Note: This material is related to a section in *AP42, Compilation of Air Pollutant Emission Factors, Volume I Stationary Point and Area Sources.* AP42 is located on the EPA web site at www.epa.gov/ttn/chief/ap42/

The file name refers to the file number, the AP42 chapter and then the section. The file name "rel01_c01s02.pdf" would mean the file relates to AP42 chapter 1 section 2. The document may be out of date and related to a previous version of the section. The document has been saved for archival and historical purposes. The primary source should always be checked. If current related information is available, it will be posted on the AP42 webpage with the current version of the section.

AP42 Section:	5.1
Related:	1
Title:	Revision of Petroleum Refinery Emission Factors. Draft Report. R G Wetherold, Radian Corp. for Bruce Tichenor US EPA, January 1980

A. MacQueen

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

DATE: May 20, 1980

SUBJECT: AP-42 Revisions for Fugitive Emissions from Petroleum References

FROM: Bruce Tichenor (MD-62)
Chemical Process Branch

TO: Charles Masser (MD-14)
OAQPS/MDAD

As we recently discussed, I am enclosing a draft copy of the subject AP-42 revisions prepared by Radian Corp. under Contract No. 68-02-2147B.

I have asked Bob Wetherold of Radian to send the reproducible master of the final copy directly to you. If you don't receive it in a few days, please give me a call.

Enclosure (1)

✓cc: A. MacQueen (MD-14) (w/encl)
K. C. Hustvedt (MD-13) (w/encl)
Bob Weber (IERL/Cinc) (w/encl)
Bob Wetherold (Radian-Austin, TX) (w/o encl)

RADIAN
CORPORATION

16 May 1980 DCN 80-219-144-11-10

Dr. Bruce A. Tichenor
Industrial Environmental Research Laboratory
Office of Research and Development (MD-62)
Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Bruce:

Enclosed are six copies of the revised section on refinery fugitive emissions for AP-42. I have included the changes suggested by you, K. C. Hustvedt, and Chuck Masser.

After some thought, I have moved the pump and compressor seals from the "Controlled Emission" column to the "Uncontrolled." As you know, we included seals with all levels of emission control in our pump/compressor seal emission factors. I feel that universal application of double mechanical seals, controlled degassing vents, and monitoring/maintenance programs should result in a significantly lower emissions level than indicated by our recently developed emission factors. There are no hard data to back up my opinions, however.

I left the cooling tower emission factors as they were presented in the draft report. The refineries in which we tested cooling towers generally analyzed their cooling water for hydrocarbon content and seemed to practice good maintenance in keeping VOC content low. This appears to be about the best reasonable control technique generally available for keeping atmospheric VOC emissions from cooling towers to a minimum.

If you have any questions or comments, please call me.

Sincerely yours,

Bob

R. G. Wetherold
Senior Staff Engineer

RGW:bj

Enclosures (6)

8500 Shoal Creek Blvd. / P.O. Box 9948 / Austin, Texas 78766 / (512)454-4797

LOG OF PREPARATION OR REVISIONS

Entry No.	Date	Author	Emission Factors Affected	Comments
1	4/73	W. M. Vatavuk	—	
2	12/77	C.C. Masser	CO & NO_2 - compressor engines VOC - blowdown systems SO_2, CO, VOC & NO_2 - vapor recovery VOC - vacuum distillation column condensers	
3	10/80	Radian	fugitive VOC emission factors added.	
4				

RADIAN
CORPORATION

REVISION OF PETROLEUM REFINERY EMISSION FACTORS

DRAFT REPORT

By:

R. G. Wetherold
RADIAN CORPORATION
Austin, Texas

For:

Dr. Bruce Tichenor
U.S. ENVIRONMENTAL PROTECTION AGENCY
Industrial Environmental Research Laboratory
Research Triangle Park, NC 27711

January 1980

ABSTRACT

The refinery air pollutant emission factors presently contained in Section 9.1 of AP-42, A Compilation of Air Pollutant Emission Factors were last revised in 1977. New emission factors for some fugitive emission sources have been developed from the results of recent testing in 13 refineries. This testing was done by Radian under EPA Contracts 68-02-2665 and 68-02-2147, Exhibit B. These factors are included in the revised draft of Section 9.1 presented in this report.

9.1 PETROLEUM REFINING[1]

9.1.1 GENERAL DESCRIPTION

The petroleum refining industry is primarily involved in the conversion of 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 crude storage at the refinery, include all petroleum handling and refining operations, and terminate with storage of the refined products at the refinery.

The petroleum refining industry employs a wide variety of processes for the conversion of crude oil to finished petroleum products. A refinery's processing flow scheme selection 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 9.1-1 shows the general processing arrangement used by U.S. refineries for major refinery processes. The arrangement of these processes will vary among refineries and few, if any, refineries employ all of these processes. Petroleum refining processes having direct emission sources are presented in bold line boxes.

In general, refinery processes and operations can be divided into five categories:

1) Separation processes
   a. atmospheric distillation
   b. vacuum distillation
   c. light ends recovery (gas processing)

