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Assessment of Atmospheric Emissions from Petroleum Refining:

Volume 5. Appendix F

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16. ABSTRACT
The report gives results of a 3-year program to assess the environmental impact of petroleum refining atmospheric emissions. This volume gives a detailed characterization of petroleum refinery technology, prepared as part of the program. Petroleum refineries in the U.S. are listed, characterized, and classified according to their types and complexities. It describes four types or sets of refinery models which could be used to simulate the entire refinery industry. It gives the characteristics of crude oils, other raw materials, and intermediate and final products. A major portion of this volume is a detailed description of current refinery process technology and auxiliary operations. It describes the purpose, operation, energy needs, and utility requirements. It includes simple flow diagrams for most processes. It gives a detailed estimate of the number of fugitive emission sources for each process type. It also includes detailed estimates of process and fugitive nonmethane hydrocarbon emissions for major refinery process units.

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Assessments	Technology	14B
Properties	Characterization	
Hydrocarbons	Nonmethane Hydrocarbons	07C

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Assessment of Atmospheric Emissions from Petroleum Refining:

Volume 5. Appendix F

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APPENDIX F: REFINERY TECHNOLOGY CHARACTERIZATION

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SECTION 1

INTRODUCTION

This appendix contains a characterization of refinery technology. The information contained here is useful as the basis for an environmental assessment of the petroleum refining industry.

Section 2 of this appendix contains information on classifying and characterizing petroleum refineries. Four types or sets of refinery models which could be used to simulate the entire United States refining industry are included.

A description of the materials used in the refining process is given in Section 3. Included are discussions on the characteristics of crude oils, other raw materials, intermediate products, and final products.

Section 4 of this appendix contains detailed information on a variety of refining processes. This information includes a description of the purpose of the process and a discussion of current process technology. In addition, estimates of atmospheric emissions which result during the operation of each process are also included.

SECTION 2

REFINERY SIMULATION AND CLASSIFICATION

To develop an environmental assessment of refineries, it is necessary to study refineries and refining processes in some detail. Representative or model refineries are generally very useful when performing this type of study. These models can include refinery flow diagrams, material balances, process types, operating conditions, product slates, plot plans, emissions sources, etc.

In developing refinery models for the simulation of the entire United States refining industry, a considerable compromise must be made between the number of refinery models used in the simulation and the accuracy of the simulation. On January 1, 1979, there were 288 operating refineries in the U.S.[1] The U.S. refining industry could be precisely and accurately simulated with 288 refinery models, each representing an existing, operating refinery. Such a large set of models would obviously be unmanageable for study purposes. A reduction in the number of refinery models provides a more manageable system, but the ability of this system to accurately simulate the refining industry is reduced.

Four types or sets of models which have been or could be developed are discussed in this document. In Section 2.1, a single representative refinery with a fixed process configuration is described. The distribution of products in the product slate of this model refinery is the same as the distribution in the total U.S. refinery production.

Another set of five refinery models could be developed from the five EPA refinery categories,[2] which are modifications of the five refinery classes proposed by the American Petroleum Institute (API). This approach is discussed in Section 2.2.

In Section 2.3, a set of "cluster" refinery models developed by Arthur D. Little, Inc.[3] is discussed. These models were developed to simulate the U.S. refining industry in order to study the impacts of SO_x emissions control and gasoline lead regulations on the industry. The cluster models are quite sophisticated and are described in some detail.

Pacific Environmental Services[4] has developed refinery plot plans for four refinery cases varying from a small existing plant to a large new refinery. Each case has a detailed plot plan and a census of fugitive emission sources for every refinery unit. The cases are discussed in Section 2.4.

2.1 SINGLE REPRESENTATIVE REFINERY MODEL

It is often customary to propose a "typical" or "representative" refinery model for purposes of illustration, discussion, or crude refinery simulation. Flow diagrams of the representative refinery can be used to describe the different types of refineries, the arrangement and integration of refinery processing units, and the origins and fates of the various product and process streams.

An example of this type of refinery model is a representative U.S. refinery model that was defined for process analysis and stream characterization purposes.[5] The flow diagram of this plant is presented in Figure F2-1. The product slate for this refinery is given in Table F2-1, and the capacities of the various individual processing units within the refinery are shown in Table F2-2. This model refinery was developed under the following assumptions:

A. The refinery capacity was 100,000 barrels/day.

B. The process units shown on the flow diagram are those in common use in the refining industry.

C. The capacities of the process units relative to the crude feedstock agree with the average 1978 capacities of all U.S. refineries, as shown in Table F2-2.

D. The refinery product distribution is reasonably consistent with that of the entire refining industry in 1974.

E. The crude feedstock was a weighted composite of crudes from the major oil fields supplying petroleum to domestic refineries in 1974.

In theory, the entire U.S. refining industry could be simulated with a number of these representative model refineries. Practically, however, there are a number of serious drawbacks to this simulation method, and only a very superficial and

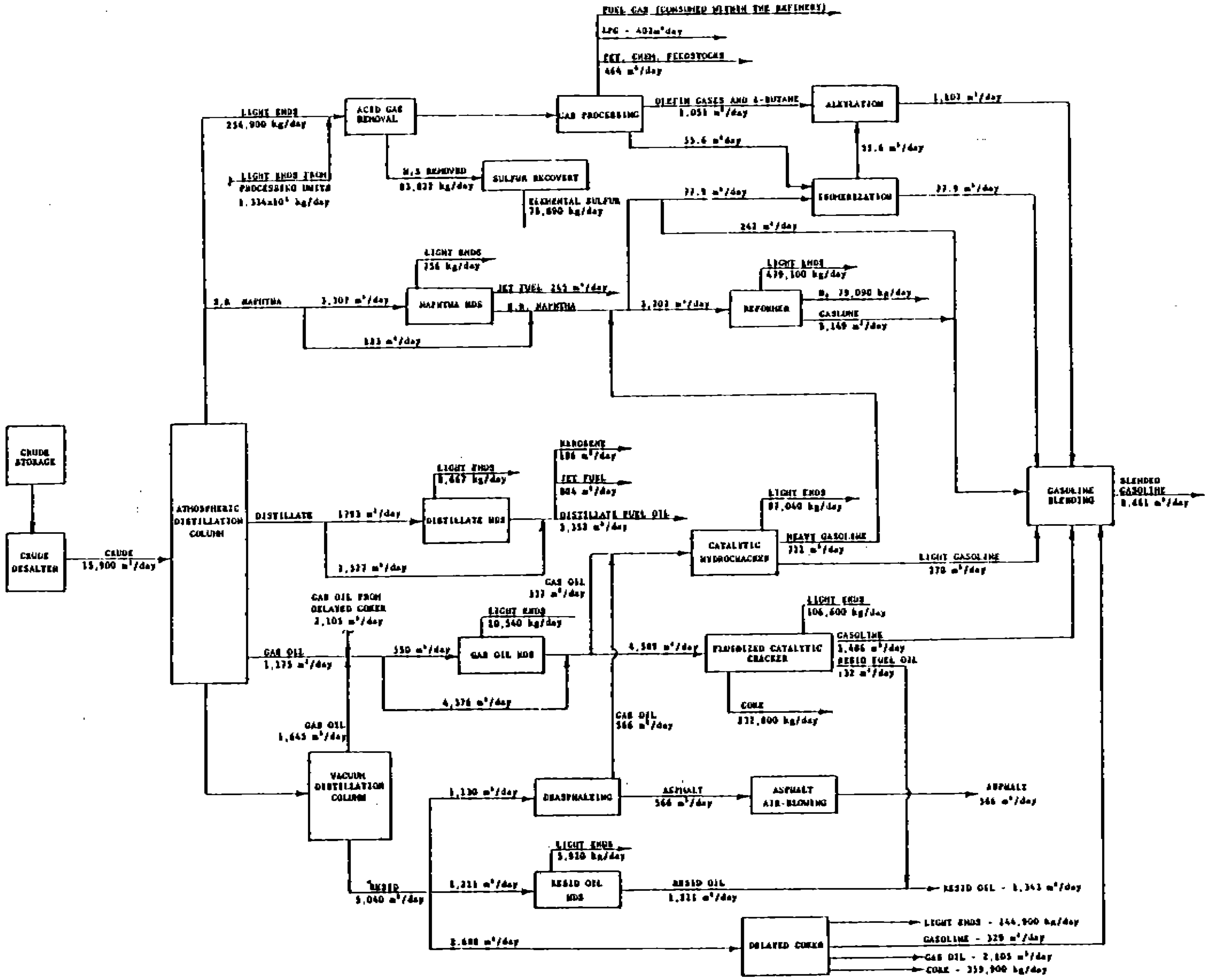


Figure F2-1. Block flow diagram for a representative U.S. refinery.

Source: Reference 5

TABLE F2-1. COMPARISON OF "REPRESENTATIVE" REFINERY PRODUCT SLATE WITH TOTAL ACTUAL U.S. PRODUCTION

Product	Volume Percent of Total Refinery Products	
	Representative Refinery Production	Total U.S. Production (1974)
Gasoline	50.3	48.9
Kerosine	1.2	1.2
Jet Fuel,		
Naphtha type	1.5	1.5
Kerosine type	5.0	4.9
Distillate Fuel Oil	20.4	20.4
Asphalt	3.4	3.4
Residual Fuel Oil	8.2	8.2
Marketable Coke	1.4	1.4
LPG	2.4	2.4
Petrochemical Feedstocks	2.8	2.8
Other (Fuels, misc.)	3.4	4.9
TOTAL	100.0	100.0

Source: References 5 and 6

TABLE F2-2. REFINERY PROCESS UNIT CAPACITIES "REPRESENTATIVE" COMPARED TO AVERAGE OF U.S. REFINERIES

Unit	Volume Percent of Crude Feedstock	
	Representative Refinery	Average of U.S. Refineries (1978)
Reformer	24.6	21.0
Fluid Cat Cracker	28.9	27.6
Hydrocracker	5.6	4.9
Coking	1.4	6.0
Asphalt	3.6	4.5
Isomerization	0.8	0.7
Alkylation	5.6	5.1
Naphtha HDS	20.8	20.0
Distillate HDS	11.3	12.3
Gas Oil HDS	3.5	5.9
Resid. Oil HDS	0.04	0.7

Source: References 1 and 5

imprecise analysis of nationwide refinery operations can be accomplished with this technique. Some of the more obvious deficiencies of this method are listed below.

A. The types of refinery process units are fixed. There are, however, many refineries which utilize fewer process modules, and a number which employ more.

B. The configuration of the process units within the refinery is also fixed. This greatly limits the flexibility of the model.

C. While the representative refinery can efficiently process the selected composite crude oil, it is not suitable for refining many of the individual crudes processed by refineries across the U.S.

D. The necessary specification of the individual processing units and the associated range of operating conditions further limits the utility of this model for representing the entire industry.

E. Total fugitive emissions cannot be calculated since the model does not provide a means of estimating the number of individual fugitive sources within each process unit.

F. The model is very general and accurate estimates for both hydrocarbon and non-hydrocarbon emissions from non-fugitive sources are difficult.

In actuality, the only major variables that can be manipulated in this type of model are the size of the refinery (in terms of crude feedstock) and the process operating conditions (within the operating constraints of each of the individual processes). For the purposes of this project, the single representative refinery model is unsuitable.

2.2 EPA/API REFINERY CLASSIFICATION AND PROPOSED MODELS

One possible means of modeling the refining industry is to categorize the nation's petroleum refineries according to a logical set of basic characteristics, and to develop a typical or representative model refinery for each of the categories. The refining industry could then be simulated with this group of models.

API has developed a classification system for refineries. All refineries are grouped into one of the following five basic refinery classes.

- <u>Class A: Topping</u> - The principal operation is the separation of crude oil into its major fractions. Excluded from this class are refineries with cracking and/or coking processes. Hydrotreating operations may be carried out in this type of refinery.

- Class B: Topping and Cracking - In addition to the crude separation and hydrotreating operations of the topping refineries, cracking and coking processes are included. Also included are refineries with production of conventional refinery-associated first-generation products and intermediates such as BTX (benzene/toluene/xylene), alkanes, alkynes, alkenes, and other miscellaneous products such as sulfur, hydrogen, and coke. Refineries which contain lube oils processing units are not included in this classification.

- Class C: Topping, Cracking, and Petrochemical - Refineries in this classification contain topping, cracking, conversion, coking and, in addition, first and second-generation petrochemical operations. No lube oils processing occurs in this class of refineries.

- Class D: Integrated - This classification includes refineries with all of the Class B operations plus lube oils processing.

- Class E: Integrated and Petrochemical - Petrochemical manufacturing units are included in this classification of refinery, along with all the processes of a Class D refinery.

The EPA has developed refinery subcategories which are reflective of the wastewater loading with respect to refinery type, processing units, and operating severity.[2] There are five subcategories that are similar to the API classifications. The characteristics of the subcategories are summarized in Table F2-3.

The topping Subcategory A is the same as the API Class A. Subcategory B (Cracking) is the same as the API Class B except that the production of first-generation petrochemicals is included only if these products amount to less than 15 percent of the refinery throughput. The petrochemical Subcategory C is similar to the API Class C. Petrochemical operations of refineries in this subcategory include production of intermediate chemicals such as cumene, phthalic anhydride, alcohols, ketones, styrene, etc. These chemicals are generally considered to be second-generation petrochemicals. Refineries which include the associated manufacture of second generation petrochemicals belong in Subcategory C.

The lube Subcategory D is the same as the API Class D. The integrated Subcategory E is identical to the API Class E except for the exclusion of refineries having first-generation petrochemical operations where the petrochemical production capacity is equivalent to less than 15 percent of refinery throughput.

There were 288 operating refineries in the U.S. as of January 1, 1979.[1] These refineries have been classified into the EPA subcategories, and are tabulated by subcategory or type in Tables F2-4 through F2-8. Included in these tables are company, location, crude capacity, major process unit capacities, and production capacities for each of the 288 refineries. They were classified using information from Oil and Gas Journal,[1] EPA,[2] and the 1976 Directory of Chemical Producers, U.S.A.[7]

TABLE F2-3. SUBCATEGORIZATION OF THE PETROLEUM REFINING INDUSTRY REFLECTING SIGNIFICANT DIFFERENCES IN WASTEWATER CHARACTERISTICS

Subcategory	Basic Refinery Operations Included
Topping	Topping and catalytic reforming whether or not the facility includes any other process in addition to topping and catalytic process. This subcategory is not applicable to facilities which include thermal processes (coking, visbreaking, etc.) or catalytic cracking.
Cracking	Topping and cracking, whether or not the facility includes any processes in addition to topping and cracking, unless specified in one of the subcategories listed below.
Petrochemical	Topping, cracking and petrochemical operations, whether or not the facility includes any process in addition to topping, cracking and petrochemical operations,* except lube oil manufacturing operations.
Lube	Topping, cracking and lube oil manufacturing processes, whether or not the facility includes any process in addition to topping, cracking and lube oil manufacturing processes, except petrochemical operations.*
Integrated	Topping, cracking, lube oil manufacturing processes, and petrochemical operations, whether or not the facility includes any processes in addition to topping, cracking, lube oil manufacturing processes and petrochemical operations.*

*The term "petrochemical operations" shall mean the production of second generation petrochemicals (i.e., alcohols, ketones, cumene, styrene, etc.) or first generation petrochemicals and isomerization products (i.e., BTX, olefins, cyclohexane, etc.) when 15% or more of refinery production is as first generation petrochemicals and isomerization products.

Source: Reference 2

TABLE F2-4. TYPE "A" REFINERIES - CAPACITIES AS OF JANUARY 1, 1979

Company - Location	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Golden Eagle Refining Co., Carson, Calif.	A		16.5	17.2	--	--	--	--	--	--	--	--	--	--	--	--
Lunday-Thagard Oil Co., South Gate, Calif.	A		12.0	10.0	2.5	--	--	--	--	--	--	--	--	--	2.2	--
MacMillan Ring-Free Oil Co., Signal Hill, Calif.	A		11.6	12.2	--	--	--	--	--	--	--	--	--	--	--	--
Mohawk Petroleum Corp., Inc., Bakersfield, Calif.	A		22.1	22.8	--	--	--	2.5	--	2.5	2.5	--	--	--	--	--
Newhall Refining Co., Inc., Newhall, Calif.	A		17.6	18.5	8.0	--	--	--	--	--	--	--	--	--	3.0	--
Road Oil Sales, Inc., Bakersfield, Calif.	A		1.5	1.6	--	--	--	--	--	--	--	--	--	--	--	--
Sabre Refining, Inc., Bakersfield, Calif.	A		8.6	9.0	--	--	--	--	--	--	--	--	--	--	--	--
San Joaquin Refining Co., Oildale, Calif.	A		27.0	28.4	--	--	--	--	--	--	--	--	--	--	--	--
Sunland Refining Corp., Bakersfield, Calif.	A		15.0	15.0	--	--	--	1.0	--	--	1.5	--	--	--	--	--
Amoco Oil Co., Savannah, Ga.	A		18.0	19.0	--	--	--	--	--	--	--	--	--	--	11.0	--
Young Refining Corp., Douglasville, Ga.	A		5.0	5.0	--	--	--	--	--	--	--	--	--	--	3.0	--
Hawaiian Independent Refinery, Inc., Oahu, Hawaii	A		62.5	65.5	--	--	--	11.0	--	--	11.0	--	--	--	--	--

Continued

TABLE F2-4. Continued

Company - Location	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Yetter Oil Co., Colmar, Ill.	A		1.0	1.1	1.0	--	--	--	--	--	--	--	--	--	--	--
Princeton Refining, Inc., Princeton, Ind.	A		4.6	4.8	--	--	--	1.5	--	--	1.5	--	--	--	--	--
Gladieux Refinery, Inc., Fort Wayne, Ind.	A		10.6	12.2	--	--	--	--	--	--	--	--	--	--	--	--
Laketon Asphalt Refining, Inc., Laketon, Ind.	A		8.1	8.5	7.5	--	--	--	--	--	--	--	--	--	3.0	--
Mid-America Refinery Co., Chanute, Kansas	A		3.1	3.3	1.8	--	--	--	--	--	--	--	--	--	--	--
Somerset Refinery, Inc., Somerset, Ky.	A		5.0	5.3	--	--	--	1.0	--	--	--	--	--	--	--	--
Atlas Processing Co., Div. of Pennzoil, Shreveport, La.	A		45.0	47.4	9.1	--	--	10.0	--	--	10.0	--	1.0	2.2	0.6	--
Calumet Refining Co., Princeton, La.	A		2.4	2.4	4.8	--	--	--	--	--	--	--	--	2.0	0.5	--
Claiborne Gasoline Co., Lilbon, La.	A		6.5	6.7	--	--	--	2.2	--	--	--	--	--	--	--	--
Evangeline Refining Co., Inc., Jennings, La.	A		4.8	5.0	--	--	--	0.6	--	--	--	--	--	--	--	--
Cotton Valley Solvents (Kerr McGee), Cotton Valley, La.	A		11.0	11.2	--	--	--	--	--	--	--	--	--	--	--	--
Lalet, Inc., St. James, La.	A		20.0	21.1	20.0	--	--	--	--	--	--	--	--	--	--	--
Placid Refining Co., Port Allen, La.	A		34.2	36.0	20.0	--	--	5.5	--	--	6.0	--	--	--	--	--

Continued

TABLE F2-4. Continued

					Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	Category		Crude Capacity													
Company - Location	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/Isom.	Lubes	Asphalts	Coke, T/D
Amoco Oil Co., Baltimore, Md.	A		15.0	17.0	--	--	--	--	--	--	--	--	--	--	10.7	--
Chevron U.S.A. Inc., Baltimore, Md.	A		13.5	14.2	13.8	--	--	--	--	--	--	--	--	--	11.0	--
Crystal Refining Co., Carson City, Mich.	A		6.2	4.0	--	--	--	--	--	--	--	--	--	--	--	--
Lakeside Refining Co., Kalamazoo, Mich.	A		5.6	5.9	--	--	--	2.0	--	--	--	--	--	--	--	--
Osceola Refining Co., West Branch, Mich.	A		12.5	10.0	--	--	--	1.6	--	--	2.8	--	--	--	--	--
Southland Oil Co., Lumberton, Miss.	A		5.8	6.6	--	--	--	--	--	--	--	--	--	--	2.8	--
Southland Oil Co., Sandersville, Miss.	A		11.0	12.5	6.9	--	--	--	--	--	--	--	--	--	5.0	--
Southland Oil Co., Yazoo City, Miss.	A		3.8	4.5	2.5	--	--	--	--	--	--	--	--	--	1.9	--
Carlbon Four Corners, Inc., Kirland, New Mexico	A		2.4	2.5	--	--	--	--	--	--	--	--	--	--	--	--
Southern Union Refining Co., Lovington, N.M.	A		36.0	37.0	--	--	--	--	--	--	--	--	--	--	--	--
Southern Union Refining Co., Monument, N.M.	A		5.0	5.2	--	--	--	--	--	--	--	--	--	--	--	--
Northland Oil & Refining Co., Dickinson, N.D.	A		5.0	5.3	--	--	--	--	--	--	--	--	--	--	--	--
Ashland Petroleum Co., Findlay, Ohio	A		20.4	21.0	8.0	--	--	--	--	--	--	--	--	--	6.5	--

Continued

TABLE F2-4. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/Isom.	Lubes	Asphalts	Coke, T/D
Allied Materials Corp., Stroud, Okla.	A		7.0	7.3	7.3	--	--	--	--	--	--	--	--	1.0	1.8	--
Tonkawa Refining Co., Arnett, Okla.	A		6.0	6.5	--	--	--	--	--	--	--	--	--	--	--	--
Standard Oil Company of Calif., Portland, Oregon	A		14.0	14.7	15.0	--	--	--	--	--	--	--	--	--	8.6	--
Pennzoil Co., Wolf's Head Division, Rouseville, Pa.	A		12.0	12.5	4.0	--	--	3.6	--	--	7.2	--	--	--	3.9	--
Kendall-Amalie Div., Witco Chemical Corp., Bradford, Pa.	A		9.0	9.5	--	--	--	2.0	--	--	2.5	--	--	4.7	--	--
Valvoline Oil Co., Division of Ashland Oil, Inc., Freedom, Pa.	A		6.8	7.0	3.6	--	--	--	--	--	--	--	--	--	1.4	--
Longview Refining Co., Division of Crystal Oil, Longview, Texas	A		8.8	9.0	--	--	--	5.5	--	3.0	4.0	--	--	--	--	--
Dorchester Refining Co., White Deer, Texas	A		1.0	1.0	--	--	--	1.0	--	--	--	--	--	--	--	--
Eddy Refining Co., Houston, Texas	A		3.7	3.5	--	--	--	--	--	--	--	--	--	--	--	--
Flint Chemical Co., San Antonio, Texas	A		1.2	1.4	--	--	--	--	--	--	--	--	--	--	--	--
Gulf States Oil & Refining Co., Corpus Christi, Texas	A		12.5	13.2	--	--	--	--	--	--	--	--	--	--	--	--
Howell Corp., San Antonio, Texas	A		3.0	4.0	--	--	--	1.3	--	--	--	--	0.8	--	--	--

Continued

TABLE F2-4. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Sector Refining Co., Tucker, Texas	A		9.7	10.0	--	--	--	--	--	--	--	--	--	--	--	--
Carbonit Refinery, Inc. Hearne, Texas	A		10.0	11.0	--	--	--	--	--	--	--	--	--	--	--	--
Pride Refining, Inc. Abilene, Texas	A		20.5	36.5	12.0	--	--	--	--	--	--	--	--	--	--	--
South Hampton Refining Co., Silsbee, Texas	A		20.5	22.5	--	--	--	4.0	--	--	--	--	--	--	--	--
Tesoro Petroleum Corp., Carrizo Springs, Texas	A		26.1	27.5	--	--	--	4.0	--	--	--	--	--	--	--	--
Texaco, Inc., Port Neches, Texas	A		47.0	49.5	26.0	--	--	--	--	--	--	--	--	--	9.0	--
Texas Asphalt & Refining Co., Euless, Texas	A		5.0	6.0	--	--	--	--	--	--	--	--	--	--	--	--
Hunt Oil Co., Tuscaloosa, Ala.	A		29.0	30.0	15.0	--	--	5.5	--	9.0	11.5	--	--	--	10.0	--
Vulcan Refining Co., Cordona, Ala.	A		10.6	11.4	--	--	--	5.5	--	--	--	--	--	--	5.0	--
Warrior Asphalt Corp., Tuscaloosa, Ala	A		2.9	3.0	--	--	--	--	--	--	--	--	--	--	1.5	--
Atlantic Richfield Co. North Slope, Alaska	A		13.0	13.7	--	--	--	--	--	--	--	--	--	--	--	--
North Pole Refining, North Pole, Alaska	A		22.6	25.0	--	--	--	--	--	--	--	--	--	--	--	--
Chevron, U.S.A. Inc. Kenai, Alaska	A		22.0	23.2	--	--	--	--	--	--	--	--	--	--	0.3	--

Continued

TABLE F2-4. Continued

Company - Location	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Tesoro Petroleum Corp., Kenai, Alaska	A		38.0	40.0	--	--	--	6.0	--	--	6.0	--	--	--	--	--
Arizona Fuels Corp., Fredonia, Arizona	A		6.0	5.4	3.5	--	--	--	--	--	--	--	--	--	--	--
Cross Oil & Refining Co., Smackover, Ark.	A		8.6	8.8	3.1	--	--	--	--	--	1.2	--	--	1.5	1.5	--
Berry Petroleum, Stevens, Ark.	A		2.9	3.0	2.0	--	--	--	--	--	--	--	--	--	1.1	--
MacMillan Ring-Free Oil Co., Norphlet, Ark.	A		4.4	4.5	3.0	--	--	--	--	--	--	--	--	2.0	1.5	--
Douglas Oil Co., Paramount, Calif.	A		46.5	48.0	28.0	--	--	11.5	--	--	29.0	--	--	--	15.0	--
Douglas Oil Co., Santa Maria, Calif.	A		9.5	10.0	7.8	--	--	--	--	--	--	--	--	--	6.8	--
Edgington Oil Co., Long Beach, Calif.	A		29.5	30.0	12.6	--	--	--	--	--	--	--	--	--	8.0	--
Edgington Oxnard Refinery, Oxnard, Calif.	A		2.5	2.5	--	--	--	--	--	--	--	--	--	--	--	--
Fletcher Oil & Refining Co., Carson, Calif.	A		25.0	26.0	--	--	--	4.0	--	--	4.0	--	--	--	--	--
Golden Bear Div., Witco Chemical Corp., Oildale, Calif.	A		10.5	11.0	9.5	--	--	--	--	--	--	--	--	4.0	3.2	--
Sound Refining, Inc., Tacoma, Wash.	A		8.0	10.0	3.5	--	--	--	--	--	--	--	--	1.9	2.6	--
Chevron U.S.A. Inc., Seattle, Wash.	A		4.5	4.7	5.0	--	--	--	--	--	--	--	--	--	4.0	--
U.S. Oil & Refining Co., Tacoma, Wash.	A		21.4	22.5	4.8	--	--	3.0	--	--	3.0	--	--	--	--	--

Continued

TABLE F2-4. Continued

					Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	Category EPA	Category ADL	Crude Capacity MBPCD	Crude Capacity MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/Isom.	Lubes	Asphalts	Coke, T/D
Pennzoil Co., Elk Refining Div., Falling Rock, W.Va.	A		4.9	5.2	2.5	--	--	2.0	--	--	2.5	--	--	1.4	--	--
Quaker State Oil Refining Corp., Newell, W.Va.	A		9.7	10.0	4.0	--	--	2.9	--	4.4	3.1	--	--	3.6	--	--
Quaker State Oil Refining Corp., St. Mary's, W.Va.	A		4.9	5.0	2.2	--	--	1.3	--	--	1.5	--	--	1.7	--	--
Mountaineer Refining Co., Inc., LaBarge, Wyo.	A		0.5	0.5	--	--	--	--	--	--	--	--	--	--	--	--
Sage Creek Refining Co., Crowley, Wyo.	A		1.0	1.2	--	--	--	0.5	--	--	--	--	--	--	--	--
Southwestern Refining Co., LaBarge, Wyo.	A		1.0	1.0	--	--	--	--	--	--	--	--	--	--	--	--
Louisiana Land & Exploration Co., Saraland, Ala.	A		41.3	40.0	--	--	--	--	--	--	--	--	--	--	--	--
Mobile Bay Refining Co., Chickasaw, Ala.	A		28.0	21.0	--	--	--	3.0	--	--	3.0	--	--	--	--	--
Basin Petroleum, Inc., Long Beach, Calif.	A		14.3	15.0	--	--	--	--	--	--	--	--	--	--	--	--
DeMenno Resources, Compton, Calif.	A		10.0	11.0	--	--	--	--	--	--	--	--	--	1.0	--	--
Eco Petroleum, Inc., Signal Hill, Calif.	A		5.6	6.0	--	--	--	--	--	--	--	--	--	--	--	--
Sierra Anchor, McKittrick, Calif.	A		10.0	10.8	2.0	--	--	--	--	--	--	--	--	--	--	--
USA Petrochem Corp., Ventura, Calif.	A		20.0	19.0	--	--	--	6.0	--	--	7.5	--	--	--	--	--

Continued

TABLE F2-4. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
West Coast Oil Co., Oildale, Calif.	A		19.0	20.0	--	--	--	--	--	--	--	--	--	6.0	--	--
Continental Oil Co., Denver, Colo.	A		10.0	11.0	2.5	--	--	6.5	--	--	7.0	--	--	--	--	--
Gary Western Co., Fruita, Colo.	A		13.0	14.0	10.0	--	--	2.0	--	--	2.0	--	--	--	0.6	--
Seminole Asphalt Refining, Inc., St. Marks, Fla.	A		9.8	9.1	5.0	--	--	--	--	--	--	--	--	--	--	--
M. T. Richards, Inc., Crossville, Ill.	A		0.7	0.7	--	--	--	--	--	--	--	--	--	--	--	--
Industrial Fuel & Asphalt of Indiana, Inc., Ind.	A		9.8	10.3	--	--	--	--	--	--	--	--	--	--	--	--
E-Z Serve Refining Inc., Shallowater, Kansas	A		4.6	4.8	--	--	--	--	--	--	--	--	--	--	--	--
Kentucky Oil & Refining Co., Inc., Betsy Layne, Ky.	A		0.5	1.0	--	--	--	--	--	--	--	--	--	--	--	--
Bayou State Oil Corp., Hosston, La.	A		5.0	5.3	2.0	--	--	--	--	--	--	--	--	--	--	--
Calcasieu Refining Ltd., Lake Charles, La.	A		5.7	6.0	--	--	--	--	--	--	--	--	--	--	--	--
Hill Petroleum Co., Krotz Springs, La.	A		10.1	10.7	--	--	--	--	--	--	--	--	--	--	--	--
Marathon Oil Co., Garyville, La.	A		200.0	205.0	100.0	--	--	37.5	--	86.5	37.5	--	--	--	20.0	--
Mt. Airy Refinery Co., Mt. Airy, La.	A		13.6	14.2	--	--	--	--	--	--	--	--	--	--	--	--

Continued

TABLE F2-4. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Shepherd Oil Inc., Mermentau, La.	A		10.0	10.0	--	--	--	--	--	--	--	--	--	--	--	--
T & S Refining Inc., Jennings, La.	A		10.2	10.9	--	--	--	--	--	--	--	--	--	--	--	--
Dow Chemical U.S.A., Bay City, Mich.	A		14.0	22.0	--	--	--	--	--	--	--	--	--	--	--	--
Ergon Refining Inc., Vicksburg, Miss.	A		10.0	10.0	--	--	--	--	--	--	--	--	--	--	--	--
Kenco Refining Inc., Wolf Point, Mont.	A		4.5	4.7	--	--	--	--	--	--	--	--	--	--	--	--
Nevada Refining Co., Tonopah, Nevada	A		4.0	4.2	--	--	--	--	--	--	--	--	--	--	--	--
ATC Petroleum, Inc., Newington, N.H.	A		12.8	13.0	--	--	--	--	--	--	--	--	--	--	--	--
Giant Industries, Inc., Farmington, N.M.	A		8.8	9.2	--	--	--	--	--	--	--	--	--	--	--	--
Cibro Petroleum Products, Inc., Albany, N.Y.	A		28.0	30.0	--	--	--	--	--	--	--	--	--	--	--	--
Quaker State Oil Refining Corp., Emlenton, Pa.	A		3.3	3.5	1.7	--	--	1.3	--	--	1.5	--	--	1.7	--	--
Quaker State Oil Refining Corp., Farmers Valley, Pa.	A		6.5	6.8	2.8	--	--	1.9	--	--	2.3	--	--	2.5	--	--
Adobe Refining Co., La Blanca, Texas	A		5.0	5.0	--	--	--	--	--	--	--	--	--	--	--	--
Pioneer Refining, Ltd., Nixon, Texas	A		4.9	5.0	--	--	--	--	--	--	--	--	--	--	--	--
Quitman Refining Co., Quitman, Texas	A		6.0	5.7	--	--	--	--	--	--	--	--	--	--	--	--

Continued

TABLE F2-4. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Rancho Refining Co., Donna, Texas	A		1.2	1.2	1.2	--	--	--	--	--	--	--	--	--	--	--
Saber Refining Co., Corpus Christi, Tx.	A		20.0	21.0	--	--	--	--	--	--	--	--	--	--	--	--
Sentry Refining, Inc., Corpus Christi, Tx.	A		10.0	10.0	--	--	--	--	--	--	--	--	--	--	--	--
Sigmor Refining Co., Three Rivers, Tx.	A		22.8	24.0	1.6	--	--	8.5	--	--	8.5	--	--	1.2	--	--
Thriftway, Inc., Graham, Tx.	A		1.8	2.5	--	--	--	--	--	--	--	--	--	--	--	--
Tipperary Corp., Ingleside, Tx.	A		6.5	6.5	--	--	--	--	--	--	--	--	--	--	--	--
Uni Refining Co., Ingleside, Tx.	A		11.9	12.5	--	--	--	--	--	--	--	--	--	--	--	--
Morrison Petroleum Co., Woods Cross, Utah	A		2.5	2.6	--	--	--	--	--	--	--	--	--	--	--	--
C & H Refinery, Inc., Lusk, Wyo.	A		0.2	0.2	--	--	--	--	--	--	--	--	--	--	--	--
Glacier Park Co., Osage, Wyo.	A		3.9	4.0	--	--	--	--	--	--	--	--	--	--	--	--
Glenrock Refinery Co., Glenrock, Wyo.	A		1.0	1.0	--	--	--	--	--	--	--	--	--	--	--	--
ATC Petroleum, Inc., Wilmington, N.C.	A		11.9	12.5	--	--	--	--	--	--	--	--	--	--	--	--
Erickson Refining Co., Port Neches, Tx.	A		30.0	32.0	--	--	--	--	--	--	--	--	--	--	--	--
United Independent Oil Oil Co., Tacoma, Wash.	A		1.0	1.0	--	--	--	--	--	--	--	--	--	--	--	--
TOTAL			1762.8	1849.0	409.0	--	--	168.2	--	105.4	183.4	--	1.8	38.4	167.0	--

Source: Reference 1

TABLE F2-5. TYPE "B" REFINERIES - CAPACITIES AS OF JANUARY 1, 1979

Company - Location	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Beacon Oil Co. Hanford, Calif.	B	--	12.3	12.4	--	0.5	--	1.7	--	--	--	--	--	--	--	--
Champlin Petroleum Co., Wilmington, Calif.	B	--	31.2	32.5	20.0	11.5	--	--	--	--	--	--	--	--	--	650
Exxon Co., Benicia, Calif.	B	--	99.0	105.0	54.0	26.0	49.0	24.0	23.0	23.0	54.0	11.5	--	--	--	1000
Gulf Oil Co., Santa Fe Springs, Calif.	B	--	51.5	53.8	25.0	20.3	13.5	22.0	11.0	--	15.0	3.0	--	--	4.0	--
Kern County Refinery, Inc., Bakersfield, Calif.	B	--	15.9	15.6	--	6.5	3.0	--	--	--	3.0	--	--	--	--	--
Mobil Oil Co., Torrance, Calif.	B	HC	123.5	131.1	95.0	62.0	60.0	36.0	21.7	--	60.5	10.0	--	--	--	2900
Powerine Oil Co., Sante Fe Springs, Calif.	B	--	44.1	46.0	15.0	--	11.5	1.5	--	8.0	10.0	2.7	--	--	1.0	--
Shell Oil Co., Wilmington, Delaware	B	--	108.0	113.0	60.0	41.5	35.0	24.0	--	--	72.4	8.6	3.8	--	--	2100
Texaco, Inc., Wilmington, Calif.	B	--	75.0	78.9	--	48.0	28.0	35.0	20.0	13.0	20.0	4.4	--	--	--	1650
Tosco Corp., Bakersfield, Calif.	B	--	39.5	40.0	23.5	7.0	12.0	15.5	14.0	--	8.4	1.8	--	--	--	250
Union Oil Co. of Calif., Los Angeles, Calif.	B	--	108.0	111.0	83.0	20.0	45.0	49.0	21.0	--	85.0	8.0	--	--	10.0	--
Asamera Oil U.S. Inc., Commerce City, Colo.	B	--	17.1	18.0	7.0	--	7.0	3.0	--	--	--	1.8	--	--	--	--
Clark Oil & Refining Corp., Hartfor, Ill.	B	--	57.0	60.0	18.0	13.0	28.0	9.2	--	--	20.0	8.0	--	--	--	--

Continued

TABLE F2-5. Continued

					Charge Capacity, MBPSD							Production Capacity				
	Category		Crude Capacity									MBPSD				
Company - Location	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Marathon Oil Co., Robinson, Ill.	B	--	195.0	205.0	62.0	21.8	38.0	47.3	22.0	6.0	22.0	7.6	--	--	--	--
Mobil Oil Corp., Joliet, Ill.	B	LM	180.0	200.0	88.0	34.0	92.0	47.0	--	75.0	74.0	23.0	--	--	--	2080
Texaco, Inc., Lawrenceville, Ill.	B	--	84.0	88.4	25.3	10.0	38.2	26.7	--	--	45.6	7.3	--	--	3.0	--
Texaco, Inc., Lockport, Ill.	B	--	72.0	75.8	14.7	30.0	33.3	21.1	--	--	40.0	8.9	--	--	--	300
Union Oil Co. of Calif., Lemont, Ill.	B	LM	151.0	158.9	55.0	21.0	55.0	31.0	--	--	86.2	15.5	3.5	--	2.5	1050
Indiana Farm Bureau Coop. Assn., Inc., Mt. Vernon, Ind.	B	--	21.5	22.6	8.0	--	7.2	3.0	--	--	--	--	--	--	--	--
Rock Island Refining Corp., Indianapolis, Ind.	B	—	43.6	44.5	17.0	--	17.0	8.7	--	--	13.5	4.2	--	--	5.0	--
Fester Refinery Co., El Dorado, Kan.	B	--	21.8	22.5	8.0	--	11.0	4.0	--	--	4.0	2.0	--	--	2.0	--
Total Petroleum, Arkansas City, Kan.	B	--	42.5	47.2	13.0	--	9.6	16.3	3.0	--	16.3	2.6	--	--	3.0	--
CRA, Inc., Phillipsburg, Kan.	B	--	26.6	27.5	10.0	--	8.5	5.3	--	--	7.5	2.3	--	--	2.0	--
Derby Refining Co., Wichita, Kan.	B	--	25.0	27.7	9.8	3.8	10.8	5.0	--	--	5.0	3.0	--	--	--	160
Mobil Oil Corp., Augusta, Kan.	B	--	50.0	52.0	18.3	4.1	21.5	22.0	--	--	11.5	3.8	--	--	8.0	--
National Coop. Refinery Assn., McPherson, Kan.	B	--	54.2	57.0	18.0	17.0	20.0	7.0	--	--	8.0	6.0	2.0	--	--	425

Continued

TABLE F2-5. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Ashland Petroleum Co., Louisville, Ky.	B	--	25.2	26.0	13.0	--	10.0	3.0	--	--	3.0	--	--	--	3.5	--
Continental Oil Co., Lake Charles, La.	B	--	87.0	90.0	11.5	15.5	25.5	18.5	--	--	19.0	4.6	0.6	--	--	--
Good Hope Refineries, Inc., Metairie, La.	B	--	86.0	95.0	60.0	--	65.0	4.5	--	--	4.5	--	2.0	--	--	--
Gulf Oil Co. - Alliance Ref., Belle Chase, La.	B	LG	195.5	202.0	73.0	16.0	78.0	37.5	--	38.0	42.0	28.4	16.5	--	--	840
Gulf Oil Co., Venice, La.	B	--	28.7	29.1	--	--	--	18.0	11.5	--	14.4	--	--	--	--	--
Murphy Oil Corp., Meraux, La.	B	--	92.5	95.4	40.0	--	10.5	23.0	--	15.5	44.0	3.0	--	--	--	--
Shell Oil Co., Norco, La.	B	LG	230.0	240.0	90.0	64.9	100.0	46.0	24.0	25.0	29.0	13.5	--	--	10.0	860
Tenneco Oil Co., Chalmette, La.	B	--	114.0	120.0	23.0	9.0	22.0	35.0	18.0	--	24.0	5.0	7.0	--	--	350
Texaco, Inc., Convent, La.	B	--	140.0	147.4	36.8	13.3	77.8	33.3	--	--	61.0	13.9	--	--	--	--
Marathon Oil Co., Detroit, Mich.	B	--	65.0	67.0	25.0	--	25.5	16.0	--	12.5	16.5	3.5	--	--	8.7	--
Total Petroleum, Inc., Alma, Mich.	B	--	40.0	42.0	--	--	16.0	10.0	--	5.0	10.0	3.0	1.0	--	--	--
Continental Oil Co., Wrenshall, Minn.	B	--	23.5	24.0	9.0	--	9.5	3.6	--	--	3.6	--	1.2	--	--	--
Koch Refining Co., Rosemont, Minn.	B	--	127.3	131.9	80.0	23.0	50.0	15.0	--	45.0	42.0	8.5	--	--	35.0	1300
Northwest Refining Co., Division of Ashland Oil, Inc., St. Paul Park, Minn.	B	--	67.0	69.0	32.0	--	23.0	12.0	--	20.0	20.2	3.3	--	--	14.0	--

Continued

TABLE F2-5. Continued

					Charge Capacity, MBPSD							Production Capacity				
	Category		Crude Capacity									MBPSD				
Company - Location	EPA	ADL^a	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Amerada Hess Corp., Purvis, Miss.	B	--	30.0	31.6	--	7.0	16.2	5.4	--	--	5.5	5.2	--	--	--	320
Amoco Oil Co., Sugar Creek, Miss.	B	--	109.0	111.0	40.0	13.5	42.0	16.0	--	--	61.5	5.0	--	--	6.5	800
Cenex Laurel, Mont.	B	--	40.4	42.5	14.0	--	12.0	12.0	--	14.0	15.0	3.0	2.0	--	6.0	--
Continental Oil Co., Billings, Mont.	B	--	52.5	56.0	17.0	--	15.0	15.8	--	--	38.0	3.8	2.6	--	4.5	--
Exxon Co., Billings, Mont.	B	--	45.0	46.0	18.0	7.0	19.2	14.5	4.9	--	35.5	3.4	--	--	3.0	310
Phillips Petroleum Co., Great Falls, Mont.	B	--	6.0	6.3	2.1	--	2.1	0.6	--	--	2.0	--	--	--	0.9	--
Westco Refining Co., Cut Bank, Mont.	B	--	5.3	6.0	--	2.2	--	2.3	--	--	3.3	--	--	--	--	--
CRA, Inc., Scottsbluff, Neb.	B	--	5.6	6.2	2.4	--	2.4	0.8	--	--	--	--	--	--	--	--
Chevron U.S.A., Inc., Perth Amboy, N.J.	B	--	168.0	176.8	96.0	--	33.0	39.0	--	60.0	59.0	3.0	--	--	30.0	--
Navajo Refining Co., South Artesia, N.M.	B	--	22.6	23.8	4.0	--	5.6	--	--	--	--	1.5	--	--	2.4	--
Shell Oil Co., Ciniza, N.M.	B	--	18.0	19.0	7.9	--	7.2	6.8	--	--	6.8	1.5	--	--	0.7	--
Mobil Oil Corp., Buffalo, N.Y.	B	--	43.0	44.0	18.0	--	19.0	11.5	--	--	12.5	2.8	--	--	7.5	--
Amoco Oil Co., Mandan, N.D.	B	--	52.0	53.0	--	--	24.0	8.2	--	--	10.0	2.6	--	--	--	--
Westland Oil Co., Williston, N.D.	B	--	4.7	5.0	--	1.1	--	2.0	--	--	1.6	--	--	--	--	--
Ashland Petroleum Co., Canton, Ohio	B	--	64.0	66.0	33.0	--	25.0	11.0	--	34.5	12.0	7.0	--	--	12.0	--

Continued

TABLE F2-5. Continued

					Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	Category		Crude Capacity													
Company - Location	EPA	ADL^a	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Gulf Oil Co., Cleves, Ohio	B	--	42.7	44.0	13.0	--	18.0	10.0	--	5.0	11.0	4.5	--	--	2.9	--
Gulf Oil Co., Toledo, Ohio	B	SM	50.3	51.0	12.5	--	19.8	11.0	--	5.5	11.0	5.5	--	--	2.0	--
Standard Oil Co. of Ohio, Toledo, Ohio	B	--	120.0	126.0	68.0	11.2	55.0	40.7	35.0	--	37.0	11.3	--	--	7.0	600
Oklahoma Refining Co., Cyril, Okla.	B	--	14.0	14.7	5.0	--	6.7	1.1	--	--	1.1	1.7	--	--	1.6	--
Kerr McGee Corp., Wynnewood, Okla.	B	--	50.0	51.0	10.0	--	11.5	7.5	4.5	--	11.5	3.5	--	--	3.5	--
Hudson Refining Co., Inc., Cushing, Okla.	B	--	19.0	19.8	7.0	4.0	7.5	4.5	--	--	8.5	2.0	--	--	--	100
OKC Refining, Inc., Okmulgee, Okla.	B	--	25.0	24.0	3.2	--	8.0	--	--	--	--	1.5	--	--	1.8	--
Sun Oil Co., Duncan, Okla.	B	--	48.5	50.0	17.0	12.0	25.0	8.0	--	--	8.0	5.8	--	--	--	400
Texaco, Inc., West Tulsa, Okla.	B	--	50.0	52.6	15.3	6.7	20.0	22.2	--	--	27.8	3.3	0.5	--	--	--
Vickers Petroleum Corp., Ardmore, Okla.	B	--	61.3	64.5	30.0	--	21.5	12.0	--	20.0	12.0	5.0	--	--	15.0	--
Atlantic Richfield Co., Philadelphia, Pa.	B	EC	185.0	185.0	106.0	--	--	56.0	30.0	74.0	54.0	--	--	--	25.0	--
BP Oil Corp., Marcus Hook, Pa.	B	--	164.0	177.0	85.0	--	48.0	50.0	25.0	48.0	105.0	8.2	0.6	--	--	--
Gulf Oil Co., Philadelphia, Pa.	B	--	208.0	214.0	80.0	--	84.6	52.0	--	62.0	52.0	15.0	5.0	--	--	--
United Refining Co., Warren, Pa.	B	--	42.0	42.8	25.0	--	11.5	10.0	--	--	16.5	1.4	--	--	5.0	--

Continued

TABLE F2-5. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Delta Refining Co., Memphis, Tenn.	B	--	42.5	43.8	12.0	--	12.5	9.3	--	--	13.5	3.6	--	--	3.0	--
Dorchester Refining Co., Mt. Pleasant, Tex.	B	--	26.0	28.5	13.0	--	10.0	4.0	--	--	10.0	2.4	--	--	8.0	--
American Petrofina, Inc., Port Arthur, Tex.	B	--	90.0	110.0	28.0	10.0	34.0	22.0	--	30.0	22.0	2.5	4.6	--	--	--
Champlin Petroleum Co., Corpus Christi, Tex.	B	--	155.0	159.0	52.0	--	65.0	31.3	--	50.0	33.3	17.6	4.1	--	--	--
Charter International Oil Co., Houston, Tex.	B	--	65.0	70.0	22.0	10.0	40.0	13.5	--	29.5	46.3	4.5	2.9	--	5.0	--
Chevron Oil Co., El Paso, Tex.	B	--	76.0	80.0	26.0	--	22.0	25.0	--	18.0	25.0	5.0	2.0	--	5.0	--
Crown Central Petroleum Corp., Houston, Tex.	B	--	100.0	103.0	38.0	9.5	520.0	22.0	--	--	22.0	10.0	4.0	--	--	300
Diamond Shamrock Oil & Gas Co., Sunray, Tex.	B	--	51.5	53.5	16.5	2.5	23.0	14.0	--	--	14.0	8.7	1.4	--	2.5	--
LaGloria Oil & Gas Co., Tyler, Tex.	B	--	29.3	29.7	--	15.0	10.0	9.5	--	--	7.0	3.0	--	--	--	80
Shell Oil Company Odessa, Tex.	B	--	32.0	35.0	10.0	--	10.5	11.0	--	--	11.0	3.0	1.0	--	--	--
Southwestern Refining Co., Inc., Corpus Christi, Tex.	B	--	120.0	122.5	36.0	--	12.0	30.0	--	18.0	59.0	4.0	6.0	--	--	--
Texaco, Inc., Amarillo, Tex.	B	--	20.0	21.1	--	4.4	8.9	5.6	--	--	5.6	1.7	--	--	--	100
Texaco, Inc., El Paso, Tex.	B	--	17.0	17.9	--	4.4	7.8	3.9	--	--	3.9	1.7	0.5	--	--	100

Continued

TABLE F2-5. Continued

Company - Location	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity					
												MBPSD					
	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Texas City Refinery, Inc., Texas City, Tex.	B	--	119.6	130.0	49.0	9.0	35.0	11.0	--	--	11.0	--	--	--	--	--
Independent Refining Corp., Winnie, Tx.	B	--	16.0	15.4	--	--	--	7.7	3.0	--	8.3	--	0.4	--	--	--
Winston Refining Co., Fort Worth, Tx.	B	--	20.0	20.5	3.5	--	3.4	1.7	--	--	--	--	--	--	--	--
Amoco Oil Co., Salt Lake City, Utah	B	--	39.0	41.5	--	--	18.0	6.0	--	--	6.0	3.8	3.0	--	9.0	--
Caribou Four Corners, Inc., Woods Cross, Utah	B	--	7.1	7.4	1.0	--	2.0	--	1.1	--	3.5	--	--	--	--	--
Chevron Oil Co., Salt Lake City, Utah	B	--	45.0	47.4	35.0	8.5	18.0	5.5	--	5.5	5.5	4.3	0.8	--	--	350
Husky Oil Co., North Salt Lake, Utah	B	--	25.0	26.0	3.8	--	4.4	5.0	--	--	6.0	1.0	--	--	--	--
Plateau, Inc., Roosevelt, Utah	B	--	8.0	8.5	--	--	5.2	--	--	--	--	--	--	--	--	--
Phillips Petroleum Co., Woods Cross, Utah	B	--	24.0	25.0	3.2	--	8.4	4.7	--	--	12.6	2.1	--	--	1.7	--
Atlantic Richfield Co., Cherry Point, Ferndale, Wash.	B	--	106.0	110.0	65.0	30.0	--	39.0	39.0	12.0	27.0	--	--	--	--	1600
Mobil Oil Corp., Ferndale, Wash.	B	--	71.5	75.0	13.0	7.0	25.5	23.0	--	--	34.0	5.9	--	--	--	--
Shell Oil Co., Anacortes, Wash.	B	--	91.0	94.0	33.0	—	36.0	20.0	--	8.5	48.0	12.1	2.9	--	--	--
Texaco, Inc., Anacortes, Wash.	B	--	78.0	82.1	26.3	--	33.3	22.2	--	--	46.7	7.3	--	--	--	--

