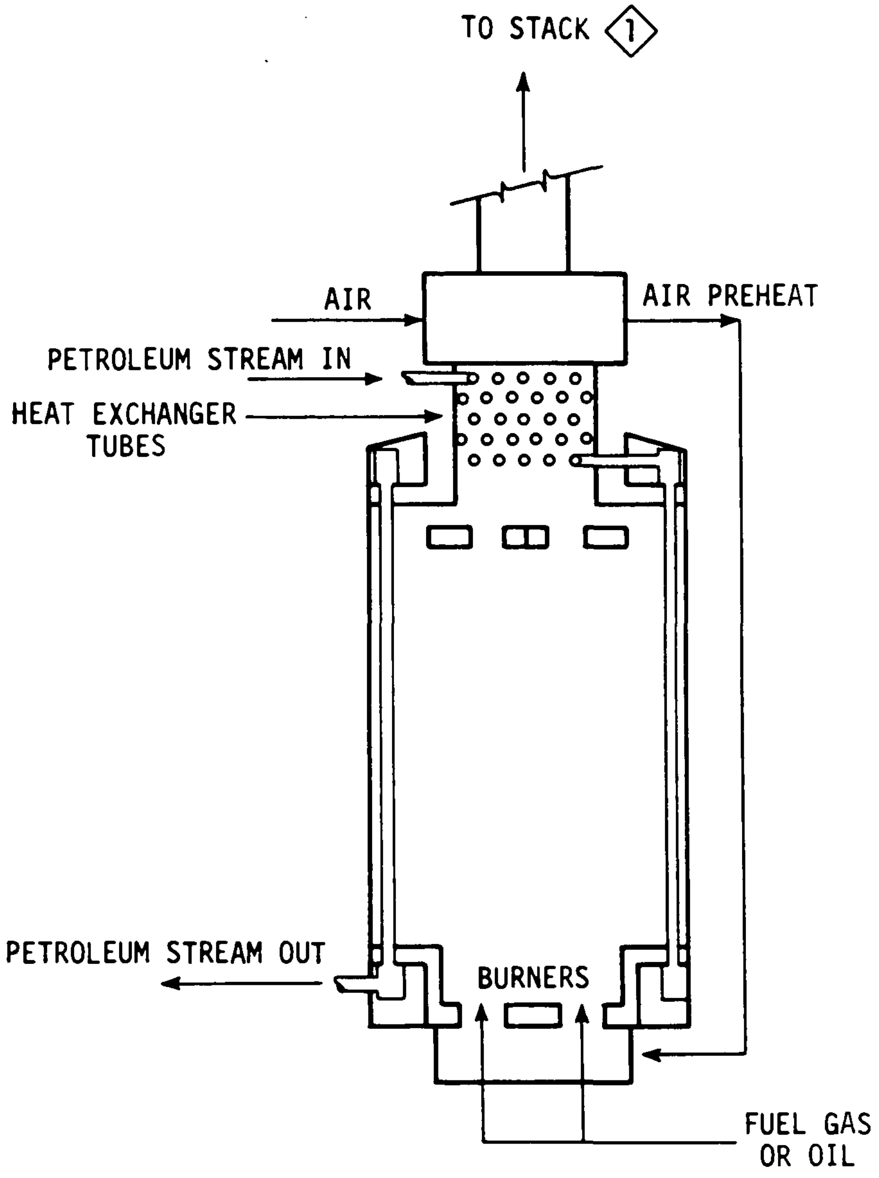

Figure 4.20-1. Typical vertical refinery process heater.

Pyrolysis heaters - Pyrolysis heaters are used to produce olefins from gaseous feedstocks such as ethane and propane and from liquid feedstocks such as naphtha and gas oil. In cracking heaters, where chemical reactions occur in the coil, the tubes and burners are arranged so as to assure pinpoint firing control. Fluid outlet temperatures in heaters designed for liquid feedstocks range from 815° to 900°C (1500° to 1650°F).

Fired heaters can also be grouped according to the methods of combustion-air supply and flue gas removal. A flow of combustion air into a fired heater can be induced when the buoyancy of hot flue gases creates "draft" (less than atmospheric pressure). Since this draft results from a natural stack effect, it is termed natural draft. Most fired heater installations are the natural-draft type, in which a stack effect introduces the combustion air and removes the flue gas. It is the function of the stack to generate sufficient draft to maintain a negative pressure throughout the heater.

An induced-draft heater incorporates a fan, in lieu of a stack, to maintain a positive pressure and to induce the flow of combustion air and the removal of flue gas. A forced-draft-fired heater is one wherein the combustion air is supplied under positive pressure by means of a fan. The flue gases are removed by the stack effect and all parts of the fired heater are maintained under negative pressure. A forced-draft/induced draft heater uses a fan to supply combustion air and a fan to remove the flue gas and maintain the heater under negative pressure. Most fired heaters equipped with air preheaters are of the forced-draft/induced-draft type.

## Steam Boilers

A typical high-pressure/high-temperature boiler is shown in Figure 4.20-2. Typical operating conditions are 10,443 kPa (1500 psig) and 540°C (1000°F). This boiler may be fired by either

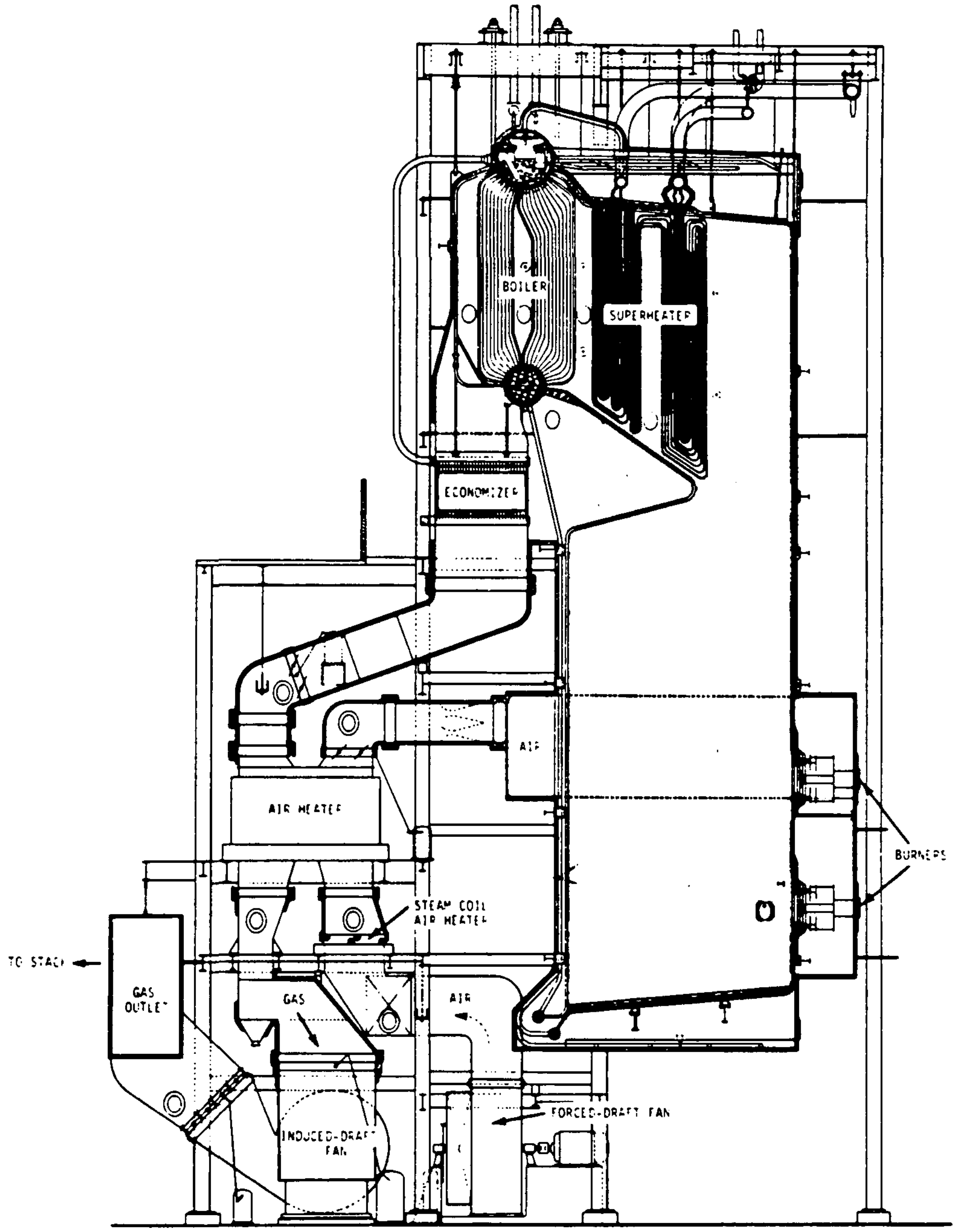

Figure 4.20-2. Typical high-pressure/high-temperature boiler.[2]

natural gas or oil, which is ignited by burners. As a result of combustion, heat is liberated. Transfer of this heat to water in the furnace tubes produces steam. All the steam is generated in the furnace, superheater, and economizer, but primarily in the furnace tubes. The convection surface consists of a superheater, economizer, and air heater.

In the superheater, heat is transferred from hot flue gases to steam in the tubes. This superheated steam can be used in a turbine for production of electricity.

In the economizer, the boiler feedwater is preheated. Hot flue gases flow vertically across horizontal tubes containing the boiler feedwater. Fins, projections, or extended surfaces may be added to the tubes in the economizer to increase the heat transfer area without affecting the flow of fluid. The fins on the outside of the tubes run vertically so as to retain a minimum of soot and fly ash from the flue gases. Soot blowers placed at right angles to the water tubes blow either steam or air to keep the tubes clean.

The air heater recovers heat from the exiting flue gases and preheats the combustion air. It provides high combustion air temperatures and reduces the temperature of the flue gas to the minimum allowable stack temperature. The intent is to keep the exiting flue gas temperature above the dew point of the products of combustion.

In a boiler operating at subcritical pressure, the temperature of the flue gases leaving the steam-generating surfaces of the boiler is determined essentially by the saturation of the boiling water. The higher the steam pressure, the higher will be this saturation temperature. Temperature of the flue gases must be high enough, usually 370° to 540°C (700° to 1000°F), to permit transfer of heat from the gases to the steam-generating surfaces. If the flue gases were exhausted to the atmosphere at such high temperatures, the boiler efficiency would be reduced significantly. The feedwater on its way to the boiler at temperatures substantially below saturation and the air on its way to the furnace absorb much of the heat from the flue gases, thus substantially improving the overall efficiency.

A CO boiler is essentially a gas-fired steam generating boiler. Waste gases from the fluid catalytic cracking unit and/or the fluid coker contain CO and other combustibles, mainly hydrocarbons; these gases are mixed with supplemental fuel and burned to utilize the heat from the combustion of CO and the sensible heat from the other waste gases. A minimum furnace temperature of 980°C (1800°F) is needed to maintain CO combustion and ensure stable operations. The CO boiler is normally equipped with a forced-draft fan. Capacities of CO boilers range from 22,700 kg/h (50,000 lb/h) of steam to more than 227,000 kg/h (500,000 lb/h).

### 4.20.2 Emission Sources

Most emissions associated with process heaters and boilers come from the fuels used for combustion. Particulates, sulfur oxides, carbon monoxide, nitrogen oxides, hydrocarbons, and aldehydes are potential emissions from the stack. Hydrocarbons are emitted from leaking valves or flanges on the process fluid side of a heater. Any sludge from treatment of boiler feedwater constitutes a solid waste.

### 4.20.3 Emission Controls

Emissions of particulate, nitrogen oxides, and hydrocarbon from process heaters are rarely if ever controlled, except by proper design and operation of the heater to ensure complete combustion. These heaters usually burn oil or natural gas, which are fairly clean fuels. Therefore, with proper operation, no control is required.

Emissions of sulfur dioxide are normally controlled by burning low-sulfur distillate oils and natural gas. Since this results in low sulfur dioxide emissions, post-combustion treatment is rarely used to remove sulfur dioxide from the flue gases.

Sulfur compounds such as hydrogen sulfide and mercaptans can be removed from fuel gas by amine scrubbing and from oil by hydrodesulfurization followed by amine scrubbing of the resulting gas. Hydrogen sulfide is stripped from the amine solution and converted to elemental sulfur in a Claus process.

### 4.20.4 Instrumentation

Close monitoring of the key variables is very important for optimum performance of a process heater or a steam boiler. The important key variables are the amount of excess air and the flue gas temperature.

Process heaters and boilers are normally operated with a small amount of excess air (5 to 10 percent above the theoretical minimum) to allow for small variations in fuel compositions and flow rates. Control of excess air is achieved by the use of air blowers and stack dampers. The quantity of excess air may be monitored by observing the oxygen content of the stack gases, either by analysis of samples drawn from the stack manually or use of fixed instruments with continuous monitoring.

Measurement of flue gas temperature leaving the radiant section serves as an index to the firing balance in the fire box. Flue gas temperatures also provide an indication of overfiring conditions and of heater efficiency.

### 4.20.5 Startup/Shutdown/Malfunctions

Startup of process heaters and boilers creates excessive emissions because the heater efficiency is low until line out. This inefficiency is caused either by too much excess air (which causes consumption of extra fuel) or by too little excess air (which causes incomplete combustion of the fuel). Line out is usually accomplished within a few hours. When dual-fired units are switched to oil, particulate emissions usually increase because of carbon deposits on the atomizing tips of the burners; these units may actually smoke until combustion air is adjusted and/or the carbon deposits are burned off.

Malfunctions of process heaters and boilers include flame-outs, hot tubes, and air leaks. Flameouts, caused by positive pressure in the firebox, lead to an increase in hydrocarbon emissions and are dangerous because of the risk of explosion from the buildup of uncombusted fuel. A hot tube is the result of coking of the inside of a tube, which causes the tube to turn cherry red. A hot tube could also be caused by metal failure due to excess thermal stress. Hot tubes necessitate shutdown for replacement of the worn tubes, which may take 2 days. Air leaks into the heater give incorrect readings of the amount of excess oxygen in the flue gas. Attempts to correct for the erroneous reading could lead to incomplete combustion and an increase in hydrocarbon emissions.

### 4.20.6 References

1. Berman, H. L. Fired Heaters, I. Chemical Engineering, June 19, 1978. pp. 99-104.

2. Babcock and Wilcox. Steam: Its Generation and Use. 38th ed., New York, 1972. p. 16-10.

## 4.21 WASTEWATER TREATMENT[1,2]

The major uses of water in petroleum refining are steam generation and heat transfer. The volume of water coming into direct contact with process streams is small when compared with the volume used for indirect cooling and heat transfer. Almost every major refining operation, however, produces a wastewater stream containing various pollutants. The following streams are waste sources: crude desalting, atmospheric distillation, pentane deasphalting, deasphalted oil, hydrogen desulfurization, asphalt blowing (partial oxidation), hydrocracking, fluid catalytic cracking, hydrofluoric alkylation, sulfur recovery, cooling towers, steam generation, and electric power generation. Wastewater treatment methods remove pollutants so that the water may be reused or discharged to a municipal sewer system or a waterway.

Refinery wastewater typically contains oil, phenols, sulfides, ammonia, and dissolved and suspended solids. Some refinery wastes contain other organic and inorganic chemicals, including toxic chemicals. The treatment processes vary with the types and concentrations of contaminants and with effluent quality requirements. Figure 4.21-1 illustrates a typical wastewater treatment system.

Wastewater treatment processes can be separated into five general categories: inplant pretreatment, primary treatment, intermediate treatment, secondary treatment, and tertiary treatment. Inplant pretreatment processes are applied to individual aqueous streams before those streams are combined with effluent flowing to primary treatment facilities. For example, sour water stripping in sulfur recovery can be considered pretreatment.

Primary treatment processes are usually designed for oil/water separation and for removal of settleable solids from the water. Primary treatment may be performed at the unit or at a central wastewater treatment plant. Two widely used designs are the American Petroleum Institute (API) separator and the corrugated plate interceptor (CPI) separator. Both processes utilize

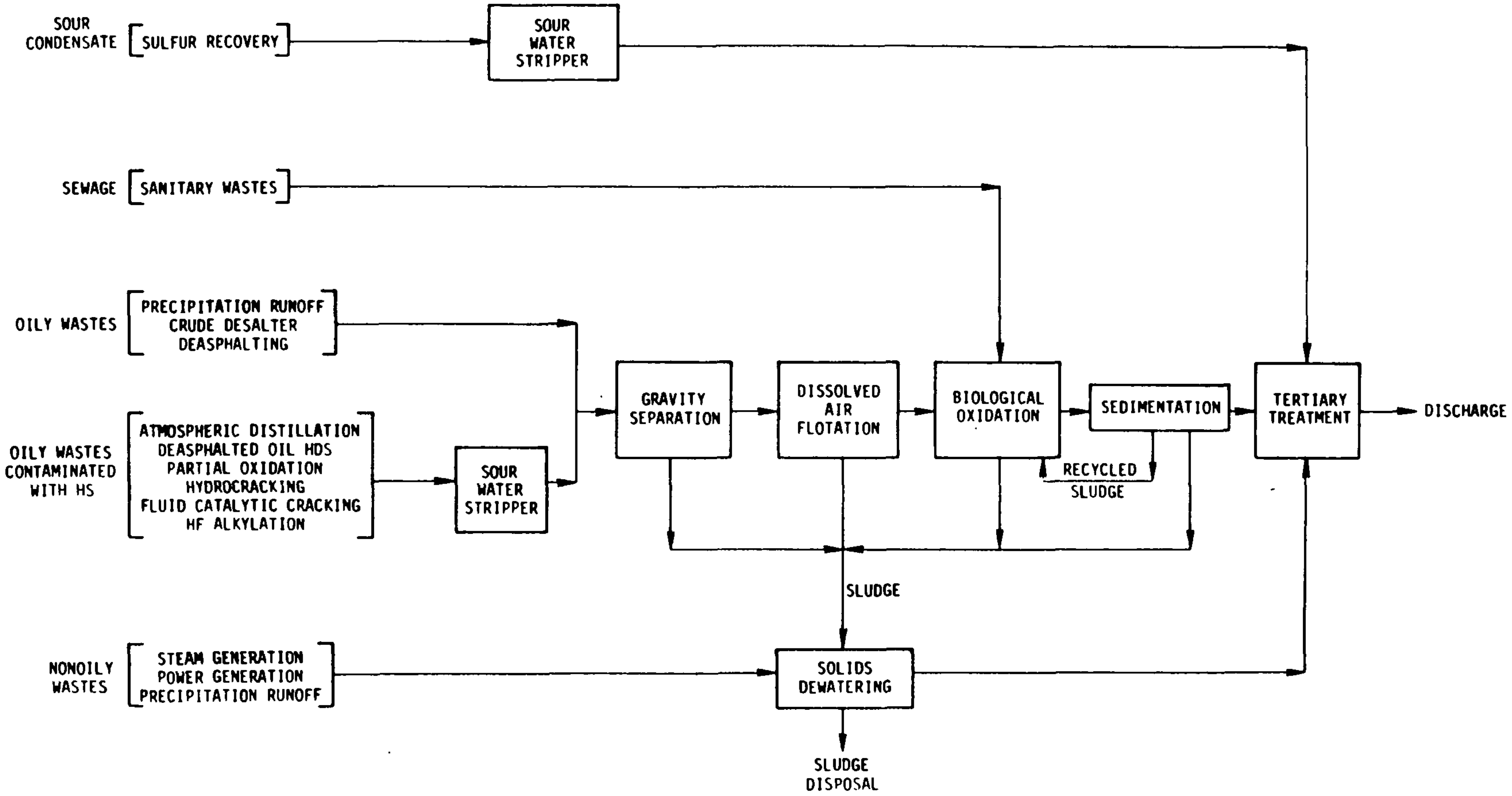

Figure 4.21-1. Wastewater treatment flow diagram.

gravity separation techniques to remove oil, oily sludge, and grit from incoming wastewater before further treatment. Sludge generated from these and other processes is usually treated in a solids dewatering process.

Intermediate treatment consists of an equilibrium holding basin having several hours of retention time to allow leveling of hydraulic and contaminant concentration surges. The basin minimizes shock loading to the secondary treatment facility. Dissolved air flotation units are sometimes used to remove additional suspended matter from the water before secondary treatment.

Secondary treatment processes utilize biological oxidation to degrade soluble organic contaminants in wastewater. In the biological processes, microorganisms and oxygen convert the soluble organic and inorganic matter to carbon dioxide ($CO_2$), sulfur dioxide ($SO_2$), nitrogen ($N_2$), and water ($H_2O$), thereby reducing the biological oxygen demand (BOD) of the wastewater. The concentration of biodegradable contaminant is measured by the BOD of the wastewater. Several biological processes are in widespread use. Oxidation ponds, usually associated with low BOD wastes, depend completely on biological oxidation without mechanical aerators. Aerated lagoons utilize mechanical mixing and aeration to handle larger BOD loadings. The trickling filter process and its variations handle relatively large BOD loadings. The activated sludge process and its variations treat wastewater with high BOD loadings. Trickling filter and activated sludge processes require a clarification step to remove biological sludge from the effluent.

Tertiary treatment processes are not now widely used but may be required as effluent quality regulations become more restrictive. Processes in limited use or in development include chlorination, ion exchange, membrane separation, activated carbon adsorption, and filtration.

## 4.21.1 Process Description

### Sour Water Stripping

Sour waters are produced in a refinery when steam is used as a stripping medium in the various cracking processes. Hydrogen sulfides ($H_2S$), ammonia ($NH_3$), and phenols distribute themselves in the condensate between the water and hydrogen phases. The concentrations of these pollutants in the water vary widely depending on the type of crude and processing involved. The purpose of treating sour water is to remove $H_2S$ and polysulfides before the wastewater enters the refinery sewer.

Sour water strippers are designed to achieve 85 to 99 percent removal of sulfides. Phenols and cyanide contaminants can also be stripped depending upon the wastewater pH, temperature, and partial pressure.* The stripper bottoms usually go to the desalter, where phenols are extracted. Chemical oxygen demand (COD) and BOD of the sour water are reduced by stripping out oxidizable sulfur compounds and by phenol removal.

Heated sour water is stripped with steam or flue gas in a single- or double-stage packed or tray column (Figures 4.21-2 and 4.21-3). If the wastewater contains $NH_3$, it is neutralized with acid before steam stripping. The waste liquid passes down the stripping column while the stripping gas passes upward. Stripped $H_2S$ is recovered as sulfuric acid or sulfur or is burned in a furnace. The bottoms have a concentration of sulfide low enough to permit discharge into the wastewater system for secondary or tertiary treatment. Refiners can incinerate the acid gases from the stripper, thereby converting the hydrogen sulfide to sulfur oxide and the ammonia to nitrogen and traces of nitrogen oxides. An alternative is to send the acid gases to a dual-burner Claus

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*If acid is not required for sulfide stripping, $NH_3$ will also be stripped, the percentage varying with the stripping temperature and pH. If acid is added to the wastewater, virtually none of the $NH_3$ will be removed.

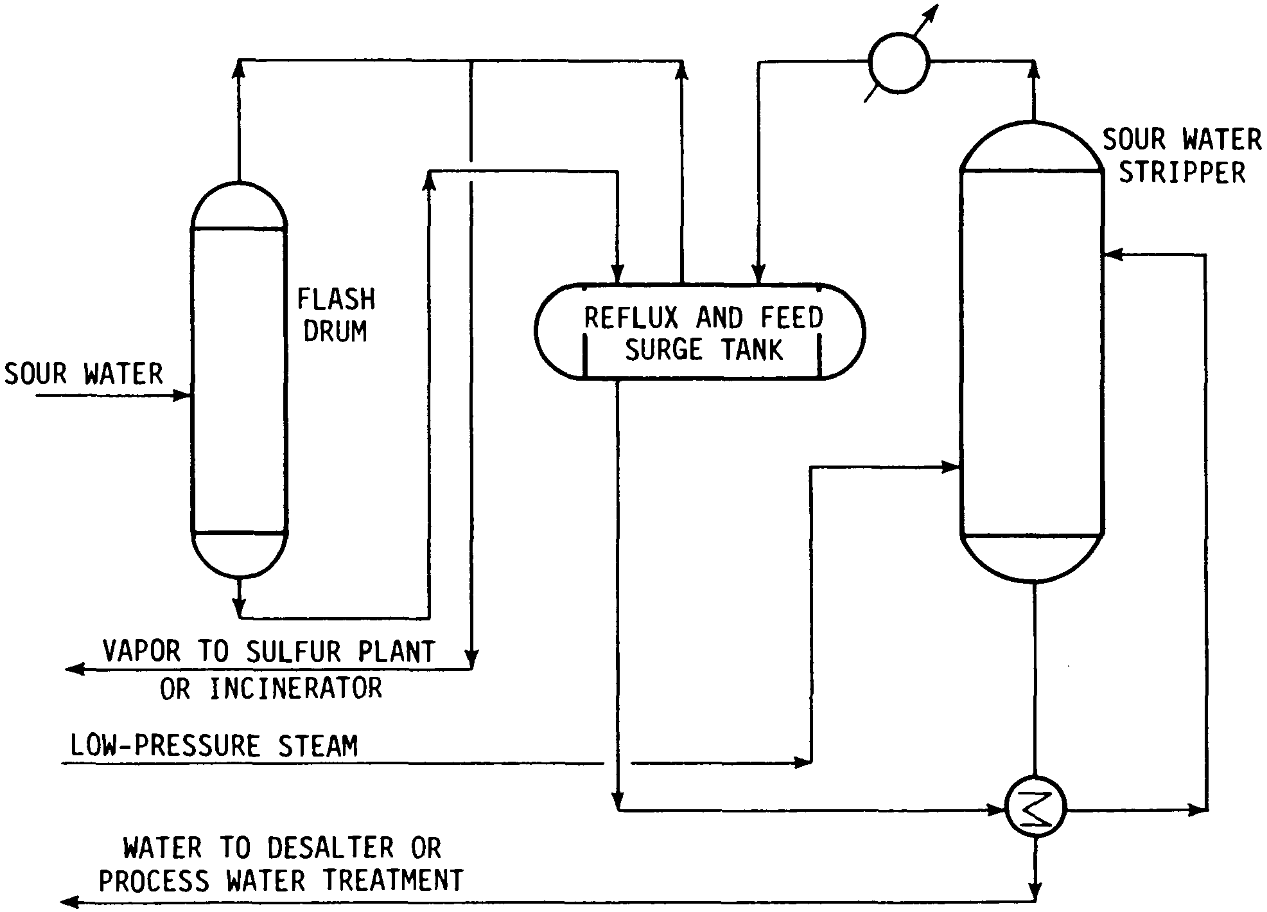


Figure 4.21-2. Single-stage sour water stripper.

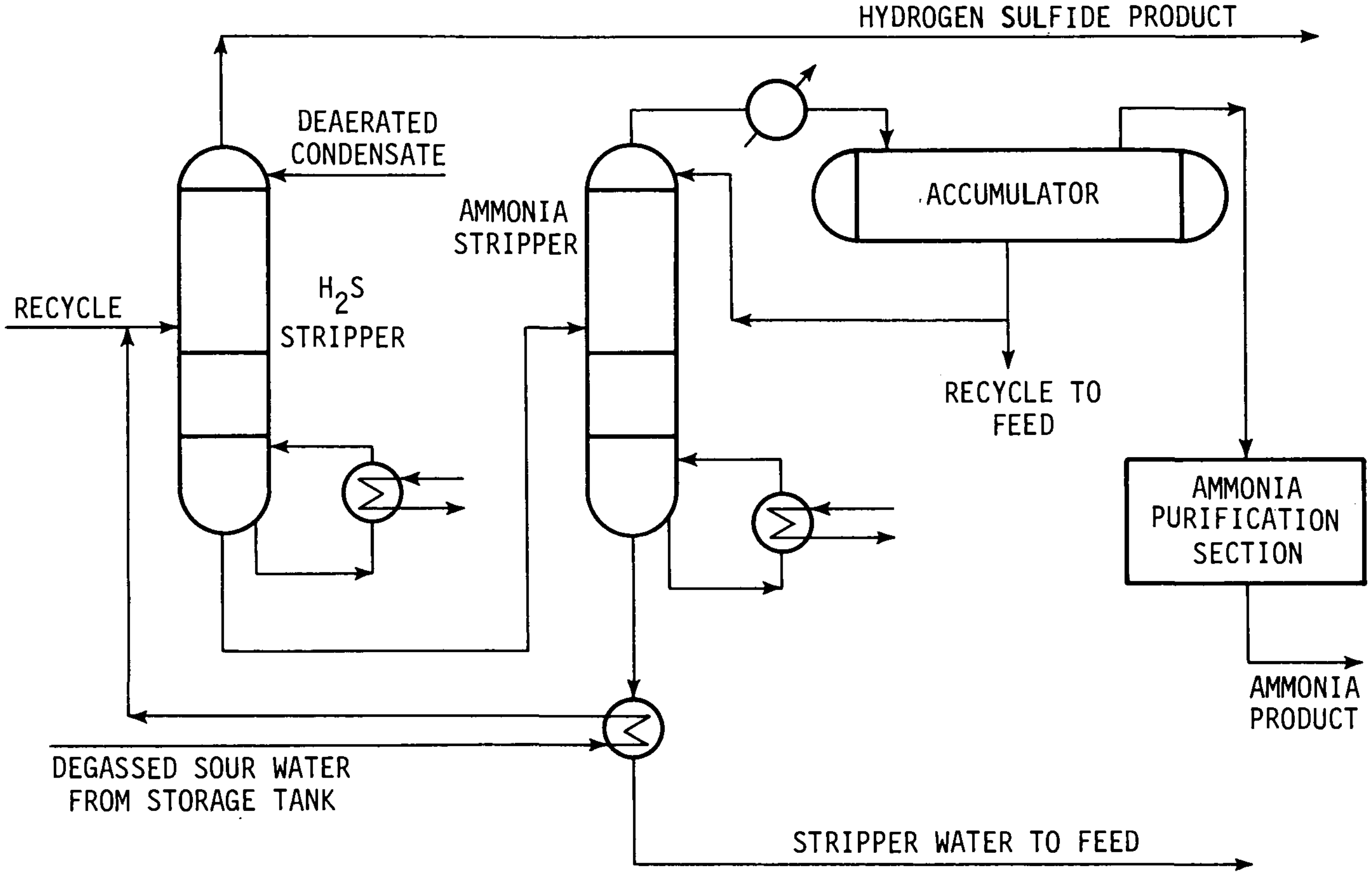


Figure 4.21-3. Double-stage sour water stripper.

plant where the hydrogen sulfide and ammonia are converted to sulfur oxides and nitrogen oxides.

A second stripper is occasionally added in series for ammonia removal (Figure 4.21-3). The use of two strippers allows for the production of high purity sulfide and ammonia offgases, which can be recovered and discarded more readily. Ammonia, if recovered in the aqueous or anhydrous form, can be sold as a byproduct of the stripping operation.

## Gravity Separation

The oily wastes from the process unit or from the sour water stripper are processed by gravity separators. Gravity separators remove 60 to 99 percent of the free oil found in refinery wastewaters. They are the most economical means of separating free oils from water. A gravity separator does not separate substances in solution or break emulsions. Its effectiveness depends on the wastewater feed temperature, the density and size of the oil globules, and the amount of suspended matter. Obviously, the greater the difference in specific gravities, the better will be the separation of oil and water.

Typical gravity devices consist of chambers equipped with influent and effluent distribution elements and with oil skimming and sludge collection devices. Grit or settling chambers may be used as preseparators. Given adequate residence time under calm conditions, the solids settle to the bottom of the separator while the oil floats to the surface. Skimmers or weirs collect the oil and other materials. Pumps move the various components to designated disposal or processing points. Gravity units often use baffles or corrugated plates to minimize turbulence, increase surface area, and achieve satisfactory throughput.

Continuous systems are usually fitted with weirs at the outlets to permit uninterrupted removal of the free oil layer. Drains allow clarified water and solid particles to be removed from the bottom. Weir heights and slopes are usually adjustable to allow optimum performance for the type and amount of oil in the stream.

Batch operations are advantageous for intermittent, low-flow waste streams. Wastewater fills the collection tanks, the oil is skimmed or decanted, and clean water and sediments are removed.

The API separators are the most widely used (Figure 4.21-4). They are usually long, rectangular tanks divided into multiple basins that maintain continuous laminar flow. Scrapers are often used to move oil to the downstream end of the separator, where it is collected in a slotted pipe or drum. The scrapers return upstream along the bottom of the basins, carrying the solids to collection troughs.

Another type of separator finding increasing use in refineries is the parallel plate separator or corrugated plate interceptor (CPI) shown in Figure 4.21-5. The separator chamber is subdivided by parallel plates set at 45 degree angles and less than 15.24 cm (6 in.) apart. This placement increases the oil collection area, thus decreasing the overall size of the unit. As the water flows through the separator, the oil droplets coalesce on the underside of the plates and travel upwards for collection. The CPI effluents contain less oil than the API effluents. The CPI can be used as a primary gravity separation device or can follow an API separator.

Separator skimmings contain excess amounts of solids and water and must be treated before reuse. Concentrations of 1 percent solids generally interfere with processing. The sludge that settles in the separator may be pumped to an incinerator, removed by tank truck for disposal, or processed further by solids dewatering.

## Dissolved Air Flotation

Dissolved air flotation is used by many refineries to treat the effluent from the oil separator and oil emulsions. The dissolved air flotation process consists of saturating a portion

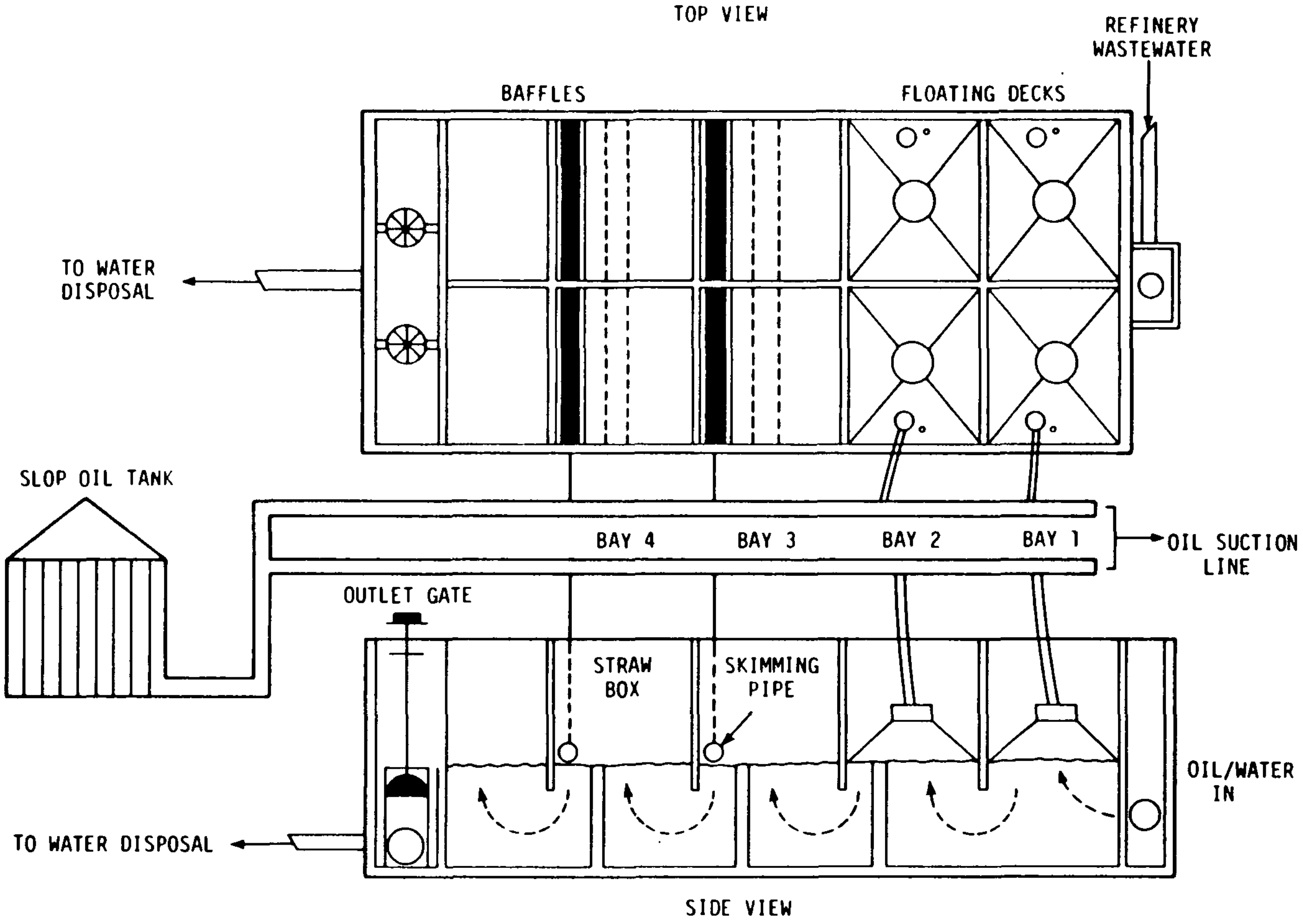


Figure 4.21-4. Top and side views of API separator.

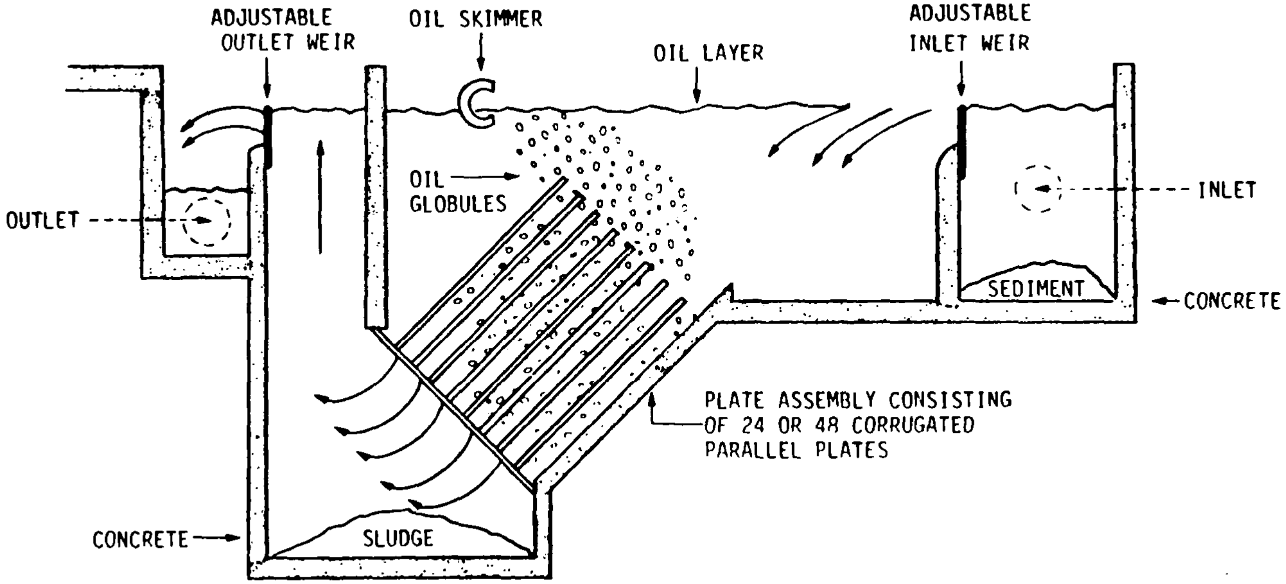


Figure 4.21-5. Corrugated plate interceptor (CPI) separator.

of the wastewater feed or recycled effluent with air. The wastewater or recycled stream is held at 380 to 515 kPa (40 to 60 psig) pressure for 1 to 5 minutes in a retention tank and then instantaneously released to the flotation chamber at atmospheric pressure. The sudden reduction in pressure results in the formation of microscopic air bubbles that attach themselves to oil and suspended particles.

Because of the entrained air, the oil and particulates have greatly increased vertical rise rates of 15 to 30 cm/min (0.5 to 1.0 ft/min). They agglomerate, rise to the surface, and form a froth layer. Specially designed flight scrapers or other skimming devices continuously remove the froth.

The retention time in the flotation chamber is usually 10 to 30 minutes. The effectiveness of the dissolved air flotation process depends on the attachment of bubbles to the suspended oil and other particles. The attraction between the air bubble and the particle depends on the particle surface and bubble size distribution.

Chemical flocculating agents, such as salts of iron and aluminum, with or without organic polyelectrolytes, are often helpful in improving the effectiveness of the air flotation process and in providing a high degree of clarification. (Details on flocculation are given in the subsection on Coagulation-Sedimentation.)

The froth skimmed from the flotation tank can be combined with other sludges (such as those from a gravity separator) for treatment and disposal. Clarified effluent from a flotation unit generally receives further treatment in a biological unit such as an activated sludge unit or a trickling filter. A discussion of the activated sludge and trickling filter processes follow.

## Trickling Filters

A trickling filter is an aerobic biological process that greatly reduces the concentration of dissolved and finely suspended organic matter in a wastewater stream. The trickling filter can be used either as the complete treatment system or as a roughing filter. Most refiners use it as a roughing device to reduce the loading on an activated sludge system.

The trickling filter has spray lines that rotate slowly over a bed of stones 3 to 6 feet thick, continuously distributing the polluted water (Figure 4.21-6). As the water trickles through the bed, the biodegradable organic contaminants are consumed or metabolized by a layer of biomass attached to the stones. A fastmoving food chain is set in motion. Various forms of bateria consume molecules of hydrocarbons. Protozoans consume the bacteria and reduce high-energy chemicals to a lower energy state.

## Activated Sludge

Activated sludge processes are preferred to trickling filters for petroleum refinery wastewater treatment (Figure 4.21-7) because a high rate and degree of organic stabilization is possible. Primary treated sewage is pumped to an aeration tank, where it is mixed with air and activated sludge. The tank has a retention time ranging from 5 to 7 hours. Activated sludge metabolizes the biodegradable organics, thereby reducing the BOD of the wastewater. The treated waters flow to a sedimentation tank, where the sludge biomass settles out and is recycled to the aerator. Some of the growing sludge mass must be removed or "wasted" to maintain steady-state conditions.

The completely mixed, activated sludge (CMS) plant uses large mechanical mixers to mix and aerate the influent wastewater with the contents of the aeration basin. This contact stabilization process is useful where the oxygen demand is in the suspended or colloidal form and where land costs are high or land is not available.

The activated sludge process has some disadvantages. Because of the amount of mechanical equipment involved, the operating and maintenance costs are higher than those of other biological

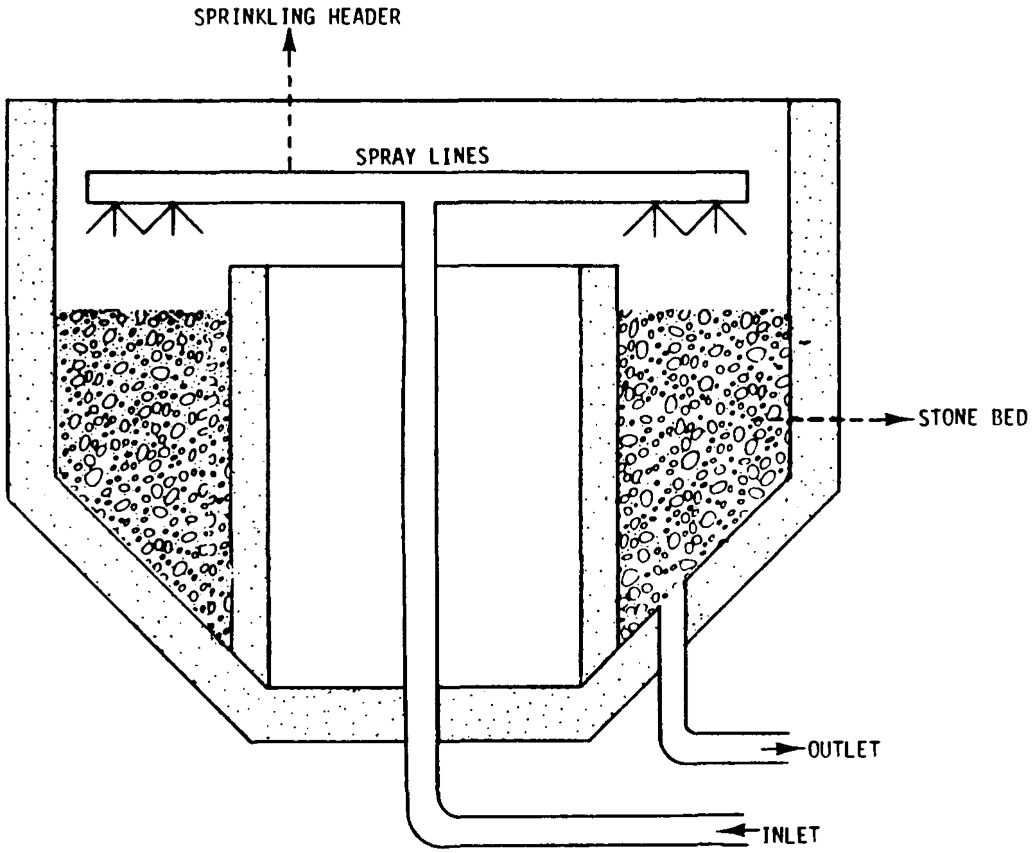


Figure 4.21-6. Trickling filter.