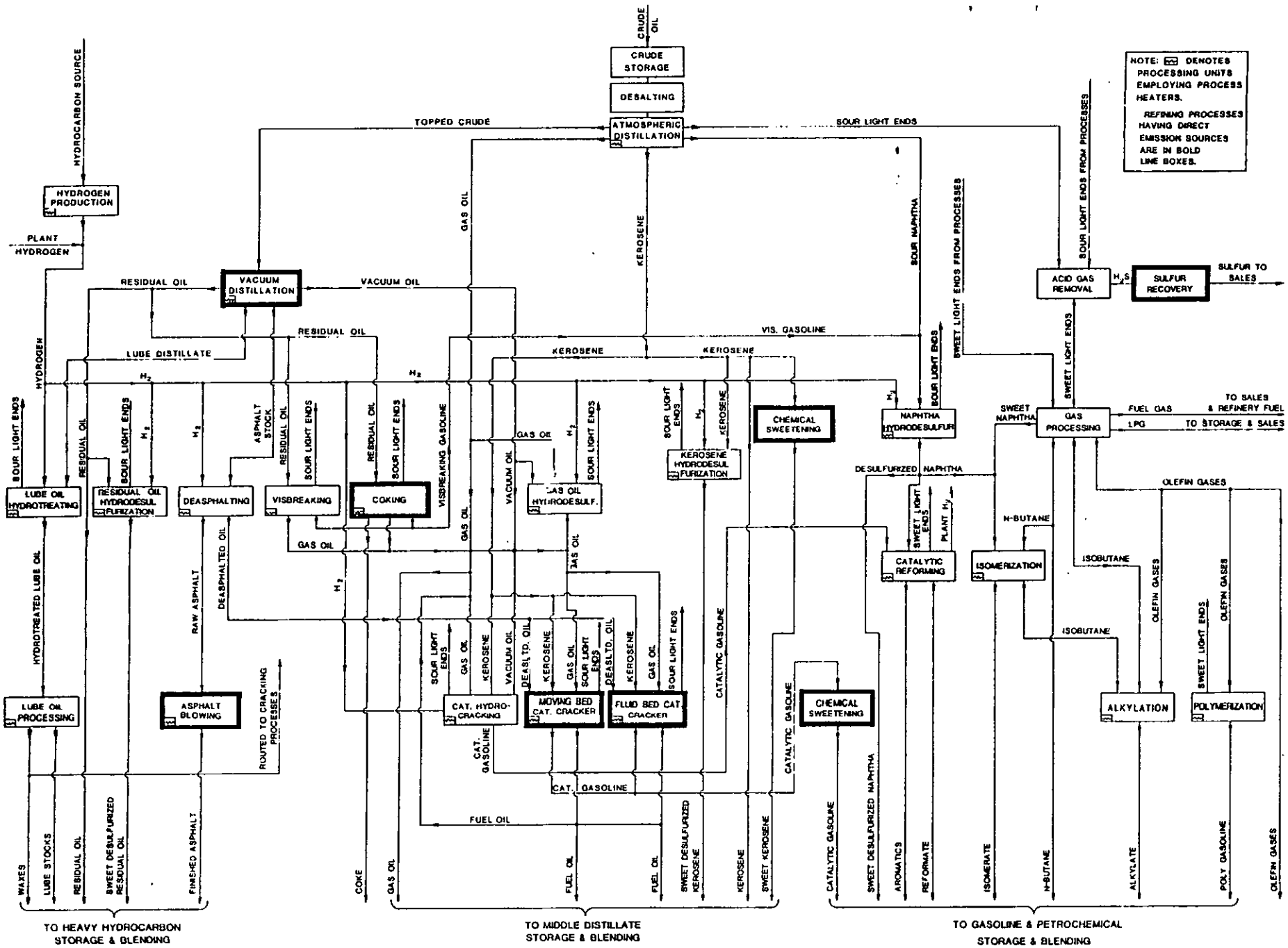

FIGURE 1-1 SCHEMATIC OF AN EXAMPLE INTEGRATED PETROLEUM REFINERY

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. wastewater treatment
   c. hydrogen production
   d. sulfur recovery plant
   e. cooling towers
   f. blowdown system
   g. compressor engines.

These refinery processes are defined in the following section along with their emission characteristics and applicable emission control technology.

Petroleum Separation Processes

The first phase in petroleum refining operations is the separation of crude oil into its major constituents using three petroleum separation processes: atmospheric distillation, vacuum distillation, and light ends recovery. Crude oil consists of a mixture of hydrocarbon compounds including paraffinic, naphthenic, and aromatic hydrocarbons plus small amounts of impurities including sulfur, nitrogen, oxygen, and metals. Refinery separation processes use such techniques as distillation, stripping, and absorption to separate these crude oil constituents into common boiling point fractions.

Petroleum Conversion Processes

Product demand and economic considerations require that less valuable components of crude oil be converted to more valuable products by using the petroleum conversion processes. To meet the demands for high octane gasoline, jet fuel, and diesel fuel, lower value residual oils, fuel oils, and light ends are often converted to gasolines and other light fractions. The cracking, coking, and visbreaking processes are used to break large petroleum molecules into smaller petroleum molecules. On the other hand, polymerization and alkylation processes are used to combine small petroleum molecules into larger ones. Isomerization and reforming processes primarily rearrange the structure of petroleum molecules to produce higher value molecules of a similar molecular size.

Petroleum Treating Processes

Petroleum treating processes stabilize and upgrade petroleum products by separating them from less desirable

petroleum products and by removing objectionable elements from petroleum products and feedstocks. Treating processes used to stabilize products and remove undesirable elements such as sulfur, nitrogen and oxygen include 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 feed stocks prior to refining. And asphalt blowing is used to polymerize and stabilize asphalt, improving its weathering characteristics.

Feedstock and Product Handling

The refinery feedstock and product handling operations consist of storage, blending, loading, and unloading activities. All feedstocks entering the refinery and all products leaving the refinery are subject to the refinery handling operations.

Auxiliary Facilities

Auxiliary facilities include a wide assortment of processes and equipment which are not directly involved in the refining of crude oil, but which perform functions vital to the operation of the refinery. These include boilers, wastewater treatment, hydrogen plants, cooling towers, sulfur recovery units, etc. Products from auxiliary facilities (clean water, steam, process heat, etc.) are required by the majority of refinery process units and are not limited to any one part of the refinery.

9.1.2 PROCESS EMISSION SOURCES AND CONTROL TECHNOLOGY

This section presents descriptions of those refining processes which are significant air pollutant contributors. Process flow schemes, emission characteristics, and emission control technology are discussed for each process. Table 9.1-1 lists the emission factors for direct process emissions in the petroleum refinery. The following process emission sources are discussed in this section on petroleum refining emissions:

- vacuum distillation,
- catalytic cracking,
- thermal cracking processes,
- utility boilers,
- heaters,
- compressor engines,
- blowdown systems, and
- sulfur recovery.

Vacuum Distillation

Topped crude withdrawn from the bottom of the atmospheric distillation column is composed of high boiling point hydrocarbons which decompose and polymerize to foul equipment when distilled at atmospheric pressures. In order to further separate topped crude into components, it must be distilled in

TABLE 9.1-1. EMISSION FACTORS FOR PETROLEUM REFINERIES

Type of Process	Particulates	Sulfur Oxides (SO_2)	Carbon Monoxide	Total[a] Hydro-Carbons	Nitrogen Oxides (NO_2)	Aldehydes	Ammonia	Emission Factor Rating
Boilers and Process Heaters[b]								
lb/10^3 bbl oil burned	840	6,720S[c]	210[d]	42[d]	2,900	25	Neg[e]	A
kg/10^3 liters oil burned	2.4	19.2S	0.6[d]	0.12[d]	8.3	0.071	Neg	A
lb/10^3 ft^3 gas burned	0.02	2.s[f]	0.02[d]	0.003[d]	0.23	0.003	Neg	A
kg/10^3 m^3 gas burned	0.32	32s	0.32[d]	0.048[d]	3.7	0.048	Neg	A
Fluid Catalytic Cracking Units[g]								
Uncontrolled								
lb/10^3 bbl fresh feed	242 (93 to 340)[h]	493 (100 to 525)	13,700	220	71.0 (37.1 to 145.0)	19	54	B
kg/10^3 liters 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
Electrostatic Precipitator and CO boiler								
lb/10^3 bbl fresh feed	45[i] (7 to 150)	493 (100 to 525)	Neg	Neg	71.0[j] (37.1 to 145.0)	Neg	Neg	B
kg/10^3 liters fresh feed	0.128 (0.020 to 0.428)	1.413 (0.286 to 1.505)	Neg	Neg	0.204[j] (0.107 to 0.416)	Neg	Neg	B
Moving-Bed Catalytic Cracking Units[b]								
lb/10^3 bbl fresh feed	17	60	3,800	87	5	12	6	B
kg/10^3 liters fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
Fluid Coking Units[k]								
Uncontrolled								
lb/10^3 bbl fresh feed	523	NA[l]	NA	NA	NA	NA	NA	C
kg/10^3 liters fresh feed	1.50	NA	NA	NA	NA	NA	NA	C
Electrostatic Precipitator and CO boiler								
lb/10^3 bbl fresh feed	6.85	NA	Neg	Neg	NA	Neg	Neg	C
kg/10^3 liters fresh feed	0.0196	NA	Neg	Neg	NA	Neg	Neg	C
Delayed Coking Units	NA	NA	NA	NA	NA	NA	NA	NA