Continued

TABLE F2-5. Continued

Company - Location	Category EPA	Category ADL[a]	Crude Capacity MBPCD	Crude Capacity MBPSD	Charge Capacity, MBPSD: Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Production Capacity, MBPSD: Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Murphy Oil Corp., Superior, Wis.	B	--	40.0	46.8	20.5	--	9.7	10.0	--	5.8	10.0	1.7	--	--	13.5	--
Husky Oil Co., Cheyenne, Wyo	B	--	24.2	25.2	14.0	--	10.0	6.2	--	--	11.1	2.8	1.5	--	3.0	--
Husky Oil Co., Cody, Wyo.	B	--	10.8	11.3	6.5	--	3.3	1.5	--	--	3.3	0.8	--	--	4.0	--
Little America Refining Co., Casper, Wyo.	B	--	24.5	25.8	8.6	--	6.5	3.8	--	--	8.8	--	--	--	2.0	--
Sinclair Oil Corp., Sinclair, Wyo.	B	--	49.0	50.0	16.1	--	17.7	9.7	--	12.2	25.0	2.2	--	--	2.6	--
Wyoming Refining Co., Newcastle, Wyo.	B	--	10.5	11.0	--	--	4.0	--	--	--	--	0.9	--	--	--	--
Texaco, Inc., Casper, Wyo.	B	--	21.0	22.1	10.5	4.4	7.8	4.4	--	4.4	4.4	--	--	--	1.7	125
Chevron U.S.A. Inc., Bakersfield, Calif.	B	--	26.0	27.4	--	9.8	--	6.0	--	--	6.0	--	--	--	--	--
Chevron U.S.A. Inc., Barbers Point, Hawaii	B	--	44.0	46.3	25.0	--	22.0	--	--	--	3.5	4.5	1.5	--	1.3	--
Pacific Refining Co., Hercules, Calif.	B	--	85.0	89.5	--	--	--	15.0	3.0	--	14.0	--	--	--	--	--
Wireback Oil Co., Inc., Plymouth, Ill.	B	--	1.8	1.8	--	1.8	--	--	--	--	--	--	--	--	--	--
Energy Cooperative Inc., East Chicago, Ind.	B	--	126.0	140.0	70.0	--	48.0	20.0	--	--	45.0	6.0	--	--	10.4	--
Navajo Refining Co., North Artesia, N.M.	B	--	6.0	6.3	--	1.5	--	7.7	--	14.4	--	--	--	--	--	--
Plateau Inc., Bloomfield, N.M.	B	--	12.9	14.0	--	--	5.0	2.3	--	--	2.3	--	--	--	--	--

Continued

TABLE F2-5. Continued

					Charge Capacity, MBPSD							Production Capacity				
	Category		Crude Capacity									MBPSD				
Company - Location	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Marathon Oil Co., Texas City, Tx.	B	--	66.0	68.0	28.0	--	38.0	8.0	--	--	--	11.0	2.5	--	--	--
Sun Co., Inc. Corpus Christi, Tx.	B	--	57.0	60.0	10.0	7.7	25.0	24.0	--	12.5	3.2	7.3	--	--	--	--
TOTAL				7329.1	2665.8	715.0	2368.6	1637.1	334.7	829.8	2251.0	484.6	87.4	--	311.3	21130

Source: Reference 1

[a] ADL Abbreviations:

LG = Louisiana Gulf Cluster

LM = Large Midwestern Cluster

SM = Small Midcontinent Cluster

WC = West Coast Cluster

EC = East Coast Cluster

TABLE F2-6. TYPE "C" REFINERIES - CAPACITIES AS OF JANUARY 1, 1979

Company - Location	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	EPA	ADL^a	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Chevron U.S.A. Inc., El Segundo, Calif.	C	WC	405.0	426.3	179.0	54.0	52.0	60.0	49.0	98.0	74.0	5.9	1.5	--	8.3	2700
Getty Oil Co., Inc., Delaware City, Del.	C	--	140.0	150.0	90.7	44.0	62.0	42.0	20.0	--	110.0	8.0	0.5	--	--	1500
Amoco Oil Co., Wood River, Ill.	C	--	105.0	107.0	40.0	--	38.0	12.3	--	--	35.6	5.5	--	--	10.3	--
Clark Oil & Refining Corp., Blue Island, Ill.	C	--	66.5	70.0	27.0	--	26.0	30.5	11.0	--	20.5	6.0	--	--	4.5	--
Getty Refining Co., El Dorado, Kan.	C	SM	80.6	82.0	27.0	11.5	31.0	21.5	--	40.0	27.3	10.0	1.4	--	--	610
Chevron U.S.A. Inc., Pascagoula, Miss.	C	--	280.0	294.7	148.0	--	56.0	90.0	68.0	56.0	48.0	9.2	6.0	--	--	--
Exxon Co., Linden, N.J.	C	EC	290.0	307.0	155.0	--	135.0	19.0	--	50.0	158.0	8.5	--	--	48.0	--
Texaco, Inc., Westville, N.J.	C	--	88.0	92.6	31.1	14.4	44.4	14.4	--	--	44.4	3.3	--	--	--	--
Ashland Petroleum Co., Tonowanda, N.Y.	C	--	64.0	66.0	25.0	--	23.0	11.5	--	20.0	27.0	1.7	3.0	--	10.5	--
Sun Co., Toledo, Ohio	C	--	125.0	130.0	22.0	--	50.0	41.0	26.0	--	27.5	7.0	8.9	--	3.6	--
Amoco Oil Co., Texas City, Tx.	C	--	415.0	432.0	191.0	33.5	184.0	114.0	42.0	--	189.0	31.0	45.0	--	5.3	1500
Coastal States Petro-Chemical Co., Corpus Christi, Tx.	C	--	185.0	194.7	45.0	12.0	19.0	35.0	--	25.0	50.0	2.5	17.5	--	0.5	500
American Petrofina Inc., Big Spring, Tx.	C	--	60.0	65.0	25.0	10.0	24.0	20.0	--	8.0	25.0	6.0	7.8	--	8.0	--
Marathon Oil Co., Texas City, Tx.	C	--	66.0	68.0	28.0	--	38.0	8.0	--	--	--	11.0	2.5	--	--	--

Continued

TABLE F2-6. Continued

Company - Location	Category EPA	Category ADL[a]	Crude Capacity MBPCD	Crude Capacity MBPSD	Charge Capacity, MBPSD Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Production Capacity MBPSD Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Phillips Petroleum Co., Borger, Tx.	C	--	97.0	100.0	--	--	52.0	28.5	--	--	66.5	16.8	35.8	--	--	--
Phillips Petroleum Co., Sweeny, Tx.	C	--	97.0	100.0	18.0	8.0	35.5	36.0	--	--	54.5	10.5	27.2	--	--	--
Sun Co. Inc., Corpus Christi, Tx.	C	--	57.0	60.0	10.0	7.7	20.0	24.0	--	12.5	3.2	7.3	--	--	--	235
Amoco Oil Co., Yorktown, Va.	C	--	53.0	55.0	29.0	15.0	28.0	9.5	--	--	26.5	--	--	--	--	--
Atlantic Richfield Co., Carson, Calif.	C	WC	180.0	186.0	76.0	84.5	56.0	38.0	19.0	--	75.0	7.2	2.5	--	--	1800
Howell Corp., Corpus Christi, Tx.	C	--	15.0	15.8	4.0	--	--	9.5	5.0	--	10.0	--	6.8	--	--	--
TOTAL			2869.1	3002.1	1170.8	294.6	973.9	684.7	240.0	309.5	1072.0	157.4	166.4	--	265.9	8545

Source: Reference 1

[a] ADL Abbreviations:

EC - East Coast Cluster

SM - Small Midcontinent Cluster

WC - West Coast Cluster

TABLE F2-7. TYPE "D" REFINERIES - CAPACITIES AS OF JANUARY 1, 1979

Company - Location	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Tosco Corp., El Dorado, Ark.	D	--	47.0	48.3	17.0	--	15.0	5.8	--	--	11.9	4.5	--	0.8	3.8	--
Tosco Corp., Martinez, Calif.	D	--	137.0	144.2	81.0	37.0	47.0	30.0	20.0	--	34.5	10.5	1.8	0.1	--	1200
Union Oil, Rodeo, Calif.	D	--	111.0	117.0	38.5	42.5	--	26.0	30.0	--	44.0	--	--	3.6	4.3	1850
Shell Oil, Wood River, Ill.	D	--	283.0	295.0	95.5	--	94.0	90.0	33.5	27.0	158.5	22.0	2.9	5.6	29.4	--
Amoco Oil, Whiting, Ind.	D	--	380.0	405.0	180.0	25.0	140.0	76.0	--	--	146.2	19.0	15.7	6.2	40.0	1200
CRA, Inc., Coffeyville, Kan.	D	--	49.9	50.0	17.0	13.0	16.0	8.6	--	3.0	19.8	6.0	--	2.5	--	450
Cities Service Oil Co., Lake Charles, La.	D	LC	291.0	306.3	83.0	28.0	125.0	46.0	--	36.0	60.0	33.0	2.3	7.0	--	2000
Standard Oil of Ohio Lima, Ohio	D	--	168.0	177.0	51.0	16.2	37.7	47.0	20.0	--	59.0	--	--	2.1	--	620
Champlin Petroleum Co., Enid, Okla.	D	SM	53.8	56.0	18.0	5.0	19.0	15.0	--	--	20.4	4.5	6.0	1.1	1.8	200
Continental Oil Co., Ponca City, Okla.	D	--	132.0	136.0	32.0	17.0	45.0	31.0	--	--	38.0	9.7	4.7	2.0	3.0	600
Sun Company, Tulsa, Okla.	D	--	88.5	90.0	31.5	8.2	30.0	23.0	--	--	35.0	8.6	6.8	9.0	4.8	300
Mobil Oil Corp., Beaumont, Tx.	D	TC	325.0	325.0	103.0	27.0	114.0	102.0	29.0	--	206.0	12.0	20.0	8.8	--	1200
Shell Oil Co., Deer Park, Tx.	D	--	285.0	310.0	125.5	65.0	70.0	68.0	--	50.0	198.0	7.9	15.6	7.9	4.2	--
Texaco, Inc., Port Arthur, Tx.	D	--	406.0	427.4	149.5	20.0	150.0	66.7	16.7	--	155.6	16.7	--	22.2	--	--

Continued

TABLE F2-7. Continued

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/Isom.	Lubes	Asphalts	Coke, T/D
Amoco Oil Co., Casper, Wyo.	D	--	47.0	48.0	15.5	--	13.0	5.8	--	--	7.1	--	1.3	1.9	1.6	--
Mobil Oil Corp., Paulsboro, N.J.	D	--	98.0	100.5	62.6	23.7	25.0	23.5	--	--	62.6	2.3	--	6.4	--	975
Ashland Petroleum Co., Catlettsburg, Ky.	D	--	135.8	140.0	72.7	4.0	55.0	26.5	--	40.0	77.5	5.5	19.5	5.0	20.0	--
TOTAL			3038.6	3185.7	1173.3	351.6	995.7	690.9	149.2	156.0	1334.1	162.2	95.6	92.2	112.9	9595

Source: Reference 1

[a] ADL Abbreviations:

LG = Louisiana Gulf Cluster

LM = Large Midwest Cluster

SM = Small Midcontinent Cluster

TG = Texas Gulf Coast Cluster

TABLE F2-8. TYPE "E" REFINERIES - CAPACITIES AS OF JANUARY 1, 1979

	Category		Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
												MBPSD				
Company - Location	EPA	ADL[a]	MBPCD	MBPSD	Vacuum Distill.	Thermal Opns.	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalts	Coke, T/D
Shell Oil, Martinez, Calif.	E	--	104.0	107.0	55.3	--	46.0	25.0	20.0	50.0	60.3	8.0	--	4.5	10.5	--
Standard (Cal.), Richmond, Calif.	E	--	365.0	384.0	226.0	--	55.0	84.0	75.0	125.0	85.2	9.2	4.0	6.3	11.0	--
Phillips Petroleum Kansas City, Kan.	E	--	78.0	85.0	23.5	--	33.5	21.0	--	--	62.0	9.5	--	2.9	6.2	--
Exxon Baton Rouge, La.	E	--	500.0	540.0	215.0	50.0	154.0	83.0	25.0	--	95.6	29.8	--	16.0	28.9	2400
Sun Co. Inc., Marcus Hook, Pa.	E	EC	165.0	180.0	48.0	--	75.0	44.3	--	--	68.0	17.3	--	17.0	--	--
ARCO, Houston, Tx.	E	--	363.0	381.0	149.0	30.0	76.0	95.0	--	169.0	109.6	9.0	11.2	6.4	--	1800
Exxon, Baytown, Tx.	E	TG	640.0	668.0	180.0	--	145.0	148.0	21.0	198.0	416.5	26.0	--	33.8	12.0	--
Gulf Oil, Port Arthur, Tx.	E	TG	334.5	342.0	157.5	30.0	120.0	65.0	15.0	65.0	65.0	20.0	12.4	13.2	--	1390
Union Oil, Nederland, Tx.	E	--	120.0	126.3	43.0	--	38.0	36.0	--	--	49.0	4.2	3.9	1.4	3.6	--
TOTAL			2669.5	2813.3	1280.9	110.0	742.5	601.3	156.0	607.0	1011.2	133.0	31.5	101.5	72.2	5590

Source: Reference 1

[a] ADL Abbreviations:

EC = East Coast Cluster

TG = Texas Gulf Coast Cluster

Some companies reported capacities only on a stream-day basis or only on a calendar-day basis. These capacities were converted to the required bases using a stream factor of 0.95 for crude and vacuum units, and a stream factor of 0.90 for all other processes.

A summary of total refining and process-unit capacities for each refinery subcategory or type is given in Table F2-9. Type A refineries are the most numerous. Howerver, more crude is refined in Type B refineries than in any other. There are over 130 Type A refineries, but only about 10 percent of the crude is processed in these plants.

A representative model of each of the five refinery types could be developed as an average of all the refineries in each classification. The processing unit charge capacities and production capacities of each model would correspond to the average capacities (expressed as percent of crude) of each of the various refinery types as shown in Table F2-9. It would be possible to simulate the process unit capacities and product output of the U.S. refining industry with selected groups of these model types. An extensive amount of work would be required, however, to calibrate these models such that they would best simulate the operating refineries within each refinery category.

For example, it would be difficult to arbitrarily choose specific types of processing units and associated operating conditions that would accurately represent actual operations in the different types of refineries. It would be necessary to obtain from the refining companies a considerable amount of data concerning the operation of the individual processing units within the specific refineries. Companies are

TABLE F2-9. TOTAL REFINING CAPACITY AS OF JANUARY 1, 1979

Refinery Type	Number of Plants	Crude Capacity		Charge Capacity, MBPSD							Production Capacity				
											MBPSD				
		MBPCD	MBPSD	Vacuum Distillation	Thermal Operations	Cat. Cracking, Fresh Feed	Cat. Reform.	Cat. Hydro-Crack.	Cat. Hydro-Refin.	Cat. Hydro-Treat	Alkylation	Aromatics/ Isom.	Lubes	Asphalt	Coke (tons/day)
A	131	1762.8	1849.0	409.1	--	--	168.2	--	105.4	183.4	--	1.8	38.4	167.0	--
B	111	6896.5	7247.1	2665.8	715.0	2368.6	1637.1	334.7	829.8	2251.0	484.6	87.4	--	313.3	21130
C	20	2869.1	3002.1	1170.8	294.6	973.9	684.7	240.0	309.5	1072.0	157.4	166.4	--	265.9	8845
D	17	3038.0	3185.7	1173.3	351.6	995.7	690.9	149.2	156.0	1334.1	162.2	95.6	92.2	112.9	9595
E	9	2669.5	2813.3	1280.9	110.0	742.5	601.3	156.0	607.0	1011.2	133.0	31.5	103.5	72.2	5590
TOTAL	288	17235.9	18097.2	6699.9	1471.2	5080.7	3782.2	879.9	2007.7	5851.7	937.2	382.7	234.1	929.3	45160

Source: Reference 1

normally very reluctant to divulge this type of proprietary information.

Linear programming models of refineries could be used with selected crude charges, average product slates, and specific processing units and configurations in order to develop sizes and operating conditions of the individual processes. Again, however, it would be difficult to ascertain the validity of these operating conditions without an extensive amount of data from operating refineries.

In summary, the use of five refinery models instead of one would provide more flexibility and inherently greater accuracy in simulating the refining industry. An extensive data base of refinery operating data would be needed to evaluate the validity of the models and for calibration purposes.

This model still falls short of providing the required data for calculating fugitive emissions since the number of individual sources within each of the process units in the five model refineries cannot be accurately estimated. However, this model should provide a better estimate of emissions from non-fugitive sources than the single representative refinery model; particularly those emissions associated with specific process units.

2.3 REFINERY CLUSTER MODELS

In some work done for the EPA, Arthur D. Little, Inc. has defined the impact of several existing or proposed environmental regulations on the U.S. refining industry.[1,8,9] The development of a method for providing a detailed simulation of the U.S. refining industry constituted an important part of these studies. The acquisition and collation of an extensive refinery data base, which was used in calibrating the refinery models, was accomplished.

2.3.1 Model Development

In the method developed by Arthur D. Little, Inc.,[3] the refining industry, as it existed in 1973, was simulated by six individual refinery models. Each of the models, called "cluster" models, lies in a different geographical area of the U.S. and consists of a group of three existing operating refineries. In terms of crude oil type, process configurations, operating conditions, and product distributions, each group consists of refineries that are typical of the refining industry. Crude capacities of the model refineries ranged from 48,000 to 350,000 barrels/day, and each cluster model represented the average operation of the three refineries selected to comprise each group. Representatives of the EPA and members of a task force from the American Petroleum Institute (API) and the National Petroleum Refineries Association (NPRA) assisted Arthur D. Little, Inc., in the selection of the six geographical areas and the three refineries within each area.

The two most important criteria observed in the selection of representative regions and refineries were: (1) each selected cluster mode was to represent, as nearly as possible a typical and realistic refinery operation with respect to type, size of processing units, and operating flexibility; and (2) the crude slate, processing configuration, and product slates for each model were to be representative of the variations peculiar to each geographical region.

The six cluster models and the refineries comprising each cluster are listed in Table F2-10. The capacities of the refineries are shown for 1973, the calibration year, and as of January 1, 1979. The cluster model refineries are also identified in the refinery tabulations in Tables F2-4 through F2-8.

The Bureau of Mines has grouped refining operations into geographical refining districts which correspond to districts designated as PAD (Petroleum Administration for Defense) districts. These districts are briefly described in Table F2-11. The number of cluster models selected to characterize each PAD district reflects the refining capacity and the variations in the type of available crude found in each of the districts. For example, sufficient refining capacity and enough crude with common characteristics are available in PAD District I to permit characterization of that district with one cluster model, the East Coast cluster. On the other hand, about 40 percent of the total U.S. refining capacity is contained in PAD District III. Two cluster models were used to simulate the refineries in this district because of its importance, and because two types of refinery configurations and crude slates were identified.

PAD District II, containing about 28 percent of domestic refining capacity, was also simulated with two refinery cluster models, since two distinctly characteristic types of refineries could be identified within the region. One was a large Midwest-type refinery processing over 100,000 barrels/day of high sulfur crudes. The other type is typified by the small Midcontinent refinery in which 50,000 - 100,000 barrels/day of low sulfur crudes are refined.

TABLE F2-10. REFINERIES SIMULATED BY CLUSTER MODELS

PAD District	Cluster Identification	Refineries Simulated	1973 Crude Capacity MB/CD	1978 Crude Capacity MB/CD
I	East Coast	Arco - Philadelphia, Pa.	160.0	185.0
		Sun Oil - Marcus Hook, Pa.	163.0	165.0
		Exxon - Linden, New Jersey	255.0	290.0
II	Large Midwest	Mobil - Joliet, Illinois	160.0	180.0
		Union - Lemont, Illinois	140.0	151.0
		Arco - East Chicago, Indiana	135.0	126.0
II	Small Midcontinent	Skelly - El Dorado, Kansas	67.0	80.6
		Gulf Oil - Toledo, Ohio	48.8	50.3
		Champlin - Enid, Oklahoma	48.0	53.8
III	Texas Gulf	Exxon - Baytown, Texas	350.0	640.0
		Gulf Oil - Port Arthur, Texas	312.1	334.5
		Mobil - Beaumont, Texas	335.0	325.0
III	Louisiana Gulf	Gulf Oil - Alliance, La.	174.0	195.9
		Shell Oil - Norco, La.	240.0	230.0
		Cities Service - Lake Charles, La.	240.0	291.0
V	West Coast	Mobil - Torrance, California	123.5	123.5
		Arco - Carson, California	165.0	180.0
		Socal - El Segundo, California	220.0	405.0

Source: References 3 and 1

TABLE F2-11. PAD DISTRICTS AND BUREAU OF MINES REFINING DISTRICTS

PAD District	
I	East Coast + Appalachian No. 1
II	Appalachian No. 2 + Indiana-Illinois-Kentucky + Oklahoma-Kansas-Missouri + Minnesota-Wisconsin-North Dakota-South Dakota
III	Texas Inland + Texas Gulf Coast + Louisiana Gulf Coast + Northern Louisiana-Arkansas + New Mexico
IV	Rocky Mountains
V	West Coast

PAD District V was characterized by a single refinery cluster model, the West Coast cluster. Since less than 5 percent of the country's refining capacity is located within PAD District IV (Rocky Mountains), it was not represented by a cluster model.

Four of the five EPA refinery types or categories (which are very similar to the five API refinery classes) are represented in the 18 refineries which make up the cluster models. The Type A (topping) refineries are not represented. Although there are 131 topping refineries in the U.S., they process only about 10 percent of the total crude.

A summary of five types of major refinery processing units and capacities in each cluster model is presented in Table F2-12. These are compared with the average processing unit capacities (1973/1974) in refineries located within the same PAD Districts as the cluster models. In general, the capacities of the cluster model(s) characterizing each PAD district agree with or bracket the average capacities of the respective PAD districts.

There are a few cases with an above average deviation between the model values and the average district capacities. In PAD District I, the East Coast cluster contains no coking processes, even though coking capacity exists within the district. Coking operations were purposely omitted in order to have one cluster model without a coking unit, since many refineries do not carry out coking operations.

The capacities of the cluster model catalytic cracking units in PAD District II are higher than the average district capacities for this process. However, the cluster model refineries contain no hydrocracking units, so the composite of cracking operations compares well with the district average.

TABLE F2-12. SUMMARY OF MAJOR REFINERY PROCESSING UNITS

(Percentage of Crude Capacity)

Processing Unit	Texas Gulf Cluster	La. Gulf Cluster	PAD III Average	Large Midwest Cluster	Small Mid-Continent Cluster	PAD II Average	East Coast Cluster	PAD I Average	West Coast Cluster	PAD V Average
Catalytic reforming	23	18	24	21	27	22	23	21	24	23
Catalytic cracking	33	41	31	35	39	34	34	33	29	24
Hydrocracking	6	4	5	0	0	4	5	3	16	15
Alkylation	6	11	6	9	9	7	4	4	4	5
Delayed coking	6	9	8	10	8	9	0	7	24	20

Source: Reference 3

2.3.2 Calibration of Models

After developing the six cluster refinery models to represent the entire refining industry, the validity of these models was verified in reflecting regional and national refinery operations.

2.3.2.1 Input/Output Data--

The crude oil slates for the cluster models were developed from Bureau of Mines data and representative crudes selected by Arthur D. Little, Inc. (ADL). The product outputs for 1973 were also supplied by the Bureau of Mines for each of the refineries in the various cluster models. This product slate was then averaged over the three refineries in each cluster in order to get a representative product slate for each of the cluster models.

2.3.2.2 Processing Configurations--

The annual refining surveys published in Oil and Gas Journal[10,11] provided the basic data used to select the cluster model processing configurations. Processing unit capacities as of January 1, 1973 and January 1, 1974 were averaged to obtain values for the calendar year 1973.

It was necessary to obtain processing conditions for the various model configurations. Much of these data are proprietary. To avoid publicly divulging this proprietary data, the individual refinery processing conditions were transmitted by the refineries to the EPA. The EPA then averaged the operating conditions for the three refineries in each cluster model, and reported the average operating conditions to ADL.

2.3.2.3 Other Calibration Data--

Gasoline production rates and properties such as sulfur content, octane ratings, vapor pressure, and maximum lead addition were obtained and compiled by the EPA. Properties of other products such as kerosene, jet fuel, residual fuel oil, and distillate fuel oil were also obtained and used in the calibration effort.

The energy consumption for each of the refineries in the cluster models was obtained from the Bureau of Mines.

2.3.2.4 Calibration Results--

Using linear programming models to represent the various refinery processing units and the process integrations within each refinery, the cluster models were simulated and calibrated. The types of crude, inputs of materials other than crude, processing conditions, and product slates were specified. The amount of crude feedstock was allowed to vary in order to close the overall material balance around the refinery. The results were compared to Bureau of Mines and industry data. Comparisons were made in four main areas. These areas were:

- overall refinery material balance;
- refinery energy consumption;
- processing configuration, throughputs, and operating severities; and
- key product properties.

As an example, the calibration results for the Louisiana Gulf cluster model are compared to the Bureau of Mines and industry data in Table F2-13. It can be seen that in the areas of material balances, energy consumption, and processing, the agreement between the model, Bureau of Mines data and industry data is good.

Refinery process flow diagrams were developed for each of the six cluster model refineries. They are shown in Figures F2-2 through F2-7.

2.3.2.5 Scale-Up of Cluster Models--

After each cluster model was calibrated with Bureau of Mines and industry data, the models were scaled-up to represent the entire U.S. refining industry. The products and inputs for each PAD district were determined by scaling-up the products and inputs for the particular model or models of that district. The scale-up was accomplished by making the gasoline production in the cluster model(s) equal to the gasoline production in the corresponding PAD district. The maximum deviation of the model predictions from the total raw material input for any single district is 6.8 percent for PAD District V. The deviation from the total U.S. refinery raw material intake was only 1 percent. The calibrated cluster models provide a good simulation of the total U.S. refining industry.

2.3.3 Utility of the Cluster Models

The cluster model method for the simulation of the U.S. refining industry appears to have a number of distinct advantages over the two potential simulation models discussed in Sections 2.1 and 2.2. Some of these advantages are:

TABLE F2-13. LOUISIANA GULF CLUSTER MODEL

Calibration Results (MB/CD)[a]

		Oil and Gas Capacity MB/SD	BOM Data	Industry Data	Model Run
Material balances					
Total crude intake			219.8	216.8	222.2
Energy consumption					
Purchased natural gas (FOE)			5.4	--	5.4
Total fuel consumption (FOE)[b]			17.2	--	17.0
Electricity MKWH/CD			606	--	744
Processing summary					
Catalytic reforming	intake	40.5		32.9	28.3
	severity RON	--		92.3	90.0
Catalytic cracking	intake	95.0		90.0	82.2
	conversion % vol.	--		70.0	69.6
Alkylation	production	24.0		17.7	17.5
Hydrocracking	intake	9.5		6.3	6.6
Coking	intake	20.0		19.1	15.8

[a] MB/CD unless otherwise noted.

[b] Excludes catalyst coke.

Source: Reference 3

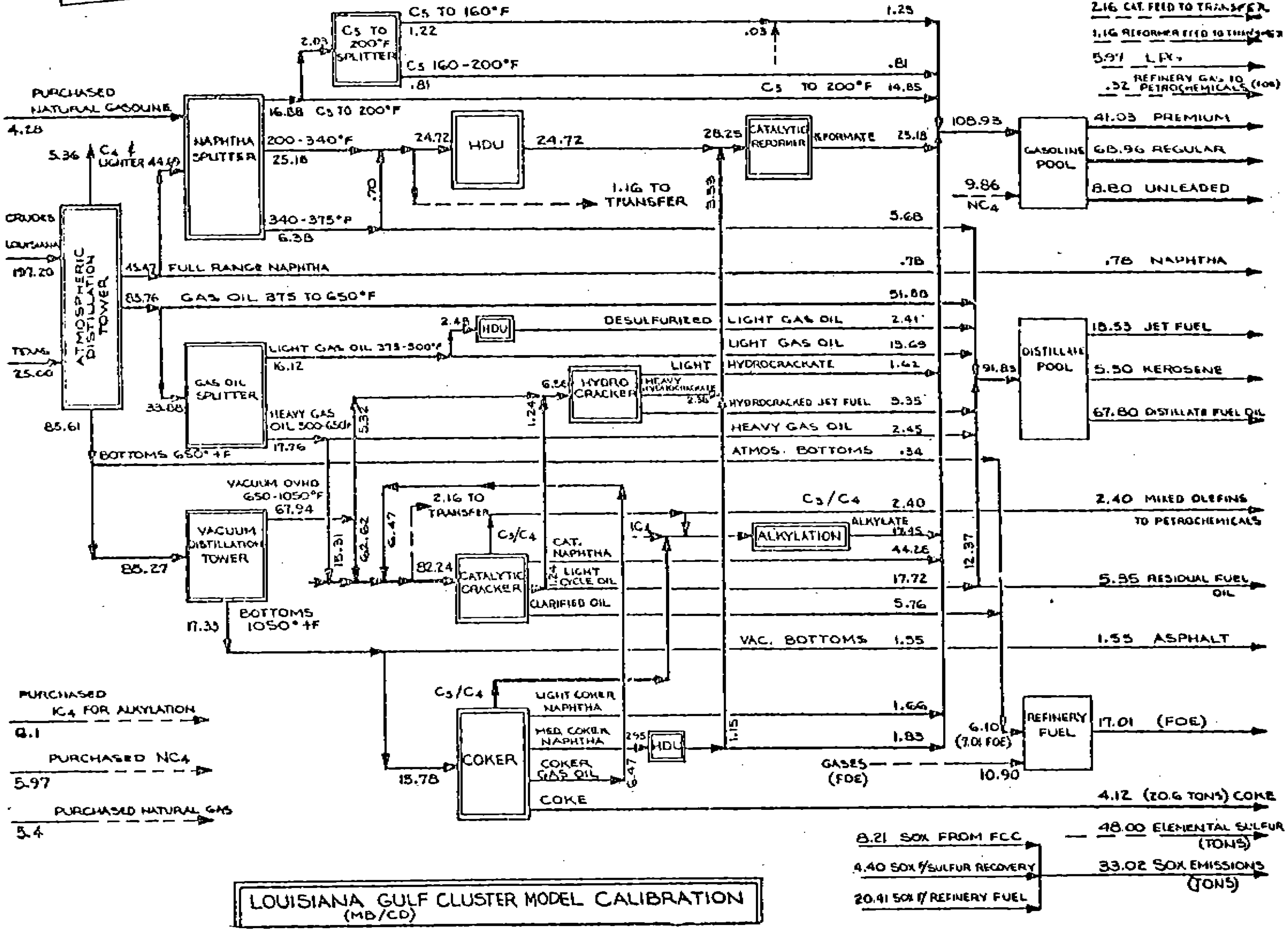
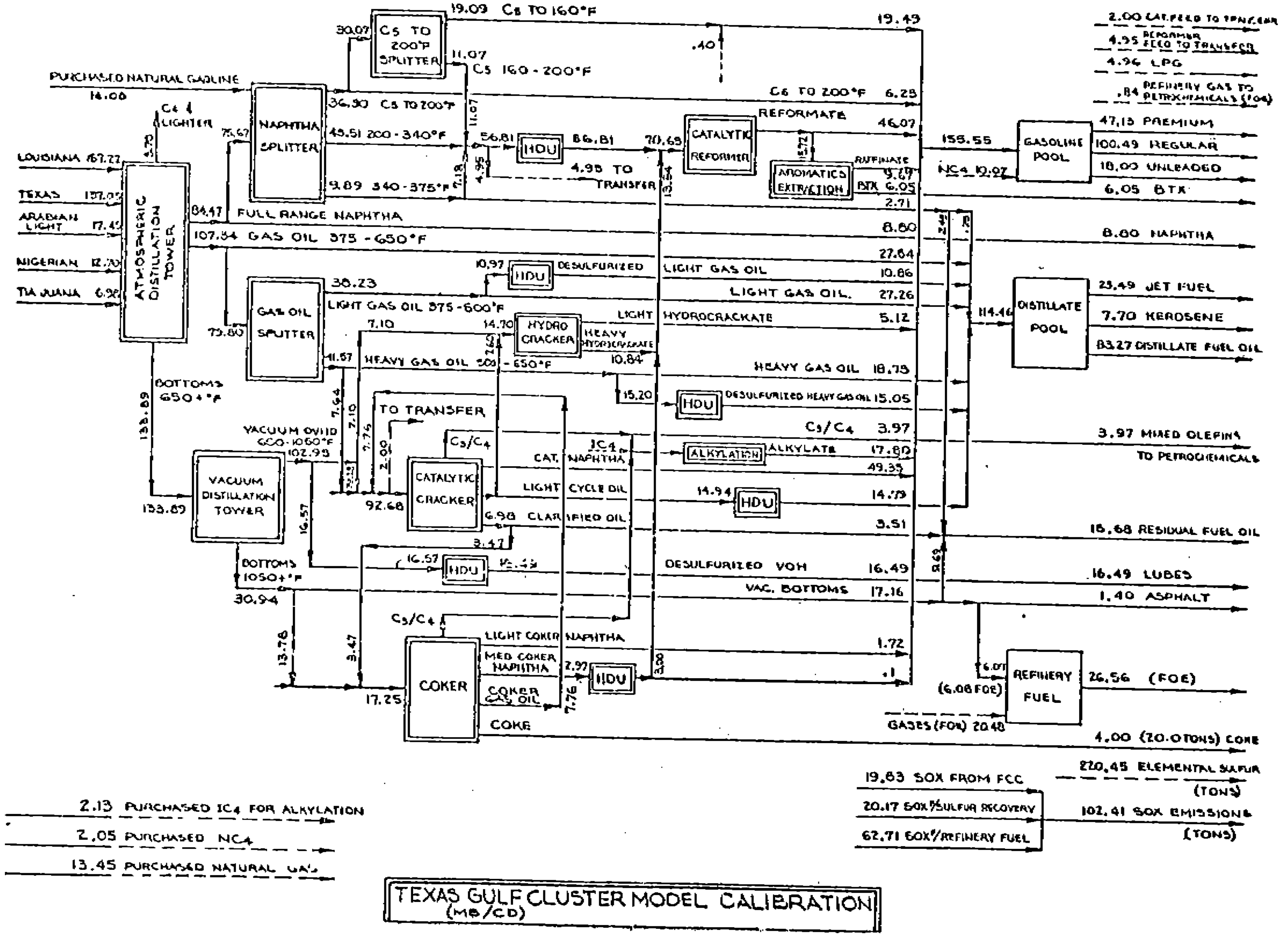


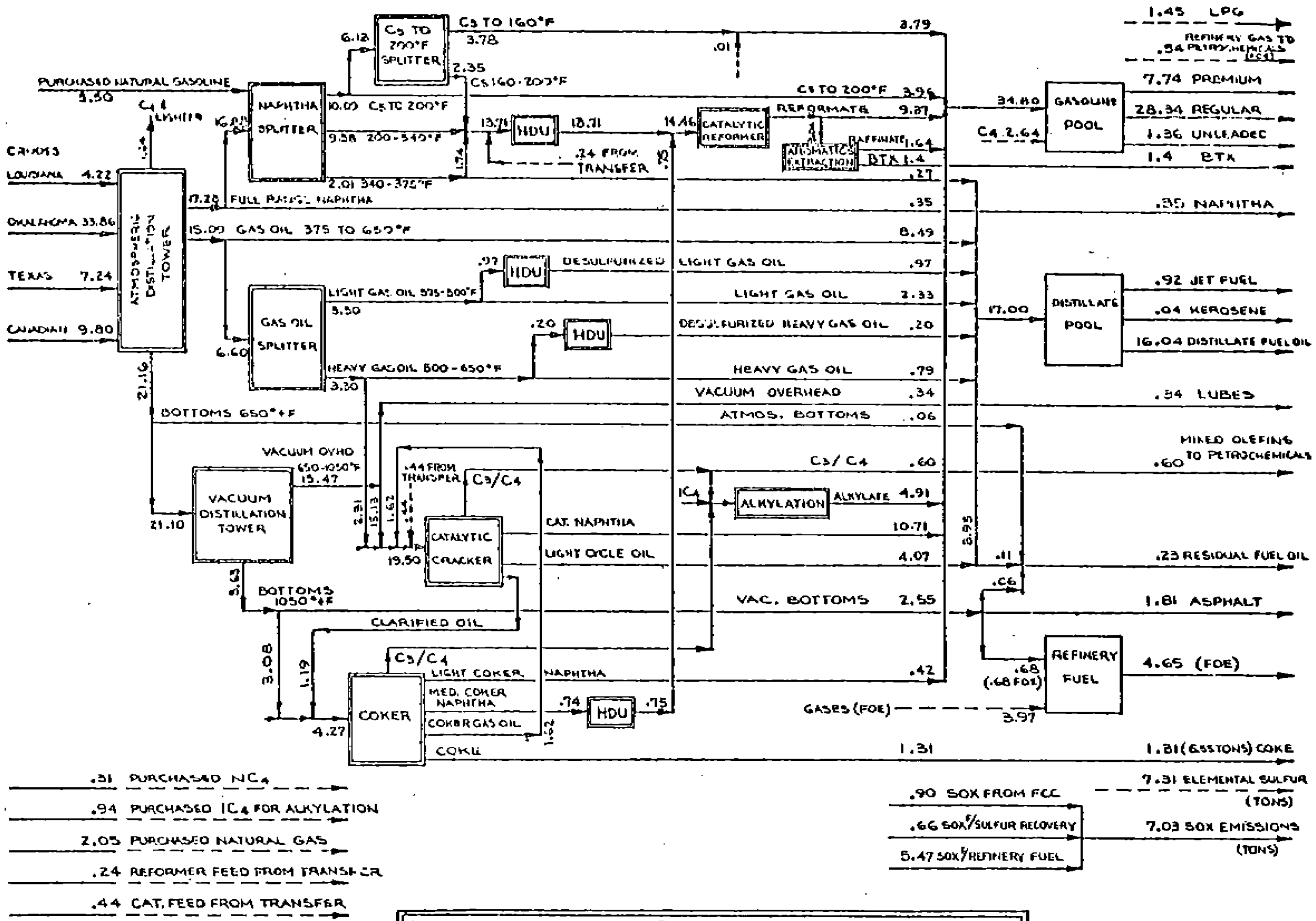
Figure F2-2

Source: Reference 3



Source: Reference 3

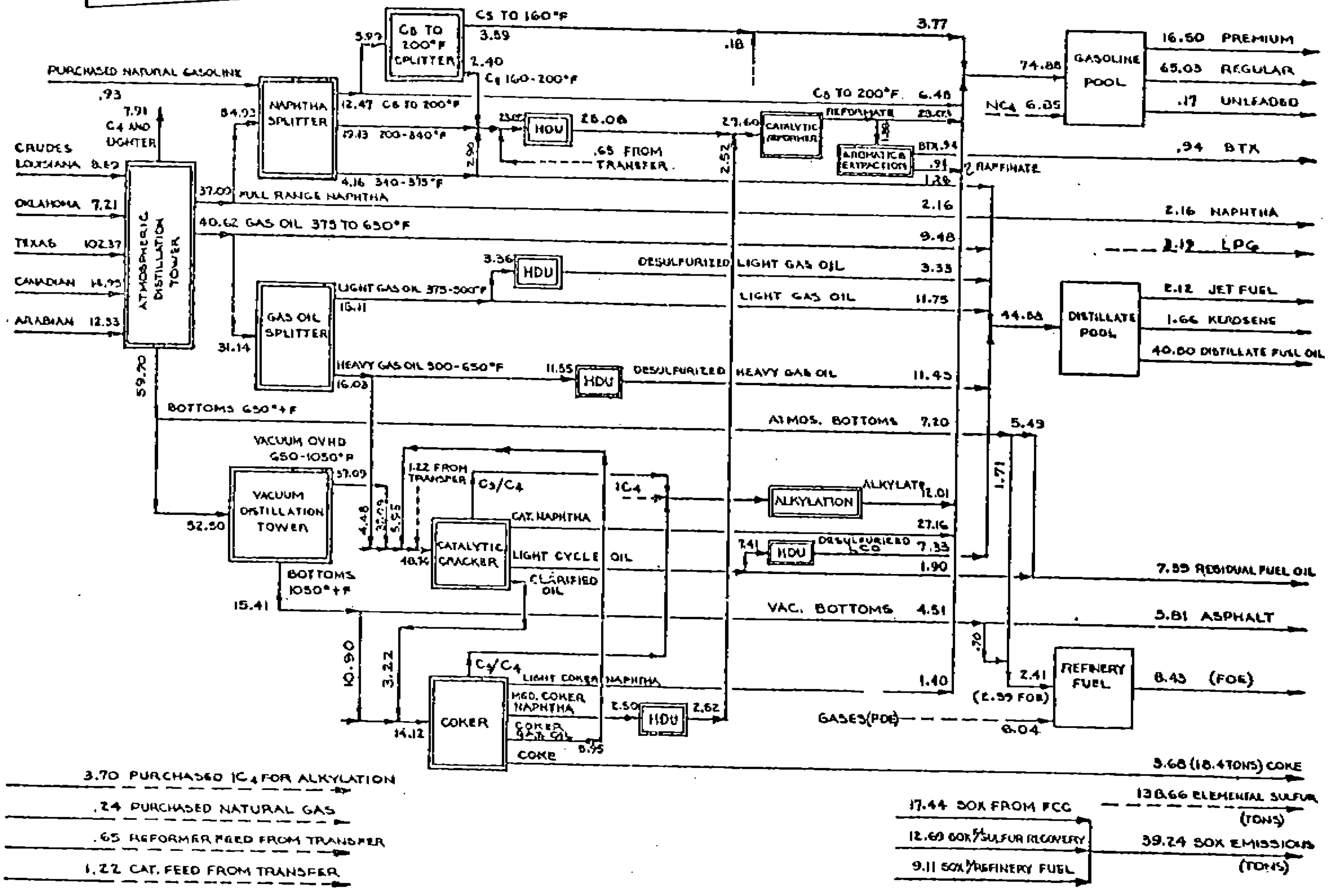
Figure F2-3



SMALL MIDCONTINENT CLUSTER MODEL CALIBRATION
(MB/CD)

Figure F2-4

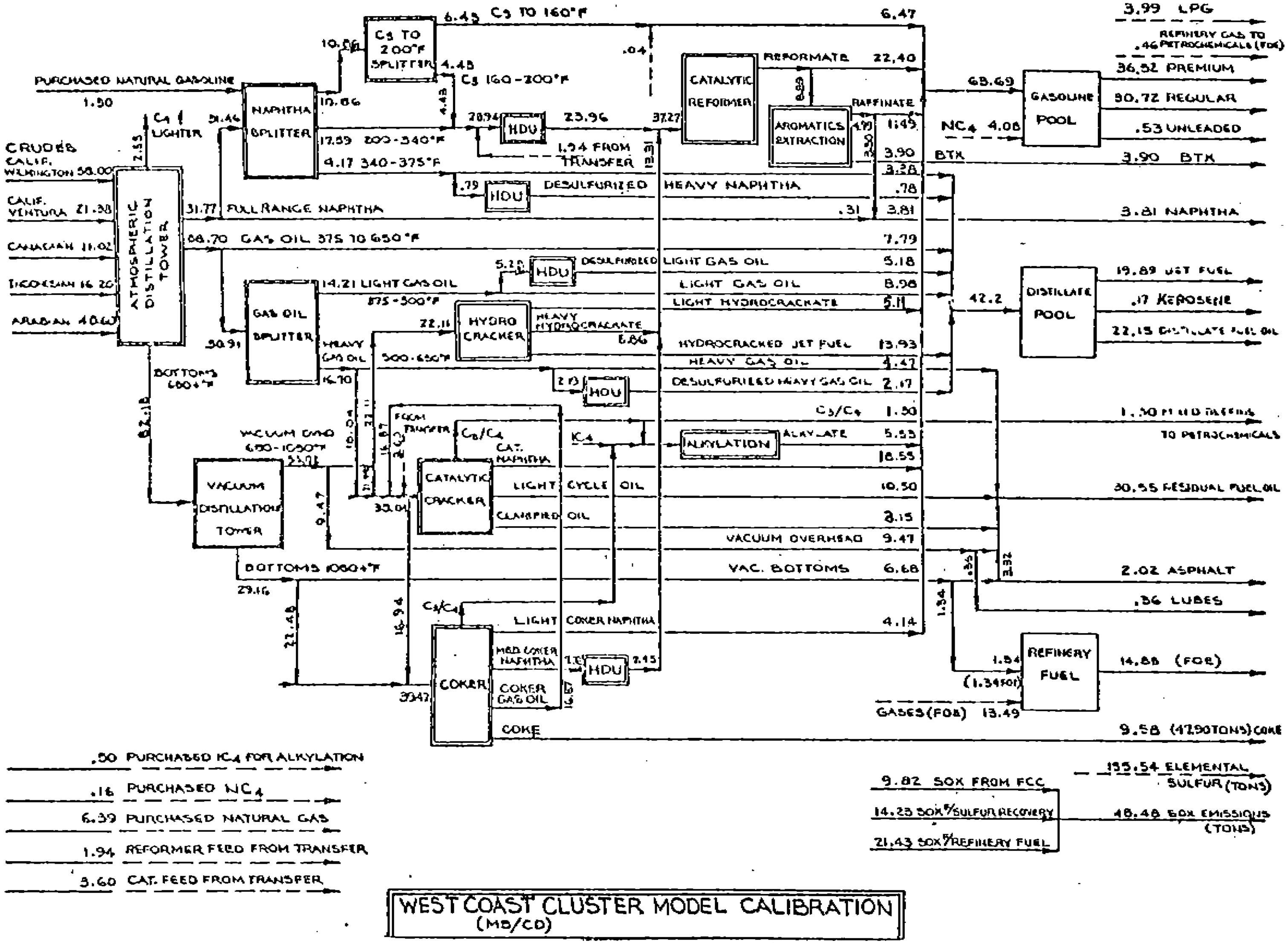
Source: Reference 3



LARGE MIDWEST CLUSTER MODEL CALIBRATION
(MB/CD)

Figure F2-5

Source: Reference 3



WEST COAST CLUSTER MODEL CALIBRATION
(MB/CD)

Figure F2-6

Source: Reference 3

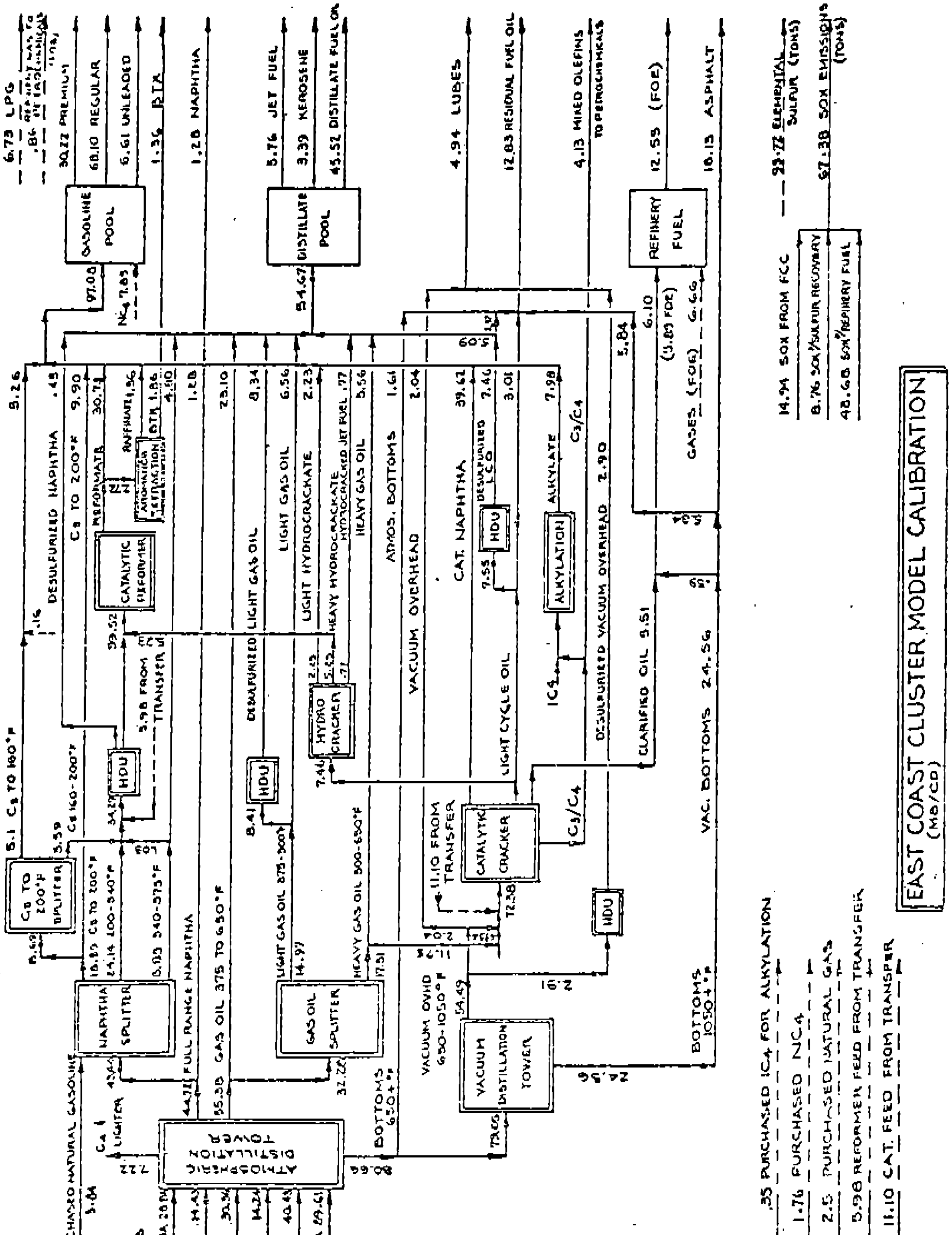


Figure F2-7

Source: Reference 3

A. The cluster models are based on individual existing and operating refineries. Thus, assumptions and conclusions based on work done with the models could be verified with existing data or through testing in these refineries.

B. An extensive data base from these refineries and their operation already exists, and much of it has been gathered and evaluated by EPA and Arthur D. Little, Inc.

C. The methodology for calibrating these models and scaling them up has been developed. The procedures for altering or updating the models are available.

D. The cluster models were developed in cooperation with API and industrial representatives. Thus, they are familiar with this simulation method.

E. From the results of scaling-up these models, it appears that they are accurate in simulating the U.S. refining industry.

F. Eighteen operating refineries were used in developing the cluster models. Eleven different companies are represented. Thus, a significant pool of existing refineries is identified as potential sampling sites.

G. The refinery cluster models are all from different geographical areas of the country, but each represents a site of significant refinery operations. Environmental assessments based on the cluster models could be developed under different, yet realistic, atmospheric conditions.

H. Each of the cluster models has, as its feed, different composite crude oils. Thus, the effect of various crude oils on refinery operation and emission characteristics could be evaluated.

I. The changing characteristics of the crude feedstock and the product slates have been projected through 1985. Future operating and emission characteristics can be evaluated if desired.

J. The processing configurations of each of the refinery cluster models is different. Thus, the characteristics of many different processes can be evaluated while using only the six cluster models.

There are some deficiencies and omissions in the cluster model simulation method.

A. There are no topping refineries (EPA Type A refineries) represented in the clusters. There are over 130 of these refineries in the U.S. Most of them are small, however, and the total refining capacity of these refineries amounts to only 10 percent of the total U.S. capacity.