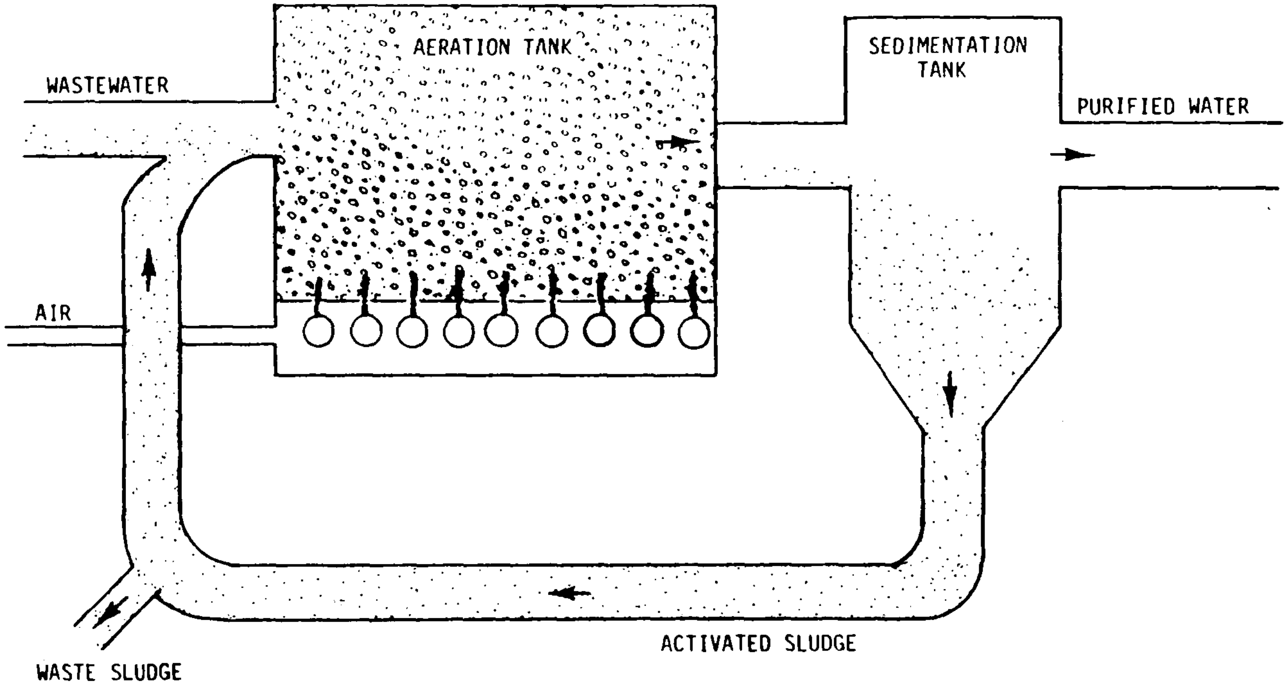


Figure 4.21-7. Activated sludge process.

systems. This process is more subject to upsets than either the trickling filter, oxidation pond, or aerated lagoon.

Shock loadings have less impact on the trickling filter process than on the activated sludge process. The high concentration of material contained in a shock loading destroys more organisms in the activated sludge unit than in the trickling filter. Consequently, most refineries maintain a basin upstream of the activated sludge unit to equilize the loadings.

## Coagulation-Sedimentation

The activated sludge effluent water is further treated by coagulation-sedimentation. In the coagulation-sedimentation process, colloids are destabilized, aggregated, and bound together for ease of sedimentation and removal from the waste stream. With sufficient addition of chemicals, this process reduces the concentration of phosphate by over 95 percent. Phosphorus is an algal nutrient.

Coagulation-sedimentation involves the formation of chemical flocs that absorb, entrap, or otherwise bring together suspended matter. The chemicals commonly used are alum, $Al_2(SO_4)_3 \cdot 18H_2O$; copperas, $FeSO_4 \cdot 7H_2O$; ferric sulfate, $Fe(SO_4)_3$; ferric chloride, $FeCl_3$; chlorinated copperas, a mixture of ferric sulfate and chloride; and polyelectrolytes (polar, synthetic, water-soluble, organic polymers of high molecular weight).

After the chemicals have been blended with the watewater, the stream passes through flocculation tanks where the smaller particles and colloids floc together into larger masses. The larger particles settle out when the effluent reaches the sedimentation or clarifier tanks.

Effective coagulation depends primarily on the wastewater pH, as well as on the amount and nature of the coagulant used. The success of sedimentation depends on sufficient retention time to permit settling. Retention ranges from 20 to 45 minutes.

Flocculating agents can agglomerate oil as well as other organic particles and suspended matter; however, capital and operating costs that are higher than for both CPI and API processes make coagulation-sedimentation less attractive for oil removal.

## Solids Dewatering

The sludge generated by gravity separation, dissolved air flotation, biological oxidation, and sedimentation is treated in solids dewatering.

## Tertiary Treatment

Tertiary processes can further improve the quality of the wastewater effluent by removing residual pollutants. In a petroleum refinery, tertiary treatment processes include oxidation ponds and aerated lagoons. A discussion of these processes follows.

The oxidation pond is practical where land is plentiful and inexpensive and BOD loadings are relatively low. An oxidation pond has a large surface area and a shallow depth, usually not exceeding 1.8 m (6 ft). These ponds have long retention periods that range from 11 to 110 days.

The shallow depth allows the oxidation pond to be operated aerobically without mechanical aerators. Algae in the pond produce oxygen through photosynthesis. This oxygen is then used by the bacteria to oxidize the wastes. Because of the decreased BOD loadings, little biological sludge is produced, and the pond is fairly resistant to upsets caused by shock loadings. Some refineries use ponds to polish the final effluent.

The aerated lagoons is smaller and deeper than an oxidation pond. It is equipped with mechanical or diffused aeration units. The addition of oxygen enables the aerated lagoon to have a higher concentration of microbes than the oxidation pond.

The retention time in aerated lagoons is usually 3 to 10 days. If the biota concentration is low, aerated lagoons are operated without final clarification. When the biota concentration is high, additional treatment is necessary. Biota discharged in the effluent, results in a high BOD and solids discharge which pollutes the stream or river.

Tertiary treatment processes may also include chlorination, ion exchange, membrane separation, activated carbon, and filtration.

Chlorination is the most commonly used process for chemical treatment of water. Chlorine, calcium hypochlorite, and sodium hypochlorite are used to chlorinate the effluent. Chlorine compounds, injected into the effluent 15 to 30 minutes before final discharge, can kill more than 99 percent of the harmful bacteria. Chlorine is suspected, however, of reacting with hydrocarbons to form polychlorinated biphenyls (PCB) and other chlorinated hydrocarbons.

Ion exchange removes the inorganic ions and nutrients from the wastewater. Three common nutrients removed are nitrates (90 percent), phosphates (70 percent), and ammonia (93 to 97 percent). Zeolite resin is the main ion exchange medium used.

Tertiary membrane treatment processes use a semipermeable membrane to concentrate the waste stream. Variations in driving force across the membrane and degree of separation desired define the specific membrane process. Examples of membrane processes include electrodialysis, reverse osmosis, ultrafiltration, and microfiltration. Particulates that can be removed from the wastewater range in diameter from $10^{-3}$ to 10 microns.

Activated carbon processes use granular activated carbon to adsorb pollutants from wastewater. Adsorption is a function of the molecular size and polarity of the adsorbed substance. Activated carbon preferentially adsorbs large nonpolar organic molecules. The process has sometimes been adopted for removal of specific compounds from waste streams. The activated carbon units are usually preceded by a sand filtration process. Sand filters remove suspended solids from the wastewater, and thus prevent plugging of the carbon pores. From the sand filter the wastewater flows to a bank of carbon columns arranged in series or parallel. As the water flows through the columns, pollutants are adsorbed by the carbon, gradually filling the pore sites. Portions of the carbon are removed to a regeneration furnace, where the adsorbed substances are burned off. The regenerated carbon is reused in the columns.

Filtering is another method of tertiary wastewater treatment. Methods include slow and rapid sand filters, multimedia filters, and moving-bed filters. As mentioned above, filtering sometimes precedes carbon adsorption.

Slow sand filters consist of a layer of sand 15 to 38 cm (6 to 15 in.) thick that is placed over a layer of coarser material of similar thickness. The filters give about 60 percent removal of suspended solids and 40 percent removal of BOC at hydraulic loading rates of 61 to 102 liters/h per $m^2$ (1.5 to 2.5 gal/h per $ft^2$). Rapid sand filters are constructed much the same as slow sand filters but are designed for loading in the range of 81 to 244 liters/min per/$m^2$ (2 to 6 gal/min per $ft^2$). These loadings, and the use of coagulants, give about 70 percent removal of suspended solids and 80 percent removal of BOD.

Multimedia filters give "in-depth" filtration of wastewater. In-depth filtration is the filtering of wastewater within the sand filter, not just on the surface (as is obtained with slow or rapid single-component sand filters). Multimedia filtration can tolerate larger loadings of suspended solids than can single-component sand filters, because the solids are dispersed throughout the filtering media.

The moving-bed filter is a new method of sand filtration. A sand filter is moved countercurrently to incoming wastewater by means of a hydraulically activated diaphragm. The sand is cleaned in a wash tower and recycled back to the sand filter. Because operation is continuous, it does not stop for backwashing (as a conventional unit does).

## 4.21.2 Emission Sources

Atmospheric emissions from oil/water treatment systems primarily result from the evaporation of volatile organic compounds (VOC). Uncovered API separators, corrugated plate interceptors, dissolved air flotation units, and associated sumps and drains contribute to VOC emissions. Separators with fixed roofs and vapor spaces are also subject to VOC leaks at sampling and maintenance hatches and vents. Floating roof separators may also leak around hatches and vents, as well as around the roof seal.

Other atmospheric emission sources include sour gas from the sour water stripper, stack gas from the sludge combustion incinerator, and, if activated carbon treatment is used, the vent gas from the carbon regenerating system.

Water pollutant discharge may include dissolved solids, oils, sulfides, phenols, ammonia, and several trace elements.

## 4.21.3 Emission Controls

Floating roofs are the best method for controlling hydrocarbon emission from oil/water separation units. An alternative control method is a fixed-roof cover with a vapor recovery system or a gas-blanketed vapor space. Floating roofs are recommended over fixed roofs, however, because they do not have a vapor space in which explosive mixtures can form.

In a sour gas stripping unit, the primary emissions are the sour gases ($SO_2$) that are removed from the effluent. The sour gases are either sent to a sulfur recovery unit where elemental sulfur is extracted and sold as a byproduct, or to an incinerator where the sour gases are burned.

Particulates are the primary emissions from a sludge combustion incinerator. The incinerator should be equipped with either a scrubber, bag filters, or an electrostatic precipitator. The type of emission control depends on the amount of sludge incinerated and its contents. Sludge charactertistics vary according to the type of crude used. The ash from the incinerator is usually suitable as landfill.

The carbon regenerating incinerator is mainly a source of carbon monoxide emissions, which can be controlled by afterburners. The afterburner brings the carbon monoxide into reaction with excess air and heat to yield carbon dioxide, which is then discharged to the atmosphere.

### 4.21.4 Instrumentation

The refinery generally monitors phenolic compounds, sulfides, several organic compounds, ammonia, pH, total dissolved solids, and trace elements. For hydrocarbon emissions, the phenolic compounds and the test performed for specific organic compounds are of prime importance for the inspector.

### 4.21.5 Startup/Shutdown/Malfunctions

No special problems arise during a well-planned startup of a wastewater treatment facility; emissions do not increase appreciably. Wastewater treatment units are usually shut down for cleaning, which can result in emissions of foul odors, especially in the sludge production and treatment units. Gases containing sulfur usually emit the most noxious odors. During maintenance and repairs, surge capacity should be available in the form of auxiliary tanks or ponds for storage of untreated waste streams. Untreated waters should not leave the plant site. Sufficient surge capacity should also be available during periods of heavy rains, or the rainwater and wastewater should be separated. Malfunctions can result from insufficient surge capacity. Large quantities of heavy metals (such as arsenic, cobalt, cyanide, copper, and chromium), acids, bases, and organics (phenols) kill the bacteria that treat the wastewater. As a result, contaminated water may be discharged from the wastewater treatment facility.

### 4.21.6 References

1. Barnhart, E. L. The Ability of Biological Systems To Assimilate Oils. American Petroleum Institute Proceedings, 1970. pp. 436-465.

2. Guide To Selecting Equipment For Oil/Water Separation. Pollution Equipment News, December 1978. pp. 65-66.

## 4.22 RELIEF AND BLOWDOWN SYSTEMS[1]

### 4.22.1 Process Description

Pressure relief and blowdown systems in a petroleum refinery provide for the safe handling and disposal of liquids and vapors. The pressure relief system is designed to prevent pressures in equipment from reaching levels at which rupture or mechanical failure may occur. It operates automatically, releasing material held within the protected piece of equipment until the pressure falls to safe limits. The blowdown system, on the other hand, is usually manually operated. In an emergency it is used to remove part or all of the contents of the protected piece of equipment. It is also used for purging the equipment by removing and disposing of most of the accumulated liquids and vapors before normal shutdown for inspection or cleaning.

The process description is divided into a discussion of the relief system, blowdown system, and handling of relief and blowdown discharges.

#### Relief System

Almost all process equipment (regardless of size or service) that contain fluids can be subjected to conditions that will raise the pressure above normal design levels. Process equipment requiring overpressure protection include tanks or pressure vessels, furnace coils, heat exchangers, pumps, and others. Most of these units involve flowing streams, the application or interchange of heat, or operations in which pressure changes occur quickly.

Various conditions can raise pressure to exceed normal levels, and not all of these conditions can be anticipated and accommodated by design and operating practices. Operators may be unable to control a rapid pressure rise in equipment during an emergency. It is for this reason that pressure relief systems are designed to operate automatically.

Many types of pressure relieving devices are on the market, including relief valves, safety valves, rupture or frangible discs, and relief hatches. A discussion of each of these devices follows. Of these, relief and safety valves are the most widely used on the process equipment.

Relief valves--Relief valves begin releasing at a set pressure, reaching their maximum discharge rate when the pressure has risen to 110 or 125 percent of the set pressure. They are primarily used for liquid service.

Relief valves may be springloaded, lever and weight, or pilot operated. Conventional spring-loaded types (Figures 4.22-1 and 4.22-2) are the most extensively used. Force due to back pressure at the valve outlet may be subtracted from or added to the force applied to the seating disc by the spring. The variable back pressure on the disc may cause wide variations in the set pressure of conventional relief valves because under these conditions the pressure is not controlled by the compression spring alone. Springloaded relief valves are commonly used where the valve discharges to the atmosphere through a short length of pipe.

Figure 4.22-1 shows a nozzle-type, spring-loaded valve that promotes streamline flow and, consequently, a higher flow coefficient. The result is maximum flow for a given size of opening. Figure 4.22-2 shows a wing-guided, spring-loaded valve. The valve stem and seat are guided by wings extending downward from the valve disc. Lacking the nozzle, the wing-guided relief valve is less efficient in streamlining the flow.

When the pressure against the disc of either the nozzle or wing-guided relief valve reaches the set pressure, the valve rises from its seat against the spring, thus permitting the flow of material through the valve and outlet port. As the pressure beneath the disc increases above the set pressure, the disc rises further, until the maximum opening and discharge capacity of the valve is reached. Maximum opening occurs at 110 percent of the set pressure when discharging vapor and 125 percent of the set

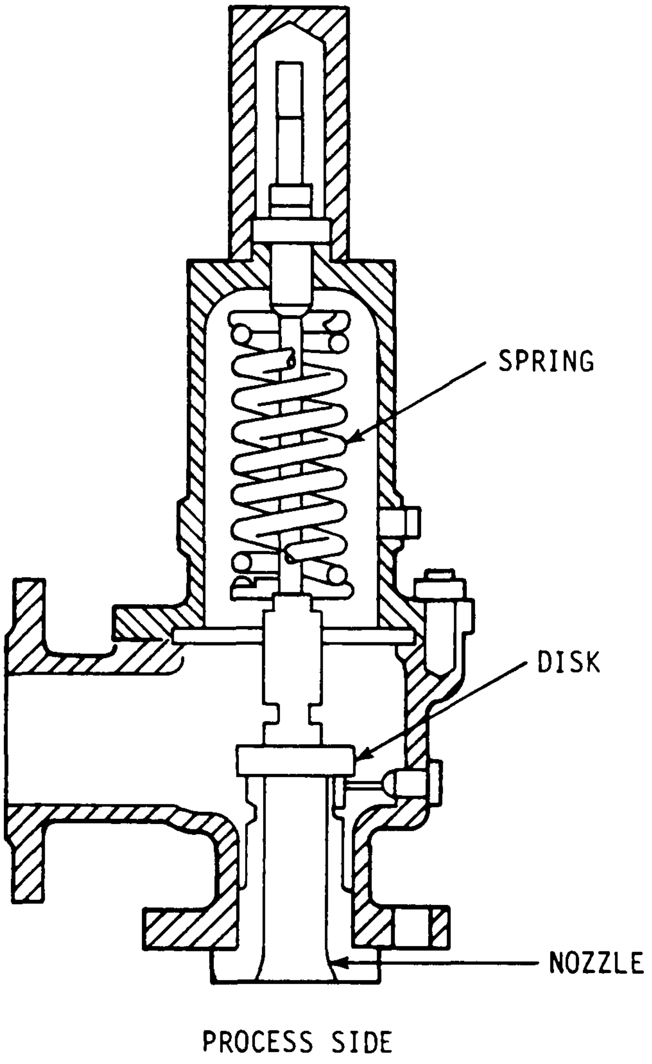


Figure 4.22-1. Nozzle-type, spring-loaded conventional relief valve.

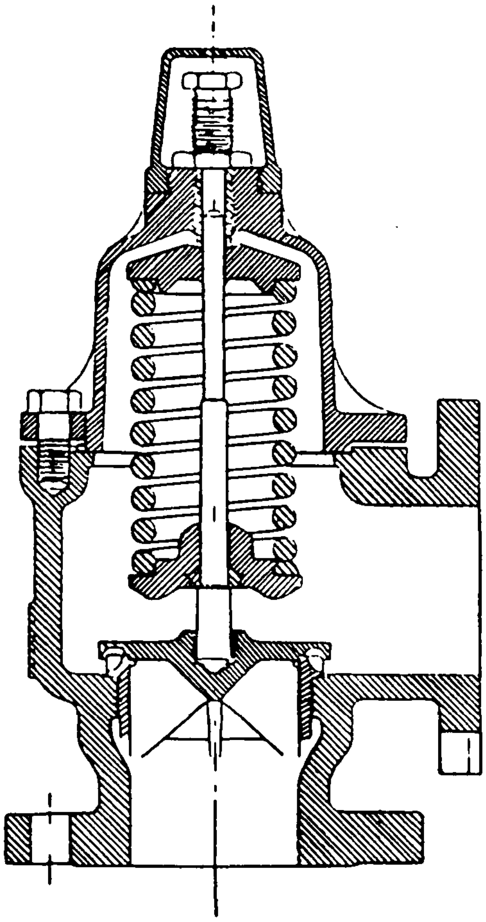


Figure 4.22-2. Wing-guided, spring-loaded conventional relief valve.

pressure when relieving liquids. When the pressure falls below that level, the valve gradually closes until the pressure reaches the set pressure, and the valve is again tightly closed.

Relief valves are used in vapor and liquid service. Relief valves designed for use in liquid service are generally simpler than valves for handling vapor (Figure 4.22-3), although in principle of operation they are the same.

Safety valves--The characteristic of safety valves that distinguishes them from relief valves is rapid opening to maximum flow at low over pressures. A safety valve in vapor service is usually fully opened at 103 percent of the set pressure. Instead of gradually opening like a relief valve, the safety valve opens with high initial flow and closes again sharply at approximately 96 percent of the set pressure. This difference between the set pressure and the resetting pressure of a valve is known as its blowdown. Figure 4.22-1 illustrates the components and assembly used in the nozzle-type safety valve.

Figure 4.22-4 shows a balanced safety valve. The bellows vent to the atmosphere so that the net force on the seating disc due to back pressure is approximately zero. The back pressure is extended on equal areas of the top and bottom of the disc; thus, the effect of back pressure is cancelled and the set pressure is controlled entirely by the compression in the spring that controls the disc.

Rupture disc--The rupture disc, sometimes known as a frangible disc or safety head, is composed of a preformed diaphragm that will rupture at a predetermined pressure level. The diaphragm or disc is held between two special flanges (Figure 4.22-5). The rupture disc is used where pressure must be quickly reduced, such as in the protection of pressurized combustion systems. When the pressure in the protected equipment reaches the level at which the disc is designed to rupture, it gives way, and the rate at which pressure is then reduced is limited more or less by the size of the disc and relief piping.

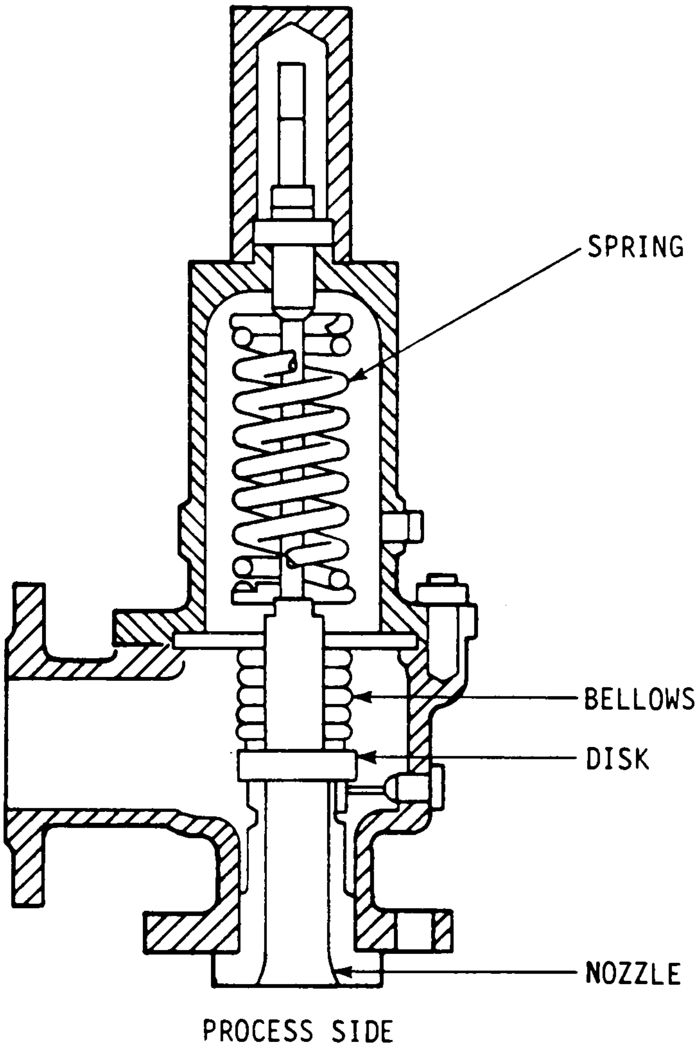


Figure 4.22-3. Bellows-type balanced pressure relief valve.

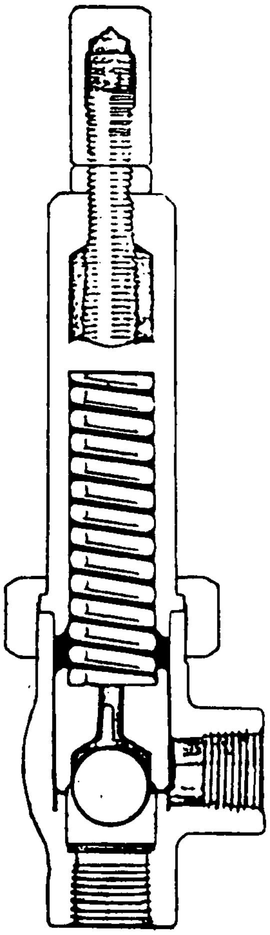


Figure 4.22-4. Relief valve for liquid service.

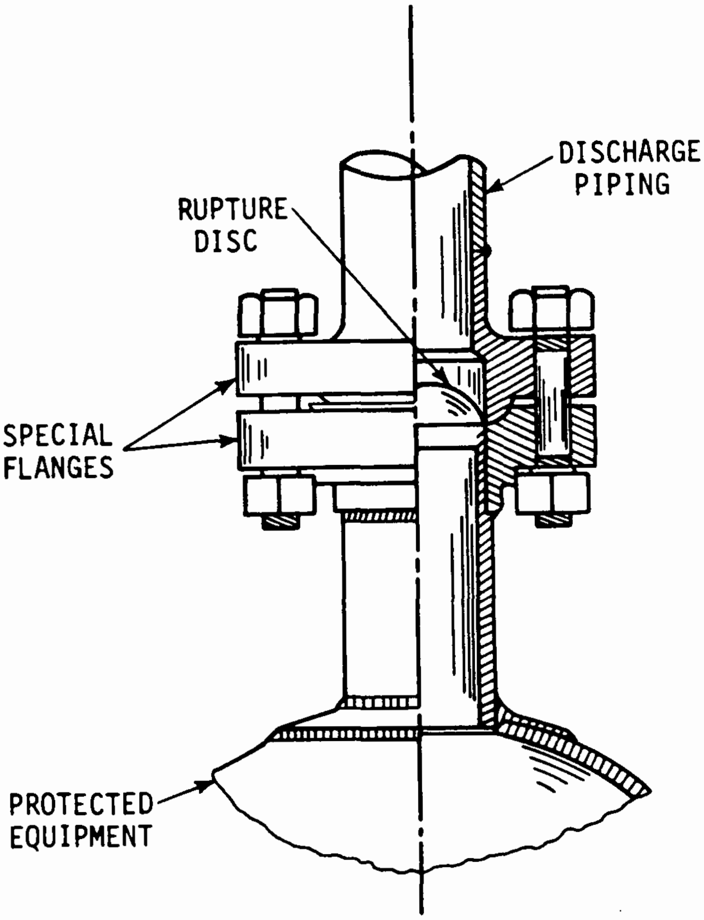


Figure 4.22-5. Typical rupture disc installation.

Relief hatch--The relief hatch, explosion hatch, or explosion door consists of a specially designed closure capable of opening under relatively low differential pressure and releasing large quantities of vapor. These devices are used to provide pressure relief on tanks, combustion chambers, and vessels that operate under relatively low pressure and where large quantities of material must be released. The set pressure of the relief hatch is usually determined by the weight of the closure itself. This method of pressure setting prevents the firm resetting of the valve; as a result, relief hatches are not suited for liquid service.

Figure 4.22-6 shows typical relief hatches. The choice of a specific hatch is determined by the situation where it will be applied. Relief hatches are the most effective way to release large quantities of vapors from low-pressure equipment.

## Blowdown System

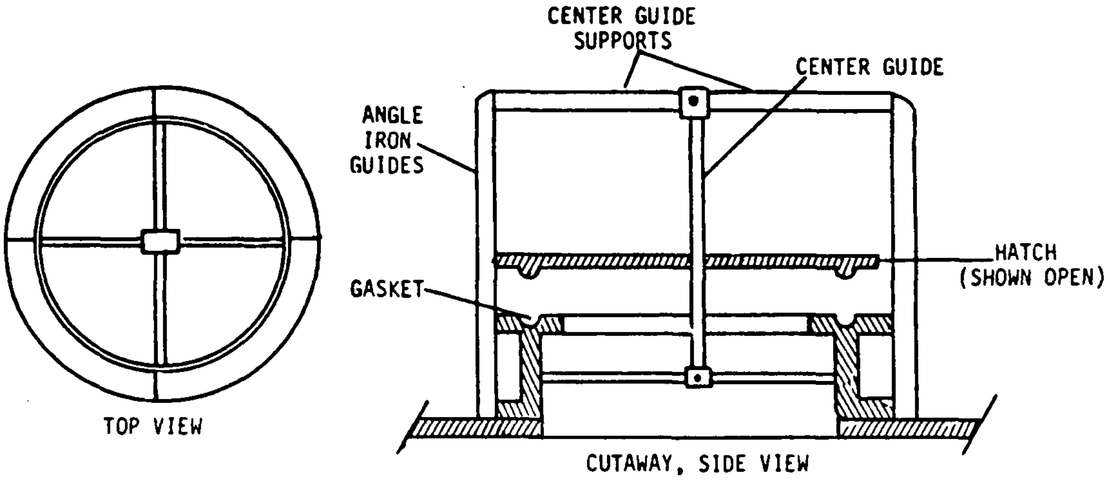
The blowdown system includes the relief valves, safety valves, manual bypass valves, blowdown headers, knockout vessels, and holding tanks. It releases quantities of vapor or liquid by self-generating pressure from equipment for one or more of the following purposes:

Reduction of pressure or control of unusual pressure surges, as from a chemical reaction

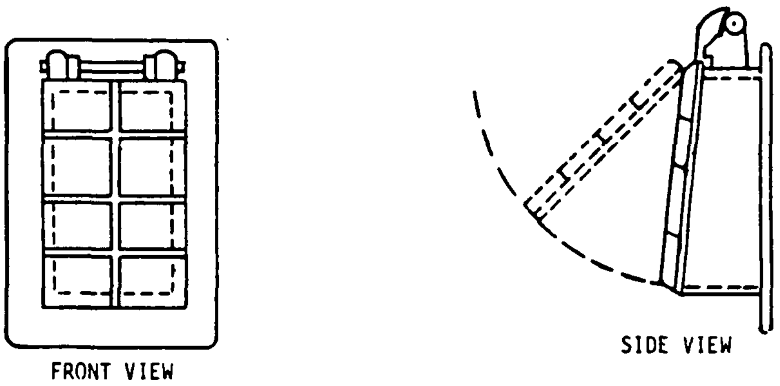
Removal of system contents under emergency conditions

Purging of equipment preparatory to maintenance work

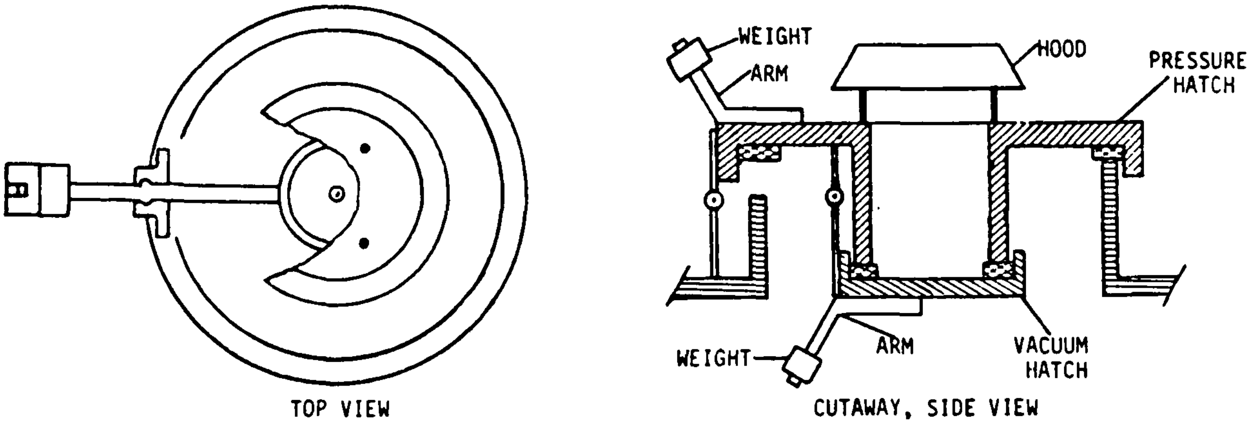
The blowdown system supplements but does not replace automatic relief valves. Blowdown equipment is typically provided on such vessels as fractionators or reactor tubes and on other pieces of equipment. Proper blowdown equipment is of great importance on process equipment, especially when volatile materials are being handled under high pressure. The equipment and vessels discharging to blowdown systems are usually segregated



a. GUIDED PRESSURE RELIEF HATCH



b. EXPLOSION DOOR



c. LEVER-AND-WEIGHT COMBINATION PRESSURE AND VACUUM RELIEF HATCH

Figure 4.22-6. Typical relief devices for the handling of large volumes of vapor, for use on low-pressure equipment where firm seating is not required.

according to their operating pressure for reasons of safety and economy. For example, high-pressure blowdown systems serve units with working pressure over 690 kPa (100 psig); low-pressure systems serve units with working pressure below 690 kPa (100 psig). Butane and propane are usually discharged to a separate blowdown drum, which is operated above atmospheric pressure to increase the recovery of liquids.

The most widely used blowdown valve is the ordinary gate valve, sometimes with minor modifications. The gate valve gives a relatively free and unobstructed flow when open. Cocks, globe valves, and diaphragm valves have also been used for blowdown purposes.

Cocks are of some advantage in manual operation because they open fully in a quarter of a turn. Globe valves are subject to sticking, which restricts their utility for blowdown purposes. Diaphragm valves do not possess the desirable flow characteristics of the gate valve.

In many applications, blowdown equipment must be able to operate under such emergency conditions as exposure to fire. Several types of operating mechanisms (including long extension stems, cable and drum arrangements, air motor drive, and electric motor drive) may be provided to permit the valve to be operated from a remote location.

## Disposition of Relief and Blowdown Discharges

The materials discharged from relief and blowdown systems are directed to one of the following: the atmosphere, a flare, a blowdown stack or tank, a sewer, or lower pressure portions of process systems. Table 4.22-1 summarizes standard practices for disposition of relief discharges. Individual circumstances may result in practices differing from those reported in the table. Because of varying wind conditions, the flare is the best way to disperse vapors to the atmosphere while preventing ground accumulations throughout the refinery. The handling of discharges of toxic materials presents a variety of special problems.

## TABLE 4.22-1. DISPOSITION OF PROCESS VAPORS FROM RELIEF VALVES, BLOWDOWN VALVES, VENTS, AND DRAINS

| Materials and conditions | Discharge directly to atmosphere | Discharge to flare system | Discharge to blowdown system | Return to process system | Discharge to sewer |
|---|---|---|---|---|---|
| PROCESS VAPORS | | | | | |
| Flammable, nontoxic vapors from relief valves and vents: | | | | | |
| Lighter than air | $X^a$ | | | | |
| Heavier than air and remaining vapors at atmospheric conditions, accompanied by steam as dispersant | $X^a$ | | | | |
| Noncondensing, heavier than air | | X | | | |
| Vapors condensable[b] at atmospheric conditions, accompanied by steam dispersant or above 300°F[c] | $X^a$ | | | | |
| Vapors condensable at atmospheric conditions, below 300°F | | | X | | |
| Flammable, toxic vapors from relief valves | Xd | $X^c$ | $X^e$ | | |
| Nonflammable, nontoxic vapors from relief valves | X | | | | |
| Nonflammable, toxic vapors from relief valves | | | | | |
| Noncondensable | $X^d$ | $X^f$ | $X^e$ | | |
| Condensable | | | $X^e$ | | |
| Vapors from blowdown valves | | | | | |
| Flammable, noncondensable | | $X^e$ | | | |
| Flammable, condensable | | | $X^e$ | | |
| Nonflammable, noncondensable, nontoxic | $X^a$ | | | | |
| Nonflammable, noncondensable, toxic | | $X^f$ | $X^e$ | | |
| Nonflammable, condensable, nontoxic | | | X | | |
| Nonflammable, condensable, toxic | | | $X^e$ | | |
| Liquid and vapor mixtures (e.g., heater steamout) | | | $X^e$ | | |

TABLE 4.22-1 (continued)

| Materials and conditions | Discharge directly to atmosphere | Discharge to flare system | Discharge to blowdown system | Return to process system | Discharge to sewer |
|---|---|---|---|---|---|
| PROCESS VAPORS (continued) | | | | | |
| Gas, excess process | | | | | |
| Flammable toxic or nontoxic | | X | | | |
| Nonflammable, toxic | | X[f] | X[e] | | |
| Nonflammable, nontoxic | X | | | | |
| PROCESS LIQUIDS | | | | | |
| Liquids[g] from relief valves | | | X[h] | X[i] | |
| Liquids from blowdown valves | | | X[e] | | |
| Liquids from drains[j] | | | | | |
| Process liquids | | | | | X[k] |
| Water | | | | | X[k] |
| Relief valve drains | | | | | X[k] |
| STEAM AND MISCELLANEOUS | | | | | |
| Excess or exhaust steam release | X | | | | |
| Boiler blowdown | | | X | | |
| Steam trap condensate | | | | | X |
| Reboiler steam condensate | | | | | X |
| Surface drains | | | | | X |

[a] With relief valve discharge properly isolated from surrounding equipment. This generally requires at least 10 ft of elevation above the highest tower or building top within a 50-ft radius.

[b] "Condensable" signifies that approximately 50 percent or more of the material is condensable at atmospheric temperature and pressure.

[c] No liquid present in the valve discharge.

[d] Under some conditions, if accompanied automatically by steam dispersant, small quantities of noncondensable toxic vapors can be vented to the atmosphere if sufficiently remote from people.

TABLE 4.22-1 (continued)

[e] Possibly requires supplementary absorption or neutralization provisions for toxic materials.

[f] Preferable to pass vapors through a burning flare if decomposable by heat without information of toxic products.

[g] Materials liquid at atmospheric pressure and temperature.

[h] Heat exchanger relief valves may discharge separately to a drum vented to the blowdown stack, by which leakage of valves may be checked and oil kept out of plant sewers. Valves likely to discharge large amounts connect directly to blowdown systems.

[i] Applies particularly to the discharges of hot oil pumps, which relieve back into the suction line. Relief valve discharges returned to system must enter zones of approximately same temperature. Opportunity should not be afforded for hot returned material to cause excessive vaporization in the zone to which returned nor for material to be returned to zones where it will be heated or vaporized excessively by the temperature therein.

[j] Contemplates very small quantities, not withdrawn continuously (except water) from valves generally measuring 1 in. and smaller.

[k] If toxic, corrosive, or otherwise dangerous, disposal in sewers may not be permissible. Liquids from sampling of liquefied petroleum gases should not be drawn to sewers.

Only certain vapors may be discharged from relief valves to the atmosphere; in these cases, the discharge lines must be elevated (Footnote a, Table 4.22-1). The relief valve may never discharge near the air intakes of air compressors, since the discharge could be drawn into the air intake stream and cause a fire.

Figure 4.22-7 shows a system of handling liquids having a high vapor pressure and containing gases such as propane. Entering liquids are segregated in the separation drum and the evolved gases pass through the stack to be burned. The drum separates out the liquids that do not vaporize at atmospheric pressure, and these liquids are pumped to proper storage. Air is excluded from the flare stack by continuously bleeding gas to the drum. A pilot (flame) at the top of the stack provides a source of ignition. Complete combustion and smokeless burning are obtained by injecting the gas stream in the combustion zone of the flare, thereby providing turbulence and the inspiration of air. Steam injection reduces nitrogen oxide emissions by lowering the flame temperature. The flare stack itself may vary in height from 100 to more than 200 feet, depending on location and proximity to other equipment.

Blowdown systems discharge to a pressure storage tank. The tank is maintained under pressure by means of a back-pressure control valve on the vapor line leaving the tank. This control valve regulates the vapor flow rate to the flare.

When condensable vapors and hot heavy oils are being discharged, the materials enter the blowdown drum and are quenched by water streams in the line, drum, and stack (Figure 4.22-8). This system is essentially a contact condenser and cooler from which the condensables and oil are sent to slop.

### 4.22.2 Emission Sources

Relief and blowdown systems are potential sources of emissions of sulfur and hydrocarbons. Sulfur emissions are generated by mercaptans and vapors containing hydrogen sulfide that are

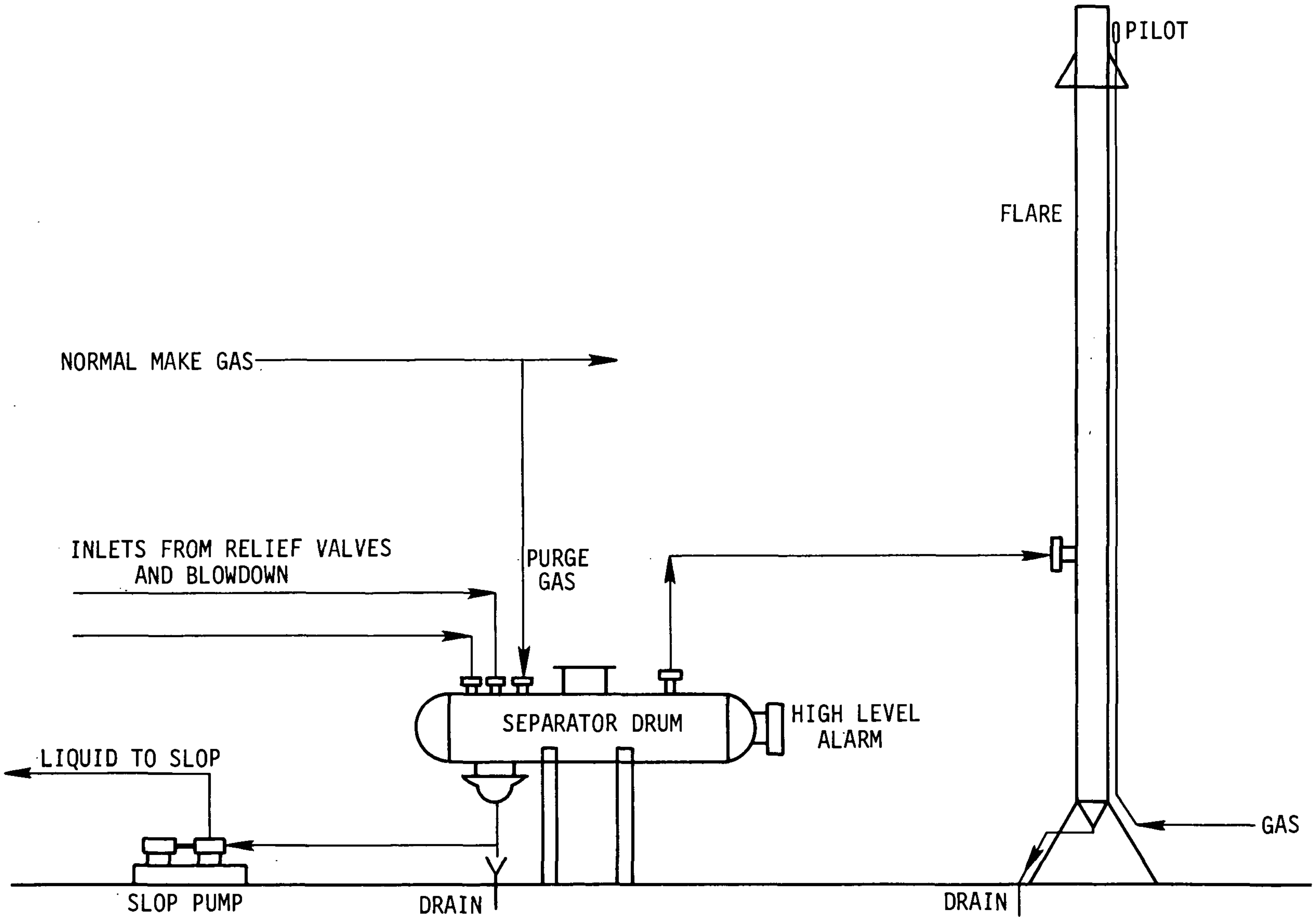


Figure 4.22-7. Flow diagram of a typical flare installation for safe disposition of flammable vapors, including separator drum for collection of condensate.

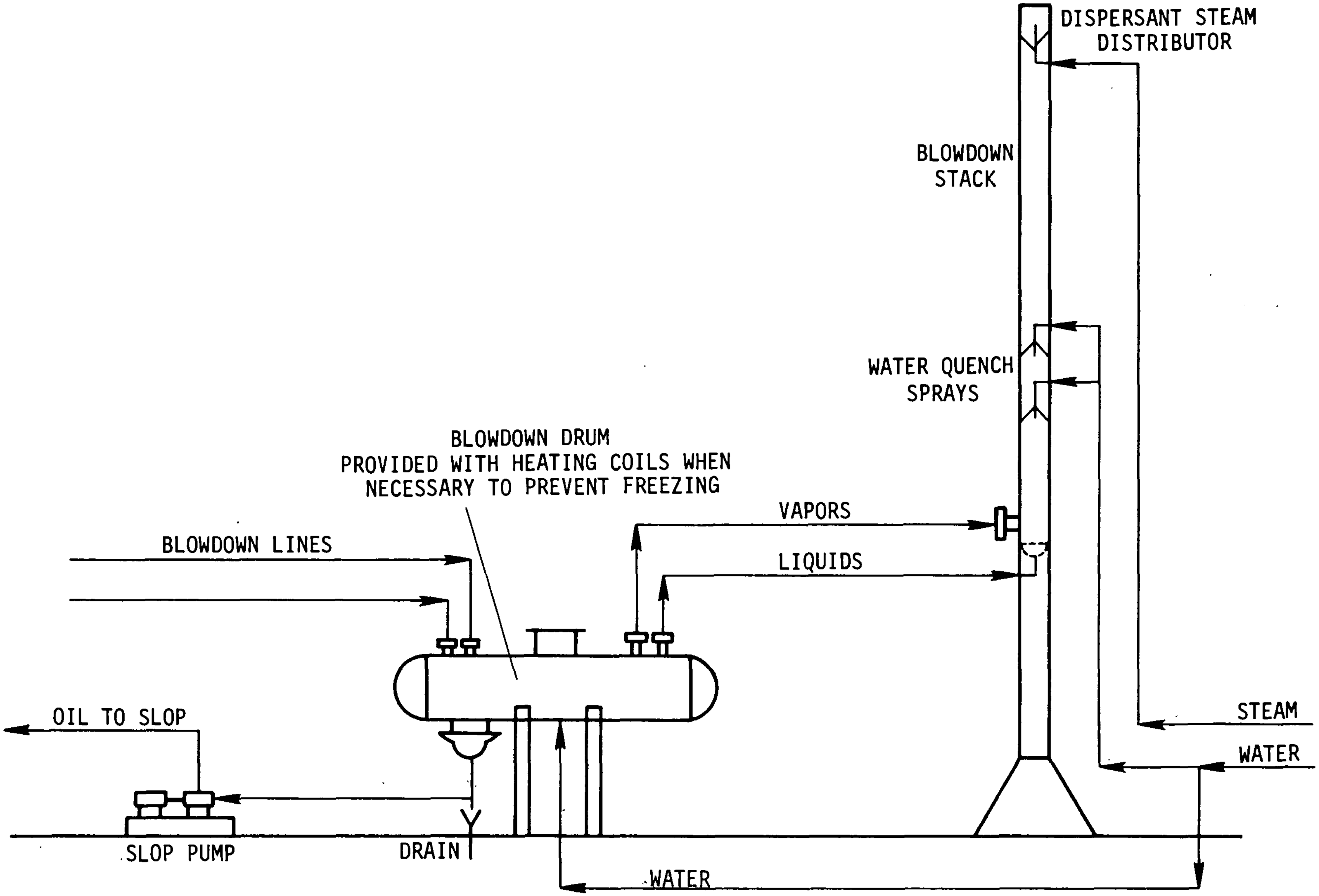


Figure 4.22-8. Flow diagram of a typical blowdown drum and stack installation.

discharged to the atmosphere or flare. These sulfur compounds are converted at the flare to sulfur oxides, which are emitted to the atmosphere. The emission rate in a blowdown system is a function of the amount of equipment manifolded into the system, the frequency of equipment discharge, and the blowdown system controls.