(Continued)

TABLE 9.1-1. EMISSION FACTORS FOR PETROLEUM REFINERIES (Continued)

Type of Process	Particulates	Sulfur Oxides (SO_2)	Carbon Monoxide	Total[a] Hydro-Carbons	Nitrogen Oxides (NO_2)	Aldehydes	Ammonia	Emission Factor Rating
Compressor Engines[m]								
Reciprocating Engines								
$lb/10^3 ft^3$ gas burned	Neg	2s	0.43	1.4	3.4	0.1	0.2	B
$kg/10^3 m^3$ gas burned	Neg	32s	7.02	21.8	55.4	1.61	3.2	B
Gas Turbines								
$lb/10^3 ft^3$ gas burned	Neg	2s	0.12	0.02	0.3	NA	NA	B
$kg/10^3 m^3$ gas burned	Neg	32s	1.94	0.28	4.7	NA	NA	B
Blowdown Systems[n]								
Uncontrolled								
$lb/10^3$ bbl refinery feed	Neg	Neg	Neg	580	Neg	Neg	Neg	C
$kg/10^3$ liters refinery feed	Neg	Neg	Neg	1.662	Neg	Neg	Neg	C
Vapor Recovery system and flaring								
$lb/10^3$ bbl refinery feed	Neg	26.9	4.3	0.8	18.9	Neg	Neg	C
$kg/10^3$ liters refinery feed	Neg	0.077	0.012	0.002	0.054	Neg	Neg	C
Vacuum Distillation[o] Column Condensers								
Uncontrolled								
$lb/10^3$ bbl refinery feed	Neg	Neg	Neg	18	Neg	Neg	Neg	C
$kg/10^3$ liters refinery feed	Neg	Neg	Neg	0.052	Neg	Neg	Neg	C
$lb/10^3$ bbl vacuum feed	Neg	Neg	Neg	50 (0-130)	Neg	Neg	Neg	C
$kg/10^3$ liters vacuum feed	Neg	Neg	Neg	0.144	Neg	Neg	Neg	C
Controlled	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C

(Continued)

TABLE 9.1-1. EMISSION FACTORS FOR PETROLEUM REFINERIES (Continued)

Type of Process	Particulates	Sulfur Oxides (SO_2)	Carbon Monoxide	Total[a] Hydro-Carbons	Nitrogen Oxides (NO_2)	Aldehydes	Ammonia	Emission Factor Rating
Claus Plant and Tail Gas Treatment	See Section 5.18							

[a] Overall, less than 1 percent by weight of the total hydrocarbon emissions are methane.

[b] Reference 2

[c] S = Fuel oil sulfur content (weight percent): factors based on 100 percent combustion of sulfur to SO_2 and assumed density of 336 lb/bbl (0.96 kg/liter).

[d] Carbon monoxide and hydrocarbon factors taken from Tables 1.3-1 and 1.4-1 of this manual.

[e] Negligible emission

[f] s = Refinery gas sulfur content (lb/1000 ft^3): factors based on 100 percent combustion of sulfur to SO_2.

[g] References 2 through 8

[h] Numbers in parenthesis indicate range of values observed.

[i] Under the New Source Performance Standards, controlled FCC regenerators will have particulate emissions lower than 19 lb/10^3 bbl fresh feed.

[j] May be higher due to the combustion of ammonia.

[k] Reference 5

[l] NA, Not Available

[m] Reference 9 and 10

[n] Reference 2, 11

[o] Reference 2, 12, 13

a vacuum distillation 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 700°F to 800°F. The heated topped crude is flashed into a multi-tray vacuum distillation column operating at vacuums ranging from 0.5 psia to 2 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 in 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 normally 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 are recovered in condensers. Historically, the noncondensable portion of the vapors has been vented to the atmosphere from the condensers. There are approximately 50 pounds of noncondensable hydrocarbons per thousand barrels 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 37,000 Btu per barrel of topped crude processed in the vacuum column. Process heater emissions and their control are discussed later in this section. 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 in this section.

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

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 650-1000°F. All of the catalytic cracking processes in use today can be classified as either fluidized-bed or moving bed units.

- Fluidized-bed Catalytic Cracking (FCC) - The FCC process uses a catalyst in the form of very fine particles which act as a fluid when aerated with a vapor. Fresh feed is preheated in a process heater and introducted 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 (880-980°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 adsorbed 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 1100 - 1250°F. The catalyst is then recycled to be mixed with fresh hydrocarbon feed.

- Moving-bed Catalytic Cracking (TCC) - In the TCC process catalyst beads (∿0.5 cm) flow by gravity 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 dis-

cussed later in this section. Emissions from the catalyst regenerator include hydrocarbons, oxides of sulfur, ammonia, aldehydes, oxides of nitrogen, cyanides, carbon monoxide, and particulates (Table 9.1-1). 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 wasteheat boilers reduce the carbon monoxide 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 9.1-1). 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 fire-box 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]

Thermal Cracking

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

- Visbreaking - Topped crude or vacuum residuals are heated and thermally cracked (850-900°F, 50-250 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 a fuel oil blending component or used as catalytic cracking feed.

- Coking - Coking is a thermal cracking process which is 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 section 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 is rapidly heated in the coking heater to a temperature of 900-1100°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 (25-30 psig), and temperature (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 removal 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% 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 removal 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 later in this section. 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 later in this section. 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, prior to 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]

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. When used 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.

The emissions from boilers, and applicable emission control technology are discussed in much greater detail in Chapter 1.0.

Sulfur Recovery Plant

Sulfur recovery plants are used in petroleum refineries to convert hydrogen sulfide (H_2S) separated from refinery gas streams into the more disposable by-product, elemental sulfur.

The emissions from sulfur recovery plants and their control are discussed in Section 5.18.

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 the blowdown system. By using a series of flash drums and condensers arranged in decreasing pressure, the blowdown 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 processed by the refinery. 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 systems's controls.

Emissions from the blowdown system can be effectively controlled by combustion of the non-condensables 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 to inspirate air. Steam injection also reduces NO_x emissions by lowering the flame temperature. Controlled emissions are listed in Table 9.1-1.[2,11]

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 temperature. They are used in many processes throughout the refinery.