B. Small refineries of less than 50,000 barrels/day capacity are not represented in the cluster models. Over half of the refineries in the U.S. fall in this category. They refine only about one-quarter of the total U.S. refinery crude input, however.

C. The models were developed in 1974-1975. If they are to be used for a detailed and comprehensive environmental assessment of refineries, recalibration of the models might be required. This could be determined from a comparison of current operations in the 18 reference refineries to those of 1977-1978.

D. Like the two models discussed previously, no method is available to accurately characterize the number of fugitive sources within the cluster models.

2.4 THE DEVELOPMENT OF REFINERY PLOT PLANS

Powell, et al.,[4] have developed for the EPA plot plans for four refinery cases. In this work, representative refinery process and auxiliary units were placed into modules. These modules were located on refinery plot plans for the purpose of generating hydrocarbon ambient dispersion models.

2.4.1 Description of Plot Plans

Four refinery cases were developed. These were:

- A small capacity existing refinery with a crude unit charge rate of 50,000 barrels per day.
- An intermediate capacity existing refinery with a crude unit charge rate of 200,000 barrels per day.
- A large capacity existing refinery with a crude unit charge rate of 350,000 barrels per day.
- A relatively new refinery with a crude unit charge rate of 250,000 barrels per day.

The following information was given for each of the four refinery cases:

- A plot plan detailing the location and area of each refinery module.
- The estimated number and description of all potential emission sources within each module. Included among these potential sources are valves, fittings, pumps, compressors, heaters, tanks, wastewater treating units, cooling towers, and flares.
- Descriptions of tall and wide structures which could affect airflow and, consequently, dispersion of pollutants.

A summary of the type and number of potential emission sources is given in Table F2-14 for the four refinery cases. The number of sources was estimated using several methods.

The number of pumps and compressors (both active and spare) was determined by counting these sources on process flow diagrams. Actual flow diagrams and generalized process flow diagrams from published literature were both used. Where not specified, the number of spare pumps and compressors was estimated using engineering judgment.

The number of valves and fittings was estimated from the number of pumps handling hydrocarbons in a process module. The number of process valves was assumed to be 70 times the number of active and spare pumps. The number of control valves was determined from process flow diagrams or was estimated from the number of control valves in similar processes.

The total number of screwed and flanged fittings was derived by multiplying the number of active and spare pumps (handling hydrocarbons) by 235. The number of vessels and columns within a module was used to estimate the number of relief valves.

Other equipment and process information given for each refinery module include: the number of process heaters and boilers, the design heat input for each device, stack heights and diameters, storage tank information, and the area and dimensions of each process module.

The plot plan for the large existing refinery case is shown in Figure F2-8. The individual modules are identified in Table F2-15. A product slate for the large existing refinery case is presented in Table F2-16.

TABLE F2-14. TYPE AND NUMBER OF POTENTIAL EMISSION SOURCES FOR FOUR REFINERY CASES

	Refinery Type			
	Small Existing Refinery	Intermediate Existing Refinery	Large Existing Refinery	New Refinery
	Capacity, bbl/day			
	50,000	200,000	350,000	250,000
Pumps - active and spare in hydrocarbon service	186	411	614	315
Compressors - active and spare in hydrocarbon service	17	37	61	24
Pumps and compressors - active and spare in aqueous service	30	43	53	25
Control valves	228	364	809	352
Process valves	16,645	28,240	48,670	24,805
Fittings	54,706	94,867	162,996	83,337
Relief valves	237	429	739	371
Sample valves	323	634	997	495
Combustion devices	29	49	91	32
Tanks	78	416	236	70
Flares	2	4	3	2

Source: Reference 4

Capacity = 350,000 bbl/day   Area = 6120 ft x 9100 ft

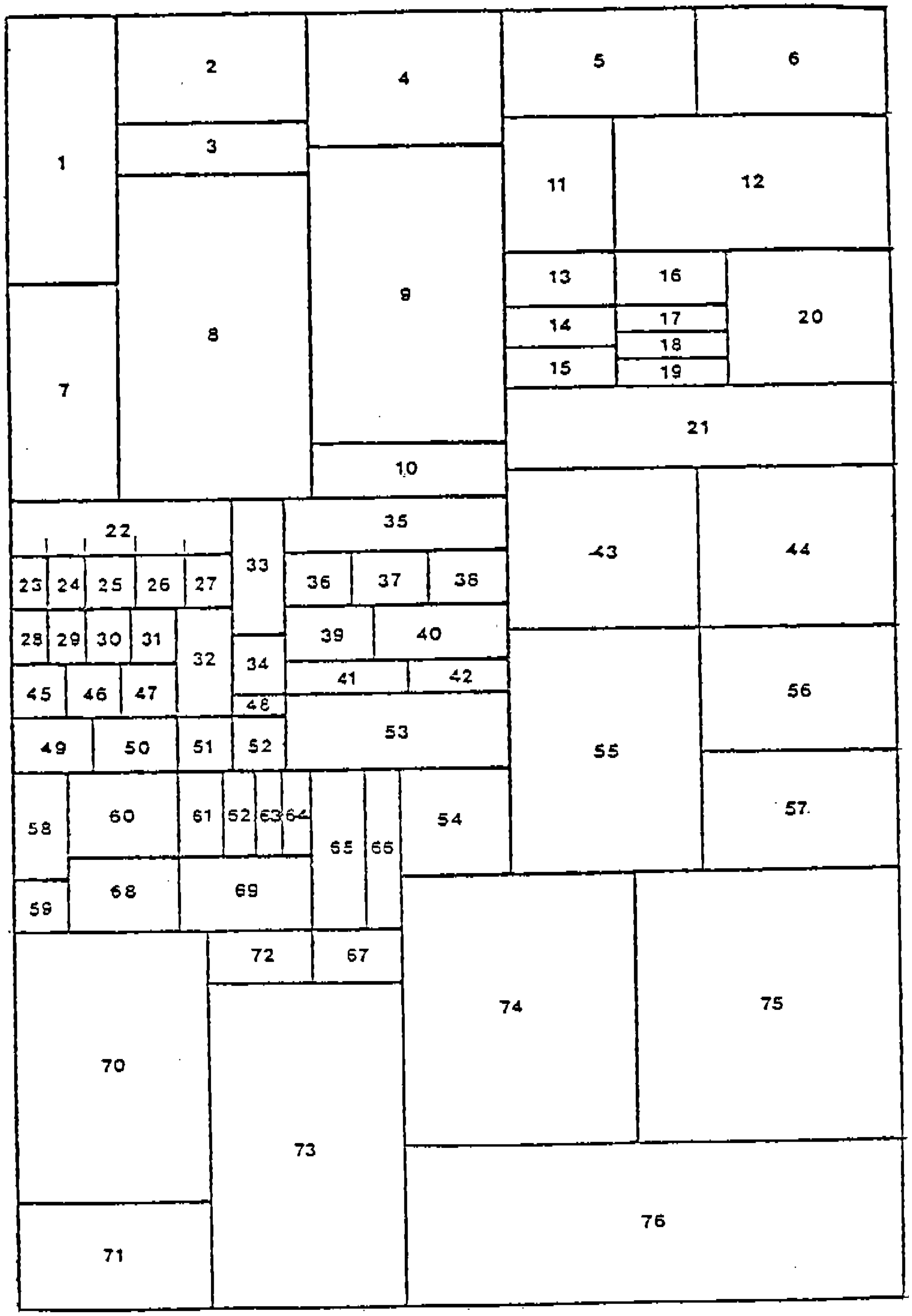


Figure F2-8. Arrangement of refinery process and auxiliary modules for a large existing refinery.

Source: Reference 4

TABLE F2-15. DESCRIPTION AND IDENTIFICATION NUMBER OF MODULES IN A LARGE EXISTING REFINERY

Module No.	Description
L1	Buffer Zone
L2	Feedstock Storage
L3	Crude Oil Storage
L4	Feedstock Storage
L5	Feedstock Storage
L6	Crude Oil Storage
L7	Feedstock and Product Storage
L8	Crude, Feedstock, and Product Storage
L9	Crude, Feedstock, and Product Storage
L10	Oil-Water Separator
L11	Product Storage
L12	Product Storage
L13	Distillation and Gas Recovery Unit
L14	Jet Hydrofiner/Catalytic Reformer
L15	Naphtha Nydrotreater
L16	Hydrotreater (lt cycle oil)
L17	Hydrogen Manufacturing
L18	Partial Oxidation Unit
L19	Future Expansion
L20	Cooling Tower
L21	Flares
L22	Feedstock and Product Storage
L23	Naphtha Hydrotreater
L24	Vacuum Gas Oil Unit
L25	Benzene Fractionation
L26	Steam Rerun Stills
L27	Future Expansion
L28	Crude Distillation
L29	Catalytic Reformer
L30	Vacuum Residuum Desulfurizer
L31	Hydrogen Manufacturing
L32	Alkylation
L33	Distillate Hydrodesulfurization (hvy gas oil)
L34	Sulfur Recovery
L35	Tanks/Cooling Towers
L36	Catalytic Reformer
L37	Aromatics Extraction
L38	Catalytic Cracking
L39	Para-Xylene Plant
L40	Delayed Coker
L41	Barrel Storage

Continued

Table F2-15. Continued

Module No.	Description
L42	Barrel Reconditioning
L43	Feedstock Storage
L44	Storm Water Impound Basin
L45	Warehouse
L46	Gas Holder/Blowdown Stack
L47	Gas Holder/Blowdown STack
L48	Fire Prevention Training Facility
L49	Oil-Water Separator
L50	Asphalt Plant
L51	Solvent Treating Plant/Boiler House
L52	SO_2 Treating Plant/Tanks
L53	Lube Oil Packaging
L54	Coke Storage
L55	Crude Oil Storage
L56	Feedstock Storage
L57	Tanks/Impound Basin
L58	Administration
L59	Oil-Water Separator
L60	Gasoline Sweetener/Crude Distillation
L61	Crude Distillation/Crude Desalter
L62	Specialty Crude Distillation
L63	Specialty Crude Distillation/Condenser Box
L64	Gasoline Fractionating Unit
L65	Tank Loading/Truck Loading/Vapor Recovery
L66	Buildings
L67	LPG Storage and Blending
L68	Vapor Recovery/Gasoline Rectifier/Tanks
L69	Main Pump House
L70	Product Storage
L71	Wastewater Treatment
L72	Building
L73	Product Storage
L74	Shops and Warehouse
L75	Crude Oil Storage
L76	Crude, Feedstock, and Product Storage

Source: Reference 4

TABLE F2-16. PRODUCT SLATE FOR LARGE CAPACITY EXISTING REFINERY

Crude Charge Rate	350,000 bbl/day
Benzene into Refinery	1,220 bbl/day

Product Slate

Product	Production Rate bbl/day
Gasoline	152,500
Fuel oil	68,770
Jet fuel	44,780
Distillate fuel oil	49,870
Coke	21,550
Naphtha	8,579
Toluene and xylene	7,189
Asphalt	4,541
Mixed olefins	2,906
Benzene	1,572
Lube oils	799
Kerosene	403
	363,500

Source: Reference 4

2.4.2 Utility of the Refinery Plot Plans

The Refinery Plot Plans described in this section have both advantages and disadvantages for potential application in the Refinery Assessment Program. The advantages include:

- Detailed refinery layouts are presented. These layouts can be used in association with atmospheric dispersion models to evaluate hydrocarbon and other pollutant concentrations in the vicinity of refineries.
- Each refinery case contains a very detailed listing of all refinery modules including process units, auxiliary/supportive units, and storage facilities.
- Detailed source counts are given for each of the modules. This allows hydrocarbon emissions to be estimated from each refinery module.
- Heaters and boilers, along with stack dimensions, are described in detail. Rated heat duties are given for each combustion source.
- Process streams through each pump and compressor are classified into one of three groups according to their volatility. This is helpful in applying valve, pump seal, and compressor seal emission factors which are functions of stream volatilities.

Some disadvantages of the refinery plot plan cases are:

- The numbers estimated for each source type were not based on actual field counts.
- All module shapes and refinery layout are rectangular.
- Standard size (capacity) modules were used to develop the plot plans for the four refinery cases.
- The four refinery cases do not necessarily correspond to any "typical" or "representative" set of model refineries.

2.5 THE PRODUCTION OF ORGANIC CHEMICALS AT REFINERIES

Processing modules for the production of organic chemicals other than BTX (benzene/toluene/xylene), LPG, and C_3/C_4 olefins are not included in either the ADL cluster models[3] or the refinery cases developed by Powell, et al.[4] The capacities and sites of chemical production facilities were surveyed to determine the need for the inclusion of additional process modules in the existing refinery simulation models.

The 20 organic chemicals produced in the greatest volume in the United States (1974) were identified. It was found that 15 of these chemicals are produced in significant quantities at refinery associated sites, often at facilities operated by chemical subsidiaries of the parent refining companies. Production site and capacity summaries for these 15 chemicals are tabulated in Table F2-17. The chemical manufacturing capacity at refinery associated sites exceeds 50 percent of the total domestic capacity for only five organic chemicals: benzene, cumene, propylene, toluene, and p-xylene. In addition, it is probable that over half of the mixed xylenes production capacity is also located at refinery associated sites, but individual site capacities were not available to verify this assumption. Only benzene, toluene and propylene are produced at more than 20 refinery associated sites.

Chemical production at sites associated with Types C (petrochemical) and E (integrated) refineries was identified. Data on production capacities for organic chemicals at these locations were obtained from the <u>1976 Directory of Chemical Producers</u>.[7] A total of 30 refinery sites were considered. Only seven organic chemicals were produced at more than 6 of the 30 refinery associated locations. These chemicals were benzene, toluene, mixed xylenes, propylene, cyclohexane, cumene and propane. The refinery associated production sites are listed in Table F2-18. Only benzene, toluene, mixed xylenes and propylene are produced at more than 10 refinery associated sites.

With the exception of BTX and propylene production, then, it is difficult to characterize the manufacture of organic chemicals at refinery associated sites. The production modules for aromatics and C_3/C_4 olefins are already included in the refinery models. In both cases, the inclusion of additional fractionation in the existing modules would provide the means for producing benzene, toluene, mixed xylenes and propylene. The addition of other chemical production modules to the existing refinery models does not appear to be justified.

TABLE F2-17. CHEMICAL PRODUCTION AT REFINERY ASSOCIATED SITES

Chemical	Total 1976 Production Capacity (Domestic)	Production Capacity at Refinery Associated Sites		Total No. of Production Sites	Refinery Associated Production Sites	
		Amount	% of Total Capacity		Number	% of Total Sites
Benzene	1,475 MM gal	1,099 MM gal	75	52	35	67
Butadiene	4,406 MM lb	700 MM lb	16	23	4	17
Cumene	3,785 MM lb	1,995 MM lb	53	13	9	69
Ethylbenzene	8,406 MM lb	1,246 MM lb	15	17	6	35
Ethylene	25,220 MM lb	8,075 MM lb	32	34	10	29
Ethylene Dichloride	12,880 MM lb	2,435 MM lb	19	17	3	17
Ethylene Glycol	3,400 MM lb	265 MM lb	8	16	1	6
Ethylene Oxide	3,960 MM lb	475 MM lb	12	14	1	7
Phenol	2,556 MM lb	238 MM lb	9	17	3	18
Propylene	13,223 MM lb	9,031 MM lb	68	60	37	62
Styrene	7,075 MM lb	1,010 MM lb	14	13	3	23
Toluene	967 MM gal	833 MM lb	86	47	27	57
Vinyl Chloride	6,165 MM lb	1,540 MM lb	25	14	2	14
Mixed Xylenes	(6,060 MM lb)*			32	18	56
P-xylene	2,530 MM lb	2,230 MM lb	88	11	10	91

*1974 Production

Source: References 7, 12

TABLE F2-18. ORGANIC CHEMICALS PRODUCED AT REFINERY ASSOCIATED SITES

Refineries/Sites	Benzene	Toluene	Mixed Xylenes	Propylene	Cyclohexane	Cumene	Propane
Standard Oil Co. (California) El Segundo, California	P/C	P		C		C	
Getty Oil Company Delaware City, Delaware				P			
Amoco Oil Company Wood River, Illinois				C			
Clark Oil & Refining Company Blue Island, Illinois				C		C	
Skelly Oil Company El Dorado, Kansas	P	P		P		P	P
Ashland Petroleum Company Tonowanda, New York	C	C	C	C			
Standard Oil Co. (Kentucky) Pascagoula, Mississippi							
Exxon Company Linden, New Jersey				C			
Texaco, Inc. Westville, New Jersey	P	P		P		P	
Ashland Petroleum Cattletsburg, Kentucky	C	C	C	C		C	
Sun Oil Co. of Pennsylvania Toledo, Ohio				P			P

Continued

TABLE F2-18. Continued

Refineries/Sites	Benzene	Toluene	Mixed Xylenes	Propylene	Cyclohexane	Cumene	Propane
Amoco Oil Company Texas City, Texas	C	C	C				
Coastal States Petrochemical Co. Corpus Christi, Texas	P	P	P	P		P	
Cosden Oil & Chemical Company Big Spring, Texas	P	P	P	P	P		
Marathon Oil Company Texas City, Texas	P	P	P	P		P	P
Phillips Petroleum Company Borger, Texas					P		
Phillips Petroleum Company Sweeny, Texas	P	P		P	P		
Suntide Refining Company Corpus Christi, Texas	P	P	P	P		P	P
Amoco Oil Company Yorktown, Virginia							
Atlantic Richfield Company Carson, California	C	C	C	C			C
Shell Oil Company Martinez, California							
Standard Oil Co. (California) Richmond, California				C			

Continued

TABLE F2-18. Continued

Refineries/Sites	Benzene	Toluene	Xylenes	Propylene	Cyclohexane	Cumene	Propane
Phillips Petroleum Company Kansas City, Kansas							
Exxon Company Baton Rouge, Louisiana	C			C			
Sun Oil Company Marcus Hook, Pennsylvania	P	P	P	P			
Atlantic Richfield Company Houston, Texas	C	C	C				
Exxon Company Baytown, Texas	C	C		C	C		
Gulf Oil Company Port Arthur, Texas	C	C		C	C	C	
Union Oil Company Nederland, Texas	P	P	P	C	P		P

P = Produced by petroleum company.

C = Produced by chemical subsidiary of petroleum company.

2.6 SUMMARY

The cluster model refineries developed by ADL[3] and the refinery cases developed by Powell, et al.,[4] seem best suited for emissions evaluation and an environmental assessment. The cluster models are useful for preliminary emissions evaluation to determine the relative importance of various types of emission sources.

The refinery plot plans and refinery cases developed by Powell, et al.,[4] are quite detailed. They were developed for use with atmospheric dispersion models. Consequently, they should be suited for use in an environmental assessment.

Actual field source counts have been obtained as a part of this program and are provided in Section 4 for a variety of process units. When these counts are compared to those developed by Powell, et al.,[4] it is evident that there are considerable differences between the two estimates. This is probably a result of real differences between the actual number of sources in process units of the same type as well as differences resulting from the methods used to obtain these estimates.

Estimates for total emissions from a variety of process units are listed in Section 4 of this Appendix. Where possible, both sets of estimates for fugitive emission sources are included. It is difficult to say which estimate is the more representative of the two. Since the results of this program indicate that there are wide variations in the number of sources between similar process units in different refineries and that these differences do not correlate with the unit capacity, the use of an "average" number of sources per process unit is probably not appropriate. Therefore, accurate estimates of total fugitive emissions from actual process units should be obtained using the number and distribution of sources actually present in that particular process unit.

2.7 REFERENCES FOR SECTION 2

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3. Arthur D. Little, Inc. Impact of SO_x Emissions Control on Petroleum Refining Industry. Final Report, Vol. II, Detailed Study Results. EPA-600/2-76-161b. Cambridge, Massachusetts, June 1976.

4. Powell, D., et al. Development of Petroleum Refinery Plot Plans. EPA-450/3-78-025. Pacific Environmental Services, June 1978.

5. Bombaugh, K. J., et al. Sampling and Analytical Strategies for Compounds in Petroleum Refinery Streams. Final Report, Volumes, PB 251 744 (Vol. 1); PB 251 (Vol. 2); EPA-600/2-76-012, Radian Corporation, Austin, Texas, January 1976.

6. U.S. Bureau of Mines. Crude Petroleum, Petroleum Products, and Natural Gas Liquids, December 1974 Mineral Industry Surveys. Petroleum Statement Monthly, Washington, D.C., April 1975.

7. Stanford Research Institute. 1976 Directory of Chemical Producers, U.S.A. Menlo Park, California, 1976.

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11. Cantrell, Ailleen. Annual Refining Survey. Oil and Gas J., 72(13): 82-106, April 1, 1974.

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SECTION 3

REFINERY RAW MATERIALS AND PRODUCTS

Each refinery has its own set of raw materials and products which varies with availability and market demand. The general categories and characteristics of each will be described in this section. A detailed description is beyond the scope of this report.

3.1 CHARACTERISTICS OF RAW MATERIALS

The raw materials for a refinery include crude oil, catalysts, acids, bases, light olefins, and gasoline additives. All are used in varying amounts.

3.1.1 Crude Oil

Crude oil is the basic raw material of any refinery. Its definition, according to ASTM D-288, is as follows:

> "A naturally occurring mixture, consisting predominantly of hydrocarbons, and/or of sulfur, nitrogen and/or oxygen derivatives of hydrocarbons, which is removed from the earth in liquid state or is capable of being removed.
>
> Crude petroleum is commonly accompanied by varying quantities of extraneous substances such as water, inorganic matter and gas. The removal of such extraneous substances alone does not change the status of the mixture as crude petroleum. If such removal

> appreciably affects the composition of the oil mixture, then the resulting product is no longer crude petroleum."

Crude is primarily a liquid; it may be light and easy-flowing or a heavy, semi-solid substance. Its color may be green, brown, black, or almost white. Specific gravities of crudes usually range between 0.8 and 0.95; most kinematic viscosities are between 0.023 and 0.23 stoke.[1]

The elemental composition of crude is amazingly uniform. The ultimate analysis is given in Table F3-1.

TABLE F3-1. ULTIMATE ANALYSIS OF CRUDE OILS, WEIGHT PERCENT

Carbon	83.9 - 86.8
Hydrogen	11.4 - 14.0
Sulphur	0.06 - 8.00
Nitrogen	0.11 - 1.70
Oxygen	0.5
Metals (Fe, V, Ni, etc.)	0.03

Source: Reference 2

3.1.1.1 Major Types--

There are as many different crudes as there are sources. Though the elementary composition is relatively uniform, small variances can greatly affect physical properties. Because crudes are so very complex and varied, there is no one simple method for classification. It has been proposed that classification systems now in use be replaced by the concept of a continuous spectrum of oils arranged in order of increasing cyclization of the components.[3] Two methods for categorization are presented here: the classification by product commonly used by refiners and a geographic classification.

Classification By Product--Refiners often classify crudes according to the residue from their nondestructive distillation. This classification method usually gives some indication of the ultimate products. There may be as many as nine categories in the classification to account for the various types of oils. Some oils are combinations of several types.

The simplest classification has two categories: paraffin-base and asphalt-base. Paraffinic crudes are good sources of paraffin wax (condensed paraffins) and high-quality motor oils and kerosenes. Asphaltic crudes are good sources of asphalt (primarily condensed aromatics), machine lubricating oils and high-quality gasoline. Asphaltic crudes usually have high sulfur, oxygen, and nitrogen content; light and intermediate fractions of asphaltic crude are higher in naphthenes.

Geographic Classification--Crudes from a certain geographic region usually have similar characteristics. Therefore, it is often convenient to classify crudes according to their region of origin.

No one geographic classification is used universally. However, the classification used by A. D. Little[5] is considered the most widely used one. This classification is presented as Table F3-2. Some general properties of the crudes categorized in Table F3-2 are listed in Table F3-3.

TABLE F3-2. GEOGRAPHIC CLASSIFICATION OF CRUDES

Name	Type
Louisiana	Louisiana and low-sulfur Texas crudes
Oklahoma	Light, sweet crudes from the mid-continent
West Texas	High-sulfur crudes from Texas and New Mexico
Wilmington	Heavy crudes from California
Ventura	Light crudes from California
Nigeria Forcados	Heavy African crudes
Algerian Hassi Messaoud	Light African crudes
Arabian Light	Considered representative of average Middle East crudes
Minas	Considered representative of Southeast Asian crude imports
Tia Juana Medium	Considered representative of Venzuelan crude exports

Source: Reference 5

TABLE F3-3. GENERAL PROPERTIES OF CRUDES ACCORDING TO GEOGRAPHIC LOCATIONS

	Domestic Crudes					
	Louisiana	West Texas Sour	Oklahoma	California Wilmington	California Ventura	Alaskan North Slope
Yield, Volume %						
Methane/ethane (FOE)	---	0.04	--	0.002	0.005	0.06
Propane	0.20	0.50	0.48	0.093	0.400	0.28
Isobutane	0.40	0.40	0.46	0.095	0.295	0.13
Normal butane	0.70	1.30	2.18	0.318	1.069	0.49
Straight-run naphtha:						
C5-160°F	4.09	5.70	7.70	2.09	5.72	3.53
Light 160-200°F	2.99	3.80	4.76	2.47	3.25	2.57
Medium 200-340°F	13.05	15.50	16.66	7.64	14.26	9.25
Heavy 340-375°F	3.47	3.30	3.93	1.50	3.34	2.69
Light gas oil 375-500°F	17.50	13.39	13.76	9.29	11.54	12.43
Heavy gas oil 500-650°F	19.50	14.11	11.77	11.96	12.53	15.50
Vacuum overhead 650-1050°F	32.50	29.60	28.04	38.54	32.08	29.49
Vacuum bottom 1050°F+	5.60	12.30	10.25	26.00	15.50	23.52
Crude properties						
Gravity (°API)	36.2	33.4	40.2	19.6	29.7	27.5
% weight sulfur	0.2[a]	1.31[a]	0.212	1.28	1.56	0.96

(Continued)

TABLE F3-3. Continued

	Foreign Crudes						
	Nigerian Forcados	Arabian Light	Venezuelan Tia Juana	Algerian Hassi Messaoud	Mixed Canadian	Indo-nesian Minas	Natural Gasoline
Yield, Volume %							
Methane/ethane (FOE)	0.04	--	0.01	0.04	0.05	0.003	--
Propane	0.04	0.17	0.59	1.21	1.13	0.139	--
Isobutane	0.51	0.17	0.27	0.53	0.49	0.141	4.71
Normal butane	0.79	1.06	0.45	3.27	1.98	0.379	7.58
Straight-run naphtha:							
C5-160°F	2.70	4.85	3.89	8.29	6.60	1.70	62.02
Light 160-200°F	3.40	3.27	2.20	5.00	3.89	1.60	13.99
Medium 200-340°F	11.70	14.93	9.09	21.19	16.50	9.10	11.70
Heavy 340-375°F	2.80	3.95	2.52	5.02	3.51	2.60	--
Light gas oil 375-500°F	18.10	13.39	10.30	15.78	14.40	10.70	--
Heavy gas oil 500-650°F	20.60	15.01	12.70	11.92	15.20	15.00	--
Vacuum overhead 650-1150°F	30.40	29.50	32.80	22.71	25.60	41.00	--
Vacuum bottom 1050°F+	8.50	13.70	25.00	4.99	10.60	18.00	--
Crude properties							
Gravity (°API)	29.4	34.6	26.3	44.7	39.0	35.3	--
% weight sulfur	0.21	1.7	1.51	0.13	0.55	0.07	--

[a] Radian calculation.

Source: Reference 4

Crudes are also often referred to by specific field.

3.1.1.2 Major Constituents--

As stated previously, crudes are basically very complex mixtures of hydrocarbons. There are probably more than 3000 compounds in any one crude.[6] Because the composition of crude influences so many aspects of refinery design and operation, it has been the subject of much research in recent years.

The hydrocarbons in the crude are normally paraffins, naphthenes (cycloparaffins) and aromatics. Their structures may be simple or complex. There is evidence of normal paraffins with as many as 78 carbon atoms. The concentration of branched paraffins appears to decrease with increasing molecular weight. There also appears to be a tendency toward methyl branches at the ends of molecules.[7]

Naphthenes usually have 5-, 6-, or 7-membered rings, whether they are monocyclic or polycyclic. Methyl substitution is quite common. Most of the alkyl derivatives of benzene, naphthalene, biphenyl, and phenanthrene with boiling points up to 300°C have been found in crude. Substituents on the ring usually consist largely of methyl groups with one long, relatively unbranched, alkyl group. In high boiling point fractions, aromatic rings and cycloalkyl rings may be combined.[7]

The hydrocarbons in crude are usually categorized according to their boiling point ranges. The terminology used to describe the fractions varies slightly. Exact boiling point cut-offs vary with the intended use for the fraction. Two example slates of fractions are given in Tables F3-4 and F3-5.

TABLE F3-4. BOILING RANGES OF TYPICAL CRUDE OIL FRACTIONS

Fraction	Boiling Range, °F
Light gases (methane, ethane, some propane)	-259 to -44
Propane	-44
Butanes	11 to 31
Light Naphtha	30 to 300
Heavy Naphtha	300 to 400
Kerosine	400 to 500
Light Gas Oil	400 to 600
Heavy Gas Oil	600 to 800
Vacuum Gas Oils	800 to 1100
Residue (source of asphalts or waxes)	1100^{+}

Source: Reference 1

TABLE F3-5. BOILING RANGES OF TYPICAL CRUDE OIL FRACTIONS

Fraction	Boiling Range, °F
Butanes and lighter	Not given
Light straight-run gasoline (LSR)	90 to 190
Naphtha (heavy straight-run gasoline)	190 to 380
Kerosine	380 to 520
Light gas oil (LGO)	520 to 610
Atmospheric gas oil	610 to 800
Vacuum gas oil (VGO)	800 to 1,050
Vacuum reduced crude	1050+

Source: Reference 8

The hydrocarbon composition of a crude fraction depends on the type of crude. This is illustrated in Table F3-6, which shows the approximate hydrocarbon compositions of some representative fractions in paraffinic and asphaltic crudes.

3.1.1.3 Potentially Hazardous Constituents--

The potentially hazardous constituents of crude oil are of four types: hydrocarbons, sulfur compounds, nitrogen compounds, and trace elements. Unlike coal, oil is subjected to processing during which essentially all components are converted into usable products. The hazardous constituents may be released during any of the processing steps. Since most oil products are fuels, the hazardous constituents may also be released when these fuels are combusted.

Hydrocarbons--Table F3-7 is a list of hydrocarbons which have been identified in crude and which have been designated as potentially hazardous. The compounds included have either been assigned a threshold limit value (TLV) by the American Conference of Governmental Industrial Hygienists or assigned a rating of 2 or 3 (capable of causing permanent damage to humans) by Irving Sax in Dangerous Properties of Industrial Materials, 1975 edition.

Sulfur Compounds--Organic sulfur compounds are present to some extent in all crudes, but the amount can vary from 0.06 to over 8 weight percent. The sulfur compounds are not distributed evenly through the crude: in general, the concentration of sulfur compounds increases as molecular weight increases. The complexity of sulfur-containing molecules also increases with increasing molecular weight.[2]

TABLE F3-6. DISTRIBUTION OF HYDROCARBON TYPES IN SOME PETROLEUM FRACTIONS

Fraction	Boiling Range 50% ASTM Distillation, °F	Paraffin-Base Crude, Wt %			Asphalt-Base Crude, Wt %			
		Paraffins	Naphthenes	Aromatics	Paraffins	Naphthenes	Aromatics	Unsaturated
Gasoline	280	65	30	5	35	55	10	--
Kerosine	450	60	30	10	25	50	25	--
Gas oil	600	35	55	15	--	65	33	2
Heavy Distillate	750	20	65	15	--	55	43	2

Source: Reference 1

TABLE F3-7. POTENTIALLY HAZARDOUS[a] HYDROCARBONS IN CRUDE OIL

Compound	Concentration[b]
Methane	T
Ethane	T
Propane	m
Methylpropane	T
Butane	m → M
Methylbutane	m
n-Pentane	m
2,2-Dimethylpropane	T → m
n-Hexane	m
2-Methylpentane	m → M
3-Methylpentane	m
2,2-Dimethylbutane	m
2,3-Dimethylbutane	m
n-Heptane	m-M
2,3-Dimethylpentane	m
2,4-Dimethylpentane	m
n-Octane	m
2-methylheptane	m
2,3-Dimethylhexane	m
2,4-Dimethyhexane	m
2,2,4-Trimethylpentane	T
n-Dodecane	T → m
Cyclopentane	m
Cyclohexane	m
Methylcyclohexane	m → M
Cycloheptane	m
Benzene	T → m
Toluene	T → m
Ethylbenzene	T → m
Dimethylbenzene (Xylene)	T → m
n-Propylbenzene	m
Isopropylbenzene (Cumene)	m
1,2,3-Trimethylbenzene	m
1,2,4-Trimethylbenzene	m
1,3,5-Trimethylbenzene	m
Isobutylbenzene	m
sec-Butylbenzene	m
tert-Butylbenzene	m
1-Methyl-5-Isopropylbenzene	m
1,2-Diethylbenzene	m
1,3-Diethylbenzene	m

(Continued)

TABLE F3-7. Continued

Compound	Concentration[b]
1,4-Diethylbenzene	m
1-Methyl-4-tert-butylbenzene	T
1-Methylnaphthalene	T
2-Methylnaphthalene	T
Pyrene	T
Coronene	T
Benzo(e)pyrene	T
1,2,3,4-Tetrahydronaphthalene	T
Biphenyl	T
Acenaphthene	T
Benzofluorenes	T
Phenanthrene	T
Benzophenanthrene	T
Naphthenophenanthrenes	T
Dinaphthenophenanthrenes	T
Trinaphthenophenanthrenes	T
Tetranaphthenophenanthrenes	T
Pentanaphthenophenanthrenes	T
Fluoranthrenes	T
Perylene	T
Phenyleneperylene	T
Dibenzoperylene	T
Chrysene	T
Benzo(g)chrysene	T
3-Methylchrysene	T
Naphthenochrysenes	T
Anthracene	T
Benzanthracene	T

Sources: References 3, 9, 10, 11, 12, 13, 14, 15, 16

[a] The compounds included in this list have either been assigned a Threshold Limit Value (TLV) by the American Conference of Governmental Industrial Hygienists or assigned a rating of 2 or 3 (capable of causing permanent damage) by Irving Sax in Dangerous Properties of Industrial Materials, 1975 edition.

[b] Key to Concentrations:

T = trace: <100 ppm
m = minor: 100 ppm to 2.99%
M = major: ≥3.0%

Trace quantities of 48 thiols, almost 200 sulfides, and a number of sulfites, sulfonates, and sulfones have been identified in crude and identified as potentially hazardous according to footnote "a" in Table F3-7. Hydrogen sulfide is known to be a dangerous chemical. Many of the sulfur compounds in crude are decomposed by normal refinery processes.

Hydrogen sulfide is often associated with the lighter gases. Elementary sulfur can also be dissolved in the oil, possibly formed by the oxidation of hydrogen sulfide.

In lower boiling point fractions (up to about 400°F), mercaptans (thiols) appear to predominate. Alkyl mercaptans with the thiol group on a primary carbon are most prevalent in fractions with boiling points up to 200°F; in higher boiling fractions, the thiol group is more likely attached to a secondary carbon.

Cyclic mercaptans appear in the kerosine range; thioethers and cyclic sulfides in naphthenes. In higher boiling fractions, the tendency appears to be toward sulfur substitution in saturated rings. Little is known of the sulfur species in the heaviest distillates; they are believed to be mostly polycyclic molecules with sulfur substitutions in the rings.

Nitrogen Compounds--As with sulfur compounds, the concentration of nitrogen compounds in crude increases with increasing boiling point. Unlike sulfur compounds, nitrogen compounds do not decompose in normal refinery processes. Also, nitrogen content is lower than sulfur content--less than one percent.

Approximately one-fourth to one-third of the nitrogen in crude is found in basic nitrogen compounds. The basic nitrogen compounds which have been isolated, mainly in gas oils, are alkyl, mainly methyl or dimethyl, substituted quinolines and pyridines. All of these alkyl quinolines and some of the pyridines have been designated potentially hazardous as defined by footnote "a" in Table F3-7. The nonbasic compounds indole and the carbazoles have also been identified in crude oils and have been designated as potentially hazardous.

Oxygen Components--Crude oil generally contains less than 2 percent oxygen. However, oxygen content increases with increasing molecular weight: residual oils may contain as much as 8 percent oxygen.[2]

The oxygen compounds in crude designated as potentially hazardous include the lower molecular weight carboxylic acids and alkyl ketones, some cyclic ketones and phenols. These compounds are present in trace amounts in crude.

Trace Metals--Trace quantities, most less than 100 ppm, of a number of metals have been found in crude. These elements are usually observed in the ash remaining from combustion. Twenty-eight metals which have been found by spectrographic examination of ash are listed in Table F3-8. Of the metals listed, vanadium, nickel and iron are usually present in the greatest quantities. Table F3-9 gives relative trace element concentrations in several representative crudes. Most of the elements are considered potentially hazardous.

TABLE F3-8. TRACE METALS FOUND BY SPECTROGRAPHIC ANALYSIS OF THE ASH FROM CRUDE OIL

Ag	Ba	Ca	K	Mo	Pb	V
Al	Ce	Cu	La	Na	Sn	Zr
As	Co	Fe	Mg	Nd	Sr	Zn
B	Cr	Ga	Mn	Ni	Tl	U

Source: Reference 17

TABLE F3-9. TRACE ELEMENT CONTENTS OF SOME CRUDE OILS BY NEUTRON ACTIVATION ANALYSIS

	Concentration in Crude Oil (ppmw)			
Element	California (Tertiary)	Libya	Venezuela (Boscan)	Alberta (Cretaceous)
V	7.5	8.2	1100.	0.682
Cl	1.47	1.81	--	25.5
I	--	--	--	1.36
Na	13.2	13.0	20.3	2.92
K	--	4.93	--	--
Mn	1.20	0.79	0.21	0.048
Cu	0.93	0.19	0.21	--
Ga	0.30	0.01	--	--
As	0.655	0.077	0.284	0.0024
Br	0.29	1.33	--	0.072
Mo	--	--	7.85	--
Cr	0.640	0.0023	0.430	--
Fe	68.9	4.94	4.77	0.696
Hg	23.1	--	0.027	0.084
Se	0.364	1.10	0.369	0.0094
Sb	0.056	0.055	0.303	--
Ni	98.4	49.1	117.	0.609
Co	13.5	0.032	0.178	0.0027
Zn	9.76	62.9	0.692	0.670
Sc	0.0088	0.0003	0.0044	--
U	--	0.015	--	--

Source: Reference 17

3.1.2 Other Raw Materials

Besides crude oil, a large number of chemicals are used at a refinery as treating agents, solvents, catalysts, and additives. Many of these chemicals are eventually emitted to the atmosphere.

3.1.2.1 Catalysts--

Petroleum refineries are the largest user of catalysts in the chemical industry.[1] The catalysts may be solid or liquid. Table F3-10 lists the commonly used catalysts and the processes in which they are used.

Catalyst fines are emitted to the atmosphere during catalyst regeneration. Most catalysts are regenerated only a few times a year; therefore, the escaping catalyst fines are considered insignificant. Fluid catalytic cracking catalysts, on the other hand, are regenerated continuously. In this case, particle collection devices are used extensively to control the emissions, both for environmental protection and for economic reasons.

3.1.2.2 Gasoline Additives--

In many refineries, gasoline is the primary product. Several chemicals are usually added to this gasoline to improve its various qualities. These additives are described below:[1,2]

Antiknock Compounds--Tetraethyl lead is the most common antiknock compound; it was used in concentrations of up to 0.08 volume percent before the lead phase-out program. By 1979, the maximum concentration approached 0.01 volume percent.

TABLE F3-10. PRINCIPAL APPLICATIONS OF CATALYST MATERIALS[a]

Catalyst Material	Processing Application Cracking	Reforming	Hydrotreating	Isomerization	Alkylation	Polymerization
Aluminia	X	X	X			
Aluminum chloride				X	X	
Antimony trichloride				X		
Bauxite	X			X		
Bentonite clay	X					
Clay	X					
Cobalt-molybdena			X			
Cobalt molybdate		X	X	X		
Cobalt oxide		X				
Copper	X					
Copper pyrophosphate						X
Hydrochloric acid				X	X	
Hydrofluoric acid					X	
Iron oxide	X					
Kaolin clay	X					
Magnesia	X					
Molybdena		X				
Molybdenum		X				
Nickel sulfide			X			
Phosphoric acid						X
Platinum		X	X			
Potassium	X					
Silica-alumina	X	X	X	X		
Sulfuric acid					X	
Tungsten nickel sulfide			X			

[a] Many catalyst materials are also used for other purposes in a refinery.

Source: Reference 1

Others which may be used are tetramethyl lead, triethylmethyl lead, diethyldimethyl lead, and ethyltrimethyl lead. Ethylene dibromide is added in a 1:1 relationship with the lead to cause the formation of volatile lead bromide instead of lead oxide which could foul the engine.

Antioxidants--Aromatic amines and alkyl-substituted phenols are used in concentrations of about 50 ppm to inhibit oxidation reactions which cause the formation of gums.

Metal Deactivators--Metal deactivators prevent the dissolution of metals, particularly copper, by the gasoline or deactivate metals already dissolved in the fuel. Copper in particular catalyzes the formation of gums. Many metal deactivators contain amine or diamine groups which combine with the metal to form a compound which does not react further.

Anti-Corrosion Additives--Surface-active chemicals are added to gasoline to emulsify any water present so that it will not rust pipelines, storage tanks, and engine parts.

Antistall Additives--Antistall additives are used to prevent carburetor icing. There are two types: cryoscopic additives such as methanol, ethanol or isopropanol lower the freezing point of condensed water so that it does not freeze; surfactants such as polyalkylene glycols, alkyl phosphates, and alkyl amines form a monomolecular hydrophobic film over metal surfaces to prevent the adherence of ice crystals. Surfactants are used at levels of 30 to 150 ppm; cryoscopic additives are used at levels of about 0.05 to 1.0 percent volume.

Antipreignition Agents--Deposit modifiers such as phosphorus compounds are used to change the character of combustion-chamber deposits. These are used at about 200 ppm.

Lubricants--About 0.2 to 0.5 percent of a light lubricating oil is often added to gasoline to lubricate the intake valves and the top ring belt area of the engine.

3.1.2.3 Other Chemicals--

Many chemicals are used in the various refining processes. Table F3-11 is a summary of major chemicals and their principal uses. Some catalysts discussed above are included in this table. The chemicals may be used alone or with other chemicals.

3.2 CHARACTERISTICS OF REFINERY PRODUCTS

3.2.1 Final Products

According to an API study a few years ago, almost 3000 individual products are produced in petroleum refineries.[1] Although there are many variations, these products are generally grouped into a few major categories. These categories will be described in this section.

3.2.1.1 Refinery Gases--

The most volatile fraction of crude oil processing is a mixture of gases in the C_1 to C_5 range. These gases may have been a part of the original crude, they may have been injected into the crude in the oilfield, or they may be a product of the processing of heavier fractions. All are considered potentially hazardous.[2]

TABLE F3-11. MAJOR CHEMICALS USED IN REFINING AND THEIR PRINCIPAL USES

Chemical	Uses
Acetic Acid	Break up emulsions Increase treating of sulfuric acid Reduce sulfur content Extract polymers from cracked distillates Separate waxes
Acetone	Regenerate clays Isolate benzene in azeotropic distillation Solvent in determining oil content of waxes
Aluminum Chloride	Cracking, alkylation, and isomerization catalyst
Aluminum Oxide (Bauxite)	Cracking catalyst
Aluminum Naphthenates Aluminum Phenates Aluminum Soaps Aluminum Stearate	Detergent additive for lubricating oils
Barium Hydroxide	Treat spent caustic solutions Neutralize acid-treated oils Precipitate naphthenic acids Prevent foaming before caustic soda treating for mercaptan removal Remove inorganic salts from furfural before refining

(Continued)

TABLE F3-11. Continued

Chemical	Uses
Barium Salts	Oxidation inhibitors, detergent additives in lube oils
Benzene	Solvent extraction to improve viscosity index of lube oils and remove waxes
Bore Char	Decolorize oil
Cadmium-Ammonium Chloride	Distillate Desulfurizing
Cadmium Hydroxide	
Cadmium Chloride	
Cadmium Sulfide	
Cadmium Oleate	Oxixation inhibitor in lube oil
Cadmium Naphthenate	
Cadmium Dithiocarbamate	Detergent additive
Cadmium Sulfonate	
Calcium Oxide	Neutralize acid-treated oils Remove hydrogen sulfide and organic acids from oils
Calcium Hydroxide	
Calcium Carbonate	
Calcium Chloride	Dessicant
Calcium Hypochlorite	Oxidize sulfides and mercaptans in oils

(Continued)

TABLE F3-11. Continued

Chemical	Uses
Chlorine	Oxidize disulfides to sulfonyl halides and to remove mercaptans Regenerate Bentonite clay Regenerate sodium plumbite "doctor solution" Prepare calcium and sodium hydroxide Improve cetane number of fuels
Clays	Adsorbents to improve color, odor, and stability of waxes and lube oils Cracking catalysts
Cupric Chloride	Convert mercaptans to insolubile disulfides
Cresol	Extraction of high-viscosity-index, light-color, low-carbon-residue lubricants from residual or distillate base stock
Dichloroethyl Ether	Solvent in chlorex extraction to improve viscosity index and yields of paraffinic oils
Ethanolamines (MEA, DEA, TEA)	Removal or recovery of water, hydrogen sulfide, or carbon dioxide from gaseous streams
Ethylene Dichloride	Removing wax from lube oil
Ethylene Glycol	Selective recovery of benzene, toluene, and xylenes from petroleum shocks
Formaldehyde	Laboratory reagent and solvent

(Continued)

TABLE F3-11. Continued

Chemical	Uses
Furfural	Extraction of diesel fuels, burning oils, cracking stocks, and crude oils Removal of low-cetane materials, unstable and acidic materials, sulfur, organometallic and nitrogen compounds. Extraction of aromatic, naphthene, olefinic, and unstable hydrocarbons from lube oils.
Hydrogen	Hydrotreating Hydrocracking Hydroalkylation
Hydrogen Fluoride	Alkylation Catalyst
Methyl Ethyl Ketone (MEK)	Remove wax from oils
Methyl Isobutyl Ketone (MIBK)	Deoiling high-quality waxes
Natural Oils	Production of lubes and greases
Nitrobenzene	Extract carbon and sludge-forming compounds from lube oils
Phenol	Extraction of high-viscosity-index, high-color, low-carbon-residue lubricants from residual or distillate base stock Improve viscosity index, color and oxidation resistance, and to reduce carbon and sludge-forming tendencies of lube oils.
Phosphorous Compounds	Polymerization catalysts
Phosphorous Pentoxide	Catalyst for air-blowing of asphalt

(Continued)

TABLE F3-11. Continued

Chemical	Uses
Potassium Hydroxide	Remove acids from petroleum
Potassium Phosphate	Remove hydrogen sulfide from gas
Propane	Solvent extractions-deasphating, dewaxing, and decarbonizing
Sodium Carbonate (Soda Ash)	Neutralize acids in processing streams
Sodium Hydroxide (Caustic Soda)	Remove acidic substances
Sodium Hypochlorite	Sweeten gasoline
Sodium Phenolate	Remove hydrogen sulfide from gasoline Stabilize color of gasoline
Sodium Plumbite	"Doctor sweetening" agent to convert mercaptans to disulfides
Sulfur Chlorides	Solvents
Sulfur Dioxide	Extract aromatic hydrocarbons and sulfur-bearing compounds from paraffins and naphthenes Improve viscosity index and remove waxes from lube oils
Sulfuric Acid	Remove aromatics from kerosene Remove or dissolve resinous and asphaltic materials and sulfur
Toluene	Remove waxes from lube oils
Trichloroethylene	Extract carbon- and sludge-forming constituents of lube oils and increase their viscosity index

Source: Reference 1

Several processing steps result in the production of refinery gases. The exact composition of a gas stream varies with its origin. Table F3-12 summarizes the compositions of the gas streams from the various processes.

One step in the production of high-octane gasoline is the catalytic reforming of hydrocarbons in the C_7 to C_{10} range. The gas produced contains hydrogen and hydrocarbons in the C_1 to C_4 range. The hydrogen is usually recycled and the C_3/C_4 fraction added to the liquified petroleum gas stream.

Catalytic cracking of heavy oils produces saturated and unsaturated hydrocarbons. Acetylenes may also be produced with severe cracking. Naphtha or gas oil may be thermally cracked to produce ethylene and propylene. Additional gases are produced by the coking, visbreaking, and hydrocracking of heavy oils.

3.2.1.2 Liquified Petroleum Gas--

Liquified petroleum gas, also called LP gas, LPG, or "bottled gas", is a mixture primarily of propane and butane, both of which are considered potentially hazardous. It may be sold either as a mixture or as individual gases. It is stored and transported as a liquid; liquefaction is achieved either by compression or refrigeration. Only about one-fourth of the LP gas used in this country is obtained from petroleum; the remainder is obtained from natural gas.[1]

Most LP gas is used as fuel either for heating or for motor vehicles. However, much of the butane from refineries is used as petrochemical feedstock.

TABLE F3-12. COMPOSITIONS OF TYPICAL REFINERY GASES

Composition % wt	Primary Fractionator Gas	Catalytic Reformer (Powerformer) Tail Gas	Fluid Cat Cracker Tail Gas	Hydrocracker Isomax Tail Gas	Steam Cracker		Hydrofiner Tail Gas
					Naphtha	Gas Oil	
					Light Ends		
H_2	--	1.5	0.6	1.4	1.2	1.3	3.0
C_1	8.5	6.0	7.9	21.8	17.4	19.6	24.0
C_2	15.4	17.5	11.5	4.4	7.0	3.5	70.0
C_2=	--	--	3.6	--	33.3	38.0	--
C_3	30.2	31.5	14.0	15.3	0.7	1.0	3.0
C_3=	--	--	16.4	--	27.0	19.7	--
C_4	45.9	43.5	21.8	57.1	13.4	16.9	--
C_4=	--	--	24.2				--
Gas yield, % wt (on feed to unit)	9.2	20.0	16.5	14.5	72.8	59.6	3.8

Source: Reference 2

3.2.1.3 Aviation Fuels--

Aviation Gasolines--Aviation gasolines consist almost entirely of hydrocarbons. In general, these fuels have a high percentage of isoparaffins and smaller percentages of naphthenes and aromatics. A typical ultimate analysis is 84 weight percent hydrogen, 15 percent carbon, and some sulfur, lead, bromine, nitrogen, and oxygen from dyes and antiknock additives. Most constituents of aviation fuel are considered potentially hazardous.[2]

Knocking in an automobile engine can be a minor problem; in aircraft engines it can be extremely serious. To prevent the problem, a small amount of tetraethyl lead is added. The lead oxide which could be formed from the tetraethyl lead would form deposits in the combustion zone of the engine and cause fouling of spark plugs and valves, so ethyl bromide is added to form volatile lead bromide. The tetraethyl lead and ethyl bromide must be in an exact 1:1 ratio because excess bromide would be corrosive to engine parts. An identifying dye and kerosene are added with the tetraethyl lead/ethylene bromide mixture. Fuels with octane ratings well above 100 are possible.[2]

Other properties of the fuel mixture must be geared to specific requirements. For instance, if the fuel is not volatile enough, it will be difficult to start a cold engine; if it is too volatile, it will vaporize in the tanks, particularly at high altitudes. A boiling range of from about 85°F to 300°F and a Reid vapor pressure of between 5.5 and 7.0 psi (vapor pressure at 100°F) is desirable. The freezing temperature must be -76°F or below. Average viscosity is 0.75 centistokes at 32°F.[2]

A large proportion of the lower paraffins and isoparaffins is desirable to minimize carbon deposits and to maximize heat energy. Antioxidants are added to retard the formation of gum and the precipitation of lead compounds during storage.