Relief and blowdown systems are sources of hydrocarbon emissions when the discharges are vented to the atmosphere. Some fugitive emissions are caused by leaking valves. These systems are well maintained, however, so that they will provide an efficient release of vapors in an emergency. Leaks are thus the exception rather than the rule.

### 4.22.3 Emission Controls

Hydrocarbons emissions can be reduced effectively by flaring the vapors. The relevant Control Technique Guideline recommends that the vapors be discharged to a flare, refinery fuel system, heater box, or vapor recovery unit until the vessel is at 35 kPa (5 psig).[2] After that point, the vapors can be discharged to the atmosphere. The ability of refineries to vent to the atmosphere at the recommended pressure cannot be determined without site-specific data.[3] The inspector should determine the blowdown procedure used at each refinery and assess its compliance with RACT.

Section 4.22.1 describes the use of flares for handling relief and blowdown discharges, and the use of blowdown systems and process units for controlling hydrocarbon emissions.

### 4.22.4 Instrumentation

Oxygen analyzers offer continuous monitoring of air leakage from plant areas into the flare system. When the analyzer shows zero to 0.3 percent oxygen by volume, the flare is operating safely. Between 0.3 and 1.0 percent oxygen by volume, the refinery should institute a procedure to eliminate oxygen from the system because an explosion could result.

Anemotherm gas flowmeters are located at strategic points on flare systems. These meters serve two purposes: they provide continuous monitoring of gas flow in major laterals to verify that adequate sweep gas is being maintained, and they measure the magnitude of safety leaks and flare dumps. Pressure gauges are also located in flare systems to detect potential plugging and ensure safe operation.

The only indication that the blowdown and relief systems are discharging emissions is to observe that the valves are open. Escaping gas cannot be noticed by odor alone because pronounced odors are usually found around process equipment. Visual indications of gas escape include the frosting of points of leakage and the wavy appearance of the air due to the changed index of refraction (as with the displaced airflows from an automobile gasoline tank during filling, or the "heat waves" observed on highways). When large quantities of liquids that are vaporous at atmospheric pressure and temperature are released to the air, a distinct, visible cloud may be formed by the condensation of moisture and the droplets of unvaporized material remaining after pressure release. A hydrocarbon detector is used to detect these fugitive emissions.

### 4.22.5 Startup/Shutdown/Malfunctions

Relief and blowdown systems are used during shutdown or malfunctions of process units.

The only malfunction that might occur in the relief and blowout systems is a flameout at the flare. This malfunction is very dangerous because it can result in an explosion. The flare is relighted as soon as possible.

### 4.22.6 References

1. Armistead, G. Safety in Petroleum Refining and Related Industries. 2d ed. John G. Simmonds & Co., New York, 1959. pp. 196-235.

2. U. S. Environmental Protection Agency. Office of Air Quality Planning and Standards. Control Technique Guideline for Volatile Organic Vapors from Process Turnarounds. December 1978.

3. Carruthers, J. E., and J. L. McClure. Overview Survey of Status of Refineries in the United States with RACT Requirements. Prepared for the U.S. Environmental Protection Agency by PEDCo Environmental, Inc., under Contract No. 68-01-4147, Tasks 65 and 74. 1979.

# ENFORCEMENT PROCEDURES

# SECTION 5

# ENFORCEMENT PROCEDURES

Each petroleum refinery is designed, engineered, constructed, and operated to process specific crude oils and produce specific products. This results in each petroleum refinery being unique in the complexity and number of processes employed. Since there is no typical refinery, a standard procedure for conducting the inspection does not exist. This section describes approaches to conducting an inspection rather than describing a standard procedure for the inspector to follow.

## 5.1 INTRODUCTION

This section describes the various levels of enforcement inspections and lists the process units and other emission sources that are to be inspected on those levels.

A thorough search should be conducted of the file for the refinery to be inspected to determine what process units are there, to note compliance history and trends, and to collect other pertinent data. The inspection checklists (which are given in Appendixes J through M) should be filled out as much as possible from file data. The data can then be verified and additional data collected during the inspection. The checklists are merely a means of organizing data; they are not official forms.

The inspector should be as informed as possible before entering the refinery, and one way to accomplish this is to review the descriptions of the various refining processes (Section 4). The inspector should review the subsections pertaining to those units that will be inspected. Appendix B and Appendix C provide additional background on the chemical engineering principles applicable to petroleum refining. The more an inspector knows about an industry he is inspecting, the better he will be able to communicate with plant personnel and the better the inspection will be. The inspector is cautioned not to appear to possess more knowledge of a subject than he actually has; by doing so, he may miss getting important information or discredit himself if plant personnel detect an area of ignorance. An honest, questioning approach is generally the most effective.

It is important that the inspector be assertive in order to assess compliance. The inspector should guide the course of the inspection and be persistent in getting and verifying important data. For example, the inspector may have a list of process units and their feed rates. Rather than accepting the word of the plant personnel aiding in the inspection, the inspector should ask to see production sheets or a logbook that will verify these data. An inspector should be confident that correct data are collected. This approach, although time consuming, is effective in uncovering additional compliance problems.

The following subsections describe three levels of inspection, which increase in degree of intensity and follow different time schedules. The Level I inspection is aimed at obtaining continuing compliance of a limited number of units. These units are the most likely to cause emission problems. The purpose of a Level II inspection is to obtain compliance with particulate, sulfur oxide, nitrous oxide, and some hydrocarbon emission regulations. In a Level II inspection more units are investigated than on a Level I inspection. The Level III inspection is aimed at obtaining strict compliance with hydrocarbon emission regulations. The number of fugitive emission sources monitored on a Level III inspection is much greater than the number monitored on a Level II inspection. Level II and III inspections are similar in the number of sources investigated for compliance with particulate, sulfur oxide, and nitrous oxide emission regulations. In the future, a fourth or very detailed inspection may be added.

This manual does not rule out that possibility, which would result from new state and Federal policies.

## 5.2 LEVEL I INSPECTION

It is recommended that a Level I inspection be performed once every 2 to 4 months. The actual frequency depends on the workload and manpower available at local, state and Federal offices. The duration of the inspection depends on the size of the refinery and the number of inspectors. A two-man inspection team can investigate a 30,000 barrel per day refinery in 2 to 3 hours.

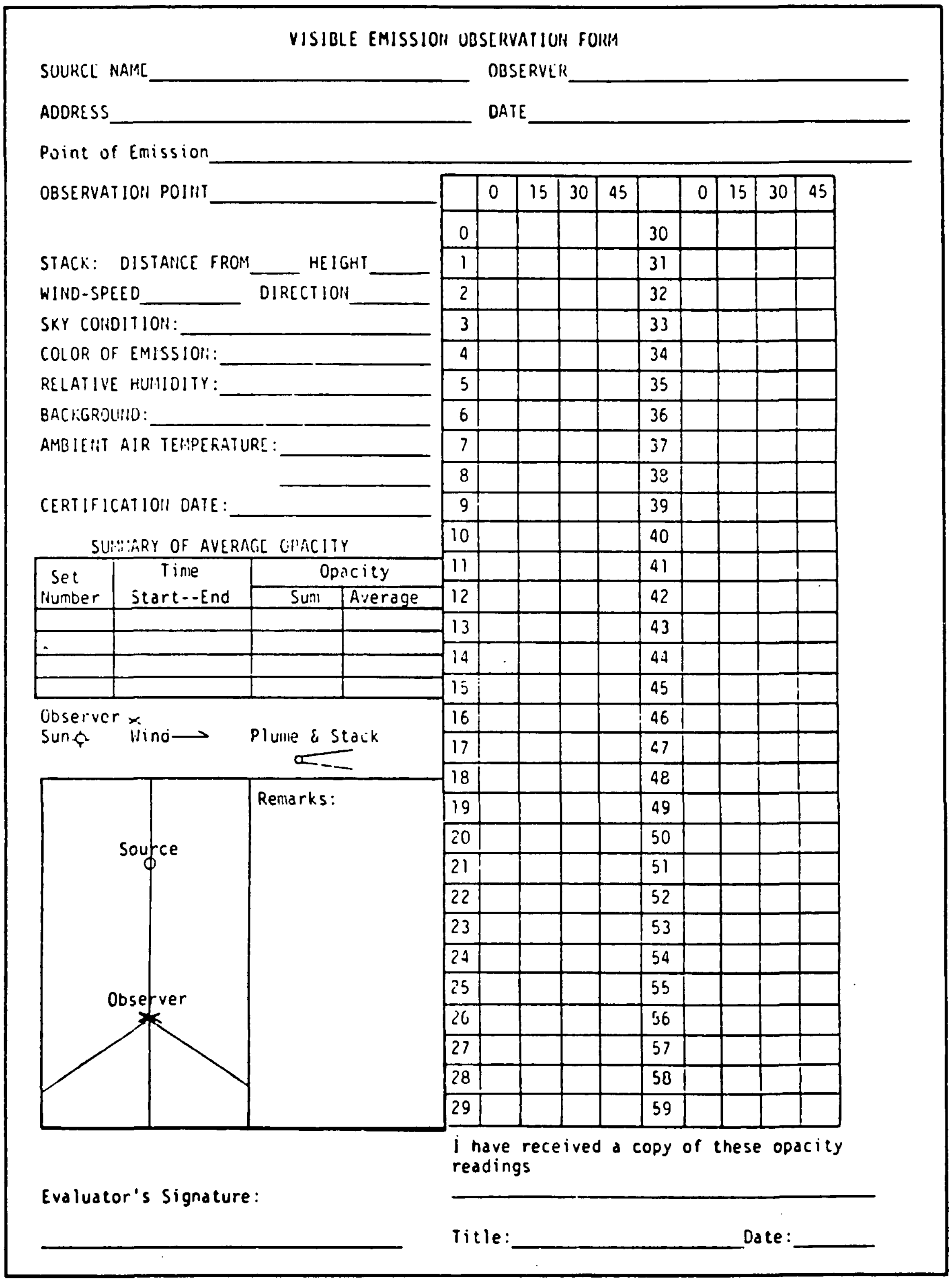
Note the overall condition of the refinery during this inspection. Dust from the unpaved roads is a source of particulate emissions, and pools of oily water are a source of hydrocarbon emissions. Observe all heater and boiler stacks to monitor opacity. When a heater or a boiler stack is out of compliance with the state visible emission standard, complete the the visible emission observation form. (This form is illustrated here in Figure 5-1.)

Review and investigate the following units:

| Unit | Pollutant |
|---|---|
| Fluid catalytic cracking | Particulates; sulfur dioxide |
| Sulfur recovery | Sulfur dioxide |

The pollution control equipment that may be present at the Fluid Catalytic Cracking (FCC) unit includes a CO boiler, an electrostatic precipitator (ESP), and internal and external cyclones. Note the type of control equipment that is used and also note whether the CO boiler or ESP is bypassed during the inspection. (A refinery that does not have a flare, bypasses the CO boiler to the FCC sump stack.)

Sulfur dioxide emissions from a sulfur plant are continuously monitored at incinerator stacks by recording the incinerator temperature. The usual incinerator temperature is about



VISIBLE EMISSION OBSERVATION FORM

SOURCE NAME________________ OBSERVER________________

ADDRESS________________ DATE________________

Point of Emission________________

OBSERVATION POINT________________

STACK: DISTANCE FROM_____ HEIGHT______

WIND-SPEED_________ DIRECTION________

SKY CONDITION:________________

COLOR OF EMISSION:________________

RELATIVE HUMIDITY:________________

BACKGROUND:________________

AMBIENT AIR TEMPERATURE:________________

________________

CERTIFICATION DATE:________________

SUMMARY OF AVERAGE OPACITY

| Set Number | Time Start--End | Opacity | |
|---|---|---|---|
| | | Sum | Average |
| | | | |
| | | | |
| | | | |
| | | | |

Observer ⨯ Sun ✧ Wind ⟶ Plume & Stack

Remarks:

| | 0 | 15 | 30 | 45 | | 0 | 15 | 30 | 45 |
|---|---|---|---|---|---|---|---|---|---|
| 0 | | | | | 30 | | | | |
| 1 | | | | | 31 | | | | |
| 2 | | | | | 32 | | | | |
| 3 | | | | | 33 | | | | |
| 4 | | | | | 34 | | | | |
| 5 | | | | | 35 | | | | |
| 6 | | | | | 36 | | | | |
| 7 | | | | | 37 | | | | |
| 8 | | | | | 38 | | | | |
| 9 | | | | | 39 | | | | |
| 10 | | | | | 40 | | | | |
| 11 | | | | | 41 | | | | |
| 12 | | | | | 42 | | | | |
| 13 | | | | | 43 | | | | |
| 14 | | | | | 44 | | | | |
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| 24 | | | | | 54 | | | | |
| 25 | | | | | 55 | | | | |
| 26 | | | | | 56 | | | | |
| 27 | | | | | 57 | | | | |
| 28 | | | | | 58 | | | | |
| 29 | | | | | 59 | | | | |

I have received a copy of these opacity readings

________________

Evaluator's Signature:

________________

Title:________________Date:________

Figure 5-1. Visible Emission Observation form.

1204°C (2200°F). This temperature increases, however, to about 1427°C (2600°F) when the acid gas feed bypasses the Claus and tail gas unit and is routed directly to the incinerator, thus increasing $SO_2$ emissions at the stack. The incinerator temperature is a good indicator of the amount of acid gas being bypassed.

Completion of the Level I checklist is further discussed in Section 5.7.

## 5.3 LEVEL II INSPECTION

It is recommended that a Level II inspection be performed once every 6 to 9 months. The actual frequency depends on the workload and manpower available at the agency. The duration of the inspection depends on the size of the refinery and the number of inspectors. It takes a two-man team 1 to 2 days to inspect a 30,000 barrel per day integrated refinery. Before the inspection, obtain the data listed below for the units being inspected; during the inspection, review the data with refinery personnel.

Process flow diagram
Process information
Heater and boiler data (type of fuel, heater duty, exit temperature, and stack data)
Storage tank data
Wastewater separator data (type of separator, type of cover, condition of cover)

Some fugitive emissions are monitored by a hydrocarbon detector, in addition to the monitoring of particulates and $SO_2$ emissions.

Review and investigate the following units:

| Unit | Pollutant |
|---|---|
| Fluid catalytic cracking | Hydrocarbon vapors; particulates; sulfur dioxide |
| Sulfur recovery | Sulfur dioxide |
| Watewater treatment | Hydrocarbon vapors |

(continued)

| Unit | Pollutant |
|---|---|
| Isomerization | Hydrocarbon vapors, particulates |
| Alkylation | Hydrocarbon vapors, particulates |
| Storage | Hydrocarbon vapors |
| Loading | Hydrocarbon vapors |
| Light-ends/gas processing | Hydrocarbon vapors |

The survey of oil refineries by the California Air Resources Board in April 1978 showed that isomerization, alkylation, storage, loading, light ends/gas processing, and FCC units accounted for about 40 percent of the fugitive hydrocarbon emissions. The CARB study also identified the items that contributed most to fugitive emissions: valves, pump seals, and compressor seals. For each process unit listed, use a hydrocarbon detector to inspect a certain number of the key emission contributors (Table 5-1). A screening procedure for monitoring fugitive emissions is provided in Appendix H. Appendix G contains operating instructions for a Century Organic Vapor Analyzer, hydrocarbon detector.

## 5.4 LEVEL III INSPECTION

It is recommended that a Level III inspection be performed once every 12 to 18 months. The frequency and duration depends on the workload and manpower available at the agency. The duration of the inspection depends on the size and complexity of the refinery. It takes a four-man team about one week to inspect a 30,000 barrel per day integrated refinery. It is a very detailed inspection of the following units:

TABLE 5-1. LEVEL II LEAK DETECTION PROGRAM

| Process unit | Valves (in gas service) |  | Pump seals |  | Compressor seals |  |
|---|---|---|---|---|---|---|
|  | Sample size | Accept No.* | Sample size | Accept No.* | Sample size | Accept No.* |
| Isomerization | 20 | 5 |  |  |  |  |
| Alkylation | 20 | 5 | 5 | 1 |  |  |
| Storage | 20 | 5 | 8 | 2 | 2 | 1 |
| Loading | 20 | 5 | 8 | 2 |  |  |
| Gas processing | 20 | 5 | 8 | 2 | 2 | 1 |
| FCC | 8 | 2 | 5 | 1 | 2 | 1 |

*The accept number is the maximum number of leaks detected in the sample size that results in statistically approving the sample. This number is based on varying quality levels and statistics. Appendix E explains the derivation of these numbers.

| Unit | Pollutant |
|---|---|
| Fluid catalytic cracking | Hydrocarbon vapors; particulates, sulfur dioxide |
| Sulfur recovery | Sulfur dioxide |
| Wastewater treatment | Hydrocarbon vapors |
| Distillation: Vacuum | Hydrocarbon vapors; particulates |
| Distillation: Atmospheric | Hydrocarbon vapors; particulates |
| Isomerization | Hydrocarbon vapors; particulates |
| Alkylation | Hydrocarbon vapors; particulates |
| Storage | Hydrocarbon vapors |
| Loading | Hydrocarbon vapors |
| Light-ends/gas processing | Hydrocarbon vapors |
| Hydrocracking | Hydrocarbon vapors; particulates |
| Reforming | Hydrocarbon vapors; particulates |
| Visbreaking | Hydrocarbon vapors |
| Hydrotreating (Hydrodesulfurization, or HDS) | Hydrocarbon vapors |

Again, the CARB study determined that the process units listed above comprise about 52 percent of the fugitive hydrocarbon emissions. For each process unit listed, use a hydrocarbon sniffer to inspect a certain number of the key emission contributors (Table 5-2). The operating instructions for using a Century Organic Vapor Analyzer to monitor fugitive emissions is provided in Appendix G. Appendix H contains a screening procedure for monitoring fugitive emissions.

## 5.5 INSPECTION SCHEDULE

Table 5-3 shows a proposed schedule of inspections by level for an individual refinery; it can be used as a guideline for planning an inspection program. The inspector may decide to

## TABLE 5-2 LEVEL III LEAK DETECTION PROGRAM

| | Valves (in gas service) | | Pump seals | | Compressor seals | |
|---|---|---|---|---|---|---|
| Process unit | Sample size | Accept No. | Sample size | Accept No. | Sample size | Accept No. |
| Isomerization | 20 | 2 | | | | |
| Alkylation | 50 | 5 | 8 | 1 | | |
| Storage | 50 | 5 | 20 | 2 | 3 | 0 |
| Loading | 50 | 5 | 20 | 2 | | |
| Gas Processing | 50 | 5 | 20 | 2 | 3 | 0 |
| FCC | 20 | 2 | 8 | 1 | 3 | 0 |
| Visbreaking | 20 | 2 | 8 | 1 | 3 | 0 |
| Hydrotreating* (HDS) | 20 | 2 | 8 | 1 | 3 | 0 |
| Hydrocracking | 20 | 2 | 8 | 1 | 3 | 0 |
| Reformer | 20 | 2 | 8 | 1 | 3 | 0 |
| Distillation: Atmospheric | 20 | 2 | 8 | 1 | | |
| Distillation: Vacuum | 20 | 2 | 8 | 1 | | |

*A refinery has hydrotreating units for several feedstreams, some of which are listed below:

HDS--reformer feed
HDS--light gas oil
HDS--heavy gas oil
Vacuum--(Residue) gas oil
Coker--Naphtha

TABLE 5-3 EXAMPLE OF AN INSPECTION SCHEDULE FOR AN INDIVIDUAL REFINERY

| Month | Inspection level |
|---|---|
| February | Level I |
| April | Level II |
| June | Level I |
| July | Level III |
| September | Level I |
| November | Level II |

perform a higher level of inspection on the basis of recurring violations or specific problems. For example, an inspector may notice a problem with the FCC unit while conducting a Level I inspection. The inspector identifies the problem by obtaining additional Level III information, then proceeds with the Level I inspection of the other units.

## 5.6 INSPECTION REPORT FORM

Complete an Inspection Report form, as shown Figure 5-2, on a separate sheet. This form is used as a cover page for each inspection report. Attach to the sheet the completed unit checklists. The cover sheet, the completed checklists, and any pertinent notes, comments, or records constitute your complete inspection report. The local, state, or federal policies may dictate the information on these proposed checklists be transferred to a designated form.

## 5.7 COMPLETION OF LEVEL I CHECKLIST

A blank checklist of a Level I inspection is shown in Figure 5-3. A copy is also provided in Appendix J. Sample checklists have been completed to show the result before and after the inspection.

From a file search prior to the inspection, the inspector knows the number and type of cracking and sulfur units in the refinery. A hypothetical refinery has one fluid catalytic cracking unit with a refinery identification of 212, as shown in Figure 5-4. The types of control, as found during the inspection and shown in Figure 5-5, are one ESP, six internal cyclones in the reactor, six internal cyclones in the regenerator, and a CO boiler. The opacity of the FCC sump stack is also recorded in the checklist at this time. The control equipment that is not operating at the time of the inspection should be listed in the checklist.

LEVEL __ INSPECTION

AQCR _____

Date(s) of Inspection __________

______________________________

Time In _________ Out _________

Company Name ____________________________________________

Mailing Address __________________________________________

__________________________________________________________

Location of Facility _____________________________________

__________________________________________________________

(Include County or Parish)

Type of Industry _________________________________________

Form of Ownership ________________________________________

Corporate Address ________________________________________

__________________________________________________________

| Company Personnel | Name | Title | Phone |
|---|---|---|---|
| Responsible for Facility | | | |
| Responsible for Environmental Matters | | | |
| Company Personnel Contacted | | | |
| | | | |
| Confidentiality Statement given to | | | |
| EPA Personnel | | | |
| | | | |
| State or Local Agency Personnel | | | |
| | | | |

Figure 5-2. Inspection report form.

### I. Heater and Boiler Information

| Identification Number | Heater description including unit location | Opacity | Comments |
|---|---|---|---|

### II. Catalytic Cracker

| Identification Number or Name | Type of Process | Pollution Control Equipment | | | FCC Sump Stack Opacity | Comments |
|---|---|---|---|---|---|---|
| | | CO Boiler | ESP | Cyclones | | |

### III. Sulfur Plant

| Identification Number or Name | Pollution Control Equipment | Incinerator Temperature (°F) | Incinerator Stack Opacity | Comments |
|---|---|---|---|---|

### IV. General Comments

(Note the general housekeeping practices of the refinery.)

Figure 5-3. Level I inspection checklist.

## I. Heater and Boiler Information

| Identification Number | Heater description including unit location | Opacity | Comments |
|---|---|---|---|
| H-1 | Crude unit | | |
| H-2 | Crude unit | | |
| H-3 | FCC | | |
| H-4 | Reformer | | |
| H-5 | Reformer | | |
| B-1 | Steam Generation | | |
| B-2 | Steam Generation | | |

## II. Catalytic Cracker

| Identification Number or Name | Type of Process | Pollution Control Equipment | | | FCC Sump Stack Opacity | Comments |
|---|---|---|---|---|---|---|
| | | CO Boiler | ESP | Cyclones | | |
| FCC 212 | Fluid | | | | | |

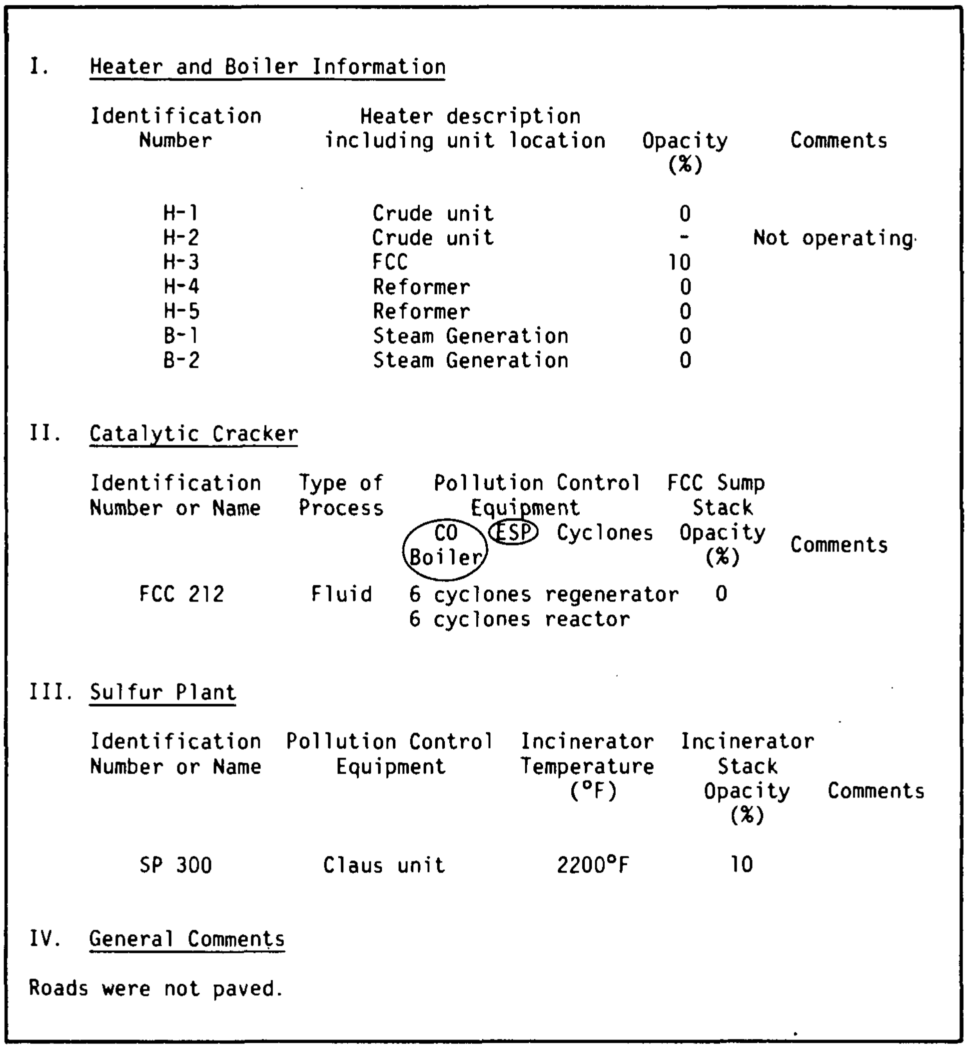
## III. Sulfur Plant

| Identification Number or Name | Pollution Control Equipment | Incinerator Temperature (°F) | Incinerator Stack Opacity | Comments |
|---|---|---|---|---|
| SP 300 | | | | |

## IV. General Comments

(Note the general housekeeping practices of the refinery.)

Figure 5-4. Example Level I inspection checklist after file research.



I. Heater and Boiler Information

| Identification Number | Heater description including unit location | Opacity (%) | Comments |
|---|---|---|---|
| H-1 | Crude unit | 0 | |
| H-2 | Crude unit | - | Not operating |
| H-3 | FCC | 10 | |
| H-4 | Reformer | 0 | |
| H-5 | Reformer | 0 | |
| B-1 | Steam Generation | 0 | |
| B-2 | Steam Generation | 0 | |

II. Catalytic Cracker

| Identification Number or Name | Type of Process | Pollution Control Equipment<br>[✓ CO Boiler] [✓ ESP] Cyclones | FCC Sump Stack Opacity (%) | Comments |
|---|---|---|---|---|
| FCC 212 | Fluid | 6 cyclones regenerator<br>6 cyclones reactor | 0 | |

III. Sulfur Plant

| Identification Number or Name | Pollution Control Equipment | Incinerator Temperature (°F) | Incinerator Stack Opacity (%) | Comments |
|---|---|---|---|---|
| SP 300 | Claus unit | 2200°F | 10 | |

IV. General Comments

Roads were not paved.

Figure 5-5. Example Level I inspection checklist after inspection.

The Level I data needed for the checklist for a sulfur plant includes the unit number or name, the control equipment, the incinerator temperature (°F), and the incinerator stack opacity. At the time of the inspection, the inspector should ask plant personnel about the type of control equipment, temperature, and stack opacity.

Heater and boiler description and unit location can usually be obtained in the state files prior to an inspection. At the time of the inspection, the inspector should verify the heater and boiler information and record the opacity of the stacks. In the hypothetical refinery, one of the heaters was not operating during the inspection. This should be noted on the checklist (as shown in Figure 5-5).

## 5.8 COMPLETION OF LEVEL II CHECKLIST

A Level II checklist includes a more detailed description of each process unit, storage tank data, and wastewater treatment facilities, in addition to heater and boiler information. Blank and completed checklists are presented in Appendixes K and L.

Prior to the inspection, an inspector may be able to search files for descriptions of process units, storage tanks, and loading facilities. During the inspection, the inspectors should observe each of the process units to verify the process descriptions obtained in the file search. All heaters and boilers should also be observed to record opacity. The data on storage tanks should be verified. Appendix D contains the vapor pressure of common petrochemical compounds found in petroleum refineries. This information is useful in completing the "Storage Tank Data" sheet of the checklist. While inspecting the wastewater treatment facility, the inspector should note on the checklist any odors and whether the separator is adequately covered.

The second part of the inspection includes the screening of selected units with a hydrocarbon detector. The data are recorded on a leak detection survey log (appearing as blank forms in

Appendix K and as a completed form in Appendix L). All the information on the form must be completed while at the refinery.

## 5.9 COMPLETION OF LEVEL III CHECKLIST

The completion of the Level III checklist provides a very detailed description of the refinery. This checklist includes all the information from the Level II checklist plus a screening survey of 10 units in the refinery and additional process data.

The checklist and leak detection survey log are completed in the same manner as the Level II checklist shown in Appendix L. A blank checklist for a Level III checklist is presented in Appendix M.

## SECTION 6

## TRENDS IN INSPECTION DATA

In addition to preparing for the inspection by reviewing the files and the Petroleum Refinery Enforcement Manual, the inspector should be informed of the trends in refinery growth and in emissions from the various units. An easy way to correlate important inspection data is to present them in a table or graph. An example is shown in Figure 6-1.

Two items of comparative data that should be noted are the type of crude oil and its sulfur content. As more high-sulfur crude is used, $SO_x$ emissions will increase and additional sulfur plants and sour gas treating units will be built.

Another trend to note is the process throughput of a unit. If throughput increases significantly when compared with a previous visit, the inspector should note the opacity reading of the heater stack at the unit. Heater duty increases with process throughput, producing higher opacity reading at that heater stack.

The summation of all the heater duties recorded during each inspection should be noted for future reference. This information is helpful in defining one of the reasons for increased visible emissions.

Violations, such as a high opacity reading, should also be included in the trend table. The table will provide a brief summary check of compliance.

If the refinery has a sulfur plant, the inspector should record the incinerator temperature of the plant on the trend table. Incinerator temperature is a good indicator of the amount of acid gas bypassed and the reasons for changes in $SO_2$ emissions.

Table 6-2 illustrates the trends observed at a petroleum refinery. This table shows that the crude being processed at this 100,000 barrel per day refinery has a higher sulfur content in 1979 and 1980 than that processed in 1977 and 1978. The total heat input has increased by 20 percent over four years. This increased heat requirement could be the result of the refinery meeting the increased demand for gasoline. Accompanying this increase in heater duties is an increase in the number of opacity violations occurring at this refinery.

The feedrate to the crude unit, fluid catalytic cracking unit (FCCU), and reforming unit increased over the four years. Accompanying this increased rate was an increase in the opacity observed at the FCCU.

The increase in the sulfur plant incinerator temperature indicates that the refinery is having difficulty processing the higher sulfur crudes (i.e. more hydrogen sulfide is not being converted). Therefore, more sulfur oxides are being emitted to the atmosphere.

## TABLE 6-1. EXAMPLE TREND TABLE.

TREND TABLE

| | Year of inspection | | | | |
|---|---|---|---|---|---|
| | 1977 | 1978 | 1979 | 1980 | 1981 |
| Crude oil: | | | | | |
| Type | | | | | |
| Sulfur, % | | | | | |
| ΣHeater duties | | | | | |
| Opacity violations | | | | | |
| Process throughput (list applicable processes) | | | | | |
| Process opacity | | | | | |
| Sulfur plant incinerator temperature | | | | | |

TABLE 6-2. SUMMARY OF TRENDS OBSERVED AT REFINERY A.

| | Year of Inspection | | | | |
|---|---|---|---|---|---|
| | 1977 | 1978 | 1979 | 1980 | 1981 |
| Crude oil: | | | | | |
| Type | Foreign | Foreign | Foreign | Foreign | |
| Sulfur, % | 2.0 | 2.0 | 2.5 | 2.5 | |
| ΣHeater duties | 320 MM Btu[1] | 330 MM Btu[1] | 370 MM Btu[1] | 385 MM Btu[1] | |
| Opacity violations | 1 | 1 | 2 | 2 | |
| Process throughput | | | | | |
| crude unit | 98,000[2] | 100,000[2] | 102,000[2] | 105,000[2] | |
| FCCU[3] | 50,000[2] | 50,000[2] | 51,000[2] | 52,000[2] | |
| reformer | 30,000[2] | 30,000[2] | 30,000[2] | 32,000[2] | |
| Process opacity | FCCU[3]<br>15 | FCCU[3]<br>15 | FCCU[3]<br>20 | FCCU[3]<br>20 | |
| Sulfur plant incinerator temperature | 2150°F | 2200°F | 2300°F | 2300°F | |

[1] MM Btu = million Btu.

[2] Expressed in barrels per day.

[3] FCCU = Fluid Catalytic Cracking Unit.

# APPENDICES

# APPENDIX A

The following tables list operating refineries located in the United States as of January 1, 1979. The designations of refineries in attainment or nonattainment areas for oxidants are based on EPA designations as published in the Federal Register and conversations with EPA regional personnel. Supplemental information has been included to explain additions to and emissions from the tables.

The data in this appendix were taken from a PEDCo report entitled "Overview Survey of Status of Refineries in the U.S. with RACT Requirements," which was prepared for the U.S. EPA Division of Stationary Souce Enforcement under Contract No. 68-01-4147, Task Nos. 65 and 74.

TABLE A-1. OPERATING PETROLEUM REFINERIES IN THE UNITED STATES[a]

| EPA region | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| I | 1 | 13,400 | 0 | 1 |
| II | 11 | 1,790,820 | 4 | 7 |
| III | 16 | 1,028,660 | 3 | 13 |
| IV | 21 | 699,800 | 14 | 7 |
| V | 40 | 2,841,398 | 10 | 30 |
| VI | 108 | 7,541,560 | 54 | 54 |
| VII | 13 | 571,339 | 11 | 2 |
| VIII | 34 | 642,898 | 25 | 9 |
| IX | 46 | 2,537,420 | 5 | 41 |
| X | 12 | 477,500 | 7 | 5 |
| Totals | 302 | 18,144,795 | 133 | 169 |

[a] The data presented in the tables of Appendix A were compiled in January 1979. Possible changes in number and status of refineries since that time are indicated in Supplemental Information, pp. A-80 through A-84.

TABLE A-2. BREAKDOWN OF OPERATING REFINERIES IN REGION I.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Connecticut | 0 | 0 | 0 | 0 |
| Maine | 0 | 0 | 0 | 0 |
| Massachusetts | 0 | 0 | 0 | 0 |
| New Hampshire | 1 | 13,400 | 0 | 1 |
| Rhode Island | 0 | 0 | 0 | 0 |
| Vermont | 0 | 0 | 0 | 0 |
| Totals | 1 | 13,400 | 0 | 1 |

TABLE A-3. BREAKDOWN OF OPERATING REFINERIES IN CONNECTICUT

REGION: I
STATE: Connecticut

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-4. BREAKDOWN OF OPERATING REFINERIES IN MAINE

REGION: I
STATE: Maine

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-5. BREAKDOWN OF OPERATING REFINERIES IN MASSACHUSETTS

REGION: I
STATE: Massachusetts

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-6. BREAKDOWN OF OPERATING REFINERIES IN NEW HAMPSHIRE

REGION: I
STATE: New Hampshire

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| ATC Petroleum, Inc.<br>Newington 03842 | Rockingham | 121 | 13,400 | | x |
| Totals 1 | | | 13,400 | 0 | 1 |

TABLE A-7. BREAKDOWN OF OPERATING REFINERIES IN RHODE ISLAND

REGION: I
STATE: Rhode Island

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

## TABLE A-8. BREAKDOWN OF OPERATING REFINERIES IN VERMONT

REGION: I
STATE: Vermont

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-9. BREAKDOWN OF OPERATING REFINERIES IN REGION II.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| New Jersey | 4 | 644,000 | 0 | 4 |
| New York | 3 | 135,020 | 0 | 3 |
| Puerto Rico | 3 | 283,800 | 3 | 0 |
| Virgin Islands | 1 | 728,000 | 1 | 0 |
| Totals | 11 | 1,790,820 | 4 | 7 |

TABLE A-10. BREAKDOWN OF OPERATING REFINERIES IN NEW JERSEY

REGION: II
STATE: New Jersey

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Chevron USA, Inc.<br>1200 State Street<br>Perth Amboy 08861 | Middlesex | 043 | 168,000 | | x |
| Exxon Co., USA<br>P.O. Box 222<br>Linden 07036 | Union | 043 | 290,000 | | x |
| Mobil Oil Corp.<br>Paulsburo 08066 | Gloucester | 045 | 98,000 | | x |
| Texaco, Inc.<br>P.O. Box 98<br>Westville 08093 | Gloucester | 045 | 88,000 | | x |
| Totals 4 | | | 644,000 | 0 | 4 |

TABLE A-11. BREAKDOWN OF OPERATING REFINERIES IN NEW YORK

REGION: II
STATE: New York

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Ashland Oil, Inc.<br>N. Tonawanda 14120 | Niagara | 162 | 64,020 | | x |
| Cibro Petroleum<br>Port of Albany 12202 | Albany | 161 | 28,000 | | x |
| Mobil Oil Corp.<br>Buffalo 14240 | Erie | 162 | 43,000 | | x |
| Totals 3 | | | 135,020 | 0 | 3 |

TABLE A-12. BREAKDOWN OF OPERATING REFINERIES IN PUERTO RICO

REGION: II
Puerto Rico

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Caribbean Gulf Refining Corp.<br>G.P.O. Box 1988<br>San Juan 00936 | — | 244 | 37,800 | x | |
| Commonwealth Oil & Refining Co.<br>(CORCO)<br>Penuelas at Guayanilla Bay 00731 | — | 244 | 161,000 | x | |
| Yubucoa Sun Oil Co., Inc.<br>P.O. Box 186<br>Yubucoa 00767 | — | 244 | 85,000 | x | |
| Totals 3 | | | 283,800 | 3 | 0 |

TABLE A-13. BREAKDOWN OF OPERATING REFINERIES IN VIRGIN ISLANDS

REGION: II
Virgin Islands

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amerada Hess Corp.<br>St. Croix 00850 | ——— | 247 | 728,000 | x | |
| Totals 1 | | | 728,000 | 1 | 0 |

TABLE A-14. BREAKDOWN OF OPERATING REFINERIES IN REGION III.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Delaware | 1 | 140,000 | 0 | 1 |
| Maryland | 1 | 15,000 | 0 | 1 |
| Pennsylvania | 10 | 801,210 | 0 | 10 |
| Virginia | 1 | 53,000 | 1 | 0 |
| West Virginia | 3 | 19,450 | 2 | 1 |
| Washington D.C. | 0 | 0 | 0 | 0 |
| Totals | 16 | 1,028,660 | 3 | 13 |

TABLE A-15. BREAKDOWN OF OPERATING REFINERIES IN DELAWARE

REGION: III
STATE: Delaware

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Getty Oil Co.<br>Delaware City 19706 | New Castle | 045 | 140,000 | | x |
| Totals 1 | | | 140,000 | 0 | 1 |

## TABLE A-16. BREAKDOWN OF OPERATING REFINERIES IN MARYLAND

REGION: III
STATE: Maryland

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>3901 Asiatic Ave.<br>Baltimore 21226 | Baltimore | 115 | 15,000 | | x |
| Totals 1 | | | 15,000 | 0 | 1 |

TABLE A-17. BREAKDOWN OF OPERATING REFINERIES IN PENNSYLVANIA

REGION: III
STATE: Pennsylvania

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Ashland Oil, Inc.<br>Freedom 15042 | Beaver | 197 | 6,790 | | x |
| Atlantic Richfield Co.<br>3144 Passyunk<br>Philadelphia 19145 | Philadelphia | 151 | 185,000 | | x |
| B.P. Oil, Inc. (subsidiary of Standard Oil Co. of Ohio)<br>P.O. Box 428<br>Marcus Hook 19061 | Delaware | 151 | 164,000 | | x |
| Gulf Oil Corp.<br>P.O. Box 7408<br>Philadelphia 19101 | Philadelphia | 151 | 207,600 | | x |
| Pennzoil Co.<br>Rouseville 16344 | Venango | 178 | 12,000 | | x |
| Quaker State Oil Refining Corp.<br>Emlenton 16373 | Venango | 178 | 3,320 | | x |
| Quaker State Oil Refining Corp.<br>Farmers Valley 16749 | McKean | 178 | 6,500 | | x |
| Sun Petroleum Products Co. (Div. of Sun Oil Co. of Pa.)<br>P.O. Box 426<br>Marcus Hook 19061 | Delaware | 151 | 165,000 | | x |

(continued)

TABLE A-17. (continued)

REGION: III
STATE: Pennsylvania (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| United Refining Co.<br>P.O. Box 780<br>Bradley and Dobson Sts.<br>Warren 16365 | Warren | 178 | 42,000 | | x |
| Witco Chemical Corp.,<br>Kendall Refining Div.<br>77 N. Kendall Ave.<br>Bradford 16701 | McKean | 178 | 9,000 | | x |
| Totals 10 | | | 801,210 | 0 | 10 |

TABLE A-18. BREAKDOWN OF OPERATING REFINERIES IN VIRGINIA

REGION: III
STATE: Virginia

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>P.O. Box 578<br>Yorktown 23490 | York | 223 | 53,000 | x | |
| Totals 1 | | | 53,000 | 1 | 0 |

TABLE A-19. BREAKDOWN OF OPERATING REFINERIES IN WEST VIRGINIA

REGION: III
STATE: West Virginia

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Elk Refining Co.<br>(Div. of Pennzoil Co.)<br>P.O. Box 68<br>Falling Rock 25079 | Kanawha | 234 | 4,900 | | x |
| Quaker State Oil Refining Corp.<br>P.O. Box 336<br>Newell 26050 | Hancock | 181 | 9,700 | x | |
| Quaker State Oil Refining Corp.<br>St. Marys 26170 | Pleasants | 179 | 4,850 | x | |
| Totals 3 | | | 19,450 | 2 | 1 |

TABLE A-20. BREAKDOWN OF OPERATING REFINERIES IN DISTRICT OF COLUMBIA

REGION: III
Washington, D.C.

