## 5.1 Petroleum Refining[1]

### 5.1.1 General Description

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry. Petroleum refinery activities start with receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and they terminate with storage preparatory to shipping the refined products from the refinery.

The petroleum refining industry employs a wide variety of processes. A refinery's processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. The example refinery flow scheme presented in Figure 5.1-1 shows the general processing arrangement used by refineries in the United States for major refinery processes. The arrangement of these processes will vary among refineries, and few, if any, employ all of these processes. Petroleum refining processes having direct emission sources are presented on the figure in bold-line boxes.

Listed below are 5 categories of general refinery processes and associated operations:

1. Separation processes
    a. Atmospheric distillation
    b. Vacuum distillation
    c. Light ends recovery (gas processing)
2. Petroleum conversion processes
    a. Cracking (thermal and catalytic)
    b. Reforming
    c. Alkylation
    d. Polymerization
    e. Isomerization
    f. Coking
    g. Visbreaking
3. Petroleum treating processes
    a. Hydrodesulfurization
    b. Hydrotreating
    c. Chemical sweetening
    d. Acid gas removal
    e. Deasphalting
4. Feedstock and product handling
    a. Storage
    b. Blending
    c. Loading
    d. Unloading
5. Auxiliary facilities
    a. Boilers
    b. Waste water treatment
    c. Hydrogen production
    d. Sulfur recovery plant

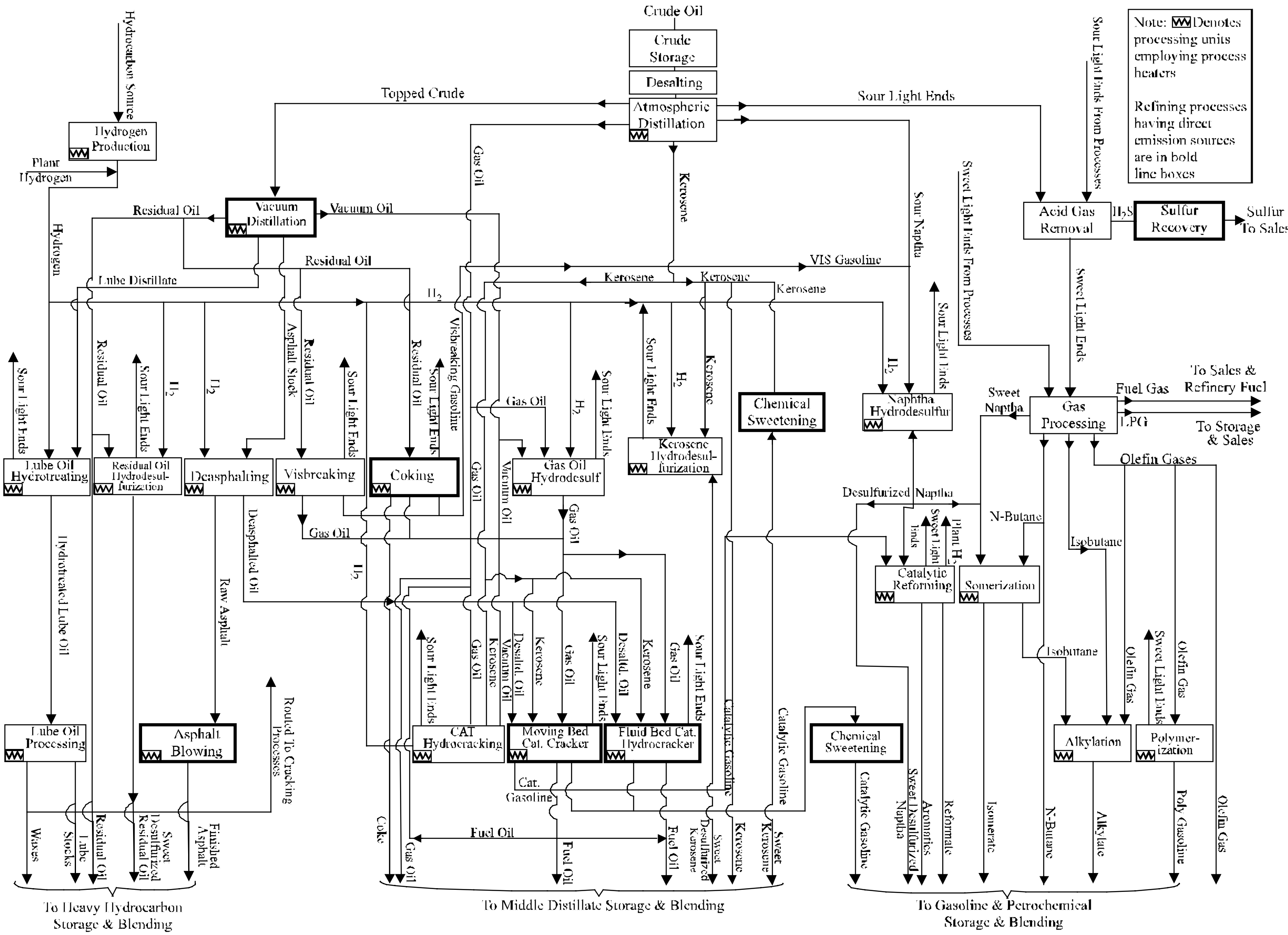


Figure 5.1-1. Schematic of an example integrated petroleum refinery.

e. Cooling towers
f. Blowdown system
g. Compressor engines

These refinery processes are defined below, and their emission characteristics and applicable emission control technology are discussed.