Jet Fuels--An approximate distribution of the hydrocarbons in jet fuels is given in Table F3-13. Aromatics are carefully limited, sometimes to even lower values than given, because they act as a solvent on fuel lines. Polynuclear aromatics are sometimes eliminated. Olefin and sulfur contents are limited, but not nitrogen and oxygen.

TABLE F3-13. APPROXIMATE DISTRIBUTION OF HYDROCARBONS IN JET FUELS

Paraffins:	33-61% volume percent
Olefins:	0.5-5% volume percent
Naphthenes:	10-45% volume percent
Total Aromatics:	12-25% volume percent

Source: Reference 2

Additives are added to the fuel to control oxidation, to chelate any copper that may be present from refining, to ensure that any water dissolved in the fuel will not freeze, to increase conductivity and thus reduce static electricity, and to inhibit corrosion. Most constituents of jet fuel are considered potentially hazardous.

The boiling range of jet fuel is about 300°F to 460°F; maximum viscosity is usually about 5 centistokes at -30°F.

Freezing temperature must be -76°F or below, though this limit may be raised as high as -40°F in some cases.

3.2.1.4 Automobile Gasoline--

Gasoline is defined as a petroleum fuel for use in reciprocating, spark-ignition, internal combustion engines. It is a complex mixture of hydrocarbons, mostly in the C_4 to C_{12} range, which distill between 85°F and 410°F. Gasolines from different refineries may vary widely in exact composition according to the processes used at the refinery. A summary of the main components of gasoline and their sources is given in Table F3-14.

In general, gasoline must meet the following criteria:

A. Burn smoothly without knocking,

B. Evaporate readily enough that a combustible fuel-air mixture is supplied when the engine is started cold and that a considerable portion is vaporized in the intake manifold when the engine is run warm,

C. Evaporate slowly enough that it will not boil in the fuel pump or fuel lines, and

D. Evaporate completely with no residue.

To meet these criteria, each refinery has its own blending scheme. Additives that may be added include antiknock compounds, anti-icing additives, anti-oxidants, metal deactivators, carburetor detergents, anti-corrosion additives, and others. These are discussed in Section 3.1.2.2.[1,2]

TABLE F3-14. MAIN COMPONENTS OF GASOLINE

Components	Source	Boiling Range, °F	Remarks
Paraffinic			
Butane	Crude oil distillation Conversion processes	30	Widely used in proportions up to 10%.
Isopentane	Crude oil distillation Conversion processes Isomerization of n-pentane	81	Widely used as high-octane, high-volatility component.
Alkylate	Alkylation process	100-300	Used widely in aviation gasoline, but less frequently in motor gasoline.
Isomerate	Isomerization process	100-160	Relatively little used at present. Excellent antiknock properties under severe engine conditions.
Straight-run Naphtha	Crude oil distillation	90-200	Widely used low-octane component.
Hydrocrackate	Hydrocracking process	100-390	Heavy products used as feed for catalytic reforming. Contains also aromatics.
Olefinic			
Thermal Reformate	Thermal reforming	100-390	Obsolescent process.
Catalytic Naphtha	Catalytic cracking	100-390	Widely used component, particularly in premium gasoline.
Steam Cracked Naphtha	Steam cracking	100-390	By-product of chemical processes.
Polymer	Polymerization of olefins	140-390	High-octane component but not widely used.
Aromatic			
Catalytic Reformate	Catalytic reforming	100-390	Most widely used high-octane component of gasolines.

Source: Reference 2

3.2.1.5 Diesel Fuel--

Diesel fuel for commercial use is divided into three categories according to ASTM Specifications:

- Grade 1-D: volatile fuel oils from kerosene in the intermediate distillates.
- Grade 2-D: distillate gas oils of lower volatility.
- Grade 4-D: more viscous distillates and blends of these distillates with residual fuel oils.

The exact composition of a diesel fuel varies with the refinery processes used and with product requirements. Most constituents are considered potentially hazardous.[1]

3.2.1.6 Heating Oils--

Heating oils include kerosene, distillate oils, and residual oils. The only uniform requirement appears to be that they be free of acid, grit, and fibrous or other foreign matter likely to clog or injure burner or valves. Other more specific requirements may vary.

Kerosene is a broad term for the virgin refinery product which has a boiling range of 350°F to 550°F and an API gravity of 43° to 45°. Characteristics of three grades of distillate oil are given in Table F3-15 and of two grades of residual oil in Table F3-16. Most constituents of heating oils are considered potentially hazardous.[1]

TABLE F3-15. CHARACTERISTICS OF THREE GRADES OF DISTILLATE HEATING OILS

Property	Grade 1	Grade 2	Grade 4
Gravity, °API	42.6	34.9	21.2
Viscosity at 100°F, cs	1.79	2.61	15.41
Sulfur, wt %	0.071	0.249	0.77
Ramsbottom carbon residue, wt %	0.052	0.116	3.30
Distillation, °F:			
Initial boiling point	349	370	422
10% point	390	432	496
50% point	437	499	674
Final boiling point	533	629	754

Source: Reference 1

TABLE F3-16. CHARACTERISTICS OF TWO RESIDUAL-TYPE HEATING OILS

Property	Grade 5	Grade 6
Gravity, °API	17.1	12.3
Viscosity:		
Kinematic at 100°F, cs	60.2	
Furol at 122°F, sec	25.8	170.2
Sulfur content, %	1.07	1.33
Ramsbottom carbon residue on 100% sample, %	6.7	10.7
Ash, %	0.035	0.41
Water and sediment, vol %	0.16	0.15

Source: Reference 1

3.2.1.7 Industrial Fuels--

The term "industrial fuels" as used here refers to gas oils and fuel oils. These may be straight-run, cracked, or a blend of both.[2]

Gas Oil--Gas oil is an intermediate between kerosene and light lubricating oil. It has no residual components and is low in sulfur. It is commonly used as a thinning agent for reducing the viscosity of heavy fuel oil without lowering the flash point too much. The characteristics of individual gas oils depend on the nature of the crude and its subsequent processing.

Fuel Oil--Fuel oils include heavy residual oils and such oils blended with varying amounts of gas oil to improve viscosity. Specific gravity may range from 0.92 to 1.0.[2]

Fuel oils for specific markets are blends of several components. Table F3-17 shows typical analyses of three example fuel oils. Most constitutents are considered potentially hazardous.

3.2.1.8 Solvents, Thinners and Diluents (Industrial Naphthas)--

Almost all industrial naphthas are clear, water-white liquids which are immiscible with water but completely miscible with other organic substances. They may be pure hydrocarbons such as benzene, toluene, xylene, ethylbenzene, hexane, or cyclohexane, or they may be blends of varying proportions of paraffins, cycloparaffins and aromatics. Solvents usually contain no olefins.

TABLE F3-17. TYPICAL ANALYSES OF INDUSTRIAL FUEL OILS

	Light	Medium	Heavy
Specific gravity at 15/59°C	0.922	0.948	0.977
Kinematic viscosity at 48.4°C, cSt, max	12.5	30	70
Calorific value, gross, Btu/lb	18,700	18,500	18,190
Ultimate analysis, % wt			
C	84.9	84.9	84.5
H	12.0	11.4	11.1
S	2.57	3.19	3.84
Ash	0.06	0.11	0.12
N,O, etc (by difference)	0.47	0.40	0.44
C:H ratio	7.1	7.4	7.6
Flashpoint, closed, Pensky-Martens,°C, min	66	66	66

Source: Reference 2

There are some standard solvents with properties specified by the ASTM Committee on Petroleum Products and Lubricants. Properties of three such solvents are given in Table F3-18. Most common constituents of industrial naphthas are considered potentially hazardous. Benzene in particular has been cited for its extremely toxic properties.

3.2.1.9 Lubricants--

An API survey, a few years ago, reported over 1100 lubricating oils and nearly 300 grease products made by U.S. companies. The great variety of applications makes a standard set of specifications impossible.[2]

Lubricants are of two types: automotive and industrial. Automotive lubricants include crankcase oils, transmission and axle lubricants, and fluids for hydraulic torque converters and fluid couplings such as automatic transmissions. Industrial lubricants include those required for the power plant and those for production equipment.

Viscosity is generally the single most important property of lubricants. Other important properties are API gravity, carbon residue, cloud and pour points, color, corrosive tendencies, foaming tendencies, sulfur content, saponification, and neutralization number.

Lubricating oils are obtained from the vacuum distillation of the residue from atmospheric distillation. Not all crudes produce acceptable lube oils; therefore several refining steps are usually necessary.

TABLE F3-18. PROPERTIES OF THREE INDUSTRIAL SOLVENTS FOR WHICH SPECIFICATIONS HAVE BEEN PREPARED BY ASTM COMMITTEE D-2 ON PETROLEUM PRODUCTS AND LUBRICANTS

PETROLEUM SPIRITS (MINERAL SPIRITS), D235	
Appearance:	Clear and free of suspended matter and water
Color:	Water white, not darker than No. 21 Saybolt Chromometer
Flash point, min:	100°F
Blackening:	Shall not blacken or corrode clean metallic copper in 30 min. at boiling point of spirits.
Distillation:	
% recovered at 350°F, min	50
End point	410°F
Acidity of distillation residue	Neutral
HEAVY PETROLEUM SPIRITS (HEAVY MINERAL SPIRITS), D965*	
Appearance:	Clear and free of suspended matter and water
Color:	Water white, not darker than No. 21 Saybolt Chromometer
Flash point, min:	125°F
Blackening:	Shall not blacken or corrode clean metallic copper in 30 min at boiling point of spirits

(Continued)

TABLE F3-18. Continued

Distillation:	
Initial boiling point, min	340°F
95% (by volume)	460°F
End point, max	485°F
Acidity of distillation residue:	Neutral

*Tentative.

STODDARD SOLVENT, D 484	
Color:	Water white or not darker than 21
Corrosion at 212°F	Not more than extremely slight discoloration of the copper test strip, or shows no greater corrosion than a mutually approved reference strip
Doctor test:	Negative
Sulfuric-Acid absorption, max, %	5
Flash point, min, °F:	100
Distillation:	
Percentage recovered at 350°F, min	50
Percentage recovered at 375°F, min	90
End point, max. °F	410
Residue, max, %	1.5
Acidity:	No acid reaction to methyl orange shown by residue from distillation

Source: Reference 1

The major hydrocarbons in lubricating oils are paraffinic compounds, polycyclic and fused ring hydrocarbons based on naphthenes, and mono- and polynuclear aromatics. Additives are added to improve the properties of the oil.

Lubricating greases are essentially lubricating oils with thickening agents added. The oil used usually has a high viscosity index. The major thickening agents are soaps of aluminum, barium, calcium, lithium, sodium, and strontium. Solid fillers such as asbestos, graphite, metal oxides, metal powders or flakes, or metal sulfide may be included and additives similar to those used for lubricating oils are also used.

3.2.1.10 Waxes--

Waxes are separated from crude fractions often more as a measure to improve the quality of the fraction rather than to recover the wax. The properties of the waxes vary with the fraction they are recovered from. A comparison of the major types of wax is given in Table F3-19.

Paraffin waxes are by far the most common waxes used today. They are composed almost entirely of normal alkanes with some isoalkanes, cycloalkanes and only a trace of aromatics. Refined paraffin wax has a light color and contains less than 0.5 percent oil.[1,2]

Less is known about the microcrystallic waxes. They have molecular weights of about 600-800 and appear to contain branched alkanes, aromates, polycycloparaffins, and monocyclopentyl, monocyclohexyl, and dicyclohexyl paraffins in addition to the normal alkanes.[1,2]

TABLE F3-19 COMPARISON OF MAJOR WAX TYPES PRODUCED IN THE UNITED STATES

Wax	Characteristic	No. of Carbon Atoms	Melting Point, °F	Viscosity at 210°F, SSU	Crystals
Paraffin	Brittle	18-56	122-140	40	Plates
Microcrystalline					
Motor Oil	Brittle	26-42	145-170	50	Needles
Residual	Flexible	36-70	145-175	65-100	Small needles
Tank bottom	Hard	40-70	180-200	---	Very small needles

Source: Reference 1

Petrolatum is a mixture of microcrystalline waxes and oil. It is described as a colloidal system in which the solid hydrocarbons are the external phase and the liquid components are the internal phase. Petrolatum is a semisolid at room temperature; its melting point ranges from 110 to 175°F.[1]

Petroleum waxes are considered to be nonhazardous if they are pure.

3.2.1.11 Asphalt--

Asphalt cement is the material remaining after the removal of light and heavy distillates from asphaltic crudes. It is usually mixed with distillates in varying proportions to obtain materials for specific purposes.

Cutback asphalts contain lighter distillates such as naphthas, gasoline or kerosene. They may be medium- or rapid-curing.

Emulsified asphalts are emulsions of asphalt cement with chemically treated water. Road oils contain a large proportion of oil which is either allowed to remain during distillation or is added during processing.

"Blown asphalt" may be produced by blowing air through a residual oil at temperatures usually about 400 to 600°F.[1] Asphalts of varying characteristics may be produced. Air may also be blown through asphalt to remove hydrogen as water. Partially dehydrogenated molecules are polymerized.

3.2.1.12 Petrochemicals--

A widely accepted definition of a petrochemical reads "a chemical compound or element recovered from petroleum or natural gas, or derived in whole or in part from petroleum or natural gas hydrocarbons and intended for chemical markets." There are hundreds of petrochemicals manufactured today.

Petrochemicals are grouped according to their chemical composition and structure as aliphatic, aromatic or inorganic. Most aliphatic petrochemicals are made from C_1 to C_4 hydrocarbons. Important aromatic petrochemicals are benzene, toluene, xylene, phenol and styrene. Typical inorganic petrochemicals are sulfur, ammonia and its derivatives, and carbon black.[1]

More than half of the petrochemicals are aliphatic. A list of 95 commercial petrochemicals, their important properties and the raw material they are derived from is given in Petroleum Processing Handbook edited by Wm. F. Bland and Robert L. Davidson, McGraw-Hill, New York, 1967.

3.2.1.13 Carbon Black and Petroleum Coke--

Carbon black, though a petrochemical, is often considered separately. It is the blackest pigment available to industry.

Carbon black is a finely divided semigraphitic form of carbon. It can be produced by the partial combustion of oil in a furnace. Its properties vary with particle size and the related surface area.

Coke is a by-product of the thermal cracking of reduced crudes and residuums. Its composition varies with the feedstock. Sulfur and metal content are important considerations.

To make coke more suitable for certain purposes, it is calcined. Calcination is a high-temperature treatment in which the carbon-hydrogen ratio is increased from about 20 to more than 1000. Volatile material is also driven off and the coke is dehydrogenated.[1]

3.2.2 Intermediate Products

An intermediate product is considered here to be any material which is produced by one refinery process and subsequently used in another. Most intermediate products used as feedstocks for major processes have been discussed previously in this section either as components of the raw crude or as final products. Others will be discussed here. Table F3-20 is a list of major processes and their major feedstocks.

Light ends include the light gases (methane, ethane, and propane) from the crude plus the light gases from a number of processes. Some light ends come from cracking operations; therefore, olefins and isoparaffins in the C_2 to C_4 range may also be present in a light ends stream. The light ends stream, like many other intermediate streams, may be sweet or sour, depending on whether or not sulfur compounds have been removed or made less objectionable. The olefin stream is simply the C_2 to C_4 olefins which have been separated from the other light ends.

TABLE F3-20. MAJOR PROCESSES AND THEIR MAJOR FEEDSTOCKS

Process	Major Feedstocks
Atmospheric Distillation	Crude oil
Vacuum Distillation	Topped Crude
Residual Oil Hydrodesulfurization	Residual Oil
Asphalt Blowing	Raw Asphalt
Lube Oil Processing (Dewaxing)	Hydrotreated Lube Oil
Coking	Residual Oil
Gas Oil Hydrodesulfurization	Vacuum Oil Gas Oil
Catalytic Hydrocracking	Gas Oil Kerosene Vacuum Oil
Fluid Catalytic Cracking	Deasphalted Oil Kerosene Gas Oil
Kerosene Hydrodesulfurization	Kerosene
Naphtha Hydrodesulfurization	Sour Naphtha
Catalytic Reforming	Gasoline Sweet Naphtha Sweet Light Ends
Isomerization	Sweet Naphtha n-butane
Gas Processing	Sweet Light Ends
Alkylation	Isobutane Olefin Gases
Sulfur Recovery	Sour Light Ends

3.3 REFERENCES FOR SECTION 3

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SECTION 4

REFINERY PROCESS TECHNOLOGY

Section 4 contains a characterization of various major refining processes or operations. All of the processes which have been utilized in the development of a "hypothetical refinery" (discussed in Section 2 of this appendix) are discussed in this section. In addition, several other common processes not included in the hypothetical refinery are also described here.

The discussion of each of the processes described in this section includes the following types of information:

- A description of each process,
- A description of process technology, and
- A discussion with appropriate estimates for atmospheric emissions from each type of process.

A process description is provided for each unit discussed in Section 4. Included is information on the function of the process, a description of significant differences between processes of the same general type (e.g., sulfuric versus hydrofluoric acid alkylation), and a discussion on how the process is integrated into the overall refining scheme.

A detailed description of the operation of each process is contained in the subsection titled "process technology". Here, specific details concerning process operations, major processing variables, feed and catalyst characteristics, recent process innovations, etc., are described.

A subsection on atmospheric emissions has been provided for most of the processes discussed in Section 4. Emissions sources can include process emissions such as those from fired heaters and catalyst regeneration operations, and fugitive emissions from various process equipment.

Three types of information necessary to estimate total atmospheric emissions from refinery process units have been studied over the course of this program:

- Fugitive hydrocarbon emission factors for each type of source have been determined as a function of the type of process fluid handled by the source.
- An estimate of the number of fugitive sources within each type of process unit was obtained, based on field source counts.
- The distribution of these sources between the process fluid groups used in the calculation of emission factors was investigated.

The development of emission factors for fugitive sources is a major result of this program and the methods used to establish these emission factors are well documented in numerous places in this report. Conversely, the estimates for the number and process fluid distribution of fugitive sources in specific process units are not as reliable.

Where possible, two estimates of the number of fugitive sources are provided for each type of process unit. The first estimates represent actual field source counts, or estimates based on these counts, which were developed as a part of this program. The second set of estimates were developed in a published EPA report, The Development of Petroleum Refinery Plot Plans (Reference 8).

The estimates developed during this program were based on field source counting in 19 process units. This is an insufficient amount of data to establish accurate average source counts for individual process units. However, it was determined that the number of sources within similar process units can vary considerably from one refinery to the next. Further, these variations in the number of sources do not correlate with the capacity of the counted process units. The methods used to estimate the number of fugitive sources and the distribution of these sources between the four process fluid groups are described in detail in Section 4.1.1.3.

The source count estimates provided in Reference 8 were based on counts developed from process flow diagrams. In particular, the numbers of pumps, compressors, and control valves were counted from flow diagrams or estimated, based on results from process units containing similar vessel types. From these counts, ratios were used to estimate the number of block valves, flanges, and screwed fittings. Relief valve and sample valve estimates were obtained by other means. Details of the methods used to estimate the sources counts presented in Reference 8 are also included in Section 4.1.1.3.

Both sets of estimates described above have been used, where possible, to allow the calculation of a range of emissions from each of the process units. It is evident that, in a number of cases, the two sets of estimates are quite different. This is probably a result of real differences between the number of sources in actual process units as well as differences resulting from the methods used to obtain these estimates. It is important that both sets of source counts be considered, at best, rough estimates. Estimates for total fugitive emissions from actual process units should be based on the number and distribution of sources actually present in that particular process unit.

4.1 SEPARATION PROCESSES

Crude oil separation describes those processes which separate crude oil into a variety of intermediate products. These products become feedstock for additional downstream refinery processing units. Distillation streams are typically classified according to boiling range, as shown in Table F4-1.

Higher efficiencies and lower costs are achieved if crude oil separation is accomplished in two steps: 1) fractionating the total crude stream at atmospheric pressure; then 2) feeding the high boiling bottoms fraction (topped crude) from the atmospheric still to a second fractionator operating under a high vacuum. Sections 4.1.1 and 4.1.2 describe process operation and process emissions for atmospheric and vacuum distillation units.

TABLE F4-1. TYPICAL BOILING RANGES FOR CRUDE OIL FRACTIONS

Fraction	Boiling Range, °F
Butanes and lighter gases	80
Light straight run gasoline (LSR)	80-220
Naphtha (heavy straight run gasoline)	180-400
Kerosene	330-540
Light gas oil	420-640
Atmospheric gas oil	550-830
Vacuum gas oil	750-1050
Vacuum reduced crude	1000

The aromatic hydrocarbon content of reformate streams is quite high. Aromatics extraction units are used to separate and concentrate these aromatic compounds for use in gasoline blending or petrochemical operations. Aromatics extraction is discussed in Section 4.1.3.

4.1.1 Atmospheric Distillation

Nearly all incoming crude oil feed must pass through a refinery's atmospheric distillation unit before it can be further processed. The purpose of atmospheric distillation is to separate the crude's hydrocarbon components into fractions by means of distillation and steam stripping.

Because it performs a function basic to refining, almost all refineries will have at least one atmospheric distillation unit. United States atmospheric distillation capacity was 17.2×10^6 bbl/day in 1978. Approximately 14.8×10^6 bbl/day of crude was processed in 1978.

4.1.1.1 Process Description--

The atmospheric distillation process is outlined in Figure F4-1. After desalting, the crude oil is pumped through a series of heat exchangers in which its temperature is elevated by heat recovered from product and reflux streams. The preheated crude is then charged to a direct-fired furnace where additional heat is supplied to achieve partial vaporization of the crude petroleum. Both the liquid and vaporized portions are charged to the atmospheric fractionator at a temperature of about 650-700°F. At temperatures above this range, thermal decomposition ("cracking") of the crude may occur. The carbon produced by cracking fouls equipment and has a deleterious effect on properties of some distillation products. In addition, some of the more valuable liquid products are cracked at high temperatures to form less valuable gases.

The crude charge is separated into several petroleum fractions within the atmospheric fractionator. A stream of naphtha and lighter material is condensed and taken from the tower overhead. This stream is essentially light straight run (LSR) gasoline containing some propane, butanes, and almost all the pentane-and-heavier components in the tower overhead vapor. Some of the condensate is returned to the top of the tower as reflux, and the remainder is sent to other refinery processes or product storage.

Several liquid side stream fractions are withdrawn from the fractionator at different elevations within the tower. These streams are charged to the side stream product strippers, where lighter hydrocarbons are stripped and returned to the fractionation tower. The stripping medium is typically steam, light petroleum gases, or reboiler vapors. In addition to the

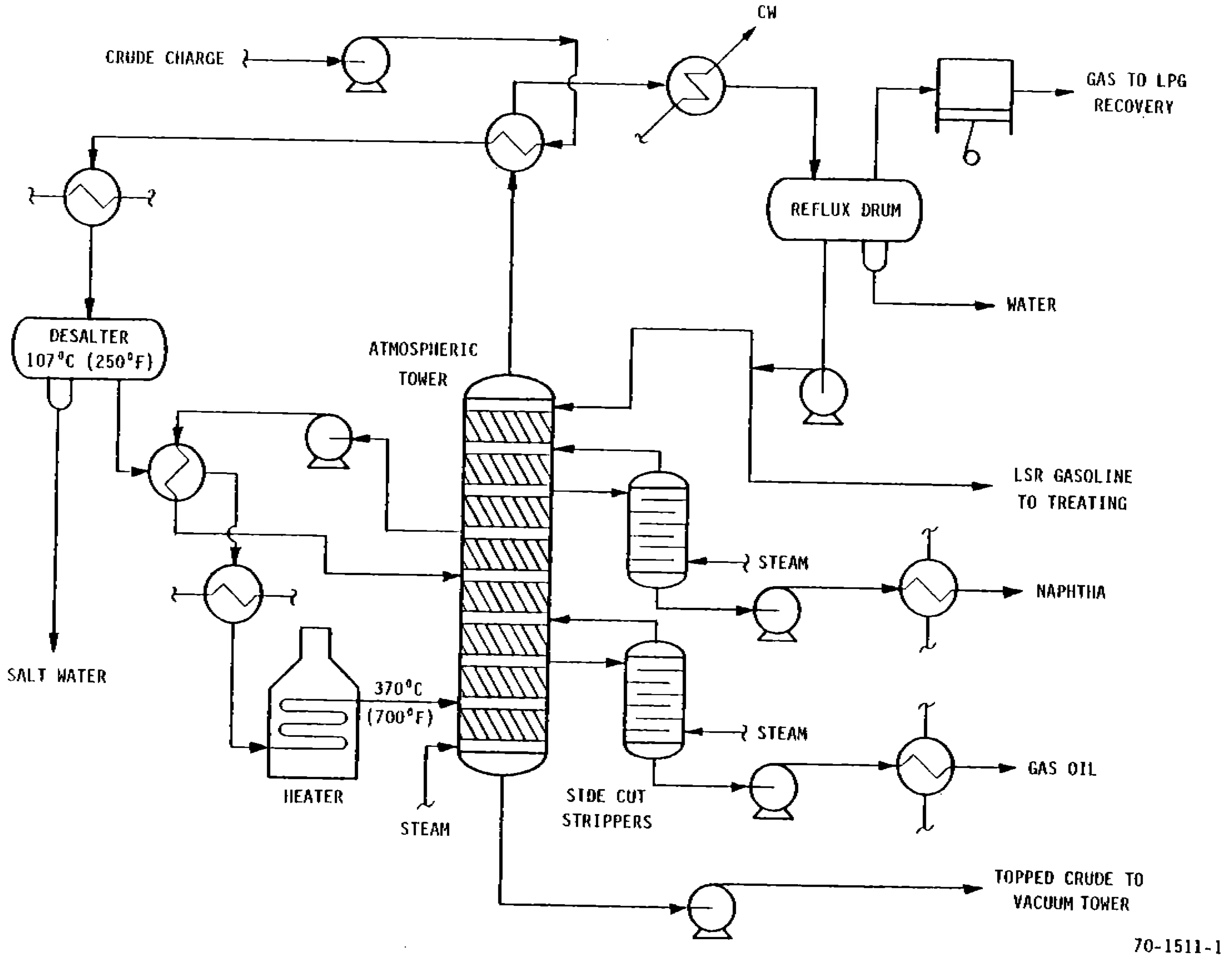

Figure F4-1. Atmospheric distillation.

side stream strippers, the atmospheric fractionator has a bottoms stripping zone in which lighter hydrocarbons are stripped from the residual product.

The stripping medium and stripped hydrocarbons are vented back to the vapor zone of the fractionator at a point above the corresponding side-stream withdrawal point.

The fractions withdrawn from the atmospheric fractionator are progressively heavier as they are removed at successively lower points. The vaporization end point of the heaviest sidestream product closely corresponds to the crude's temperature when charged to the fractionator.

Fractionator bottoms (topped crude) is the heaviest petroleum fraction in the crude. Because this fraction cannot be further separated at atmospheric pressure, it is charged to the vacuum distillation unit.

Relative product amounts from crude atmospheric distillation vary with the type of crude being processed. Variances in product amount range from 10 to 50 percent.

In general, the intermediate products from atmospheric distillation include liquid petroleum gases (LPG), light straight run gasoline (LSR), naphtha, kerosene, distillate or diesel oil, gas oil, and topped crude. The naphtha may be blended into motor fuels or any of several other refinery products, or further processed to improve octane rating and/or reduce sulfur content. The kerosene may be chemically sweetened or hydrogen treated and sold directly or blended with other petroleum products. The distillate or diesel oil may be sold directly as diesel fuel or fuel oil. It may also be hydrogen treated, hydrocracked, catalytically cracked, or blended with other refinery products. Gas oil is not usually used directly, but may be processed similarly to distillate oil. Although the topped crude fraction is usually the feed for the vacuum distillation process, it may also be sold for fuel, blended into fuels, hydrogen treated, catalytically cracked, or sent to a coking unit.

4.1.1.2 Process Technology--

Process Conditions, Fuel, and Utility Requirements--Typical operating parameters for an atmospheric distillation unit with a capacity of 24,000 bbl/day are listed below:

- Pressure: Atmospheric
- Temperature: 250°F - at top of fractionator
  700°F - at bottom of fractionator
- Electricity: 4.1 kW/bbl
- Thermal Energy: 10^5 Btu/bbl
- Steam: 50 lb/bbl
- Process Water: 50 gal/bbl

Process Equipment--The major pieces of process equipment used in atmospheric distillation include heat exchangers, a direct fired furnace, an atmospheric fractionation column, and side stream product strippers. A brief description of each of these items follows.

Heat exchangers are employed for a number of uses: feedstock preheating and vaporization, condensation of overhead vapor, and cooling liquid products before discharge to further processing or storage. The most common type of heat exchanger used in refineries is the shell-and-tube type, which permits high heat transfer rates by allowing high fluid velocities and countercurrent flow between tube side and shell side fluids. Commonly used shell-and-tube exchangers include fixed tube sheet, floating head, and hairpin-type tube units.

Heat exchangers may be air or water cooled. Initial capital costs and space requirements for air-cooled units are usually higher than those for water-cooled units. However, operating costs for water-cooled units are often higher because of higher costs for cooling water, wastewater disposal, and tube maintenance.

A direct-fired furnace ("pipestill") is used to heat the crude charge so that it is partially vaporized when it enters the fractionation tower. A typical furnace consists of an array of tubes arranged in a refractory lined shell that may be cylindrically- or box-shaped. Burners located in the heater shell wall provide heat, which is transferred by both radiation and convection to the crude oil inside the tubes.

The type of heater used depends on the heat load as well as the thermal efficiency and pressure drop of the fluid to be heated. The high heat loads required in crude distillation units necessitate the use of box furnaces, which are usually designed for heat absorption rates greater than 150 x 10^6 Btu/hr.

The atmospheric fractionator is a vertical cylindrical column in which vapor is bubbled through the liquid retained on a vertical array of horizontal trays. The fractionation tower normally contains 30 to 50 fractionation trays. Five to eight trays are needed for each sidestream product, and the same number is required above and below the feed point.

Several different types of trays are used in atmospheric distillation towers: bubble cap trays, perforated trays, grid trays, and valve trays. Valve and perforated trays are most widely used in atmospheric distillation units. Bubble cap trays are highly flexible and efficient but have a high initial cost. Perforated trays are lower in cost, but are also lower in efficiency at low vapor loadings. Grid trays, while economical, are relatively inflexible in handling varying loads. Valve trays are considerably less expensive than bubble cap trays, and are also capable of operating at high efficiencies over a wide range of loadings.

Any number of sidestream stripping towers may be employed in an atmospheric distillation unit, depending on the number of distillation cuts being taken. Each stripping tower contains four to ten trays. Steam is introduced under the bottom tray.

4.1.1.3 Atmospheric Emissions--

Emissions sources from atmospheric distillation operations include:

- Process heater flue gas emissions, and
- Fugitive emissions.

<u>Process Heater Emissions</u>--Emission factors for various pollutants from fired heaters are given in Table F4-2. A typical atmospheric distillation unit will require a process heater to raise the temperature of the crude oil prior to its entry into the fractionator. Additional process heat is required to reboil the fractionator bottoms.

Total emissions from an atmospheric distillation unit process heater are also given in Table F4-2. These figures are given as pounds of pollutant per thousand barrels of feed using a typical heat input requirement of 1.0×10^5 Btu per barrel of feed.

<u>Fugitive Emissions</u>--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical crude distillation unit are given in Table F4-3. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and

TABLE F4-2. TYPICAL EMISSIONS FROM ATMOSPHERIC DISTILLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of crude oil feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.4
- Residual oil		
Grade 4	7	5.0
Grade 5	10	7.1
Grade 6	10(S)+3	7.1(S)+2.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	101(S)
- Residual oil	157(S)	112(S)
Sulfur Trioxide[c]	2(S)	1.4(S)
Carbon Monoxide[d]	5	3.6
Hydrocarbons (as CH_4)[d]	1	0.71
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	16
- Residual oil[e]	$22+400(N)^2$	$16+286(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.48-1.43
Sulfur Oxides (as SO_2)[f]	0.6	0.057
Carbon Monoxide	17	1.6
Hydrocarbons (as CH_4)	3	0.29
Nitrogen Oxides (as NO_2)	120-230	11.4-21.9

[a] Source: Reference 9

[b] Based on a heat input of $1.0x10^5$ Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the fuel oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE F4-3. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL CRUDE DISTILLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d,e]		
Valves	Gas/Vapor	89	263 - 270	0.059	5.25 - 15.9
	Light Liquid (VP > 0.1 psia @ 100°F)	281	1663 - 1727	0.024	6.74 - 41.4
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	523	704 - 703	0.0005	0.262 - 0.352
	Hydrogen Service	0	0	0.018	0.0
	Total	893[a]	2630 - 2700[c]		12.3 - 57.7
Open-End (Sample) Valves	All	-	56 - 57[b]	0.005	0.280 - 0.285
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	11(15)	26(36)-27(38)	0.25	3.75 - 9.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	20(28)	11(15)-11(15)	0.046	0.690 - 1.29
	Total	31(43)[a]	37(52)-38(53)[b]		4.44 - 10.8
Drains	All	69[a]	-	0.070	4.83
Flanges & Fittings	All	3997[a]	8695 - 8930[c]	0.00056	2.24 - 5.00
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	1(2)	0	1.4	0.0 - 2.80
	Hydrogen	0	0	0.11	0.0
	Total	1(2)[a]	0		0.0 - 2.80
					25.2 - 82.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 8

[e] This PES estimate includes vacuum distillation as part of the crude distillation unit. Radian estimates for emissions from vacuum distillation are listed in Section 4.1.2.3 and may be added to the Radian estimates for atmospheric distillation for comparison to the PES estimates.

- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[8]

The methods used to develop estimates for the number and process fluid distribution of each source type from data taken during this program are discussed below. These methods have been used throughout this appendix wherever estimates of process unit source counts are provided. The source count data on which these estimates are based is provided in Section 2.7 of Appendix B (Detailed results).

Pumps - The number of pumps within a given process unit was determined from field data collected during this program. For process units which were not physically counted, the number of pumps was estimated, based on a comparison to similar process units or information from available process flowsheets.

The distribution of these pumps between light and heavy streams was based on field data taken during this program or estimated, based on results in similar process units.

The number of seals (on which total emissions were based) was assumed to average 1.4 seals per pump. This value was obtained from the Los Angeles Joint Study[10] and is indicated in parenthesis behind the actual number of pumps in Table F4-3.

Valves - From an analysis of field data, the number of valves in a process unit was determined to average 41 valves per pump. The Los Angeles Joint Study[10] concluded that 23.6 percent of all valves were in gas/vapor service. Thus, 31 of the 41 valves per pump were assumed to be in liquid service. The distribution of these valves between light and heavy liquid service was the same as that for the pumps.

The remaining valve distribution for hydrocarbon vapor service, hydrogen service and light and heavy liquid service was determined as follows:

1) Valves in liquid service = 31 x (number of pumps in the process unit).

2) Valves in gas service = Total counted valves -valves in liquid service (Step 1). It was assumed that at least 10 percent of the valves in a process unit are in gas stream service. The number of valves calculated in this step can amount to less than 10 percent of the total valves. If so, the number of gas valves is set at 10 percent of the total number of valves.

3) Valves in hydrogen service = 30 percent of the total number of valves in gas service for units which utilize significant quantities of hydrogen (reforming, HDS, hydrocracking).

4) Valve liquid distribution = Ratio of pump liquid stream service as determined from this study.

Flanges - The number of flanges and other fittings was determined to average 3.6 flanges per valve. This factor was used to estimate the flange counts in Table F4-3.

Compressors - The number of compressors was estimated in a manner identical to that given for pumps. The hydrocarbon-hydrogen categories are intended to distinguish between light hydrocarbon service compressors and compressors in predominantly hydrogen service. The number of seals (on which total emissions were based) was determined to average two seals per compressor. This value is given in parenthesis behind the actual compressor count in Table F4-3.

Relief valves - From actual field counts, the number of relief valves was determined to average six atmospherically vented relief valves per process unit. This factor was used to determine atmospheric emissions.

Drains - The number of drains per pump was determined to average 2.6 in all counted process units. This factor was used to estimate the drain counts in Table F4-3.

The source counts given in Table F4-3 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process types, and processing flexibility. Hence, the number of sources shown in Table F4-3 is not necessarily representative of all or even the majority of atmospheric distillation units.

In addition to the source counts and estimates developed by Radian, a second column of source counts is also given in Table F4-3. These counts were based on information contained in Reference 8, The Development of Petroleum Refinery Plot Plans. In this study, process flow diagrams were used to determine the number of pumps and compressors within the unit. The distribution of pumps between the light and heavy liquid service categories was based on pump service information obtained from the process flow sheets. The number of valves and fittings was based on the number of pumps. For purposes of data comparison, the valve counts listed in Reference 8 have been distributed between the various service categories. This was accomplished using the procedures described above for distributing the Radian valve totals. In this case, however, the light and heavy liquid service split was based on the pump distribution given in Reference 8.

The final column in Table F4-3 shows the estimated fugitive emissions from each source category as well as an estimate of emissions from the entire unit. Many of these estimates are listed as a range, based on the two sets of source counts described above.

It must be emphasized that all of the source counts and stream service distributions given in Appendix B are, at best, rough estimates. Even those values based on actual source count data should be considered rough estimates since only a small number of process units were counted. In addition, source counts for similar types of process units showed large variations. Therefore, reliable estimates for emissions source counts and distributions should be obtained for the particular process unit in question rather than using the estimates which are designed to characterize typical refinery operation.

The estimated composition of fugitive non-methane hydrocarbon emissions from an atmospheric distillation unit is given in Table F4-4. These estimates indicate the types of

TABLE F4-4. ESTIMATED COMPOSITION OF NON-METHANE HYDROCARBON FUGITIVE EMISSIONS FROM A CRUDE DISTILLATION UNIT

	Stream				
	Crude Oil	Straight run naphtha	Middle distillate	Atmospheric gas oil	Totals
Estimated percentage of emissions attributed to each stream - %	74	24	1	1	100%
Weighted contribution of each component to unit emissions - ppmw					
Benzene	46	59	0	0	105
Toluene	522	617	0	0	1139
Ethylbenzene	169	208	0	0	377
Xylenes	676	382	1	0	1059
Other Alkylbenzenes	2871	3904	8	1	6784
Naphthalene	660	344	1	0	1005
Anthracene	108	1	1	0	110
Biphenyl	246	147	0	0	393
Other Polynuclear aromatics	6051	3528	56	2	9637
n-Hexane	13820	9167	0	0	22987
Other Alkanes	673680	117660	8627	9724	809691
Olefins	0	0	0	0	0
Cyclo Alkanes	44770	99503	1024	512	145809
					999096

hydrocarbons contributed by sources on a number of process streams found within this unit. Additional information about these estimates may be found in Appendix D.

4.1.2 Vacuum Distillation

Vacuum distillation is employed to fractionate topped crude from the atmospheric distillation unit into a heavy residual oil and one or more heavy gas oil streams. The temperatures necessary to distill the heavier crude fractions at atmospheric pressure are so high that thermal cracking would occur. These fractions are therefore distilled under vacuum to prevent equipment fouling and product loss resulting from cracking.

A vacuum distillation unit is an integral part of most refineries. Charge capacity of U.S. vacuum distillation units was more than 6.5 x 10^6 barrels per stream day in 1978.

4.1.2.1 Process Description--

A schematic diagram of a single-stage vacuum distillation unit is shown in Figure F4-2. Lubricant production sometimes necessitates adding a second stage to the primary vacuum fractionator.

Distillation is carried out with absolute pressures in the tower flash zone of 0.4-0.7 psi. In most units, the vacuum inside the fractionator is maintained with steam ejectors, although mechanical vacuum pumps may also be used. This system is also designed to remove noncondensible hydrocarbon vapors produced as the charge is heated.

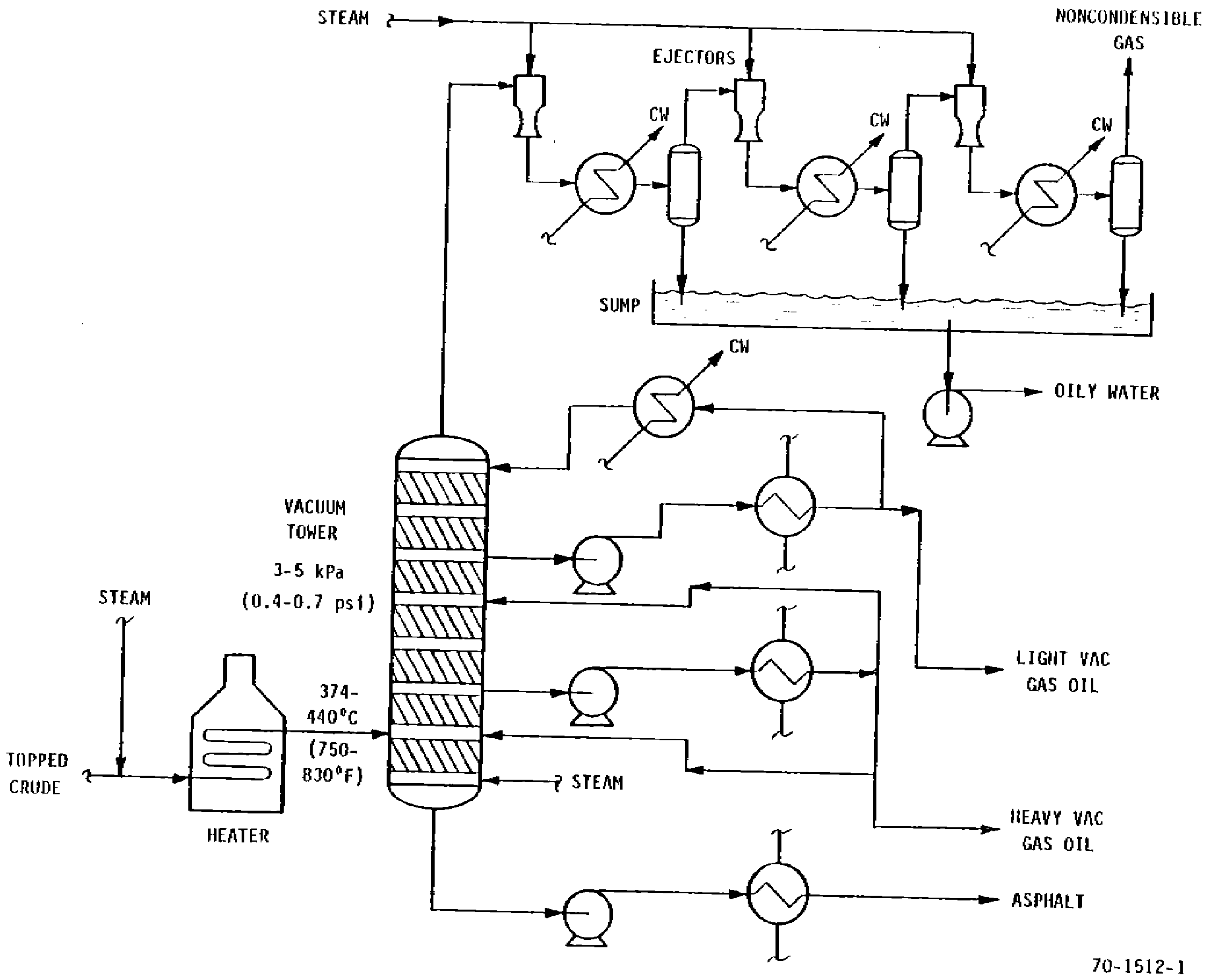

Figure F4-2. Vacuum distillation.

Topped crude is heated in a direct-fired furnace and charged to the vacuum fractionator. Vacuum distillation plus steam stripping may be used to produce narrow boiling range lube oil stocks for further processing. The injection of superheated steam at the base of the column further reduces the partial pressure of hydrocarbons in the fractionator to approximately 0.2 psi. Steam stripping is not required in the fractionation of vacuum distillates for catalytic cracking or visbreaking feedstocks.

Distillation products are pumped from the fractionation tower at various points on the tower, with lighter components distilling higher in the fractionator. Product specifications depend on the crude feed and refinery design. Typical vacuum distillation products include noncondensible refinery gas, asphalt, and light and heavy vacuum gas oils. These gas oils may be sent to a coker to be thermally cracked into gasoline feedstocks, or sent to a visbreaker to be cracked into distillate fuel. Another alternative is hydrotreating, where sulfur can be removed to upgrade the gas oils.

4.1.2.2 Process Technology

Process Conditions, Fuel, and Utility Requirements--Typical operating parameters for a vacuum distillation unit are listed below:

- Temperature: 750-830°F
- Pressure: 0.4-0.7 psi
- Thermal energy: 74,900 Btu/bbl

- Electricity: 0.10-0.20 kW/bbl
- Steam: 8 lb/bbl

Process Equipment--The major pieces of process equipment in vacuum distillation units include heat exchangers, a direct fired furnace, a vacuum fractionator, and a vacuum producing system (usually steam ejectors). The vacuum fractionator and steam ejectors are described briefly below.

Trays similar to those used in atmospheric fractionators may also be used in vacuum fractionators. Tray efficiency in vacuum columns tends to be much lower than that in atmospheric columns, primarily because of the increased vapor loads and the minimal liquid holding time on each tray. (Holding time must be kept low to maintain low pressure drops across the trays.) Tray efficiency may be increased by increasing the diameter of the fractionation tower to a maximum of 40-45 feet.

Packed vacuum fractionation columns with diameters of 3-6 feet are replacing older, larger columns. These units contain grid packing instead of trays, and operate with the liquid phase trickling over the packing, countercurrent to the vapor phase. A number of proprietary packing designs are in current use.

Steam ejectors and barometric or surface condensers are used in many vacuum distillation units to maintain operating pressure. The size and number of ejectors and condensers used is determined by the vacuum needed and the vapor load. To maintain a fractionator pressure of no more than 0.4 psia, three ejector stages are usually required. The first stage condenses the steam and compresses the fractionated noncondensible gases.

The second and third stages remove the noncondensible gases from the condensers.

The trend in vacuum distillation unit design is toward the use of surface condensers rather than barometric condensers. Surface condensers, although more costly than barometric condensers, are much more effective in reducing hydrocarbon emissions from the steam ejectors.

4.1.2.3 Atmospheric Emissions--

Emission sources from vacuum distillation units include:

- Emissions from steam ejectors and barometric condensers,
- Process heater flue gas emissions, and
- Fugitive emissions.

Vacuum System Emissions--Process hydrocarbon emissions from steam vacuum ejectors have been estimated at 50 $lb/10^3$ bbl charge. Using barometric condensers rather than surface condensers may result in process emissions of as much as 1060 $lb/10^3$ bbl charge. Noncondensible hydrocarbon vapors removed by the ejector system are released to the atmosphere unless combusted in a furnace firebox or other type of combustion device.

Process Heater Emissions--Emission factors for various pollutants from fired heaters are given in Table F4-5. A typical vacuum distillation unit will require process heaters to raise the temperature of the topped crude to between 750-830°F.

TABLE F4-5. TYPICAL EMISSIONS FROM VACUUM DISTILLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.1
- Residual oil		
Grade 4	7	3.8
Grade 5	10	5.4
Grade 6	10(S)+3	5.4(S)+1.6
Sulfur Dioxide[c]		
- Distillate oil	142(S)	76.1(S)
- Residual oil	157(S)	84.1(S)
Sulfur Trioxide[c]	2(S)	1.1(S)
Carbon Monoxide[d]	5	2.7
Hydrocarbons (as CH_4)[d]	1	0.54
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	12
- Residual oil[e]	$22+400(N)^2$	$12+214(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.36-1.07
Sulfur Oxides (as SO_2)[f]	0.6	0.043
Carbon Monoxide	17	1.2
Hydrocarbons (as CH_4)	3	0.21
Nitrogen Oxides (as NO_2)	120-230	9.6-16.4

[a] Source: Reference 9

[b] Based on a heat input of 7.5×10^4 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the fuel oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

Total emissions from vacuum unit heaters are also given in Table F4-5. These figures are given as pounds of pollutant per thousand barrels of feed using a typical heat input of 7.5 x 10^4 Btu per barrel of feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical vacuum distillation unit are given in Table F4-6. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[8]

The methods used to develop estimates for the number of each source type are discussed in Section 4.1.1.3 of this appendix.

TABLE F4-6. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL VACUUM DISTILLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit: Counts or Estimates From Radian Study	Number of Sources in Process Unit: Counts or Estimates From PES Study[c]	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	50	71	0.059	2.95 - 4.19
	Light Liquid (VP > 0.1 psia @ 100°F)	45	142	0.024	1.08 - 3.41
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	405	497	0.0005	0.203- 0.249
	Hydrogen Service	0	0	0.018	0.0
	Total	500[b]	710[b]		4.23 - 7.85
Open-End (Sample) Valves	All	-	14[a]	0.005	0.070
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(2)	2(3)	0.25	0.50 - 0.75
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	14(20)	7(10)	0.046	0.46 - 0.92
	Total	16(22)[b]	9(13)[a]		0.96 - 1.67
Drains	All	42[b]	-	0.070	2.94
Flanges & Fittings	All	1785[b]	2350[b]	0.00056	1.00 - 1.32
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	0	1.4	0.0
	Hydrogen	0	0	0.11	0.0
	Total	0	0		0.0
					10.3 - 15.0

[a] Counted From Flow Diagrams

[b] Estimated

[c] Reference 8

The source counts given in Table F4-6 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Hence, the number of sources shown in Table F4-6 are not necessarily representative of all or even the majority of vacuum distillation units.

4.1.3 Aromatics Extraction

The products of aromatic extraction--principally benzene, toluene, and the xylenes (BTX)--are used in the petrochemical industry as intermediates in the production of plastics, synthetic fibers, detergents, insecticides, synthetic rubber, etc. Toluene is increasingly in demand as an ingredient in the blending of gasoline to increase the octane rating of unleaded gasoline. The extraction process is also used to produce aromatic-free solvents for special applications.

Before the 1950s, the principal source of aromatic hydrocarbons was coal tar. Now, virtually all aromatics are extracted from two sources: the reformate produced by the catalytic reforming of naphtha, and pyrolysis gasoline, produced by the steam cracking of naphtha. Reformate has been for many years the principal route to BTX in the U.S. Pyrolysis gasoline is still important in Japan and, to a lesser extent, in western Europe.

4.1.3.1 Process Description--

Aromatics extraction is a liquid/liquid solvent extraction process. The several proprietary processes are broadly similar; the main difference between them is in the solvent that is used.

Fresh feed, preheated to approximately 210°F, enters the extraction column countercurrent to the lean solvent. Some processes use rotating disks as contact stages; most use a series of trays. Aromatics are selectively dissolved, and an almost aromatic-free raffinate stream is withdrawn from the top of the extractor. The raffinate is then cooled, and washed with water to remove solvent.

The rich solvent leaves the bottom of the extractor and is charged to a steam stripper. Some processes use a single extractive stripping process to distill the extract into benzene, toluene, and xylenes and to recover the solvent, but others accomplish this in two stages. The stripper overhead is condensed into a stream containing some remaining aromatics and saturated hydrocarbons. This stream is returned to the bottom of the extractor column as reflux. The lean solvent is recycled.

Tetraethylene glycol, mixtures of several glycols, dimethyl-sulfoxide, formal-morpholine, and tetrahydrothiphene-dioxide are some of the solvents used.

There are a number of proprietary commercial extraction processes. The Sulfolane and Udex processes account for the majority of commercial installations for aromatics extraction: each is in use in more than 50 refineries throughout the world. The Tetra process is installed in more than 35 refineries.