Process heaters are designed to raise petroleum fluid temperatures to a maximum of about 950°F. The fuel burned may

be refinery gas, natural gas, residual fuel oils, or combinations, depending on the economics, operating conditions, and pollution requirements. The process heaters may also use carbon monoxide-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 oxide emissions can be controlled by fuel desulfurization or flue gas treatment. Carbon monoxide and hydrocarbons can be limited by better combustion efficiency. Current technology is investigating four general techniques or modifications for the control of NO_x emissions. These include combustion modification, fuel modification, alternate furnace design, and flue gas treatment. Several of these NO_x control techniques are presently being applied to large utility boilers, but their applicability to process heaters is undefined.[2,14]

Compressor Engines

Many older refineries use reciprocating and gas turbine engines fired with natural gas to run high pressure compressors. Natural gas has traditionally been a cheap abundant source of energy. Examples of refining units operating at high pressure include hydrodesulfurization, isomerization, reforming, and hydrocracking units. Internal combustion engines are less reliable and harder to maintain than 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 are combustion products in the exhaust gas. These emissions include carbon monoxide, hydrocarbons, nitrogen oxides, aldehydes, and ammonia. Sulfur oxides may also be present depending on the sulfur content of the natural gas. All of 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 applied to automobiles may also be effective in reducing emissions but are currently undefined for this application.

only F, E, S, C, E mentioned.

9.1.3 FUGITIVE EMISSION SOURCES AND CONTROL EQUIPMENT

This section presents descriptions of refinery processes and operations which are significant sources of fugitive emissions. Process flow schemes, emission characteristics and emission control technology are discussed for each process. Emission factors for both uncontrolled and controlled fugitive ~~emission~~ sources are listed in Table 9.1-2. The ~~following~~ fugitive emission sources ~~are~~ discussed in this section on petroleum refining emissions are ;

- oil-water separators,
- cooling towers,
- pipeline valves,
- pipeline flanges,
- relief valves,
- pump and compressor seals,
- asphalt blowing,
- blind changing,

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES[a,b]

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Pipeline Valves	B	lb/hr-source kg/day-source	0.059(0.030,0.110)[d]	NA[e]	Monitoring and maintenance program	A
	C	lb/hr-source kg/day-source	0.024(0.017,0.036)	NA		A
	D	lb/hr-source kg/day-source	0.0005(0.0002,0.0015)	NA		A
	E	lb/hr-source kg/day-source	0.018(0.007,0.045)	NA		A
Open-Ended Valves[f]	A	lb/hr-source kg/day-source	0.005(0.0016,0.016)	NA	Installation of cap or plug on open end of valve/line	
Flanges	A	lb/hr-source kg/day-source	0.00056(0.0002,0.0025)	NA	Monitoring and maintenance program	A
Pump Seals	C	lb/hr-source kg/day-source	NA	0.25(0.16,0.37)	Mechanical seals, dual seals, purged seals, visual monitoring	A
	D	lb/hr-source kg/day-source	NA	0.046(0.019,0.11)		A
Compressor Seals	B	lb/hr-source kg/day-source	NA	1.4(0.66,2.9)	Mechanical seals, dual seals, purged seals, visual monitoring	A
	E	lb/hr-source kg/hr-source	NA	0.11(0.05,0.23)		
Drains	A	lb/hr-source kg/day-source	0.070(0.023,0.20)	NA	Traps and covers	A
Vessel Relief Valves	A	lb/hr-source kg/day-source	0.19(0.070,0.49)	Negligible	Rupture disks upstream of relief valves and/or venturi to blowdown system	A
Cooling Towers	-	lb/10^6 gal cooling water kg/10^6 liters cooling water lb/10^3 bbl refinery feed[g] kg/10^6 liters refinery feed	6 0.7 10 0.0	0.70	Minimization of hydrocarbon leaks into cooling water system. Monitoring of cooling water for hydrocarbons	D

(Continued)

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES[a,b] (Continued)

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Oil-Water Separators	-	lb/10^3 gal wastewater	5	0.2		D
		kg/10^3 liter wastewater	0.6	0.024		
		lb/10^3 bbl refinery feed	200	10		
		kg/10^3 liters refinery feed	0.6	0.03		
Asphalt Blowing	-	lb/ton of asphalt	60	Negligible		D
		kg/metric ton of asphalt	30	Negligible		
Blind Changing	-	lb/10^3 bbl refinery feed	0.3	Negligible		D
		kg/10^3 liters refinery feed	0.001	Negligible		
Miscellaneous: sampling, non-asphalt blowing (sweetening), purging, etc.	-	lb/10^3 bbl refinery feed	10	NA		D
		kg/10^3 liters refinery feed	0.03	NA		
Storage		See Section 4.3				
Loading		See Section 4.4				

[a]References 2, 4, 12, 13, 17

[b]Overall, less than 2 percent by weight of the total hydrocarbon emissions are methane.

[c]The volatility and hydrogen content of the process streams have a substantial effect on the emission rate of some fugitive emission sources. The stream identification letter, stream group description, and stream group name are given below.

Stream Identification Letter	Stream Name	Stream Group Description
A	All Streams	All streams
B	Gas Streams	Hydrocarbon gas/vapor at process conditions (containing less than 50% hydrogen, by volume)
C	Light Liquid and Gas/Liquid Streams	Liquid or gas-liquid stream (based on the most volatile class present at ≥20 percent) boiling below kerosene (vapor pressure = 0.1 psia @ 100°F).
D	Heavy Liquid Stream	Liquid stream (based on the most volatile class present at ≥20 percent) boiling above naphtha (vapor pressure = 0.1 psia @ 100°F).
E	Hydrogen Streams	Gas streams containing more than 50% hydrogen (by volume)

[d]Numbers in parentheses are the upper and lower bounds of the 95% confidence interval for the emission factor.

[e]NA - These emission factors are not available.

[f]The downstream side of these valves is open to the atmosphere. Emissions are through the valve seat of the closed valve.

[g]Refinery rate is defined as the crude oil feed rate to the atmospheric distillation column.

Cap only 1 first letter as marked

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES[a, b]

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Pipeline Valves[d]	B	lb/hr-source kg/day-source	0.059(0.030,0.110)[e] 0.637(0.32,1.19)	NA	Monitoring and maintenance program	A
	C	lb/hr-source kg/day-source	0.024(0.017,0.036) 0.26(0.18,0.39)	NA		A
	D	lb/hr-source kg/day-source	0.0005(0.0002,0.0015) 0.005(0.002,0.016)	NA		A
	E	lb/hr-source kg/day-source	0.018(0.007,0.045) 0.19(0.08,0.49)	NA		A
Open-Ended Valves[f,d]	A	lb/hr-source kg/day-source	0.005(0.0016,0.016) 0.05(0.017,0.17)	NA	Installation of cap or plug on open end of valve/line	
Flanges[d]	A	lb/hr-source kg/day-source	0.00056(0.0002,0.0025) 0.0060(0.002,0.027)	NA	Monitoring and maintenance program	A
Pump Seals[d]	C	lb/hr-source kg/day-source	NA	0.25(0.16,0.37) 2.7(1.7,4.0)	Mechanical seals, dual seals, purged seals, visual monitoring	A
	D	lb/hr-source kg/day-source	NA	0.046(0.019,0.11) 0.50(0.21,1.2)		A
Compressor Seals[d]	B	lb/hr-source kg/day-source	NA	1.4(0.66,2.9) 15(7.1,31)	Mechanical seals, dual seals, purged seals, visual monitoring	A
	E	lb/hr-source kg/hr-source	NA	0.11(0.05,0.23) 1.2(0.5,2.5)		
Drains[d]	A	lb/hr-source kg/day-source	0.070(0.023,0.20)	NA	Traps and covers	A
Vessel Relief Valves[d]	A	lb/hr-source kg/day-source	0.19(0.070,0.49)	Negligible	Rupture disks upstream of relief valves and/or venting to blowdown system	A
Cooling Towers[b]	-	lb/10^6 gal cooling water kg/10^6 liters cooling water lb/10^3 bbl refinery feed[g] kg/10^6 liters refinery feed	6.0 0.7 10.0 0.03	0.70 0.083 1.2 0.004	Minimization of hydrocarbon leaks into cooling water system. Monitoring of cooling water for hydrocarbons	D

(Continued)

(cont.)