5.1.1.1 Separation Processes -

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using 3 petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery (gas processing). Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons with small amounts of impurities including sulfur, nitrogen, oxygen, and metals. Refinery separation processes separate these crude oil constituents into common boiling-point fractions.

5.1.1.2 Conversion Processes -

To meet the demands for high-octane gasoline, jet fuel, and diesel fuel, components such as residual oils, fuel oils, and light ends are converted to gasolines and other light fractions. Cracking, coking, and visbreaking processes are used to break large petroleum molecules into smaller ones. Polymerization and alkylation processes are used to combine small petroleum molecules into larger ones. Isomerization and reforming processes are applied to rearrange the structure of petroleum molecules to produce higher-value molecules of a similar molecular size.

5.1.1.3 Treating Processes -

Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable products and by removing objectionable elements. Undesirable elements such as sulfur, nitrogen, and oxygen are removed by hydrodesulfurization, hydrotreating, chemical sweetening, and acid gas removal. Treating processes, employed primarily for the separation of petroleum products, include such processes as deasphalting. Desalting is used to remove salt, minerals, grit, and water from crude oil feedstocks before refining. Asphalt blowing is used for polymerizing and stabilizing asphalt to improve its weathering characteristics.

5.1.1.4 Feedstock And Product Handling -

The refinery feedstock and product handling operations consist of unloading, storage, blending, and loading activities.

5.1.1.5 Auxiliary Facilities -

A wide assortment of processes and equipment not directly involved in the refining of crude oil is used in functions vital to the operation of the refinery. Examples are boilers, waste water treatment facilities, hydrogen plants, cooling towers, and sulfur recovery units. Products from auxiliary facilities (clean water, steam, and process heat) are required by most process units throughout the refinery.

## 5.1.2 Process Emission Sources And Control Technology

This section presents descriptions of those refining processes that are significant air pollutant contributors. Process flow schemes, emission characteristics, and emission control technology are discussed for each process. Table 5.1-1 lists the emission factors for direct-process emissions in

Table 5.1-1 (Metric And English Units). EMISSION FACTORS FOR PETROLEUM REFINERIES[a]

| Process | Particulate | Sulfur Oxides (as $SO_2$) | Carbon Monoxide | Total Hydro-carbons[b] | Nitrogen Oxides (as $NO_2$) | Aldehydes | Ammonia | EMISSION FACTOR RATING |
|---|---|---|---|---|---|---|---|---|
| Boilers and process heaters | | | | | | | | |
| Fuel oil | See Section 1.3 - "Fuel Oil Combustion" | | | | | | | |
| Natural gas | See Section 1.4 - "Natural Gas Combustion" | | | | | | | |
| Fluid catalytic cracking units (FCC)[c] | | | | | | | | |
| Uncontrolled | | | | | | | | |
| kg/$10^3$ L fresh feed | 0.695 (0.267 to 0.976) | 1.413 (0.286 to 1.505) | 39.2 | 0.630 | 0.204 (0.107 to 0.416) | 0.054 | 0.155 | B |
| lb/$10^3$ bbl fresh feed | 242 (93 to 340) | 493 (100 to 525) | 13,700 | 220 | 71.0 (37.1 to 145.0) | 19 | 54 | B |
| Electrostatic precipitator and CO boiler | | | | | | | | |
| kg/$10^3$ L fresh feed | 0.128[d] (0.020 to 0.428) | 1.413 (0.286 to 1.505) | Neg | Neg | 0.204[e] (0.107 to 0.416) | Neg | Neg | B |
| lb/$10^3$ bbl fresh feed | 45[d] (7 to 150) | 493 (100 to 525) | Neg | Neg | 71.0[e] (37.1 to 145.0) | Neg | Neg | B |
| Moving-bed catalytic cracking units[f] | | | | | | | | |
| kg/$10^3$ L fresh feed | 0.049 | 0.171 | 10.8 | 0.250 | 0.014 | 0.034 | 0.017 | B |
| lb/$10^3$ bbl fresh feed | 17 | 60 | 3,800 | 87 | 5 | 12 | 6 | B |
| Fluid coking units[g] | | | | | | | | |
| Uncontrolled | | | | | | | | |
| kg/$10^3$ L fresh feed | 1.50 | ND | ND | ND | ND | ND | ND | C |
| lb/$10^3$ bbl fresh feed | 523 | ND | ND | ND | ND | ND | ND | C |
| Electrostatic precipitator and CO boiler | | | | | | | | |
| kg/$10^3$ L fresh feed | 0.0196 | ND | Neg | Neg | ND | Neg | Neg | C |
| lb/$10^3$ bbl fresh feed | 6.85 | ND | Neg | Neg | ND | Neg | Neg | C |