Sulfolane, originally developed by Royal Dutch/Shell, is licensed by the UOP Process Division of UOP, Inc., as is Udex. The Tetra licensor is Union Carbide Corporation. Most of the remaining commercial installations are processes licensed by Howe-Baker Engineers (Aromex), Snamprogetti S.p.A. (Formex), and the Institut Francais du Petrole (IFP).

4.1.3.2 Process Technology--

The aromatic content of a typical reformate is (vol. %) benzene 5; toluene 24; ethylbenzene 4; para-, meta-, and ortho-xylene 18; and C_9 and C_{10} aromatics 4. The aromatic content of typical pyrolysis gasoline is (weight %) benzene 32; toluene 14; C_8 aromatics 11; and C_9+ aromatics 13. On the average, 100 percent of the benzene, 99 percent of the toluene, and 95-98 percent of the xylenes are recovered in the extraction process.

Fuel and utility requirements for the three most widely used processes--Sulfolane, Udex, and Tetra--are given below.

Utility per Bbl Feed	Udex Process	Sulfolane Process	Tetra Process
Steam, lb	400	2.5	125
Fuel, 10^3 Btu	-	190	-
Cooling Water, gal	1200	530	650
Electric Power, kWh	1.3	0.8	0.3

Operating parameters for the two most widely used processes, Sulfolane and Udex, are given below.

Operating Condition	Udex Process	Sulfolane Process
Stripping steam ratio, wt/wt	0.6	0.13
Stripper bottom temperature, °F	290	375
Extractor top temperature, °F	290	212
Extractor pressure, psig	110	15
Feed temperature, °F	240	240

Process Equipment--The main equipment components of the process are the extractor column, which contains trays or rotating disks to mix the feed and the solvent; one or more steam stripping columns, which contain trays beneath which steam is introduced to contact steam and rich solvent; and a conventional fractional distillation unit where the extract is separated into benzene, toluene, and xylenes.

Depending on the particular proprietary process, a water still and a vacuum solvent regenerator may also be required.

4.1.3.3 Atmospheric Emissions--

Since aromatics extraction is a closed process, the only significant emissions are fugitive hydrocarbon emissions.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low.

However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical aromatics extraction unit are given in Table F4-7. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[8]

The methods used to develop estimates for the number of each source type are discussed in Section 4.1.1.3 of this appendix.

The source counts given in Table F4-7 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Hence, the number of sources shown in

TABLE F4-7. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL AROMATIC EXTRACTION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[c]		
Valves	Gas/Vapor	60	206	0.059	3.54 - 12.2
	Light Liquid (VP > 0.1 psia @ 100°F)	486	1370	0.024	11.7 - 32.9
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	54	483	0.0005	0.027 - 0.242
	Hydrogen Service	0	0	0.018	0.0
	Total	600[b]	2059[b]		15.3 - 45.3
Open-End (Sample) Valves	All	-	29[a]	0.005	0.145
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	16(23)	17(24)	0.25	5.75 - 6.00
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	2(3)	6(8)	0.046	0.138 - 0.368
	Total	18(25)[b]	23(32)[a]		5.89 - 6.37
Drains	All		-	0.070	3.29
Flanges & Fittings	All	2142[b]	6815[b]	0.00056	1.20 - 3.82
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	0	1.4	0.0
	Hydrogen	0	0	0.11	0.0
	Total	0	0		0.0
					27.0 - 59.6

[a] Counted From Flow Diagrams

[b] Estimated

[c] Reference 8

Table F4-7 are not necessarily representative of all or even the majority of aromatics extraction units.

The estimated composition of fugitive non-methane hydrocarbon emissions from an aromatics extraction unit is given in Table F4-8. These estimates indicate the types of hydrocarbons contributed by sources on a number of process streams found within this unit. Additional information about these estimates may be found in Section 2.4 of Appendix D.

4.1.4 References for Section 4.1

1. Refining Process Handbook. Hydrocarbon Processing, 57(9), 1978.
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3. Good Vaccum Unit Design Pays Off. Oil and Gas Journal, 76 (12): 72-79, March 13, 1978.
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5. Gary, J. H., and G. E. Handwerk. Petroleum Refining: Technology and Economics. Manual Dekker, Inc., New York, 1975. pp. 31-46.
6. Dickerman, J. C., et al. Industrial Process Profiles for Environmental Use: Chapter 3. Petroleum Refining Industry. EPA-600/2-77-023c. U.S. Environmental Protection Agency, Washington, D.C., January 1977.
7. Wetherold, R. G. The Distribution of Selected Fugitive Hydrocarbon Emission Sources Among Petroleum Refinery Process Streams. EPA Contract No. 68-0202665. U.S. Environmental Protection Agency, Research Triangle Park, N.C, 1979, unpublished.
8. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards. Development of Petroleum Refinery Plot Plans. EPA-450/3-78-025. Research Triangle Park, North Carolina, 1978.

TABLE F4-8. ESTIMATED COMPOSITION OF FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM AN AROMATICS EXTRACTION UNIT

	Stream				
	Reformate	Solvent	Aromatic Extract	Raffinate	Totals
Estimated percentage of emissions attributed to each stream - %	12	0	44	44	100%
Weighted contribution of each component to unit emissions - ppmw					
Benzene	648	0	7850	22	8520
Toluene	9324	0	112948	330	122602
Ethylbenzene	4020	0	48695	132	52847
Xylenes	20508	0	248420	660	269588
Other Alkylbenzenes	38928	0	21120	1012	61060
Naphthalene	858	0	44	22	954
Anthracene	0	0	0	0	0
Biphenyl	0	0	0	0	0
Other Polynuclear aromatics	84	0	44	22	150
n-Hexane	2880	0	44	27720	30644
Other Alkanes	42720	0	836	410080	453637
Olefins	0	0	0	0	0
Cyclo Alkanes	0	0	0	0	0
					1000000

9. Environmental Protection Agency. Compilation of Air Pollutant Emission Factors. Third Edition, Supplement No. 8. AP-42. Research Triangle Park, NC, May 1978.

10. Air Pollution Control District, County of Los Angeles; State of California, Department of Public Health; U.S. Department of Health, Education and Welfare; Western Oil and Gas Association. Emissions to the Atmosphere from Eight Miscellaneous Sources in Oil Refineries. June 1958.

11. Deal, G. H., Jr., et al., A Better Way to Extract Aromatics. Petroleum Refiner, September 1959, p. 195.

4.2 THERMAL OPERATIONS

Thermal operations are noncatalytic processes used to convert large hydrocarbon molecules into smaller molecules at high temperatures. These processes convert low value stocks such as heavy gas oil into lighter, more valuable products.

Cracking is the phenomenon by which large oil molecules are thermally decomposed into smaller, lower boiling molecules. At the same time, certain of these smaller molecules may combine with one another to give even larger molecules than those in the original stock. The more stable materials leave the system as cracked gasoline or light hydrocarbon gases, and the more reactive materials polymerize to form cracked fuel oil or coke. In addition, materials having boiling ranges between fuel oil and gasoline are also produced.[7]

The thermal processes currently in operation in U.S. refineries include:

- Delayed coking
- Fluid coking
- Visbreaking
- Thermal cracking

Delayed coking is a semicontinuous process in which the heated charge (heavy gas oil or residuum) is transferred to large coking drums. The coking drums provide sufficient residence time for the cracking reactions to proceed to completion. During the reaction, coke is produced and deposited within the coke drum.

This coke is then recovered and sold as a by-product; its value is dependent on the quality of the feedstock.[1]

Delayed coking is likely to remain an important refining process since it simultaneously converts low value materials to lighter, more valuable materials while producing coke as a valuable by-product. More detailed information on this process is contained in Section 4.2.1.

Fluid coking is a continuous process which converts heavy feedstocks such as residuum and pitch into lighter, more valuable products. The heated feed is sprayed into a fluidized bed of hot coke particles causing additional coke to form. The cracked oil vapors leave the reactor and are fractionated into a heavy recycle stream, various gas oil streams, and gasoline. The coke particles are sent to a burner where they are heated by burning a portion of the coke with a limited amount of air. The hot coke particles are then recirculated back to the reactor where they furnish much of the heat required for the cracking reactions. Since there is a net production of coke in the unit, coke is removed from the burner as a by-product.[1]

Unlike delayed coke, fluid coke is often unsuitable for many end uses, and is consequently less valuable than delayed coke. Additional information on fluid coking is presented in Section 4.2.2.

Visbreaking is a relatively mild cracking operation used to reduce the viscosity of straight-run residues such as pitch. These heavy residues are often blended with lighter heating oils to produce fuel oils of acceptable viscosity. This procedure, however, uses a high value product, light heating oil, to produce a lower value product, fuel oil. By reducing the viscosity of the pitch fraction, visbreaking reduces the amount of required light heating oil.[1]

The visbreaking reactions occur within specially designed tubes in a fired heater. The heated product is then fractionated into low quality gasoline, light and heavy gas oil, and a residual tar of reduced viscosity. Visbreaking is discussed in further detail in Section 4.2.3.

Various thermal cracking operations have been used in petroleum refining since 1910. However, thermal cracking of high boiling materials is no longer a major source of motor gasoline since its octane rating is low.

A few thermal cracking units are still in operation. These processes utilize temperatures of 850-1000°F and pressures ranging from 100-1000 psig. Products include light hydrocarbon gases, cracked gasoline, light heating oil, and thermal tar. Thermal tar can be used as coker feedstock or it can be blended into fuel oil.

The current (1979) utilization by U.S. refiners of the processes described above is supplied below.[3]

Process	Number of Units	Total Capacity, bbl/sd
Delayed coking	48	997,900
Fluid coking	4	77,000
Visbreaking	13	160,500
Thermal cracking (gas oil or reduced crude feed)	15	150,600

4.2.1 Delayed Coking

The delayed coking process was developed as a method to reduce the yield of residual fuel oil by severe thermal cracking of feeds such as atmospheric or vacuum residuals, and thermal tars. In addition, delayed cokers are capable of processing other materials including full range crude oils, shale oil, bitumin, gilsonite, and coal tar pitch.

Products from delayed coking consist of light gases, gasoline, diesel, light and heavy gas oil, and coke. Gas oils, which constitute the largest portion of the liquid products, are typically utilized as catalytic cracking feedstock for the production of high octane gasoline. Technological improvements in downstream processing now permit the economical upgrading of other coker products. For example, coker gasoline can be catalytically reformed to high octane gasoline after suitable hydrotreating for the removal of metals, nitrogen, or sulfur contaminants.

Solid petroleum coke is produced as a product in delayed coking operations. The main uses of petroleum coke include:[2]

- Manufacture of electrodes for the electric furnace production of elemental phosphorus, titanium dioxide, steel, calcium carbide, and silicon carbide.
- Manufacture of anodes for electrolytic cell reduction of alumina.

- Direct use as carbon source for production of phosphorus, calcium carbide, and silicon carbide.

- Manufacture of graphite.

- Direct use as fuel.

The quality of the coke produced in delayed coking depends in part on the operating conditions and the quality of the feed. Desirable qualities in petroleum coke include low porosity, a low coefficient of thermal expansion, good electrical conductivity, and low ash, metals, and sulfur content.

The most common form of coke is produced as hard, irregular-shaped lumps called sponge coke. Sponge coke is generally produced when using low quality feeds such as vacuum residuals with high asphaltene content. During the coking process, the asphaltenes, which exist as colloidal suspensions, form a highly cross-linked amorphous coke with a high concentration of impurities. These impurities, which include sulfur, nickel, and vanadium, make sponge coke unsuitable for high grade anodes.[6]

Some highly aromatic materials, such as catalytic cracker cycle oil and thermal cracking tars, are used to produce high quality "needle" coke. Needle coke derives its name from its microscopic elongated crystalline structure. This structure is a result of condensation and polymerization of large aromatic molecules. Since needle coke is produced from previously cracked oils which contain less sulfur than residues, the sulfur content of needle coke is generally lower than that of sponge coke. An additional reason for lower needle coke sulfur content could be the differences in sulfur distribution between the aromatic and asphaltene molecules. That is, sulfur is not readily released from the interior of asphaltene molecules which form sponge coke. Needle coke is preferred over sponge coke for electrode manufacture because of its lower electrical resistivity and its lower coefficient of thermal expansion.[5,6]

4.2.1.1 Process Description

A simplified flow diagram for the delayed coking process is given in Figure F4-3. The process flow is quite simple and has remained relatively unchanged since the process was developed. Fresh feed is fed directly to the bottom of the main fractionator where materials lighter than the desired end point of the heavy gas oil product are flashed off. The remaining material combines with the recycle and is pumped to the coking heater where the temperature of the oil is quickly raised to around 950°F. The liquid-vapor mixture leaving the coking heater passes to a coke drum where the coking reactions occur. The coke drum is actually just a wide spot in the line where sufficient residence time is provided for the reactions to go to completion.

Most coking units use two drums (or two sets of drums). After the first drum becomes filled with coke, the flow of hot oil is diverted to the second drum. Thus, a semicontinuous processing scheme is established by alternating the coking and decoking operations for each drum. The coke drums are often sized so that each one operates on a 48-hour cycle, permitting the decoking operation to be scheduled at the same time each day on a 24-hour cycle.

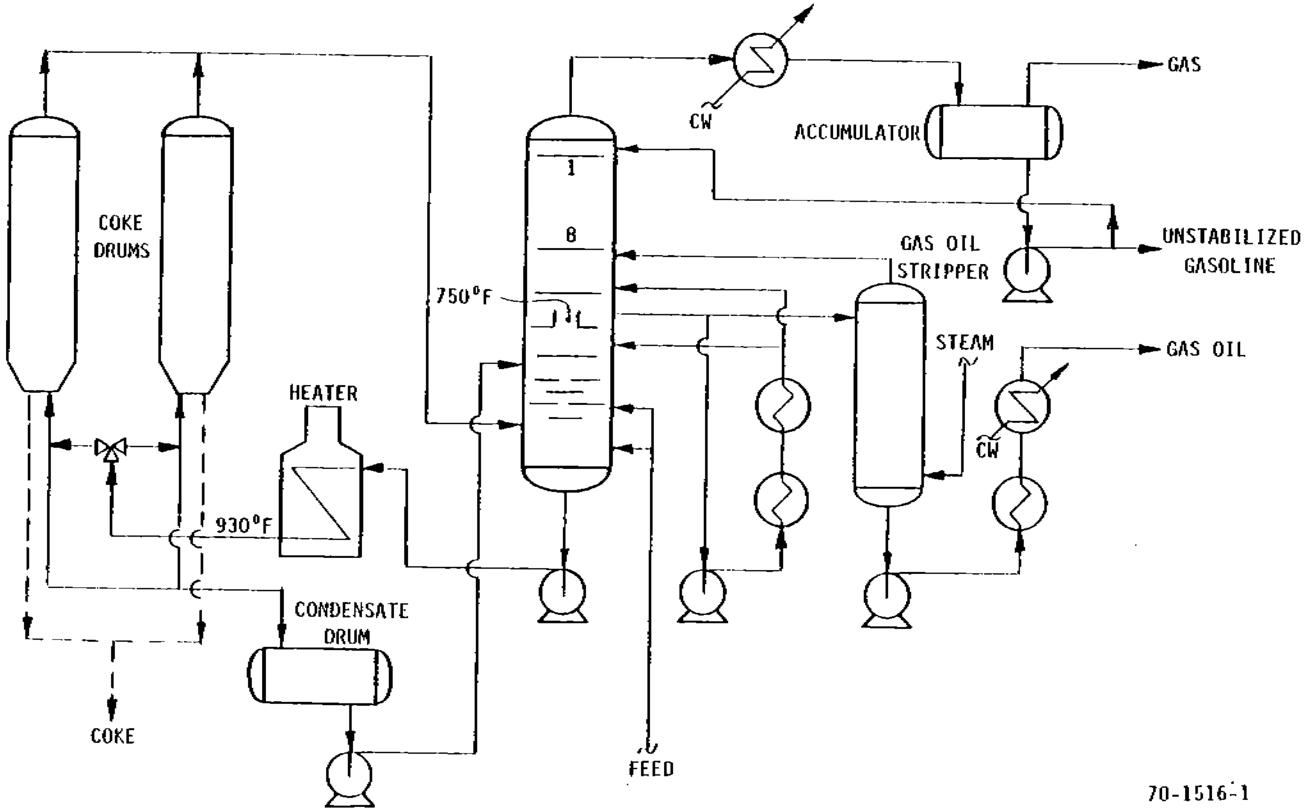

Figure F4-3. Process flow diagram - delayed coking.

Source: Reference 5

Hot vapor from the coke drum returns to the fractionator for product separation. The heaviest portion combines with fresh feed in the fractionator and is recycled back to the heater.

The design of the fractionator above the gas oil tray is similar to that employed for crude towers. Below that point, however, special designs are required. As mentioned previously, fresh feed is introduced near the bottom of the tower, perhaps 2 to 4 trays above the bottom vapor space. This accomplishes the following:[2]

- Hot vapors from the coke drum are quenched preventing significant coke formation within the fractionator.
- A portion of the hot coke drum vapors are condensed for recycle.
- Any material lighter than the desired coke drum feed is stripped from the fresh feed.
- The fresh feed liquid is further preheated.

The design of the coker heater is also important to the economical operation of the unit. Since the mixture is heated to temperatures above the coking temperature, steps must be taken to suppress coke buildup in the heater tubes. Generally, coke formation is suppressed by passing the oil through the heater at high velocity. As the oil nears the coking temperature, an increasing quantity of the feed is vaporized, serving to increase the velocity and turbulence even further.

If insufficient velocity is obtained by vaporization of the oil, steam or water can be injected. With sufficient precautions, coker heaters can operate for periods of well over a year before decoking of the heater tubes is required.[5,2]

Decoking the coke drums consists of numerous individual operations. After switching drums, steam is introduced to the bed for removal of volatile combustion matter (VCM). Then, water is injected at a controlled rate to cool the coke. After the excess water is drained, the coke drum is opened and the coke removed.

The first step in the decoking operation is to drill a pilot hole through the bed. This pilot hole is then enlarged to permit lumps of coke to fall through the bed without the danger of coke buildup around the drill stem. The coke is then cut away from the drum using either a mechanical drill or, more commonly, a hydraulic system. The hydraulic system consists of a number of high pressure (2000 to 3000 psig) water jets which are lowered into the bed on a rotating stem. The coke is then cut from the drum, a layer at a time, starting from either the top or the bottom.[5]

Several methods of collecting the coke are available. In many cases, the coker is mounted over a railroad track so that the coke can be discharged directly into railroad cars. The coke is retained in the cars while water and coke fines drain off and flow to a sump. Alternatively, the coke can be directed to a concrete apron or pit. The water and coke fines drain off, and the coke is moved using a scoop or bridge crane. In either system, water collected in the sump is usually sent to a clarifier for fines removal. Clarified water is then sent to a storage tank for reuse.

After all coke has been removed, the drum is closed, pressure tested, and reheated at a controlled rate. The entire decoking operation is completed in 24 hours using a schedule similar to that given below.[2,5]

Operation	Time, hours
Fill drum with coke	24.0
Switch drums	0.5
Steam Out	3.0
Cooling	3.0
Drain	2.0
Unhead and Decoke	5.0
Head up test	2.0
Warm-up	7.0
Spare time	1.5
Total	48.0

4.2.1.2 Process Technology--

Processing Variables--Important process variables for delayed coking include the heater outlet temperature, the fractionator pressure, the vapor temperature at the heavy gas oil draw-off tray, and the Conradson "free" carbon content of the feed. At higher heater outlet temperatures, the rate of the cracking and coking reactions increases. This increases the yield of gas, naphtha, and coke at the expense of a lower gas oil yield. Typical heater outlet temperatures range from 900-975°F.[5]

Increasing the fractionator pressure has much the same effect as an increase in temperature. Higher pressure in the fractionator serves to condense more recycle within the fractionator for return to the heater and coke drums. Thus, less gas oil is produced relative to the amount of gas, naphtha, and coke. Typical pressures used in delayed coking range from 20-60 psig. However, when high quality aromatic feedstocks are used, the pressure can be increased to around 100 psig in the coke drum to promote the formation and yield of valuable needle coke.

The temperature of the vapor at the gas oil draw-off tray determines the end point of the gas oil product. If this temperature is raised, less gas oil is available for recycle. Thus, the yield of gas oil is increased at the expense of gas, naphtha, and coke. Often, the gas oil end point temperature is dictated by the allowable metals content.

The Conradson carbon residue (CCR) is a laboratory measurement of the coke forming potential of a particular stock. And, a number of correlations are available which relate CCR to the expected commercial coke yield.[5]

The recycle ratio is often given as an operating variable in coking operations. Actually, the recycle ratio is a function of the fractionator pressure and the gas oil draw-off tray vapor temperature. High recycle ratios are used when processing for maximum gas oil. Typical recycle ratios range from 0.1-1.0.[2]

The following is a summary of operating conditions for delayed coking:[1,2,4,5]

Heater Outlet Temperature, °F	900-975
Coke Drum Pressure, psig	20-100
Recycle Ratio	0.1-1.0

4.2.1.3 Process Emissions--

Emission sources from delayed coking operations include:

- Emissions during decoking operations,
- Process heater flue gas, and
- Fugitive emissions.

Emissions During Decoking Operations--At the end of each coking cycle, coke is removed from the coke drum. This procedure has been described in a previous section (4.2.1.1). Part of the cooling operation involves injecting steam into the coke drum. The procedure serves to remove the majority of the hydrocarbons remaining in the drum. The steam is then condensed and the remaining vapors are usually flared.

Following the cool-down procedure, the drum is opened and the coke is removed. This operation is a source of particulate emissions to the atmosphere. In addition, hydrocarbon vapors entrained in the coke may be released during the cutting operation. A water quench is often used to minimize particulate emissions. Since this water will contain some sulfur compounds, it may be a source of objectionable odors. Emission factors for the decoking operation are unavailable.

Process Heater Emissions--Emission factors for various pollutants from fired heaters are given in Table F4-9. A typical delayed coking unit will require process heaters to raise the temperature of the coke drum feed to the desired coking temperature.

Total emissions from the delayed coking heaters are also given in Table F4-9. These figures are given as pounds of pollutant per thousand barrels of feed using a typical heat input of 2.4 x 10^5 Btu per barrel of feed.[14]

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical delayed cooking unit are given in Table F4-10. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

TABLE F4-9. TYPICAL EMISSIONS FROM DELAYED COKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of coker feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	3.4
- Residual oil		
Grade 4	7	12
Grade 5	10	17
Grade 6	10(S) + 3	17(S) + 5.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	243(S)
- Residual oil	157(S)	269(S)
Sulfur Trioxide[c]	2(S)	3.4(S)
Carbon Monoxide[d]	5	8.6
Hydrocarbons (as CH_4)[d]	1	1.7
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	38
- Residual oil[e]	$22+400(N)^2$	$38+686(N)^2$
Gas Fired Heaters		
Particulates	5-15	1.1-3.4
Sulfur Oxides (as SO_2)[f]	0.6	0.14
Carbon Monoxide	17	3.9
Hydrocarbons (as CH_4)	3	0.69
Nitrogen Oxides (as NO_2)	120-230	27-53

[a] Source: Reference 15

[b] Based on a heat input of 2.4×10^5 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the fuel oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% (N<.5) nitrogen content. For oil with higher nitrogen content (N>0.5), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE F4-10. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL DELAYED COKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit: Counts or Estimates From Radian Study	Number of Sources in Process Unit: Counts or Estimates From PES Study[c]	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	30	178	0.059	1.77 - 10.5
	Light Liquid (VP > 0.1 psia @ 100°F)	57	1308	0.024	1.37 - 31.4
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	213	291	0.0005	0.107 - 0.146
	Hydrogen Service	0	0	0.018	0.0
	Total	300[b]	1777[b]		3.25 - 42.0
Open-End (Sample) Valves	All	-	43[a]	0.005	0.215
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(3)	18(25)	0.25	0.750 - 6.25
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	7(10)	4(6)	0.046	0.460 - 0.276
	Total	9(13)[b]	22(31)[a]		1.21 - 6.53
Drains	All	23[b]	-	0.070	1.61
Flanges & Fittings	All	1071[b]	5875[b]	0.00056	0.60 - 3.29
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	3(6)	1.4	0.0 - 8.4
	Hydrogen	0	0(0)	0.11	0.0
	Total	0	3(6)		0.0 - 8.4
					8.03 - 63.5

[a] Counted From Flow Diagrams

[b] Estimated

[c] Reference 14

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[14]

The methods used to develop estimates for the number of each source type are discussed in Section 4.1.1.3 of this appendix.

The source counts given in Table F4-10 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Hence, the number of sources shown in Table F4-10 are not necessarily representative of all or even the majority of fluid coking units.

The estimated composition of fugitive non-methane hydrocarbon emissions from a delayed coking unit is given in Table F4-11. These estimates indicate the types of hydrocarbons contributed by sources on a number of streams within the process unit. Additional information about these estimates may be found in Section 2.4 of Appendix D.

TABLE F4-11. ESTIMATED COMPOSITION OF FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A DELAYED COKING UNIT

	Stream					
	Vacuum Resid	Coke	Cracked Naphtha	LPG Olefins	Fuel Gas	Totals
Estimated percentage of emissions attributed to each stream - %	0	0	57	14	29	100%
Weighted contribution of each component to unit emissions - ppmw						
Benzene	0	0	1642	0	0	1642
Toluene	0	0	51175	0	0	51175
Ethylbenzene	0	0	12215	0	0	12215
Xylenes	0	0	97727	0	0	97727
Other Alkylbenzenes	0	0	138778	0	0	138778
Naphthalene	0	0	6242	0	0	6242
Anthracene	0	0	0	0	0	0
Biphenyl	0	0	0	0	0	0
Other Polynuclear aromatics	0	0	3694	0	0	3694
n-Hexane	0	0	6743	0	0	6743
Other Alkanes	0	0	116340	56000	266800	439140
Olefins	0	0	97322	84000	17400	198722
Cyclo Alkanes	0	0	38122	0	0	38122
Hydrogen	0	0	0	0	5800	5800
						1000000

4.2.2 Fluid Coking

Fluid coking, like delayed coking, was developed as a method of reducing the overall yield of residuals, tars, and resins produced during certain refining operations. These materials are converted to lighter, more valuable liquid products and coke.

4.2.2.1 Process Description--

The yield of liquid products from fluid coking is similar to that of delayed coking. Coke production, however, is significantly lower in fluid coking. Factors leading to decreased coke production include:

- Higher yields of heavy gas oil, and
- A substantial portion of the coke is consumed within the unit to provide process heat.

The coke produced by the fluid coking process is usually of insufficient quality for most industrial uses. Consequently, most of this coke is sold as fuel or used within the refinery to produce steam.[1,10] The fact that many delayed coking units are now being operated to produce valuable premium cokes may account for the limited use of fluid coking process. In fact, the number of fluid coking units in operation has actually decreased from 10 units in 1970 to just 4 units in 1979.[3]

A relatively recent advancement in coking processes is Flexicoking, developed by the Exxon Research and Engineering

Company. Flexicoking integrates conventional fluid coking with coke gasification to produce a coke gas containing significant quantities of carbon monoxide, hydrogen, carbon dioxide, water vapor, and nitrogen. The coke gas may be substituted for refinery fuel gas or natural gas to fire process heaters or boilers.[9] The net coke production from Flexicoking is reported to be in the range of 1-2 wt. percent of the feed as compared to 10-20 percent for conventional fluid coking. Up to 99 percent of the metals are concentrated in the coke by-product. At this time no commercial Flexicokers have been installed in the United States.[9] Extensive commercial experience has been accrued abroad, however, mainly in Japan.

4.2.2.2 Process Technology--

As indicated in the simplified process flow diagram given in Figure F4-4, fluid coker units contain two major process vessels: a fluidized bed reactor and a coke burner. Coke particles are continuously circulated between these two vessels to provide process heat. The oil or pitch feed is injected directly into the bed of hot coke particles. Part of the feed is vaporized while the remainder is distributed on the surface of the coke where the cracking reactions occur. The cracked products vaporize leaving a thin layer of new coke on the particles. Steam, injected into the bottom of the bed, keeps the bed fluidized and promotes mixing. This steam also serves to strip any remaining hydrocarbons from the coke particles as they leave the reactor bed.

The vapor products are passed through cyclones and charged to the bottom of a scrubber. The scrubber serves to condense the heaviest components which are recycled to the reactor. The vapors leaving the scrubber are sent to a fractionator for product separation.

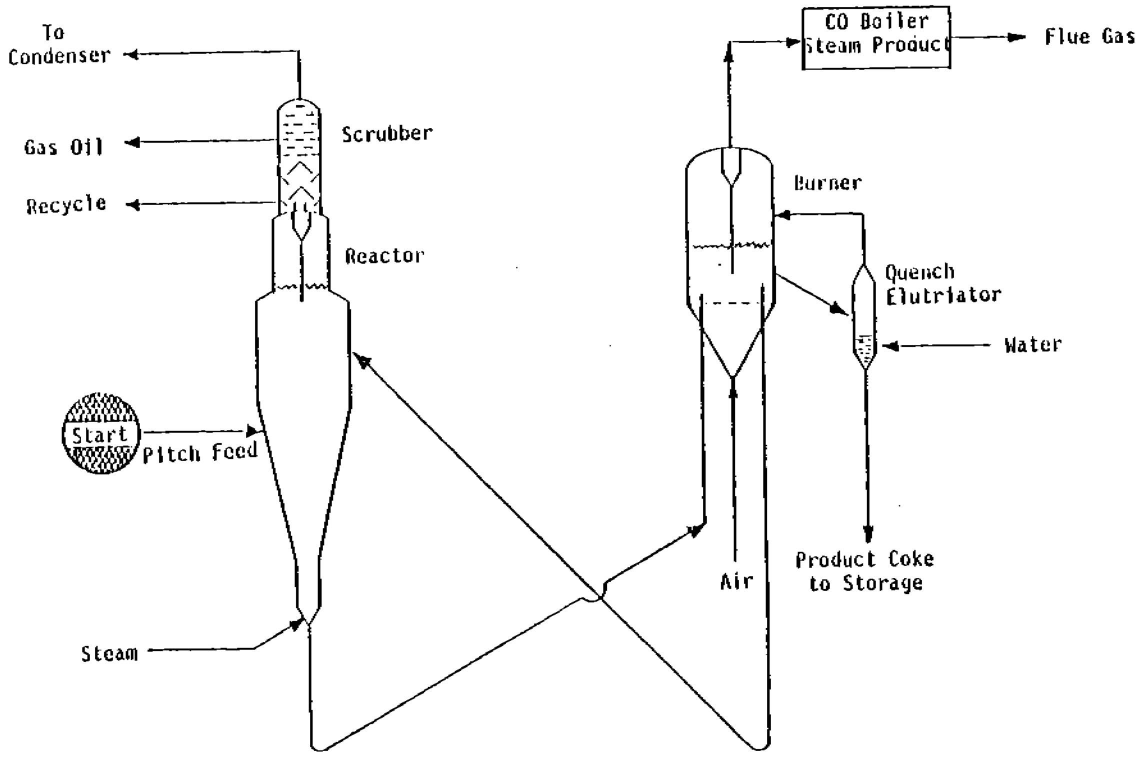

Figure F4-4. Process flow diagram - fluid coking.

Source: Reference 14

The steam-stripped coke particles leaving the reactor proceed to the burner vessel. Within the burner, approximately 25 percent of the coke formed in the reactor is consumed.[8] The heat produced by combustion heats the remaining coke particles which are then returned to the reactor. No preheat furnace for the feed is required since the circulating hot coke particles provide the heat necessary for the coking reactions.

Since more coke is produced in the reactor than is consumed in the burner, a stream of coke is withdrawn from the burner. The coke is water-cooled in a quench elutriator and sent to storage.

The flue gas from the burner bed normally contains significant quantities of carbon monoxide and has a heating value of around 43 Btu/scf.[11] Hence, this stream is usually discharged through cyclones to a waste heat recovery device such as a CO boiler or process heater.

A simplified flow diagram for the Flexicoking process is given in Figure F4-5. This process is a combination of conventional fluid coking and coke gasification. The Flexicoking process utilizes three process vessels; a reactor, a coke burner, and a coke gasifier. The operation of the reactor and burner vessels is nearly identical to that of conventional fluid coking. However, most of the coke produced within the unit is sent from the burner to the gasifier. The gasification is similar to fluid bed coal gasification practiced commercially since the 1920's in the Winkler process. Basically, steam and air are reacted with the coke at elevated temperatures to produce a coke gas with a heating value of 100-130 Btu/scf.[9]

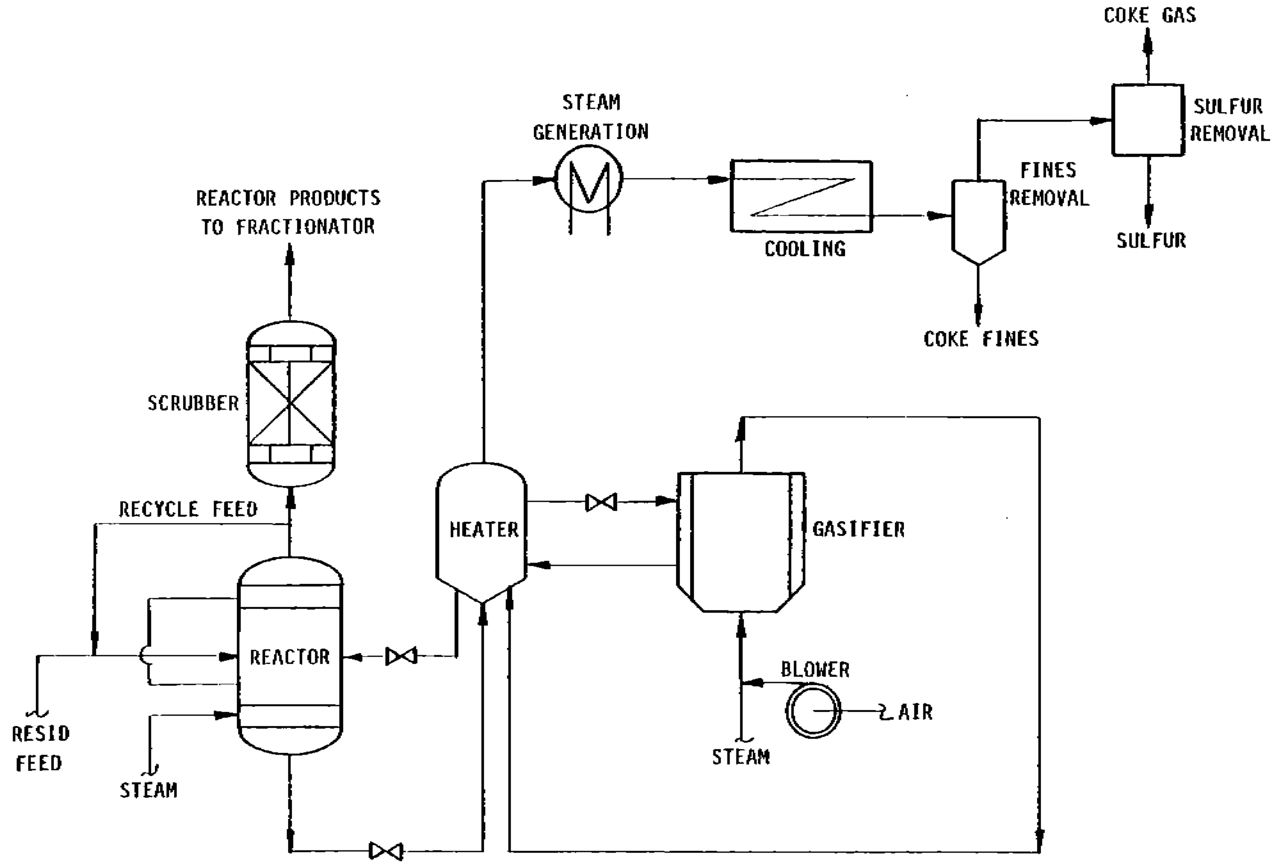

Figure F4-5. Process flow diagram - Flexicoking.

Source: Reference 12

The coke gas is returned to the burner vessel where it is cooled to provide a portion of the heat carried back to the reactor. The combined coke gas and burner flue gas stream leaves the burner vessel where it is cooled and desulfurized.[9]

Approximately 95 percent of the total coke produced is either consumed in the burner or converted to coke gas in the gasifier. The remaining 5 percent (≈1-2 wt. percent of the fresh feed) is removed from the burner. This coke has been substantially desulfurized but contains up to 99 percent of the metals present in the feed.[9]

Fluid coking and Flexicoking operating conditions are summarized in Table F4-12.

TABLE F4-12. PROCESS CONDITIONS FOR FLUID COKING AND FLEXICOKING

	Fluid Coking	Flexicoking
Temperature, °F		
Reactor	950	950
Burner	1150	1150
Gasifier	-	1300-1800
Pressure, psig		
Reactor	10	10
Burner	11	11
Gasifier	-	25-45
Utilities - per barrel feed		
Electric Power, kWh	5.5	13
Fuel, MM Btu	0	0

Source: References 1, 4, 8 and 9

4.2.2.3 Process Emissions--

Emission sources for the fluid coking process include:

- The burner vessel flue gas
- Fugitive emissions.

Operating fluid cokers do not require the use of a process heater since heat is obtained from burning coke produced by the unit.

Burner Vessel Emissions--

Approximately 25 percent of the coke formed within the fluid coker reactor is consumed within the burner vessel. And, the heat generated by combustion heats the remaining coke particles which are then returned to the reactor. The combustion process produces a flue gas containing substantial quantities of carbon monoxide with lesser amounts of SO_x, NO_x, organics, and particulates.

CO emission rates have been estimated at 30 pounds per barrel of feed.[13] And, venting of this gas would represent a substantial loss of energy. At present, all four domestic fluid coking units utilize either a CO boiler or a fired heater to recover this energy.

Use of a CO boiler will reduce the concentration of CO and other combustible materials to low levels. There may also be a reduction in particulate emissions. However, high combustion temperatures may cause an increase in NO_x emissions and both SO_x and NO_x will increase if auxiliary fuel is required.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical fluid coking unit are given in Table F4-13. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[14]

The methods used to develop estimates for the number of each source type are discussed in Section 4.1.1.3 of this appendix.

The source counts given in Table F4-13 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

TABLE F4-13. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL FLUID COKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	30	0.059	1.77
	Light Liquid (VP > 0.1 psia @ 100°F)	58	0.024	1.39
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	216	0.0005	0.108
	Hydrogen Service	0	0.018	0.0
	Total	304[a]		3.27
Open-End (Sample) Valves	All	-	0.005	-
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(3)	0.25	0.75
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	7(10)	0.046	0.46
	Total	9(13)[a]		1.21
Drains	All	28[a]	0.070	1.96
Flanges & Fittings	All	1047[a]	0.00056	0.586
Relief Valves	All	6[b]	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	4(8)	1.4	11.2
	Hydrogen	0(0)	0.11	0.0
	Total	4(8)[a]		11.2
				19.4

[a] Physically Counted

[b] Estimated

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Hence, the number of sources shown in Table F4-13 are not necessarily representative of all or even the majority of fluid coking units.

4.2.3 Visbreaking

Viscosity breaking or visbreaking is a mild thermal cracking operation used to reduce the viscosity of materials such as atmospheric or vacuum residuals and pitch. This procedure reduces the amount of valuable light heating oil which must be blended with the residuum to produce a fuel oil of acceptable viscosity. Currently, 13 visbreaking units are in operation with a total capacity of 160,500 bbl/day.[3]

4.2.3.1 Process Description and Technology--

A flow diagram for the visbreaking process is given in Figure F4-6. The reduced crude charge is heated in a fired heater where mild liquid phase cracking occurs. The heater effluent is quenched and then flashed in a combination tower. The flashed vapors can be fractionated into gas, low quality gasoline, light and heavy gas oil, and a visbreaker tar of reduced viscosity. Alternatively, the gas oil fraction can be included with the bottoms product which can further reduce the amount of lighter cutter stock required to meet viscosity specifications.[4]

Visbreaking processes utilize temperatures at the heater outlet of 850-950°F. And, the pressure at this point is in the range of 50-300 psig. These conditions are obtained within specially designed heating coils. The heating coils

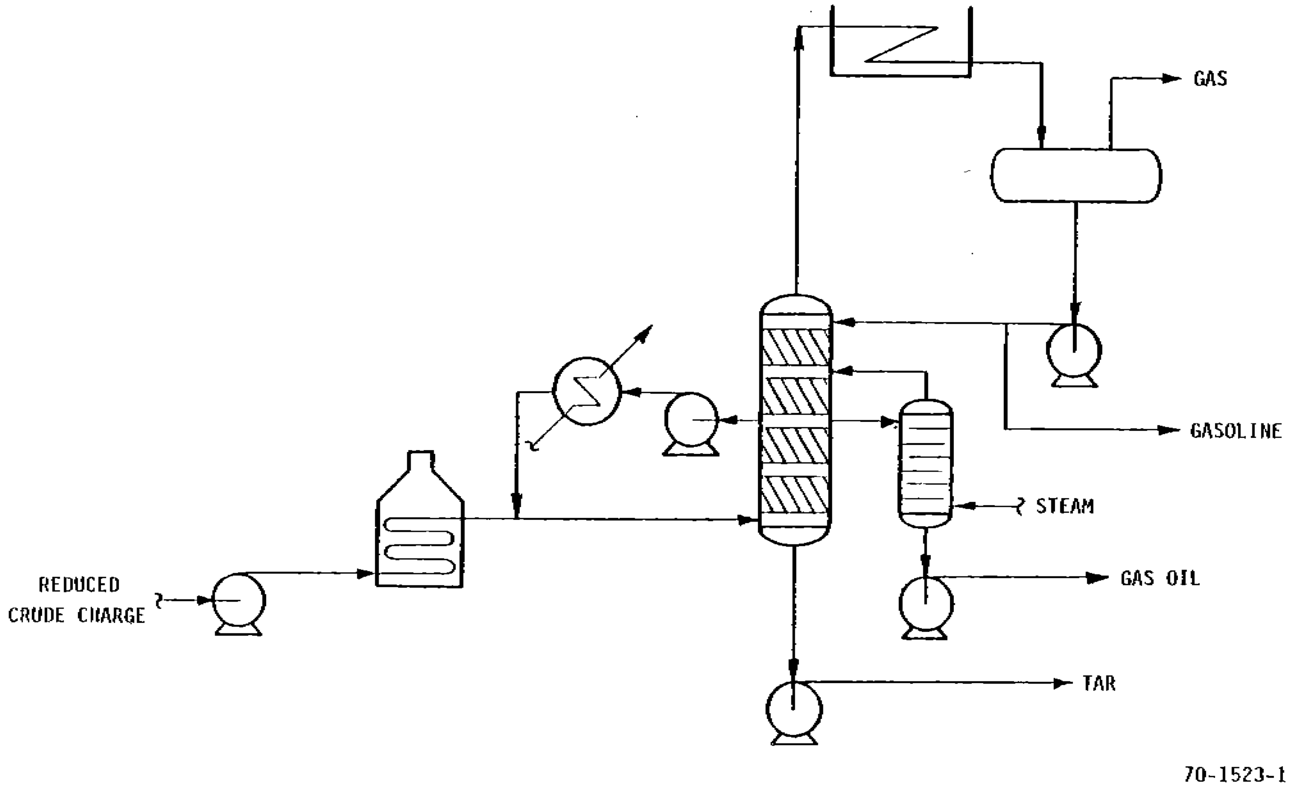

Figure F4-6. Process flow diagram - visbreaking.

Source: Reference 2

can be arranged to provide a soaking section of relatively low heat density. The charge remains in the coils until the visbreaking reactions are completed.[1]

An example of typical charge and products specifications is given in Table F4-14. Operating information and utility requirements are included in Table F4-15.

TABLE F4-14. TYPICAL VISBREAKING CHARGE AND PRODUCT PROPERTIES

	Atmospheric Residue	Vacuum Residue
Charge		
Gravity, API	17.7	6.6
Pour Point, °F	50.0	120.0
Viscosity, CS at 122°F	175.0	1900.0
CS at 210°F	22.0	-
Products, Wt %		
Gas	2.5	2.5
Unstabilized Gasoline (350°F E.P.)	7.5	7.5
350-650°F Gas Oil	24.0	14.0
650°F+ Residue	66.0	76.0
Properties of 350°F+ Visbreaker Product		
°API	21.5	10.6
Viscosity, CS at 210°F	10.0	380.0
Pour Point, °F	40.0	105.0

Source: Reference 4

TABLE F4-15. VISBREAKER OPERATING AND UTILITY INFORMATION

Temperature, °F	850-950
Pressure, psig	50-300
Utilities - per barrel feed	
Electricity, kWh	0.47
Steam (300 psig), lb	8.7
Fuel, 10^3 Btu	88

Source: References 1, 4

4.2.3.2 Process Emissions--

Emission sources from visbreaking units include:

- Process heater flue gas, and
- Fugitive emissions.

Process Heater Flue Gas--Emission factors for various pollutants from fired heaters are given in Table F4-16. A typical visbreaking unit will utilize one process heater. It is used to heat the feed to temperatures required for the visbreaking reactions to proceed.

Total emissions from the visbreaker heater are also given in Table F4-16. These figures are given as pounds of pollutant per thousand barrels of fresh feed using a heat input of 9.0 x 10^4 Btu per barrel of feed.[4]

TABLE F4-16. TYPICAL EMISSIONS FROM VISBREAKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.3
- Residual oil		
Grade 4	7	4.5
Grade 5	10	6.4
Grade 6	10(S)+3	6.4(S)+1.9
Sulfur Dioxide[c]		
- Distillate oil	142(S)	91.3(S)
- Residual oil	157(S)	101(S)
Sulfur Trioxide[c]	2(S)	1.3(S)
Carbon Monoxide[d]	5	3.2
Hydrocarbons (as CH_4)[d]	1	0.64
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	14
- Residual oil[e]	$22+400(N)^2$	$14+257(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.43-1.29
Sulfur Oxides (as SO_2)[f]	0.6	0.051
Carbon Monoxide	17	1.5
Hydrocarbons (as CH_4)	3	0.26
Nitrogen Oxides (as NO_2)	120-230	10.3-19.7

[a] Source: Reference 15

[b] Based on a heat input of 9.0×10^4 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical visbreaking unit are given in Table F4-17. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained elsewhere in this report (see Appendices B and C).

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[14]

The methods used to develop estimates for the number of each source type have been discussed in Section 4.1.1.3 of this appendix.

The source counts described in Table F4-17 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

TABLE F4-17. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL VISBREAKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	30	0.059	1.77
	Light Liquid (VP > 0.1 psia @ 100°F)	46	0.024	1.10
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	224	0.0005	0.112
	Hydrogen Service	0	0.018	0.0
	Total	300[a]		2.98
Open-End (Sample) Valves	All	20[a]	0.005	0.100
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	2(2)	0.25	0.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	7(10)	0.046	0.46
	Total	9(12)[a]		0.96
Drains	All	23[a]	0.070	1.61
Flanges & Fittings	All	1071[a]	0.00056	0.60
Relief Valves	All	6[a]	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	1.4	0.0
	Hydrogen	0	0.11	0.0
	Total	0		0.0
				7.29

[a] Estimated

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Hence, these source counts are not necessarily representative of all or even the majority of visbreaking units.

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4.3 CRACKING OPERATIONS

The primary function of cracking operations is to convert heavy petroleum fractions into lighter, more valuable products. Two processes, catalytic cracking and hydrocracking, provide a substantial portion of the cracking capacity in the United States. Although these processes are similar in that they crack heavy fractions to produce lighter products, there are considerable differences between them in both the operating principles and the pollution potential..

Catalytic cracking is a high temperature-low pressure process which produces a relatively unsaturated product. The removal of contaminants such as sulfur and nitrogen compounds from the product streams is low and the conversion of feed to lighter products is generally limited by the level of heavy aromatics in the feed. If contaminant removal or higher conversions are required, hydrogenation of feed, product, or recycle streams may be incorporated into the processing scheme. More detailed information on catalytic cracking is provided in Section 4.3.1.

Hydrocracking is a high temperature-high pressure process which consumes hydrogen to produce highly saturated, contaminant free products. Sulfur and nitrogen compounds in the feed are converted to hydrogen sulfide and ammonia.

The hydrocracking process is characterized by its flexibility. By varying the severity of the process conditions, a variety of feedstocks, including those with high aromatics concentrations, can be processed to yield a wide range of product streams. Detailed information on hydrocracking processes is given in Section 4.3.2.

The decision by the refiners as to which of these processes to employ is complicated by a number of factors. These include the availability of hydrogen, the desired product slate, product quality requirements, and the degree of flexibility desired. Since each process has its own particular requirements for downstream processing, the choice of one process over the other is usually based on an economic evaluation covering the operation of the entire refinery.

4.3.1 Catalytic Cracking

The catalytic cracking process often serves as the heart of the modern refinery by substantially increasing the production of gasoline from a given amount of crude oil. This is accomplished by cracking heavy feedstocks such as atmospheric or vacuum gas oils to produce slurry oil, light cycle oil, cracked gasoline, light gases, and coke.

Several types of catalytic cracking processes have been developed: fluid-bed catalytic cracking (FCC) units, and moving bed designs such as Thermofor (TCC) and Houdriflow (HCC) cracking units. Table F4-18 gives a breakdown by process type of catalytic cracking capacity in the United States as of January 1979.

TABLE F4-18. DOMESTIC CATALYTIC CRACKING CAPACITY, 1979

Type	Fresh Feed Bbl/Sd	% of Total Feed Capacity	# of Units in Operation
FCC	4,592,500	94.0	119[a]
TCC	242,900	5.0	19
HCC	51,500	1.0	3

[a] This value is somewhat low as some refineries have multiple catalytic cracking units.

Source: Reference 2

4.3.1.1 Process Description--

Figure F4-7 shows a diagram of a typical FCC unit. Hot regenerated catalyst, mixed with hydrocarbon feed, is transported into the reactor. The reactor contains a bed of powdered catalyst which is kept in a fluidized state by the flow of vaporized feed material and steam. Cracking of the feed, which occurs in both the riser leading to the reactor and in the fluidized bed, causes a deposit of coke to form on the catalyst particles. A continuous stream of spent catalyst is withdrawn from the reactor. The catalyst is steam stripped to remove hydrocarbons and conveyed to the regenerator by airflow. The hydrocarbon vapor from the reactor is fractionated into a variety of products including light hydrocarbons, cracked gasoline, and fuel oil, while a portion of the fractionator bottoms can be recycled to the reactor.[3]

Air is injected into the regenerator to burn off the coke deposit and the regenerated catalyst is continuously returned to the reactor. Heat added to the catalyst during coke burn-off furnishes much of the required heat for the cracking reaction.[4]

Thermofor and Houdriflow catalytic cracking units utilize beaded or pelleted catalysts. Regenerated catalyst and vaporized feed enter the top of the reactor chamber and travel cocurrently downward through the vessel. The catalyst is purged with steam at the base of the reactor and travels by gravity into the regenerator chamber. Combustion air is admitted at a controlled rate to burn off coke deposits. From the bottom of the regenerator, the catalyst is conveyed by airlift to a surge hopper above the reactor. A diagram of a typical TCC unit is given in Figure F4-8.