Cap only 1 first letter as marked

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES[a, b]
~~(Continued)~~

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Oil/Water Separators[b]	-	lb/10³ gal wastewater kg/10³ liter wastewater	5.0 0.6	0.2 0.024	Covered separators and/or vapor recovery systems	D
		lb/10³ bbl refinery feed kg/10³ liters refinery feed	200.0 0.6	10.0 0.03		
Asphalt Blowing[b]	-	lb/ton of asphalt kg/metric ton of asphalt	60.0 30.0	Negligible Negligible	Incineration of vapors	D
Blind Changing[b]	-	lb/10³ bbl refinery feed kg/10³ liters refinery feed	0.3 0.001	Negligible Negligible	Fine flushing, "line" blinds, blind insulation with gate valves	D
Miscellaneous: sampling, non-asphalt blowing (sweetening), purging, etc.	-	lb/10³ bbl refinery feed kg/10³ liters refinery feed	10.0 0.03	NA NA	Good housekeeping and maintenance	D
Storage[b]		See Section 4.3				
Loading[b]		See Section 4.4				

[a] References 2, 4, 12, 13, 17. NA = not available

[b] Overall, less than 1 ~~percent~~ % by weight of the total hydrocarbon emissions are methane.

[c] The volatility and hydrogen content of the process streams have a substantial effect on the emission rate of some fugitive emission sources. The stream identification letter, stream group description, and stream group name are given below.

Cap only 1 first letter

Stream Identification Letter	Stream Name	Stream Group Description
A	All Streams	All streams
B	Gas Streams	Hydrocarbon gas/vapor at process conditions (containing less than 50% hydrogen, by volume)
C	Light Liquid and Gas/Liquid Streams	Liquid or gas/liquid stream (based on the most volatile class present at ≥20 ~~percent~~ %) boiling below kerosene (vapor pressure = 0.1 psia @ 100°F). °C also
D	Heavy Liquid Stream	Liquid stream (based on the most volatile class present at ≥20 percent) boiling above naphtha (vapor pressure = 0.1 psia @ 100°F). °C
E	Hydrogen Streams	Gas streams containing more than 50% hydrogen (by volume)

[e] Numbers in parentheses are the upper and lower bounds of the 95% confidence interval for the emission factor.

[f] ~~NA - These emission factors are not available.~~

[g] The downstream side of these valves is open to the atmosphere. Emissions are through the valve seat of the closed valve.

[d] Refinery rate is defined as the crude oil feed rate to the atmospheric distillation column.

Hydrocarbon emissions are nonmethane hydrocarbons.

- sweetening,
- process drains,
- storage, ~~and~~
- transfer operations.

Average emission factors are presented, and, where available, 95 percent confidence intervals for the emission factors are also given. The 95 percent confidence interval is the interval or range of values expected to include the true emission factor with 95 percent confidence. For example, the true emission factor for vessel relief valves (if all relief valve emission rates could be measured and averaged) should be between 0.070 and 0.49 lb/hr (metric) kg/hr

~~Miscellaneous Fugitive Sources~~

Miscellaneous fugitive emission sources are generally defined as hydrocarbon emission sources ~~which are~~ not associated with a particular ~~refining~~ process, but ~~which are~~ scattered throughout the refinery. Fugitive emission sources include valves, flanges, pump and compressor seals, process drains, relief valves, blind changing, and sample line purging. Hydrocarbon emissions from fugitive emission sources are attributable to the evaporation of leaked or spilled petroleum liquids and gases. Normally, ~~the~~ control of fugitive emissions involves ~~the~~ minimizing ~~ation of~~ leaks and spills through equipment changes, procedural changes, and improved monitoring, housekeeping and maintenance practices.

The fugitive emission rates from valves, pump seals, and compressor seals were found to be a function of the volatility and/or composition of the refinery stream being processed.[17]

The emission factors for these sources are presented for five general categories of process stream groups. The stream categories are described below:

Stream Category A: All streams

Stream Category B: Streams which contain more than 50% hydrocarbons by volume, and which are in the gas phase at process conditions.

Stream Category C: Liquid stream or gas/liquid stream which contains 20% or more of a hydrocarbon or class of hydrocarbons whose boiling point is below that of kerosene (vapor pressure ≥ 0.1 psia @ 100°F). Contains less than 50% hydrogen.

Stream Category D: Heavy liquid streams which contain less than 20% of a hydrocarbon or class of hydrocarbons whose boiling point is below that of kerosene (vapor pressure ≥ 0.1 psia @ 100°F).

Stream Category E: Gas streams which contain more than 50% by volume of hydrogen.

The size of sources such as valves, flanges, pump and seals, compressor seals, relief valves, and process drains do not affect the leak rates.[17] Thus, the emission factors are independent of process unit or refinery throughput. The number and

stream distribution of the various source types must be known or estimated before total source emissions can be determined.

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 large water supplies required by 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. Heat in the cooling water is transferred to the air. Cooling water circulation rates for refineries commonly range from 0.3 to 3.0 gpm/bbl per day of refinery capacity.[2,16]

Atmospheric emissions from the cooling tower consist of fugitive hydrocarbons 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 contaminant in cooling water is hydrocarbons, dissolved gases such as H_2S and NH_3 may also be found in cooling water (Table 9.1-2).[2,4]

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]

Wastewater Treatment Facilities

All refineries employ some form of wastewater treatment to upgrade the quality of water effluents such that they can be safely returned to the environment or reused within the refinery.

The design of wastewater treatment plants is complicated by the diversity of refinery pollutants including oil, phenols, sulfides, dissolved solids, suspended solids, and toxic chemicals. Although the wastewater 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 conveyed through sewers and ditches to the wastewater treatment plant. Most of the wastewater treatment processing occurs in open ponds and tanks.

The main components of atmospheric emissions from wastewater treatment plants are fugitive hydrocarbons and dissolved gases which evaporate from the surfaces of wastewaters residing in oil-water separators and wastewater ponds (Table 9.1-2). Treatment processes which involve the extensive contacting of wastewater with air such as aeration ponds and dissolved air flotation create an even greater potential for atmospheric emissions.

The control of wastewater treatment plant emissions involves covering wastewater systems where emission generation is greatest (such as covering API separators and settling basins) and removing dissolved gases from wastewater streams with sour water strippers and phenol recovery units prior to their contact

with the atmosphere. These control techniques can potentially achieve greater than 90 percent reduction of wastewater system emissions.[13]

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 preheated batch mixture or, in the 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 impart special characteristics to the asphalt. Blowing is stopped when the asphalt reaches the desired product specifications.