Table 5.1-1 (cont.).

| Process | Particulate | Sulfur Oxides (as $SO_2$) | Carbon Monoxide | Total Hydro-carbons[b] | Nitrogen Oxides (as $NO_2$) | Aldehydes | Ammonia | EMISSION FACTOR RATING |
|---|---|---|---|---|---|---|---|---|
| Delayed coking units | ND | ND | ND | ND | ND | ND | ND | NA |
| Compressor engines[h] | | | | | | | | |
| Reciprocating engines | | | | | | | | |
| $kg/10^3\ m^3$ gas burned | Neg | 2s[j] | 7.02 | 21.8 | 55.4 | 1.61 | 3.2 | B |
| $lb/10^3\ ft^3$ gas burned | Neg | 2s | 0.43 | 1.4 | 3.4 | 0.1 | 0.2 | B |
| Gas turbines | | | | | | | | |
| $kg/10^3\ m^3$ gas burned | Neg | 2s | 1.94 | 0.28 | 4.7 | ND | ND | B |
| $lb/10^3\ ft^3$ gas burned | Neg | 2s | 0.12 | 0.02 | 0.3 | ND | ND | B |
| Blowdown systems[k] | | | | | | | | |
| Uncontrolled | | | | | | | | |
| $kg/10^3$ L refinery feed | Neg | Neg | Neg | 1,662 | Neg | Neg | Neg | C |
| $lb/10^3$ bbl refinery feed | Neg | Neg | Neg | 580 | Neg | Neg | Neg | C |
| Vapor recovery system and flaring | | | | | | | | |
| $kg/10^3$ L refinery feed | Neg | 0.077 | 0.012 | 0.002 | 0.054 | Neg | Neg | C |
| $lb/10^3$ bbl refinery feed | Neg | 26.9 | 4.3 | 0.8 | 18.9 | Neg | Neg | C |
| Vacuum distillation column condensers[m] | | | | | | | | |
| Uncontrolled | | | | | | | | |
| $kg/10^3$ L vacuum feed | Neg | Neg | Neg | 0.14 (0 to 0.37) | Neg | Neg | Neg | C |
| $lb/10^3$ bbl vacuum feed | Neg | Neg | Neg | 50 (0 to 130) | Neg | Neg | Neg | C |
| Controlled (vented to heater or incinerator) | Neg | Neg | Neg | Neg | Neg | Neg | Neg | C |

Table 5.1-1 (cont.).

| Process | Particulate | Sulfur Oxides (as $SO_2$) | Carbon Monoxide | Total Hydro-carbons[b] | Nitrogen Oxides (as $NO_2$) | Aldehydes | Ammonia | EMISSION FACTOR RATING |
|---|---|---|---|---|---|---|---|---|
| Claus plant and tail gas treatment | See Section 8.13 - "Sulfur Recovery" | | | | | | | |

[a] Numbers in parentheses indicate range of values observed. Neg = negligible. ND = no data.
[b] Overall, less than 1 weight % of total hydrocarbon emissions is methane.
[c] References 2-8.
[d] Under the New Source Performance Standards, controlled FCC regenerators must have particulate emissions lower than 0.054 kg/$10^3$ L (19 lb/$10^3$ bbl) fresh feed.
[e] May be higher, from the combustion of ammonia.
[g] Reference 2.
[g] Reference 5.
[h] References 9-10.
[j] Based on 100% combustion of sulfur to $SO_2$. s = refinery gas sulfur content (in kg/1000 $m^3$ or lb/1000 $ft^3$, depending on desired units for emission factor).
[k] References 2,11.
[m] References 2,12-13. If refinery feed rate is known, rather than vacuum feed rate, assume vacuum feed is 36% of refinery feed. Refinery feed rate is defined as the crude oil feed rate to the atmospheric distillation column.

petroleum refineries. Factors are expressed in units of kilograms per 1000 liters (kg/$10^3$ L) or kilograms per 1000 cubic meters (kg/$10^3$ $m^3$) and pounds per 1000 barrels (lb/$10^3$ bbl) or pounds per 1000 cubic feet (lb/$10^3$ $ft^3$). The following process emission sources are discussed here:

1. Vacuum distillation
2. Catalytic cracking
3. Thermal cracking processes
4. Utility boilers
5. Heaters
6. Compressor engines
7. Blowdown systems
8. Sulfur recovery

5.1.2.1 Vacuum Distillation -

Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high boiling-point hydrocarbons. When distilled at atmospheric pressures, the crude oil decomposes and polymerizes and will foul equipment. To separate topped crude into components, it must be distilled in a vacuum column at a very low pressure and in a steam atmosphere.