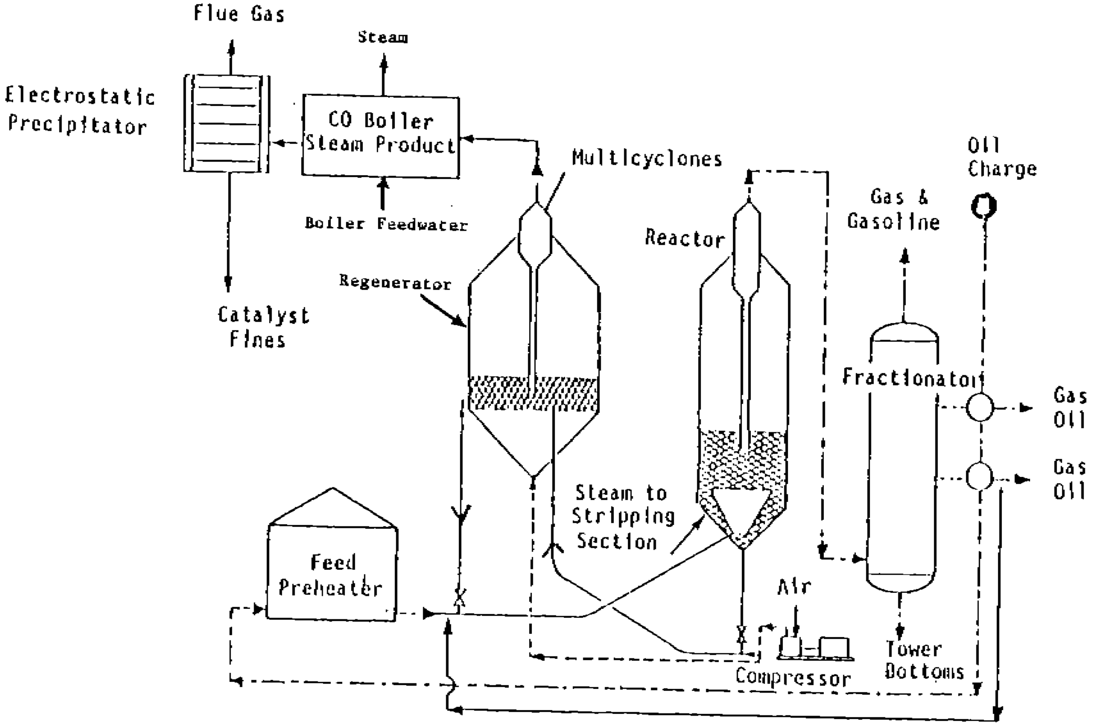

Figure F4-7. Fluid catalytic cracking unit (FCC).

Source: Reference 5

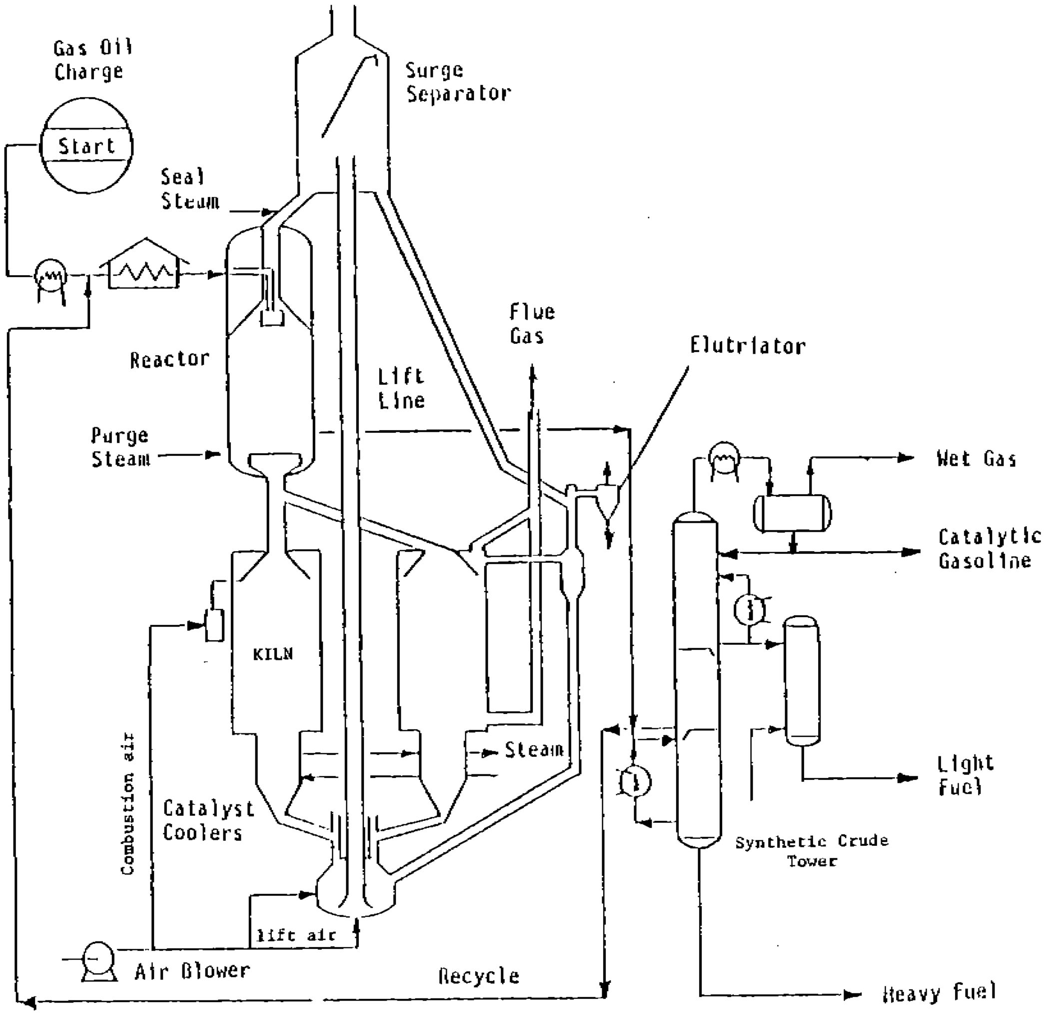

Figure F4-8. Thermofor moving-bed catalytic cracker (TCC).

Source: Reference 14

With the advent of new catalysts, major design and operational changes have been incorporated in FCC unit operation. By contrast, no major changes in moving bed type units have been observed and these units are being phased out.

4.3.1.2 Process Technology--

Conventional FCC Operation--Coke is removed from cracking catalysts to restore their activity. Spent catalyst contains roughly 6 percent coke while coke levels on the regenerated catalyst vary from 0.2-0.3 percent. The amount of air supplied to the regenerator is insufficient for complete combustion which results in flue gas CO concentrations of 5-10 percent. The oxygen level in the flue gas is low enough so that only a limited amount of combustion occurs in the regenerator "dilute phase" where no catalyst heat sink is available. Combustion in the dilute phase, called afterburning, can result in damage to the catalyst, the cyclones, and other regenerator equipment due to high temperatures. To avoid equipment damage, the regenerator is operated below 1150°F.[5,6,7]

High Temperature Regeneration--Zeolite catalysts first appeared on the market in the mid-1960's. The major features of these catalysts are summarized below:[6,8]

- Naphthenes and paraffins are cracked rapidly with excellent selectivity,
- Aromatic nuclei crack slowly with poor selectivity,
- High hydrogen transfer rates are observed,

- The rate of cracking is relatively unaffected by boiling range, and

- Efficiency is adversely affected by coke deposits which limit zeolite availability.

The use of zeolite catalysts has accelerated the trend to more fully regenerate these coke sensitive catalysts. Very low carbon on regenerated catalyst (CRC) levels have been achieved using a technique called high temperature regeneration (HTR). The key to this process is complete conversion of coke to CO_2 within the regenerator. This situation is quite different from that of conventional regeneration where conversion of CO to CO_2 is carefully controlled to about 50 percent.[7] High temperature regeneration can be utilized in new units, or applied as a retrofit to existing units. The major features of high temperature regeneration are:

- Extremely low coke on regenerated catalyst levels are possible. Typical values are 0.05-0.1 percent coke while Amoco Oil Company reported CRC levels of 0.01 percent with their UltraCat regeneration technique.[5,7]

- CO emission levels of 500 ppm in the regenerator flue gas can be obtained. This level is sufficiently low to meet federal NSPS and most state emissions regulations.[7,9,10,11]

- Complete regeneration increases catalyst activity which means a lower catalyst-to-oil ratio is possible. Thus, unit capacity can be increased if bottlenecks are removed from the rest of the process.[5,6,7,8,9]

- Temperatures in the regenerator vary from 1100-1350°F. This is 100-150°F higher than conventional regeneration. Since CO afterburn is possible, flue gas temperatures can be several hundred degrees higher than the dense-phase temperature. Normally, however, only 50 to 100°F of temperature differential results.[4,7,9,10]

- The extremely active catalyst produced from HTR is most effectively used in a short contact time riser cracking reactor. The advantage of riser cracking over bed cracking lies in avoiding secondary reactions such as the recracking of gasoline components.[6,9]

- Increased catalyst selectivity and the use of riser cracking can result in a 20 to 30 percent reduction in the amount of coke produced. Therefore, the increase in combustion air required to completely burn CO and coke to CO_2 can be offset in some cases by lower coke production such that overall combustion air usage can remain essentially constant.[5]

The operating conditions for conventional FCC's and units using HRT are compared in Table F4-19.

Existing FCC units may be revamped to incorporate HTR. The required changes to convert to HTR depend on the design of the unit and the desired coke content on the regenerated catalyst. To withstand higher regenerator temperatures, steel components within the regenerator usually require replacement with components made of more heat resistant materials such as chromium-nickel alloy stainless steels. Other modifications might include an improved combustion air distribution system or the installation of a riser cracking reactor. In general, switching to HTR increases the capacity of the process and some modifications in downstream equipment may be required to remove bottlenecks.[8,9]

TABLE F4-19. TYPICAL OPERATING CONDITIONS FOR FLUID CATALYTIC CRACKING

Reactor Temperature, °F	885 - 1025
Regenerator Temperature, °F	
Conventional Regeneration	1000 - 1100
HTR	1100 - 1350
Coke Content of Spent Catalyst, Wt %	
Conventional Regeneration	6
HTR	5
Coke Content on Regenerated Catalyst, Wt %	
Conventional Regeneration	0.2 - 0.3
HTR	0.01 - 0.1

Source: References 5, 9

Combustion Promotion Catalysts--The most recent development in FCC technology is the use of "promotion" catalysts to aid the conversion of CO to CO_2. The first type to become available (1975) was an FCC catalyst modified with a small concentration of noble metal promotion agent. In 1977, a number of manufacturers came out with a solid promoter. This powder is mixed with make-up catalyst, roughly 1-10 pounds per ton of fresh catalyst. Liquid promoters, injected directly into the regenerator, are also available.[11]

The advantage of using combustion promoters is that CO is converted to CO_2 within the dense-phase of the regenerator. This avoids the problem of CO afterburn in the regenerator dilute phase which is common in units using HTR. Thus, in units where temperature limitations prohibit the use of HTR, CO emissions below 500 ppm can be obtained without the use of a CO boiler. Essentially complete conversion of CO can be obtained with bed temperatures of 1150-1200°F.[7,9] However, regeneration of the catalyst is not quite as effective at the lower temperature and selectivity of the catalyst is slightly poorer in that more coke is produced.[9] Typically, FCC units with CO promoted regeneration have regenerator bed temperatures around 1300°F and dilute phase temperatures are generally 10 to 30°F higher.

Industry acceptance of high temperature regeneration and promotion catalysts has been high, given the relatively short time they have been available. A breakdown of the regeneration techniques being used by U.S. refiners is given in Table F4-20.

TABLE F4-20. DOMESTIC FCC REGENERATION TECHNIQUES (August 1978)

Regeneration Technique	% of All FCC Units that Use This Technique	Remarks
Conventional regeneration	53	Most units have CO boilers
High temperature regeneration	26	May be used in conjunction with a CO boiler
Combustion promoting catalysts	10	May be used in conjunction with a CO boiler
Combustion promotion, separate from catalyst	11	May be used in conjunction with a CO boiler

Source: Reference 15

Energy Factors--There are a number of factors involved in determining the energy requirements of the fluid catalytic cracking process. The cracking reaction itself is endothermic and the heat of reaction is around 150 Btu/lb feed. The heat of combustion of the coke provides the majority of the required energy. That is, coke burning in the regenerator heats the catalyst and this heat is transferred to the oil in the riser. The remainder of the required heat is obtained by preheating the feed in a fired heater.

The flue gas from conventional FCC operation contains from 5-10 percent CO which represents a substantial energy loss if released to the atmosphere. This energy can be recovered in a CO boiler by producing steam. Energy recovery from a typical CO boiler, operating with a conventional FCC unit, has been estimated to be 60 x 10^3 Btu/bbl of fresh feed.[12] Often the entire cost of a CO boiler can be justified on the basis of steam production alone.

Required utilities for the FCC process include fuel for the fired heater and auxiliary fuel for the CO boiler (if necessary). Steam is used in the stripper to strip oil from the catalyst particles and additional energy is required to power the regenerator air blower.

Energy recovery from high temperature regeneration is about the same as for CO boilers, estimated at 60 x 10^3 Btu/bbl of fresh feed.[12] In high temperature regeneration, the combustion of CO to CO_2 occurs within the regenerator rather than in the CO boiler. This energy produces higher flue gas temperatures which results in more steam production in the waste heat boiler, greater heat transfer to the catalyst which reduces the preheater duty, and increased yields of more valuable liquid products.

Many refiners operate their FCC regenerator at higher pressures (25 to 40 psig) to take advantage of higher CO combustion rates resulting from the increased oxygen partial pressure. Power recovery equipment, used to recover mechanical energy from the higher pressure flue gas, has been installed on some of these units. The system consists of a flue gas expander, the FCC air blower, an induction motor-generator, and a start-up steam turbine, all mounted in tandem. The flue gas passes through an efficient third stage cyclone system to the flue gas expander as shown in Figure F4-9. The expander produces power for the FCC air blower. The induction motor-generator smoothes any imbalance in power load by adding power if necessary or by producing electricity if the power generated by the flue gas expander is in excess of air blower requirements. Efficiency and design improvements in the third stage separator and the use of erosion-temperature resistant expander blades have made the system economically attractive for new FCC units.[6]

The energy recovery potential of various power recovery schemes are compared in Table F4-21.

4.3.1.3 Process Emissions--

Emission sources from catalytic cracking units include:

- Catalyst regeneration operations,
- Process heater flue gas,
- Fugitive emissions.

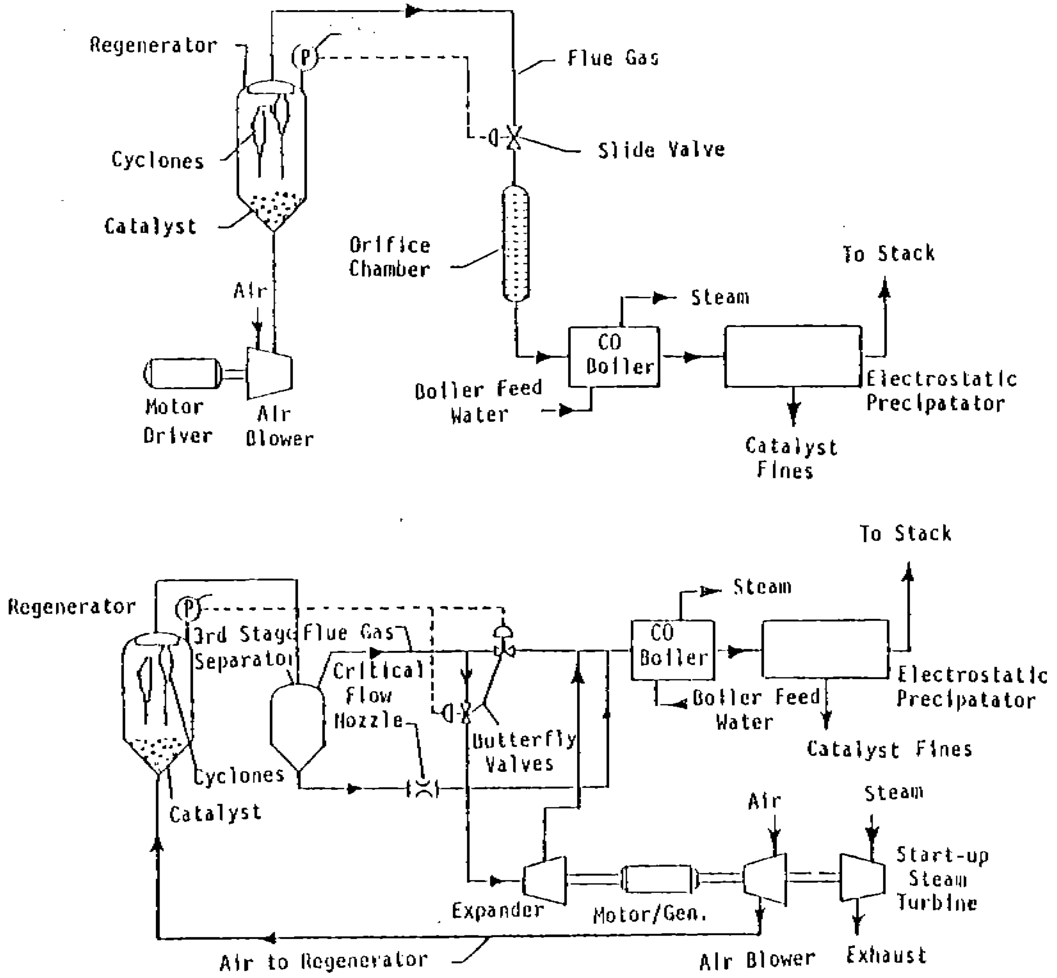

Figure F4-9. FCC unit power recovery system.

Source: Reference 13

TABLE F4-21. ENERGY RECOVERY TECHNIQUES FOR FCC REGENERATORS

Power Recovery Technique	Available Energy-Horsepower per Pound per Second of Flue Gas[a]
Waste heat boiler alone	45
Power recovery alone	78
Power recovery plus waste heat boiler	106
CO burning waste heat boiler	145
Power recovery plus CO burning waste heat boiler	206

[a] Flue gas at 20 psig - 1000°F.

Source: Reference 3

Note: This table assumes that the regenerator is operating in "conventional" regeneration mode. If a complete combustion regeneration mode is used (high temperature regeneration or CO promoted catalyst), then the incremental recoveries shown for CO burning will be obtained in the regenerator and in the unfired waste heat boiler.

Catalyst Regeneration Operations--Coke is deposited on cracking catalysts during processing, and it must be removed to restore catalytic activity and selectivity. This is accomplished by introducing air into the regenerator which burns the coke to CO and CO_2.

In conventional operation, the conversion of CO to CO_2 is minimized to avoid high temperatures which might damage internal regenerator materials. The resulting flue gas contains from 5-10 percent CO.

Many refiners utilize a CO-burning waste heat boiler to recover the energy contained in the flue gas. In addition to energy recovery, this procedure reduces CO emissions to low levels. And, other combustible contaminants may be removed, depending on the operating temperature of the boiler. Increased emissions of "thermal NO_x" may, however, result at boiler temperatures and sulfur in the auxiliary fuel will be converted to SO_x. Typical emission levels for regenerator flue gas with and without the use of a CO boiler are listed in Table F4-22. Also given in Table F4-22 are the results of sampling conducted during this program. The table lists a summary of data obtained from five FCC unit CO boiler stacks. Detailed information on these sampling results is given in Appendix B of this report.

Cracking units utilizing high temperature regeneration produce a flue gas with CO concentrations ranging from 200-2000 ppm. And, many of the applicable governmental regulations have been set or altered to allow the use of this technology.

TABLE F4-22. EMISSION RATES FROM FCC REGENERATORS, BEFORE AND AFTER CO BOILER

Chemical Species[a]	Emissions without CO Boiler	Emissions with CO Boiler		
	(Reference 9)	(Reference 9)	Data from Current Program[b]	Total Emissions Based on Data from Current Program - (lb/1000 bbl feed)
SO_2, ppmv	130-3300	Up to 2700	14.4-871	9.11-504
SO_3, ppmv	NA[c]	NA[c]	0.65-13.5	0.37-10.3
NO_x (as NO_2), ppmv	8-394	Up to 500	94.1-453	37.2-215
CO, % Vol.	7.2-12.0	0-14 ppmv	0.0-1.0	0.0-2680
CO_2, % Vol.	10.5-11.3	11.2-14.0	13.5-16.1	-
O_2, % Vol.	0.2-2.4	2.0-6.4	3.2-7.0	-
N_2, % Vol.	78.5-80.3	82.0-84.2	77-82.7	-
H_2O, % Vol.	13.9-26.3	13.4-23.9	9.2-22.7	-
Hydrocarbons, ppmv	98-1213	NA[c]	0.28-46.2	0.17-29.8
Ammonia, ppmv	0-675	NA[c]	0.0-15.4	0.0-2.37
Aldehydes, ppmv	3-130	NA[c]	0.0-19.6	0.003-5.31
Cyanides, ppmv	0.19-0.94	NA[c]	0.0-19.1	0.0-4.66
Particulates, gr/SCF	0.08-1.39	0.017-1.03	0.012-0.304	6.8-236
Temperature, °F	1000-1200	485-820	386-727	-

[a] All concentrations on dry basis
[b] Based on sampling of 5 stacks
[c] Not available

High temperature regeneration can reduce the uncontrolled emissions of other pollutants. Since the maximum temperatures used in high temperature regeneration are well below those used in CO boilers, thermal NO_x emissions are somewhat lower.[9] And, nitrogen and sulfur emissions from CO boiler auxiliary fuel use are avoided.

CO emissions from various operating schemes are summarized in Table F4-23.

TABLE F4-23. SUMMARY OF CO EMISSIONS FROM VARIOUS REGENERATION TECHNIQUES

Control Technique	Typical Emissions Level
Conventional regeneration, (uncontrolled)	5-10% CO in regenerator flue gas; AP-42 emission factor=13,700 lb CO/1000 bbl feed
Conventional regeneration, (CO boiler)	<50 ppm CO in CO boiler flue gas
High temperature regeneration or combustion promotion	200-2000 ppm CO in regenerator flue gas; <500 ppm CO can usually be obtained

Source: Reference 9

Process Heaters--Emission factors for various pollutants from fired heaters are given in Table F4-24. A typical catalytic cracking unit will require a process heater for heating the feed, prior to its contact with catalyst in the riser and reactor.

TABLE F4-24. TYPICAL EMISSIONS FROM CATALYTIC CRACKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.4
- Residual oil		
Grade 4	7	5.0
Grade 5	10	7.1
Grade 6	10(S)+3	7.1(S)+2.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	101(S)
- Residual oil	157(S)	112(S)
Sulfur Trioxide[c]	2(S)	1.4(S)
Carbon Monoxide[d]	5	3.6
Hydrocarbons (as CH_4)[d]	1	0.7
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	15.7
- Residual oil[e]	$22+400(N)^2$	$15.7+286(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.5-1.4
Sulfur Oxides (as SO_2)[f]	0.6	0.06
Carbon Monoxide	17	1.6
Hydrocarbons (as CH_4)	3	0.29
Nitrogen Oxides (as NO_2)	120-230	11.4-21.9

[a] Source: Reference 17

[b] Based on a heat input of 100,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

Total emissions from the catalytic cracking unit heaters are also given in Table F4-24. These figures are given as pounds of pollutant per thousand barrels of fresh feed based on a representative heat input of 100,000 Btu per barrel of fresh feed.[16,28]

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical catalytic cracking unit are given in Table F4-25. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[18]

The methods used to develop estimates for the number of each source type have been described in Section 4.1.1.3 of this appendix.

TABLE F4-25. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL CATALYTIC CRACKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	384	849	0.059	22.7 - 50.1
	Light Liquid (VP > 0.1 psia @ 100°F)	409	889	0.024	9.82 - 21.3
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	521	1167	0.0005	0.261 - 0.584
	Hydrogen Service	0	0	0.018	0.0
	Total	1314[a]	2905[c]		32.8 - 72.0
Open-End (Sample) Valves	All	-	67[b]	0.005	0.335
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	16(22)	0.25	4.5 - 5.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	17(24)	21(29)	0.046	1.10 - 1.33
	Total	30(42)[a]	37(52)[b]		5.60 - 6.83
Drains	All	65[a]	-	0.070	4.55
Flanges & Fittings	All	4214[a]	9635[c]	0.00056	2.36 - 5.40
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	4(8)	4(8)	1.4	11.2
	Hydrogen	0	0	0.11	0.0
	Total	4(8)[a]	4(8)[b]		11.2
					58.0 - 101

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 18

The source counts given in Table F4-25 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process types, and processing flexibility. The source counts presented in Table F4-25 are not necessarily representative of all or even the majority of catalytic cracking units.

The estimated composition of fugitive non-methane emissions from a catalytic cracking unit is given in Table F4-26. These estimates indicate the types of hydrocarbons contributed by sources on a number of process streams found within the unit. Additional information about these estimates may be found in Section 2.4 of Appendix D.

4.3.2 Hydrocracking

Hydrocracking refers to the process of converting heavy feedstocks into lighter products in the presence of hydrogen and a suitable catalyst or series of catalysts. Hydrocracking applications extend from cracking naphtha for LPG production to cracking heavy gas oil or residuum for products including gasoline, catalytic cracking feedstock, and desulfurized fuel oils.[24] The products of the hydrocracking process are highly saturated, that is, non-olefinic, and are characterized by low levels of sulfur and nitrogen. Generally, branched paraffin isomers predominate and very little methane or ethane is formed.[25]

TABLE F4-26. ESTIMATED COMPOSITION OF FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A FLUID CATALYTIC CRACKING UNIT

	Stream						
	Atmospheric Gas Oil	Fuel Gas	LPG Olefins	Cracked Naphtha	Lt. Cycle Gas Oil	Hvy. Cycle Gas Oil	Totals
Estimated percentage of emissions attributed to each stream - %	1	30	23	45	1	0	100%
Weighted contribution of each component to unit emissions - ppmw							
Benzene	0	0	0	1296	0	0	1296
Toluene	0	0	0	40401	0	0	40401
Ethylbenzene	0	0	0	9644	0	0	9644
Xylenes	0	0	0	77153	6	0	77159
Other Alkylbenzenes	1	0	0	109562	267	0	109830
Naphthalene	0	0	0	4928	590	0	5518
Anthracene	0	0	0	0	103	0	103
Biphenyl	0	0	0	0	102	0	102
Other Polynuclear aromatics	2	0	0	2916	6245	0	9163
n-Hexane	0	0	0	5324	0	0	5324
Other Alkanes	9495	216000	92000	91850	1906	0	471251
Olefins	0	18000	138000	76833	368	0	233201
Cyclo Alkanes	500	0	0	30096	412	0	31008
Hydrogen	0	6000	0	0	0	0	6000
							1000000

Catalytic reforming of the gasoline boiling range product is usually required to produce high octane gasoline. However, the hydrocracking product makes excellent reformer feedstock and the hydrogen produced in the reformer can provide much of the hydrogen required in the hydrocracker.

The total hydrocracking capacity in the United States has shown only limited growth in the last few years. This is due primarily to the development of new catalysts for the fluid-bed catalytic cracking process, and the high hydrogen requirements of hydrocracking units.[22] Today, hydrocracking is being used as a companion process to catalytic cracking. That is, feedstocks which would present difficulties for catalytic cracking are processed in the hydrocracker. Examples of such feedstocks include coker gas oils and catalytic cracker cycle oils which are high in aromatics.[20,26] Current hydrocracking capacity in the United States is given in Table F4-27.

TABLE F4-27. U. S. HYDROCRACKING CAPACITY, 1979

Feedstock	Number of Units	Total Capacity, bbl/sd
Distillate Streams	37	755,400
Residual Streams	1	20,000
Other	4	110,000
	42	885,400

Source: Reference 2

Several types of reactions occur during hydrocracking. The first group of reactions results in the removal of sulfur and nitrogen impurities as indicated below:[23]

$$RS + H_2 \rightarrow R + H_2S$$

$$2RN + 3H_2 \rightarrow 2R + 2NH_3$$

This is followed by the cracking and hydrogenation reaction:[23]

$$R + H_2 \rightarrow R^1 + C_1 + C_2 + etc$$

Hydrocracking catalysts serve two functions. They are (1) cracking of high molecular weight hydrocarbons, and (2) hydrogenation of the unsaturates formed during the cracking step or otherwise present in the feedstock.

A typical hydrocracking catalyst contains a cracking component such as silica-alumina. The silica alumina may be in the form of acid treated aluminosilicates, amorphous synthetic silica-alumina combinations, or the silica-alumina combinations known as zeolites or molecular sieves. These materials are all high temperature acids and their cracking activity is attributed to their acidity.

The hydrogenation activity of hydrocracking catalysts is obtained by incorporating a base metal or noble metal on the silica-alumina base. Typical hydrogenating metals include nickel, palladium, molybdenum, and cobalt.[23] These may be altered by promotion with another metal or by pretreatment techniques such as sulfiding.[20,21]

4.3.2.1 Process Description

Hydrocracking processes can be classified according to differences in the process design and the type of catalyst employed.

Two different types of hydrocracking processes are evident. In one, the feedstock is severely pretreated over a hydrogenating catalyst of low acidity to remove essentially all of the sulfur and nitrogen from the feed. Hydrocracking is carried out after ammonia removal in a separate stage over a relatively acidic cracking catalyst. This type of processing is particularly useful with high nitrogen containing feedstocks since nitrogen, present in both the feed and the resulting ammonia, tends to poison cracking catalysts.

In the other approach, zeolite catalysts are employed which can accomplish substantial cracking in the presence of sulfur and nitrogen compounds.[27] This allows single stage operation. Although there is a drop in catalytic activity over that of the two stage design, less equipment is required and recompression costs can be avoided.[21]

The process flow diagram for a typical single stage hydrocracker is shown in Figure F4-10. Heavy oil feed is mixed with recycle and make-up hydrogen. The mixture is heated and charged to the reactor where substantial cracking and hydrogenation of the feed occurs. In addition, sulfur and nitrogen compounds in the feed are converted to hydrogen sulfide and ammonia. The product mixture is sent to a high pressure separator where hydrogen is recovered and recycled to the reactor. The liquid stream is fractionated into a number of products and a heavy uncracked stream is recycled to the reactor. In some units, 100 percent conversion from feed to lighter products is obtained.

A flow diagram for the two stage process is given in Figure F4-11. In the two stage design, the effluent from the first reactor is flashed, allowing separation of liquid

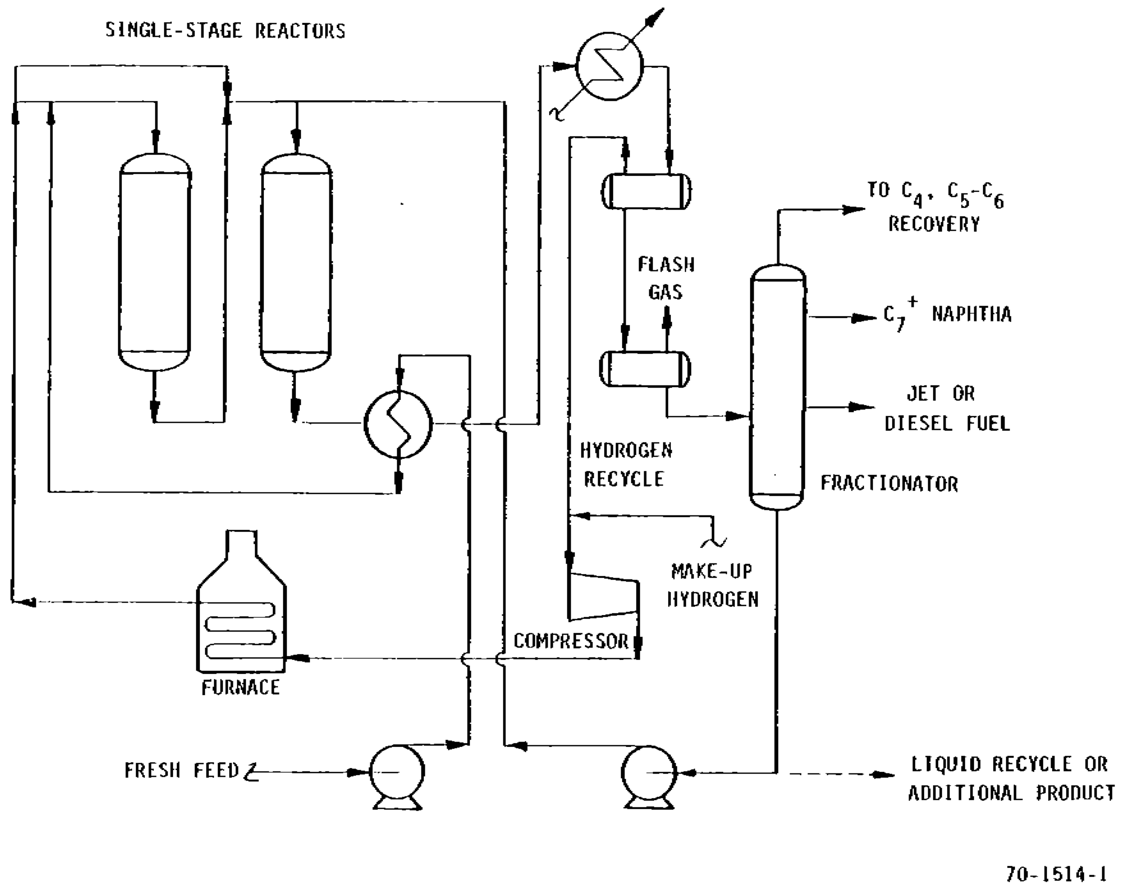

Figure F4-10. Process flow diagram - single stage hydrocracker.

Source: Reference 27

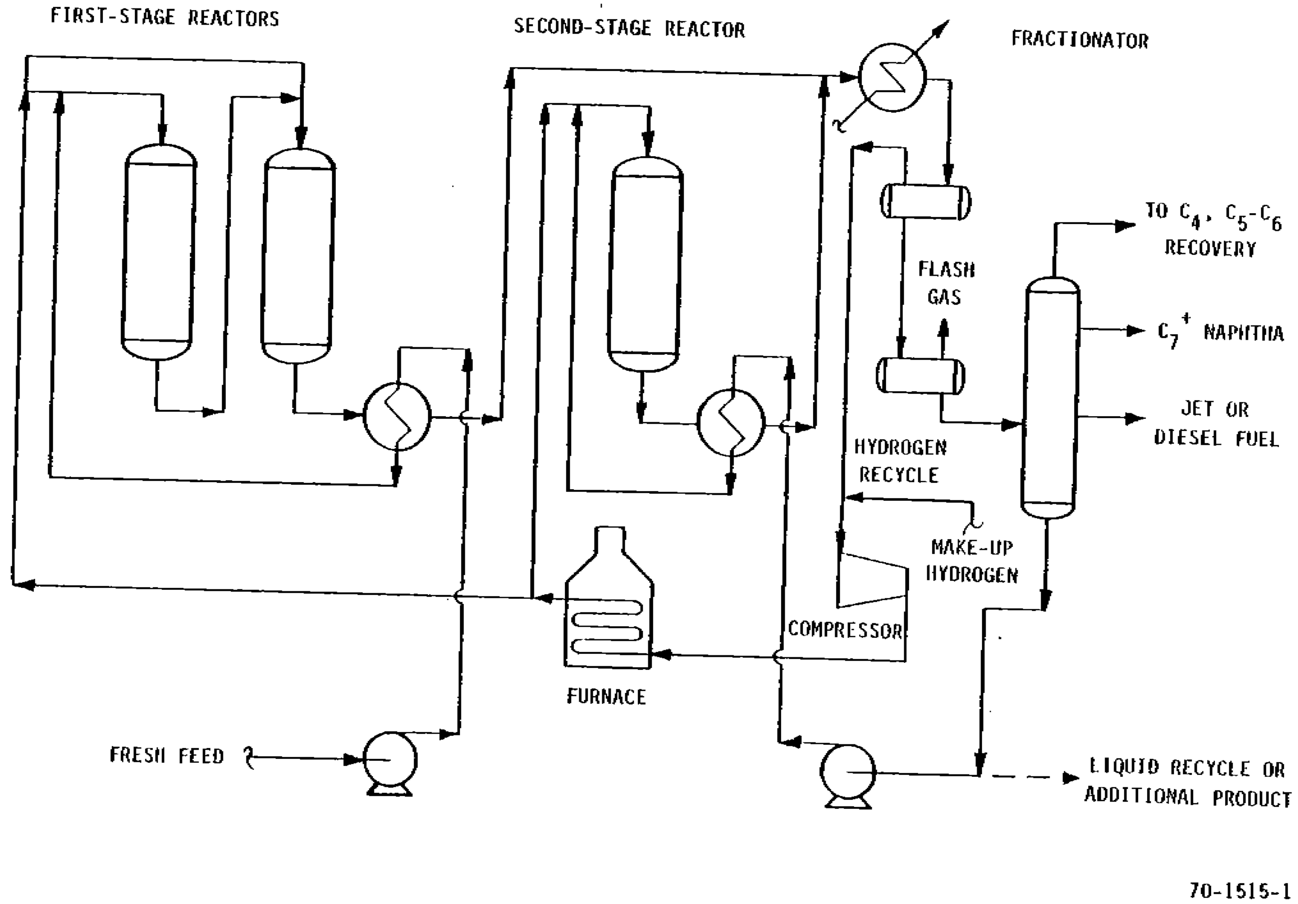

Figure F4-11. Process flow diagram - two stage hydrocracker.

Source: Reference 27

from light gases containing the hydrogen sulfide and ammonia formed in the first stage. The lack of nitrogen compounds in the second stage feed allows the reactor to obtain a high degree of cracking at conditions of lower severity.

Several licensed hydrocracker processes have been offered to the industry, many of which are available in both one and two stage designs. Some of the more prevalent designs are listed in Table F4-28.

TABLE F4-28. LICENSED HYDROCRACKING PROCESSES

Process	Licensor
Isocracking	Chevron Research Co.
Unicracking-JHC	Union Oil Co. and Esso Research
H-Oil	Hydrocarbon Research Inc. and Cities Service Research and Development Co.
H-G Hydrocracking	Gulf Research and Development Co. and the Houdry Div. of Air Products and Chemicals Inc.
Hycracking	Exxon Research and Development Co.

Most of these processes use a fixed bed reactor where the feed enters the top of the unit and travels downward through the catalyst bed. An exception to this is the H-Oil process which uses an ebullient bed reactor. In the H-Oil process, catalyst is continuously withdrawn and regenerated outside of the reactor. Thus, feeds which contain high concentrations of metals, sulfur, or nitrogen can be processed. The H-Oil process is commonly used to upgrade residuum.[14]

4.3.2.2 Process Technology--

The severity of the process conditions required for hydrocracking depends on the type of feedstock and the degree of cracking desired. In general, operating conditions must be more severe when processing a heavy feedstock or when cracking to increasingly lighter products.

Process Variables--The primary reaction variables are the reactor temperature and pressure, and the nitrogen and sulfur concentrations in the feed and off gases. The effects of these variables are discussed below.[3]

Reactor temperature is the primary means of control over the level of conversion. At normal reactor conditions, a 20°F increase in temperature nearly doubles the reaction rate. However, the effect on conversion is somewhat less as substantial recracking of material which has already been converted can occur. Since catalyst activity decreases with time, it is usually necessary to increase the temperature by 0.1 to 0.2°F per day, depending on the rate of catalyst deactivation, over the duration of the cycle.

An increase in reactor pressure serves to increase the partial pressures of hydrogen and ammonia. Conversion increases with increasing hydrogen partial pressure and decreases with increasing ammonia partial pressure. The hydrogen effect is greater, however, and the net effect of an increase in total pressure is an increase in conversion.

The organic nitrogen content of the feed is important since hydrocracking catalysts are deactivated by organic nitrogen compounds. A decrease in catalytic activity decreases conversion.

Low concentrations of hydrogen sulfide can serve as an inhibitor for reactions involving the saturation of aromatic rings.[3] This reduces hydrogen consumption and prevents the destruction of high octane aromatics. Higher hydrogen sulfide concentrations, however, can decrease cracking activity and may result in increased equipment corrosion rates.

Typical operating conditions and information on process utility requirements are given in Table F4-29.

TABLE F4-29. HYDROCRACKING - TYPICAL PROCESSING CONDITIONS AND UTILITY DATA

Pressure, psig	1000 - 4000
Temperature, °F	400 - 850
Hydrogen recycle, scf/bbl feed	8000 - 15000
Hydrogen consumption, scf/bbl feed	1500 - 2500
Fuel, 10^3 Btu/bbl feed	100 - 250
Power, kwh/bbl feed	6 - 15
Space velocity, v/hr/v	0.2 - 1.0

Source: References 3, 14, 20, 24

The high pressures required for hydrocracking result in special problems when designing the reactors. In addition to high pressures, several other factors add to reactor design difficulties. These include:

- High hydrogen partial pressures,
- High H_2S and NH_3 partial pressures,

- High operating and regenerating temperatures, and
- High exothermic heat of reaction.

The heat of reaction depends on the amount of hydrogen absorbed and usually ranges between 55-70 Btu/scf H_2. For a feed absorbing 2000 SCF H_2/bbl, the heat of reaction would be about 400 Btu/lb feed. This heat can be removed from the reactor by one of several methods:[14]

- Injection of cold recycle gas,
- Injection of cold recycle liquid, or
- Inter-bed exchangers.

The first method, which cools the reaction mixture by increasing vaporization, is most favored. Often, several reactors are used for each stage to facilitate injecting the recycle gas.[3] Liquid recycle causes difficulty in proper liquid distribution across the bed, and inter-bed exchangers raise difficult mechanical design problems under the high severity conditions in the reactor.

4.3.2.3 Process Emissions--

Emissions from hydrocracking processes include:

- Emissions during periodic catalyst regeneration,

- Process heater flue gas, and

- Fugitive emissions.

Emissions from Catalyst Regeneration Operations--During the hydrocracking process, deposits form on the catalyst which must be removed to restore catalyst activity and selectivity. This regeneration procedure involves burning the deposits by admitting air into the reactors.

During regeneration, large quantities of carbon monoxide and other pollutants may be released. However, regeneration may be required only after several months or even years of operation. Hence, total averaged emissions from this source are generally insignificant.

Process Heater Flue Gas--Emission factors for various pollutants from fired heaters are given in Table F4-30. A typical hydrocracker will require a process heater to heat the combined hydrocarbon-hydrogen feed to the reactor. In addition, a process heater may be required as a reboiler for the main fractionator. Heat input requirements vary, ranging from 100,000 to 250,000 Btu per barrel of oil feed.[14,20]

Total estimated emissions from typical hydrocracker heaters are also given in Table F4-30. These figures are given as pounds of pollutant per thousand barrels of hydrocracker feed using a total required heat input of 200,000 Btu per barrel of feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low.

TABLE F4-30. TYPICAL EMISSIONS FROM HYDROCRACKING UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	2.9
- Residual oil		
Grade 4	7	10
Grade 5	10	14
Grade 6	10(S)+3	14(S)+4.3
Sulfur Dioxide[c]		
- Distillate oil	142(S)	203(S)
- Residual oil	157(S)	224(S)
Sulfur Trioxide[c]	2(S)	2.9(S)
Carbon Monoxide[d]	5	7.1
Hydrocarbons (as CH_4)[d]	1	1.4
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	31
- Residual oil[e]	$22+400(N)^2$	$31+571(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.95-2.9
Sulfur Oxides (as SO_2)[f]	0.6	0.11
Carbon Monoxide	17	3.2
Hydrocarbons (as CH_4)	3	0.57
Nitrogen Oxides (as NO_2)	120-230	22.9-43.8

[a] Source: Reference 17

[b] Based on a heat input of 200,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = Wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical hydrocracking unit are given in Table F4-31. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[18]

The methods used to develop estimates for the number of each source type have been previously described in Section 4.1.1.3 of this appendix.

The source counts listed in Table F4-31 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. The source counts given in Table F4-31 are not necessarily representative of all or even the majority of hydrocracking units.

TABLE F4-31. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDROCRACKING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	175	0.059	10.3
	Light Liquid (VP > 0.1 psia @ 100°F)	375	0.024	9.00
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	307	0.0005	0.154
	Hydrogen Service	75	0.018	1.35
	Total	931[a]		20.8
Open-End (Sample) Valves	All	-	0.005	-
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	12(17)	0.25	4.25
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	10(14)	0.046	0.644
	Total	22(31)[a]		4.9
Drains	All	58[a]	0.070	4.1
Flanges & Fittings	All	1955[b]	0.00056	1.09
Relief Valves	All	6[b]	0.19	1.1
Compressors (Compressor Seals)	Hydrocarbon	0(0)	1.4	0.0
	Hydrogen	3(6)	0.11	0.66
	Total	3(6)[a]		0.7
				32.7

[a] Physically Counted

[b] Estimated

4.3.3 References for Section 4.3

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4.4 HYDROPROCESSING

Hydroprocessing refers to those processes in which hydrogen is mixed with a variety of feedstocks and passed over a catalyst at elevated temperature and pressure. The hydrogen reacts with sulfur- and nitrogen-containing compounds in the feedstock to form hydrogen sulfide and ammonia. Heavy metals, oxygen and halides are also removed via hydroprocessing. Hydroprocessing may also be used to stabilize unsaturated hydrocarbons such as olefins by converting them to saturated materials.

Hydroprocessing operations may be divided into three categories, based on the severity of the process: 1) hydrocracking, in which 50 percent or more of the feed is reduced in molecular weight; 2) hydrorefining, in which 10 percent or less of the feed is reduced in molecular weight; and 3) hydrotreating, in which essentially no reduction in molecular weight occurs.

Hydrocracking is discussed in detail in Section 4.3.2. The following sections describe hydrorefining and hydrotreating processes.

4.4.1 Hydrorefining

Hydrorefining includes processes in which heavier distillation cuts (e.g. residuals, heavy gas oils, topped crudes, or middle distillates) are refined or cleaned for further processing, blending, or direct use. Pretreatment of light and heavy feedstocks for catalytic cracking or reforming is also included in this category. A number of similar processes are available from various licensors which reduce the sulfur, nitrogen, or metal content of heavy feedstocks. These are discussed in the following paragraphs.

4.4.1.1 Process Description and Technology--

Hydrodesulfurization of Residual Oil--The purpose of hydrodesulfurization of residual oils is to remove contaminating sulfur, nitrogen, and metals and thus upgrade the residual feedstock for use in fuel oil production or catalytic cracking. Use of residual hydrodesulfurization has historically been limited due to the high rate of hydrogen consumption and the short catalyst life. Table F4-32 lists licensors currently offering residual hydrodesulfurization processes and the number of each type of unit in commercial operation. Figure F4-12 is a schematic diagram for residual hydrodesulfurization. The basic process involves heating a mixture of feedstock and hydrogen and passing the mixture through a reactor containing a catalyst bed. The reactions occur in the liquid phase. Both fixed and ebullient catalyst beds are used. In the reactor, sulfur in the feed is converted to H_2S; nitrogen is converted to NH_3; and metal contaminants are deposited on the catalyst. After products from the reactor are cooled, hydrogen and H_2S are flashed in a series of high and low pressure separators. The hydrogen is recycled and the H_2S is recovered for further processing. The remaining oil product is steam-stripped to remove residual H_2S, and may pass through a fractionator for removal of light hydrocarbons. The desulfurized residuum may be blended into fuel oil or further processed.

Feed to the residual hydrodesulfurization unit is usually residuum with boiling points ranging from 650-850°F and a sulfur content higher than the parent crude oil. Hydrogen is added at the rate of 400-700 scf/bbl. Although a variety of

TABLE F4-32. LICENSORS OF RESIDUAL HYDRODESULFURIZATION PROCESSES[a]

Name of Process	Licensor(s)	No. Units Operating Commercially	Total Unit Capacity
Fuel Hydrodesulfurization	BASF AG & IFP	NA	NA
Hydrodesulfurization, Residual Oil	Shell Development Co.	1	6,800 tpd
RDS/VRDS Hydrotreating	Chevron Research Co.	1	23,000 b/cd
Resid HDS	Gulf Research & Development Company	5	NA
Unicracking/HDS	Union Oil Co. of California	1	60,000 b/sd
VGO/DAO Hydrotreating	Chevron Research Co.	24	845,000 b/d

[a] Feedstocks are primarily atmospheric or vacuum residual; however, some processes also use whole crude or lighter gas oils as well.

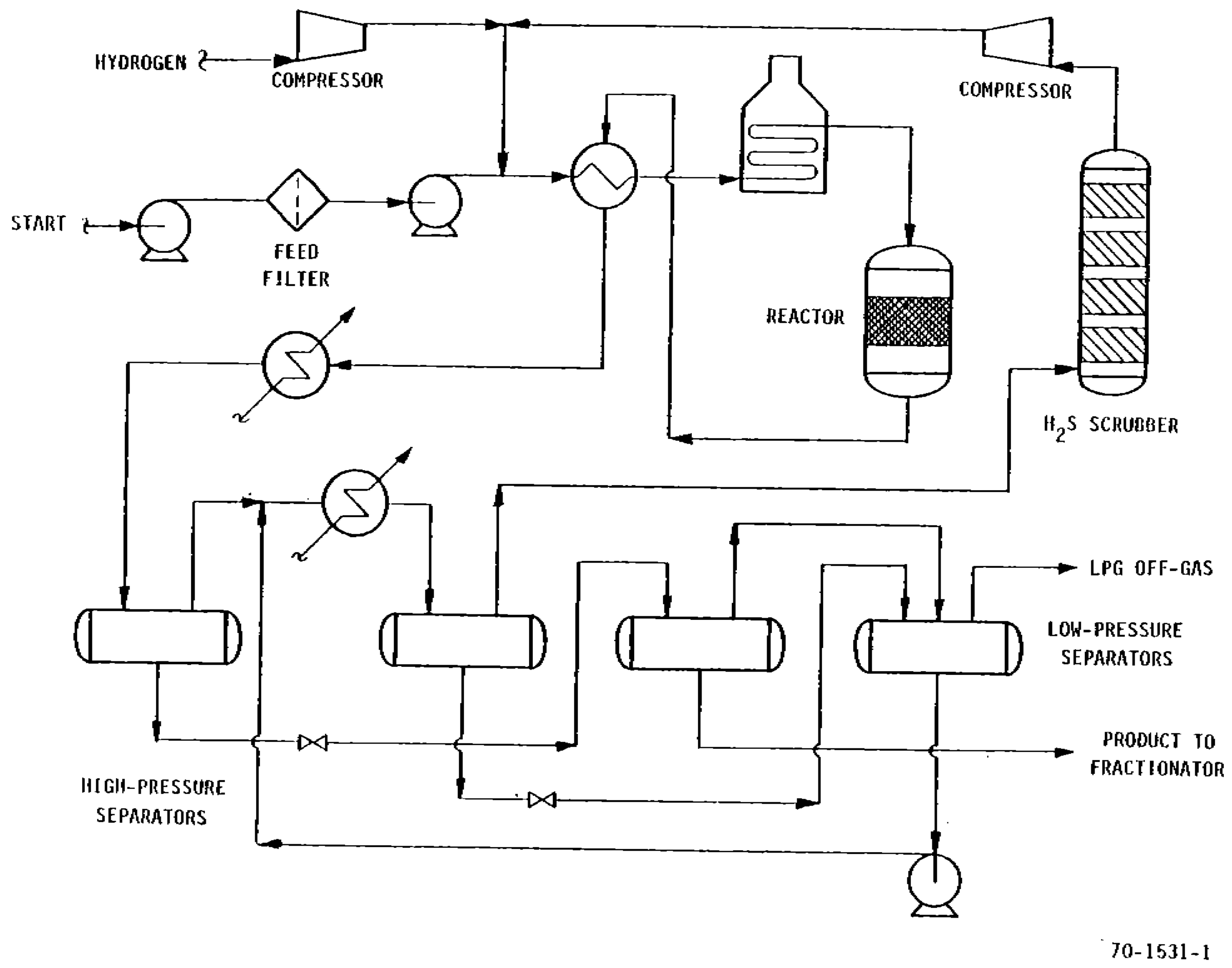

Figure F4-12. Residual hydrodesulfurization.

proprietary catalysts are in use, the most commonly used are cobalt-molybdenum or cobalt-nickel based.

The sulfur content of the desulfurized residuum varies with the feedstock sulfur content and the severity of the desulfurization process. Table F4-33 shows typical product yields and properties, investment, utility requirements and catalyst costs as reported by Gulf Research and Development Co. for the Resid HDS process.