Air emissions from asphalt blowing are primarily fugitive 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.[2,4,13,15]

Emissions from asphalt blowing can be controlled to negligible levels by vapor scrubbing, by incineration, or by a combination of the two.[4,13]

Storage

All refineries have a feedstock and product storage area, termed a "tank farm", which provides surge storage capacity to insure smooth, uninterrupted refinery operations. Individual storage tank capacities range from less than 1000 barrels to more than 500,000 barrels, and total tank farm storage capacities commonly range from several days to several weeks. Storage tank designs, emissions, and emission control technologies are discussed in detail in Section 4.3.

Sweetening

Sweetening of distillates is accomplished by the conversion of mercaptans to alkyl-disulfides in the presence of a catalyst. The conversion process may be followed by an extraction step for the removal of the alkyl-disulfides.

In the conversion process sulfur is added to the sour distillate with a small amount of caustic and air. This mixture is then passed upward through a fixed-bed catalyst countercurrent to a flow of caustic entering at the top of the vessel.

In the conversion and extraction process the sour distillate is prewashed with caustic and then is contacted with a solution of catalyst and caustic in the extractor. 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 separating the disulfides and excess air.

The major source of air emissions are fugitive hydrocarbon emissions generated when the distillate product is contacted with air in the "air blowing" step. These emissions are dependent upon equipment type and configuration as well as on operating conditions and maintenance practices.[4]

Transfer Operations

Although most refinery feedstocks and products are transported by pipeline, many feedstocks and products are transported by trucks, rail cars, and marine vessels. The refinery feedstocks and products are transferred to and from these transport vehicles in the refinery tank farm area using specialized pumps and piping systems. The emissions from transfer operations and applicable emission control technology are discussed in much greater detail in Section 4.4.

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Radian Corp. Austin TX

US Environmental Protection Agency

ABSTRACT

The refinery air pollutant emission factors presently contained in Section 9.1 of AP-42, A Compilation of Air Pollutant Emission Factors were last revised in 1977. New emission factors for some fugitive emission sources have been developed from the results of recent testing in 13 refineries. This testing was done by Radian under EPA Contracts 68-02-2665 and 68-02-2147, Exhibit B. These factors are included in the revised ~~draft of~~ subsection ~~Section 9.1~~ presented in this report.
9.1.3 (Fugitive Emission Sources and Control Equipment)

The major source of emissions from compressor engines are combustion products in the exhaust gas. These emissions include carbon monoxide, hydrocarbons, nitrogen oxides, aldehydes, and ammonia. Sulfur oxides may also be present depending on the sulfur content of the natural gas. All of 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 applied to automobiles may also be effective in reducing emissions but are currently undefined for this application.

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9.1.3 FUGITIVE EMISSION SOURCES AND CONTROL EQUIPMENT

This section presents descriptions of refinery processes and operations which are significant sources of fugitive emissions. Process flow schemes, emission characteristics and emission control technology are discussed for each process. Emission factors for both uncontrolled and controlled fugitive ~~emission~~ sources are listed in Table 9.1-2. The ~~following~~ fugitive emission sources ~~are~~ discussed in this section on petroleum refining emissions are:

- oil-water separators
- cooling towers
- pipeline valves
- pipeline flanges
- relief valves
- pump and compressor seals
- asphalt blowing
- blind changing

Cap only first letter in phrase as underlined

VOLATILE ORGANIC COMPOUND

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES[a,b]

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Pipeline Valves[d,i]	II	lb/hr-source kg/day-source	0.059(0.030,0.110)[d,e] 0.637(0.32,1.19)	NA[e,f]	Monitoring and maintenance program	A
	III	lb/hr-source kg/day-source	0.024(0.017,0.036) 0.26(0.18,0.39)	NA		A
	IV	lb/hr-source kg/day-source	0.0005(0.0002,0.0015) 0.005(0.002,0.016)	NA		A
	V	lb/hr-source kg/day-source	0.018(0.007,0.045) 0.19(0.08,0.49)	NA		A
Open-Ended Valves[d,g]	I	lb/hr-source kg/day-source	0.005(0.0016,0.016) 0.05(0.017,0.17)	NA	Installation of cap or plug on open end of valve/line	
Flanges[d]	I	lb/hr-source kg/day-source	0.00056(0.0002,0.0025) 0.0060(0.[illegible]2,0.027)	NA	Monitoring and maintenance program	A
Pump Seals[d]	III C	lb/hr-source kg/day-source	NA	0.25(0.16,0.37) 2.7(1.7,4.0)	Mechanical seals, dual seals, purged seals, visual monitoring	A
	IV D	lb/hr-source kg/day-source	NA	0.046(0.019,0.11) 0.50(0.21,1.2)		A
Compressor Seals[d]	II B	lb/hr-source kg/day-source	NA	1.4(0.66,2.9) 15(7.1,31)	Mechanical seals, dual seals, purged seals, visual monitoring	A
	V B	lb/hr-source kg/hr-source	NA	0.11(0.05,0.23) 1.2(0.5,2.5)		
Drains[d]	I A	lb/hr-source kg/day-source	0.070(0.023,0.20) metric #s	NA	Traps and covers	A
Vessel Relief Valves[d]	I	lb/hr-source kg/day-source	0.19(0.070,0.49)	Negligible	Rupture disks upstream of relief valves and/or venting to blowdown system	A
Cooling Towers[i]	-	lb/10[6] gal cooling water kg/10[6] liters cooling water lb/10[3] bbl refinery feed[h] kg/10[6] liters refinery feed	6[illegible] 0.7 10 0.03	0.70 0.083 1.2 0.004	Minimization of hydrocarbon leaks into cooling water system. Monitoring of cooling water for hydrocarbons	D

(Continued)

(A-22)

(cont.)

VOLATILE ORGANIC COMPOUND

TABLE 9.1-2. FUGITIVE HYDROCARBON EMISSION FACTORS FOR PETROLEUM REFINERIES[a,b] ~~(Continued)~~

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Oil/Water Separators[h]	-	lb/10³ gal wastewater kg/10³ liter wastewater	5 0.6	0.2 0.024	Covered separators and/or vapor recovery systems	D
		lb/10³ bbl refinery feed kg/10³ liters refinery feed	200 0.6	10 0.03		
Asphalt Blowing[h]	-	lb/ton of asphalt kg/metric ton of asphalt	60 30	Negligible Negligible	Incineration of vapors	D
Blind Changing[h]	-	lb/10³ bbl refinery feed kg/10³ liters refinery feed	0.3 0.001	Negligible Negligible	Fine flushing, "line" blinds, blind insulation with gate valves	D
Miscellaneous: sampling, non-asphalt blowing (sweetening), purging, etc.	-	lb/10³ bbl refinery feed kg/10³ liters refinery feed	10 0.03	NA NA	Good housekeeping and maintenance	D
Storage[h]		See Section 4.3				
Loading[h]		See Section 4.4				

[a] ~~References 2, 4, 12, 13, 17~~ Data from references 2, 4, 12, and 13 except as noted.

[b] Overall, less than 1 percent by weight of the total ~~hydrocarbon~~ VOC emissions are methane.