In the vacuum distillation unit, topped crude is heated with a process heater to temperatures ranging from 370 to 425°C (700 to 800°F). The heated topped crude is flashed into a multitray vacuum distillation column operating at absolute pressures ranging from 350 to 1400 kilograms per square meter (kg/$m^2$) (0.5 to 2 pounds per square inch absolute [psia]). In the vacuum column, the topped crude is separated into common boiling-point fractions by vaporization and condensation. Stripping steam is normally injected into the bottom of the vacuum distillation column to assist the separation by lowering the effective partial pressures of the components. Standard petroleum fractions withdrawn from the vacuum distillation column include lube distillates, vacuum oil, asphalt stocks, and residual oils. The vacuum in the vacuum distillation column is usually maintained by the use of steam ejectors but may be maintained by the use of vacuum pumps.

The major sources of atmospheric emissions from the vacuum distillation column are associated with the steam ejectors or vacuum pumps. A major portion of the vapors withdrawn from the column by the ejectors or pumps is recovered in condensers. Historically, the noncondensable portion of the vapors has been vented to the atmosphere from the condensers. There are approximately 0.14 kg of noncondensable hydrocarbons per $m^3$ (50 lb/$10^3$ bbl) of topped crude processed in the vacuum distillation column.[2,12-13] A second source of atmospheric emissions from vacuum distillation columns is combustion products from the process heater. Process heater requirements for the vacuum distillation column are approximately 245 megajoules per cubic meter (MJ/$m^3$) (37,000 British thermal units per barrel [Btu/bbl]) of topped crude processed in the vacuum column. Process heater emissions and their control are discussed below. Fugitive hydrocarbon emissions from leaking seals and fittings are also associated with the vacuum distillation unit, but these are minimized by the low operating pressures and low vapor pressures in the unit. Fugitive emission sources are also discussed later.

Control technology applicable to the noncondensable emissions vented from the vacuum ejectors or pumps includes venting into blowdown systems or fuel gas systems, and incineration in furnaces or waste heat boilers.[2,12-13] These control techniques are generally greater than 99 percent efficient in the control of hydrocarbon emissions, but they also contribute to the emission of combustion products.

5.1.2.2 Catalytic Cracking -

Catalytic cracking, using heat, pressure, and catalysts, converts heavy oils into lighter products with product distributions favoring the more valuable gasoline and distillate blending components. Feedstocks are usually gas oils from atmospheric distillation, vacuum distillation, coking, and deasphalting processes. These feedstocks typically have a boiling range of 340 to 540°C (650 to 1000°F). All of the catalytic cracking processes in use today can be classified as either fluidized-bed or moving-bed units.

5.1.2.2.1 Fluidized-bed Catalytic Cracking (FCC) -

The FCC process uses a catalyst in the form of very fine particles that act as a fluid when aerated with a vapor. Fresh feed is preheated in a process heater and introduced into the bottom of a vertical transfer line or riser with hot regenerated catalyst. The hot catalyst vaporizes the feed, bringing both to the desired reaction temperature, 470 to 525°C (880 to 980°F) The high activity of modern catalysts causes most of the cracking reactions to take place in the riser as the catalyst and oil mixture flows upward into the reactor. The hydrocarbon vapors are separated from the catalyst particles by cyclones in the reactor. The reaction products are sent to a fractionator for separation.

The spent catalyst falls to the bottom of the reactor and is steam stripped as it exits the reactor bottom to remove absorbed hydrocarbons. The spent catalyst is then conveyed to a regenerator. In the regenerator, coke deposited on the catalyst as a result of the cracking reactions is burned off in a controlled combustion process with preheated air. Regenerator temperature is usually 590 to 675°C (1100 to 1250°F). The catalyst is then recycled to be mixed with fresh hydrocarbon feed.

5.1.2.2.2 Moving-bed Catalytic Cracking-

In the moving-bed system, typified by the Thermafor Catalytic Cracking (TCC) units, catalyst beads (~0.5 centimeters [cm] [0.2 inches (in.)]) flow into the top of the reactor, where they contact a mixed-phase hydrocarbon feed. Cracking reactions take place as the catalyst and hydrocarbons move concurrently downward through the reactor to a zone where the catalyst is separated from the vapors. The gaseous reaction products flow out of the reactor to the fractionation section of the unit. The catalyst is steam stripped to remove any adsorbed hydrocarbons. It then falls into the regenerator, where coke is burned from the catalyst with air. The regenerated catalyst is separated from the flue gases and recycled to be mixed with fresh hydrocarbon feed. The operating temperatures of the reactor and regenerator in the TCC process are comparable to those in the FCC process.