Process equipment - The major pieces of process equipment used in hydrodesulfurization processes include a process heater, a fixed-bed or ebullient catalytic reactor, separator drums, an absorber/scrubber for H_2S, and a steam stripper. All of these pieces of equipment have been discussed in previous sections of this appendix.

Hydrodesulfurization of Heavy Gas Oils and Middle Distillates--Heavy gas oils and middle distillates are hydrodesulfurized to remove sulfur, nitrogen and metallic compounds. The process is used extensively to produce high-quality, low sulfur kerosine and light gas oils for the production of jet fuels, diesel fuels, and heating oils. The process is also used to treat heavy gas oils for blending or for high quality catalytic cracking feed.

Hydrodesulfurization is particularly important in pretreating catalytic cracker feeds. Removal of sulfur and other impurities results in reduced catalyst poisoning, longer catalyst life, better cracking selectivity and better product quality. Additionally, lower-sulfur feed results in less sulfur deposition on the catalyst; thus, catalyst regeneration produces less SO_2 emissions.

TABLE F4-33. RESIDUAL HYDRODESULFURIZATION

Yields - Average for run:

Charge (650°F+)	Kuwait Atm Resid.
Gravity, °API	16.6
Sulfur, wt %	3.8
Ni + V, ppm	60

HDS Severity	Mild	Moderate	Severe
Product Yield			
H_2S, wt %	3.1	3.7	3.9
C_1-C_4, wt %	0.6	0.9	1.1
C_5-375°F Naphtha, vol %	2.6	3.8	4.6
375-600°F Distillate, vol %	8.5	-	-
650°F Fuel Oil, vol %	90.1	-	-
375°F Fuel Oil, vol %	-	98.0	97.4
Chemical H_2 cons., scf/bbl	490	640	720

Economics - For processing 50,000 bpsd, 650°F + Kuwait Atm tower bottoms, 2 cycles per year:

HDS Severity	Mild	Moderate	Severe
Investment			
(U.S. Gulf Coast, includes catalyst, excludes hydrogen and sulfur) ¢ per bpsd	704	937	1166
Utilities (per bbl feed)			
Power, kwh	4.7	5.5	6.4
Steam (600 psig, 750°F) lb	9	7	17
Steam (50 psig, sat'd), lb	26	39	51
Fuel, heat released, 10^3 Btu	76	76	81
Cooling water (20°F rise), gal	200	230	360
Condensate (deaerated), gal	1.3	1.7	2.2
Catalyst Cost (¢ per bbl)	14	36	62

Source: Reference 8

A number of proprietary hydrodesulfurization processes are currently in use. Table F4-34 lists major processes, their frequencies, capacities, and licensors.

Feed to a typical hydrodesulfurization unit may be kerosine, light gas oil, distillate oil, or heavy gas oil. Hydrogen requirements vary with feed type and the severity of the desulfurization process. Kerosine hydrodesulfurization requires about 400 scf hydrogen per barrel feed while heavy gas oils require up to 1700 scf/bbl.

A simplified process diagram of a typical heavy gas oil hydrodesulfurization unit is shown in Figure F4-13. The oil is mixed with make-up and recycle hydrogen, heated, and charged to a fixed bed reactor containing a non-noble metal catalyst (generally nickel or cobalt-molybdenum). The reactions occur essentially in the liquid phase and sulfur and nitrogen in the feed react with hydrogen to form H_2S and NH_3. A hydrogen-rich stream is flashed from the reactor product in a high pressure separator and returned to the reactor. Reactor product flows to a low pressure separator where most of the H_2S, NH_3, and light ends are recovered. The oil product is then steam-stripped or fractionated to remove the remaining impurities.

Product yield varies with the type of feed processed. Licensors of most processes report sulfur-removing capabilities of 90 percent or greater, with product yields ranging from 98-100 volume precent of charge.[2]

TABLE F4-34. HEAVY GAS OIL AND MIDDLE DISTILLATE HYDRODESULFURIZATION PROCESSES

Name of Process	Licensor	No. Units Operating Commercially	Total Capacity
GO-fining	Exxon Research & Engineering Company	23	10^6 b/sd
Gulfing	Gulf Research & Development Co. & Houdry Div. of Air Products & Chemicals, Inc.	6	NA
Hydrodesulfurization Trickle Flow	Shell Development Co.	91	185,000 t/d
Hydrofining	BP Trading Ltd.	49	720,000 b/sd
Hydrofining	Exxon Research & Engineering Co.	225	4 x 10^6 b/sd
RCD Unibon	UOP Process Div. of UOP Inc.	NA	NA

NA - Not available
Source: Reference 2

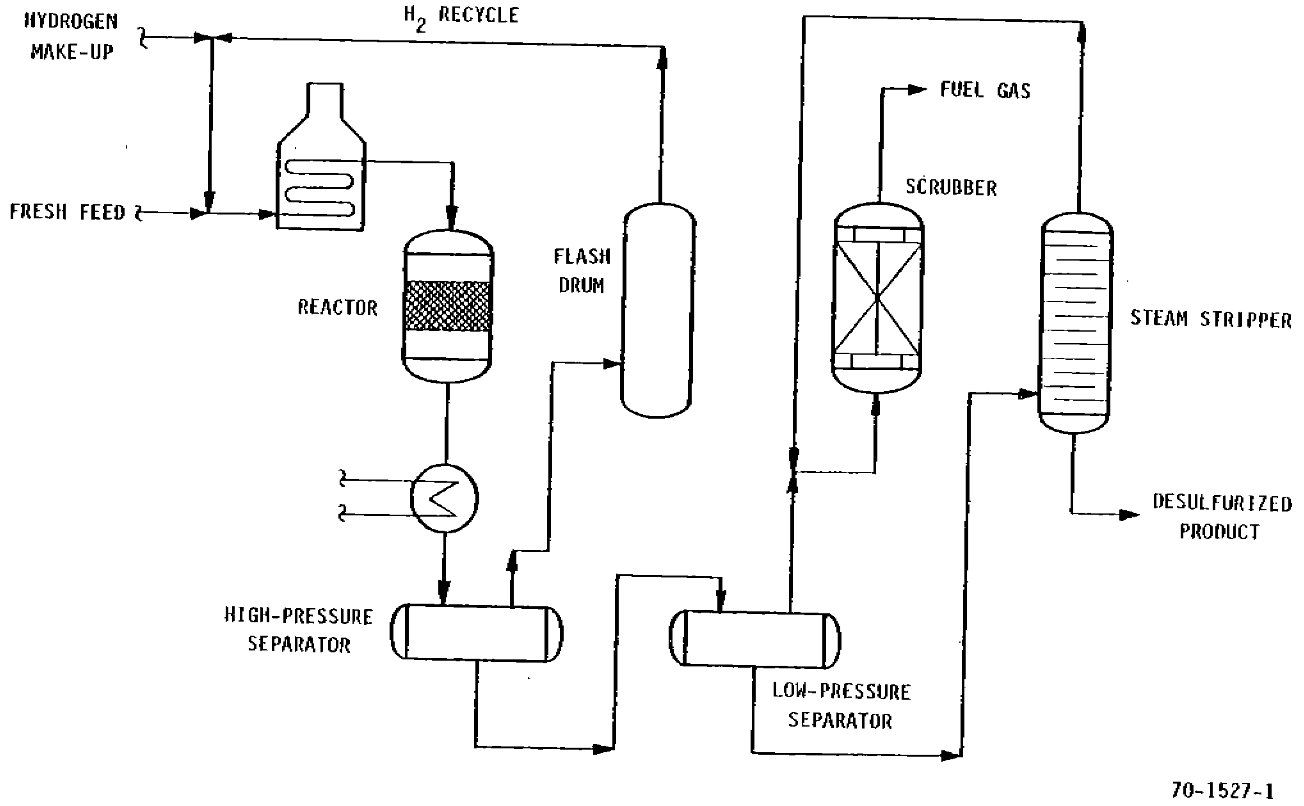

Figure F4-13. Heavy gas oil hydrodesulfurization.

Process conditions, fuel and utility requirements -

Temperature: 390-800°F
Pressure: 500-800 psi
Electricity: 19-365 kWh/bbl
Heater Fuel: 0-70,000 Btu/bbl
Steam: 1-10 lb/bbl
Cooling Water: 160 gal/bbl

Process equipment - The major pieces of process equipment used in heavy gas oil hydrodesulfurization are process heaters, a fixed bed catalytic reactor, high- and low-pressure separator drums, and a steam stripping column. All have been previously described in this appendix.

4.4.1.2 Atmospheric Emissions--

Emissions from hydrorefining processes include:

- Emissions during periodic catalyst regeneration,
- Process heater flue gas, and
- Fugitive emissions.

Emissions from Catalyst Regeneration Operations-- During the hydrorefining process, deposits form on the catalyst which must be removed to restore catalyst activity and selectivity. This regeneration procedure involves burning the deposits by admitting air into the reactors.

During regeneration, large quantities of carbon monoxide and other pollutants may be released. However, regeneration may be required only after several months or even years of operation. Hence, total averaged emissions from this source are generally insignificant.

Process Heater Flue Gas--Emission factors for various pollutants from fired heaters are given in Table F4-35. A typical hydrorefiner will require a process heater to heat the combined hydrocarbon-hydrogen feed to the reactor. Heat input requirements vary, and may be as high as 100,000 Btu per barrel of oil feed.

Total estimated emissions from typical gas oil hydrodesulfurization heaters are also given in Tabel F4-35. These figures are given as pounds of pollutant per thousand barrels of feed using a representative heat input of 60,000 Btu per barrel feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical gas oil hydrodesulfurization unit are given in Table F4-36. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

TABLE F4-35. TYPICAL EMISSIONS FROM GAS OIL HYDRODESULFURIZATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	0.86
- Residual oil		
Grade 4	7	3.0
Grade 5	10	4.3
Grade 6	10(S)+3	4.3(S)+1.3
Sulfur Dioxide[c]		
- Distillate oil	142(S)	60.9(S)
- Residual oil	157(S)	67.3(S)
Sulfur Trioxide[c]	2(S)	0.86(S)
Carbon Monoxide[d]	5	2.1
Hydrocarbons (as CH_4)[d]	1	0.43
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	9.4
- Residual oil[e]	$22+400(N)^2$	$9.4+171(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.29-0.86
Sulfur Oxides (as SO_2)[f]	0.6	0.034
Carbon Monoxide	17	0.97
Hydrocarbons (as CH_4)	3	0.17
Nitrogen Oxides (as NO_2)	120-230	6.86-13.1

[a] Source: Reference 6

[b] Based on a heat input of 60,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE F4-36. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL GAS OIL HYDRODESULFURIZATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	235	205	0.059	13.9 - 12.1
	Light Liquid (VP > 0.1 psia @ 100°F)	208	244	0.024	4.99 - 5.86
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	102	97	0.0005	0.049- 0.051
	Hydrogen Service	101	164	0.018	1.82 - 2.95
	Total	645[a]	710[c]		20.8 - 21.0
Open-End (Sample) Valves	All	-	16[b]	0.005	0.080
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	6(9)	5(7)	0.25	1.75 - 2.25
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	4(5)	2(3)	0.046	0.14 - 0.23
	Total	10(14)[a]	7(10)[b]		1.89 - 2.48
Drains	All	24[a]	-	0.070	1.68
Flanges & Fittings	All	2743[a]	2350[c]	0.00056	1.44 - 1.54
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[a]	3(6)[b]		0.66
					27.7 - 28.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 7

- Actual field source counts conducted during the course of this program, and

- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[7]

The methods used to develop estimates for the number of each source type have been previously described in Section 4.1.1.3 of this appendix.

The source counts listed in Table F4-36 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. The source counts given in Table F4-36 are not necessarily representative of all or even the majority of hydrocracking units.

The estimated composition of fugitive non-methane hydrocarbon emissions from a gas oil hydrodesulfurization unit is given in Table F4-37. These estimates indicate the types of hydrocarbons contributed by sources on a number of streams within the process unit. Additional information about these estimates may be found in Section 2.4 of Appendix D.

4.4.2 Hydrotreating

Hydrotreating processes are generally less severe than hydrorefining processes. Feedstocks for these operations include

TABLE F4-37. ESTIMATED COMPOSITION OF FUGITIVE NON-METHANE EMISSIONS FROM A GAS OIL HYDRODESULFURIZATION UNIT

	Stream			
	Gas Oil	Desulfurized Gas Oil	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - %	22	22	56	100%
Weighted contribution of each component to unit emissions - ppmw				
Benzene	0	0	0	0
Toluene	1	1	0	2
Ethylbenzene	1	1	0	2
Xylenes	5	5	0	10
Other Alkylbenzenes	8	81	0	162
Naphthalene	6	6	0	12
Anthracene	2	2	0	4
Biphenyl	2	2	0	4
Other Polynuclear aromatics	146	146	0	292
n-Hexane	0	0	0	0
Other Alkanes	208756	208756	364000	781512
Olefins	0	0	0	0
Cyclo Alkanes	11000	11000	0	22000
Hydrogen	0	0	196000	196000 1000000

naphtha, straight run distillate, olefins, aromatics and processed lube oil. As in hydrorefining, the hydrotreating process serves to remove sulfur, nitrogen, and metallic compounds from the feed. Hydrotreating is also used to saturate, and thus stabilize, olefins and aromatics, and to polish and dewax lube oil stocks.

The following sections describe three types of hydrotreating processes in current commercial use: naphtha/SR distillate desulfurization; aromatic saturation, and lube oil hydrotreating.

4.4.2.1 Process Description and Technology--

Light Hydrocarbon Hydrodesulfurization--The light hydrocarbon hydrodesulfurization unit is used to desulfurize and denitrogenate the naphtha and straight run (SR) distillate streams from the crude distillation unit. Both sulfur and ammonia must be removed because the light hydrocarbon streams are primary feeds for the isommerization and catalytic reforming units.

A number of proprietary processes in commercial use are listed in Table F4-38. Information describing unit frequency, capacity, and licensor is also included.

Feed to the light distillate hydrodesulfurization unit is typically a mixed stream of light hydrocarbons (sour naphtha, kerosine, diesel oil, and other light straight-run or cracked distillates) with a boiling range of 100-430°F. Make-up hydrogen is usually necessary to produce the desired degree of hydrogenation, although one licensor offers a process based on simultaneous dehydrogenation and desulfurization in which no make-up hydrogen is required.[2]

TABLE F4-38. LIGHT DISTILLATE HYDRODESULFURIZATION PROCESS

Name of Process	Licensor	Number of Commercial Units	Capacity
Autofining	BP Trading Ltd.	4	9,800 b/sd
Distillate Hydrodesulfurization	Institut Francais du Petrole	50	NA
Hydrodesulfurization, Vapor Phase	Shell Development Co.	72	185,000 tpd
Hydrofining	BP Trading Ltd.	49	720,000 b/sd
Hydrofining	Exxon Research & Engineering Co.	225	4 x 10^6 b/sd
Unionfining	Union Oil of California	75	NA

NA = Not available

Source: Reference 2

A schematic diagram of light distillate hydrodesulfurization is shown in Figure F4-14. Gaseous-phase feedstock is mixed with a hydrogen-rich gas and heated to reaction temperature. The mixture is then passed through a fixed-bed reactor containing a non-noble metal catalyst, usually cobalt-molybdenum or cobalt-nickel. In the reactor, organic sulfur and nitrogen compounds react with hydrogen to form H_2S and NH_3. Some cracking of naphthas into lighter fractions may occur as a side reaction.

The hot effluent is cooled in heat exchangers and is then sent to a high pressure separator where hydrogen is flashed and recycled to the feed stream. The liquid from the separator is sent to a fractionator where H_2S, NH_3, and light hydrocarbons boil off and are sent to an amine unit for removal of the acid gases. The remaining liquid product is further fractionated or continues to the reformer or isomerization units. Product yields of 99 percent or greater are reported for most commercial processes.

Process conditions, fuel, and utility requirements - The operating conditions and fuel/utility requirements of light hydrocarbon hydrodesulfurization units vary depending on feedstock composition. However, the following operating ranges are typical for most commercial processes:

Temperature: 600-800°F
Pressure: 300-1000 psi
Electricity: 2.6 kWh/bbl
Heater Fuel: 36,000-75,000 Btu/bbl
Cooling Water: 264 gal/bbl
Steam: 30-90 lb/bbl if steam stripper used, 5 lb/bbl without steam stripper

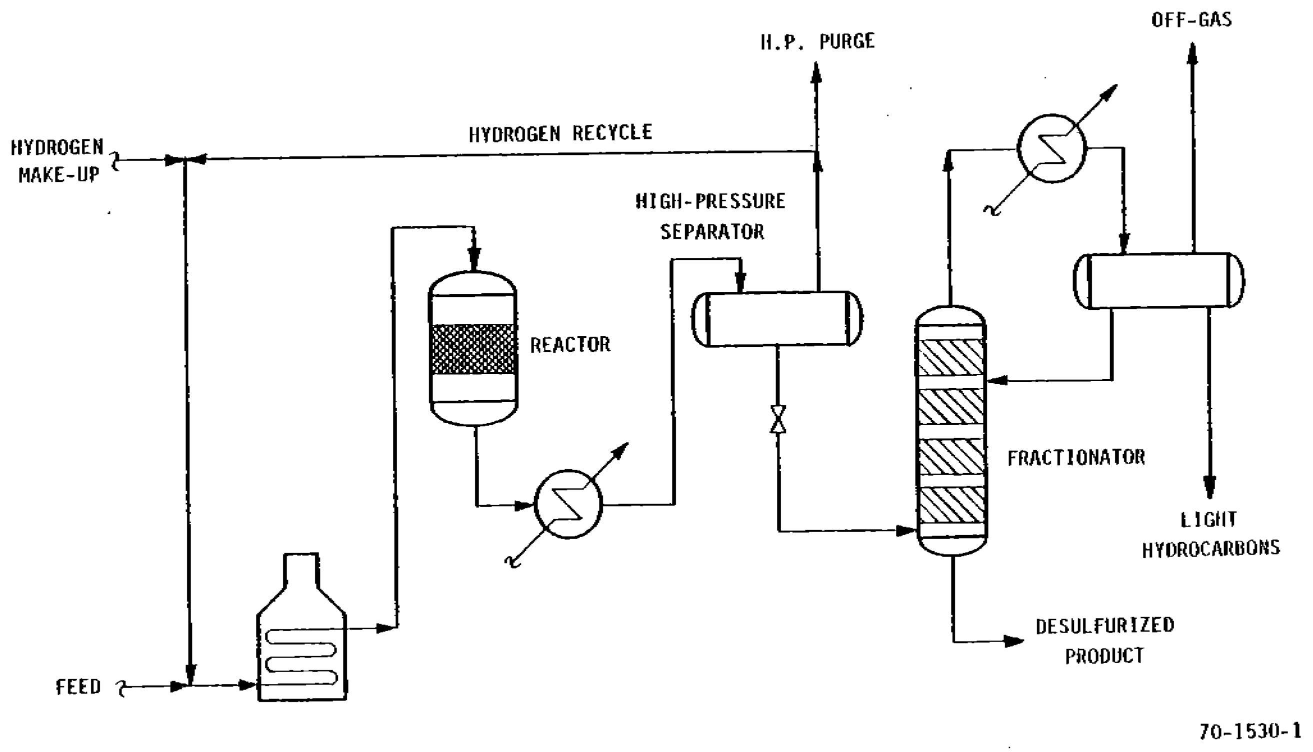

Figure F4-14. Light distillate hydrodesulfurization.

Source: Reference 9

Process equipment - The major pieces of process equipment in light hydrocarbon hydrodesulfurization units include process heaters, a fixed bed catalytic reactor, heat exchangers, a high pressure separator drum, a fractionation column, and (optionally) a steam stripper. This equipment is described in detail in previous sections of this appendix.

Olefin/Aromatics Saturation--The purpose of olefin/ aromatic saturation is to stabilize these compounds by converting aromatics to paraffins and by de-gumming olefins and diolefins. The stabilized products may be used as feedstocks and blending stocks for gasoline, aviation fuels, and turbine fuels. Some processes produce high-purity aromatic streams which may be sent to the aromatics extraction unit.

Several commercial processes are available for saturating olefins and aromatics. These processes are listed in Table F4-39.

Feed to the saturation unit may be pyrolysis naphtha, turbine fuel stocks, olefins, diolefins, and other petroleum streams with high aromatic content. Hydrogen requirements vary with the type of feedstock charged, but generally range between 450-700 scf/bbl charge.

Figure F4-15 is a simplified process diagram for olefin/aromatic saturation. Feed to the unit is combined with make-up and recycled hydrogen and heated in a fired heater. The heated mixture then enters a fixed-bed reactor containing a platinum-, palladium- or nickel-alumina catalyst. Reactor effluent is cooled and separated into liquid and vapor phases in the separator. The resulting vapor phase is recycled to the

TABLE F4-39. PROCESSES FOR OLEFIN/AROMATICS SATURATION

Name of Process	Licensor	Number of Commercial Units	Total Capacity
Arosat	C. E. Lummus	1	NA
DPG Hydrogenation	C. E. Lummus	23	160,000 b/sd
HPN	Engelhard Industries	25	NA
Unisar	Union Oil of California	6	50,000 b/d

NA = Not available

Source: Reference 2

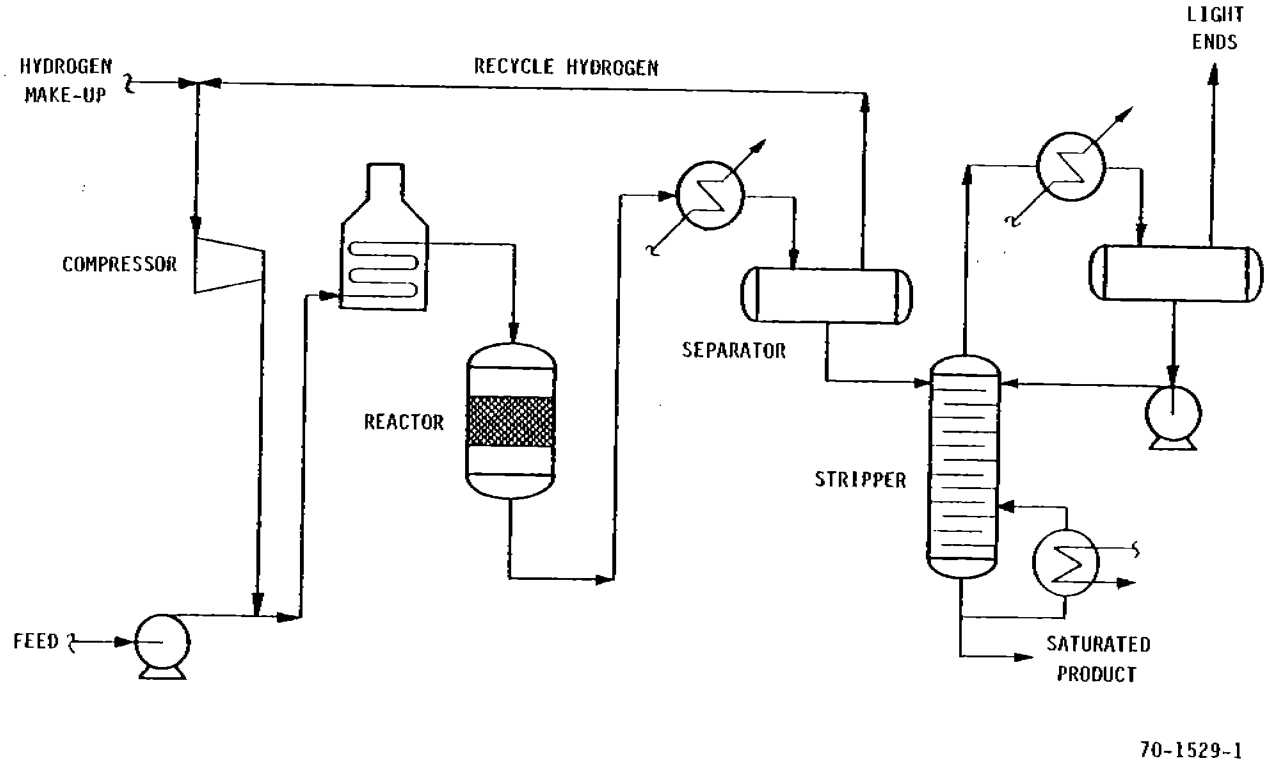

Figure F4-15. Saturation of aromatics/olefins.

Source: Reference 2, p. 155

reactor and the saturated liquid product is sent to the stripper to remove light ends. After stripping, the saturated product may be sent to further processing or blending operations.

Product yields range from 100-104 volume percent feed depending on the feedstock charged. The relative amounts of paraffins, naphthas, and aromatics in the charge also depend on the type of charge.

Process conditions, fuel, and utility requirements -
Temperature: 480-660°F
Pressure: 100-1500 psi
Electricity: 0.5-2.5 kWh/bbl feed
Steam: 12-35 lb/bbl
Fuel: 10^3 Btu/bbl
Cooling Water: 120-680 gal/bbl

Process equipment - The major equipment items in an olefin/aromatic saturation unit are a process heater, a fixed-bed catalytic reactor, a pressurized separator drum, and a steam stripping column. All have been described in detail in previous sections of this appendix.

Lube and Wax Hydrotreating--Lube oil and wax stocks are hydrotreated to improve product quality in several ways: viscosity index improvement, desulfurization, denitrogenation, demetallization, removal of gum-forming compounds, and color improvement. The products of this unit are primarily finished single- or multi-grade lube oils, but gasoline, naphtha, kerosine, furnace oil, and waxes are valuable by-products.

Table F4-40 lists major commercial processes for lube, fuel, and specialty oil hydrotreating and dewaxing.

TABLE F4-40. HYDROTREATING PROCESSES FOR OILS AND WAXES

Name of Process	Licensor	Number of Commercial Units	Total Capacity
Distillate Dewaxing	Mobil Oil Corporation	1	NA
Ferrofining	BP Trading Ltd.	NA	54,200 b/sd
Hydrogen Finishing	Texaco Development Corp.	NA	NA
Lube, Wax, and Specialty Oil Hydrotreating	Institut Francais due Petrole, and Total Companie Francais de Raffinage	10	NA
Lube Oil Hydrotreating	Gulf Research and Development Co.	4	NA
Wax Hydrofinishing	BP Trading Ltd.	1	50 tons/day

NA = Not available

Source: Reference 2

Feed to a lube/wax hydrotreating unit may be either solvent-refined lube oils and waxes, or raw distillates and deasphalted oils. Hydrogen requirements vary from 100-200 scf/bbl charge.

A simplified process diagram for lube oil/wax hydrotreating is shown in Figure F4-16. The oil feed is mixed with make-up hydrogen and charged to a fixed bed reactor. The catalyst is usually either cobalt- or nickel-molybdenum on an alumina base. Reactor effluent flows through high and low pressure separators to remove hydrogen for recycle and light ends, respectively. The product is then charged to a double stage column where it is steam-stripped and vacuum dried.

Product yields are very high, varying with the severity of the process. Table F4-41 lists product yields from a typical lube oil/wax hydrotreating unit.

TABLE F4-41. PRODUCT YIELDS FROM LUBE OIL/WAS HYDROTREATING

Product (Volume % Charge)	Severity	
	Medium	High
C_3-C_5 Hydrocarbons	1.5	3.0
C_6 Furnace Oil	18.9	57.0
Light Lube	4.6	14.4
Light Neutral	24.0	20.5
Heavy Neutral	33.9	11.6
Bright Stock	10.6	-
Slack Wax (4% Oil Content)	13.0	8.0
TOTAL	106.5	114.5

Source: Reference 2, p. 143.

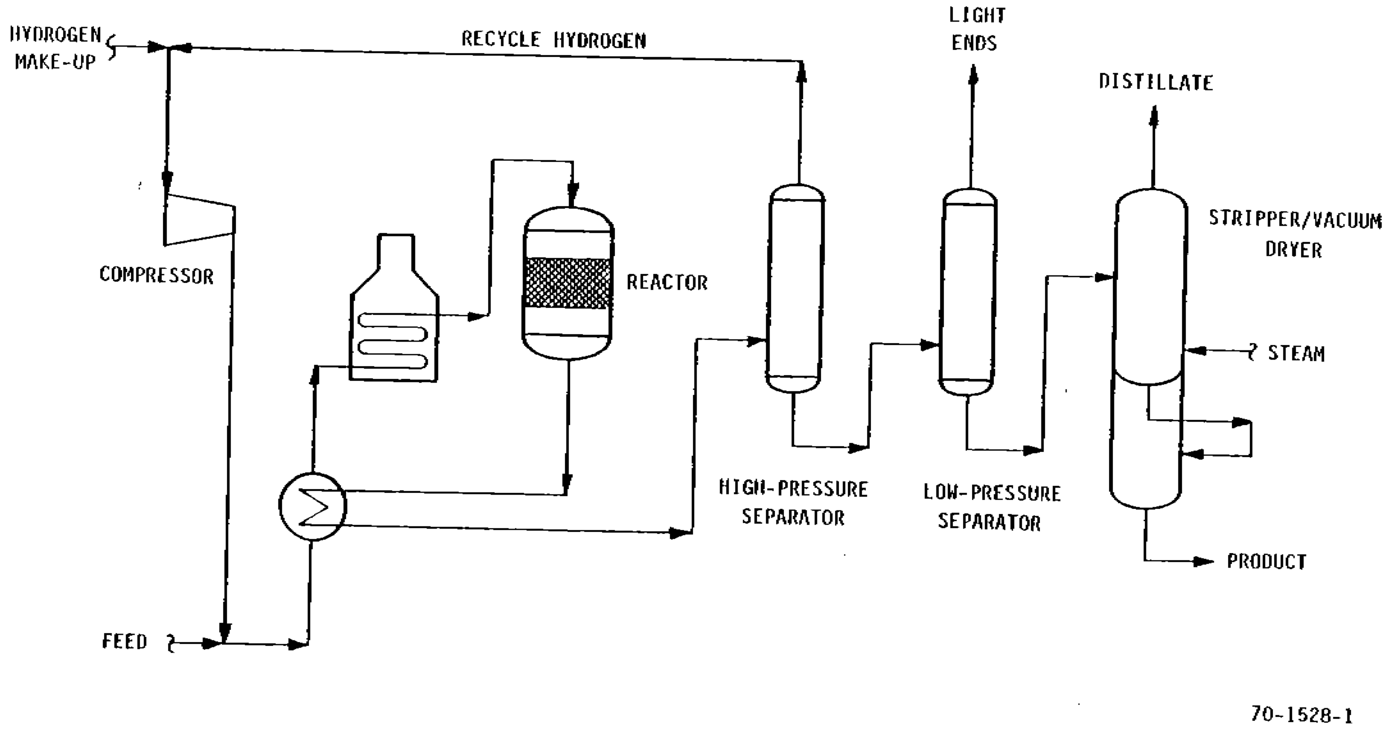

Figure F4-16. Lube oil hydrotreating.

Source: Reference 2, p. 142

Process conditions, fuel, and utility requirements -
Reactor Temperature: 600-750°F
Reactor Pressure: 500-700 psi
Electricity: 2.5 kWh/bbl charge
Steam: 15-30 lb/bbl charge
Heater Fuel: 35,000-140,000 Btu/bbl charge

Process equipment - The major pieces of process equipment in a lube oil/wax hydrotreating unit are a process heater, fixed-bed reactor, high and low pressure separators, and a double stage steam stripping/vacuum drying column. All of this equipment has been described in previous sections of this appendix.

4.4.2.2 Atmospheric Emissions--

Emissions from hydrotreating processes include:

- Emissions during periodic catalyst regeneration,
- Process heater flue gas, and
- Fugitive emissions.

Emissions from Catalyst Regeneration Operations--During hydrotreating processes, deposits form on the catalyst which must be removed to restore catalyst activity and selectivity. The regeneration procedure involves burning the deposits by admitting air into the reactors.

During regeneration, large quantities of carbon monoxide and other pollutants may be released. However, regeneration may be required only after several months or even years of operation. Hence, total averaged emissions from this source are generally insignificant.

Process Heater Flue Gas--Emission factors for various pollutants from fired heaters are given in Table F4-42. A typical hydrotreater will require a process heater to heat the combined hydrocarbon-hydrogen feed to the reactor. Heat input requirements vary, ranging from 35,000-140,000 Btu per barrel of oil feed.

Total estimated emissions from typical hydrotreater heaters are also given in Table F4-42. These figures are given as pounds of pollutant per thousand barrels of feed using a total required heat input of 75,000 Btu per barrel feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical hydrotreating unit are given in Table F4-43. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

TABLE F4-42. TYPICAL EMISSIONS FROM HYDROTREATING UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	1.1
- Residual oil		
Grade 4	7	3.8
Grade 5	10	5.4
Grade 6	10(S)+3	5.4(S)+1.6
Sulfur Dioxide[c]		
- Distillate oil	142(S)	76.1(S)
- Residual oil	157(S)	84.1(S)
Sulfur Trioxide[c]	2(S)	1.1(S)
Carbon Monoxide[d]	5	2.7
Hydrocarbons (as CH_4)[d]	1	0.54
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	12
- Residual oil[e]	$22+400(N)^2$	$12+214(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.36-1.1
Sulfur Oxides (as SO_2)[f]	0.6	0.043
Carbon Monoxide	17	1.2
Hydrocarbons (as CH_4)	3	0.21
Nitrogen Oxides (as NO_2)	120-230	8.6-16.4

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[a] Source: Reference 6

[b] Based on a heat input of 75,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE F4-43. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDROTREATING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	235	226 - 389	0.059	13.3 - 23.0
	Light Liquid (VP > 0.1 psia @ 100°F)	208	378 - 648	0.024	4.99 - 15.6
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	102	0	0.0005	0.0 - 0.051
	Hydrogen Service	101	181 - 312	0.018	1.82 - 5.62
	Total	645[a]	785 - 1349[c]		20.1 - 44.3
Open-End (Sample) Valves	All	-	17 - 29[b]	0.005	0.085- 0.145
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	6(9)	8(11)-16(22)	0.25	2.25 - 5.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	4(5)	0	0.046	0.0 - 0.23
	Total	10(14)[a]	8(11)-16(22)[b]		2.25 - 5.73
Drains	All	24[a]	-	0.070	1.68
Flanges & Fittings	All	2743[a]	2585 - 4465[c]	0.00056	1.44 - 2.50
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[a]	3(6)[b]		0.66
					27.4 - 56.0

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 7

- Actual field source counts conducted during the course of this program, and

- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[7]

The methods used to develop estimates for the number of each source type have been previously described in Section 4.1.1.3 of this appendix.

The source counts listed in Table F4-43 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. The source counts given in Table F4-43 are not necessarily representative of all or even the majority of hydrotreating units.

The estimated composition of fugitive non-methane emissions from a hydrotreating unit is given in Table F4-44. These estimates indicate the types of hydrocarbons contributed by sources on a number of process streams found within the unit. Additional information about these estimates may be found in Section 2.4 of Appendix D.

TABLE F4-44. ESTIMATED COMPOSITION OF FUGITIVE NON-METHANE EMISSIONS FROM A HYDROTREATING UNIT

	Stream			
	Straight Run Naphtha	Desulfurized Naphtha	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - %	47	47	6	100%
Weighted contribution of each component to unit emissions - ppmw				
Benzene	119	119	0	238
Toluene	1232	1232	0	2464
Ethylbenzene	417	417	0	834
Xylenes	763	763	0	1526
Other Alkylbenzenes	7792	7792	0	15584
Naphthalene	688	688	0	1376
Anthracene	2	2	0	4
Biphenyl	295	295	0	590
Other Polynuclear aromatics	7042	7042	0	14084
n-Hexane	18254	18254	0	36508
Other Alkanes	234817	234817	39000	508634
Olefins	0	0	0	0
Cyclo Alkanes	198579	198579	0	397158
Hydrogen	0	0	21000	21000
				1000000

4.4.3 References for Section 4.4

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7. Environmental Protection Agency. Development of Petroleum Refinery Plot Plans. EPA-450/3-78-025. Research Triangle Park, North Carolina, 1978.

8. Ondish, G. F., et al. Save Crude: Feed Resid to FCC. Hydrocarbon Processing, 55(7): 105-108. July 1976.

9. Refinery Process Handbook. Hydrocarbon Processing, 57(9), September 1978.

4.5 CONVERSION PROCESSES

Conversion processes may be characterized as those processes which utilize catalyzed chemical reactions to upgrade certain refinery streams or produce valuable products from less valuable materials. Conversion processes allow refiners to:

- Increase the octane value of gasolines produced within certain refining operations,
- Provide flexibility to control product distribution to meet market requirements,
- "Rebuild" certain light hydrocarbon gases into gasoline, and
- Produce petrochemical feedstocks.

The conversion processes considered here include:

- Catalytic reforming,
- Alkylation,
- Isomerization, and
- Hydrodealkylation.

Catalytic reforming is the process of converting C_6 and heavier paraffins and naphthenes into aromatics. Common feedstocks include straight run gasoline, hydrocracker gasoline, and coker gasoline. The feedstocks are generally hydrotreated to remove sulfur, nitrogen and metallic contaminants which adversely affect the catalyst.

The products include a highly aromatic high octane reformate, and hydrogen. The reformate can be used as a gasoline component, or as a source of aromatics for the production of petrochemicals. The hydrogen can be used for hydrocracking or for other hydrogen consuming processes. The catalytic reforming process is discussed in detail in Section 4.5.1.

Alkylation refers to the chemical combination of isobutane and olefins such as propylene and butylene to produce a high octane material in the gasoline boiling range. This process was originally developed to provide high octane aviation fuel and has continued as a major refining operation due to the continued upward trend of gasoline octane requirements.

The olefin feedstocks for alkylation are generally obtained from the catalytic cracking process. Isobutane sources include:

- Naturally occurring isobutane in crude oil,
- Isobutane produced by hydrocracking processes,
- Isobutane produced by the isomerization of normal butane, and
- Butanes purchased from sources outside the refinery.

Two distinctly different types of alkylation processes are available: sulfuric acid catalyzed processes, and hydrofluoric acid catalyzed processes. Both of these processes are discussed in detail in Section 4.5.2.

Isomerization processes are used by refiners to convert normal paraffins into isoparaffins. The feedstocks most commonly isomerized are butanes, pentanes, and hexanes.

Butane isomerization units are typically used in conjunction with alkylation units as a source of isobutane. In some cases, these units have been constructed with the alkylation process using common distillation equipment.

Pentane and pentane-hexane isomerization units serve to produce isopentane and/or isohexane. The octane ratings of these isoparaffins are considerably higher than their corresponding normal paraffin isomers. The isoparaffins produced may be used as high octane-low boiling range gasoline components. This is particularly important in view of regulations limiting the volatility, aromatics content, and lead content of gasoline. More detailed information on isomerization is included in Section 4.5.3.

Hydrodealkylation is used by some refiners for the preparation of petrochemical feedstocks. The most common use of this process is the dealkylation of toluene and the xylenes to produce more valuable benzene. Other applications include the production of naphthalene from alkyl-naphthalenes. Further information on this process is contained in Section 4.5.4.

An additional conversion process utilized by some refiners is polymerization. Polymerization processes utilize sulfuric or phosphoric acid catalysts to polymerize light olefins such as propylene, butylene, or isobutylene into gasoline boiling range materials. This process, however, appears to have been replaced by alkylation as a means of producing gasoline from light olefins. Hence, further discussion of this process has been omitted.

4.5.1 Catalytic Reforming

Catalytic reforming is one of the most important of all refining process operations. In catalytic reforming, relatively low octane naphthas are converted to highly aromatic, high octane gasoline blending stocks. Modern units are capable of continuous production of reformates with octane ratings over 100 RON clear. This is particularly important in light of continuous increases in the octane ratings required of modern gasoline.

Since its commercial introduction in 1939, reforming capacity has continued to expand rapidly. U.S. reforming capacity now (1979) exceeds 3,700,000 barrels per day.[3]

4.5.1.1 Process Description--

Basically, the reforming operation consists of contacting oil and hydrogen with catalyst in a series of 3 to 6 reactors. Because the overall reaction is endothermic, the mixture must be heated in a fired heater prior to its introduction into each of the reactors.

A flow diagram for a typical semi-regenerative reformer is given in Figure F4-17. As indicated in the diagram, the mixture from the final reactor is cooled and sent to a

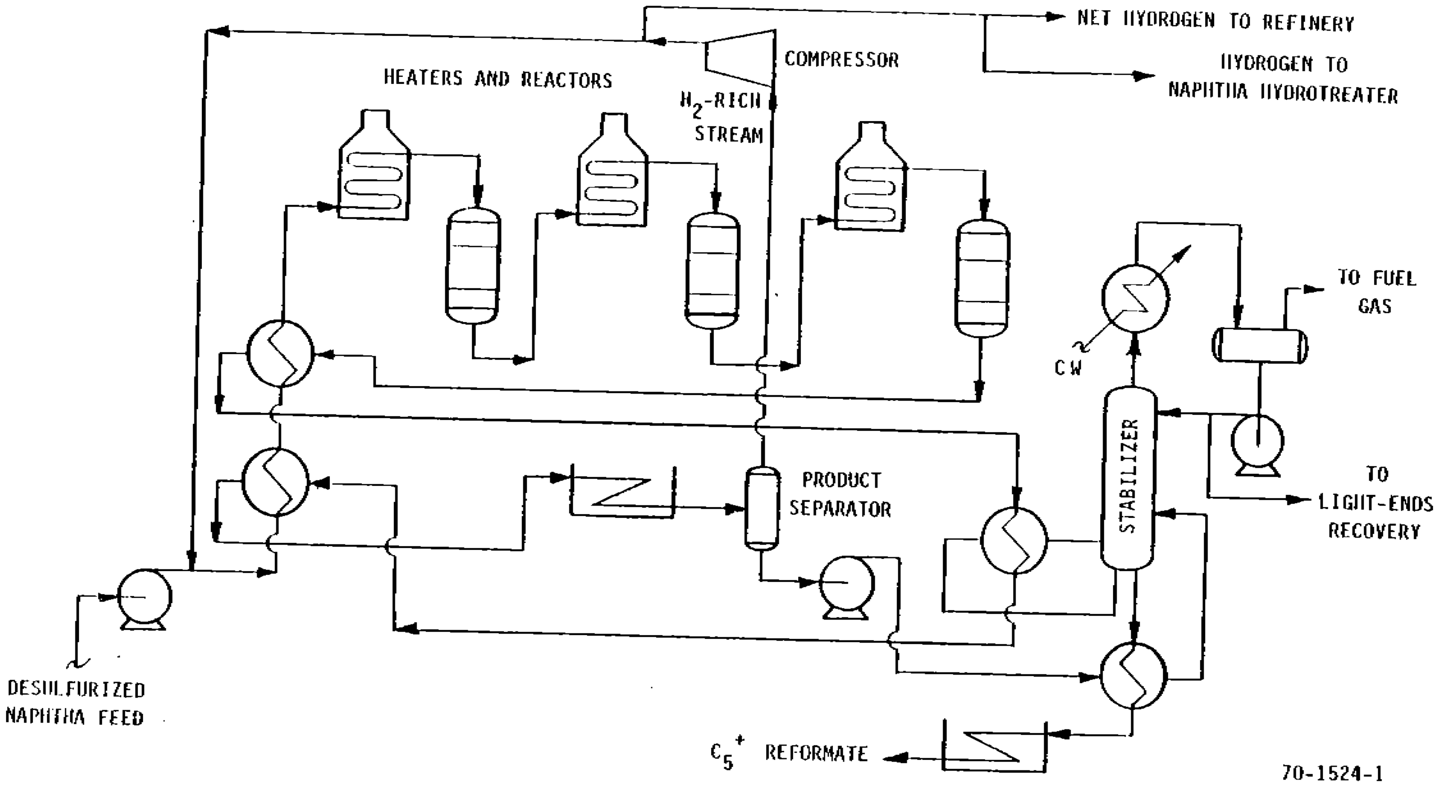


Figure F4-17. Process flow diagram - catalytic reforming.

Source: Reference 7, p. 165

separator where hydrogen produced during the reaction is removed. A portion of this hydrogen is recycled back to the reactors while the remainder is available for use in a variety of hydrogen consuming processes.

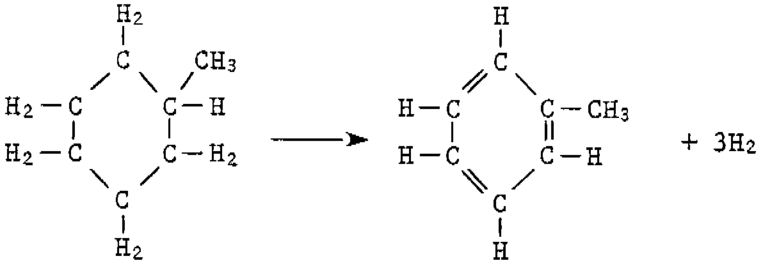
The separator liquid is sent to a stabilizer for separation of light hydrocarbons from the reformate product. The reformate can then be blended into gasoline or processed in an aromatics extraction unit for chemical production.

4.5.1.2 Process Technology--

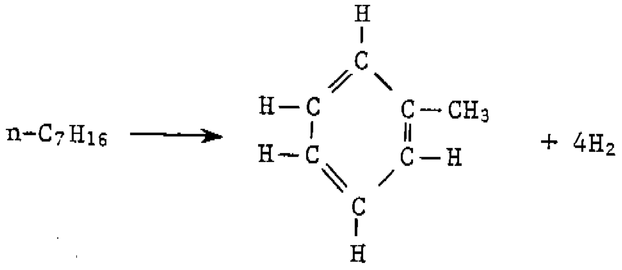
A variety of reactions occur simultaneously during the reforming process. Some of the more important reactions are discussed below.[1,2]

A. Dehydrogenation reactions

1. Dehydrogenation of alkylcyclohexanes to aromatics.

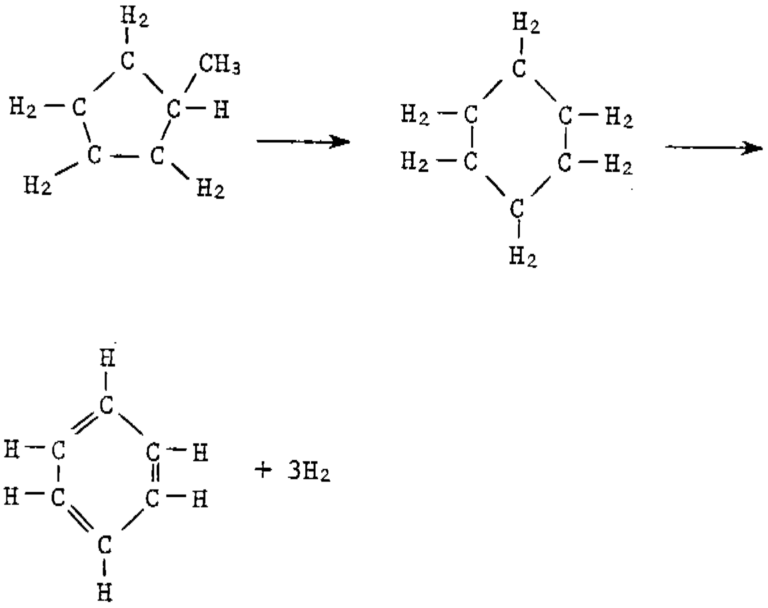


2. Dehydrocyclization of paraffins to aromatics.

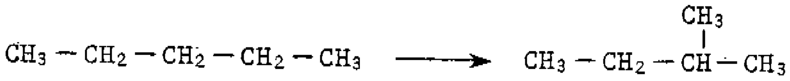


B. Isomerization reactions

1. Isomerization of alkylcyclopentanes followed by dehydrogenation to aromatics.



2. Isomerization of normal paraffins to isoparaffins.



$$CH_3-CH_2-CH_2-CH_2-CH_3 \longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

C. Hydrocracking reactions

$$C_{10}H_{22} + H_2 \longrightarrow C_6H_{14} + C_4H_{10}$$

The dehydrogenation reactions are highly endothermic (800-1000 Btu/lb) and cause a decrease in temperature as the reaction proceeds. Hence, the reaction mixture is reheated prior to entering each of the reactors.[1]

Dehydrogenation reactions are highly desirable in that they produce aromatics. The yield of aromatics is favored by:[2]

- High temperature (increases the reaction rate but adversely affects chemical equilibrium)
- Low pressure (shifts equilibrium in favor of aromatic products)
- Low space velocity (promotes approach to equilibrium)
- Low hydrogen to hydrocarbon mole ratios (shifts equilibrium in favor of aromatics).

The isomerization of normal paraffins to isoparaffins is not as important in terms of raising the product octane as are the reactions producing aromatics. Although the octane numbers of isoparaffins are considerably higher than those of normal paraffins, the equilibrium concentrations of the isoparaffins fall off rapidly with increasing temperature and are quite low at the temperatures used in reforming operations.[2]

The effect of hydrocracking reactions is twofold. Hydrocracking reactions generally improve the octane number of the reformates by breaking up low octane paraffins. However, the cracked products may be light hydrocarbons, thereby reducing the overall yield of gasoline boiling range components. Hydrocracking reactions are favored by high temperature, high pressure, and low space velocity.

In addition to the reactions discussed above, reactions which lead to the formation of coke on the catalyst are also important. Within the reactor, small amounts of aromatic polymers containing naphthalene, anthracene, and heavier compounds are formed. Reactions involving these compounds probably lead to the formation of coke on the catalyst surface. Since coke buildup causes a gradual decrease in catalytic activity, the catalyst must be regenerated periodically.

The formation of coke is enhanced by high temperature and low hydrogen partial pressure. Therefore, the choice of reactor operating conditions is a compromise between high conversion to aromatics with high coke deposition on the catalyst (low pressure operation), and long catalyst on-stream times between regeneration with lower conversion to aromatics (high pressure operation).[1]

<u>Process Types</u>--Catalytic reforming processes can be classified by the method or frequency of catalyst regeneration. Currently, three regeneration schemes are available:[6]

- Cyclic regeneration,
- Semi-regeneration, and

- Continuous regeneration.

Flow diagrams for reformers featuring each of these regeneration techniques are given in Figure F4-18.

Cyclic regeneration processes utilize an extra reactor, called a swing reactor. This allows the reactors to be regenerated, one at a time, without affecting the operation of the unit. Units using this regeneration technique are capable of processing poor quality feedstocks under severe conditions because the catalyst can be regenerated frequently. Regeneration frequencies of one to two reactors per day are typical.[2]

In semi-regenerative processes, all of the reactors are regenerated simultaneously at the end of a cycle which may range from 3-24 months in length.[2] Since long run times are desired, conditions which result in rapid coke formation are avoided. Generally, this requires higher operating pressures with a drop in gasoline yield and octane over that of cyclic regeneration systems. However, this is compensated to a degree because the swing reactor and the more complex piping system needed for cyclic operations are not required.

In comparing the relative merits of these two regeneration schemes, the following generalizations can be made.[6]

These factors favor the semi-regenerative system:

- Octane numbers above 98 RON are not required.
- Minimum plant cost is desired.
- Gasoline and hydrogen have relatively low value compared to LPG and fuel gas.