[c] The volatility and hydrogen content of the process streams have a substantial effect on the emission rate of some fugitive emission sources. The stream identification letter, stream group description, and stream group name are given below.

Stream Identification Letter	Stream Name	Stream Group Description
I	All Streams	All streams
II	Gas Streams	~~Hydrocarbon~~ VOC gas/vapor at process conditions (containing less than 50% hydrogen, by volume)
III	Light Liquid and Gas/Liquid Streams	Liquid or gas-liquid stream (based on the most volatile class present at ≥20 percent) boiling below kerosene (vapor pressure = 0.1 psia @ 100°F).
IV	Heavy Liquid Stream	Liquid stream (based on the most volatile class present at ≥20 percent) boiling above naphtha (vapor pressure = 0.1 psia @ 100°F).
V	Hydrogen Streams	Gas streams containing more than 50% hydrogen (by volume)

[d] Data from reference 17

[e] Numbers in parentheses are the upper and lower bounds of the 95% confidence interval for the emission factor.

[f] NA - ~~Fugitive emission factors are~~ not available.

[g] The downstream side of these valves is open to the atmosphere. Emissions are through the valve seat of the closed valve.

[h] Refinery rate is defined as the crude oil feed rate to the atmospheric distillation column.

~~[i] Hydrocarbon emissions are nonmethane hydrocarbons.~~

- sweetening,
- process drains,
- storage, ~~and~~
- transfer operations.

Average emission factors are presented, and, where available, 95 percent confidence intervals for the emission factors are also given. The 95 percent confidence interval is the interval or range of values expected to include the true emission factor with 95 percent confidence. For example, the true emission factor for vessel relief valves (if all relief valve emission rates could be measured and averaged) should be between 0.07~~0~~ and 0.49 lb/hr (include metric units).

~~Miscellaneous Fugitive Sources~~

Miscellaneous fugitive emission sources are generally defined as ~~hydrocarbon~~ volatile organic compound (VOC) emission sources ~~which are~~ not associated with a particular ~~refining~~ process, but ~~which~~ are scattered throughout the refinery. Fugitive emission sources include valves, flanges, pump and compressor seals, process drains, relief valves, blind changing, and sample line purging. ~~Hydrocarbon~~ VOC emissions from fugitive emission sources are attributable to the evaporation of leaked or spilled petroleum liquids and gases. Normally, ~~the~~ control of fugitive emissions involves ~~the~~ minimiz~~ation of~~ing leaks and spills through equipment changes, procedural changes, and improved monitoring, housekeeping and maintenance practices.

The fugitive emission rates from valves, pump seals, and compressor seals were found to be a function of the volatility and/or composition of the refinery stream being processed.[17]

The emission factors for these sources are presented for five general categories of process stream groups. The stream categories are described below:

Stream Category ~~A~~ I: All streams

Stream Category ~~B~~ II: Streams which contain more than 50% ~~hydrocarbons~~ VOC by volume, and which are in the gas phase at process conditions. spell

Stream Category ~~C~~ III: Liquid stream or gas/liquid stream which contains 20% or more of a ~~hydrocarbon~~ VOC or class of ~~hydrocarbons~~ VOC's whose boiling point is below that of kerosene (vapor pressure ≥ 0.1 psia @ 100°F). Contains less than 50% hydrogen. spell include metric unit

Stream Category ~~D~~ IV: Heavy liquid streams which contain less than 20% of a ~~hydrocarbon~~ VOC or class of ~~hydrocarbons~~ VOC's whose boiling point is below that of kerosene (vapor pressure ≥ 0.1 psia @ 100°F). spell include metric unit.

Stream Category ~~E~~ V: Gas streams which contain more than 50% by volume of hydrogen. spell

The size of sources such as valves, flanges, pump ~~and~~ seals, compressor seals, relief valves, and process drains ~~do~~ does not affect the leak rates.[17] Thus, the emission factors are independent of process unit or refinery throughput. The number and

stream distribution of the various source types must be known or estimated before total source emissions can be determined.

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 large water supplies required by 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. Heat in the cooling water is transferred to the air. Cooling water circulation rates for refineries commonly range from 0.3 to 3.0 gpm/bbl per day of refinery capacity.[2,16]

Atmospheric emissions from the cooling tower consist of fugitive hydrocarbons 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 contaminant in cooling water is hydrocarbons, dissolved gases such as H_2S and NH_3 may also be found in cooling water (Table 9.1-2).[2,4]

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]

REFERENCES (Continued)

14. Brown, R.A., H.B. Mason, and R.J. Schreiber, Systems Analysis Requirements for Nitrogen Oxide Control of Stationary Sources, Aerotherm/Acurex Corporation, Mountain View, CA. Prepared for the U.S. Environmental Protection Agency, Report No. EPA 650/2-74-091, 1974.

15. Hangebrauck, R.P., *et al.*, Sources of Polynuclear Hydrocarbons in the Atmosphere. 999-AP-33, Public Health Service, 1967.

16. Crumlish, Wm. S., "Review of Thermal Pollution Problems, Standards and Controls at the State Government Level", Presented at the Cooling Tower Institute Symp., New Orleans, Jan. 30, 1966.

17. The Assessment of Environmental Emissions From Oil Refining: Draft Appendix B: Detailed Results, report to EPA - ~~prepared for EPA, IERL~~, Research Triangle Park, N.C., August 23, 1979.

U.S. Environmental Protection Agency

ABSTRACT

The refinery air pollutant emission factors presently contained in Section 9.1 of AP-42, "A Compilation of Air Pollutant Emission Factors," were last revised in 1977. New emission factors for some fugitive emission sources have been developed from the results of recent testing in 13 refineries. This testing was done by Radian Corporation under EPA Contracts 68-02-2665 and 68-02-2147, Exhibit B. These factors are included in the revised subsection 9.1.3 (Fugitive Emission Sources and Control Equipment) presented in this report.

9.1.3 Fugitive Emission Sources and Control Equipment - This section presents descriptions of refinery processes and operations which are significant sources of fugitive emissions. Process flow schemes, emission characteristics and emission control technology are discussed for each process. Emission factors for both uncontrolled and controlled fugitive sources are listed in Table 9.1-2. The fugitive emission sources discussed in this section on petroleum refining emissions are:

- oil-water separators
- cooling towers
- pipeline valves
- pipeline flanges
- relief valves
- pump and compressor seals
- asphalt blowing
- blind changing
- sweetening
- process drains
- storage
- transfer operations

Average emission factors are presented, and where available, 95 percent confidence intervals for the emission factors are also given. The 95 percent confidence interval is the interval or range of values expected to include the true emission factor with 95 percent confidence. For example, the true emission factor for vessel relief valves (if all relief valve emission rates could be measured and averaged) should be between 0.07 and 0.49 lb/hr (0.76 and 5.3 kg/day).