Air emissions from catalytic cracking processes are (1) combustion products from process heaters and (2) flue gas from catalyst regeneration. Emissions from process heaters are discussed below. Emissions from the catalyst regenerator include hydrocarbons, oxides of sulfur, ammonia, aldehydes, oxides of nitrogen, cyanides, carbon monoxide (CO), and particulates (Table 5.1-1). The particulate emissions from FCC units are much greater than those from TCC units because of the higher catalyst circulation rates used.[2-3,5]

FCC particulate emissions are controlled by cyclones and/or electrostatic precipitators. Particulate control efficiencies are as high as 80 to 85 percent.[3,5] Carbon monoxide waste heat boilers reduce the CO and hydrocarbon emissions from FCC units to negligible levels.[3] TCC catalyst regeneration produces similar pollutants to FCC units, but in much smaller quantities (Table 5.1-1). The particulate emissions from a TCC unit are normally controlled by high-efficiency cyclones. Carbon monoxide and hydrocarbon emissions from a TCC unit are incinerated to negligible levels by passing the flue gases through a process heater firebox or smoke plume burner. In some installations, sulfur oxides are removed by passing the regenerator flue gases through a water or caustic scrubber.[2-3,5]

5.1.2.3 Thermal Cracking -

Thermal cracking processes include visbreaking and coking, which break heavy oil molecules by exposing them to high temperatures.

5.1.2.3.1 Visbreaking -

Topped crude or vacuum residuals are heated and thermally cracked (455 to 480°C, 3.5 to 17.6 $kg/cm^2$ [850 to 900°F, 50 to 250 pounds per square inch gauge (psig)]) in the visbreaker furnace to reduce the viscosity, or pour point, of the charge. The cracked products are quenched with gas oil and flashed into a fractionator. The vapor overhead from the fractionator is separated into light distillate products. A heavy distillate recovered from the fractionator liquid can be used as either a fuel oil blending component or catalytic cracking feed.

5.1.2.3.2 Coking -

Coking is a thermal cracking process used to convert low value residual fuel oil to higher-value gas oil and petroleum coke. Vacuum residuals and thermal tars are cracked in the coking process at high temperature and low pressure. Products are petroleum coke, gas oils, and lighter petroleum stocks. Delayed coking is the most widely used process today, but fluid coking is expected to become an important process in the future.

In the delayed coking process, heated charge stock is fed into the bottom of a fractionator, where light ends are stripped from the feed. The stripped feed is then combined with recycle products from the coke drum and rapidly heated in the coking heater to a temperature of 480 to 590°C (900 to 1100°F). Steam injection is used to control the residence time in the heater. The vapor-liquid feed leaves the heater, passing to a coke drum where, with controlled residence time, pressure (1.8 to 2.1 $kg/cm^2$ [25 to 30 psig]), and temperature (400°C [750°F]), it is cracked to form coke and vapors. Vapors from the drum return to the fractionator, where the thermal cracking products are recovered.

In the fluid coking process, typified by Flexicoking, residual oil feeds are injected into the reactor, where they are thermally cracked, yielding coke and a wide range of vapor products. Vapors leave the reactor and are quenched in a scrubber, where entrained coke fines are removed. The vapors are then fractionated. Coke from the reactor enters a heater and is devolatilized. The volatiles from the heater are treated for fines and sulfur removal to yield a particulate-free, low-sulfur fuel gas. The devolatilized coke is circulated from the heater to a gasifier where 95 percent of the reactor coke is gasified at high temperature with steam and air or oxygen. The gaseous products and coke from the gasifier are returned to the heater to supply heat for the devolatilization. These gases exit the heater with the heater volatiles through the same fines and sulfur removal processes.

From available literature, it is unclear what emissions are released and where they are released. Air emissions from thermal cracking processes include coke dust from decoking operations, combustion gases from the visbreaking and coking process heaters, and fugitive emissions. Emissions from the process heaters are discussed below. Fugitive emissions from miscellaneous leaks are significant because of the high temperatures involved, and are dependent upon equipment type and configuration, operating conditions, and general maintenance practices. Fugitive emissions are also discussed below. Particulate emissions from delayed coking operations are potentially very significant. These emissions are associated with removing the coke from the coke drum and subsequent handling and storage operations. Hydrocarbon emissions are also associated with cooling and venting the coke drum before coke removal. However, comprehensive data for delayed coking emissions have not been included in available literature.[4-5]

Particulate emission control is accomplished in the decoking operation by wetting down the coke.[5] Generally, there is no control of hydrocarbon emissions from delayed coking. However, some facilities are now collecting coke drum emissions in an enclosed system and routing them to a refinery flare.[4-5]

### 5.1.2.4 Utilities Plant -

The utilities plant supplies the steam necessary for the refinery. Although the steam can be used to produce electricity by throttling through a turbine, it is primarily used for heating and separating hydrocarbon streams. When used for heating, the steam usually heats the petroleum indirectly in heat exchangers and returns to the boiler. In direct contact operations, the steam can serve as a stripping medium or a process fluid. Steam may also be used in vacuum ejectors to produce a vacuum. Boiler emissions and applicable emission control technology are discussed in much greater detail in Chapter 1.