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-21. BREAKDOWN OF OPERATING REFINERIES IN REGION IV.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Alabama | 6 | 108,300 | 3 | 3 |
| Florida | 1 | 6,000 | 1 | 0 |
| Georgia | 2 | 20,000 | 1 | 1 |
| Kentucky | 4 | 169,000 | 2 | 2 |
| Mississippi | 6 | 340,700 | 6 | 0 |
| North Carolina | 1 | 11,900 | 1 | 0 |
| South Carolina | 0 | 0 | 0 | 0 |
| Tennessee | 1 | 43,900 | 0 | 1 |
| Totals | 21 | 699,800 | 14 | 7 |

TABLE A-22. BREAKDOWN OF OPERATING REFINERIES IN ALABAMA

REGION: IV
STATE: Alabama

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Hunt Oil Co.<br>P.O. Box 1850<br>Tuscaloosa 35402 | Tuscaloosa | 004 | 29,000 | x | |
| Louisiana Land & Exploration Co.<br>Saraland 36571 | Mobile | 005 | 41,300 | | x |
| Marion Corp.<br>P.O. Box 526<br>Theodore 36582 | Mobile | 005 | 20,000 | | x |
| Mobile Bay Refining Co.<br>P.O. Box 11526<br>Chickasaw 36611 | Mobile | 005 | 10,000 | | x |
| Vulcan Asphalt Refining Co.<br>P.O. Box 80<br>Cordova 35550 | Walker | 004 | 5,000 | x | |
| Warrior Asphalt Co. of Alabama, Inc.<br>Holt 35401 | Tuscaloosa | 004 | 3,000 | x | |
| Totals 6 | | | 108,300 | 3 | 3 |

# TABLE A-23. BREAKDOWN OF OPERATING REFINERIES IN FLORIDA

REGION: IV
STATE: Florida

| Name and address of refinery | County | AOCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Seminole Asphalt Refining, Inc.<br>P.O. Box 128<br>St. Marks 32355 | Wakulla | 049 | 6,000 | x | |
| Totals 1 | | | 6,000 | 1 | 0 |

TABLE A-24. BREAKDOWN OF OPERATING REFINERIES IN GEORGIA

REGION: IV
STATE: Georgia

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>P.O. Box 1881<br>Savannah 31402 | Chatham | 058 | 15,000 | x | |
| Young Refining Corp.<br>P.O. Box 775<br>Douglasville 30134 | Douglas | 056 | 5,000 | | x |
| Totals 2 | | | 20,000 | 1 | 1 |

TABLE A-25. BREAKDOWN OF OPERATING REFINERIES IN KENTUCKY

REGION: IV
STATE: Kentucky

| Name and address of refinery | County | AOCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Ashland Oil, Inc.<br>Catlettsburg 41129 | Boyd | 103 | 135,800 | | x |
| Ashland Oil, Inc.<br>224 East Broadway<br>Louisville 40202 | Jefferson | 078 | 25,200 | | x |
| Kentucky Oil & Refining, Inc.<br>Rt. 1, P.O. Box 63<br>Betsy Lane 41605 | Floyd | 101 | 3,000 | x | |
| Somerset Refinery, Inc.<br>Somerset 42501 | Pulaski | 105 | 5,000 | x | |
| Totals 4 | | | 169,000 | 2 | 2 |

TABLE A-26. BREAKDOWN OF OPERATING REFINERIES IN MISSISSIPPI

REGION: IV
STATE: Mississippi

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amerada Hess Corp.<br>P.O. Box 425<br>Purvis 39475 | Lamar | 005 | 30,000 | x | |
| Chevron USA, Inc.<br>P.O. Box 1300<br>Pascagoula 39567 | Jackson | 005 | 280,000 | x | |
| Ergon, Inc.<br>Vicksburg 39180 | Warren | 005 | 10,000 | x | |
| Southland Oil Co.<br>Lumberton 39455 | Lamar | 005 | 5,500 | x | |
| Southland Oil Co.<br>Sandersville 39477 | Jones | 005 | 11,000 | x | |
| Southland Oil Co.<br>Yazoo City 39194 | Yazoo | 134 | 4,200 | x | |
| Totals 6 | | | 340,700 | 6 | 0 |

TABLE A-27. BREAKDOWN OF OPERATING REFINERIES IN NORTH CAROLINA

REGION: IV
STATE: North Carolina

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| ATC Petroleum Co. (subsidiary of C. H. Sprague & Sons Co.)<br>816 Surry Street<br>Wilmington 28401 | New Hanover | 170 | 11,900 | x | |
| Totals 1 | | | 11,900 | 1 | 0 |

TABLE A-28. BREAKDOWN OF OPERATING REFINERIES IN SOUTH CAROLINA

REGION: IV
STATE: South Carolina

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-29. BREAKDOWN OF OPERATING REFINERIES IN TENNESSEE

REGION: IV
STATE: Tennessee

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Delta Refining Co. (Div. of Earth Resources Co.)<br>P.O. Box 9097<br>Memphis 38109 | Shelby | 018 | 43,900 | | x |
| Totals 1 | | | 43,900 | 0 | 1 |

TABLE A-30. BREAKDOWN OF OPERATING REFINERIES IN REGION V.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Illinois | 14 | 1,201,200 | 7 | 7 |
| Indiana | 8 | 605,900 | 3 | 5 |
| Michigan | 7 | 185,955 | 0 | 7 |
| Minnesota | 3 | 217,943 | 0 | 3 |
| Ohio | 7 | 590,400 | 0 | 7 |
| Wisconsin | 1 | 40,000 | 0 | 1 |
| Totals | 40 | 2,841,398 | 10 | 30 |

## TABLE A-31. BREAKDOWN OF OPERATING REFINERIES IN ILLINOIS

REGION: V
STATE: Illinois

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>P.O. Box 182<br>Wood River 62095 | Madison | 070 | 105,000 | | x |
| Bi-Petro, Inc.<br>Pana 62557 | Christian | 075 | 1,500 | x | |
| Clark Oil & Refining Corp.<br>P.O. Box 297<br>Blue Island 60406 | Cook | 067 | 70,000 | | x |
| Clark Oil & Refining Corp.<br>P.O. Box 145<br>Hartford 62048 | Madison | 070 | 55,000 | | x |
| Dillman Oil Recovery, Inc.<br>Robinson 62449 | Crawford | 074 | 1,200 | x | |
| Marathon Oil Co.<br>Robinson 62454 | Crawford | 074 | 195,000 | x | |
| Mobil Oil Corp.<br>P.O. Box 874<br>Joliet 60434 | Will | 067 | 180,000 | | x |
| Richards, M. T., Inc.<br>P.O. Box 429<br>Crossville 62827 | White | 074 | 700 | x | |

(continued)

TABLE A-31. (continued)

REGION: V
STATE: Illinois (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Shell Oil Co.<br>P.O. Box 262<br>Wood River 62095 | Madison | 070 | 283,000 | | x |
| Texaco, Inc.<br>P.O. Box 311<br>Lawrenceville 62439 | Lawrence | 074 | 84,000 | x | |
| Texaco, Inc.<br>P.O. Box 200<br>Lockport 60441 | Will | 067 | 72,000 | | x |
| Union Oil Co. of California<br>P.O. Box 339<br>Lemont 60439 | Cook | 067 | 151,000 | | x |
| Wireback Oil Co.<br>Plymouth 62367 | Hancock | 065 | 1,800 | x | |
| Yetter Oil Co.<br>Colmar 62327 | McDonough | 065 | 1,000 | x | |
| Totals 14 | | | 1,201,200 | 7 | 7 |

TABLE A-32. BREAKDOWN OF OPERATING REFINERIES IN INDIANA

REGION: V
STATE: Indiana

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>P.O. Box 710<br>Whiting 46394 | Lake | 067 | 380,000 |  | x |
| Energy Cooperative, Inc.<br>3500 Indianapolis Blvd.<br>E. Chicago 46312 | Lake | 067 | 126,000 |  | x |
| Gladieux Refinery, Inc.<br>4133 New Haven Ave.<br>Ft. Wayne 46803 | Allen | 081 | 12,200 |  | x |
| Indiana Farm Bureau Cooperative Assn., Inc.<br>P.O. Box 271<br>Mt. Vernon 47620 | Posey | 077 | 21,200 | x |  |
| Industrial Fuel Asphalt of Indiana<br>Hammond 46320 | Lake | 067 | 9,800 |  | x |
| Laketon Asphalt Refinery Co.<br>P.O. Box 231<br>Laketon 46943 | Wabash | 084 | 8,500 | x |  |
| Princeton Refinery, Inc.<br>Princeton 47670 | Gibson | 077 | 4,600 | x |  |

(continued)

TABLE A-32. (continued)

REGION: V
STATE: Indiana (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Rock Island Refining Corp.<br>P.O. Box 68007<br>Indianapolis 46268 | Marion | 080 | 43,600 | | x |
| Totals 8 | | | 605,900 | 3 | 5 |

TABLE A-33. BREAKDOWN OF OPERATING REFINERIES IN MICHIGAN

REGION: V
STATE: Michigan

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Consumers Power Co.<br>Marysville 48040 | St. Clair | 123 | 37,655 | | x |
| Crystal Refining Co. of Carson City, Inc.<br>Carson City 48811 | Montcalm | 122 | 6,200 | | x |
| Dow Chemical, USA<br>4868 Wilder Road<br>Bay City 48706 | Bay | 122 | 17,000 | | x |
| Lakeside Refining Co.<br>P.O. Box 909<br>Kalamazoo 49005 | Kalamazoo | 125 | 5,600 | | x |
| Marathon Oil Co.<br>1300 S. Fort Street<br>Detroit 48217 | Wayne | 123 | 65,000 | | x |
| Osceola Refining Co. (subsidiary of Texas American Petrochemical)<br>2790 Refinery Rd.<br>West Branch 48661 | Ogemaw | 122 | 12,500 | | x |
| Total Petroleum, Inc. (subsidiary of Total Petroleum (North American), Ltd.)<br>East Superior St., Alma 48801 | Gratiot | 122 | 42,000 | | x |
| Totals 7 | | | 185,955 | 0 | 7 |

TABLE A-34. BREAKDOWN OF OPERATING REFINERIES IN MINNESOTA

REGION: V
STATE: Minnesota

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Continental Oil Co.<br>P.O. Box 8<br>Wrenshall 55797 | Carlton | 129 | 23,500 | | x |
| Koch Refining Co. (subsidiary of Koch Industries, Inc.)<br>P.O. Box 43596<br>St. Paul 55164 | Dakota | 131 | 127,300 | | x |
| Northwestern Refining Co. (subsidiary of Ashland Oil, Inc.)<br>P.O. Drawer 9<br>St. Paul Park 55071 | Washington | 131 | 67,143 | | x |
| Totals 3 | | | 217,943 | 0 | 3 |

TABLE A-35. BREAKDOWN OF OPERATING REFINERIES IN OHIO

REGION: V
STATE: Ohio

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Ashland Oil, Inc.<br>P.O. Box 8170<br>Canton 44701 | Stark | 174 | 64,000 | | x |
| Ashland Oil Inc.<br>Findlay 45848 | Hancock | 177 | 20,400 | | x |
| Gulf Oil Corp.<br>P.O. Box 7<br>Cleves 45202 | Hamilton | 079 | 42,700 | | x |
| Gulf Oil Corp.<br>P.O. Box 1023<br>Toledo 43601 | Lucas | 124 | 50,300 | | x |
| Standard Oil Co. of Ohio<br>1150 S. Metcalf St.<br>Lima 45804 | Allen | 177 | 168,000 | | x |
| Standard Oil Co. of Ohio<br>P.O. Box 696<br>Toledo 43601 | Lucas | 124 | 120,000 | | x |
| Sun Co., Inc.<br>P.O. Box 920<br>Toledo 43601 | Lucas | 124 | 125,000 | | x |
| Totals 7 | | | 590,400 | 0 | 7 |

TABLE A-36. BREAKDOWN OF OPERATING REFINERIES IN WISCONSIN

REGION: V
STATE: Wisconsin

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Murphy Oil Corp.<br>Superior 54880 | Douglas | 129 | 40,000 | | x |
| Totals 1 | | | 40,000 | 0 | 1 |

TABLE A-37. BREAKDOWN OF OPERATING REFINERIES IN REGION VI.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Arkansas | 4 | 64,100 | 4 | 0 |
| Louisiana | 28 | 2,172,280 | 10 | 18 |
| New Mexico | 8 | 119,630 | 8 | 0 |
| Oklahoma | 12 | 550,400 | 10 | 2 |
| Texas | 56 | 4,635,150 | 22 | 34 |
| Totals | 108 | 7,541,560 | 54 | 54 |

## TABLE A-38. BREAKDOWN OF OPERATING REFINERIES IN ARKANSAS

REGION: VI
STATE: Arkansas

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Berry Petroleum Co. (subsidiary of Crystal Oil Co.)<br>Stephens 71764 | Ouachita | 019 | 3,500 | x | |
| Cross Oil & Refinery Co. of Ark.<br>P.O. Box 105<br>Smackover 71762 | Union | 019 | 9,200 | x | |
| Lion Oil (Div. of Tosco Corp.)<br>El Dorado 71730 | Union | 019 | 47,000 | x | |
| MacMillan Ring-Free Oil Co., Inc.<br>Norphlet 71759 | Union | 019 | 4,400 | x | |
| Totals 4 | | | 64,100 | 4 | 0 |

## TABLE A-39. BREAKDOWN OF OPERATING REFINERIES IN LOUISIANA

REGION: VI
STATE: Louisiana

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Atlas Processing Co. (subsidiary of Pennzoil Co.)<br>P.O. Box 9389<br>Shreveport 71109 | Caddo | 022 | 45,000 |  | x |
| Bayou State Oil Corp.<br>P.O. Box 158<br>Hosston 71043 | Caddo | 022 | 5,000 |  | x |
| Bruin Refining, Inc.<br>P.O. Box 156<br>St. James 70086 | St. James | 106 | 19,300 |  | x |
| Calcasieu Refining, Ltd.<br>Lake Charles 70601 | Calcasieu | 106 | 5,000 |  | x |
| Calumet Refinery Co. (Div. of Calumet Industries, Inc.)<br>Princeton 71067 | Bossier | 022 | 2,400 |  | x |
| Canal Refinery Co.<br>Church Point 70525 | Acadia | 106 | 6,400 | x |  |
| Cities Service Oil Co.<br>P.O. Box 1562<br>Lake Charles 70601 | Calcasieu | 106 | 268,000 |  | x |

(continued)

TABLE A-39. (continued)

REGION: VI
STATE: Louisiana (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Claiborne Gasoline Co.<br>P.O. Box 75<br>Lisbon 71048 | Claiborne | 022 | 6,500 | | x |
| Continental Oil Co.<br>Egan 70531 | Acadia | 106 | 15,000 | x | |
| Continental Oil Co.<br>P.O. Box 37<br>Westlake 70669 | Calcasieu | 106 | 83,000 | | x |
| Cotton Valley Solvents Co. (owned by Triangle Refineries, Inc., wholly owned subsidiary of Kerr-McGee Refining Corp.)<br>P.O. Box 97<br>Cotton Valley 71018 | Webster | 022 | 7,000 | x | |
| Evangeline Refinery Co., Inc.<br>P.O. Box 726<br>Jennings 70546 | Jefferson Davis | 106 | 5,000 | x | |
| Exxon Co., USA<br>P.O. Box 551<br>Baton Rouge 70821 | E. Baton Rouge | 106 | 510,000 | | x |
| Good Hope Refineries, Inc.<br>P.O. Drawer 537<br>Good Hope 70079 | St. Charles | 106 | 80,000 | | x |

(continued)

TABLE A-39. (continued)

REGION: VI
STATE: Louisiana (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Gulf Oil Co.-US<br>P.O. Box 395<br>Belle Chasse 70037 | Plaquemines | 106 | 195,900 | x | |
| Gulf Oil Co.-US<br>P.O. Box G<br>Venice 70091 | Plaquemines | 106 | 28,700 | x | |
| Hill Petroleum (subsidiary of Goldking Petroleum Co.)<br>P.O. Box 453<br>Krotz Springs 70750 | St. Landry | 106 | 10,000 | x | |
| LaJet, Inc. (branch of No. American Petroleum)<br>P.O. Box 47<br>St. James 70086 | St. James | 106 | 20,000 | | x |
| Marathon Oil Co.<br>P.O. Box A-C<br>Garyville 70051 | St. John the Baptist | 106 | 200,000 | | x |
| Mt. Airy Refining Co.<br>P.O. Box T<br>Garyville 70051 | St. John the Baptist | 106 | 11,580 | | x |
| Murphy Oil Corp.<br>Meraux 70075 | St. Bernard | 106 | 92,500 | | x |

(continued)

TABLE A-39. (continued)

REGION: VI
STATE: Louisiana (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Placid Refining Co.<br>P.O. Box 350 B<br>Port Allen 70767 | W. Baton Rouge | 106 | 36,000 | | x |
| Shell Oil Co.<br>P.O. Box 10<br>Norco 70079 | St. Charles | 106 | 230,000 | | x |
| Shepherd Oil, Inc.<br>P.O. Box 609<br>Jennings 70546 | Jefferson Davis | 106 | 10,000 | x | |
| South Louisiana Production Co.<br>Mermentau 70556 | Acadia | 106 | 10,000 | x | |
| T & S Refining, Inc.<br>Mermentau 70556 | Acadia | 106 | 10,000 | x | |
| Tenneco Oil Co.<br>P.O. Box 1007<br>Chalmette 70043 | St. Bernard | 106 | 120,000* | | x |
| Texaco, Inc.<br>P.O. Box 37<br>Convent 70723 | St. James | 106 | 140,000 | | x |
| Totals 28 | | | 2,172,280 | 10 | 18 |

*Barrels per stream day

## TABLE A-40. BREAKDOWN OF OPERATING REFINERIES IN NEW MEXICO

REGION: VI
STATE: New Mexico

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Caribou-Four Corners Oil Co.<br>P.O. Box 175<br>Kirtland 87417 | San Juan | 014 | 2,500 | x | |
| Giant Refining Co.<br>Bloomfield 87413 | San Juan | 014 | 6,000 | x | |
| Navajo Refinery Co. (owned by Holly Corp.)<br>P.O. Box 159<br>Artesia 88210 | Eddy | 155 | 29,900 | x | |
| Plateau, Inc.<br>Bloomfield 87413 | San Juan | 014 | 14,000 | x | |
| Shell Oil Co., Ciniza Refinery<br>Wingate Star Route<br>Gallup 87301 | McKinley | 014 | 18,000 | x | |
| Southern Union Refining Co.<br>Lovington 88260 | Lea | 155 | 36,430 | x | |
| Southern Union Refining Co.<br>Monument 88265 | Lea | 155 | 5,300 | x | |
| Thriftway Oil Co.<br>Bloomfield 87413 | San Juan | 014 | 7,500 | x | |
| Totals 8 | | | 119,630 | 8 | 0 |

TABLE A-41. BREAKDOWN OF OPERATING REFINERIES IN OKLAHOMA

REGION: VI
STATE: Oklahoma

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Allied Materials Corp.<br>P.O. Box 516<br>Stroud 74079 | Lincoln | 184 | 5,500 | x | |
| Bell Oil & Gas Co. (Div. of Vicker Petroleum Co.)<br>P.O. Box 188<br>Ardmore 73401 | Carter | 188 | 64,100 | x | |
| Champlin Petroleum Co. (subsidiary of Union Pacific)<br>P.O. Box 552<br>Enid 73701 | Ellis | 187 | 53,800 | x | |
| Continental Oil Co.<br>P.O. Box 1267<br>Ponca City 74601 | Kay | 185 | 126,000 | x | |
| Hudson Oil Co.<br>P.O. Box 1111<br>Cushing 74023 | Payne | 185 | 19,000 | x | |
| Kerr-McGee Corp.<br>P.O. Box 305<br>Wynnewood 73098 | Garvin | 188 | 50,000 | x | |
| OKC Refining Co.<br>P.O. Box 918<br>Okmulgee 74447 | Okmulgee | 186 | 25,000 | x | |

(continued)

TABLE A-41. (continued)

REGION: VI
STATE: Oklahoma (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Oklahoma Refining Co.<br>Cyril 73029 | Caddo | 189 | 14,000 | x | |
| Sun Petroleum Products Co. (Div. of Sun Oil Co. of Pa.)<br>P.O. Box 820<br>Duncan 73533 | Stephens | 189 | 48,500 | x | |
| Sun Petroleum Products Co. (Div. of Sun Oil Co. of Pa.)<br>P.O. Box 2039<br>Tulsa 74102 | Tulsa | 186 | 88,500 | | x |
| Texaco, Inc.<br>P.O. Box 2389<br>Tulsa 74101 | Tulsa | 186 | 50,000 | | x |
| Tonkawa Refining Co.<br>Route 1, Box 30<br>Arnett 73832 | Ellis | 187 | 6,000 | x | |
| Totals 12 | | | 550,400 | 10 | 2 |

TABLE A-42. BREAKDOWN OF OPERATING REFINERIES IN TEXAS

REGION: VI
STATE: Texas

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Adobe Refining Co. (subsidiary of Crystal Oil Co., La Blanca Refining Div.)<br>P.O. Box 3<br>La Blanca 78558 | Hidalgo | 213 | 5,000 | x | |
| American Petrofina Co.<br>P.O. Box 849<br>Port Arthur 77640 | Jefferson | 106 | 110,000 | | x |
| Amoco Oil Co.<br>P.O. Box 401<br>Texas City 77590 | Galveston | 216 | 360,000 | | x |
| Atlantic Richfield Co.<br>P.O. Box 2451<br>Houston 77001 | Harris | 216 | 322,000 | | x |
| Champlin Petroleum Co. (subsidiary of Union Pacific)<br>1801 Nueces Bay Blvd.<br>Corpus Christi 78408 | Nueces | 214 | 155,000 | | x |
| Charter Int'l Oil Co.<br>P.O. Box 5008<br>Houston 77012 | Harris | 216 | 65,500 | | x |
| Chevron USA, Inc.<br>P.O. Box 20002<br>El Paso 79998 | El Paso | 153 | 76,000 | | x |

(continued)

TABLE A-42. (continued)

REGION: VI
STATE: Texas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Coastal States Petrochemical Co.<br>(subsidiary of Coastal States Gas Producing Co.)<br>1300 Cantwell Lane<br>Corpus Christi 78407 | Nueces | 214 | 185,000 | | x |
| Cosden Oil & Chemical Co.<br>Big Spring 79720 | Howard | 218 | 65,000 | x | |
| Crown Central Petroleum Co.<br>Pasadena 77501 | Harris | 216 | 100,000 | | x |
| Diamond Shamrock Oil & Gas Co.<br>P.O. Box 36, Star Route 1<br>Sunray 79086 | Moore | 211 | 51,500 | x | |
| Dorchester Refining Co. (subsidiary of Dorchester Gas Corp.)<br>P.O. Box 1011<br>Mt. Pleasant 75455 | Titus | 022 | 26,000 | x | |
| Eddy Refining Co.<br>P.O. Box 185<br>Houston 77001 | Harris | 216 | 3,250 | | x |
| Erickson Refining Corp.<br>Port Neches 77651 | Jefferson | 106 | 30,000 | | x |

(continued)

TABLE A-42. (continued)

REGION: VI
STATE: Texas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Exxon Co. USA<br>P.O. Box 3950<br>Baytown 77520 | Harris | 216 | 640,000 | | x |
| Flint Chemical Co.<br>403 Somerset<br>San Antonio 78211 | Bexar | 217 | 1,200 | | x |
| Gulf Oil Corp.<br>P.O. Box 701<br>Port Arthur 77640 | Jefferson | 106 | 334,500 | | x |
| Gulf States Oil & Refining Co.<br>7501 Up River Rd.<br>Corpus Christi 78410 | Nueces | 214 | 12,500 | | x |
| Gulf States Oil & Refining Co.<br>P.O. Box 896<br>Quitman 75783 | Wood | 022 | 6,000 | x | |
| Howell Hydrocarbons, Inc.<br>P.O. Box 2776<br>San Antonio 78299 | Bexar | 217 | 5,000 | | x |
| Independent Refining Corp.<br>Winnie 77665 | Chambers | 216 | 16,000 | x | |
| J.W. Refining Co.<br>Tucker 75801 | Anderson | 022 | 4,000 | x | |

(continued)

TABLE A-42. (continued)

REGION: VI
STATE: Texas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| LaGloria Oil & Gas Co. (subsidiary of Texas Eastern Transmission Corp.)<br>P.O. Box 840<br>Tyler 75702 | Smith | 022 | 29,300 | x | |
| Longview Refining Co. (Div. of Crystal Oil Co.)<br>P.O. Box 1512<br>Longview 75601 | Gregg | 022 | 9,000 | | x |
| Marathon Oil Co.<br>P.O. Box 1191<br>Texas City 77590 | Galveston | 216 | 66,700 | | x |
| Mid-Tex Refinery (owned by Electro-Form, Inc.)<br>Hearne 77859 | Robertson | 212 | 3,000 | x | |
| Mobil Oil Corp.<br>P.O. Box 3311<br>Beaumont 77704 | Jefferson | 106 | 335,000 | | x |
| Petrolite Corp.<br>Kilgore 75662 | Gregg | 022 | 1,000 | | x |
| Phillips Petroleum Corp.<br>P.O. Box 271<br>Borger 79007 | Hutchinson | 211 | 100,000 | x | |

(continued)

TABLE A-42. (continued)

REGION: VI
STATE: Texas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Phillips Petroleum Corp.<br>P.O. Box 866<br>Sweeny 77480 | Brazoria | 216 | 104,000 | | x |
| Pioneer Refining Co.<br>Nixon 78140 | Deaf Smith | 211 | 5,000 | x | |
| Pride Refining Co.<br>P.O. Box 3237<br>Abilene 79604 | Taylor | 210 | 36,500 | x | |
| Quintana-Howell, Joint Venture<br>(owned by Howell Corp.)<br>P.O. Box 4656<br>Corpus Christi 78408 | Nueces | 214 | 35,000 | | x |
| Rancho Refining Co., Inc. (Div. of Southwest Petrochemical, Inc.)<br>Donna 78537 | Hidalgo | 213 | 1,000 | x | |
| Raymal Refining, Ltd.<br>Ingleside 78362 | San Patricio | 214 | 2,000 | x | |
| Saber Petroleum Co.<br>6560 Up River Rd.<br>Corpus Christi 78410 | Nueces | 214 | 20,000 | | x |
| Sentry Refining, Inc.<br>Corpus Christi 78407 | Nueces | 214 | 10,000 | | x |

(continued)

TABLE A-42. (continued)

REGION: VI
STATE: Texas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Shell Oil Co.<br>P.O. Box 100<br>Deer Park 77536 | Harris | 216 | 285,000 | | x |
| Shell Oil Co.<br>P.O. Box 2352<br>Odessa 79760 | Ector | 218 | 32,000 | | x |
| Sigmore Refining Co. (subsidiary of Sigmore Corp.)<br>P.O. Box 490<br>Three Rivers 78071 | Live Oak | 214 | 10,000 | x | |
| South Hampton Co.<br>P.O. Box 605<br>Silsbee 77656 | Hardin | 106 | 18,100 | x | |
| Southwestern Refining Co., Inc. (subsidiary of Kerr-McGee Corp.)<br>P.O. Box 9217<br>Corpus Christi 78408 | Nueces | 214 | 124,000 | | x |
| Sun Petroleum Products Co. (Div. of Sun Oil Co. of Pa.)<br>P.O. Box 2608<br>Corpus Christi 78403 | Nueces | 214 | 57,000 | | x |
| Tesoro Petroleum Corp.<br>P.O. Box 156<br>Carrizo Springs 78834 | Dimmit | 217 | 26,100 | x | |

(continued)

TABLE A-42. (continued)

REGION: VI
STATE: Texas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Texaco, Inc.<br>P.O. Box 30110<br>Amarillo 79120 | Potter | 211 | 20,000 | x | |
| Texaco, Inc.<br>P.O. Box 20005<br>El Paso 79998 | El Paso | 153 | 17,000 | | x |
| Texaco, Inc.<br>P.O. Box 712<br>Port Arthur 77640 | Jefferson | 106 | 367,000 | | x |
| Texaco, Inc.<br>P.O. Box 787<br>Port Neches 77651 | Jefferson | 106 | 47,000 | | x |
| Texas Asphalt & Refining Co.<br>P.O. Box 416<br>Euless 76039 | Tarrant | 215 | 6,000 | | x |
| Texas City Refining Co.<br>P.O. Box 1271<br>Texas City 77590 | Galveston | 216 | 130,000 | | x |
| Thriftway, Inc.<br>P.O. Box 195<br>Graham 76046 | Young | 210 | 1,000 | x | |

(continued)

TABLE A-42. (continued)

REGION: VI
STATE: Texas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Tipperary Corp.<br>P.O. Box 659<br>Ingleside 78362 | San Patricio | 214 | 6,000 | x | |
| Uni Oil, Inc.<br>Ingleside 78362 | San Patricio | 214 | 10,000 | x | |
| Union Oil Co. of California<br>P.O. Box 237<br>Nederland 77627 | Jefferson | 106 | 120,000 | | x |
| Wickett Refining Co.<br>Wickett 79788 | Ward | 218 | 8,000 | x | |
| Winston Refining Co.<br>28th St. & Sylvania Ave.<br>Ft. Worth 76111 | Tarrant | 215 | 20,000 | | x |
| Totals 56 | | | 4,635,150 | 22 | 34 |

TABLE A-43. BREAKDOWN OF OPERATING REFINERIES IN REGION VII.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Iowa | 0 | 0 | 0 | 0 |
| Kansas | 11 | 459,339 | 10 | 1 |
| Missouri | 1 | 107,000 | 0 | 1 |
| Nebraska | 1 | 5,000 | 1 | 0 |
| Totals | 13 | 571,339 | 11 | 2 |

## TABLE A-44. BREAKDOWN OF OPERATING REFINERIES IN IOWA

REGION: VII
STATE: Iowa

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

## TABLE A-45. BREAKDOWN OF OPERATING REFINERIES IN KANSAS

REGION: VII
STATE: Kansas

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| CRA, Inc. (subsidiary of Farmland Industries, Inc.)<br>P.O. Box 570<br>North Linden St.<br>Coffeyville 67337 | Montgomery | 098 | 48,000 | x | |
| CRA, Inc. (subsidiary of Farmland Industries, Inc.)<br>P.O. Box 608<br>Phillipsburg 67661 | Phillips | 097 | 26,400 | x | |
| Derby Refining Co.<br>P.O. Box 1030<br>Wichita 67201 | Sedgwick | 099 | 27,982 | x | |
| E-Z Serve, Inc.<br>Route 2<br>Scott City 67871 | Scott | 100 | 10,000 | x | |
| Getty Refining & Marketing Co.<br>P.O. Box 1121<br>El Dorado 67042 | Butler | 099 | 80,577 | x | |
| Mid-American Refining Co., Inc.<br>P.O. Box 31<br>Chanute 66720 | Neosho | 098 | 3,500 | x | |
| Mobil Oil Corp.<br>P.O. Box 546<br>Augusta 67010 | Butler | 099 | 50,000 | x | |

(continued)

TABLE A-45. (continued)

REGION: VII
STATE: Kansas (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| National Co-Op Refining Assoc.<br>P.O. Box 1167<br>McPherson 67460 | McPherson | 096 | 54,150 | x | |
| Pester Refining Co.<br>P.O. Box 751<br>El Dorado 67042 | Butler | 099 | 22,500 | x | |
| Phillips Petroleum Co.<br>2029 Fairfax Rd.<br>Kansas City 66115 | Wyandotte | 094 | 90,000 | | x |
| Total Petroleum, Inc.<br>Arkansas City 67005 | Cowley | 099 | 46,230 | x | |
| Totals 11 | | | 459,339 | 10 | 1 |

TABLE A-46. BREAKDOWN OF OPERATING REFINERIES IN MISSOURI

REGION: VII
STATE: Missouri

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>P.O. Box 8507<br>Sugar Creek 64054 | Jackson | 094 | 107,000 | | x |
| Totals 1 | | | 107,000 | 0 | 1 |

TABLE A-47. BREAKDOWN OF OPERATING REFINERIES IN NEBRASKA

REGION: VII
STATE: Nebraska

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| CRA, Inc. (subsidiary of Farmland Industries, Inc.)<br>P.O. Box 311<br>Scottsbluff 69361 | Scotts Bluff | 146 | 5,000 | x | |
| Totals 1 | | | 5,000 | 1 | 0 |

TABLE A-48. BREAKDOWN OF OPERATING REFINERIES IN REGION VIII.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Colorado | 3 | 64,000 | 1 | 2 |
| Montana | 6 | 144,950 | 6 | 0 |
| North Dakota | 3 | 58,658 | 3 | 0 |
| South Dakota | 0 | 0 | 0 | 0 |
| Utah | 8 | 159,500 | 1 | 7 |
| Wyoming | 14 | 215,790 | 14 | 0 |
| Totals | 34 | 642,898 | 25 | 9 |

TABLE A-49. BREAKDOWN OF OPERATING REFINERIES IN COLORADO

REGION: VIII
STATE: Colorado

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Asamera Oil (U.S.), Inc.<br>5800 Brighton Blvd.<br>Commerce City 80022 | Adams | 003 | 21,500 | | x |
| Continental Oil Co.<br>5801 Brighton Blvd.<br>Commerce City 80022 | Adams | 003 | 32,500 | | x |
| Gary Western Co.<br>Gary Community Rural Station<br>Fruita 81521 | Mesa | 011 | 10,000 | x | |
| Totals 3 | | | 64,000 | 1 | 2 |

## TABLE A-50. BREAKDOWN OF OPERATING REFINERIES IN MONTANA

REGION: VIII
STATE: Montana

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Continental Oil Co.<br>P.O. Box 2548<br>Billings 59103 | Yellowstone | 140 | 52,500 | x | |
| Exxon Co. USA<br>P.O. Box 1163<br>Billings 59103 | Yellowstone | 140 | 45,000 | x | |
| Farmers Union Central Exchange Inc. (Cenex)<br>P.O. Box 126<br>Laurel 59044 | Yellowstone | 140 | 33,650 | x | |
| Kenco Refining, Inc.<br>P.O. Box 699<br>Wolf Point 59201 | Roosevelt | 143 | 2,500 | x | |
| Phillips Petroleum<br>1900 10th St.<br>Black Eagle 59414 | Cascade | 141 | 6,000 | x | |
| Westco Refining Co.<br>(Div. of Thunderbird Resources, Inc.)<br>P.O. Box 318<br>Cut Bank 59427 | Glacier | 141 | 5,300 | x | |
| Totals 6 | | | 144,950 | 6 | 0 |

## TABLE A-51. BREAKDOWN OF OPERATING REFINERIES IN NORTH DAKOTA

REGION: VIII
STATE: North Dakota

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>P.O. Box 549<br>Mandan 58554 | Morton | 172 | 49,000 | x | |
| Northland Oil & Refining Co.<br>P.O. Box 1246<br>Dickinson 58601 | Stark | 172 | 5,000 | x | |
| Westland Oil Refinery<br>(Div. of Thunderbird Resources, Inc.)<br>P.O. Box 849<br>Williston 58801 | Williams | 172 | 4,658 | x | |
| Totals 3 | | | 58,658 | 3 | 0 |

TABLE A-52. BREAKDOWN OF OPERATING REFINERIES IN SOUTH DAKOTA

REGION: VIII
STATE: South Dakota

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-53. BREAKDOWN OF OPERATING REFINERIES IN UTAH

REGION: VIII
STATE: Utah

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>474 W. 900 N.<br>Salt Lake City 84103 | Salt Lake | 220 | 39,000 | | x |
| Caribou-Four Corners, Inc.<br>P.O. Box 54<br>Woods Cross 84087 | Davis | 220 | 7,500 | | x |
| Chevron USA, Inc.<br>2351 N. 11th W.<br>P.O. Box 25117<br>Salt Lake City 84125 | Salt Lake | 220 | 45,000 | | x |
| Husky Oil Co.<br>P.O. Box 175<br>North Salt Lake 84054 | Davis | 220 | 25,000 | | x |
| Morrison Petroleum Co.<br>P.O. Box 227<br>Woods Cross 84087 | Davis | 220 | 2,500 | | x |
| Phillips Petroleum Co.<br>Wood Cross 84087 | Davis | 220 | 23,000 | | x |
| Plateau, Inc.<br>Roosevelt 84066 | Duchesne | 219 | 7,500 | x | |
| Western Refining Co.<br>Woods Cross 84087 | Davis | 220 | 10,000 | | x |
| Totals 8 | | | 159,500 | 1 | 7 |

TABLE A-54. BREAKDOWN OF OPERATING REFINERIES IN WYOMING

REGION: VIII
STATE: Wyoming

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Amoco Oil Co.<br>P.O. Box 160<br>Casper 82602 | Natrona | 241 | 43,000 | x | |
| C & H Refinery, Inc.<br>P.O. Box 278<br>Lusk 82225 | Niobrara | 243 | 190 | x | |
| Glacier Park Co.<br>P.O. Box 3155<br>Osage 82723 | Weston | 243 | 3,900 | x | |
| Glenrock Refining Co.<br>P.O. Box 992<br>Glenrock 82637 | Converse | 241 | 1,000 | x | |
| Husky Oil Co.<br>P.O. Box 1588<br>Cheyenne 82001 | Laramie | 242 | 23,600 | x | |
| Husky Oil Co.<br>P.O. Box 380<br>Cody 82414 | Park | 243 | 10,800 | x | |
| Johnson Oil Co.<br>La Barge 83123 | Lincoln | 243 | 2,000 | x | |

(continued)

TABLE A-54. (continued)

REGION: VIII
STATE: Wyoming (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Little American Refining Co.<br>P.O. Box 510<br>Evansville 82636 | Natrona | 241 | 24,500 | x | |
| Mountaineer Refining Co., Inc.<br>P.O. Box 127<br>La Barge 83123 | Lincoln | 243 | 600 | x | |
| Sage Creek Refining Co.<br>P.O. Box 37<br>Cowley 82420 | Big Horn | 243 | 1,200 | x | |
| Sinclair Oil Corp.<br>P.O. Box 227<br>Sinclair 82334 | Carbon | 243 | 72,000 | x | |
| Southwestern Refining Co.<br>La Barge 83123 | Lincoln | 243 | 1,500 | x | |
| Texaco, Inc.<br>P.O. Box 320<br>Casper 82601 | Nartona | 241 | 21,000 | x | |
| Wyoming Refining Co. (subsidiary of Hermes Products)<br>P.O. Box 820<br>Newcastle 82701 | Weston | 243 | 10,500 | x | |
| Totals 14 | | | 215,790 | 14 | 0 |

TABLE A-55. BREAKDOWN OF OPERATING REFINERIES IN REGION IX.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Arizona | 1 | 6,000 | 1 | 0 |
| California | 41 | 2,395,120 | 0 | 41 |
| Hawaii | 2 | 105,000 | 2 | 0 |
| Nevada | 1 | 1,800 | 1 | 0 |
| American Samoa | 0 | 0 | 0 | 0 |
| Guam | 1 | 29,500 | 1 | 0 |
| Totals | 46 | 2,537,420 | 5 | 41 |

TABLE A-56. BREAKDOWN OF OPERATING REFINERIES IN ARIZONA

REGION: IX
STATE: Arizona

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Arizona Fuels, Inc.<br>Fredonia 86022 | Coconino | 014 | 6,000 | x | |
| Totals 1 | | | 6,000 | 1 | 0 |

TABLE A-57. BREAKDOWN OF OPERATING REFINERIES IN CALIFORNIA

REGION: IX
STATE: California

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Atlantic Richfield Co.<br>1801 E. Sepulveda Blvd.<br>Carson 90745 | Los Angeles | 024 | 180,000 | | x |
| Basin Petroleum, Inc.<br>1825 E. Spring<br>Long Beach 90806 | Los Angeles | 024 | 10,700 | | x |
| Beacon Oil Co.<br>525 W. Third St.<br>Hanford 93230 | Kings | 031 | 12,100 | | x |
| Champlin Petroleum<br>2402 E. Anaheim<br>Wilmington 90748 | Los Angeles | 024 | 31,000 | | x |
| Chevron USA, Inc.<br>P.O. Box 5097<br>Bakersfield 93308 | Kern | 031 | 26,000 | | x |
| Chevron USA, Inc.<br>P.O. Box 97<br>El Segundo 90245 | Los Angeles | 024 | 405,000 | | x |
| Chevron USA, Inc.<br>P.O. Box 1272<br>Richmond 94802 | Contra Costa | 030 | 365,000 | | x |

(continued)

TABLE A-57. (continued)

REGION: IX
STATE: California (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| DeMenno Resources<br>2000 N. Alameda<br>Compton 90222 | Los Angeles | 024 | 5,000 | | x |
| Douglas Oil Co. of California<br>P.O. Box 198<br>Paramount 90723 | Los Angeles | 024 | 46,500 | | x |
| Douglas Oil Co. of California<br>P.O. Box 1260<br>Santa Maria 93454 | Santa Barbara | 032 | 9,500 | | x |
| ECO Petroleum, Inc.<br>1840 E. 29th St.<br>Signal Hill 90806 | Los Angeles | 024 | 5,000 | | x |
| Edgington Oil Co.<br>2400 E. Artesia Blvd.<br>Long Beach 90805 | Los Angeles | 024 | 29,500 | | x |
| Exxon Co., USA<br>3400 E. 2nd St.<br>Benicia 94510 | Solano | 030 | 93,000 | | x |
| Fletcher Oil & Refining Co.<br>P.O. Box 548<br>Wilmington 90748 | Los Angeles | 024 | 20,100 | | x |

(continued)

TABLE A-57. (continued)

REGION: IX
STATE: California (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Golden Eagle Refining Co.<br>21,000 S. Figueroa St.<br>Torrance 90502 | Los Angeles | 024 | 16,500 | | x |
| Gulf Oil Co.<br>13539 E. Foster Rd.<br>Santa Fe Springs 90670 | Los Angeles | 024 | 51,500 | | x |
| Kern County Refining, Inc.<br>Route 6<br>Bakersfield 93307 | Kern | 031 | 15,900 | | x |
| Lion Oil Co.<br>Bakersfield 93308 | Kern | 031 | 40,000 | | x |
| Lion Oil Co.<br>Martinez 94553 | Contra Costa | 030 | 126,000 | | x |
| Lunday-Thagard Oil Co.<br>9301 Garfield Ave.<br>South Gate 90280 | Los Angeles | 024 | 10,000 | | x |
| MacMillan Ring Free Oil Co., Inc.<br>2020 Walnut Ave.<br>Signal Hill 90806 | Los Angeles | 024 | 12,200 | | x |
| Mobil Oil Corp.<br>3700 W. 190th St.<br>Torrance 90509 | Los Angeles | 024 | 123,500 | | x |

(continued)

TABLE A-57. (continued)

REGION: IX
STATE: California (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Mohawk Petroleum Corp. (subsidiary of Reserve Oil and Gas Co.)<br>P.O. Box 1476<br>Bakersfield 93302 | Kern | 031 | 22,100 | | x |
| Newhall Refining Co., Inc. (owned by Pauley Petroleum, Inc.)<br>P.O. Box 938<br>Newhall 91322 | Los Angeles | 024 | 11,500 | | x |
| Oxnard Oil Co.<br>P.O. Box 258<br>Oxnard 93032 | Ventura | 024 | 2,500 | | x |
| Pacific Refining Co. (subsidiary of Coastal States Gas Corp.)<br>P.O. Box 68<br>Hercules 94547 | Contra Costa | 030 | 53,500 | | x |
| Powerine Oil Co.<br>12354 E. Lakeland Rd.<br>Santa Fe Springs 90670 | Los Angeles | 024 | 44,120 | | x |
| Road Oil Sales, Inc.<br>P.O. Box 5356<br>Bakersfield 93308 | Kern | 031 | 1,500 | | x |
| Sabre Oil & Refining, Inc.<br>3121 Standard St.<br>Bakersfield 93308 | Kern | 031 | 3,500 | | x |

(continued)

TABLE A-57. (continued)

REGION: IX
STATE: California (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Union Oil Co. of California<br>P.O. Box 758<br>Wilmington 90744 | Los Angeles | 024 | 108,000 | | x |
| USA Petrochemical Corp.<br>4777 Crooked Palm Rd.<br>Ventura 93001 | Ventura | 024 | 20,000 | | x |
| West Coast Oil Co.<br>P.O. Box 5475<br>Oildale 93308 | Kern | 031 | 19,000 | | x |
| Witco Chemical Corp.<br>P.O. Box 5446<br>Oildale 93308 | Kern | 031 | 11,000 | | x |
| Totals 41 | | | 2,395,120 | 0 | 41 |

TABLE A-57. (continued)

REGION: IX
STATE: California (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| San Joaquin Oil Co.<br>P.O. Box 5576<br>Bakersfield 93308 | Kern | 031 | 27,000 | | x |
| Shell Oil Co.<br>P.O. Box 711<br>Martinez 94553 | Contra Costa | 030 | 92,400 | | x |
| Shell Oil Co.<br>P.O. Box 6249<br>Wilmington 90749 | Los Angeles | 024 | 93,000 | | x |
| Sierra Anchor Oil Refinery<br>McKittrick 93251 | Kern | 031 | 10,000 | | x |
| Sunland Refining Corp.<br>P.O. Box 1345<br>Bakersfield 93302 | Kern | 031 | 15,000 | | x |
| Texaco, Inc.<br>P.O. Box 817<br>Wilmington 90748 | Los Angeles | 024 | 75,000 | | x |
| Union Oil Co. of California<br>Route 1, P.O. Box 7600<br>Arroyo Grande 93420 | San Luis Obispo | 032 | 41,000 | | x |
| Union Oil Co. of California<br>Rodeo 94572 | Contra Costa | 030 | 111,000 | | x |

(continued)

TABLE A-58. BREAKDOWN OF OPERATING REFINERIES IN HAWAII

REGION: IX
STATE: Hawaii

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Chevron USA, Inc.<br>P.O. Box 29789, Barber's Point<br>Honolulu 96820 | Honolulu | 060 | 40,000 | x | |
| Hawaii Independent Refinery<br>1060 Bishop St., Box 3379<br>Honolulu 96842 | Honolulu | 060 | 65,000 | x | |
| Totals 2 | | | 105,000 | 2 | 0 |

TABLE A-59. BREAKDOWN OF OPERATING REFINERIES IN NEVADA

REGION: IX
STATE: Nevada

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Nevada Refining Co.<br>Tonopah 89049 | Nye | 147 | 1,800 | x | |
| Totals 1 | | | 1,800 | 1 | 0 |

## TABLE A-60. BREAKDOWN OF OPERATING REFINERIES IN AMERICAN SAMOA

REGION: IX
STATE: American Samoa

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-61. BREAKDOWN OF OPERATING REFINERIES IN GUAM

REGION: IX
Guam

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Guam Oil & Refining Co.<br>P.O. Box 3190<br>Agana 96910 | ——— | 246 | 29,500 | x | |
| Totals 1 | | | 29,500 | 1 | 0 |

TABLE A-62. BREAKDOWN OF OPERATING REFINERIES IN REGION X.

| | Total refineries | Total capacity, bbl/day | Refineries in attainment areas | Refineries in nonattainment areas |
|---|---|---|---|---|
| Alaska | 3 | 82,600 | 3 | 0 |
| Idaho | 0 | 0 | 0 | 0 |
| Oregon | 1 | 14,000 | 0 | 1 |
| Washington | 8 | 380,900 | 4 | 4 |
| Totals | 12 | 477,500 | 7 | 5 |

TABLE A-63. BREAKDOWN OF OPERATING REFINERIES IN ALASKA

REGION: X
STATE: Alaska

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Chevron USA, Inc.<br>Drawer F<br>Kenai 99611 | Kenai-Cook Inlet | 008 | 22,000 | x | |
| North Pole Refining (Div. of Earth Resources Co. of Alaska, Energy Co. of Alaska)<br>P.O. Box 5028<br>North Pole 99705 | Fairbanks | 009 | 22,600 | x | |
| Tesoro-Alaskan Petroleum Corp.<br>P.O. Box 3691<br>Kenai 99611 | Kenai-Cook Inlet | 008 | 38,000 | x | |
| Totals 3 | | | 82,600 | 3 | 0 |

TABLE A-64. BREAKDOWN OF OPERATING REFINERIES IN IDAHO

REGION: X
STATE: Idaho

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| None | | | | | |
| Totals 0 | | | 0 | 0 | 0 |

TABLE A-65. BREAKDOWN OF OPERATING REFINERIES IN OREGON

REGION: X
STATE: Oregon

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Chevron USA, Inc.<br>5501 N.W. Front Ave.<br>Portland 97210 | Multnomah | 193 | 14,000 | | x |
| Totals 1 | | | 14,000 | 0 | 1 |

TABLE A-66. BREAKDOWN OF OPERATING REFINERIES IN WASHINGTON

REGION: X
STATE: Washington

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| Atlantic Richfield Co.<br>P.O. Box 1127<br>Ferndale 98248 | Whatcom | 228 | 106,000 | x | |
| Chevron USA, Inc.<br>Foot of Richmond Drive<br>Richmond Beach 98160 | King | 229 | 4,500 | | x |
| Mobil Oil Corp.<br>P.O. Box 8<br>Ferndale 98248 | Whatcom | 228 | 71,500 | x | |
| Shell Oil Co.<br>P.O. Box 700<br>Anacortes 98221 | Skagit | 228 | 91,000 | x | |
| Sound Refining, Inc. (subsidiary of Kalama Chemical, Inc.)<br>P.O. Box 1372<br>Tacoma 98401 | Pierce | 229 | 7,500 | | x |
| Texaco, Inc.<br>P.O. Box 622<br>Anacortes 98221 | Skagit | 228 | 78,000 | x | |
| United Independent Oil Co.<br>709 Alexander Ave.<br>Tacoma 98401 | Pierce | 229 | 1,000 | | x |

(continued)

TABLE A-66. (continued)

REGION: X
STATE: Washington (continued)

| Name and address of refinery | County | AQCR No. | Capacity bbl/day | Attainment area for photochemical oxidant standards | Nonattainment area for photochemical oxidant standards |
|---|---|---|---|---|---|
| U.S. Oil & Refining Co.<br>3001 Marshall Ave.<br>Tacoma 98401 | Pierce | 229 | 21,400 | | x |
| Totals 8 | | | 380,900 | 4 | 4 |

# SUPPLEMENTAL INFORMATION

In the petroleum refining industry continual changes take place in ownership, operation, and size of refineries. This section is intended to clarify inventory omissions and to indicate additions or changes that may be necessary in the near future.