Miscellaneous fugitive emission sources are generally defined as volatile organic compound (VOC) emission

TABLE 9.1-2. FUGITIVE VOLATILE ORGANIC COMPOUND EMISSION FACTORS FOR PETROLEUM REFINERIES[a]

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Pipeline valves[d]	II	lb/hr-source kg/day-source	0.059(0.030,0.110)[e] 0.637(0.32,1.19)	NA[f]	Monitoring and maintenance program	A
	III	lb/hr-source kg/day-source	0.024(0.017,0.036) 0.26(0.18,0.39)	NA		A
	IV	lb/hr-source kg/day-source	0.0005(0.0002,0.0015) 0.005(0.002,0.016)	NA		A
	V	lb/hr-source kg/day-source	0.018(0.007,0.045) 0.19(0.08,0.49)	NA		A
Open-ended valves[d,g]	I	lb/hr-source kg/day-source	0.005(0.0016,0.016) 0.05(0.017,0.17)	NA	Installation of cap or plug on open end of valve/line	
Flanges[d]	I	lb/hr-source kg/day-source	0.00056(0.0002,0.0025) 0.0060(0.002,0.027)	NA	Monitoring and maintenance program	A
Pump seals[d]	III	lb/hr-source kg/day-source	0.25(0.16,0.37) 2.7(1.7,4.0)	NA	Mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlled degassing vents	A
	IV	lb/hr-source kg/day-source	0.046(0.019,0.11) 0.50(0.21,1.2)	NA		A
Compressor seals[d]	II	lb/hr-source kg/day-source	1.4(0.66,2.9) 15(7.1,31)	NA	Mechanical seals, dual seals, purged seals, monitoring and maintenance programs, controlled degassing vents.	A
	V	lb/hr-source kg/hr-source	0.11(0.05,0.23) 1.2(0.5,2.5)	NA		
Drains[d]	I	lb/hr-source kg/day-source	0.070(0.023,0.20) 0.76 (0.25, 2.2)	NA	Traps and covers	A
Vessel relief valves[d] (gas service)	I	lb/hr-source kg/day-source	0.19(0.070,0.49) 2.1 (0.76, 5.3)	Negligible	Rupture disks upstream of relief valves and/or venting to a flare	A
Cooling towers	-	$lb/10^6$ gal cooling water $kg/10^6$ liters cooling water $lb/10^3$ bbl refinery feed[i] $kg/10^6$ liters refinery feed	6 0.7 10 0.03	0.70 0.083 1.2 0.004	Minimization of hydrocarbon leaks into cooling water system. Monitoring of cooling water for hydrocarbons	D

(Continued)

TABLE 9.1-2(cont.). FUGITIVE VOLATILE ORGANIC COMPOUND EMISSION FACTORS FOR PETROLEUM REFINERIES

Emission Source	Process Stream Type[c]	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology	Emission Factor Rating
Oil-water separators	-	$lb/10^3$ gal wastewater	5	0.2	Covered separators and/or vapor recovery systems	D
		$kg/10^3$ liter wastewater	0.6	0.024		
		$lb/10^3$ bbl refinery feed	200	10		
		$kg/10^3$ liters refinery feed	0.6	0.03		
Asphalt blowing	-	lb/ton of asphalt	60	Negligible	Incineration of vapors	D
		kg/metric ton of asphalt	30	Negligible		
Blind changing	-	$lb/10^3$ bbl refinery feed	0.3	Negligible	Line flushing, "line" blinds, blind insulation with gate valves	D
		$kg/10^3$ liters refinery feed	0.001	Negligible		
Miscellaneous: sampling, non-asphalt blowing (sweetening), purging, etc.	-	$lb/10^3$ bbl refinery feed	10	NA	Good housekeeping and maintenance	D
		$kg/10^3$ liters refinery feed	0.03	NA		
Storage		See Section 4.3				
Loading		See Section 4.4				

[a] Data from references 2, 4, 12, and 13 except as noted.

[b] Overall, less than 1 percent by weight of the total VOC emissions are methane.

[c] The volatility and hydrogen content of the process streams have a substantial effect on the emission rate of some fugitive emission sources. The stream identification letter, stream group description, and stream group name are given below.

Stream Identification Letter	Stream Name	Stream Group Description
I	All streams	All streams
II	Gas streams	Hydrocarbon gas/vapor at process conditions (containing less than 50% hydrogen, by volume)
III	Light liquid and gas/liquid streams	Liquid or gas-liquid stream (based on the most volatile class present at >20 percent by volume) with a vapor pressure greater than kerosene (vapor pressure $\geq$ 0.1 psia @ 100°F or 689 Pa @ 38°C)
IV	Heavy liquid streams	Liquid stream (based on the most volatile class present at >20 percent by volume) with a vapor pressure equal to or less than kerosene (vapor pressure $\leq$0.1 psia @ 100°F or 689 Pa @ 38°C)
V	Hydrogen streams	Gas streams containing more than 50 percent hydrogen (by volume)

[d] Data from reference 17.

[e] Numbers in parentheses are the upper and lower bounds of the 95 percent confidence interval for the emission factor.

[f] NA - These emission factors are not available.

[g] The downstream side of these valves is open to the atmosphere. Emissions are through the valve seat of the closed valve.

[h] Emission factor for relief valves in gas service is for leakage, not for emissions caused by vessel pressure relief.

[i] Refinery rate is defined as the crude oil feed rate to the atmospheric distillation column.

sources not associated with a particular process, but scattered throughout the refinery. Fugitive emission sources include valves, flanges, pump and compressor seals, process drains, relief valves, blind changing, and sample line purging. VOC emissions from fugitive emission sources 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, procedural changes, and improved monitoring, housekeeping and maintenance practices.

The fugitive emission rates from valves, pump seals, and compressor seals were found to be a function of the volatility and/or composition of the refinery stream being processed.[17] The emission factors for these sources are presented for five general categories of process stream groups. The stream categories are described below:

Stream Category I:	All Streams
Stream Category II:	Streams which contain more than 50 percent VOC by volume, and which are in the gas phase at process conditions.
Stream Category III:	Liquid stream or gas/liquid stream which contains 20 percent or more by volume of a VOC or class of VOC's whose boiling point is below that of kerosene (vapor pressure >0.1 psia @ 100°F or 689 Pa @ 38°C). Contains less than 50 percent by volume of hydrogen.

Stream Category IV:	Heavy liquid streams which contain less than 20 percent of a VOC or class of VOC's whose boiling point is equal to or above that of kerosene (vapor pressure $\leq$ 0.1 psia @ 100°F or 689 Pa @ 38°C).
Stream Category E:	Gas streams which contain more than 50 percent volume of hydrogen.

The size of sources such as valves, flanges, pump seals, compressor seals, relief valves, and process drains does not affect the leak rates.[17] The emission factors are independent of process unit or refinery throughput. The number and stream distribution of the various source types must be known or estimated before total source emissions can be determined.

REFERENCES (Continued)

14. Brown, R.A., H.B. Mason, and R.J. Schreiber, Systems Analysis Requirements for Nitrogen Oxide Control of Stationary Sources, Aerotherm/Acurex Corporation, Mountain View, CA. Prepared for the U.S. Environmental Protection Agency, Report No. EPA 650/2-74-091, 1974.

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17. U.S. Environmental Protection Agency, Assessment of Atmospheric Emissions from Petroleum Refining: Volume III - Appendix B, EPA (600/2-80-075c), Research Triangle Park, NC, 1980.