### 5.1.2.5 Sulfur Recovery Plant -

Sulfur recovery plants are used in petroleum refineries to convert the hydrogen sulfide ($H_2S$) separated from refinery gas streams into the more disposable byproduct, elemental sulfur. Emissions from sulfur recovery plants and their control are discussed in Section 8.13, "Sulfur Recovery".

### 5.1.2.6 Blowdown System -

The blowdown system provides for the safe disposal of hydrocarbons (vapor and liquid) discharged from pressure relief devices.

Most refining processing units and equipment subject to planned or unplanned hydrocarbon discharges are manifolded into a collection unit, called blowdown system. By using a series of flash drums and condensers arranged in decreasing pressure, blowdown material is separated into vapor and liquid cuts. The separated liquid is recycled into the refinery. The gaseous cuts can either be smokelessly flared or recycled.

Uncontrolled blowdown emissions primarily consist of hydrocarbons but can also include any of the other criteria pollutants. The emission rate in a blowdown system is a function of the amount of equipment manifolded into the system, the frequency of equipment discharges, and the blowdown system controls.

Emissions from the blowdown system can be effectively controlled by combustion of the noncondensables in a flare. To obtain complete combustion or smokeless burning (as required by most states), steam is injected in the combustion zone of the flare to provide turbulence and air. Steam injection also reduces emissions of nitrogen oxides by lowering the flame temperature. Controlled emissions are listed in Table 5.1-1.[2,11]

### 5.1.2.7 Process Heaters -

Process heaters (furnaces) are used extensively in refineries to supply the heat necessary to raise the temperature of feed materials to reaction or distillation level. They are designed to raise petroleum fluid temperatures to a maximum of about 510°C (950°F). The fuel burned may be refinery gas, natural gas, residual fuel oils, or combinations, depending on economics, operating conditions, and emission requirements. Process heaters may also use CO-rich regenerator flue gas as fuel.

All the criteria pollutants are emitted from process heaters. The quantity of these emissions is a function of the type of fuel burned, the nature of the contaminants in the fuel, and the heat duty of the furnace. Sulfur oxides can be controlled by fuel desulfurization or flue gas treatment. Carbon monoxide and hydrocarbons can be controlled by more combustion efficiency. Currently, 4 general techniques or modifications for the control of nitrogen oxides are being investigated: combustion modification, fuel modification, furnace design, and flue gas treatment. Several of these techniques are being applied to large utility boilers, but their applicability to process heaters has not been established.[2,14]

5.1.2.8 Compressor Engines -

Many older refineries run high-pressure compressors with reciprocating and gas turbine engines fired with natural gas. Natural gas has usually been a cheap, abundant source of energy. Examples of refining units operating at high pressure include hydrodesulfurization, isomerization, reforming, and hydrocracking. Internal combustion engines are less reliable and harder to maintain than are steam engines or electric motors. For this reason, and because of increasing natural gas costs, very few such units have been installed in the last few years.

The major source of emissions from compressor engines is combustion products in the exhaust gas. These emissions include CO, hydrocarbons, nitrogen oxides, aldehydes, and ammonia. Sulfur oxides may also be present, depending on the sulfur content of the natural gas. All these emissions are significantly higher in exhaust from reciprocating engines than from turbine engines.

The major emission control technique applied to compressor engines is carburetion adjustment similar to that applied on automobiles. Catalyst systems similar to those of automobiles may also be effective in reducing emissions, but their use has not been reported.

5.1.2.9 Sweetening -

Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl disulfides in the presence of a catalyst. Conversion may be followed by an extraction step for removal of the alkyl disulfides. In the conversion process, sulfur is added to the sour distillate with a small amount of caustic and air. The mixture is then passed upward through a fixed-bed catalyst, counter to a flow of caustic entering at the top of the vessel. In the conversion and extraction process, the sour distillate is washed with caustic and then is contacted in the extractor with a solution of catalyst and caustic. The extracted distillate is then contacted with air to convert mercaptans to disulfides. After oxidation, the distillate is settled, inhibitors are added, and the distillate is sent to storage. Regeneration is accomplished by mixing caustic from the bottom of the extractor with air and then separating the disulfides and excess air.