## REFINERIES RECENTLY SHUT DOWN

Although the following U.S. refineries may have appeared on earlier reference lists, they are omitted from the Appendix A inventory because they have been recently shut down:

| | |
|---|---|
| Region I: | Mobil Oil Corp., East Providence, Rhode Island |
| Region II: | Amerada Hess Corp., Port Reading, New Jersey |
| Region III: | Wolf's Head Oil Refinery, Inc., Reno, Pennsylvania |
| Region IV: | Young Refining Corp., Moundville, Alabama |
| Region V: | Cities Service Oil Co., East Chicago, Indiana<br>Mobil Oil Corp., East Chicago, Indiana<br>Mobil Oil Corp., Woodhaven, Michigan<br>Petroleum Specialists, Inc., Flat Rock, Michigan<br>Somerset Refinery, Inc., Troy, Indiana |
| Region VI: | Bayou Refining Co., Pasadena, Texas<br>Monarch Oil & Gas, San Antonio, Texas |
| Region VIII: | Big West Oil Co. of Montana, Kevin, Montana<br>Jet Fuel Refining, Mosby, Montana<br>John Wight, Inc., Shelby, Montana, temporarily shut down<br>Morrison Refining Co., Grand Junction, Colorado<br>Oriental Refining Co., Greybull, Wyoming |

NEW REFINERIES*

The following companies either plan to build or are now building new refineries in the locations indicated. When these refineries are in operation, the inventory will be updated accordingly.

| | |
|---|---|
| Region I: | Pittstone Oil Refinery, Eastport, Maine<br>Capacity: 250,000 bbl/day; Status: C |
| Region II: | Virgin Islands Refinery Corp., St. Croix, Virgin Islands<br>Capacity: 200,000 bbl/day; Status: E |
| Region III: | Crown Central Petroleum Corp., Baltimore, Maryland<br>Capacity: 200,000 bbl/day; Status: E<br>Hampton Roads Energy Co., Portsmouth, Virginia<br>Capacity: 184,100 bbl/day; Status: E, 1980<br>Steuart Petroleum Co., Piney Point, Maryland<br>Capacity: 100,000 bbl/day; Status: P |
| Region IV: | Wallace & Wallace Chem. & Oil Corp., Tuskegee, Alabama<br>Capacity: 150,000 bbl/day; Status: C |
| Region V: | Akron Hydrocarbons, Akron, Michigan<br>Capacity: 1,000 bbl/day; Status: E |

(continued)

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*The following abbreviations are used in pages A-81 through A-84:

| | | | |
|---|---|---|---|
| P | In planning | To | Total capacity after construction |
| E | In engineering | Re | Being revamped, modernized, or debottlenecked; not reported whether increment increase or final capacity |
| C | Under construction | | |
| 1978, 1979, etc. | Projected year of completion | Ex | Expansion; not classified |
| N.A. | Not available | | |

Region VI: Dow Chemical Co., Freeport, Texas
Capacity: 210,000 bbl/day; Status: C, 1979
Harbor Refining Co., Derby, Texas
Capacity: 5,000 bbl/day; Status: E, 1979
Lake Charles Refining Co., Lake Charles, Louisiana
Capacity: 30,000 bbl/day; Status: E, 1979
Refinery Services, Inc., Westwego, Louisiana
Capacity: N.A.; Status: P
Resource Refining Co., Lake Charles, Louisiana
Capacity: 30,000 bbl/day; Status: C
Tetrak Oil, Inc., Hahnville, Louisiana
Capacity: 30,000 bbl/day; Status: P

Region IX: Hawaiian Oil & Refining Co., Hawaii
Capacity: N.A.; Status: N.A.

Region X: Alpetco, Valdez, Alaska
Capacity: 150,000 bbl/day; Status: P, 1981
Cascade Energy, St. Helens, Oregon
Capacity: 30,000 bbl/day; Status: E, 1982

## EXPANSIONS OF EXISTING REFINERIES

The following companies are expanding or modernizing their existing refineries. Upon completion of each project, it will be necessary to change the capacity entry in this inventory.

Region III: Elk Refining Co., Falling Rock, West Virginia
Capacity: N.A., Ex; Status: N.A.

Region IV: Ashland Oil, Inc., Catlettsburg, Kentucky
Capacity: 25,000 bbl/day, Re; Status: C
Marion Corp., Mobile, Alabama
Capacity: 5,000 bbl/day; Status: P, 1980
Mobile Bay Refining Co., Chickasaw, Alabama
Capacity: 10,000 bbl/day; Status: C
Seminole Asphalt & Refining, Inc., St. Marks, Florida
Capacity: 6,000 bbl/day; Ex; Status: C
Warrior Asphalt of Alabama, Tuscaloosa, Alabama
Capacity: N.A.; Status: C

Region V: Bi-Petro, Inc., Pana, Illinois
Capacity: 4,500 bbl/day; Status: C
Total Petroleum, Alma, Michigan
Capacity: 15,000 bbl/day, Ex; Status: N.A.

Region VI: Amoco Oil Co., Texas City, Texas
Capacity: 47,000 bbl/day, Ex; Status: C, 1979
Capacity: N.A., Re; Status: U, 1979

Region VI:
(Continued)

Atlas Processing Co., Shreveport, Louisiana
    Capacity: 60,000 bbl/day, To; Status: C
Cities Service Co., Lake Charles, Louisiana
    Capacity: N.A., Re; Status: E, 1978
Continental Oil Co., Westlake, Louisiana
    Capacity: 100,000 bbl/day, Ex; Status: E, 1980
Good Hope Refineries, Inc., Good Hope, Louisiana
    Capacity: 60,000 bbl/day; Status: C, 1978
Gulf States Oil & Refining Co., Corpus Christi, Texas
    Capacity: 30,000 bbl/day, To; Status: P, 1979
Kerr-McGee Corp., Wynnewood, Oklahoma
    Capacity: 50,000 bbl/day, To; Status: E, 1979
LaGloria Oil & Gas Co., Tyler, Texas
    Capacity: 17,000 bbl/day, Ex; Status: E, 1979
Lion Oil Co., El Dorado, Arkansas
    Capacity: 36,500 bbl/day, Re; Status: C
Marathon Oil Co., Garyville, Louisiana
    Capacity: N.A., Ex; Status: E, 1979
Mid Tex Refining Co., Hearne, Texas
    Capacity: 7,500 bbl/day; Status: C, 1978
Phillips Petroleum Corp., Sweeny, Texas
    Capacity: 190,000 bbl/day, To; Status: E, 1979
Placid Refining Co., Port Allen, Louisiana
    Capacity: 42,000 bbl/day; Status: E
Sigmore Refining Co., Three Rivers, Texas
    Capacity: 20,000 bbl/day, To; Status: E, 1978
Thriftway Oil Co., Graham, Texas
    Capacity: 3,000 bbl/day; Status: C
Uni Oil, Ingleside, Texas
    Capacity: 20,000 bbl/day, Ex; Status: C, 1979

Region VIII:

Asamera Oil, Inc., Commerce City, Colorado
    Capacity: 30,000 bbl/day; Status: E, 1979
C & H Refinery, Inc., Lusk, Wyoming
    Capacity: 3,310 bbl/day; Status: C
Exxon Co. USA, Billings, Montana
    Capacity: N.A.; Status: C, 1978
Husky Oil Co., Cheyenne, Wyoming
    Capacity: 30,000 bbl/day; Status: C, 1978

Region IX: Atlantic Richfield Co., Carson, California
Capacity: 20,000 bbl/day, Ex; Status: P
DeMenno Resources, Compton, California
Capacity: 8,000 bbl/day, To; Status: C, 1978
Lion Oil Co., Bakersfield, California
Capacity: N.A., Re; Status: P, 1979
Mohawk Petroleum Corp., Bakersfield, California
Capacity: 33,000 bbl/day, Ex; Status: E, 1979
Pacific Refining Co., Hercules, California
Capacity: 20,000 bbl/day; Status: C
Sabre Oil & Refining, Inc., Bakersfield, California
Capacity: 10,000 bbl/day, To; Status: C, 1978
Union Oil Co. of California, Rodeo, California
Capacity: N.A., Re; Status: E, 1979
U.S.A. Petrochemical Corp., Ventura, California
Capacity: 15,000 bbl/day, Ex; Status: E, 1979

## REFINERIES NOT MEETING SIC CODE 2911

The following companies may be listed as petroleum refineries in other references, but they have been omitted from this inventory because they do not meet the criteria for SIC Code 2911 (Petroleum Refining):

Region III: Chevron U.S.A., Inc., Baltimore, Maryland
No longer refines crude oil.

Region VI: Dorchester Gas Producing Co., White Deer, Texas
Does not sell any SIC 2911 refinery products.
Monsanto Chemical Co., Texas City, Texas
Buys gas well distillates to use as feedstocks to olefin units. Residuals are sold to refineries in the Texas City area for refining; therefore, Monsanto does not sell any SIC 2911 refinery products.

Region X: Alyeska Pump Stations, Alaska
Topping plants 6, 8, and 10 distill diesel fuel off of crude oil from the Alaskan Pipeline and use this fuel to run pipeline pumps. No products are sold. Therefore, these plants do not meet the SIC criteria for refineries.

# APPENDIX B

# SIMPLIFIED THEORY OF REACTORS

Under appropriate conditions, feed materials may be transformed in a reactor into new and different materials that constitute different chemical species. If this transformation occurs by rearrangement or redistribution of structures, a chemical reaction has occurred.

Reactor design theory incorporates knowledge of thermodynamics, chemical kinetics, fluid mechanics, heat transfer, mass transfer, and economics. Principles of thermodynamics provide the designer with two important pieces of information: the amount of heat to be liberated or absorbed during reaction and the maximum possible extent of reaction (that is, the maximum potential yield of the products of a reaction). Principles of chemical kinetics deal with the mode and mechanisms of a reaction, the physical and energy changes involved, and the rate of formation of products.

A reaction is classified as homogeneous if it occurs in one phase (such as entirely in the vapor phase) or as heterogeneous if the reaction requires at least two phases (such as liquid and vapor phases). Cutting across this classification is the catalytic reaction, whose rate is altered by a material that is neither a reactant nor a product. Such a material, called a catalyst, may either impede or accelerate the reaction process while its own physical and chemical characteristics are modified relatively slowly, if at all. A catalyst that impedes a reaction is called a negative catalyst, and one that accelerates a reaction is called a positive catalyst. Although catalysts may be solids or fluids, in petroleum refining they are most often solids.

A solid-catalyst reaction usually involves high-energy rupture or high-energy synthesis of materials. In processes where a variety of reactions occur the catalyst may be selective, changing the rates of only certain reactions (often a single reaction) without affecting the rates of others. Thus, in the presence of a specific catalyst, a given feed may yield a reaction product containing relatively uniform types and concentrations of materials.

Catalyst activity decreases as the catalyst is used. The term "fouling" is often used if catalyst deactivation is rapid and is caused by deposition of a solid that physically blocks the catalytic surface. Removal of this solid is referred to as regeneration. Deposition of carbon during catalytic cracking is an example of fouling, after which the deactivated catalyst is regenerated or replaced.

Poisoning of the catalyst can occur if its active surface is modified by chemisorption (chemical adsorption) of materials that are not easily removed. When catalyst activity can be restored after poisoning, the restoration process is called reactivation. When the adsorption is reversible, a change in operating conditions may be sufficient to regenerate the catalyst. When the adsorption is not reversible, the poisoning is permanent. The surface of the catalyst may be treated chemically, or the spent catalyst may be replaced.

Many variables other than the catalysts affect the rate of a chemical reaction. In both homogeneous and heterogeneous systems the temperature, pressure, and composition are variables. In heterogeneous systems, the rate of mass and heat transfer may also be variables.

# APPENDIX C

## BASIC PRINCIPLES OF FRACTIONATION

Fractionation may be broadly defined as any method in which a liquid or vapor mixture is separated into individual components by vaporization or condensation. The components may be pure compounds, or, if the original material is a complex mixture, they may be products that are still mixtures but whose distillation range is limited by the fractionation process. The various means of separation are given special names: distillation, fractionation, stabilization, absorption, and stripping. The glossary gives simple definitions of these terms.

Fractionation is based on the difference in equilibrium composition of the liquid and vapor phases. The main function of industrial equipment for vapor-liquid transfer operations is to provide for the intimate contact of vapor and liquid phases and for subsequent separation and handling of the products of fractionation. In typical equipment, vapors may bubble through a continuous liquid phase, droplets of liquid may fall through a continuous vapor phase, an extended interface may provide contact between the two phases, or these methods may be used in combination.

Fractionating towers and related equipment are mechanical devices that repeatedly establish equilibrium between ascending vapor and descending liquid, and repeatedly separate the two phases. Duration and violence of the contact are of little significance; any sucessful design, however, must incorporate a means of attaining a large interface for contact and of completely separating the two phases.

A plate tower is a fractionating tower in which the vapor and liquid phases flow countercurrently. A typical arrangement consists of a vertical shell in which are mounted a large number of equally spaced circular plates. At one side of each plate, a conduit known as a downcomer allows passage of liquid to the plate below. At the opposite side of the plate, a similar conduit feeds liquid from the plate above.

A bubble-cap plate is pierced with holes into which are fitted risers or "chimneys," through which vapors from the plate below may pass. The vapors rise through the chimneys, are directed downwards by the cap, and are discharged as small bubbles from slots or notches at the bottom of the cap beneath the liquid. A weir maintains the liquid level on the plate. Liquid fed to the plate passes across it and through the downcomers to the plate below; the vapors pass upward through the plate, mixing intimately with the liquid on the plate because of dispersion produced by the slots in the bubble caps. The vapors separate at the liquid surface and pass to the plate above. A plate tower with bubble caps is sometimes called a "bubble tower."

A perforated plate, or sieve plate, is pierced with small holes that replace the bubble-cap assembly. The passage of vapors through the perforations prevents liquid from draining through them. The tower has weirs and downcomers identical to those used in a bubble-cap tower.

A valve tray is perforated with openings of variable areas for gas flow. The perforations are covered with movable caps, which rise as the flow rate of gas increases. Action of the gas prevents liquid from flowing through the perforations. At low flow rates, the liquid does not drain through the perforations because the valves close.

The packed tower consists of a vertical shell filled with packing material. The liquid flows over the surface of the packing in thin films and thereby presents a large surface for contact with ascending gases. The packing is supported on a grid. The liquid is introduced at the top of the packing by means of a distribution plate (a perforated plate), and the vapor is introduced beneath the grid that supports the packing. A packed tower offers the advantages of multiple contact and countercurrent flow, but the efficiency of contact is usually lower than that obtained in a plate-type tower.

In computing the degree of fractionation to be accomplished in a fractionating system, the designer must know the relationship between the compositions of the liquid and the vapor at equilibrium. The designer either uses experimental data or computes the needed data from known laws.

In determining the number of trays or plates in a tower, the designer first calculates the number of theoretical plates required. That is, he assumes ideal contacting and other conditions to determine the number of plates required to perform the desired separation. The overall efficiency of the tower is the ratio of the theoretical number of plates to the actual number required for a particular separation.

A fractionating tower must operate between two impractical extremes. At one extreme, the reflux rate is the minimum that can be used, and an infinite number of plates is required; at the other, the reflux rate is infinite and a minimum number of plates is required. In practice, the engineer must decide whether it is more economical to purchase a large number of plates or to operate at a higher daily operating cost.

# APPENDIX D

## SELECTED PHYSICAL PROPERTIES OF COMMON PETROCHEMICAL COMPOUNDS

The table found in this appendix lists various petrochemical compounds and their true vapor pressure at various temperatures. These data are useful in determining the type of storage vessel and vapor control equipment required to store a given material.

## TABLE D-1 SELECTED PHYSICAL PROPERTIES OF COMMON PETROCHEMICAL COMPOUNDS

| Chemical names and abbreviations | True vapor pressure, psia[a] 60°F | 70°F | 80°F | 90°F |
|---|---|---|---|---|
| 1. Acetic acid (AcOH or IUPAC), ethanoic acid | 0.2 | 0.3 | 0.3 | 0.5 |
| 2. Acetone (DMK) | 2.9 | 3.7 | 4.7 | 6.0 |
| 3. Acetonitrile | 1.1 | 1.4 | 1.9 | 2.5 |
| 4. Acrylonitrile | 1.4 | 1.8 | 2.4 | 3.1 |
| 5. Allyl alcohol | 0.3 | 0.4 | 0.5 | 0.7 |
| 6. Allyl chloride | 4.8 | 6.0 | 7.4 | 9.1 |
| 7. Ammonium hydroxide (28.8% solution) | 8.5 | 10.8 | 13.5 | 16.8 |
| 8. Benzene | 1.2 | 1.5 | 2.0 | 2.6 |
| 9. Butyl "Cellosolve"[b] (see No. 49)<br>Butyl "Oxitol"[c] (BUOX), 2-butoxyethanol | | | | |
| 10. Butyl formate[d] | 0.3 | 0.4 | 0.6 | 0.8 |
| 11. Butyl methacrylate, butyl acrylate | 0.1 | 0.1 | 0.1 | 0.2 |
| 12. Butyl phenol | Negligible | | | |
| 13. Isobutyl acetate (IBAc) | 0.2 | 0.3 | 0.4 | 0.5 |
| 14. Isobutyl alcohol (IBA or IBUOH)[d] | 0.1 | 0.2 | 0.3 | 0.4 |
| 15. Isobutyl isobutyrate (IBIB) | 0.2 | 0.3 | 0.4 | 0.5 |
| 16. n-Butyl acetate (NBAc) | 0.1 | 0.2 | 0.2 | 0.3 |
| 17. n-Butyl alcohol (NBA) | 0.1 | 0.1 | 0.2 | 0.2 |
| 18. Secondary butyl alcohol (SBA) | 0.2 | 0.3 | 0.4 | 0.6 |
| 19. Tertiary butyl alcohol (TBA) | 0.5 | 0.6 | 0.9 | 1.2 |
| 20. n-Butyl chloride | 1.3 | 1.7 | 2.2 | 2.7 |
| 21. Diisobutylene, diisobutene | | | | |

(continued)

TABLE D-1 (continued)

| Chemical names and abbreviations | True vapor pressure, psia[a] | | | |
|---|---|---|---|---|
| | 60°F | 70°F | 80°F | 90°F |
| 22. Carbon disulfide | 4.8 | 6.0 | 7.4 | 9.2 |
| 23. Carbon tetrachloride | 1.4 | 1.8 | 2.3 | 3.0 |
| 24. "Cellosolve"[b] solvent (see No. 51 following) | | | | |
| 25. Chloroform | 2.5 | 3.2 | 4.1 | 5.2 |
| 26. Chloroprene | 2.9 | 3.7 | 4.6 | 5.7 |
| 27. Cumene (isopropyl benzene) | 0.1 | 0.1 | 0.1 | 0.2 |
| 28. Cresylic acid (Cresol)[e] | 0.2 | 0.3 | 0.5 | 0.8 |
| 29. Cyclohexane | 1.2 | 1.6 | 2.1 | 2.6 |
| 30. Cyclopentane | 4.2 | 5.2 | 6.5 | 8.1 |
| 31. n-Decyl alcohol (1-decanol) | Negligible | | | |
| 32. Diacetone alcohol (see No. 57) | | | | |
| 33. 1, 1-Dichloroethane | 2.9 | 3.8 | 4.7 | 5.8 |
| 34. 1, 2-Dichloroethane | 1.0 | 1.4 | 1.7 | 2.2 |
| 35. cis -1, 2-Dichloroethylene | 2.7 | 3.5 | 4.4 | 5.6 |
| 36. trans-1, 2-Dichloroethylene | 4.4 | 5.5 | 6.8 | 8.3 |
| 37. Diethyl ether | 7.0 | 8.7 | 10.4 | 13.3 |
| 38. Diethylamine | 2.9 | 3.9 | 4.9 | 6.1 |
| 39. Diisobutyl ketone | | | | |
| 40. Diisopropyl ether | 2.1 | 2.7 | 3.5 | 4.3 |
| 41. 1-4 Dioxane | 0.4 | 0.6 | 0.8 | 1.1 |
| 42. Dipropyl ether | 0.8 | 1.1 | 1.4 | 1.9 |

(continued)

TABLE D-1 (continued)

| Chemical names and abbreviations | True vapor pressure, psia[a] | | | |
|---|---|---|---|---|
| | 60°F | 70°F | 80°F | 90°F |
| 43. Ethyl acetate (EAc) | 1.1 | 1.5 | 1.9 | 2.5 |
| 44. Ethyl acrylate | 0.4 | 0.6 | 0.8 | 1.1 |
| 45. Ethyl alcohol | 0.6 | 0.9 | 1.2 | 1.7 |
| 46. Ethyl amyl ketone (EAK) 5-methyl-3-hexanone | | | | |
| 47. Ethyl glycol | Negligible | | | |
| 48. Ethylene glycol diethyl ether | | | | |
| 49. Ethylene glycol monobutyl ether | Negligible | | | |
| 50. Ethylene glycol monoethyl ether | 0.2 | 0.2 | 0.2 | 0.2 |
| 51. Ethylene glycol monomethyl ether (see Nos. 73 and 83) | 0.1 | 0.2 | 0.3 | 0.4 |
| 52. "Freon 11",[e] trichlorofluoromethane | 10.9 | 13.4 | 16.3 | 19.7 |
| 53. n-Heptane | 0.5 | 0.7 | 1.0 | 1.2 |
| 54. n-Hexane | 0.9 | 2.4 | 3.1 | 3.9 |
| 55. Hexylene glycol (HG), 2-methyl-2,4 pentane-diol | 9.5 | 11.9 | 15.4 | 18.6 |
| 56. Hydrogen cyanide (HCN) | 9.5 | 11.9 | 15.4 | 18.6 |
| 57. 4-Hydroxy-4 methyl-2 pentanone (same as No. 32) | Negligible | | | |
| 58. Isobutyl acetate (IBAc) (see No. 13) | | | | |
| 59. Iso-octane | 0.5 | 0.8 | 1.1 | 1.4 |
| 60. Isopentane | 10.0 | 12.5 | 15.3 | 18.4 |
| 61. Isoprene | 7.7 | 9.7 | 11.7 | 14.5 |

(continued)

TABLE D-1 (continued)

| Chemical names and abbreviations | True vapor pressure, psia[a] | | | |
|---|---|---|---|---|
| | 60°F | 70°F | 80°F | 90°F |
| 62. Isopropyl alcohol (IPA) | 0.5 | 0.7 | 0.9 | 1.3 |
| 63. Isopropyl ether (IPE) | 2.1 | 2.8 | 3.6 | 4.6 |
| 64. Mesityl oxide (MO, isopropylideneacetone) | 0.1 | 0.1 | 0.2 | 0.3 |
| 65. Methanol[e] (methyl alcohol, carbinol, MEOH) | 1.4 | 2.0 | 2.6 | 3.5 |
| 66. 4-Methoxy-4 methyl-pentanone-2, pent-oxone (see No. 91) | | | | |
| 67. Methyl acetate | 2.7 | 3.7 | 4.7 | 5.8 |
| 68. Methyl acrylate | 1.0 | 1.4 | 1.8 | 2.4 |
| 69. Methyl alcohol (see No. 65) | | | | |
| 70. Methylamyl acetate (MAAc) | | | | |
| 71. Methylamyl alcohol (MIBC), methylisobutyl carbinol | | | | |
| 72. Methyl butyl keton (MBK) | Neg. | 0.1 | 0.1 | 0.1 |
| 73. Methyl "Cellosolve"[f] (see Nos. 51 and 83) | | | | |
| 74. Methacrylonitrile | 0.9 | 1.2 | 1.5 | 1.9 |
| 75. Methylcyclohexane | 0.5 | 0.7 | 1.0 | 1.3 |
| 76. Methylcyclopentane | 1.6 | 2.2 | 2.9 | 3.6 |
| 77. Methylene chloride | 5.4 | 6.8 | 8.7 | 10.3 |
| 78. Methyl ethyl ketone (MEK) | 1.2 | 1.5 | 2.1 | 2.7 |
| 79. Methylisobutyl acetate (MIBAc) isopropyl acetate | | | | |

(continued)

TABLE D-1 (continued)

| Chemical names and abbreviations | True vapor pressure, psia[a] | | | |
|---|---|---|---|---|
| | 60°F | 70°F | 80°F | 90°F |
| 80. Methylisobutyl carbinol (MIBC, see No. 71) | | | | |
| 81. Methylisobutyl ketone (MIBK) | 0.1 | 0.1 | 0.2 | 0.2 |
| 82. Methyl methacrylate | 0.3 | 0.5 | 0.8 | 1.1 |
| 83. Methyl "Oxitol"[c] (see Nos. 51 and 73) | | | | |
| 84. Methyl propyl ether | 6.1 | 7.1 | 9.4 | 11.6 |
| 85. Naphthenic acid, hexahydrobenzoic acid cyclohexanecarboxylic acid | | | | |
| 86. "Neosol A"[c,g] | 0.6 | 0.9 | 1.2 | 1.7 |
| 87. Nitromethane | 0.3 | 0.5 | 0.7 | 1.0 |
| 88. "Oxitol"[c] (see Nos. 51, 73, and 83) | | | | |
| 89. n-Pentane | 6.8 | 8.4 | 10.4 | 13.0 |
| 90. "Pentoxone"[c] (see No. 66) | | | | |
| 91. Perchloroethylene, tetrachloroethylene | 0.2 | 0.3 | 0.4 | 0.5 |
| 92. Propyl acetate[d] | 0.4 | 0.5 | 0.7 | 0.9 |
| 93. n-Propylamine | 4.2 | 5.3 | 6.5 | 8.0 |
| 94. Styrene, phenyl-ethylene | 0.1 | 0.1 | 0.2 | 0.2 |
| 95. Super VM and P-66[c,h,i] | 0.2 | 0.3 | 0.3 | 0.4 |
| 96. Tetrahydrofuran (THF) | 2.1 | 2.6 | 3.3 | 4.1 |
| 97. Toluene | 0.3 | 0.4 | 0.6 | 0.7 |
| 98. "Tolu-Sol 6"[c,h] | 0.6 | 0.8 | 1.0 | 1.4 |
| 99. 1, 1, 1-Trichloroethane | 1.6 | 2.0 | 2.6 | 3.3 |

(continued)

TABLE D-1 (continued)

| Chemical names and abbreviations | True vapor pressure, psia[a] | | | |
|---|---|---|---|---|
| | 60° F | 70° F | 80° F | 90° F |
| **100. Trichloroethylene** | 0.9 | 1.2 | 1.5 | 2.0 |
| **101. Vinyl acetate** | 1.3 | 1.7 | 2.3 | 3.1 |
| **102. Vinylidene chloride** | 7.9 | 9.8 | 11.8 | 15.3 |
| **103. Xylene** [d,j] (meta-, ortho- and para-) | 0.1 | 0.1 | 0.2 | 0.2 |

[a] All values are from API Bulletin entitled Petrochemical Evaporation Loss From Storage Tanks, Bulletin No. 2523, 1st ed., November 1969, unless otherwise indicated. Metric conversion factors are as follows: °F = 9/5 (°C) + 32; psia = 6.8947 kPa.

[b] Union Carbide trademark.

[c] Shell Chemical Company trademark.

[d] Weast, R. C. Handbook of Chemistry and Physics. 55th ed. CRC Press Cleveland, Ohio, 1974.

[e] Dean, J. A. Lang's Handbook of Chemistry, 11th ed. McGraw-Hill Company, New York, 1973. pp. 10-31/10-45.

[f] du Pont trademark.

[g] Bureau of Internal Revenue approved denatured alcohol

| | |
|---|---|
| No. 1 (190 proof) | 100 parts by volume |
| Methyl isobutyl ketone | 1 part by volume |
| Ethyl acetate | 1 part by volume |
| Aviation gasoline | 1 part by volume |

(For calculations, use ethyl alcohol, No. 45)

[h] Shell Oil Company data, Dominguez Research Laboratories, October 28, 1975.

[i] Molecular weight is a calculated value based on boiling point range.

[j] Kirk-Othmer Encyclopedia of Chemical Technology. 2nd ed., Vol. 22. John Wiley & Sons, New York, 1970. p. 486.

# APPENDIX E

## STORAGE TANK INSPECTION BY STATISTICAL SAMPLING

During a Level II or Level III inspection, a number of storage tanks are checked to determine compliance with state and Federal regulation of hydrocarbon emissions. From both a time and cost viewpoint, it is impractical to check every storage tank in a refinery. A statistical sampling approach enables the inspector to test only a small percentage of the total number of tanks in a refinery and thereby to determine with confidence the compliance status of the entire tank farm. The statistical technique to be applied is acceptance control. The objective is to ensure that the final product (in this case, storage tanks) is consistent with a specified quality, i.e., is in compliance with state and Federal regulations. Four general types of acceptance control are practiced: spot checks, 100% inspection, certification, and acceptance sampling.

Acceptance sampling by attributes (go/no-go) is widely accepted as the preferred method of acceptance control. Tables, charts, and graphs have been developed to facilitate implementation of acceptance sampling and selection of specific sampling plans. The guidelines MIL-STD-105D[1] and MIL-STD-404[2] are sources of widely used information on military acceptance control. These standards define a range of acceptable quality levels (AQL), which limit the percentage of allowable defects. The charts developed for acceptance sampling define criteria for the size of the sample to be tested based on the size of the production lot (i.e., number of storage tanks in a refinery) and also define criteria for the maximum number of defective units permitted in the sample. When these criteria are met, the probability of accepting lots with this defective rate is specified by the applicable plan. The inherent risk in all acceptance sampling plans is rejecting lots that should be accepted, and vice versa.

Acceptance sampling evaluates a group of units, drawn from a production lot, in order to assess the acceptability of the whole lot. Since only a portion of the whole lot is inspected, there is always a risk that the quality of the sample will not reflect the quality of the lot. As a result, lots may be rejected undeservedly and faulty lots accepted. The former situation is mainly of interest to the producer (refinery owner), who wants to minimize the risk of having good lots rejected, and is defined as the producer's risk. The risk of accepting bad lots in a sampling scheme is mainly the concern of the consumer (inspector), and is called the consumer's risk. Both risks are quantified statistically by constructing an operating characteristic curve (OC curve).

The producer's risk, 'a', is the probability of having production lots rejected as a result of a sampling plan, even though they meet the specified acceptable quality requirements. The most frequently used value for the producer's risk is 0.05. This means the producer has a 95 percent chance of having production lots accepted that meet the quality requirements.

The consumer's risk, 'b', is the probability of accepting production lots that do not meet the poorest tolerable quality requirements. The risk assumed by the consumer is usually set at 0.1 or 10 percent. This quality level is designated as the lot tolerance percent defective (LTPD). The consumer has a 90 percent chance that the sampling plan will reject production lots of LTPD quality.

The acceptable quality level (AQL) is the maximum percentage of defective units that, for purposes of the sampling inspection, can be considered satisfactory as a process average (the lot has a high probability of acceptance, usually 95 percent).

The lot tolerance percent defective (LTPD) is that quality level (in percent defective) that has a low probability of acceptance, usually 10 percent. The usual sampling plan therefore accepts good lots (lot quality = AQL) 95 percent of the time and rejects the not-quite-so-tolerable lots (lot quality = LTPD) 90 percent of the time. Lot quality levels between the AQL and LTPD values have probabilities of acceptance as defined by the OC curve, which is a graph depicting the relationship between process defect percentage and the corresponding probability of acceptance of such lots by the sampling plan. A typical OC curve is shown in Figure E-1.

Points 'a' and 'b' on the OC curve refer, respectively, to the AQL and the LTPD. These probability percentages agree with the common AQL and LTPD acceptance probabilities. The OC curve permits the determination of the probability of acceptance for lots of varying quality. For example, in Figure E-1 the probability of acceptance can be determined for any lot defective rate between zero and 12 percent. For a submitted lot that is 3 percent defective, the probability of acceptance is 70 percent (see point 'P').

A sampling plan and its associated OC curve are fully defined by the sample size, 'n', and the acceptance number, 'c'. A range of values of percentage defective 'p', is assumed, and the expected number of defects, 'np', is calculated. Then the Poisson distribution is used to determine the probability of 'c' or fewer defectives occurring for each value of 'np'. This is the probability of acceptance and is plotted against the percent defective as the OC curve. Values of the acceptance number depend on the particular level of quality desired and the amount of protection afforded by the plan. The MIL-STD-105D contains a large number of inspection plans that define sample size and accept/reject numbers as related to acceptable quality levels and OC curves. The guideline is used to define the inspection plan for each refinery tank farm inspected.

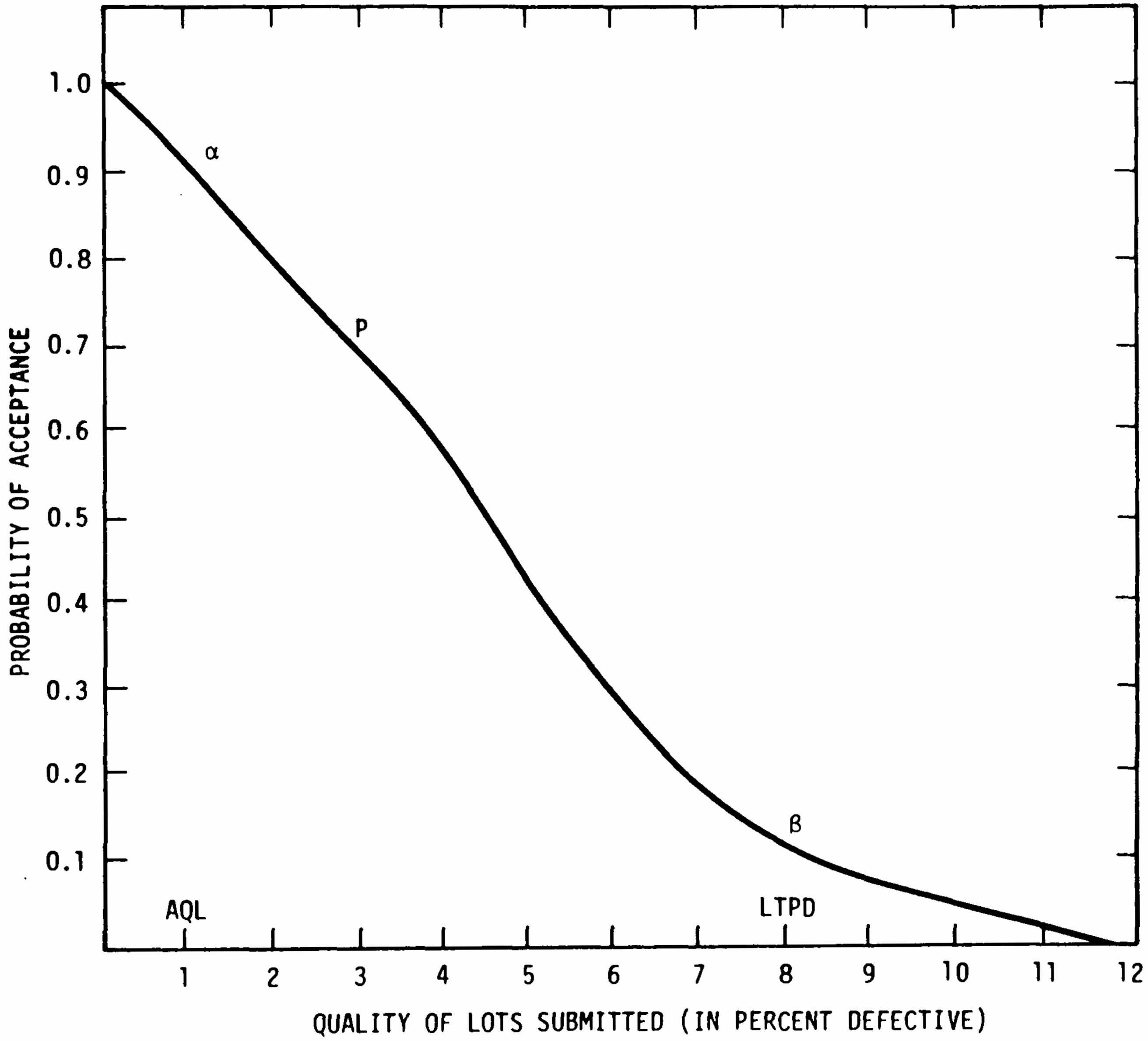

Figure E-1. Typical operating characteristic curve for sampling plan.

For a given lot size (number of tanks in the refinery), a sample size can be determined depending on the inspection level desired. In MIL-STD-105D, a code letter designates the inspection sample size. There are three general inspection levels: I, II, and III. Inspection Level I provides less discrimination (60 percent less than Level II) because it uses smaller sample sizes; Level III increases the discrimination to 1.6 times that of a Level I inspection because of larger sample sizes for the same lot size.

Four special inspection levels are designated '$s_1$' through '$s_4$'. These special levels are used when the inspection involves destructive testing or when the cost of inspection is high.

After selection of the inspection level and corresponding sample size, the acceptance and rejection numbers are determined for varying acceptable quality levels. For each sample inspected, the entire lot is considered acceptable (passes the inspection) if the number of defectives found (tanks not passing the inspection) is equal to or less than the acceptance number. If the number of defectives exceeds the acceptance number, the lot is rejected (the tank farm does not pass the inspection). Appendix F contains selected tables from MIL-STD-105D.

For the refinery tank farm inspections (Level II and III inspections), sample sizes have been determined and the acceptance number chosen for two different acceptable quality levels. A Level II inspection is based on a MIL-STD-105D inspection level of I and an acceptable quality level of 10. A Level III inspection is based on a MIL-STD-105D inspection level of II and an acceptable quality level of 4. Table E-1 summarizes the sampling plan for the two levels of refinery inspections.

Plans for double and multiple sampling are also available. Inspection plans for double sampling give two sample sizes per sample size code letter with the corresponding acceptance and rejection number. Inspections start with the first sample size and the applicable accept/reject criterion. As in the single sampling plan, if the number of defectives found is equal to or

TABLE E-1. REFINERY TANK INSPECTION PLAN

| No. of tanks | Inspection level | Sample size | Accept No. | Reject No. |
|---|---|---|---|---|
| 2 to 8 | 2 | 2 | 1 | 2 |
| | 3 | 3 | 0 | 1 |
| 9 to 15 | 2 | 2 | 1 | 2 |
| | 3 | 3 | 0 | 1 |
| 16 to 25 | 2 | 3 | 1 | 2 |
| | 3 | 5 | 0 | 1 |
| 26 to 50 | 2 | 5 | 1 | 2 |
| | 3 | 8 | 1 | 2 |
| 51 to 90 | 2 | 5 | 1 | 2 |
| | 3 | 13 | 1 | 2 |
| 91 to 150 | 2 | 8 | 2 | 3 |
| | 3 | 20 | 2 | 3 |
| 151 to 280 | 2 | 13 | 3 | 4 |
| | 3 | 32 | 3 | 4 |
| 281 to 500 | 2 | 20 | 5 | 6 |
| | 3 | 50 | 5 | 6 |

less than the accept number, the lot is accepted. If the number of defectives exceeds the accept number and is equal to or greater than the reject number, the production lot is rejected.

If the number of defectives found in the first sample is between the first acceptance and rejection numbers, a second sample of the size given by the plan is inspected. If the sum of the number of defectives found in the first and second inspection samples equals or is less than the second acceptance number, the lot is accepted. If the sum of the number of defectives in the first and second inspection samples is equal to or exceeds the second rejection number, the lot is rejected.

Multiple sampling plans are an extension of the double sampling plans. The difference is that more than two successive samples may be needed as a basis for decision regarding the acceptance of the production lot.

Storage tanks can be categorized in two broad classes: floating roof and fixed roof. Each group should be individually inspected in the sampling plan so far submitted. Once the inspector has determined the number of tanks in each classification, he can determine the sample size and accept/reject criterion for each group. Each tank should have an individual tank number and be listed on a master sheet (provided by the refinery). A random number generator can be used to select the tanks for the sample lot.

## REFERENCES

1. U.S. Department of Defense. Sampling Procedures and Tables for Inspection by Attributes. MIL-STD-105D. April 29, 1963.

2. U.S. Department of Defense. Sampling Procedures and Tables for Inspection by Variables. MIL-STD-414. June 11, 1957.

# APPENDIX F

## MIL-STD TABLES FOR USE IN STATISTICAL SAMPLING OF STORAGE TANKS

Table F-1 contains sample size code letters. An inspector is to determine the lot or batch size (i.e., the number of tanks) and select the type and level of inspection to be performed; the sample size code letter can be determined from Table F-1 based on this information. The sample size and the accept and reject numbers are presented in Tables F-2 and F-3. Appendix E contains further information on the use of these tables.

## REFERENCE

1. U.S. Department of Defense. Sampling Procedures and Tables for Inspection by Attribute. MIL-STD 105D. April 29, 1963.

## TABLE F-1. SAMPLE SIZE CODE LETTERS

| Lot or batch size | Special inspection levels | | | | General inspection levels | | |
|---|---|---|---|---|---|---|---|
| | S-1 | S-2 | S-3 | S-4 | I | II | III |
| 2 to 8 | A | A | A | A | A | A | B |
| 9 to 15 | A | A | A | A | A | B | C |
| 16 to 25 | A | A | B | B | B | C | D |
| 26 to 50 | A | B | B | C | C | D | E |
| 51 to 90 | B | B | C | C | C | E | F |
| 91 to 150 | B | B | C | D | D | F | G |
| 151 to 280 | B | C | D | E | E | G | H |
| 281 to 500 | B | C | D | E | F | H | J |
| 501 to 1200 | C | C | E | F | G | J | K |
| 1201 to 3200 | C | D | E | G | H | K | L |
| 3201 to 10000 | C | D | F | G | J | L | M |
| 10001 to 35000 | C | D | F | H | K | M | N |
| 35001 to 150000 | D | E | G | J | L | N | P |
| 150001 to 500000 | D | E | G | J | M | P | Q |
| 500001 and over | D | E | H | K | N | Q | R |

## TABLE F-2. SINGLE SAMPLING PLANS FOR NORMAL INSPECTION (MASTER TABLE)

| Sample size code letter | Sample size | Acceptable quality levels (normal inspection) | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.010 | | 0.015 | | 0.025 | | 0.040 | | 0.065 | | 0.10 | | 0.15 | | 0.25 | | 0.40 | | 0.65 | | 1.0 | |
| | | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re |
| A | 2 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| B | 3 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| C | 5 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| D | 8 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| E | 13 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | 0 | 1 |
| F | 20 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | 0 | 1 | ↑ | |
| G | 32 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | 0 | 1 | ↑ | | ↓ | |
| H | 50 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | 0 | 1 | ↑ | | ↓ | | 1 | 2 |
| J | 80 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 |
| K | 125 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 |
| L | 200 | ↓ | | ↓ | | ↓ | | ↓ | | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 |
| M | 315 | ↓ | | ↓ | | ↓ | | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 |
| N | 600 | ↓ | | ↓ | | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 |
| P | 800 | ↓ | | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 |
| Q | 1250 | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 |
| R | 2000 | ↑ | | ↑ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | ↑ | |

(continued)

TABLE F-2 (continued)

| Acceptable quality levels (normal inspection) | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1.5 | | 2.5 | | 4.0 | | 6.5 | | 10 | | 15 | | 25 | | 40 | | 65 | | 100 | | 150 | | 250 | | 400 | | 650 | | 1000 | |
| Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re |
| ↓ | | ↓ | | ↓ | | 0 | 1 | ↓ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | 30 | 31 |
| | | | | C | 1 | ↑ | | | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | 30 | 31 | 44 | 45 |
| | | 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | 30 | 31 | 44 | 45 | ↑ | |
| 0 | 1 | ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | 30 | 31 | 44 | 45 | ↑ | | | |
| ↑ | | ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | 30 | 31 | 44 | 45 | ↑ | | | | | |
| ↓ | | 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | ↑ | | ↑ | | ↑ | | | | | | | |
| 1 | 2 | 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | ↑ | | | | | | | | | | | | | |
| 2 | 3 | 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | ↑ | | | | | | | | | | | | | | | |
| 3 | 4 | 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | ↑ | | | | | | | | | | | | | | | | | |
| 5 | 6 | 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | ↑ | | | | | | | | | | | | | | | | | | | |
| 7 | 8 | 10 | 11 | 14 | 15 | 21 | 22 | ↑ | | | | | | | | | | | | | | | | | | | | | |
| 10 | 11 | 14 | 15 | 21 | 22 | ↑ | | | | | | | | | | | | | | | | | | | | | | | |
| 14 | 15 | 21 | 22 | ↑ | | | | | | | | | | | | | | | | | | | | | | | | | |
| 21 | 22 | ↑ | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| ↑ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

↓ = Use first sampling plan below arrow. If sample size equals, or exceed, lot or batch size, do 100-percent inspection.

↑ = Use first sampling plan above arrow.

Ac = Acceptance number.
Re = Rejection number.

## TABLE F-3. DOUBLING SAMPLING PLANS FOR NORMAL INSPECTION (MASTER TABLE)

| Sample size code letter | Sample | Sample size | Cumulative sample size | Acceptable quality levels (normal inspection) | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 0.010 | | 0.015 | | 0.025 | | 0.040 | | 0.065 | | 0.10 | | 0.15 | | 0.25 | | 0.40 | | 0.65 | | 1.0 | |
| | | | | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re |
| A | First | | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| | Second | | | | | | | | | | | | | | | | | | | | | | | | |
| B | First | 2 | 2 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| | Second | 2 | 4 | | | | | | | | | | | | | | | | | | | | | | |
| C | First | 3 | 3 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| | Second | 3 | 6 | | | | | | | | | | | | | | | | | | | | | | |
| D | First | 5 | 5 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | |
| | Second | 5 | 10 | | | | | | | | | | | | | | | | | | | | | | |
| E | First | 8 | 8 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | a | |
| | Second | 8 | 16 | | | | | | | | | | | | | | | | | | | | | | |
| F | First | 13 | 13 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | a | | ↑ | |
| | Second | 13 | 26 | | | | | | | | | | | | | | | | | | | | | | |
| G | First | 20 | 20 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | a | | ↑ | | ↓ | |
| | Second | 20 | 40 | | | | | | | | | | | | | | | | | | | | | | |
| H | First | 32 | 32 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | a | | ↑ | | ↓ | | 0 | 2 |
| | Second | 32 | 64 | | | | | | | | | | | | | | | | | | | | | 1 | 2 |
| J | First | 50 | 50 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | a | | ↑ | | ↓ | | 0 | 2 | 0 | 3 |
| | Second | 50 | 100 | | | | | | | | | | | | | | | | | | | 1 | 2 | 3 | 4 |
| K | First | 80 | 80 | ↓ | | ↓ | | ↓ | | ↓ | | ↓ | | a | | ↑ | | ↓ | | 0 | 2 | 0 | 3 | 1 | 4 |
| | Second | 80 | 160 | | | | | | | | | | | | | | | | | 1 | 2 | 3 | 4 | 4 | 5 |
| L | First | 125 | 125 | ↓ | | ↓ | | ↓ | | ↓ | | a | | ↑ | | ↓ | | 0 | 2 | 0 | 3 | 1 | 4 | 2 | 5 |
| | Second | 125 | 250 | | | | | | | | | | | | | | | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 |
| M | First | 200 | 200 | ↓ | | ↓ | | ↓ | | a | | ↑ | | ↓ | | 0 | 2 | 0 | 3 | 1 | 4 | 2 | 5 | 3 | 7 |
| | Second | 200 | 400 | | | | | | | | | | | | | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 | 9 |
| N | First | 315 | 315 | ↓ | | ↓ | | a | | ↑ | | ↓ | | 0 | 2 | 0 | 3 | 1 | 4 | 2 | 5 | 3 | 7 | 5 | 9 |
| | Second | 315 | 630 | | | | | | | | | | | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 | 9 | 12 | 13 |
| P | First | 500 | 500 | ↓ | | a | | ↑ | | ↓ | | 0 | 2 | 0 | 3 | 1 | 4 | 2 | 5 | 3 | 7 | 5 | 9 | 7 | 11 |
| | Second | 500 | 1000 | | | | | | | | | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 | 9 | 12 | 13 | 18 | 19 |
| Q | First | 800 | 800 | a | | ↑ | | ↓ | | 0 | 2 | 0 | 3 | 1 | 4 | 2 | 5 | 3 | 7 | 5 | 9 | 7 | 11 | 11 | 16 |
| | Second | 800 | 1600 | | | | | | | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 | 9 | 12 | 13 | 18 | 19 | 26 | 27 |
| R | First | 1250 | 1250 | ↑ | | ↑ | | 0 | 2 | 0 | 3 | 1 | 4 | 2 | 5 | 3 | 7 | 5 | 9 | 7 | 11 | 11 | 16 | ↑ | |
| | Second | 1250 | 2500 | | | | | 1 | 2 | 3 | 4 | 4 | 5 | 6 | 7 | 8 | 9 | 12 | 13 | 18 | 19 | 26 | 27 | | |

(continued)

TABLE F-3 (continued)

**Acceptable quality levels (normal inspection)**

| 1.5 | | 2.5 | | 4.0 | | 6.5 | | 10 | | 15 | | 25 | | 40 | | 65 | | 100 | | 150 | | 250 | | 400 | | 650 | | 1000 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re | Ac | Re |
| ↓ | | ↓ | | ↓ | | a | | ↓ | | ↓ | | a | | a | | a | | a | | a | | a | | a | | a | | a | |
| | | | | a | | ↑ | | | | 0 | 2 | 0 | 3 | 1 | 4 | 2 | 5 | 3 | 7 | 5 | 9 | 7 | 11 | 11 | 16 | 17 | 22 | 25 | 31 |
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| ↑ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

**↓ = Use first sampling plan below arrow. If sample size equals or exceeds lot or batch size, do 100-percent inspection.**

**↑ = Use first sampling plan above arrow.**

**Ac = Acceptance number.**
**Re = Rejection number.**
**a = Use corresponding single sampling plan (or alternatively, use double sampling plan below, where available).**

# APPENDIX G

# OPERATING INSTRUCTIONS FOR AN ORGANIC VAPOR ANALYZER (OVA)

## 1. GENERAL INSTRUCTIONS

### 1.1 INTRODUCTION

The Century Systems Corporation Model OVA-128 is a portable, lightweight, sensitive instrument designed to measure trace amounts of organic vapors in air. It utilizes a hydrogen flame ionization detector and can be calibrated to measure almost all organic vapors. It is a quantitative type instrument with sensitivity to 0.1 ppm methane. Figure G-1 illustrates the OVA-128. Figure G-2 shows the instrument in use.

### 1.2 DESCRIPTION OF MAJOR PARTS

### 1.2.1 Probe/Readout Assembly

The output meter and high alarm level adjustments are located in this assembly, along with the sample probe assembly. This assembly can be handled with one hand. It is connected to the side pack by a knurled nut on the sample line, and a five-pin push type connector on the umbilical cord. When the instrument is supplied with a sample dilutor to read vapor concentrations greater than 1000 ppm, the dilutor is mounted on the sample probe.

### 1.2.2 Side Pack Assembly

This unit contains the remaining operating controls and indicators, the electronic circuitry, flame ionization detector chamber, hydrogen fuel supply, and the battery pack power supply.

Figure G-1. Portable organic vapor analyzer (Model OVA-128).

Courtesy of Century Systems Corporation, Arkansas City, Kansas.

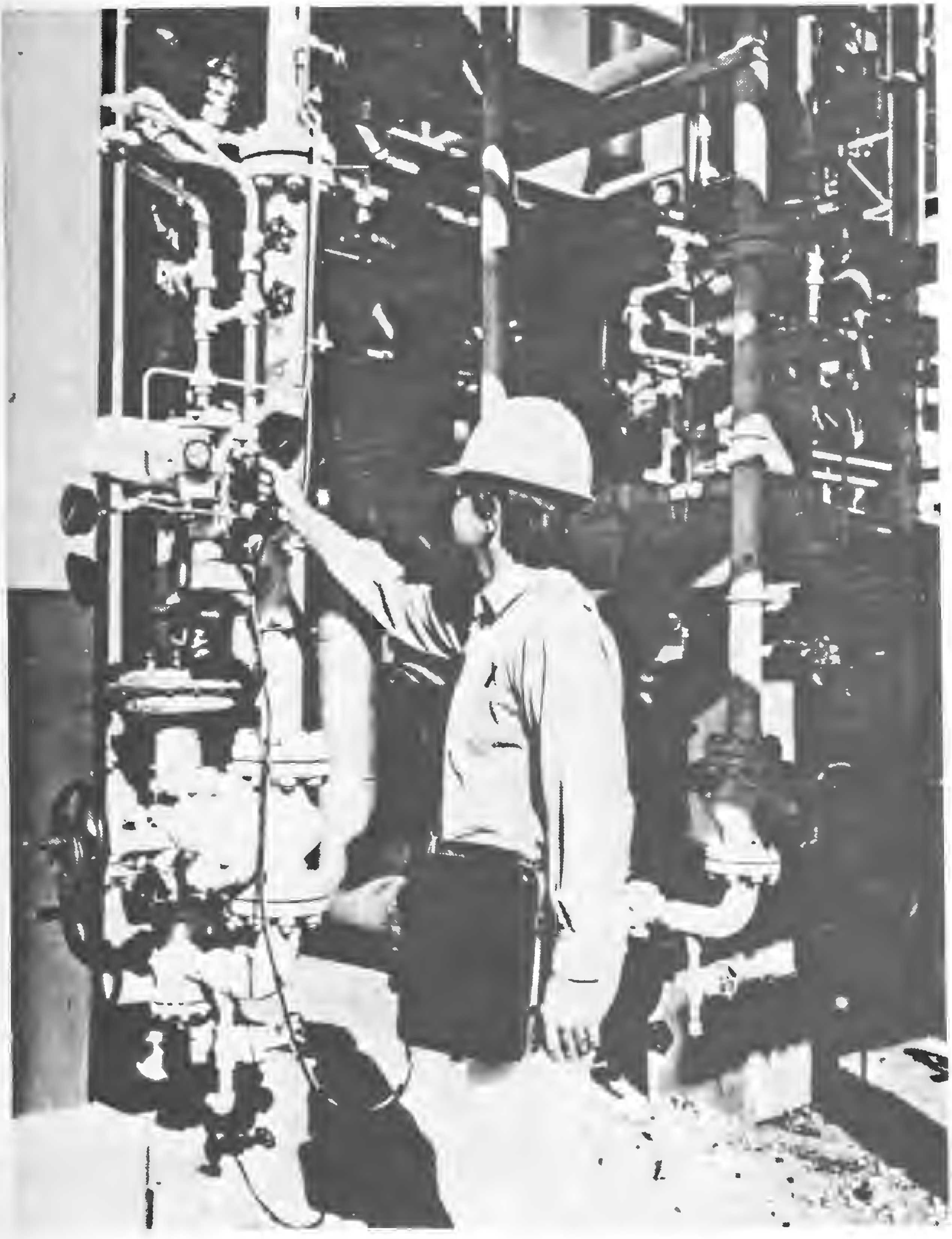


Figure G-2. Illustration of the use of the organic vapor analyzer.

### 1.2.3 Safety Considerations

Hydrogen gas is contained under pressure in the side pack. All safety precautions for handling hydrogen gas must be observed. The instrument is safe when proper operating procedures are followed. Section 5 of the Century System Manual provides detailed safety precautions, which should be read and understood before operating the OVA.

### 1.2.4 General Operating Principles

The instrument is used for detecting hydrocarbons in air. The sample is pulled in at a constant rate, by the internal pump, through the sample probe attached to the probe/readout assembly. When hydrocarbons are present, they are burned in the hydrogen flame. The ionization detector generates a signal that is sent to the readout meter. This meter has a 0 to 10 scale. The instrument has a range switch with X1, X10, and X100 settings, which allows reading vapor concentrations from 1 to 1000 ppm. If the vapor concentration is higher than 1000 ppm, the sample dilutor may be used. The diluter makes it possible to measure concentrations of 10,000 ppm, or higher.

The instrument is certified as safe by Factory Mutual Research Corporation for use in Class I, Division 1, Groups A, B, C, and D hazardous environments. Therefore, it is essential to maintain the certification that the instrument not be modified in any way.

## 2. OPERATING PROCEDURES

### 2.1 INITIAL STARTUP OF THE INSTRUMENT

Startup cannot be attempted until the internal hydrogen fuel supply tank is filled (instructions in Section 2.6 of the Century manual), and the battery pack is charged. The battery may be checked with the INSTR/BATT test switch. Move the switch to the

BATT position and note the reading to see if it is within the "battery charged" section on the meter.

The GAS SELECT control should be preset to the desired dial indication prior to turn on. The instrument as received from the factory is set to measure methane in air. Settings for other vapors may be determined by the procedure in Section 4 of the Century manual.

Following are the startup instructions for the Model OVA-128:

1. Move the INSTR switch to ON and allow 5 minutes for warmup.

2. Select the sample probe suitable for the work to be performed. The adjustable length probe is used for normal survey work, and the "close area" probe for special work where the sample is easily within reach. Attach the probe to the readout assembly with the captive locking nut. Insert a pickup fixture in the probe. If there is a chance that dust or liquids may be drawn into the probe, a particle filter should be assembly to the side pack with the push-in plug, making sure that the connector pins are properly aligned. Connect the sample line to the pump connection with the knurled nut.

3. Turn the pump switch to ON and observe the sample flow rate indicator. The indication should be about 2 units. The audible alarm may be set now if so desired. Adjust the meter pointer to the desired alarm level using the CALIBRATE ADJUST knob. Turn the alarm level adjust knob on the back of the readout assembly until the audible alarm just comes on. Adjust speaker volume with the VOLUME knob.

4. Move the CALIBRATE switch to X10 and adjust the meter reading to zero with the CALIBRATE ADJUST knob.

5. Open the $H_2$ TANK VALVE one turn and observe the reading on the $H_2$ TANK PRESSURE indicator. The tank pressure should be sufficient to allow for 150 psi of pressure drop for each hour of operation.

6. Open the $H_2$ SUPPLY VALVE one turn and observe the reading on the $H_2$ SUPPLY PRESSURE indicator. CAUTION: Be sure the pump is running while the $H_2$ SUPPLY VALVE is open. Otherwise, hydrogen will accumulate in the detector chamber which could damage the instrument or cause an internal explosion.

7. Readjust the meter reading to zero if necessary.

8. Depress the igniter button. There should be a slight "pop" sound as the hydrogen ignites and the meter pointer will move upscale. Release the igniter button immediately after ignition. If the burner does not ignite, let the instrument run for several minutes before depressing the igniter button again. After ignition, the meter pointer will indicate the hydrocarbon background concentration.

   CAUTION: Do not depress the igniter button for more than 6 seconds at one time.

9. Move the instrument to an area that is representative of the lowest ambient background concentration to be surveyed. Move the CALIBRATE switch to X1 and adjust the meter to read 1 ppm with the CALIBRATE ADJUST knob.

   NOTE: Adjustment to 1 ppm, rather than 0, is necessary in the X1 range because of the sensitivity of the OVA. This permits minor downward fluctuations in the normal background level without dropping below 0, which would actuate the flame-out alarm. Also, remember during subsequent surveys that 1 ppm must be subtracted from all readings. Thus a reading of 2.8 ppm would be only 1.8 ppm.

The instrument is now ready for use.

## 2.2 MONITORING TECHNIQUES

Start with the CALIBRATE switch in the X1 range for maximum sensitivity. Using one-hand operation, survey the areas of interest while observing the meter. For ease of operation, use the shoulder strap to carry the side pack assembly on the side opposite the hand holding the probe/readout. For area surveys, outdoors, the pickup fixture should be positioned several feet above ground level. When making quantitative readings or pin-pointing leaks, the probe should be positioned at the point of interest. When testing for leaks, the probe pickup should be held at the source, leaving the pickup in one spot for 5 seconds or more to allow for the instrument response time. When the wind is blowing, the probe pickup should be positioned on the downwind side of the pipe connection or equipment for the initial leak test.

When organic vapors are detected, the meter pointer will move upscale and the audible alarm will sound when the preset point is exceeded. The frequency of the alarm will increase as the detection level increases. Move the CALIBRATE switch to the appropriate scale position to determine the extent of the leak.

If flame-out occurs, the flame-out alarm actuates; ensure that the pump is running before pressing the igniter button. Usually flame-out results from sampling a gas mixture that is above the lower explosive level, which causes the $H_2$ flame to extinguish. When this happens, as soon as the explosive mixture passes or is pumped out of the detector, reignition is all that is required.

Another cause of flame-out is a restriction of the sample flow line, which would not allow sufficient air for combustion to enter the chamber. This condition could be caused by a clogged particle filter or other restriction in the sample line, or by blocking the exhaust port that is located on the bottom of the case.

### 2.3 SHUTDOWN PROCEDURE

1. Close the $H_2$ SUPPLY VALVE.
2. Close the $H_2$ TANK VALVE.
3. Move the INSTR switch to OFF.
4. Wait 5 seconds and move the PUMP switch to OFF.

The instrument is now shut down.

## 3. REFUELING

### 3.1 REFILLING THE HYDROGEN FUEL SUPPLY

The instrument must be completely shut down as described in the previous section. The refilling should be done in a well-ventilated area to prevent a possible buildup of explosive mixtures of hydrogen and air. Also there should be no potential igniters or flame in the area.

1. If you are making the first filling of the instrument or if the filling hose has been allowed to fill with air, the filling hose must be purged with hydrogen prior to filling the instrument tank. This can be accomplished by connecting the filling hose to the cylinder and turning the valve on the other end to the fill position for a few short blasts and then to the bleed position for a short time with the cylinder valve open slightly. Turn the bleed valve to the OFF position.

2. Connect the hose to the refill connection on the side pack assembly. Open the hydrogen supply bottle valve slightly. Open the REFILL VALVE and the $H_2$ TANK VALVE on the instrument panel and place the FILL/BLEED valve on the filling hose assembly in the FILL position. The new pressure in the instrument tank will now be indicated on the $H_2$ TANK PRESSURE indicator.

3. After the instrument fuel tank is filled, shut off the REFILL VALVE on the panel, the FILL/BLEED valve on the filling hose assembly, and the hydrogen supply bottle valve.

   The hydrogen in the filling hose must now be bled off by turning the FILL/BLEED valve to the BLEED position. CAUTION: <u>Hydrogen under high pressure is in this hose.</u> After the pressure in this line is down to atmospheric pressure, turn the REFILL/BLEED valve to FILL for a short time to allow the high-pressure hydrogen in the connectors to enter the refilling hose. Again turn the FILL/BLEED valve to BLEED to lower pressure to atmospheric in the hose. Turn FILL/BLEED valve to the OFF position and disconnect it from the REFILL VALVE. Leave connected to the cylinder and it will not need purging again.

4. Close the $H_2$ TANK VALVE on the side pack and observe the pressure on the pressure indicator that is reading the pressure of the trapped hydrogen in the line. If this pressure decreases more than 350 psig/h, it indicates a significant hydrogen leak and it should be repaired.

## 3.2 BATTERY RECHARGING

1. Plug the charger BNC connector into mating connector on battery cover and insert the AC plug into 115 VAC wall outlet. Never charge in a hazardous area.

2. Move the battery charger switch to the ON position. The light above the switch button should illuminate.

3. Battery charge condition is indicated by the meter on the front panel of the charger; the meter will deflect to the right when charging. When fully charged, the pointer will be in line with the "charged" marker above the scale.

4. Approximately 1 hour of charging time is required for each hour of operation. However, overnight charging is recommended, and the charger can be left on indefinitely without damaging the batteries. If the battery has been allowed to discharge completely and does not charge by the above procedure, the procedure in the Century manual, Section 2.7.1, pages 6 and 7, must be followed.

## 4. CALIBRATION

### 4.1 GENERAL

The instrument is factory calibrated to a methane in air standard at a GAS SELECT control setting of 300. The instrument will respond to nearly all organic compounds and can be easily and rapidly calibrated to other organic compounds of interest. the GAS SELECT control on the panel is used to set the electronic gain to a particular compound. The instrument is adjusted at the factory to read linearly from one range to another.

### 4.2 CALIBRATION TO OTHER ORGANIC VAPORS

Primary calibration of the instrument is accomplished using a known mixture of a specific organic vapor compound. Commercially available standard samples offer the most convenient and reliable calibration standards and are recommended for the most precise analyses. Always obtain the cylinder with the desired sample concentration and the "balance as air." The calibration gas should be drawn from the cylinder into a collapsed sample bag, then drawn from the bag by the instrument pump to prevent a pressure or vacuum at the sample inlet.

Calibration of the instrument to other organic compounds by the following procedure is recommended:

> After the instrument is in operation and the normal background is "zeroed out," draw a sample of the calibration gas into the instrument. The GAS SELECT knob on the panel is used to shift the readout meter indication to correspond to

the concentration of the calibration gas mixture. The setting on the GAS SELECT dial is read and recorded for that particular organic compound. This exercise can be performed for a large variety of compounds; when the operator wants to read a particular compound, the GAS SELECT control is turned to the predetermined setting for that compound. Calibration on any one range automatically calibrates the other two ranges.

Calibration can be accomplished by means of pure gases or liquids and preparing individual standards using collapsible bags made of inert material such as polyethylene or mylar. Bags may be purchased from laboratory supply houses or some instrument manufacturers. Polyethylene trash can liners could be used. Before using this method of making calibration standards, the user should read and understand Section 4.3 on calibration, pages 8 and 9, in the Century manual.

For liquid samples, use of the following equation will allow the calculation of the microliters of organic liquid needed to make 100 ppm of vapor calibration gas.

$V_1 = V_2 \times Mw/244\ D$

where $V_1$ = volume of liquid in microliters (for 100 ppm mixture)

$V_2$ = volume of bottle or bag in liters

Mw = molecular weight of organic liquid

D = density of organic liquid.

Therefore, to make up a 100 ppm hexane calibration gas,

$V_1$ = 5 liters x 86/244 (0.659) = 2.67 microliters of hexane.

A microliter syringe is required to measure these small amounts of liquid.

## 5. SAFETY CONSIDERATIONS

The Century Systems Models OVA-108, OVA-128, and OVA-138 have been tested and certified by Factory Mutual Research Corporation (FM) as intrinsically safe for use in Class I, Division

1, Groups A, B, C, and D hazardous atmospheres. All flame ionization hydrocarbon detectors are potentially hazardous since they burn hydrogen in the detector cell. Mixtures of hydrogen and air are flammable over a wide range of concentrations. Safety was a major factor in the design of the OVA. To protect against external ignition of flammable gas mixtures, the flame detection chamber has porous metal flame arresters on the sample input and exhaust ports, as well as on the hydrogen inlet connector. The standard battery pack and other circuits are internally current limited to an intrinsically safe level.

When monitoring organic vapors in a refinery, the following safety practices are suggested:

1. Do not insert the probe too close to a moving part such as a rotating pump shaft.
2. Do not place the probe too close to a liquid stream. Blockage of the probe could result.
3. Do not place the umbilical cord on a heated surface such as a pipe, valve, heat exchanger or furnace.
4. Turn the instrument off after a flame-out and ignite it in a safe area.
5. Read the operating and service manual for the portable OVA prior to operating it in the field.
6. Carefully read the hydrogen filling instructions prior to refilling.
7. Read the operating and service manual prior to troubleshooting.
8. Make arrangements for hexane or methane and hydrogen cylinders to arrive at the inspection site.

## 6. MONITORING PROBLEMS

One of the main problems in monitoring organic vapors is pinpointing leaks. As discussed in the monitoring procedures, it is important that the probe be moved slowly. The 5-second response time of the instrument requires a slow, methodical monitoring procedure. Because the organic vapors are dispersed by the wind, it is difficult to determine their source. When a slight increase in organic vapors is detected, locate the source by moving the probe slowly and noting differences in concentration. Move the probe in the direction of highest concentration. To help in pinpointing the leaks, note such usual indications of gas escape as the frosting of points of leakage and the wavy appearance of the air due to a change in the index of refraction.

Because the organic vapors are dispersed by the wind, placing a notebook on the upwind side or adjacent to the suspected valve or flange aids in finding the leak.

The OVA will sometimes detect leaks at sources that do not contain hydrocarbons. This usually happens when the OVA detects hydrocarbons from one valve and the wind moves these vapors over another valve. Be aware of the possibility of false readings and make attempts to correct them.

# APPENDIX H

## EMISSIONS FROM VALVES, PUMP AND COMPRESSOR SEALS, AND OTHER REFINERY EQUIPMENT COMPONENTS

Potential sources of volatile organic compound (VOC) emissions at petroleum refineries include valves, flanges, threaded fittings, pump seals, and compressor seals. Emissions occur when the volatile material flowing through a refinery component leaks through the component because the seal is inadequate. This appendix describes these refinery components and discusses factors that contribute to the development of leaks.

Reasonably available control technology (as described in EPA's control technique guidelines series) is an active inspection and maintenance (I&M) program. An I&M program requires that refinery personnel monitor all valves, flanges, threaded fittings, pump seals, and compressor seals for leaks. When a leak is found, it is to be tagged and repaired within 15 days of its detection. Air pollution control inspectors are to screen periodically a random sample of refinery equipment associated with various process units to determine the number of leaks. Records of the refinery's I&M program are also to be reviewed by the inspector.

An organic vapor analyzer (OVA) that meets the specifications listed in the control technique guideline is to be used in detecting VOC leaks. The instrument is to be calibrated with methane gas. A leak is defined as a concentration greater than or equal to 10,000 ppm of hydrocarbons when sampling is conducted at the source (i.e., 1 cm from the source).

The locations on the various refinery components where screening is to be done is indicated on the illustrations. These are the points where VOC leaks generally occur.

## VALVES

Large numbers of pipeline valves are associated with every type of equipment used in petroleum processing. Although many types exist, they perform one of three functions:

On/off flow control and throttling
Flow rate control (control valves)
Flow direction control (check valves)

The gate and plug valves are the most common types used for on/off flow control in a refinery, while globe valves are the most common type for flow control. Almost all check valves are enclosed within the process piping, but their access connections to the working parts may be sources of fugitive emissions. All other valves consist of internal parts connected to an external actuator by means of a valve stem. A packing around the valve stem is used to prevent process fluid from escaping from the valve. On/off flow control and throttling valves are actuated by the operation of a handwheel or crank. Control valves are frequently automatically operated, often by air pressure.

Because of heat, pressure, vibration, friction, and corrosion, leaks can develop in the packing surrounding the valve stem. Figures H-1 through H-8 show the potential leak areas for common refinery valves. The California Air Resources Board (CARB) found in its inspection of refineries that 9 percent of the valves leaked hydrocarbons. Most of this valve leak rate was from gas service valves, which constitute 25 percent of the refinery valve population but produce 85 percent of the total hydrocarbon emissions from valves.

Emissions originating from product leaks at valves can be controlled only by regular inspection and prompt repair of the leak. CARB requires gas service valves to be inspected by the

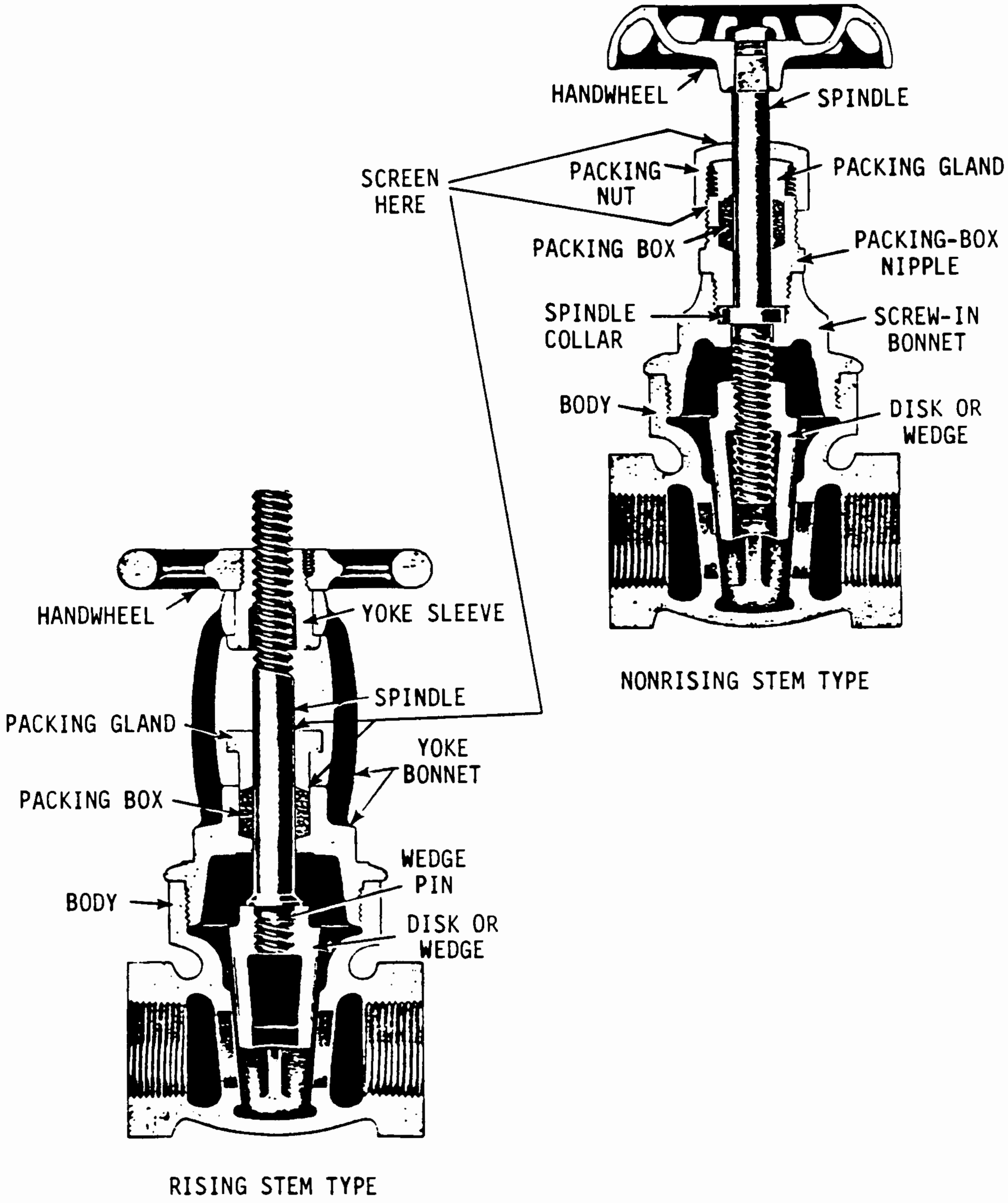
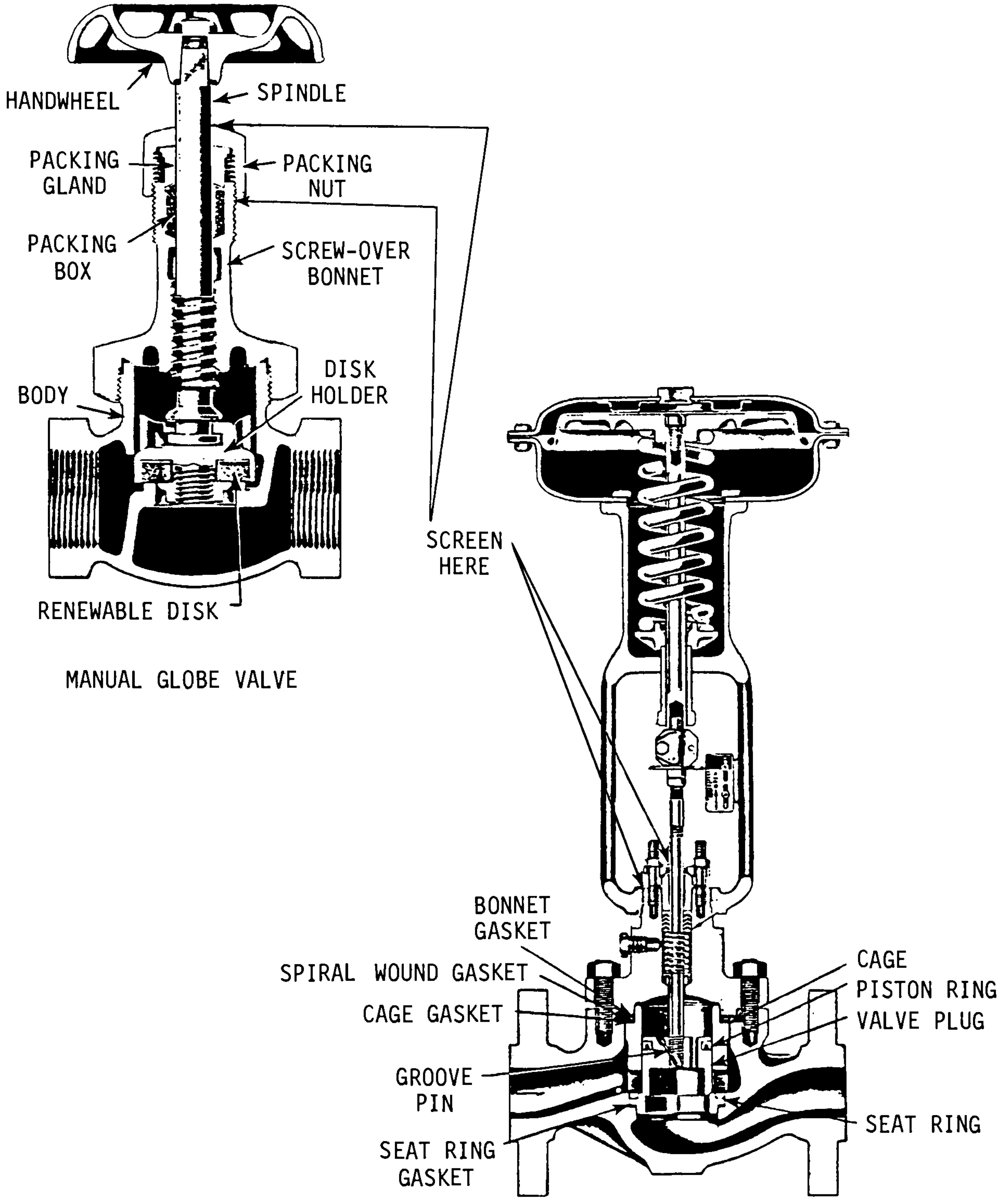


Figure H-1. Gate valves.[1]



MANUAL GLOBE VALVE

GLOBE-TYPE CONTROL VALVE

Figure H-2. Globe valves.[1]

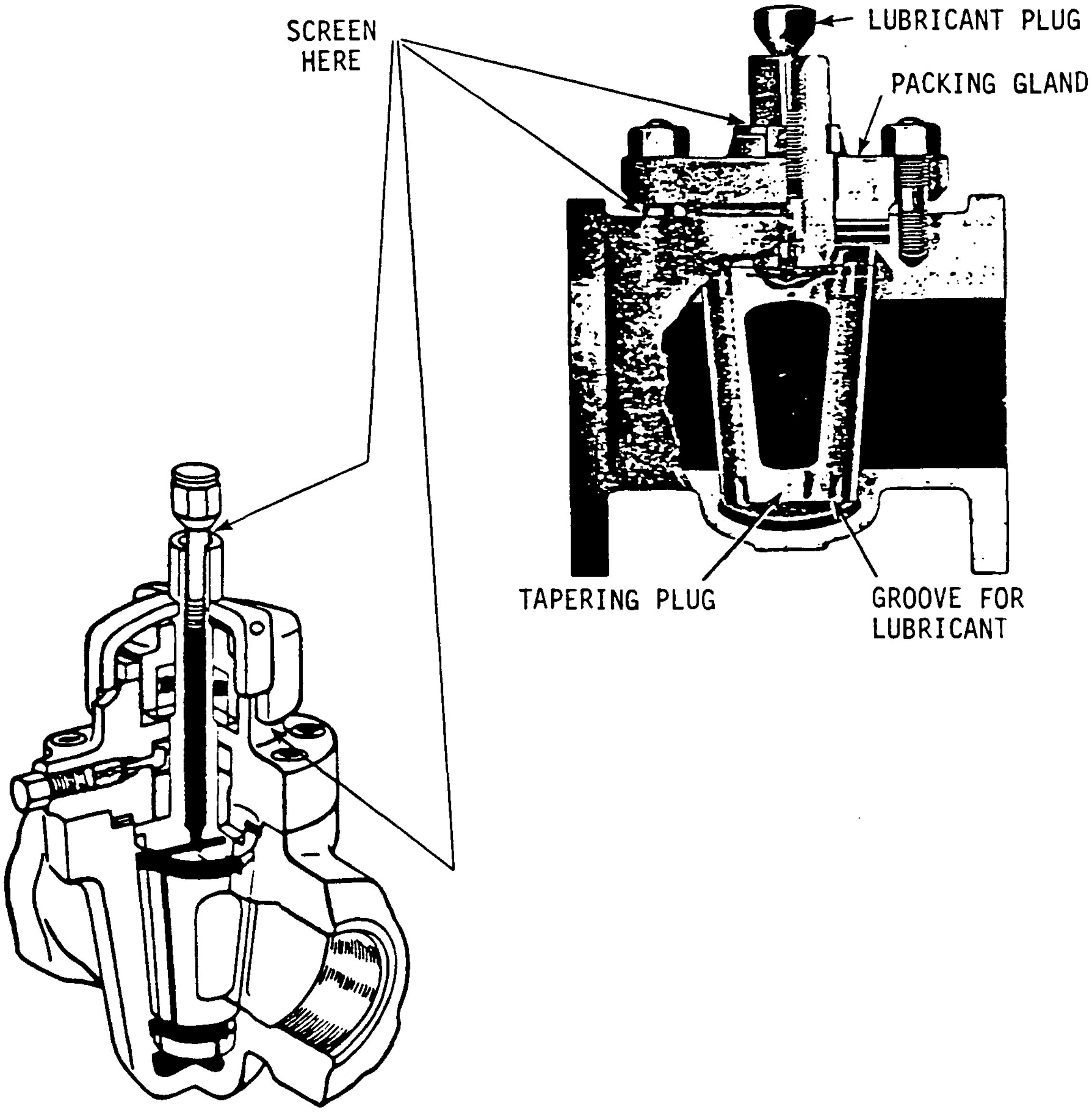


Figure H-3. Lubricated plug valves.[1]

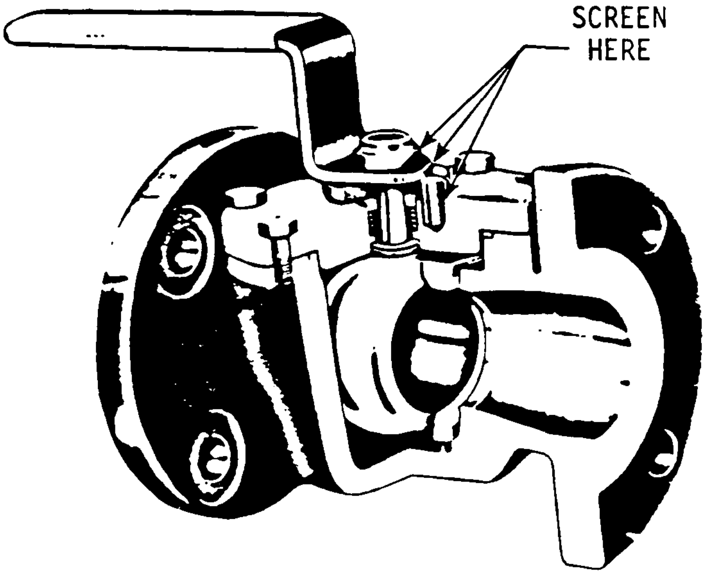


Figure H-4. Ball valve.[1]

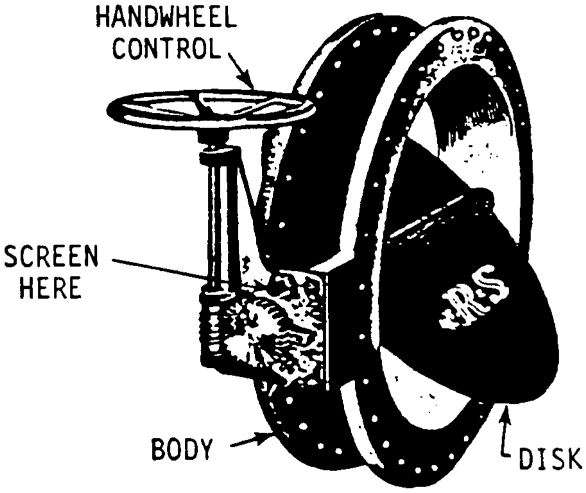


Figure H-5. Butterfly valve.[1]

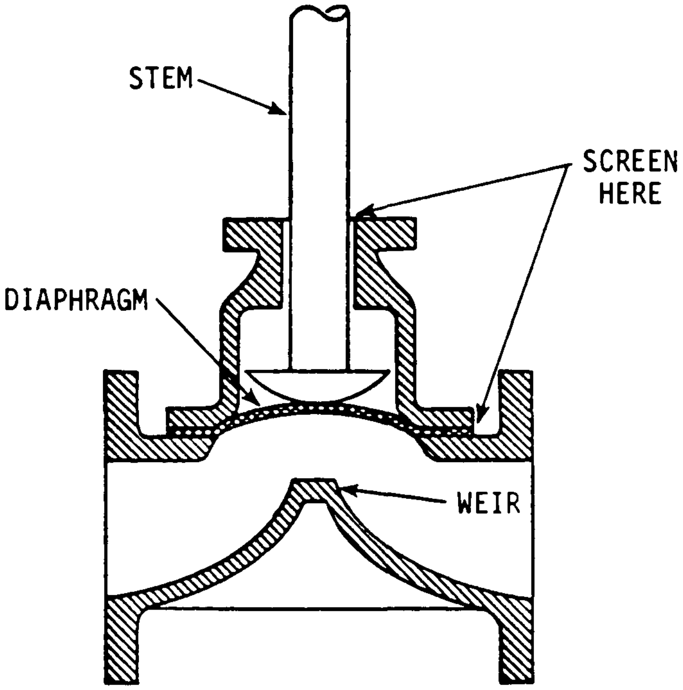


Figure H-6. Weir-type diaphragm valve.[1]

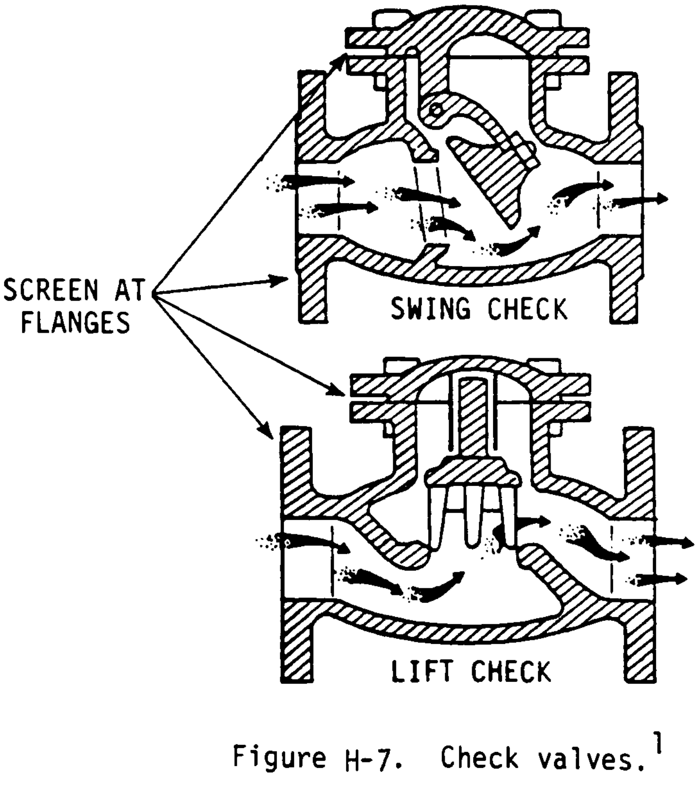


Figure H-7. Check valves.[1]

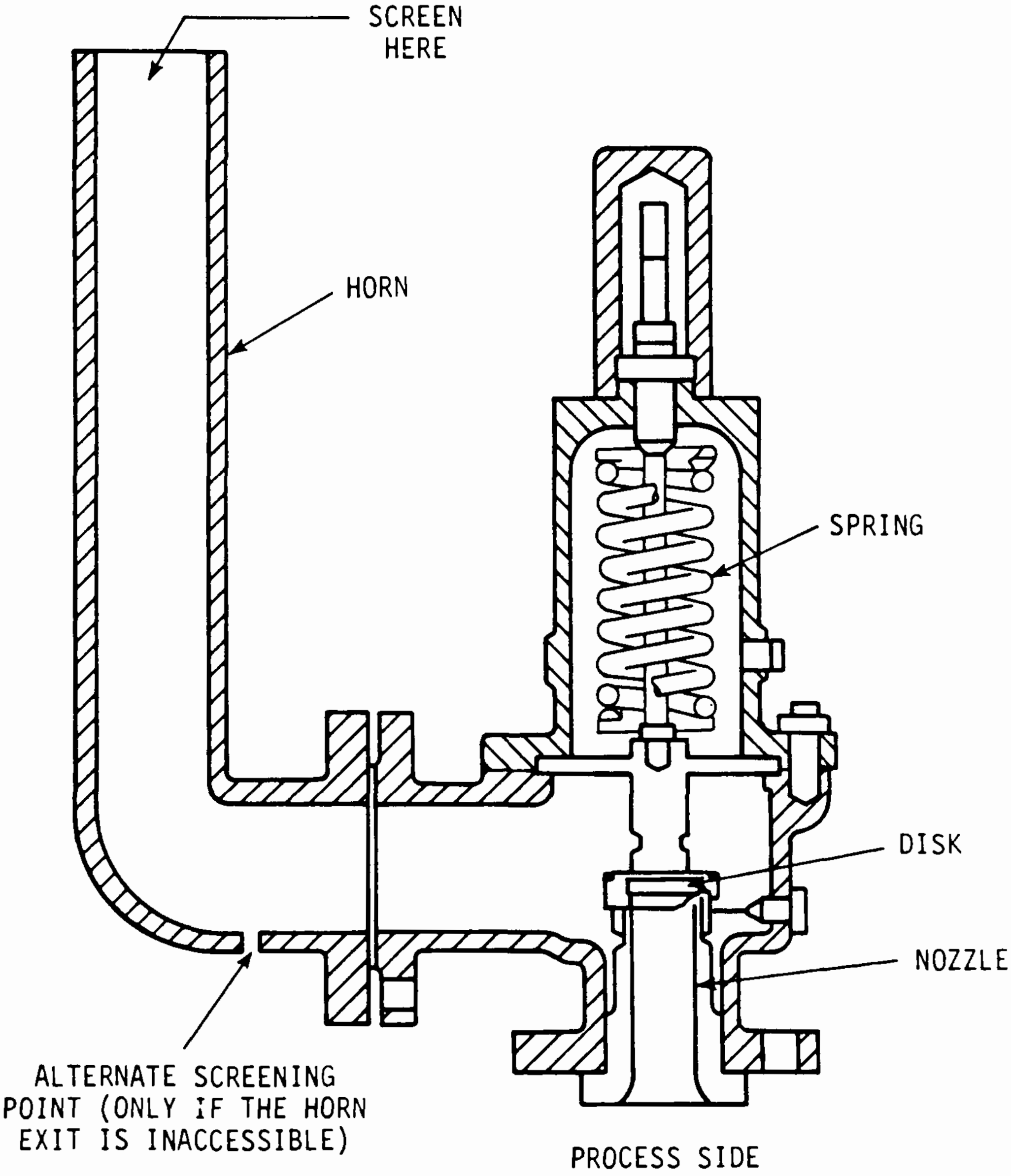


Figure H-8. Spring-loaded relief valve.[1]

refinery once every 3 months and inspection records to be kept. CARB concluded that a standard of no leaks for refinery gas service valves is feasible when a mandated inspection and maintenance plan is applied to these valves. A no-leak standard can be achieved from liquid-service valves with only marginally improved maintenance by refineries.