The major emission problem is hydrocarbons from contact of the distillate product and air in the "air blowing" step. These emissions are related to equipment type and configuration, as well as to operating conditions and maintenance practices.[4]

5.1.2.10 Asphalt Blowing -

The asphalt blowing process polymerizes asphaltic residual oils by oxidation, increasing their melting temperature and hardness to achieve an increased resistance to weathering. The oils, containing a large quantity of polycyclic aromatic compounds (asphaltic oils), are oxidized by blowing heated air through a heated batch mixture or, in a continuous process, by passing hot air countercurrent to the oil flow. The reaction is exothermic, and quench steam is sometimes needed for temperature control. In some cases, ferric chloride or phosphorus pentoxide is used as a catalyst to increase the reaction rate and to impart special characteristics to the asphalt.

Air emissions from asphalt blowing are primarily hydrocarbon vapors vented with the blowing air. The quantities of emissions are small because of the prior removal of volatile hydrocarbons in the distillation units, but the emissions may contain hazardous polynuclear organics. Emissions are 30 kg/megagram (Mg) (60 lb/ton) of asphalt.[13] Emissions from asphalt blowing can be controlled to negligible levels by vapor scrubbing, incineration, or both.[4,13]

### 5.1.3 Fugitive Emissions And Controls

Fugitive emission sources include leaks of hydrocarbon vapors from process equipment and evaporation of hydrocarbons from open areas, rather than through a stack or vent. Fugitive emission sources include valves of all types, flanges, pump and compressor seals, process drains, cooling towers, and oil/water separators. Fugitive emissions are attributable to the evaporation of leaked or spilled petroleum liquids and gases. Normally, control of fugitive emissions involves minimizing leaks and spills through equipment changes, procedure changes, and improved monitoring, housekeeping, and maintenance practices. Controlled and uncontrolled fugitive emission factors for the following sources are listed in Table 5.1-2:

- Oil/water separators (waste water treatment)
- Storage
- Transfer operations
- Cooling towers

Emission factors for fugitive leaks from the following types of process equipment can be found in *Protocol For Equipment Leak Emission Estimates*, EPA-453/R-93-026, June 1993, or subsequent updates:

- Valves (pipeline, open ended, vessel relief)
- Flanges
- Seals (pump, compressor)
- Process drains

#### 5.1.3.1 Valves, Flanges, Seals, And Drains -

For these sources, a very high correlation has been found between mass emission rates and the type of stream service in which the sources are employed. The four stream service types are (1) hydrocarbon gas/vapor streams (including gas streams with up to 50 percent hydrogen by volume), (2) light liquid and gas/liquid streams, (3) kerosene and heavier liquid streams (includes all crude oils), and (4) gas streams containing more than 50 percent hydrogen by volume. It is found that sources in gas/vapor stream service have higher emission rates than those in heavier stream service. This trend is especially pronounced for valves and pump seals. The size of valves, flanges, pump seals, compressor seals, relief valves, and process drains does not affect their leak rates.[17] The emission factors are independent of process unit or refinery throughput.

Valves, because of their number and relatively high emission factor, are the major emission source. This conclusion is based on an analysis of a hypothetical refinery coupled with the emission rates. The total quantity of fugitive VOC emissions in a typical oil refinery with a capacity of 52,500 $m^3$ (330,000 bbl) per day is estimated as 20,500 kg (45,000 lb) per day (see Table 5.1-3). This estimate is based on a typical late 1970s refinery without a leak inspection and maintenance (I/M) program. See the *Protocol* document for details on how to estimate emissions for a specific refinery.

Table 5.1-2 (Metric And English Units). FUGITIVE EMISSION FACTORS FOR PETROLEUM REFINERIES[a]

EMISSION FACTOR RATING: D

| Emission Source | Emission Factor Units | Emission Factors | | Applicable Control Technology |
|---|---|---|---|---|
| | | Uncontrolled Emissions | Controlled Emissions | |
| Cooling towers[b] | $kg/10^6$ L cooling water | 0.7 | 0.08 | Minimization of hydrocarbon leaks into cooling water system; monitoring of cooling water for hydrocarbons |
| | $lb/10^6$ gal cooling water | 6 | 0.7 | Minimization of hydrocarbon leaks into cooling water system; monitoring of cooling water for hydrocarbons |
| Oil/water separators[c] | $kg/10^3$ L waste water | 0.6 | 0.024 | Covered separators and/or vapor recovery systems |
| | $lb/10^3$ gal waste water | 5 | 0.2 | Covered separators and/or vapor recovery systems |
| Storage | See Chapter 7 - Liquid Storage Tanks | | | |
| Loading | See Section 5.2 - Transportation And Marketing Of Petroleum Liquids | | | |

[a] References 2,4,12-13.
[b] If cooling water rate is unknown (in liters or gallons) assume it is 40 times the refinery feed rate (in liters or gallons). Refinery feed rate is defined as the crude oil feed rate to the atmospheric distillation column. 1 bbl (oil) = 42 gallons (gal), 1 $m^3$ = 1000 L.
[c] If waste water flow rate to oil/water separators is unknown (in liters or gallons) assume it is 0.95 times the refinery feed rate (in liters or gallons). Refinery feed rate is defined as the crude oil feed rate to the atmospheric distillation column. 1 bbl (oil) = 42 gal, 1 $m^3$ = 1000 L.