CARB emphasis on valve maintenance by the refineries requires that an inspector be able to recognize a lack of routine maintenance. During field inspection, typical indicators of a lack of routine maintenance are the following:

Leak is large enough to be seen, heard, or smelled.

Gland flange nuts are rusted on the bolts.

Valves are covered with undisturbed grime.

During the screening, the inspector should compare the leak frequency of valves at similar process units in different refineries. Considerable variation in these leak frequencies indicates a cause for leaks other than the nature of the valve service.

Inspection and maintenance of valve packing boxes are routinely performed by many refineries. Maintenance activities to stop valve leakage include:

Simple tightening of the gland flange on gate or globe valves, or

Lubrication of plug valves.

Sometimes, instead of improved maintenance, the valves need to be modified or different designs selected. For example, valves packed with alternate rings of braided graphite and containing steam at a temperature of 315°C (600°F) and a pressure of 2860 kPa (400 psig) have undergone 50,000 cycles (turns) before leaking. Such valves were completely leak-free for 15,000 cycles. Additionally, hermetically sealed diaphragm or bellows valves are advertised as zero-leak valves.

Because the leakage rate of a valve depends on the nature of the products handled, the degree of maintenance, and the characteristics of the equipment, the level of emission reduction achieved by I&M programs is difficult to estimate. The costs of I&M programs are the cost of labor for inspection and the cost of materials for repairs and maintenance. I&M program credits are received for product recovery and improved process operations.

## PUMP AND COMPRESSOR SEALS

Pumps and compressors most frequently leak at the seal between the moving shaft and the stationary casing. However, there are some types of pumps that are nonleaking. Examples of nonleaking pumps are the completely enclosed or "canned" pumps in which there are no seals, diaphragm pumps in which a flexible diaphragm prevents the product from contacting the working parts of the pump, and pumps with magnetic drivers in which magnetics are used to transmit mechanical energy across a sealed pump housing.

Pumps may be classified under two general headings, positive displacement and centrifugal. Positive-displacement pumps have as their principle of operation the displacement of the liquid from the pump case by reciprocating action of a piston or diaphragm or by the rotating action of a gear, cam, vane, or screw. The type of action may be used further to classify positive-displacement pumps as reciprocating or rotary. Reciprocating positive-displacement pumps are the most common type of positive-displacement pump used in refineries. Centrifugal pumps operate by the principle of converting velocity pressure generated by centrifugal force to static pressure. Velocity is imparted to the fluid by an impeller that is rotated at high speeds inside a housing containing the fluid. The fluid enters the housing at the center of the impeller and is discharged from the housing at the impeller's periphery. These pumps, which are illustrated in Figures H-9 and H-10, are commonly used by refineries.

Compressors are pumps that are used in gas service. They operate on the principle of volume reduction through the reciprocating action of a piston and by pressure increase through the centrifugal action of a vane just like a pump.

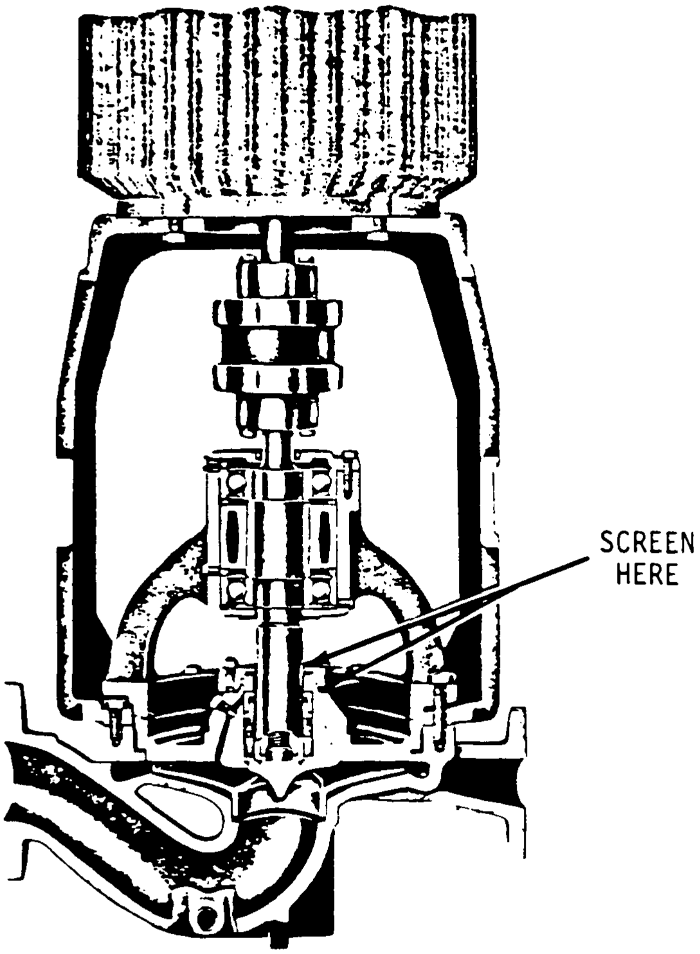


Figure H-9. Vertical centrifugal pump.[1]

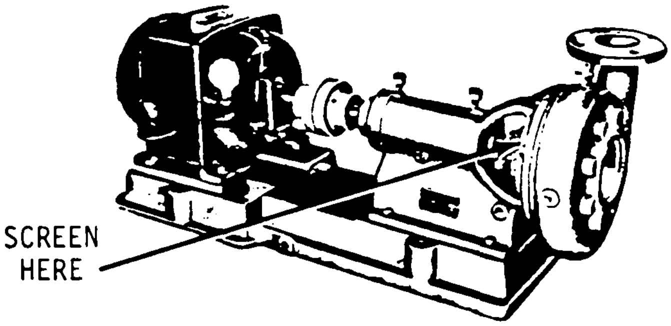


Figure H-10. Horizontal centrifugal pump.[1]

The seals normally used on pumps are mechanical or packed. A packed seal generally consists of a stationary stuffing box, much like the packing gland on a valve. The stuffing box surrounds the moving shaft and is filled with fiber, leather, or other elastic material. The stuffing box is provided with takeup rings that allow compression of the packing. Compression forces the packing material against the shaft and effects the seal. A mechanical seal consists of two plates situated perpendicular to the shaft and forced tightly together. One plate is attached to the shaft and one is attached to the casing. Packed seals can be used on reciprocating or rotating shafts; mechanical seals are for rotating shafts only. Figures H-11 through H-13 illustrate the packed and mechanical seals and show areas where leakage may occur.

In normal service both packed and mechanical seals can leak. These losses may be vapor or liquid and occur when shafts become scarred, move eccentrically, or through failure of the packing or seal faces. The rate at which this destruction of seal efficiency progresses depends upon the abrasive and corrosive properties of the product handled and the type of maintenance applied.

The CARB found that centrifugal pumps with packed seals lost 2.2 kg of hydrocarbons/day-seal (4.8 lb/day-seal), centrifugal pumps with mechanical seals lost 1.5 kg of hydrocarbons/day-seal (3.2 lb/day-seal), reciprocating pumps with packed seals lost 2.4 kg of hydrocarbons/day-seal (5.4 lb/day-seal), and compressors lost 3.9 kg of hydrocarbons/day-seal (8.5 lb/day-seal). A total of 20 percent of the pumps in liquid service leaked, while 18 percent of those processing gas leaked. Of the pumps and compressors inspected by CARB, 11 percent of the compressors leaked and 20 percent of the pumps leaked. Compressor seals are illustrated in Figures H-14 and H-15.

Both packed and mechanical seals inherently leak, but emissions from centrifugal pumps can be reduced 33 percent by replacing packed seals with mechanical seals. Emissions from dual mechanical seals can be eliminated by using a circulating, inert

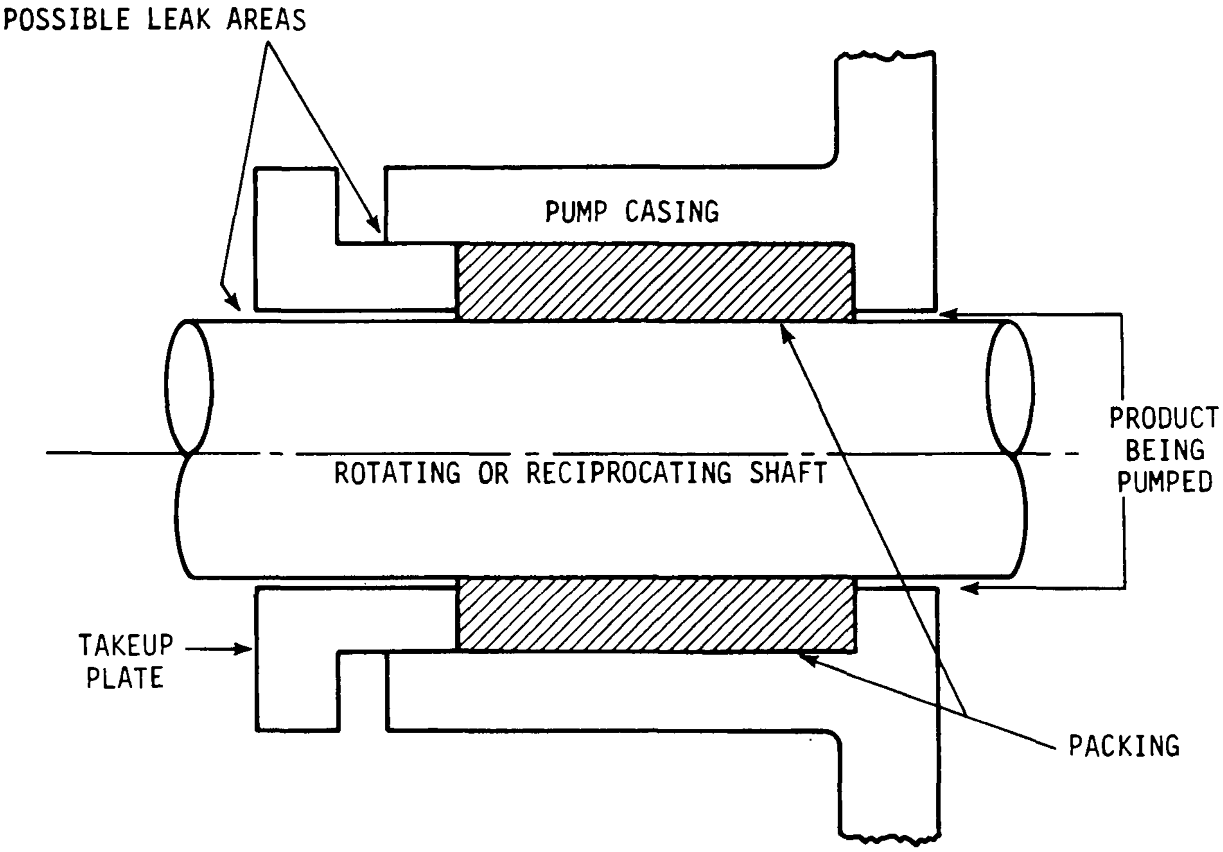


Figure H-11. Simple packed seal.[1]

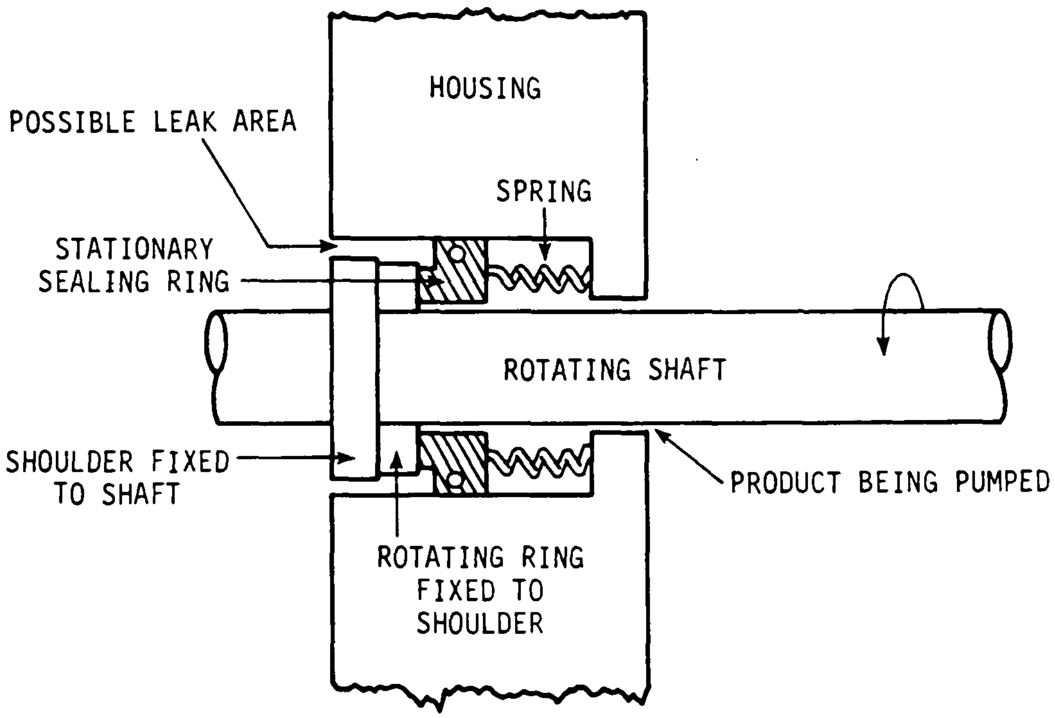
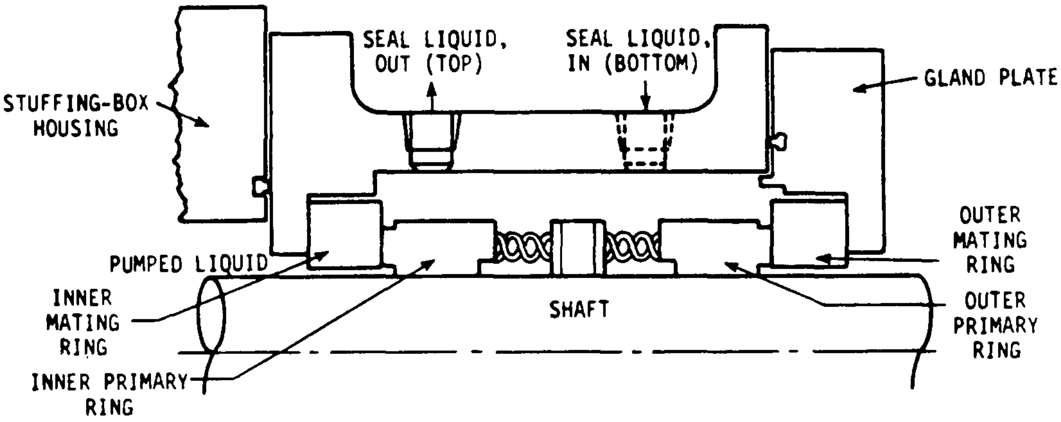
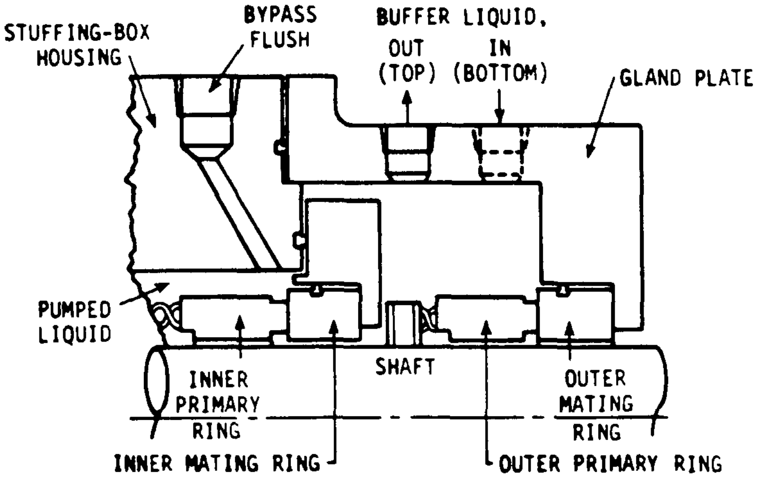


Figure H-12. Simple mechanical seal.[1]



TYPICAL DOUBLE MECHANICAL SEAL



TANDEM MECHANICAL SEALS

Figure H-13. Double mechanical seals for pumps.[1]

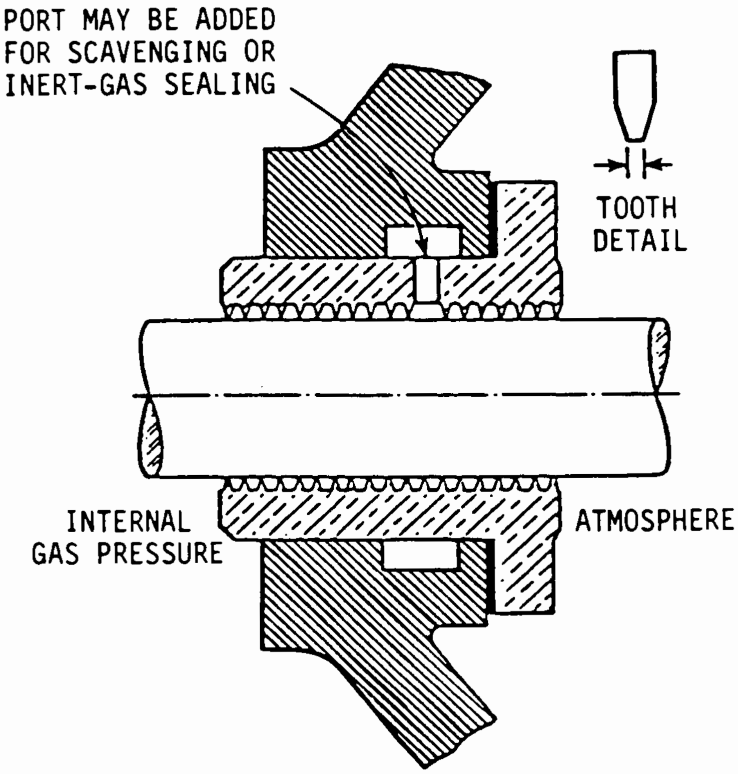
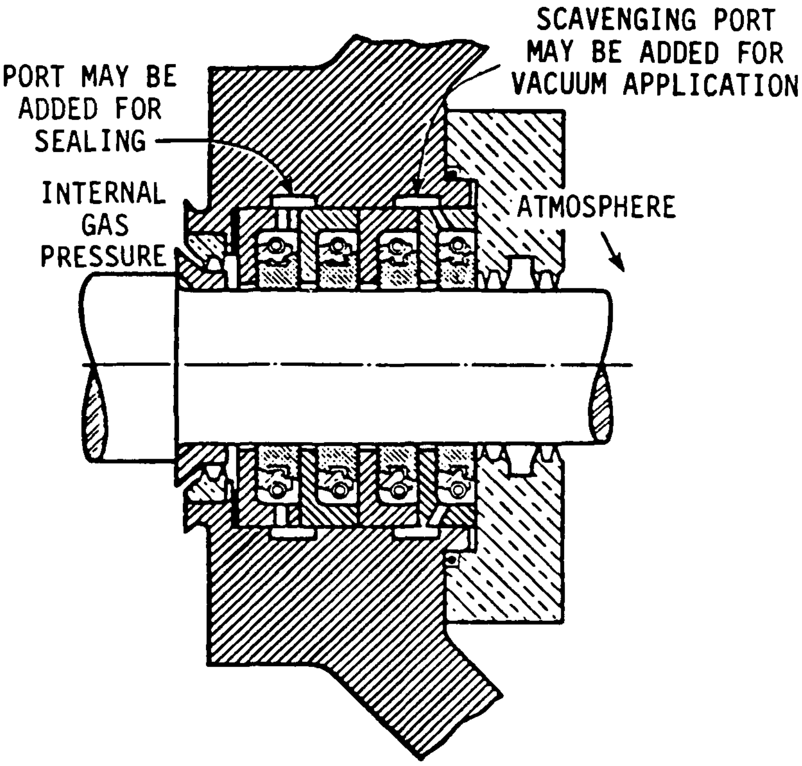


Figure H-14. Honeycomb labyrinth compressor seal.[1]



RESTRICTIVE CARBON RING SEALS

Figure H-15. Mechanical seals for compressors.[1]

fluid to pressurize the seals. According to several refiners, the highest temperatures in which mechanical seals can be used range from 210° to 360°C (410 to 680°F). Emissions from reciprocating pumps can be controlled by installation of dual packed seals with provisions to vent the volatile vapors that leak past the first seal into a vapor recovery system.

Emissions from any kind of pump or compressor seal can be minimized by frequent inspection and corrective maintenance. Major indications of leakage at or near the seal/shaft are a visible mist, hissing sound, or strong odor.

## FLANGES AND OTHER PIPE JOINING TECHNIQUES

Process piping can be joined to process vessels and equipment or to other lengths of piping in as many as 17 different ways. There are, however, three principal types of joining techniques used in petroleum refining:

Threaded fittings
Flanges
Welds

Threaded fittings are a joining technique where threaded lengths of pipe are screwed together using other threaded parts. They are most commonly used for pipes of 0.05-m (2-inch) diameter or smaller. The most common threaded fitting is the "bull plug." Bull plugs are used to cap off valve outlets or other threaded outlets that are normally used for sampling. A valve outlet is the same type of equipment without a threaded fitting in place. Some refineries have bull plugs in all exposed valve outlets.

Flanges provide pipe joints that can easily be disassembled. They consist of circular discs (faces) welded or threaded to the outer circumference of pipe ends. A gasket forms the seal between flanges. The gasket is held in place by bolts connecting the two flange faces. Gasket material for flanges is typically asbestos fiber sheet (similar to brake shoe material), metal/asbestos for high temperature and pressure, and steel alloys for corrosive service. Flanges are the most common joining technique used in refineries.

Welds are used to connect pieces of pipe when disassembly will not be needed. Welding produces a seal almost as complete as the pipe itself. Welding is a desirable pipe joining technique whenever practical.

The influences of heat, pressure, vibration, friction, and corrosion can cause leakage in joints. Of the three kinds of joints described, threaded fittings that have been frequently assembled and disassembled are the most likely to leak. The CARB inspected 346 threaded fittings and found that 23 percent of them leaked. Some refineries require bull plugs in exposed valve outlets after a leak is detected from the valve outlet. Threaded fittings, however, are not the predominant type of connecting device. Therefore, many refineries do not have procedures for them. Welds are virtually leak-proof because they are rigid joints less susceptible to the effects of vibration, etc., that disturb the original seal. Flanges can leak if the gasket material is damaged, if the flange is not aligned properly, or because of seal deformation due to thermal stresses on the piping system. CARB inspected 24,826 flanges and found that only 0.4 percent leaked. Therefore, flanges are a negligible source of emissions.

Emissions from product leaks at flanges and threaded fittings can be controlled by regular inspection and prompt maintenance. CARB recommends an annual undocumented inspection program for flanges. The board and other governmental agencies focused their regulations on the control of emissions from flanges, because they are the most common type of connecting device in a refinery.

## REFERENCE

1. Harris, G. E., and G. J. Langley. Detailed Screening Plan For Fugitive Emissions From SOCMI Process Units. Prepared by Radian Corporation for the U.S. Environmental Protection Agency. DCN 79-203-001-01-05, December 1979.

# APPENDIX I

## INFORMATION CHECKLISTS FOR PSD REVIEW

The data sheets in this appendix list the source information that is required for a TIER I and TIER II PSD review (Prevention of Significant Deterioration of Air Quality).

## SOURCE INFORMATION

1. General Information
   - Facility name
   - Proposed location
   - Parent company
   - Principal products
   - New or modified source

2. An Enforceable State Permit

   If an enforceable state permit has been obtained, submit that; if not, submit the data required in Items 1, 3 and 4.

3. Major Activity Throughputs

   - Description of major activity
   - Major activity products
   - Maximum capacity
   - Operating schedule

4. Potential Emissions

   - Annual potential emissions
   - The calcultion by which the above emissions were estimated

   If the applicant would like EPA to calculate the annual potential emissions, they should submit the data required in Items 1, 5, 6, and 7 as applicable.

5. Process/Operating Data

   - Descriptions of process/operating units
   - Process/operating units
     - Feed materials
     - Maximum annual rates
   - Process/operating units outputs
     - Products
     - Maximum annual rates
   - Fuel usage
     - Type of combustion unit
     - Size
   - Fuel
     - Type
     - Heat content
     - Percent sulfur
     - Percent lead
     - Percent ash
   - Annual fuel consumption

6. <u>Storage Tank Data</u>

   - Tank capacity
   - Throughputs
   - Roof type
   - Product stored
   - Reid vapor pressure

7. <u>Solvent Usage</u>

   - Feed material
   - Common name of solvent
   - Chemical composition
   - Solvent as a percent of feed material
     - By volume
     - By weight
   - Solvent recovered
     - Amount by volume
     - Amount by weight
     - Method for recovery
   - Disposal of solvent
     - Amount
     - Method

# INFORMATION REQUIREMENTS FOR A TIER I REVIEW

1. General Information

   Facility name
   Proposed location
   Parent company
   Company contact
   Principal products
   New or modified source
   Distance to Class I areas

2. Detailed Construction Schedule

3. An Enforceable State Permit

   If an enforceable state permit has been obtained, submit it along with Items 9 and 10, if they are not included as part of the state permit. If a state permit has not been obtained, submit Items 1, 4, 5, 9, 10, as applicable.

4. Major Activity Throughputs

   Description of major activity
   Major activity products
   Maximum capacity
   Operating schedule

5. Allowable Emissions

   Annual, daily, and hourly allowable emissions
   The calculation by which the above emissions were estimated

   If the applicant would like EPA to calculate the allowable emissions, they should submit the data required in Items 1, 6, 7, 8, 9, and 10 as applicable.

6. Process/Operating Data

   Process flow diagram describing the entire facility
   Process flow diagram describing each major activity affected by the modification
   Descriptions of process/operating units
   Operating schedule (h/yr)
   Process/operating units
     Feed materials
     Maximum annual, daily, and hourly rates
   Process/operating unit outputs
     Products
     Maximum annual, daily, and hourly rates

- Fuel usage
  - Type of combustion unit
  - Size
- Fuel
  - Type
  - Heat content
  - Percent sulfur
  - Percent lead
  - Percent ash
- Annual, daily, and hourly fuel consumption

7. Storage Tank Data

- Tank capacity
- Throughputs
- Roof type
- Product stored
- Reid vapor pressure

8. Solvent Usage

- Feed material
- Common name of solvent
- Chemical composition
- Solvent as a percent of feed material
  - By volume
  - By weight
- Solvent recovered
  - Amount of volume
  - Amount of weight
  - Method for recovery
- Disposal of solvent
  - Amount
  - Method

9. Stack and Vent Data

- Location of emission points
  - Stack, vent, fugitive, immediately after process unit (prior to combination with other units)
- Stack height
- Cross-sectional area
- Exit gas flow rate
  - Maximum
  - Normal
- Exit gas velocity

10. Air Cleaning Equipment

- Type
- Specifications (design criteria)
- Pollutant removed
- Percent collection efficiency (design criteria)

## INFORMATION REQUIREMENTS FOR A TIER II REVIEW

1. General Information

   - Facility name
   - Proposed location
   - Parent company
   - Company contact
   - Principal products
   - New or modified source
   - Distance to Class I area

2. Detailed Construction Schedule

3. Process/Operating Data

   - Process flow diagram describing the entire facility
   - Process flow diagram describing each major activity affected by the modification
     - If it is not apparent from the process flow diagrams, describe how process/operating units, air cleaning equipment, and stacks and vents are interconnected.
   - Descriptions of process/operating units
   - Operating schedule (h/yr)
   - Process/operating units
     - Feed materials
     - Maximum annual, daily, and hourly rates
   - Process/operating unit outputs
     - Products
     - Maximum annual, daily, and hourly rates
   - Fuel usage
     - Type of combustion unit
     - Size
   - Fuel
     - Type
     - Heat content
     - Percent sulfur
     - Percent lead
     - Percent ash
   - Maximum annual, daily, and hourly fuel consumption

4. Storage Tank Data (as applicable)

   - Tank measurements
     - Capacity
     - Throughputs
     - Diameter
     - Height

- Tank characteristics
  - Location (above or below ground)
  - Fill mouth (submerged, splash, bottom loading)
  - Roof type
  - Roof seal
- Product stored
  - Density
  - Vapor mole weight
  - Reid vapor pressure
  - Storage temperature
    - Maximum
    - Normal

5. <u>Solvent Usage</u> (as applicable)

- Feed material
- Common name of solvent
- Chemical composition
- Solvent as a percent of feed material
  - By volume
  - By weight
- Solvent recovered
  - Amount by volume
  - Amount by weight
  - Method for recovery
- Disposal of solvent
  - Amount
  - Method

6. <u>Stack and Vent Data</u>

- Location of emission points
  - Stack, vent, fugitive, immediately after process unit (prior to combination with other units)
- Stack height
- Cross sectional area
- Exit gas temperature
- Exit gas flow rate
  - Maximum
  - Normal
- Exit gas velocity

7. <u>Control Technology</u>

a. Flue Gas Treatment
  - (1) ESP
  - (2) Fabric Filter
  - (3) Scrubber
  - (4) Other

b. Process Modification (if applicable)

   (1) Description of how the process modifications (including fuel cleaning, or treatment or innovative fuel combustion techniques) reduce emissions
   (2) Emission reductions gained by using the modified process
   (3) Direct costs as indicated in Part A, "Guidelines for Determining BACT".

c. Design, Equipment, Work Practice or Operational Standard
   (1) Description
   (2) Emissions reductions
   (3) Direct costs

# PRECIPITATOR DATA

## Part I - Preliminary design or design criteria

1. Estimated total gas flow at full load and ESP operating temperature (acfm)
2. ESP operating temperature (°F) range
3. Number of separate ESP modules under consideration
4. Estimated total collecting surface area of each module
5. Estimated total collecting surface for all modules
6. Number of separate electrical sections for each module under consideration
7. Type of power control

   Manual power
   or Manual spark rate
   or Automatic power
   or Automatic spark rate
8. Instrumentation for each electrically isolated section

   Primary voltage
   Primary current
   Secondary voltage
   Secondary current
   Spark rate
9. Estimated linear velocity of gas through each module at full load (actual ft/s) or range of acceptable velocities
10. Briefly describe techniques used to ensure uniform linear velocity within ESP
11. Briefly describe system used to remove and convey collected ash to final disposal.
12. Vendor guarantee and terms of guarantee if available

## Part II - Reference plant example

1. General flow diagram for the precipitator
2. Provide design criteria or preliminary engineering data for the major elements of the ESP for the particular plant under consideration or a similar plant where the major elements have been designed and exact detailed specifications are available.

## FABRIC FILTER

Part I - Preliminary design or design criteria

1. Estimated total gas flow at the full load and fabric filter operation temperature (acfm)
2. Fabric filter operation temperature (°F) range
3. Estimated number of separate fabric filters
4. Estimated number of isolated compartments per fabric filter
5. Estimated number of filters per compartment
6. Estimated filter length (ft) and filter diameter (inches) or range of acceptable alternative lengths or diameters
7. Estimated total cloth area of all filters ($ft^2$)
8. Design criteria for air to cloth ratio or range of acceptable ratio (cloth area divided by total acfm)
9. Briefly describe cloth

   Material
   Weave
   Weight ($oz/yd^2$)
   Permeability

10. Type of filter cleaning under consideration

    Reverse air
    Pulse jet
    Shake
    Other

11. Type filter cleaning controls

    Pressure drop actuated
    Time actuated

12. Briefly describe how faulty filters will be detected and replaced
13. Briefly describe ash handling system from fabric filter to final disposal
14. Vendor guarantee and terms of guarantee if available

Part II - Reference plant example

1. General flow diagram for the fabric filter
2. Provide design criteria or preliminary engineering data for the major elements of the fabric filter for the particular plant under consideration or a similar plant where the above elements have been designed and exact detailed specifications are available.

## SCRUBBER DATA

Part I - Preliminary design or design criteria

1. Design data or criteria for the scrubber modules to include:
   - Scrubber type (TCS, spray tower, etc.)
   - Absorbent type
   - Possible scrubber liquor additives (e.g., Mg)
   - Prescrubber design criteria, or acceptable ranges for l/g, inlet and outlet chloride, etc.
   - Design criteria for acceptable ranges for inlet and outlet gas flow and temperature and volume percent $H_2O$, $O_3$, and $SO_2$
   - Specific design criteria or acceptable ranges for liquid/gas ratio
   - Estimated scrubber gas velocity
   - Design criteria or acceptable range for scrubber inlet and outlet pH
   - Design criteria or acceptable range of pressure drop across the scrubber (inches $H_2O$)
2. For turbulent contact absorber (TCA) also supply:
   - Design criteria or acceptable ranges for diameter of spheres
   - Design criteria or acceptable ranges for the height of sphere in TCA
   - Design criteria or acceptable ranges for number of grids or screens in TCA
3. Indicate total number of scrubber modules and number of spare modules during maximum boiler loading
4. What special precautions will be taken with modules internals and other components (pumps, mist eliminators, fans, etc.) to ensure that corrosion, scaling, and plugging do not cause failure of the system?
5. What special precautions will be taken with the pH control system, e.g., spare probes, probe site location, probe sheaths, backup instrumentaion, to ensure that failure will not lead to excess emissions or fouling of components via scaling?
6. How will other key variables such as process stoichiometry, liquid to gas ratios (l/g), etc., be monitored to ensure good operations?
7. Indicate which key components of the scrubber will be spared, e.g., pumps, fans, nozzles, etc.
8. If reheat of gases is planned, indicate reason for reheat, location and mechanism of reheat, auxiliary fuel requirements, and percentage of exhaust gas reheated. If reheat will not be performed, indicate what measures are being

taken to eliminate stack corrosion or provide data to verify that stack corrosion will not be a problem area.

9. Outline routine maintenance and inspection procedures for the scrubber system hardware to ensure continuous and reliable scrubber performance.
10. Describe the general design standard for the material to be used and type of mist eliminator system, and describe the techniques under consideration to guarantee uniform gas distribution across the mist eliminator and to the scrubber modules.
11. Vendor guarantees and terms of guarantee if available

Part II - Reference plant example

1. General flow diagram of the scrubber system including mix tanks, prequench section, scrubber modules, mist eliminator and reheat. General design standards for materials to be used to construct above elements.
2. Provide design criteria or design criteria data for the major scrubber and system components (e.g., sizing of pumps, clarifier, recirculation tanks, alkali handling systems, etc.) for the particular plant under consideration or a similar plant where the above items have been already designed and exact detailed specifications are available.

OTHER CONTROL DEVICES

Type
Specifications (design criteria)
Pollutant removed
Percent collection efficiency (design criteria)
Inlet gas temperature
Inlet gas flow rate
Inlet gas pressure
Pressure drop

# APPENDIX J

## LEVEL I INSPECTION: BLANK CHECKLIST FORMS

This appendix provides the cover sheet and checklist form to be used in conducting a Level I inspection.

## LEVEL __ INSPECTION

AQCR ______

Date(s) of Inspection ___________

______________________________

Time In __________ Out __________

Company Name ______________________________________________

Mailing Address ___________________________________________

___________________________________________________________

Location of Facility ______________________________________

___________________________________________________________

(Include County or Parish)

Type of Industry __________________________________________

Form of Ownership _________________________________________

Corporate Address _________________________________________

___________________________________________________________

| Company Personnel | Name | Title | Phone |
|---|---|---|---|
| Responsible for Facility | | | |
| Responsible for Environmental Matters | | | |
| Company Personnel Contacted | | | |
| | | | |
| Confidentiality Statement given to | | | |
| EPA Personnel | | | |
| | | | |
| State or Local Agency Personnel | | | |
| | | | |

# VISIBLE EMISSION OBSERVATION FORM

SOURCE NAME____________________ OBSERVER____________________

ADDRESS____________________ DATE____________________

Point of Emission____________________

OBSERVATION POINT____________________

STACK: DISTANCE FROM_____ HEIGHT_____

WIND-SPEED________ DIRECTION________

SKY CONDITION:________________

COLOR OF EMISSION:________________

RELATIVE HUMIDITY:________________

BACKGROUND:________________

AMBIENT AIR TEMPERATURE:________________

________________

CERTIFICATION DATE:________________

| | 0 | 15 | 30 | 45 | | 0 | 15 | 30 | 45 |
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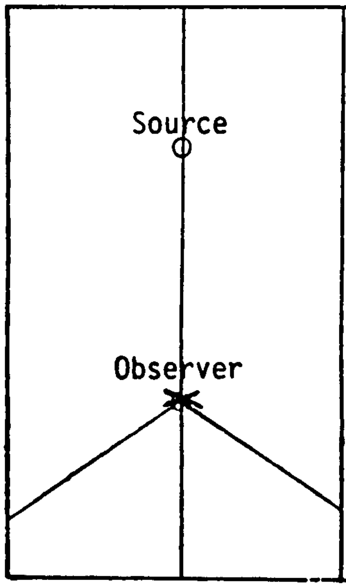
| 28 | | | | | 58 | | | | |
| 29 | | | | | 59 | | | | |

## SUMMARY OF AVERAGE OPACITY

| Set Number | Time Start--End | Opacity | |
|---|---|---|---|
| | | Sum | Average |
| | | | |
| | | | |
| | | | |
| | | | |

Observer ×

Sun ⊕ Wind ⟶ Plume & Stack



Remarks:

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Evaluator's Signature:

____________________

Title:________________ Date:________

## LEVEL I INSPECTION CHECKLIST

### I. Heater and Boiler Information

| Identification Number | Heater description including unit location | Opacity | Comments |
|---|---|---|---|

### II. Catalytic Cracker

| Identification Number or Name | Type of Process | Pollution Control Equipment | | | FCC Sump Stack Opacity | Comments |
|---|---|---|---|---|---|---|
| | | CO Boiler | ESP | Cyclones | | |

### III. Sulfur Plant

| Identification Number or Name | Pollution Control Equipment | Incinerator Temperature (°F) | Incinerator Stack Opacity | Comments |
|---|---|---|---|---|

### IV. General Comments

(Note the general housekeeping practices of the refinery.)

# APPENDIX K

## LEVEL II INSPECTION: BLANK CHECKLIST FORMS

This appendix provides the cover sheet and checklist form to be used in conducting a Level II inspection.

## LEVEL __ INSPECTION

AQCR ______

Date(s) of Inspection ____________

____________________________

Time In __________ Out __________

Company Name ____________________________

Mailing Address ____________________________

____________________________

Location of Facility ____________________________

____________________________

(Include County or Parish)

Type of Industry ____________________________

Form of Ownership ____________________________

Corporate Address ____________________________

____________________________

| <u>Company Personnel</u> | <u>Name</u> | <u>Title</u> | <u>Phone</u> |
|---|---|---|---|
| Responsible for Facility | ____________ | ____________ | ____________ |
| Responsible for Environmental Matters | ____________ | ____________ | ____________ |
| Company Personnel Contacted | ____________ | ____________ | ____________ |
| | ____________ | ____________ | ____________ |
| Confidentiality Statement given to | ____________ | ____________ | ____________ |
| EPA Personnel | ____________ | ____________ | ____________ |
| | ____________ | ____________ | ____________ |
| State or Local Agency Personnel | ____________ | ____________ | ____________ |
| | ____________ | ____________ | ____________ |

# VISIBLE EMISSION OBSERVATION FORM

SOURCE NAME______________________________ OBSERVER______________________________

ADDRESS______________________________ DATE______________________________

Point of Emission______________________________

OBSERVATION POINT______________________________

STACK: DISTANCE FROM_____ HEIGHT______

WIND-SPEED_________ DIRECTION________

SKY CONDITION:______________________

COLOR OF EMISSION:__________________

RELATIVE HUMIDITY:__________________

BACKGROUND:_________________________

AMBIENT AIR TEMPERATURE:____________

____________

CERTIFICATION DATE:_________________

| | 0 | 15 | 30 | 45 | | 0 | 15 | 30 | 45 |
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| 27 | | | | | 57 | | | | |
| 28 | | | | | 58 | | | | |
| 29 | | | | | 59 | | | | |

SUMMARY OF AVERAGE OPACITY

| Set Number | Time Start--End | Opacity | |
|---|---|---|---|
| | | Sum | Average |
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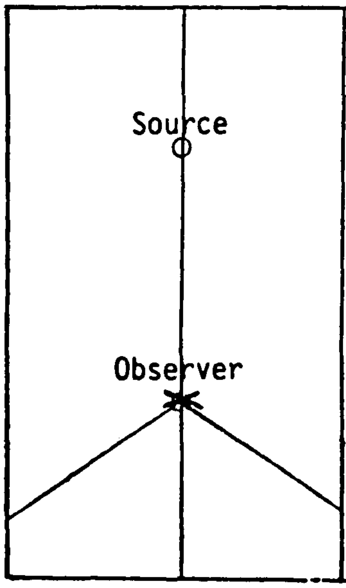
| | | | |

Observer ×
Sun ⌖ Wind ⟶ Plume & Stack



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Evaluator's Signature:

______________________________

Title:______________________ Date:________

(Insert refinery flow diagram here.)

Simple process flow diagram.

# PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Crude distillation | | | Number of atmospheric towers -<br>Description of towers - preflash, primary, secondary, tertiary fractionating towers | |
| | | | Number of atmospheric towers -<br>Description of towers - preflash, primary, secondary, tertiary fractionating towers | |
| Vacuum distillation | | | Pressure of tower -<br>Type of vacuum producing system | |
| | | | Pressure of tower<br>Type of vacuum producing system | |
| Catalytic reforming | | | | |
| Isomerization | | | Type -<br>Catalyst - | |

## PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Crude distillation | | | | | | |
| Vacuum distillation | | | | | | |
| Catalytic reforming | | | | | | |
| Isomerization | | | | | | |

PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Crude distillation | | |
| Vacuum distillation | All hot wells must be covered | |
| Catalytic reforming | Recommended venting to atmosphere after 5 psig during turnaround | |
| | Last shutdown date<br>Next shutdown date | |
| Isomerization | Last shutdown date<br>Next shutdown date | |

PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Polymerization | | | Type -<br>Catalyst - | |
| Alkylation | | | Type of process - | |
| Hydrocracking | | | | |
| Catalytic cracking | | | Type of process - | |
| Coking | | | Type of process - | |
| Visbreaking | | | | |
| Deasphalting | | | Solvent employed | |

## PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Polymerization | | | | | | |
| Alkylation | | | | | | |
| Hydrocracking | | | | | | |
| Catalytic cracking | | | | | | |
| Coking | | | | | | |
| Visbreaking | | | | | | |
| Deasphalting | | | | | | |

PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Polymerization | Last shutdown date<br>Next shutdown date | |
| Alkylation | | |
| Hydrocracking | | |
| Catalytic cracking | | |
| Coking | | |
| Visbreaking | | |
| Deasphalting | | |

PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Hydrotreating | | | | |
| Wax production | | | | |
| Grease production | | | | |
| Lube production | | | | |
| Asphalt | | | | |
| Gas processing | | | | |
| Sulfur plant | | | | |
| Furfural extraction | | | | |

## PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Hydrotreating | | | | | | |
| Wax production | | | | | | |
| Grease production | | | | | | |
| Lube production | | | | | | |
| Asphalt | | | | | | |
| Gas processing | | | | | | |
| Sulfur plant | | | | | | |
| Furfural extraction | | | | | | |

## PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Hydrotreating | | |
| Wax production | | |
| Grease production | | |
| Lube production | | |
| Asphalt | | |
| Gas processing | | |
| Sulfur plant | | |
| Furfural extraction | | |

PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Amine treating | | | Type of solvent - | |
| Other | | | | |

PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Amine treating | | | | | | |
| Other | | | | | | |

## PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Amine treating | | |
| Other | | |

# HEATER AND BOILER INFORMATION

| Identification Number | Heater description including unit location | Fuel capability | Current fuel | Duty million Btu/h |  | Number of Stacks | Stack Data |  | Exit Temp. (°F) | Opacit |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Maximum | Current |  | Height (ft) | Diameter (ft) |  |  |
|  |  |  |  |  |  |  |  |  |  |  |

HEATER AND BOILER INFORMATION (continued)

| Identification No. | Heater description including unit location | Opacity |
|---|---|---|
| | | |

For Particulate, sulfur dioxide, and nitrogen oxide emission information.

| Type of Fuel used in Boilers and Heaters | Heat Content Btu/lb or Btu/scf | Sulfur Content |
|---|---|---|
| | | |

## TANK INFORMATION

| Tank Number | Capacity (Units) | Type (1) | Product Stored | True Vapor Pressure (Units) | Tank Color | Construction: Welded or Riveted | Vapor Controls (2) | Remarks* |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |

Footnotes:

(1) C = fixed roof: F = floating roof; P = pressure; O = open top; S = spheroid; H = horizontal; U = underground

(2) N = None, CV = conservation vents; F = floating roof (SS = single seal; DS = double seal); VR = Vapor recovery (describe); VD = vapor disposal (describe); VB = vapor balance; SF = submerged fill

* Date installed, etc.

## VOLATILE HYDROCARBON LOADING/UNLOADING FACILITIES

| LOADING FACILITY DESIGNATION | SOURCE | TYPE TRANSFER/SIZE (RR CARS, TRUCKS) | MONTHLY THRU-PUT (1000 GAL) | VAPOR CONTROL SYSTEM | SUBMERGED LOADING | PRODUCTS | |
|---|---|---|---|---|---|---|---|
| | | | | | | TYPE | VAPOR PRESSURE (PSIA) |
| | | | | | | | |

# WASTEWASTER TREATMENT

| Treatment Facility | Observation | | | | |
|---|---|---|---|---|---|
| In-Plant Treatment: Sour Water Stripper | Noticable emissions (1) | Disposition of sulfides (1) | | | |
| | Yes No | incinerated recovered in sulfur recovery unit | | | |
| Primary treatment: - Gravity Separators | Type(s) of separator | gaps (or) leaks in cover - inspect with hydrocarbon detector | (1) | Type of cover | Noticable emissions (1) |
| | | | covered<br>uncovered | | Yes No |
| 1) Intermediate treatment: Dissolved Air Flotation Unit and holding basin | Type(s) | Capacity of each | | | |
| | | | | | |
| Secondary treatment: Biological Oxidation | Type(s) | Capacity of each | | | |
| | | | | | |
| Tertiary treatment | Type(s) | Capacity of each | | | |
| | | | | | |
| (1) Solids Disposal | Type(s) | Disposal (1) | | | |
| | | onsite offsite | | | |
| Surge storage capability | Type(s) | Capacity of each | | | |
| | | | | | |

Footnotes:
(1) Circle one

# LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 20

Unit Isomerization

Accept No. 5

Component Valves

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 20

Unit Alkylation

Accept No. 5

Component Valves

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit Alkylation

Component Pump seals

Sample size 5

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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## LEAK DETECTION SURVEY LOG

Inspection level II

Unit Storage

Component Valves

Sample size 20

Accept No. 5

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit Storage

Component Pump seals

Sample size 8

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit Storage

Component Compressor seals

Sample size 2

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 20

Unit Loading

Accept No. 5

Component Valves

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 8

Unit Loading

Accept No. 2

Component Pump seals

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit Gas processing

Component Valves

Sample size 20

Accept No. 5

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 8

Unit Gas processing

Accept No. 2

Component Pump seals

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit Gas processing

Component Compressor seals

Sample size 2

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit FCC

Component Valves

Sample size 8

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit FCC

Component Pump seals

Sample size 5

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level II

Unit FCC

Component Compressor seals

Sample size 2

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# APPENDIX L

## LEVEL II INSPECTION: EXAMPLE COMPLETED CHECKLIST FORMS

This appendix provides an example of a completed Level II checklist.

# LEVEL II INSPECTION

AQCR 003

Date(s) of Inspection

March 17-18, 1980

Time In 8:00/9:00 Out 4:00/2:00

Company Name Refinery A

Mailing Address 201 Oil Blvd. Oil City, U.S.A.

Location of Facility County

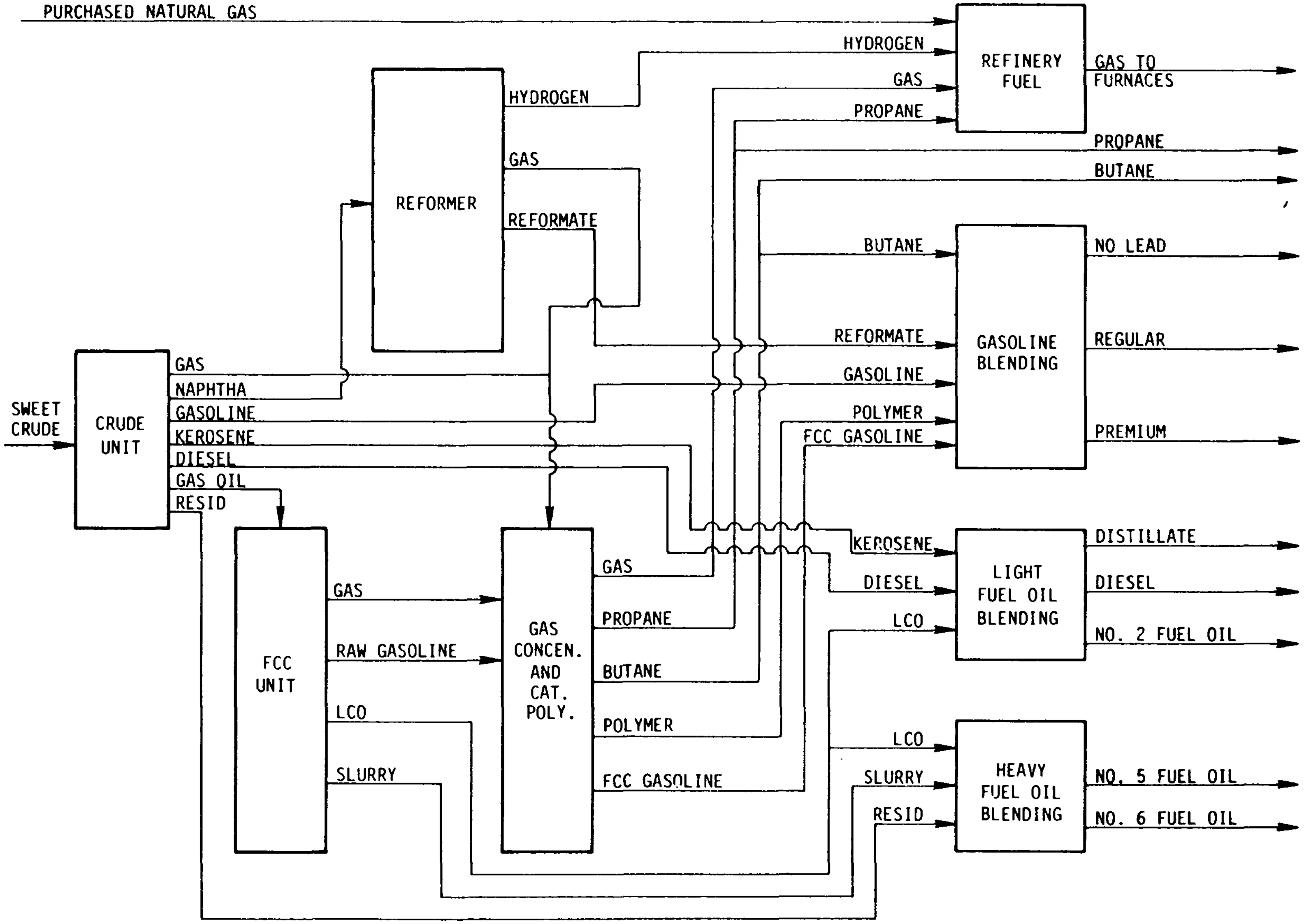
(Include County or Parish)

Type of Industry Petroleum Refinery

Form of Ownership

Corporate Address

| Company Personnel | Name | Title | Phone |
|---|---|---|---|
| Responsible for Facility | | Refinery Manager | |
| Responsible for Environmental Matters | | Assistant Manager | |
| Company Personnel Contacted | | Refinery Manager | |
| | | | |
| Confidentiality Statement given to | | | |
| EPA Personnel | | | |
| | | | |
| State or Local Agency Personnel | | | |
| | | | |



FCC: FLUID CATALYTIC CRACKING
LCO: LIGHT CYCLE OIL

REFINERY FLOW DIAGRAM

## PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Crude distillation | 1 | 212 | Number of atmospheric towers - 2<br>Description of towers - preflash, primary, secondary, tertiary fractionating towers | |
| | | | Number of atmospheric towers -<br>Description of towers - preflash, primary, secondary, tertiary fractionating towers | |
| Vacuum distillation | 1 | | Pressure of tower - 10 mm Hg absoulte<br>Type of vacuum producing system - 3 stage job<br>1 contact condenser<br>1 surface condenser | |
| | | | Pressure of tower<br>Type of vacuum producing system | |
| Catalytic reforming | 1 | 300 | 3 Fixed bed reactors | Powerformer |
| Isomerization | | | Type -<br>Catalyst - | |

PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Crude distillation | Sweet crude | Gas<br>Naphtha<br>Kerosene<br>Diesel<br>Gas oil |  | 20,000 |  |  |
| Vacuum distillation | Atmospheric bottoms | Gas oil<br>Resid |  | 5,000 |  |  |
| Catalytic reforming | Naphtha | Hydrogen<br>Gas<br>Reformate |  | 3,100 |  |  |
| Isomerization |  |  |  |  |  |  |

PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Crude distillation | | |
| Vacuum distillation | All hot wells must be covered<br>1 covered hot well | Hydrocarbon vapors from surface condensers are flared. |
| Catalytic reforming | Recommended venting to atmosphere after 5 psig during turnaround<br>Last shutdown date February, 1980<br>Next shutdown date | |
| Isomerization | Last shutdown date<br>Next shutdown date | |

PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Polymerization | 1 | 400 | Type - Solid phosphonic acid<br>Catalyst - | |
| Alkylation | | | Type of process - | |
| Hydrocracking | | | | |
| Catalytic cracking | 1 | 500 | Type of process - Fluid - UOP design | |
| Coking | | | Type of process - | |
| Visbreaking | | | | |
| Deasphalting | | | Solvent employed | |

## PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Polymerization | Gas<br>Raw gasoline | Gas<br>Propane<br>Butane<br>Polymer | | 2,000 | | |
| Alkylation | | | | | | |
| Hydrocracking | | | | | | |
| Catalytic cracking | Gas oil and wax crude oil | Gas<br>Raw gasoline<br>Slurry | | 7,000 | | Primary and secondary cyclones 99.9 percent efficiency |
| Coking | | | | | | |
| Visbreaking | | | | | | |
| Deasphalting | | | | | | |

PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Polymerization | Last shutdown date February, 1980<br>Next shutdown date | |
| Alkylation | | |
| Hydrocracking | | |
| Catalytic cracking | | Installed 1958 |
| Coking | | |
| Visbreaking | | |
| Deasphalting | | |

PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Hydrotreating | 1 | 600 | | |
| Wax production | | | | |
| Grease production | | | | |
| Lube production | | | | |
| Asphalt | | | | |
| Gas processing | | | | |
| Sulfur plant | 1 | 700 | Amine treating and claus sulfur plant | |
| Furfural extraction | | | | |

PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Hydrotreating | | | | | | |
| Wax production | | | | | | |
| Grease production | | | | | | |
| Lube production | | | | | | |
| Asphalt | | | | | | |
| Gas processing | | | | | | |
| Sulfur plant | Sour waste gas | Sulfur | | 10 tons/day | | |
| Furfural extraction | | | | | | |

PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Hydrotreating | | |
| Wax production | | |
| Grease production | | |
| Lube production | | |
| Asphalt | | |
| Gas processing | | |
| Sulfur plant | | |
| Furfural extraction | | |

PROCESS INFORMATION

| Process unit | Number of units | Identification number or name | Process description | Refinery terminology |
|---|---|---|---|---|
| Amine treating | 1 | Sulfur plant | Type of solvent - Monoethgnolamine (MEA) | |
| Other | | | | |

PROCESS INFORMATION

| Process unit | Feed | Products | Maximum rate, barrels/day | Current rate, barrels/day | Evaluated for RACT particulates, carbon monoxide sulfur oxide | Pollution abatement equipment |
|---|---|---|---|---|---|---|
| Amine treating | | | | | | |
| Other | | | | | | |

PROCESS INFORMATION

| Process unit | RACT requirements | Comments |
|---|---|---|
| Amine treating | | |
| Other | | |

HEATER AND BOILER INFORMATION

| Identification No. | Heater description, including unit location | Fuel capability | Current fuel | Duty, million Btu/h |  | Number of stacks | Stack data |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Maximum | Current |  | Height, ft | Diameter, ft | Exit temp., °F |
| H-1 | Crude distillation unit |  | 1, 2 | 40 |  | 2 | 55 | 3.0 | 350 |
| H-2 | Crude distillation unit |  | 1, 2 | 20 |  | 2 | 95 | 6.0 | 350 |
| H-3 | Reformer |  | 3 | 15 |  | 1 | 40 | 4.0 | 800 |
| H-4 | Reformer |  | 3 | 15 |  | 2 | 40 | 3.5 | 800 |
| H-5 | FCC |  | 3 | 8 |  | 2 | 50 | 3.0 | 1200 |

1 = Refinery gas. 2 = Natural gas. 3 = No. 6 Fuel oil.

HEATER AND BOILER INFORMATION (continued)

| Identification No. | Heater description including unit location | Opacity |
|---|---|---|
| H-1 | Crude distillation unit | 0 |
| H-2 | Crude distillation unit | 0 |
| H-3 | Reformer | 0 |
| H-4 | Reformer | 10 |
| H-5 | FCC | 0 |

For Particulate, sulfur dioxide, and nitrogen oxide emission information.

| Type of Fuel used in Boilers and Heaters | Heat Content Btu/lb or Btu/scf | Sulfur Content |
|---|---|---|
| Refinery gas | 800 Btu/scf | 100 grains $H_2S$/scf |
| No. 6 Fuel oil | 6 Btu/bbl | 0.9% |

## TANK INFORMATION

| Tank Number | Capacity (Units) | Type (1) | Product Stored | True Vapor Pressure (Units) psia | Tank Color | Construction: Welded or Riveted | Vapor Controls (2) | Remarks* |
|---|---|---|---|---|---|---|---|---|
| 1 | 600 | C | Crude oil | 2.2 | Gray | Welded | F | |
| 2 | 600 | C | Crude oil | 2.2 | Gray | Welded | F | |
| 3 | 100 | C | Gas oil | <1.0 | Gray | Welded | N | |
| 4 | 100 | C | Gas oil | <1.0 | Gray | Welded | N | |
| 5 | 100 | C | Gas oil | <1.0 | Gray | Welded | N | |
| 6 | 25 | C | Diesel | 0.2 | Gray | Welded | N | |
| 7 | 75 | C | Unleaded gasoline | 5-12 | Gray | Welded | VR | Vapor recovery compressor system |
| 8 | 75 | C | Unleaded gasoline | 5-12 | Gray | Welded | VR | Vapor recovery compressor system |
| 9 | 560 | C | Regular gasoline | 5-12 | Gray | Welded | VR | Vapor recovery compressor system |
| 10 | 560 | C | Regular gasoline | 5-12 | Gray | Welded | VR | Vapor recovery compressor system |

Footnotes:

(1) C = fixed roof: F = floating roof; P = pressure; O = open top; S = spheroid; H = horizontal; U = underground

(2) N = None, CV = conservation vents; F = floating roof (SS = single seal; DS = double seal); VR = Vapor recovery (describe); VD = vapor disposal (describe); VB = vapor balance; SF = submerged fill

* Date installed, etc.

VOLATILE HYDROCARBON LOADING/UNLOADING FACILITIES

| LOADING FACILITY DESIGNATION | SOURCE | TYPE TRANSFER/SIZE (RR CARS, TRUCKS) | MONTHLY THRU-PUT (1000 GAL) | VAPOR CONTROL SYSTEM | SUBMERGED LOADING | PRODUCTS | |
|---|---|---|---|---|---|---|---|
| | | | | | | TYPE | VAPOR PRESSURE (PSIA) |
| Loading | | Truck | 1,500 | | yes (100%) | Gasoline | 10 |
| Loading | | Truck | 1,560 | | no | Propane<br>Butane | 200<br>60 |

## WASTEWATER TREATMENT

| Treatment facility | Observations | | | | |
|---|---|---|---|---|---|
| In-plant treatment: Sour water stripper | Noticeable emissions[a] | Disposition of sulfides[a] | | | |
| | Yes No | Incinerated Recovered in sulfur recovery unit | | | |
| Primary treatment: Gravity separators | Type(s) of separator | Gaps (or) leaks in cover: Inspect with hydrocarbon detector | a | Type of cover | Noticeable emissions[a] |
| | 3 API | 2<br>1 | Covered<br>Uncovered | fabric | Yes [✓ No] |
| Intermediate treatment: Dissolved air flotation unit and holding basin | Type(s) | Capacity of each | | | |
| | | | | | |
| Secondary treatment: Biological oxidation | Type(s) | Capacity of each | | | |
| | | | | | |
| Tertiary treatment | Type(s) | Capacity of each | | | |
| | | | | | |
| Solids disposal | Type(s) | Disposal[a] | | | |
| | | Onsite Offsite | | | |
| Surge storage capability | Type(s) | Capacity of each | | | |
| | | | | | |

[a] Circle one.

# LEAK DETECTION SURVEY LOG

Inspection level II

Sample size 20

Unit Gas Processing

Accept No. 5

Component Valves

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
| Gate valve | X | | X | | 100 ppm |
| Gate valve | X | | X | | 40 ppm |
| Control globe valve | X | | X | | 100 ppm |
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# APPENDIX M

## LEVEL III INSPECTION: BLANK CHECKLIST FORMS

This appendix provides the cover sheet and additional forms to be used in conducting a Level III inspection. When combined with the Level II checklist forms (Appendix K), this material constitutes a Level III inspection report.

LEVEL __ INSPECTION

AQCR ______

Date(s) of Inspection ____________

____________________________

Time In __________ Out __________

Company Name ________________________________________

Mailing Address ________________________________________

________________________________________________

Location of Facility ________________________________________

________________________________________________

(Include County or Parish)

Type of Industry ________________________________________

Form of Ownership ________________________________________

Corporate Address ________________________________________

________________________________________________

| Company Personnel | Name | Title | Phone |
|---|---|---|---|
| Responsible for Facility | | | |
| Responsible for Environmental Matters | | | |
| Company Personnel Contacted | | | |
| | | | |
| Confidentiality Statement given to | | | |
| EPA Personnel | | | |
| | | | |
| State or Local Agency Personnel | | | |
| | | | |

## ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTIONS

| Process unit | | |
|---|---|---|
| Crude distillation | | |
| Vacuum distillation | Number of ejectors | |
| | Type of ejectors | |
| | Type of condensers | |
| | Is hot well covered? | |
| Catalytic cracking | Reactor temperature, °F | |
| | CO boiler temperature, °F | |
| | Oxygen analyzer, % $O_2$ | |
| | ESP status: | |
| | Primary voltage, kW | |
| | Primary current, amp | |
| | Secondary current, amp | |
| | Hopper heaters (on, off) | |
| | Hopper level indicators (full, empty) | |
| Isomerization | Reactor temperature, °F | |

## ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTIONS

| Process unit | | |
|---|---|---|
| Polymerization | Reactor temperature, °F | |
| Alkylation | Reactor temperature, °F | |
| Hydrocracking | | |
| Catalytic reforming | Reactor temperature, °F<br>Reactor pressure, psig<br>Hydrogen pressure, psig | |
| Coking | | |

## ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTION

| Process unit | | |
|---|---|---|
| Visbreaking | | |
| Deasphalting | | |
| Hydrotreating | Reactor temperature, °F<br>Reactor pressure, psig<br>Hydrogen pressure, psig | |
| Wax production | | |
| Grease production | | |

## ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTION

| Process unit | | |
|---|---|---|
| Lube production | | |
| Asphalt | | |
| Gas processing | | |
| Sulfur plant | Air/acid gas ratio | |
| | Air/stripper gas ratio | |
| | Inlet catalytic reactor temperature, °F | |
| | Outlet catalytic reactor temperature, °F | |
| | Incinerator temperature, °F | |
| Furfural refining | | |

## ADDITIONAL PROCESS INFORMATION FOR LEVEL III INSPECTION

| Process unit | | |
|---|---|---|
| Amine treating | Hydrocarbon in acid gas feed | |

# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Isomerization

Component Valves

Sample size 20

Accept No. 2

| Description of source | Stream composition |  | Stream volatility |  | Maximum VOC reading |
|---|---|---|---|---|---|
|  | Gas | Liquid | High | Low |  |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Alkylation

Component Valves

Sample size 50

Accept No. 5

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Alkylation

Component Pump seals

Sample size 8

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Storage

Component Valves

Sample size 50

Accept No. 5

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Storage

Component Pump seals

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 3

Unit Storage

Accept No. 0

Component Compressor seals

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Loading

Component Valves

Sample size 50

Accept No. 5

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Loading

Component Pump seals

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 50

Unit Gas processing

Accept No. 5

Component Valves

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Gas processing

Component Pump seals

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Gas processing

Component Compressor seals

Sample size 3

Accept No. 0

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit FCC

Component Valves

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 8

Unit FCC

Accept No. 1

Component Pump seals

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit FCC

Component Compressor seals

Sample size 3

Accept No. 0

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Visbreaking

Component Valves

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 8

Unit Visbreaking

Accept No. 1

Component Pump seals

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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## LEAK DETECTION SURVEY LOG

Inspection level III

Unit Visbreaking

Component Compressor seals

Sample size 3

Accept No. 0

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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## LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrotreating

Component Valves

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrotreating

Component Pump seals

Sample size 8

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrotreating

Component Compressor seals

Sample size 3

Accept No. 0

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrocracking

Component Valves

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Hydrocracking

Component Pump seals

Sample size 8

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 3

Unit Hydrocracking

Accept No. 0

Component Compressor seals

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Reformer

Component Valves

Sample size 20

Accept No. 2

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Reformer

Component Pump seals

Sample size 8

Accept No. 1

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# LEAK DETECTION SURVEY LOG

Inspection level III

Unit Reformer

Component Compressor seals

Sample size 3

Accept No. 0

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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## LEAK DETECTION SURVEY LOG

Inspection level III

Sample size 20

Unit Distillation - atmospheric

Accept No. 2

Component Valves

| Description of source | Stream composition | | Stream volatility | | Maximum VOC reading |
|---|---|---|---|---|---|
| | Gas | Liquid | High | Low | |
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# GLOSSARY

The definitions herein are those in current use in the United States refining industry. Conversions of units of measure to the metric system have not been included in most cases, because the English system continues to dominate the industry.

An ASTM number is a reference to a testing method defined by the American Society for Testing and Materials.

ABSORPTION: An operation in which the significant or desired transfer of materials is from the vapor phase to the liquid phase. Absorption usually designates an operation in which liquid is supplied as a separate stream independent of the vapor being treated.

ACID HEAT TEST: A test indicative of unsaturated components in petroleum distillates. The test measures the amount of reaction of unsaturated hydrocarbons with sulfuric acid ($H_2SO_4$).

ADSORPTION: A separation process in which gas molecules condense or liquid molecules crystallize onto a solid that has a porous surface. The pore size dictates the selectivity of the solid for a particular solute.

ALKYLATE: The product of an alkylation process.

ALKYLATE BOTTOMS: A thick, dark-brown oil containing high-molecular-weight polymerization products of alkylation reactions.

ALKYLATION: A polymerization process uniting olefins and isoparaffins: particularly, the reacting of butylene and isobutane, with sulfuric acid or hydrofluoric acid as a catalyst, to produce a high-octane, low-sensitivity blending agent for gasoline.

ALUMINUM CHLORIDE TREATING: A process that improves the quality of steam-cracked naphthas by use of aluminum chloride ($AlCl_3$) as a catalyst. The process improves the color and odor of the naphtha by polymerization of undesirable olefins into resins. Aluminum chloride treating is also used when production of resins is desirable.

ANILINE POINT: The minimum temperature for complete miscibility of equal volumes of aniline and the test sample. The point test is considered an indication of the paraffinicity of the sample. The aniline point is also used in classifying the ignition quality of diesel fuels.

API GRAVITY: An arbitrary gravity indicator defined as:

$$°\text{API} = \frac{141.5}{\text{Specific gravity } 60/60°\text{F}} - 131.5$$

This formula allows representation of the specific gravity of oils, which on the 60/60° scale (density of substance at 60°F divided by the density of pure water at 60°F) varies over a range of only 0.776 by a scale that ranges from less than 0 (heavy residual oil) to 340 (methane). API gravities are not usually accompanied by temperature; they correspond to a temperature of 60°F unless otherwise indicated.

AROMATICS: Cyclic hydrocarbons in which five, six, or seven carbon atoms are linked in a ring structure with alternating double and single bonds. Common aromatics in refinery streams are benzene, toluene, xylene, and naphthalene.

ASTM: American Society for Testing and Materials.

ASTM DISTILLATION: A standardized laboratory batch process for distillation of naphthas and middle distillates carried out at atmospheric pressure without fractionation.

BARREL: 42 gallons.

BARRELS PER CALENDAR DAY (BPCD): Average flow rates based on operating 365 days per year.

BARRELS PER STREAM DAY (BPSD): Flow rates based on actual on-stream time of a unit or group of units. This notation equals barrels per calendar day divided by the service factor.

BATTERY LIMITS (BL): The periphery of the area surrounding any process unit, including the equipment used in the process.

B-B: Butane-butylene fraction.

BFOE: Barrels fuel oil equivalent based on net heating value (LHV) of 6,050,000 Btu per BFOE.

BITUMEN: That component of petroleum, asphalt, and tar products that will dissolve completely in carbon disulfide ($CS_2$). This dissolving ability permits a complete separation from foreign products not soluble in carbon disulfide.

BLENDING: One of the final operations in refining, in which two or more components are mixed to obtain a specified range of properties in the finished product.

BLOCKED OPERATION: Operation of a unit, e.g., a pipe still, under periodic change of feed or internal conditions that will yield a required range of raw products. Blocked operation is needed to meet critical specifications of various finished products. No mixed stocks are charged; therefore, the efficiency of operation is often increased because each charge stock is processed at its optimum operating conditions.

BOTTOMS: In general, the higher boiling residue that is removed from the bottom of a fractionating column.

BRIGHT STOCK: Heavy lube oils from which waxy paraffins and asphaltic compounds have been removed. Bright stock is the feed to a lube oil blending plant.

BROMINE INDEX: Measure of amount of bromine-reactive material in a sample; ASTM D-2710.

BROMINE NUMBER: Indicator of the degree of unsaturation in a test sample; ASTM D-1159.

CABP: Cubic average boiling point.

$$\text{CABP} = \sum_{i=1}^{h} X_{vi} T_{bi}^{1/3} \, {}^{3}$$

where

$X_{vi}$ = volume fraction of component i.

$T_{bi}$ = normal boiling point of component i.

CAFFEINE NUMBER: A value indicating the amount of carcinogenic compounds (high-molecular-weight aromatics, or "tars") in an oil.

CATALYST: A substance that assists or deters a chemical reaction but is not itself chemically changed as a result.

CATALYST/OIL RATIO (C/O): The weight of circulating catalyst fed to the reactor of a fluid-bed catalytic cracking unit, divided by the weight of the hydrocarbons charged during the same interval.

CATALYTIC CYCLE STOCK: The portion of a catalytic cracker effluent that is not converted to naphtha and lighter products. This material, generally at temperatures of 340°F or more, may either be completely recycled or it may be partly recycled, in which case the remainder is blended to products or further processed.

CETANE NUMBER: A number designating the percentage of pure cetane in a blend of cetane and alphamethyl-naphthalene that matches the ignition quality of a diesel fuel sample. This number, specified for middle distillate fuels, is synonymous with the octane number of gasolines.

CFR: Code of Federal Regulations.

CFR: Combined feed ratio. Ratio of total feed (including recycle) to fresh feed.

CHARACTERIZATION FACTOR: An index of feedstock quality, also useful for correlating data based on physical properties such as average boiling point and specific gravity.

CLAY TREATING: A process conducted at high temperatures and pressures, usually applied to thermally cracked naphthas to improve stability and color. Stability is increased by the adsorption and polymerization of reactive diolefins in the cracked naphtha. Clay treating is now used extensively for treating jet fuel to remove surface-active agents that adversely affect the wastewater separator.

CLOUD POINT: The temperature at which solidifiable compounds in a sample begin to crystallize or separate from the solution under prescribed conditions of chilling. Cloud point is a typical specification of middle distillate fuels; ASTM D-2500.

CONRADSON CARBON TEST: A test used to determine the amount of carbon residue left after evaporation and pyrolysis of an oil under specified conditions. Expressed as percent by weight; ASTM D-189.

CRACKING: The breaking down of higher-molecular-weight hydrocarbons to lighter components by application of heat. Cracking in the presence of a catalyst improves product yield and quality over those obtained in simple thermal cracking.

CRUDE ASSAY DISTILLATION: See fifteen/five distillation.

CUT: The portion of a crude that boils within certain temperature limits. Usually the limits are specified on a crude assay true boiling point basis.

CUT POINT: The temperature limit of a cut, usually on a true boiling point basis. ASTM distillation cut points are not uncommon.

DEBUTANIZER: A tower in which butane is removed by distillation from a hydrocarbon stream.

DEISOBUTANIZER: A distillation column in which isobutane is removed from a petroleum fraction.

DEWAXING: The removal of wax from lubricating oils, either by chilling and filtering or by solvent extraction.

DIESEL INDEX (DI): A measure of the ignition quality of a diesel fuel. The diesel index is defined as

$$\text{DI} = \text{gravity}\ \frac{(^\circ\text{API})\ \text{x aniline point}\ (^\circ\text{F})}{100}$$

The higher the diesel index, the higher the ignition quality of the fuel. By means of correlations unique to each crude and manufacturing process, this index can be used to predict cetane number if no standardized test for the latter is available.

DISTILLATE: A product of distillation, or the fluid condensed from the vapor driven off during distillation. Gasoline, naphtha, kerosene, and light lubricating oils are examples of distillates.

DISTILLATION: A physical separation process in which different hydrocarbon fractions are separated by means of heating, vaporization, fractionation, condensation, and cooling.

DOCTOR TEST: A method of determining the presence of mercaptan sulfur in petroleum products. This test is used for products in which a "sweet" odor is desirable for commercial reasons, especially naphthas; ASTM D-484.

DRY GAS: All methane ($C_1$) to propane ($C_3$) material, whether associated with a crude or produced as a byproduct of refinery processing. By convention, hydrogen is often included in dry-gas yields.

END POINT (EP): Upper temperature limit of a distillation.

ENDOTHERMIC REACTION: A reaction in which heat must be added to maintain reactants and products at a constant temperature.

EXOTHERMIC REACTION: A reaction in which heat is evolved. Alkylation, polymerization, and hydrogenation reactions are exothermic.

FBP: The final boiling point of a cut, in degrees Fahrenheit, usually on an ASTM distillation basis.

FIFTEEN/FIVE (15/5) DISTILLATION: A laboratory batch distillation performed in a theoretical plate fractionating column with a three-to-one reflux ratio. A good fractionation results in accurate boiling temperatures. For this reason, the distillation is referred to as the true-boiling-point (TBP) distillation.

FIXED CARBON: The organic portion of the residual coke obtained when hydrocarbon products are evaporated to dryness in the absence of air..

FLASH POINT: The temperature to which a product must be heated under prescribed conditions to release sufficient vapor to form a mixture with air that can be readily ignited. Flash point is generally used as an indication of the fire and explosion potential of a product; ASTM D-56, D-92, D-93, E-134, D-1310.

FLUX: A material blended in small amounts with a product to meet some specification of the final product.

FOE: Fuel oil equivalent.

FRACTIONATION: A countercurrent operation in which a vapor mixture is repeatedly brought in contact with liquids having nearly the same composition as the respective vapors. Liquids are at their boiling points; hence part of the vapor is condensed and part of the liquid is vaporized during each contact. In a series of contact treatments, the vapor finally becomes rich in low-boiling components, and the liquid becomes rich in high-boiling components.

FRACTIONATOR: A closed cylindrical tower arranged with trays through which distilled gas/liquid is caused to bubble. The trays retain a portion of the condensed liquid and thus separate the heavier fractions of the gas/liquid from the lighter fractions of gas/liquid. Also called stabilizer column, fractionating tower, or bubble tower.

FREE CARBON: The organic matter in tars that is insoluble in carbon disulfide ($CS_2$).

FUEL OIL EQUIVALENT (FOE): The heating value of a standard barrel of fuel oil, equal to $6.05 \times 10^6$ Btu. On a yield chart, dry gas and refinery fuel gas are usually expressed in FOE barrels.

FVT: The final vapor temperature of a cut, in degrees Fahrenheit. Boiling ranges expressed in this manner are usually on a crude assay, true-boiling-point basis.

GAS OIL: That material boiling within the general range of 300° to 750°F. This range usually includes kerosene, diesel fuel, heating oils, and light fuel oils. Actual initial and final cut points are determined by specifications of the desired products.

GHV: Gross heating value of fuels.

GILSONITE: A trade name for uintaite, a black, lustrous asphalt.

HEART CUT RECYCLE: The unconverted portion of catalytically cracked material that is recycled to the catalytic cracker. This recycle is usually in the boiling range of the feed and, by definition, contains no bottoms. Recycle allows less severe operation and suppresses the cracking of desirable products.

HEMPEL DISTILLATION: Routine distillation method of the U.S. Bureau of Mines. Results are frequently used interchangeably with those of true boiling point (TBP) or 15/5 distillation.

IBP: Initial boiling point of a cut, usually on an ASTM distillation basis.

ISOBUTANE: A branched-chain butane compound ($C_4H_{10}$).

ISOMERIZATE: The product of an isomerization process.

ISOMERIZATION: The rearrangement of straight-chain hydrocarbon molecules to form branched-chain products. Pentanes and hexanes, which are difficult to reform, are isomerized by use of aluminum chloride or precious-metal catalysts to form gasoline-blending components of high octane value. Normal butane may be isomerized to provide a portion of the isobutane feed needed for alkylation processes.

IVT: Initial vapor temperature of a cut, in degrees Fahrenheit, usually based on a crude assay distillation.

KEROSENE: A middle-distillate product composed of material of 300° to 550° FVT. The exact cut is determined by various specifications of the finished kerosene.

LAMP SULFUR: The total amount of sulfur present per unit of liquid product. The analysis is made by burning a sample so that the sulfur content is converted to sulfur dioxide, which can be measured quantitatively. Lamp sulfur is a critical specification of all motor, tractor, and burner fuels; ASTM D-1266, D-2784.

LEAD SUSCEPTIBILITY: The variation of the octane number of a gasoline as a function of the tetraethyl lead content.

LHSV: Liquid hour space velocity: volume of feed per hour per volume of catalyst.

LHV: Lower heating value of fuels (net heat of combustion).

LIGHT ENDS: Hydrocarbon fractions in the butane and lighter boiling range.

LIQUEFIED PETROLEUM GAS (LPG): Liquefied light-end gases used for home heating and cooking. This gas is usually 95 percent propane, and the remainder consists of equal parts of ethane and butane.

LNG: Liquefied natural gas.

LUBRICATING OILS: A fluid used to reduce friction when introduced between solid surfaces. The major constituents of lubricating oils are from distillate or residual fractions of the crude. The manufacture and compounding of lubricating oils are highly specialized and confined to a few major refineries. Some refineries produce lube base stocks (bright oils), which are transferred to a refinery specializing in lube oil finishing and compounding.

MABP: Molal average boiling point.

$$\text{MABP} = \sum_{i=1}^{h} X_i T_{bi}$$

MeABP: Mean average boiling point.

$$\text{MeABP} = \frac{\text{MABP} + \text{CABP}}{2}$$

METAXYLENE: One of the three isomers of xylene.

MID-BOILING POINT: That temperature, usually based on a crude assay distillation, at which one-half of the material of a cut has been vaporized.

MIDDLE DISTILLATES: Atmospheric pipe-still cuts boiling in the range of 300° to 700° FVT. The exact cut is determined by the specifications of the products.

MID-PERCENT POINT: The vapor temperature at which one-half of the material of a cut has been vaporized. Mid-percent point is often used in place of temperature to characterize a cut.

MONOMER: A reactive species fed to a polymerization unit which reacts in a repetitive manner to form long polymer chains. Typical monomers are ethylene, propylene, styrene, and vinyl chloride.

MOTOR OCTANE NUMBER (MON, ASTM ON, F-2): The percentage by volume of isooctane in a blend of isooctane and n-heptane that knocks with the same intensity as a fuel being tested. A standardized test engine operating under standardized conditions (900 rpm) is used to approximate cruising conditions of an automobile; ASTM D-2723.

NAPHTHA: A pipe-still cut in the range of 160° to 420°F. Pentanes ($C_5$) are the lower boiling naphthas, at approximately 160°F. Naphthas are subdivided according to the actual pipe-still cuts into light, intermediate, heavy, and very heavy virgin naphthas. The quantity of the individual cut varies with the crude. A typical pipe-still operation would yield:

$C_5$-160°F - Light virgin naphtha
160°-280°F - Intermediate virgin naphtha
280°-330°F - Heavy virgin naphtha
330°-420°F - Very heavy virgin naphtha

Naphthas, the major constituents of gasoline, generally must be further processed to make suitable quality gasoline.

NEUTRALIZATION NUMBER: The quantity of acid or base that is required to neutralize all basic or acidic components present in a sample of specified quantity. This is a measure of the amount of oxidation of a product in storage or in service; ASTM D-664, D-974.

OLEFIN SPACE VELOCITY: Volume of olefin charged per hour to an alkylation reactor, divided by the volume of acid in the reactor.

ORTHOXYLENE: One of the three isomers of xylene.

PARAFFINIC RAFFINATES: Straight-chain, saturated hydrocarbon fraction remaining after distillation or extraction.

PARAXYLENE: One of the three isomers of xylene.

PERFORMANCE RATING: A method of expressing the quality of a high-octane gasoline relative to isooctane. This rating is used for fuels of higher quality than isooctane.

PETROLEUM FRACTION: A major product that may be separated from petroleum, i.e., gasoline, kerosene, gas oil; an elementary compound with a constant boiling range. Heavier fractions have higher boiling ranges than lighter fractions.

PIPE STILL: A heater or furnace containing tubes through which oil is pumped while being heated or vaporized. Pipe stills are fired with waste gas, natural gas, or heavy oils. With provision for rapid heating under conditions of high pressure and temperature, pipe stills are useful for thermal cracking as well as distillation applications.

POLYMERIZATION: The combination of two or more unsaturated molecules to form a molecule of higher molecular weight. Propylenes and butylenes are the primary feed material for refinery polymerization processes, which use solid or liquid phosphoric acid catalysts.

POUR BLENDING INDEX (PBI): An empirical quantity related to pour point, which allows volumetric blending of pour points of various blend components. This method of blending is most accurate for blending of similar fractions of the same crude.

POUR POINT: The lowest temperature at which a petroleum oil will flow or pour when it is chilled, and poured without disturbance at a standard rate. Pour point is a critical specification of middle distillate products used in cold climates; ASTM D-99.

PROPYLENE: A hydrocarbon compound containing three carbon atoms, seven hydrogen atoms, and a double bond making it unsaturated and highly reactive.

RAFFINATE: The residue recovered from an extraction process. An example is the $SO_2$ extraction of raw kerosene. The $SO_2$ raffinate is relatively free of aromatics and other impurities that have poor burning characteristics.

RAMSBOTTOM CARBON: Recommended to replace Conradson Carbon; ASTM D-524. Carbon residue expressed in percent by weight.

RECONSTITUTED CRUDE: A crude to which has been added a specific crude fraction for the purpose of meeting some product volume unattainable with the original crude.

REDUCED CRUDE: A crude whose API gravity has been reduced by distillation of the lighter, lower boiling constituents.

REFORMATE: A reformed naphtha that is upgraded in octane value by means of catalytic or thermal reforming.

REFORMING: The conversion of naphtha fractions to products of higher octane value. Thermal reforming is essentially a light cracking process applied to heavy naphthas to increase the yields of hydrocarbons in the gasoline boiling range. Catalytic reforming is applied to various straight-run cracked naphtha fractions and consists primarily of the dehydrogenation of naphthenes to aromatics. A number of catalysts are used, including platinum, platinum-rhenium, and the oxides of aluminum, chromium, molybdenum, cobalt, and silicon. A high partial pressure of hydrogen is maintained to prevent the formation of excessive coke.

REID VAPOR PRESSURE (RVP): The vapor pressure of a product determined in a volume of air 4 times the liquid volume at 100°F. Reid vapor pressure is an indication of the vapor-lock tendency of a motor gasoline, as well as of explosion and evaporation hazards; ASTM D-323.

RESEARCH OCTANE NUMBER (RON, CFRR, F-1): The percentage by volume of isooctane in a blend of isooctane and n-heptane that knocks with the same intensity as a fuel being tested. A standardized test engine operating under standardized conditions (600 rpm) is used. Results are comparable to those obtained in an automatic engine operated at low speed; ASTM D-2722.

ROAD OCTANE NUMBER: The percentage by volume of isooctane that would be required in a blend of isooctane and n-heptane to give incipient knock in an automobile engine operating under the same conditions of engine load, speed, and degree of spark advance as that of a fuel being tested.

SCF: Volume of gas in "standard cubic feet." Standard conditions in petroleum and natural gas usage refer to a pressure base of 14.696 psia and a temperature base of 60°F.

SELECTIVITY: Ratio of desirable to undesirable products.

SENSITIVITY: The difference between the research octane number and the motor octane number of a given gasoline. Alkylate is an excellent low-sensitivity gasoline component.

SERVICE FACTOR: A quantity that relates the actual on-stream time of a process unit to the total time available for use. Service factors include both expected and unexpected unit shutdowns.

SEVERITY: The degree of intensity of the operating conditions of a process unit. Severity may be indicated by clear research octane number of the product, percent yield of the product, or operating conditions alone.

SMOKE POINT: A test measuring the burning quality of jet fuels, kerosene, and illuminating oils. It is defined as the height of the flame in millimeters beyond which smoking takes place; ASTM D-1322.

SOUR OR SWEET CRUDE: A general classification of crudes according to sulfur content. Various definitions are available:

Sour Crude: A crude that contains sulfur in amounts greater than 0.5 to 1 percent or that contains 0.05 $ft^3$ or more of hydrogen sulfide ($H_2S$) per 100 gal, except West Texas crude, which is always considered sour regardless of its hydrogen sulfide content. Arabian crudes, although of high sulfur content, are not always considered sour because they do not contain highly active sulfur compounds.

Sweet Crude: A sweet crude contains little or no dissolved hydrogen sulfide and relatively small amounts of mercaptans and other sulfur compounds.

SPACE VELOCITY: The volume (or weight) of gas or liquid passing through a given catalyst or reaction space per unit time, divided by the volume (or weight) of catalyst through which the fluid passes. High space velocities correspond to short reaction times. See LHSV and WHSV.

STABILIZATION: A fractionation operation conducted for the purpose of removing high-vapor-pressure components.

STRAIGHT-RUN GASOLINE: An uncracked gasoline fraction distilled from crude. Straight-run gasolines contain primarily paraffinic hydrocarbons and have lower octane values than cracked gasolines from the same feedstocks.

STRIPPING: An operation in which the significant or desired transfer of material is from the liquid to the vapor phase.

SWEETENING: The removal of sulfur compounds or their conversion to innocuous substances in a petroleum product by any of several processes (doctor treating, caustic and water washing, etc.).

SYNTHETIC CRUDE: Wide-boiling-range product of catalytic cracking.

TA: Total alkylate.

TAIL GAS: Light gases ($C_1$ to $C_3$ and $H_2$) produced as byproducts of refinery processing.

TBP DISTILLATION: See fifteen-five (15/5) distillation.

TETRAETHYL LEAD (TEL): An antiknock additive for gasoline.

THEORETICAL PLATE: A theoretical contacting unit useful in distillation calculations. Vapors and liquid leaving any such unit are required to be in equilibrium under the applicable conditions of temperature and pressure. An actual fractionator tray or plate is generally less effective than a theoretical plate. The ratio of the number of theoretical plates required to perform a given distillation separation to the number of actual plates used gives the tray efficiency of the fractionator.

TOPPING: Removal by distillation of the light products from crude oil, leaving in the still all the heavier constituents.

TREAT GAS: Light gas, usually high in hydrogen, which is required for refinery hydrotreating processes such as hydrodesulfurization. The treat gas for hydrodesulfurization is usually the tail gas from catalytic reforming.

TUBE STILL: See pipe still.

U.S. BUREAU OF MINES ROUTINE METHOD DISTILLATION: See Hempel distillation.

VAPOR LOCK INDEX: A measure of the tendency of a gasoline to generate excessive vapors in the fuel line, thus causing displacement of liquid fuel and subsequent interruption of normal engine operation. The vapor lock index generally is related to RVP and to percentages distilled at 158°F.

VIRGIN STOCKS: Petroleum oils that have not been cracked or otherwise subjected to any treatment that would produce appreciable chemical change.

VISCOSITY: The property of liquids under flow conditions that causes them to resist instantaneous change of shape or instantaneous rearrangement of their parts due to internal friction. Viscosity is generally measured as the number of seconds, at a definite temperature, required for a standard quantity of oil to flow through a standard apparatus.

Common viscosity scales in use are Saybolt Universal, Saybolt Furol, and Kinematic (Stokes).

VOLATILITY FACTOR: An empirical quantity that indicates good gasoline performance with respect to volatility. It involves actual automobile operating conditions and climatic factors. The volatility factor is generally defined as a function of RVP, and of percentages distilled at 158° and 212°F. This factor is used to predict the vapor-lock tendency of a gasoline.

WABP: Weight average boiling point.

$$\mathrm{WABP} = \sum_{i=1}^{n} X_{wi} T_{bi}$$

where

$X_{wi}$ = weight fraction of component i.

WHSV: Weight hour space velocity: weight of feed per hour per weight of catalyst.

WICK CHAR TEST: A test used to indicate the burning quality of a kerosene or illuminating oil. Wick char is defined as the weight of deposits remaining on the wick after a specified quantity of sample is burned.

XYLENE: Special name given to dimethylbenzene.

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