5.1.3.2 Storage -

All refineries have a feedstock and product storage area, termed a "tank farm", which provides surge storage capacity to ensure smooth, uninterrupted refinery operations. Individual storage tank capacities range from less than 160 $m^3$ to more than 79,500 $m^3$ (1,000 to 500,000 bbl). Storage tank designs, emissions, and emission control technology are discussed in detail in AP-42 Chapter 7, and the *TANKS* software program is available to perform the emissions calculations, if desired.

Table 5.1-3 (Metric And English Units). FUGITIVE VOC EMISSIONS FROM AN UNCONTROLLED OIL REFINERY OF 52,500 $m^3$/day (330,000 bbl/day) CAPACITY[a]

| Source | Number | VOC Emissions | |
|---|---|---|---|
| | | kg/day | lb/day |
| Valves | 11,500 | 3,100 | 6,800 |
| Flanges | 46,500 | 300 | 600 |
| Pump seals | 350 | 590 | 1,300 |
| Compressor seals | 70 | 500 | 1,100 |
| Relief valves | 100 | 200 | 500 |
| Drains | 650 | 450 | 1,000 |
| Cooling towers[b] | 1 | 730 | 1,600 |
| Oil/water separators (uncovered)[b] | 1 | 14,600 | 32,100 |
| TOTAL | — | 20,500 | 45,000 |

[a] Reference 17.
[b] Based on limited data.

5.1.3.3 Transfer Operations -

Although most refinery feedstocks and products are transported by pipeline, some are transported by trucks, rail cars, and marine vessels. They are transferred to and from these transport vehicles in the refinery tank farm area by specialized pumps and piping systems. The emissions from transfer operations and applicable emission control technology are discussed in much greater detail in Section 5.2, "Transportation And Marketing Of Petroleum Liquids".

5.1.3.4 Waste Water Treatment Plant -

All refineries employ some form of waste water treatment so water effluents can safely be returned to the environment or reused in the refinery. The design of waste water treatment plants is complicated by the diversity of refinery pollutants, including oil, phenols, sulfides, dissolved solids, and toxic chemicals. Although the treatment processes employed by refineries vary greatly, they generally include neutralizers, oil/water separators, settling chambers, clarifiers, dissolved air flotation systems, coagulators, aerated lagoons, and activated sludge ponds. Refinery water effluents are collected from various processing units and are conveyed through sewers and ditches to the treatment plant. Most of the treatment occurs in open ponds and tanks.

The main components of atmospheric emissions from waste water treatment plants are fugitive VOCs and dissolved gases that evaporate from the surfaces of waste water residing in open process drains, separators, and ponds (Table 5.1-2). Treatment processes that involve extensive contact of waste water and air, such as aeration ponds and dissolved air flotation, have an even greater potential for atmospheric emissions. Section 4.3, "Waste Water Collection, Treatment And Storage", discusses estimation techniques for such water treatment operations. *WATER8* and *SIMS* software models are available to perform the calculations.

The control of waste water treatment plant emissions involves covering systems where emission generation is greatest (such as oil/water separators and settling basins) and removing dissolved gases from water streams with sour water strippers and phenol recovery units before their contact with the atmosphere. These control techniques potentially can achieve greater than 90 percent reduction of waste water system emissions.[13]

5.1.3.5 Cooling Towers -

Cooling towers are used extensively in refinery cooling water systems to transfer waste heat from the cooling water to the atmosphere. The only refineries not employing cooling towers are those with once-through cooling. The increasing scarcity of a large water supply required for once-through cooling is contributing to the disappearance of that form of refinery cooling. In the cooling tower, warm cooling water returning from refinery processes is contacted with air by cascading through packing. Cooling water circulation rates for refineries commonly range from 7 to 70 L/minute per $m^3$/day (0.3 to 3.0 gal/minute per bbl/day) of refinery capacity.[2,16]

Atmospheric emissions from the cooling tower consist of fugitive VOCs and gases stripped from the cooling water as the air and water come into contact. These contaminants enter the cooling water system from leaking heat exchangers and condensers. Although the predominant contaminants in cooling water are VOCs, dissolved gases such as $H_2S$ and ammonia may also be found (see Table 5.1-2).[2,4,17]

Control of cooling tower emissions is accomplished by reducing contamination of cooling water through the proper maintenance of heat exchangers and condensers. The effectiveness of cooling tower controls is highly variable, depending on refinery configuration and existing maintenance practices.[4]

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