A. Cyclic Regeneration Scheme

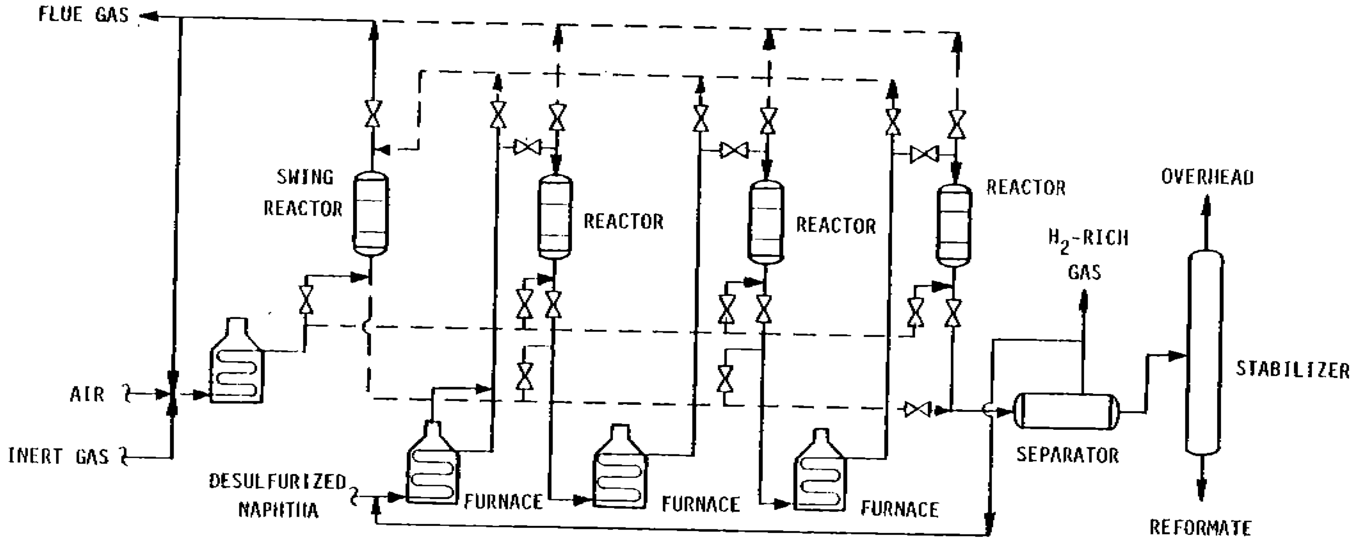


Figure F4-18. Process flow diagram - catalytic reforming.

Source: Reference 7

B. Semi-Regeneration Scheme

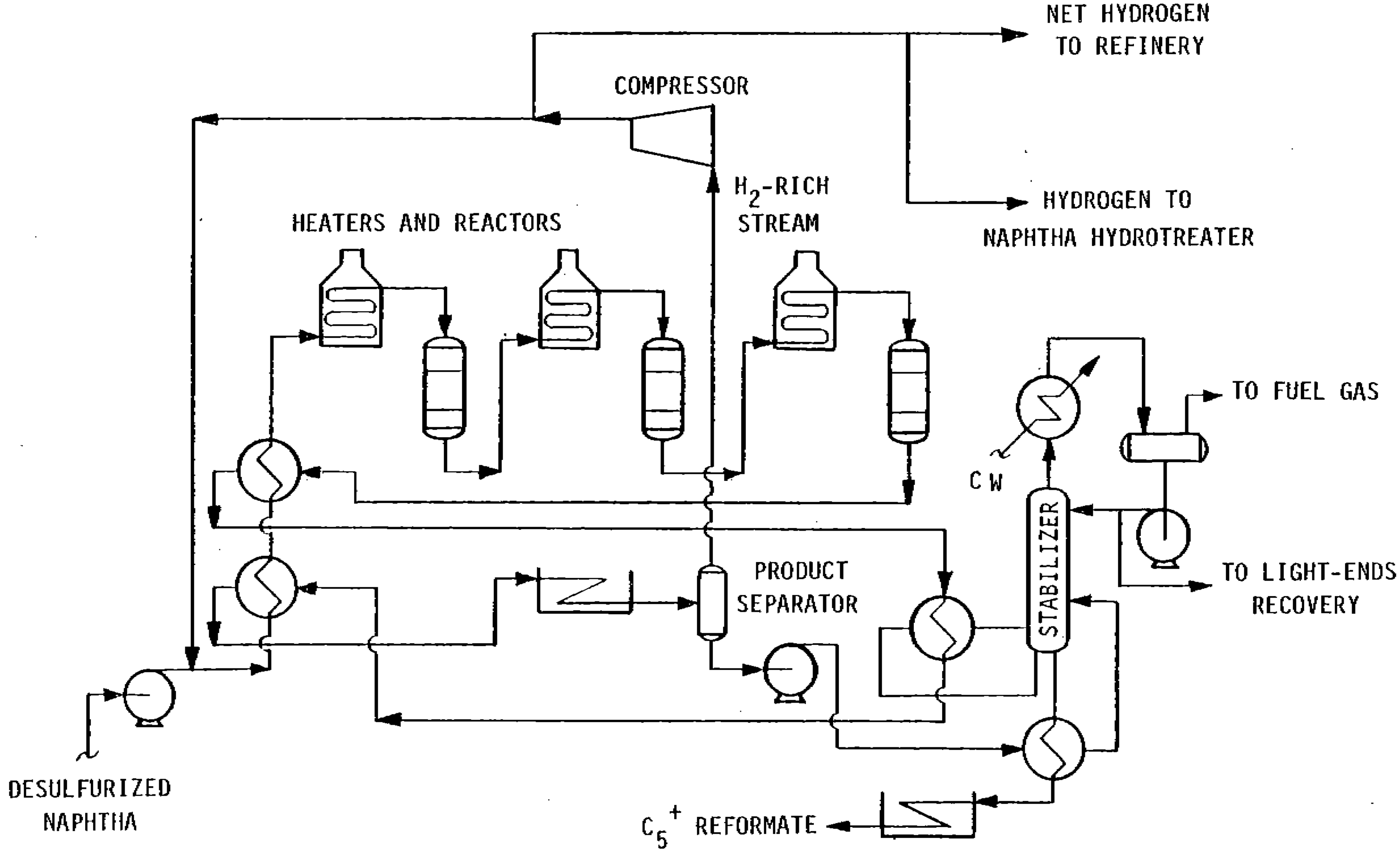


Figure F4-18. Continued.

Source: Reference 7, p. 165

C. Continuous Regeneration Scheme

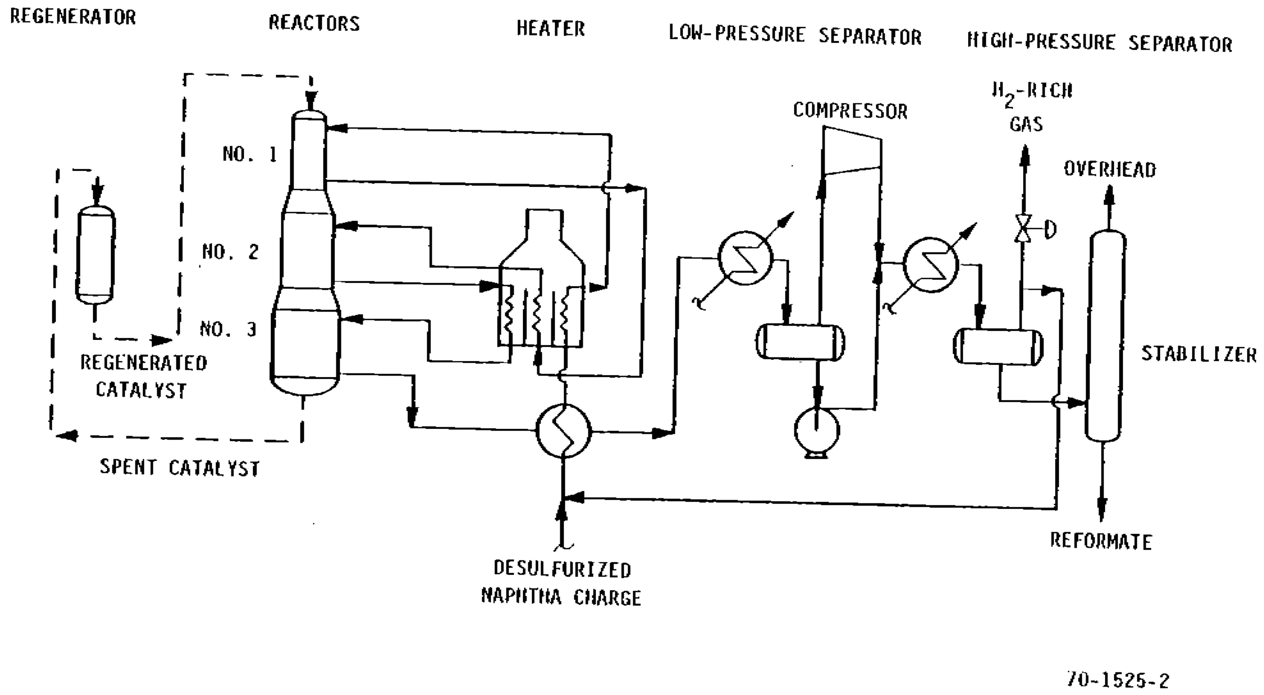


Figure F4-18. Continued

Source: Reference 7

- Small unit size or limited plot space.
- Unit shutdown for catalyst regeneration at periodic intervals is acceptable.
- High quality feeds are available.

Factors favoring cyclic operation include:

- Octane numbers greater than 98 RON clear are desired.
- Larger capacity units.
- Gasoline and hydrogen have high values compared to LPG and fuel gas.
- Poor quality feeds are available.
- Return on investment more important than initial investment.
- Greater operating flexibility.

The introduction of bimetallic catalysts (1968) allowed reformers to be operated at lower pressures (higher severity), particularly semi-regenerative units. Conventional platinum catalysts, which dominated the field through the 1960's, are quite sensitive to coke deposits. Bimetallic catalysts retain their activity and selectivity at higher coke levels and permit operation at lower pressures and lower hydrogen recycle ratios without sacrificing cycle length. The most common bimetallic combination is platinum and rhenium although other combinations are available.[5,6]

The trend toward even higher severity-lower pressure operation led to the development of continuous reforming. A continuous reformer utilizing three reactors is diagrammed in Figure F4-18. Catalyst is continuously withdrawn (in small batches) from the bottom of the third reactor while the unit is in operation. The catalyst is regenerated in a separate regeneration system and returned to the top of the first reactor.

In four reactor systems, the fourth reactor stands beside the stack containing the first three reactors. Catalyst is withdrawn from the bottom of the third and fourth reactors, sent to the regeneration system, and returned to the top of the first and fourth reactors. In four reactor systems, the first three reactors and the fourth reactor contain approximately equal amounts of catalyst.[8]

Desirable features of continuous reforming include:[8]

- Both the reactor and regenerator systems operate continuously and the unit need not be shut down for periodic catalyst regeneration.
- High severity-low pressure operation for maximum product octane is possible since the catalyst activity and selectivity is continuously restored.
- A continuous stream of high purity hydrogen is available to other process units.

- The catalyst is not regenerated within the reactor; hence, both the reactor and regenerator systems can be designed and operated to perform their functions under optimum conditions.

Economical operation at low pressures necessitated some changes in the process flow and mechanical design of the continuous reformer. As indicated in Figure F4-18, the cooled reaction products flow into a low pressure separator where the gas and liquid phases are separated. These two streams are remixed at higher pressure, cooled, and separated in a high pressure separator. Hence, high pressure separation is used in a low pressure process. This increases the hydrogen purity and reduces the amount of light hydrocarbons recycled to the reactors. In addition, the pressure drop across the recycle hydrogen loop was minimized to reduce recycle compressor costs.[8]

One additional feature of the continuous reforming process is that it can be installed without the regeneration facilities as a semi-regenerative process. This substantially reduces initial investment costs. Then, when higher octane products are required, the unit can be converted to continuous operation by installation of regeneration facilities.

Since the initial development of catalytic reforming, many proprietary processes have been offered to the industry. Many of these are available as either cyclic or semi-regenerative processes. However, only UOP and IFP offer continuous processes at present.[8,9]

A breakdown of current reforming capacity by the method of regeneration is given in Table F4-45.

TABLE F4-45. REGENERATION SCHEMES USED FOR U.S. REFORMING CAPACITY

Regeneration Method	Number of Units	Total Capacity, bbl/sd
Semi-regeneration		
Conventional Catalyst	42	522,200
Bimetallic Catalyst	125	2,081,445
Cyclic Regeneration		
Conventional Catalyst	21	687,100
Bimetallic Catalyst	7	236,300
Other[1]		
Conventional Catalyst	3	63,150
Bimetallic Catalyst	3	93,000
	201	3,683,200

[1] Other includes nonregenerative systems, i.e., catalyst replaced by fresh catalyst, and continuous reforming processes.

Source: Reference 3.

Processing Variables--

Feedstock - Catalytic reformer feedstocks are usually saturated (i.e., not olefinic) materials boiling up to a maximum of 375°F. Generally, C_5 and lighter materials are not included in catalytic reformer feeds as only the isomerization reactions lead to octane improvement. Equilibrium concentrations of the isoparaffins are quite low at process temperatures.

The most common feedstock is straight run naphtha. Other feedstocks include hydrocracked naphtha or suitably treated coker naphtha.

The yield of gasoline of a given octane number at given operating conditions depends on the type of hydrocarbons present in the feed. Highly naphthenic feeds, which convert readily to aromatics, are the easiest to reform. Paraffin stocks, however, are more difficult to reform since they depend on the more difficult isomerization, dehydrocyclization, and hydrocracking reactions. Hence, paraffin stocks give lower gasoline yields than naphthenic stocks.

Contaminants in the feed can poison platinum catalysts, reducing gasoline yield and catalyst life. Some of the more important contaminants include sulfur, nitrogen, metals, water, and chlorine.[1]

Hydrogen sulfide is a reversible poison for platinum catalysts, particularly the bimetallics, and causes a decrease in the dehydrogenation and dehydrocyclization activity. Hydrogen sulfide is formed under reactor conditions from sulfur compounds in the feed and can accumulate in the recycle hydrogen stream. Therefore, hydrodesulfurization of the reformer feed to protect catalyst activity is quite common.

Nitrogen compounds in the feed are converted to ammonia under reactor conditions. The ammonia neutralizes the acid sites on the catalyst causing a decrease in isomerization, hydrocracking, and dehydrocyclization activity. Organic nitrogen can be a problem with such feeds as coker naphtha, and high pressure hydrotreating may be required for nitrogen removal.

Extremely low concentrations of metals such as arsenic, lead, and copper can deactivate platinum catalyst. These metals, however, can be removed when desulfurizing the feed as the metals are deposited on the desulfurizer catalyst, which is less sensitive than the platinum catalyst.

The immediate effect of an increase in either the water or chlorine content of the feed is to increase the hydrocracking activity of the catalyst. Thus, the yield of gasoline is reduced due to the formation of C_1-C_4 cracking products. C_1-C_4 products are present as diluents in the recycle gas stream. This reduces the hydrogen partial pressure resulting in increased coke formation on the catalyst. Some water content, however, is necessary as excessive demethylation of substituted aromatics has been reported with water content in the feed of less than 10 ppm.[1]

Some reforming catalysts contain chlorine as the acid function promoter. Excess water, under these conditions, serves to strip chlorine off the catalyst. The effect of this is a net reduction in hydrocracking activity as opposed to an increase in the short term. With this type of catalyst, a balance between the chloride content and water is maintained by adjusting the water content and injecting organic chlorides into the reactor train.[1]

Temperature - Increasing the reactor temperatures can increase product octane by increasing the reaction rates. Typical reactor temperatures range from 850-1000°F. At temperatures below 850°F, the reactions are too slow, while at temperatures greater than 1000°F, hydrocracking reactions become excessive, reducing gasoline yield. In addition, some thermal cracking can occur above this temperature, leading to coke formation on the catalyst.

Space Velocity - The space velocity (vol. feed per hour per vol. catalyst) required to achieve a given severity depends on the hydrocarbon types present in the feed; higher space velocity for naphthenic feeds and lower space velocity for paraffinic feeds. Generally, space velocities in the range of 1.5-3.0 v/hr/v are used for gasoline production.[1]

Pressure - As mentioned previously, a reduction in the reactor pressure increases the yield of high octane aromatics by increasing the aromatic equilibrium concentration. However, coke formation is increased when pressure is reduced since less hydrogen is available to suppress coke formation.

Since the development of the catalytic reforming process, there has been a trend to reduce operating pressures to obtain substantial yield and octane benefits. The early units, utilizing platinum catalysts, showed rapid coke deactivation. These processes were forced to operate at pressures in excess of 500 psig to provide acceptable run lengths. The introduction of bimetallic catalysts resulted in a decrease in the allowable reactor pressure. These catalysts appear to be more effective in dispersing the coke formed during the reaction and retain their activity at much higher coke levels. Thus, semi-regenerative units utilizing bimetallics can retain acceptable run lengths at pressures ranging from 150-200 psig. Cyclic and continuous regenerative units now operate at even lower pressures, ranging from 90-150 psig, due to more frequent regeneration.

Hydrogen/Oil Ratio - The hydrogen to oil ratio changes the hydrogen partial pressure in the reactor, and its effects are therefore related to total pressure. Typical hydrogen/oil ratios range from 2.0-5.5.

A summary of typical operating conditions along with utility information is given in Table F4-46.

TABLE F4-46. OPERATING CONDITIONS FOR CATALYTIC REFORMING

Reactor Pressure, psig	
Semi-regenerative	150-500
Cyclic Regenerative	90-200
Continuous Regeneration	90-200
Reactor Temperature, °F	850-1000
Space Velocity, vol/hr/vol	1.5-3.0
Hydrogen to Hydrocarbon Ratio	2.0-5.5
Hydrogen Recycle Purity, vol. %	80-85
Utilities - per barrel feed	
Power, kwh	5-7
Fuel, 10^6 Btu	0.15-0.32

Source: References 1, 2, 4

4.5.1.3 Process Emissions--

Emission sources from catalytic reformers include:

- Catalyst regeneration operations,
- Process heater flue gas, and
- Fugitive emissions.

Catalyst Regeneration--During the reforming operation, coke is deposited on the catalyst. The rate of coke formation is a function of the type of feedstock and the severity of the operating conditions. This coke must be removed from the catalyst to restore catalytic activity.

The regeneration procedure consists of burning these deposits off the catalyst by injecting air into the reactor. During this process, a flue gas stream is generated which contains carbon monoxide and low concentrations of sulfur and nitrogen oxides. Total mass emissions from regeneration, however, are quite low because only small amounts of coke are produced, and the frequency of regeneration may be low.

Perhaps the highest potential for emissions from regeneration operations occurs with the so-called continuous reformers, since they can be operated at conditions of highest severity. Carbon monoxide emissions from continuous reformers have been estimated at 0.002-0.02 pounds per barrel of fresh feed.[12] Hence, emissions from this source are relatively insignificant.

Process Heaters--Emission factors for various pollutants from fired heaters are given in Table F4-47. A typical reforming unit will require a process heater to heat the feed stream prior to entering each of the reactors. In some cases, one large heater is used for this purpose. In addition, a heater may be required as a stabilizer reboiler. Heat input requirements vary, ranging from 150,000-320,000 Btu per barrel feed.

Total emissions from the reformer heaters are also given in Table F4-47. These figures are given as pounds of pollutant per thousand barrels of fresh feed using a heat input of 200,000 Btu per barrel feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical catalytic reforming unit are given in Table F4-48. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

TABLE F4-47. TYPICAL EMISSIONS FROM CATALYTIC REFORMING UNIT PROCESS HEATERS

	EPA Emission Factor[a] ($lb/10^3$ gal-oil fired) ($lb/10^6$ scf-gas fired)	Total Emissions[b] ($lb/10^3$ bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	2.9
- Residual oil		
Grade 4	7	10
Grade 5	10	14
Grade 6	10(S)+3	14(S)+4.3
Sulfur Dioxide[c]		
- Distillate oil	142(S)	203(S)
- Residual oil	157(S)	224(S)
Sulfur Trioxide[c]	2(S)	2.9(S)
Carbon Monoxide[d]	5	7.1
Hydrocarbons (as CH_4)[d]	1	1.4
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	31
- Residual oil[e]	$22+400(N)^2$	$31+571(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.95-2.9
Sulfur Oxides (as SO_2)[f]	0.6	0.11
Carbon Monoxide	17	3.2
Hydrocarbons (as CH_4)	3	0.57
Nitrogen Oxides (as NO_2)	120-230	22.9-43.8

[a] Source: Reference 11

[b] Based on a heat input of 200,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 $lb/10^3$ gal

[f] Based on sulfur content of 2000 $gr/10^6$ scf

TABLE F4-48. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL CATALYTIC REFORMING UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit: Counts or Estimates From Radian Study	Number of Sources in Process Unit: Counts or Estimates From PES Study[d]	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	180	154 - 291	0.059	9.09 - 17.2
	Light Liquid (VP > 0.1 psia @ 100°F)	391	493 - 938	0.024	9.38 - 22.5
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	43	0	0.0005	0.0
	Hydrogen Service	77	139 - 263	0.018	1.39 - 4.73
	Total	691[a]	786 - 1492[c]		19.9 - 44.4
Open-End (Sample) Valves	All	-	16 - 30[b]	0.005	0.080 - 0.15
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	8(11)-17(24)	0.25	2.75 - 6.00
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	1(2)	0	0.046	0.0 - 0.092
	Total	14(20)[a]	8(11)-17(24)[b]		2.75 - 6.09
Drains	All	49[a]	-	0.070	3.43
Flanges & Fittings	All	2961[a]	2585 - 4935[c]	0.00056	1.45 - 2.76
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[a]	3(6)		0.66
					29.4 - 58.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 10

- Actual field source counts conducted during the course of this program, and

- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025[10]

The methods used to develop estimates for each source type have been previously described in Section 4.1.1.3 of this appendix.

The source counts described in Table F4-48 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Hence, these source counts may not be representative of all or even the majority of reforming units.

The estimated composition of fugitive non-methane hydrocarbon emissions from a catalytic reforming unit is given in Table F4-49. These estimates indicate the types of hydrocarbons emitted by sources on a number of process streams found within the unit. Additional information about these estimates may be found in Section 2.4 of Appendix D.

4.5.2 Alkylation

Alkylation refers to the chemical combination of two hydrocarbon molecules, an olefin and an isoparaffin, to produce higher molecular weight isoparaffins. Typical olefin feedstocks

TABLE F4-49. ESTIMATED COMPOSITION OF FUGITIVE NON-METHANE EMISSIONS FROM A CATALYTIC REFORMING UNIT

	Stream			
	Desulfurized Naphtha	Reformate	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - %	47	47	6	100%
Weighted contribution of each component to unit emissions - ppmw				
Benzene	119	2538	0	2657
Toluene	1232	36519	0	37751
Ethylbenzene	417	15745	0	16162
Xylenes	763	80323	0	81086
Other Alkylbenzenes	7792	152468	0	160260
Naphthalene	688	3478	0	4166
Anthracene	2	0	0	2
Biphenyl	295	0	0	295
Other Polynuclear aromatics	7042	329	0	7371
n-Hexane	18254	11280	0	29534
Other Alkanes	234817	167320	39000	441137
Olefins	0	0	0	0
Cyclo Alkanes	198579	0	0	198579
Hydrogen	0	0	21000	21000
				1000000

consist of butylene or a mixture of propylene and butylene, while the isoparaffin most commonly used is isobutane. The resulting product is a branched isoparaffin containing from six to nine carbon atoms which has a high octane rating. The alkylate product is usually used to upgrade the octane rating of the motor gasoline pool.

The growth of alkylation to its present status as a major refining process is due to the excellent characteristics of the alkylate product. It has a high octane rating, a high heat of combustion, a low vapor pressure, and a desirable boiling range. In addition, the alkylate has good lead susceptibility with low or even negative sensitivity (RON-MON).[14]

The first commercial alkylation unit went onstream in 1939 and by 1946, 59 alkylation units were in operation. These units helped to provide the large quantities of aviation fuel required by the military during World War II. After the war, many of these units were shut down or dismantled because the octane levels required for motor gasoline were not high enough to justify the continued use of this relatively expensive process.[14]

Alkylation capacity began another sharp increase during the Korean War. With ever increasing octane requirements for motor gasoline, alkylation capacity continued to expand. Today, the total U.S. alkylation capacity is in excess of 900,000 barrels per day.[3]

4.5.2.1 Process Description--

Almost all of the commercial alkylation units utilize either sulfuric acid (H_2SO_4) or hydrofluoric acid (HF) as catalysts. The sulfuric acid process was offered to the industry in the late 1930's as a means of utilizing light olefins produced in the thermal and catalytic cracking processes. This early experimental work indicated that the alkylation reactions would proceed in the absence of a catalyst at elevated temperatures and that catalysts other than sulfuric acid (such as hydrofluoric acid or aluminum chloride) could also be used. Successful processes were developed using hydrofluoric acid catalyst and the first commercial unit was built in 1942. The thermal and aluminum chloride processes, however, found only limited commercial acceptance.[14]

The current use of sulfuric and hydrofluoric acid alkylation processes by U.S. refiners is given below in Table F4-50.

TABLE F4-50. U.S. ALKYLATION CAPACITY, 1979

Process	Number of Units	Capacity, bbl/sd
Sulfuric Acid Alkylation	61	522,100
Hydrofluoric Acid Alkylation	66	384,100
	127	906,200

Source: Reference 3

4.5.2.2 Process Technology

Sulfuric Acid Alkylation--Process flow diagrams for two typical sulfuric acid alkylation units are given in Figures F4-19 and F4-20. The olefin feed, recycle and makeup isobutane, and acid are mixed within a specially designed reactor. In the reactor, the olefin and isobutane combine to form higher

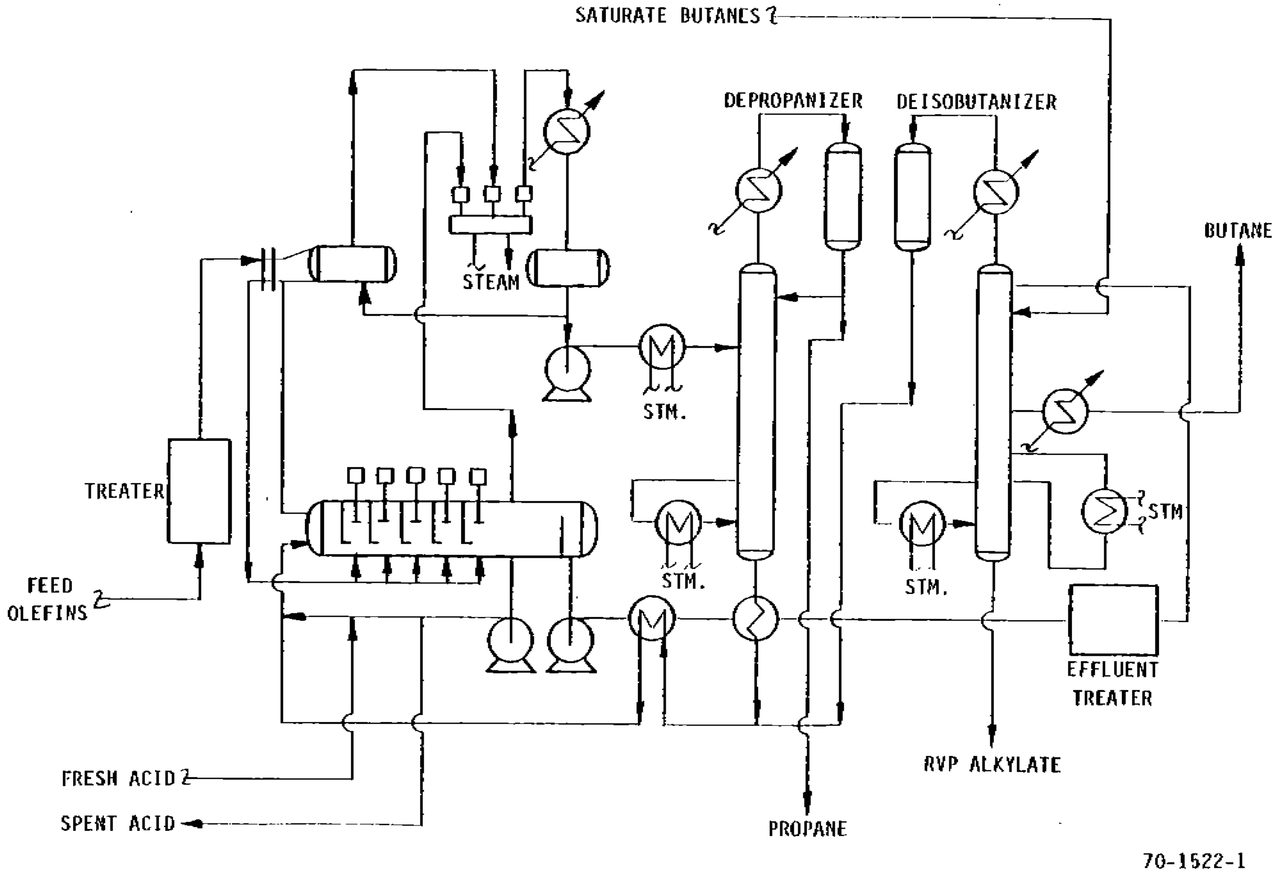


Figure F4-19. Process flow diagram - H_2SO_4 alkylation, cascade auto-refrigeration system.

Source: Reference 18, p. 69

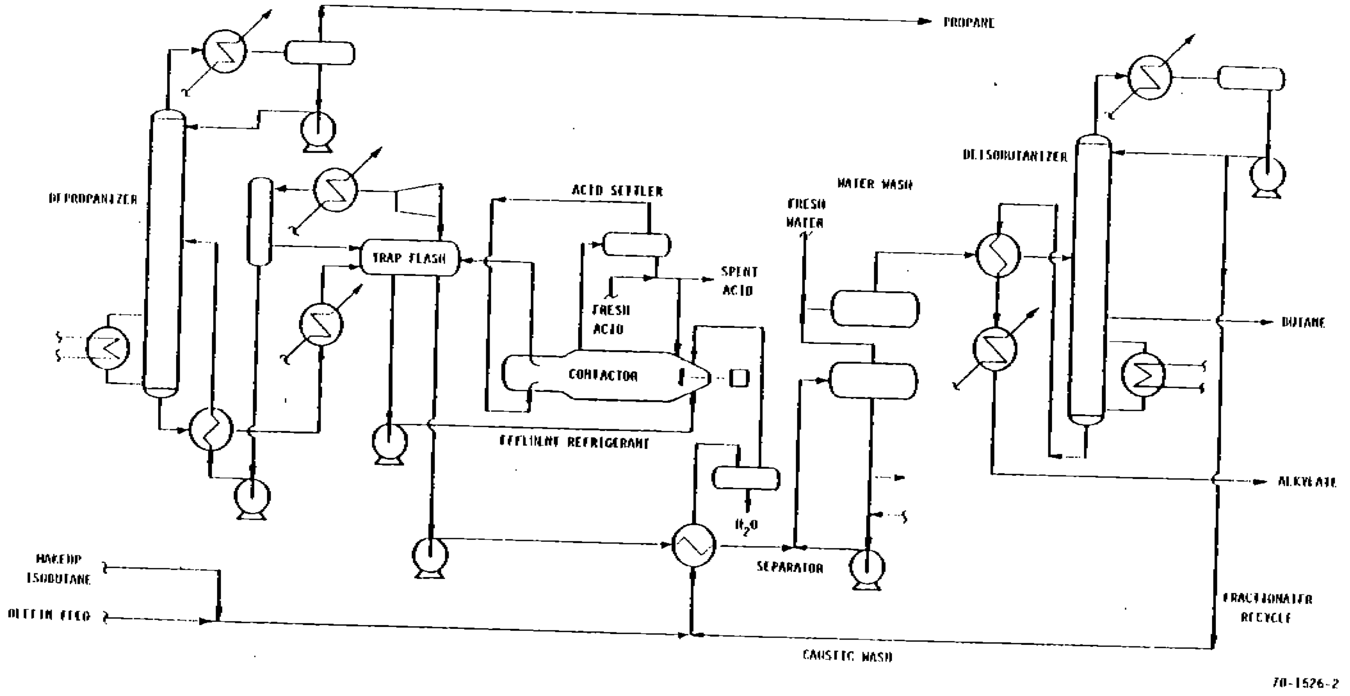


Figure F4-20. Process flow diagram - H_2SO_4 alkylation, Stratco effluent refrigeration system.

Source: Reference 18, p. 68

molecular weight isoparaffins. The contents of the reactor are thoroughly agitated to promote contact between the hydrocarbon phase and the acid catalyst. The emulsion is then sent to an acid settler where the hydrocarbon and acid form separate phases. The hydrocarbon phase is caustic treated and/or water washed and charged to a deisobutanizer for fractionation into an isobutane recycle stream, a normal butane stream, and the alkylate product. Part of the acid phase is returned to the reactor while the remainder is removed from the system as spent acid. In some cases, this acid is regenerated and returned to the system.

Reactor design - The sulfuric acid alkylation reactor must be designed to perform several important functions including:

- Removal of heat generated by the reaction, and
- Maintenance of a high isobutane to olefin ratio.

The heat of reaction ranges from 270-360 Btu per pound of alkylate. This heat must be removed from the reactor to maintain the desired reactor temperature. High isobutane to olefin ratios are important in order to minimize side reactions such as the polymerization of the olefins.[15]

Several types of reactors have been designed to meet these requirements. And, the two most prevalent designs are the Kellogg auto-refrigerated or cascade reactor and the Stratco stirred contactor. These are shown in Figures F4-19 and F4-20.

In the cascade system, a dilute olefin concentration is obtained by splitting the olefin feed into a number of parallel streams. Each stream is fed to a separate reactor compartment, each with its own mixer. The isobutane-acid mixture flows in series from one reactor compartment to the next and ends up in the acid settler. This flow scheme provides the highest effective isobutane concentration for the entire reactor.

Low reactor temperatures are maintained by allowing a portion of the reactor contents to vaporize, thus removing heat from the reaction mixture. The vapors are compressed and charged to a depropanizer to prevent propane from accumulating within the system. Butanes from the depropanizer bottoms are combined with recycle isobutane from the deisobutanizer and returned to the reactor.[14]

The Stratco system utilizes external cooling to remove heat generated during the reaction. The reactor contains a tube bundle similar to that of a heat exchanger. The reactor contents are mixed and circulated around the tubes by an internal axial flow impeller.[15]

The hydrocarbon phase from the acid settler is passed through the tube bundle within the reactor. Much of the isobutane is allowed to flash, dropping the temperature of this stream some 20-30°F. And, heat generated within the reactor is removed by heat exchange with this stream. The isobutane vapors are compressed, depropanized, and returned to the reactor along with isobutane from the deisobutanizer.[3,14]

Both of the above reactor systems maintain high isobutane to olefin ratios to prevent side reactions. In the cascade system, the olefin feed is split into several streams. Each stream is introduced into a separator reactor compartment which keeps the olefin concentration low during the entire reaction sequence. In the Stratco system, the olefin feed is rapidly dispersed by the mixer. None of the isobutane in the reactor need be vaporized for cooling. Hence, the isobutane concentration remains high.

Process variables - The most important process variables in sulfuric acid alkylation are reaction temperature, acid strength, isobutane concentration, and olefin space velocity.[2]

The reaction temperature is usually kept between 35-55°F. At lower temperatures, sulfuric acid becomes so viscous that good mixing in the reactor and subsequent phase separation of the emulsion become very difficult. At higher temperatures, polymerization of the olefins causes yields to decrease.[2]

The highest quality alkylate is obtained using acid strengths of 93-95 percent by weight. A decrease in acid strength lessens its catalytic activity and a decrease in product octane results.

The isobutane concentration is usually expressed as the isobutane to olefin ratio. High isobutane to olefin ratios increase the octane of the alkylate, minimize the number of side reactions, and decrease the level of acid consumption. The external isobutane to olefin ratio generally ranges from 5:1 to 15:1. However, internal ratios may reach as high as 1000:1 in well mixed reactors.[2] Units with higher external isobutane to olefin ratios require more investment and consume more utilities. These costs are associated with the increased stream flows requiring larger compressors, lines, and fractionation systems.

In general, the lower the olefin space velocity, the higher the octane of the alkylate. Lower space velocity can also reduce acid consumption and decrease the amount of high boiling hydrocarbons produced by side reactions. Space velocities for sulfuric acid alkylation range from 0.1-0.6 v/hr/v.[2] A summary of sulfuric acid alkylation process conditions along with utility requirements are given in Table F4-51.

Hydrofluoric Acid Alkylation--A flow diagram for a typical hydrofluoric alkylation unit is given in Figure F4-21. Olefin feed (C_3-C_4) and isobutane are mixed with acid within a specially designed reactor. The resulting emulsion is sent to an acid settler for separation of the hydrocarbon and acid phases. As is the case with sulfuric acid alkylation, the heat produced by the reaction must be removed from the reactor to maintain the desired temperature. And, the method of heat removal depends on the reactor design.[17]

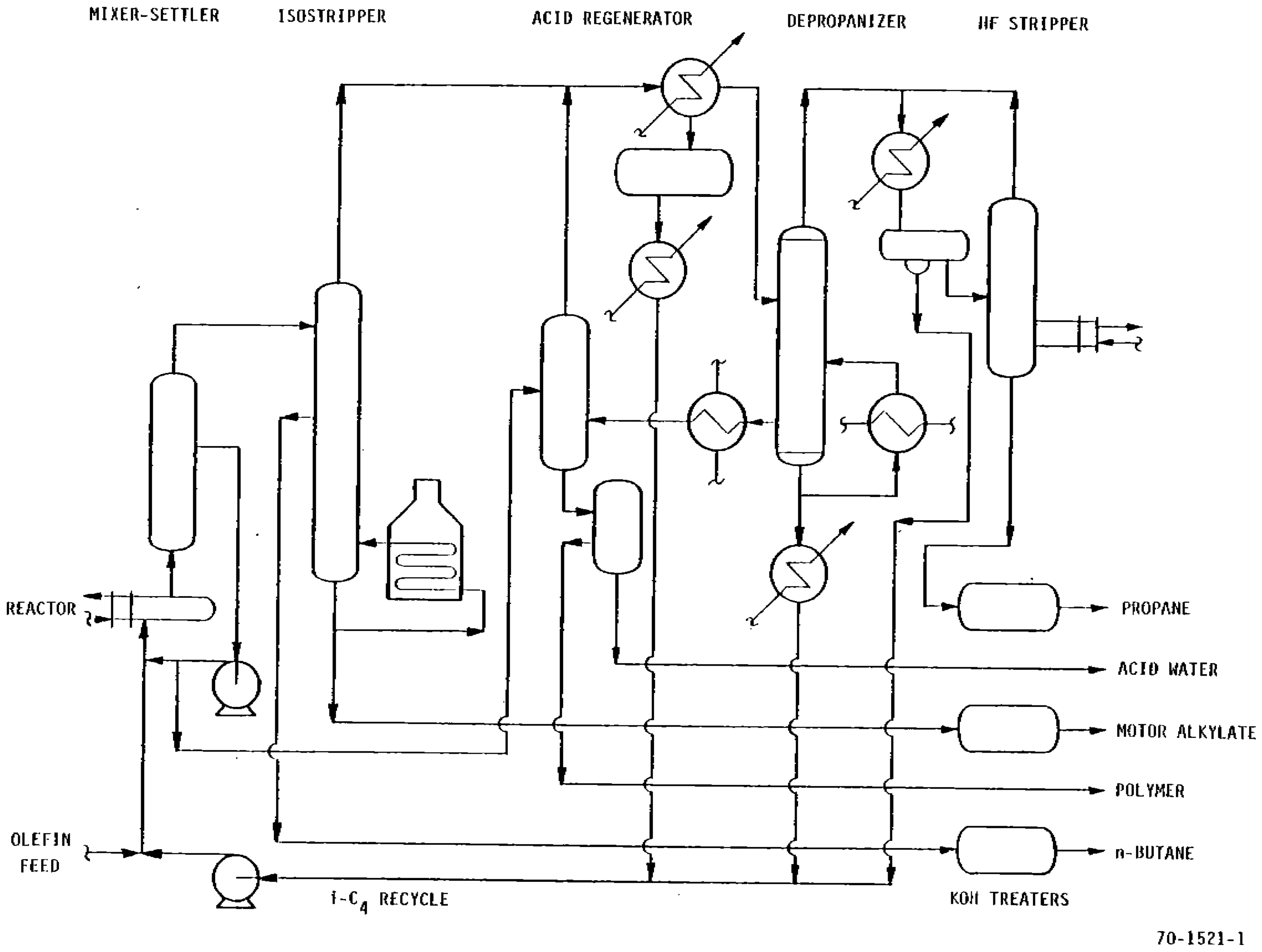


Figure F4-21. Process flow diagram - HF alkylation.

Source: Reference 18, p. 67.

TABLE F4-51. OPERATING INFORMATION FOR SULFURIC ACID ALKYLATION

Isobutane Concentration	
Vol. % in reaction zone	40 - 80
External ratio to olefins	3-12:1
Internal ratio to olefins	50-1000:1
Olefin Concentration	
Total hydrocarbon contact time, min.	20 - 30
Olefin space velocity, v/hr/v	0.1 - 0.6
Reactor Temperature, °F	35 - 60
Sulfuric Acid Concentration, wt %	88 - 95
Acid in Emulsion, wt %	40 - 60
Reactor Pressure	
Stratco contactor system, psig	>50
Kellogg cascade system, psig	5 - 15
Utility Data - per bbl total alkylate	
Steam, lb	300 - 400
Power, kwh	2.5 - 5.0
Chemical Requirements - per bbl total alkylate	
H_2SO_4, lb	18 - 30
Caustic, lb	0.2

Source: References 1, 2, 4, 18

The hydrocarbon phase in the settler contains the alkylate product, excess isobutane, and a small amount of acid. This mixture is sent to an isostripper for fractionation into a recycle isobutane stream and the alkylate product. As indicated in Figure F4-21, field butanes (a mixture of butane isomers) can also be charged to the isostripper. Hence, outputs from the isostripper include an isobutane overhead stream, a normal butane stream, and the alkylate bottoms product.[16]

The normal butane stream is withdrawn from the isostripper as a vapor sidecut. In addition to removing normal butane from the system, removing the butane in this manner provides control over the vapor pressure of the alkylate product.[16]

A portion of the isostripper overhead is sent to a depropanizer to prevent accumulation of propane within the system. The depropanizer overhead contains a small amount of acid. This acid is removed in an HF stripper and returned to the reactor.[16]

Most of the acid phase in the acid settler is recycled back to the reactor. However, a slipstream of acid from the settler is sent to an acid regenerator to effect separation of the acid from water which enters with the feed and polymers which are formed in small volumes in the reactor. The column produces reconstituted acid as an overhead product which is returned to the reactor. The bottoms product, containing the polymer and water, is commonly burned as fuel.[2]

Corrosion in HF alkylation is largely iron fluoride deposition and stress corrosion. Hydrogen fluoride attacks the slag formations in welds, and process vessels must be stress relieved. Any part of the plant which is in direct contact with HF is made of monel metal.[1] An additional corrosion prevention method is the dehydration of the olefin and isobutane feeds over a solid bed desiccant. This operation reduces the water in the feed to less than one percent.

Defluorination of the alkylate product can be accomplished by proper design of the isostripper reboiler. The alkylate is passed through the tubes of a fired heater and the concentration of combined fluorides decreases, often to less than 10 ppm.

Reactor design - Most of the HF units presently in operation have been designed by either UOP Inc. or Phillips Petroleum Co. The reactors designed by UOP are similar to shell and tube heat exchangers. Cooling water flows inside the tubes to remove the heat of reaction. Mixing of the emulsion is accomplished by using an external recirculation pump to force the mixture through the reactor.[15]

The reactors designed by Phillips can be described as vertical lift, plug flow reactors. Hydrocarbon feed enters the bottom of the vertical tube reactor through a jet-eductor device and is contacted with acid from an acid cooler. The jet-eductor helps to mix the hydrocarbon and acid phases. The mixture flows upward to a settler for separation of the acid and hydrocarbon phases. The settled acid flows downward to the acid cooler and is remixed with fresh hycrocarbon. Acid circulation in this system is promoted by the hydrocarbon jet-eductor and by the gravity differential between the HF acid recycle leg and the acid-hydrocarbon mixture in the reactor tube. In this design, an acid recirculation pump is not necessary.[2,15]

Process variables - The important variables in hydrofluoric acid alkylation include the isobutane concentration, the reactor temperature, and the acid strength. High isobutane concentrations are required to produce high octane alkylate while minimizing side reactions.

The reactor temperatures used in HF alkylation are generally between 70-100°F. The effects of temperature, however, are not as critical as those encountered in sulfuric acid alkylation.[2]

In hydrofluoric acid alkylation, the highest octane alkylate is obtained when using acid concentrations of 86-90 percent by weight. In commercial operations, acid concentrations range from 83-92 percent with less than one percent water.

A summary of hydrofluoric acid alkylation operating conditions and utility requirements given in Table F4-52.

TABLE F4-52. OPERATING INFORMATION FOR HYDROFLUORIC ACID ALKYLATION

Isobutane Concentration	
Vol % in reaction zone	30 - 80
External ratio to olefins	3-12:1
Hydrocarbon Contact Time, min	8 - 20
Reactor Temperature, °F	60 - 120
Hydrofluoric Acid Concentration, wt %	83 - 92
Acid in Emulsion, wt %	25 - 80
Utility Data - per barrel total alkylate	
Power, kwh	3 - 7
Fuel, 10^6 Btu	0.3 - 1.1
Chemical Data - per barrel total alkylate	
Acid, lb	0.1 - 0.5
Caustic, lb	0.1 - 0.2

Source: References 1, 2, 4, 18

4.5.2.3 Process Emissions--

The alkylation process is a closed system; that is, there are no process vents to the atmosphere. The only air emissions are those associated with process heaters and fugitive emissions from process equipment and fittings.

Process Heaters--Emission factors for various pollutants from fired heaters are given in Table F4-53. Typically, an HF alkylation unit will require a process heater. It is used as a reboiler for the main fractionator. Heat input requirements vary, ranging from 300,000 to 1,100,000 Btu per barrel of total alkylate.[4,18]

Total emissions from the alkylation heater are also given in Table F4-53. These figures are given as pounds of pollutant per thousand barrels of total alkylate using a heat input of 360,000 Btu per barrel total alkylate.[12]

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pump seals, compressor seals, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical sulfuric acid alkylation unit are given in Table F4-54. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

TABLE F4-53. TYPICAL EMISSIONS FROM ALKYLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of total alkylate)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	5.1
- Residual oil		
Grade 4	7	18
Grade 5	10	26
Grade 6	10(S)+3	26(S)+7.7
Sulfur Dioxide[c]		
- Distillate oil	142(S)	365(S)
- Residual oil	157(S)	404(S)
Sulfur Trioxide[c]	2(S)	5.1(S)
Carbon Monoxide[d]	5	13
Hydrocarbons (as CH_4)[d]	1	2.6
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	57
- Residual oil[e]	$22+400(N)^2$	$57+1030(N)^2$
Gas Fired Heaters		
Particulates	5-15	1.7-5.1
Sulfur Oxides (as SO_2)[f]	0.6	0.21
Carbon Monoxide	17	5.8
Hydrocarbons (as CH_4)	3	1.0
Nitrogen Oxides (as NO_2)	120-230	41.1-78.9

[a] Source: Reference 11

[b] Based on a heat input of 360,000 Btu/bbl of total alkylate with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE F4-54. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL SULFURIC ACID ALKYLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[d]		
Valves	Gas/Vapor	274	429 - 719	0.059	16.2 - 42.4
	Light Liquid (VP > 0.1 psia @ 100°F)	403	636 - 1067	0.024	9.67 - 25.6
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0	0	0.0005	0.0
	Hydrogen Service	0	0	0.018	0.0
	Total	677[a]	1065 - 1786[c]		25.9 - 68.0
Open-End (Sample) Valves	All	-	26 - 30[b]	0.005	0.13 - 0.15
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	13(18)-23(32)	0.25	4.50 - 8.00
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0(0)	0(0)- 0(0)	0.046	0.0
	Total	13(18)[a]	13(18)-23(32)[b]		4.50 - 8.00
Drains	All	41[a]	-	0.070	2.87
Flanges & Fittings	All	2407[a]	3525 - 5875[c]	0.00056	1.35 - 3.29
Relief Valves	All	6[c]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0	0(0) - 2(4)	1.4	0.0 - 5.60
	Hydrogen	0	0(0) - 0(0)	0.11	0.0
	Total	0	0(0) - 2(4)[b]		0.0 - 5.60
					35.9 - 89.1

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 10

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025[10]

The methods used to develop estimates for each source type have been previously described in Section 4.1.1.3 of this Appendix.

The source counts presented in Table F4-54 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Thus, the number of sources presented in Table F4-54 may not be representative of all or even the majority of alkylation units.

The estimated composition of fugitive non-methane hydrocarbon emissions from an alkylation unit is given in Table F4-55. These estimates indicate the types of hydrocarbons contributed by sources on a number of process lines within the unit. Additional information about these estimates may be found in Section 2.4 of Appendix D.

TABLE F4-55. ESTIMATED COMPOSITION OF FUGITIVE NONMETHANE HYDROCARBON EMISSIONS FROM AN ALKYLATION UNIT

	Stream				
	LPG Olefins	LPG	H_2SO_4	Alkylate	Totals
Estimated percentage of emissions attributed to each stream - %	24	35	0	41	
Weighted contribution of each component to unit emissions - ppmw					
Benzene	0	0	0	0	0
Toluene	0	0	0	0	0
Ethylbenzene	0	0	0	0	0
Xylenes	0	0	0	1	1
Other Alkylbenzenes	0	0	0	1	1
Naphthalene	0	0	0	0	0
Anthracene	0	0	0	0	0
Biphenyl	0	0	0	0	0
Other Polynuclear aromatics	0	0	0	1	1
n-Hexane	0	0	0	39	39
Other Alkanes	96000	350000	0	409572	855572
Olefins	144000	0	0	381	144381
Cyclo Alkanes	0	0	0	5	5
					1000000

4.5.3 Isomerization

Isomerization processes are used to convert normal paraffins into isoparaffins. The value of this type of processing is indicated in Table F4-56, which is a listing of the octane number of various light hydrocarbons. In general, the octane numbers of the isoparaffins are considerably higher than those of the normal paraffins.

TABLE F4-56. OCTANE NUMBERS OF PARAFFIN HYDROCARBONS

Paraffin Hydrocarbon	RON Clear	MON Clear	RON 3 cc TEL	MON 3 cc TEL
n-butane	94.0	89.1	104.1	104.7
Isobutane	102.1	97.0	118.3	-
n-pentane	61.7	61.3	84.7	83.6
Isopentane	92.6	90.3	103.5	106.9
n-hexane	34.0	25.0	65.3	63.5
3-methylpentane	74.5	74.0	92.3	92.6
2-methylpentane	73.4	72.9	92.2	92.4
2,3-dimethylbutane	103.5	94.3	112.0	109.7
2,2-dimethylbutane	92.3	92.9	103.4	114.6

Source: References 1, 20

4.5.3.1 Process Description--

The isomerization process was originally developed and used to provide isobutane for the alkylation process. Catalytic cracking processes provided an abundant source of olefins, but the amount of isobutane present in refinery streams was insufficient to meet alkylation feed requirements. Consequently, isomerization was used to convert normal butane to isobutane. Alkylation and isomerization processes helped to provide the large quantities of high octane aviation fuel required during World War II.[20]

The isomerization of pentane and hexane to their isomers has become increasingly important for a number of reasons. Until recently, refiners have had little reason to isomerize C_5/C_6 streams because the octane of these materials could be significantly improved with the addition of lead compounds. However, with the reduction in allowable lead content and increasing octane requirements for modern gasolines, some refiners have turned to isomerization as a means of utilizing these low octane materials.[21]

The current domestic isomerization capacity, as a function of the feedstock, is given in Table F4-57.

TABLE F4-57. CURRENT U.S. ISOMERIZATION CAPACITY (1979)

Feedstock	Number of Units	Total Capacity, bbl/sd
Butane	19	44,550
Pentane	5	60,400
Pentane-hexane	3	26,300

Source: Reference 3

4.5.3.2 Process Technology--

Basically, the isomerization process consists of contacting hydrocarbon and catalyst in a reactor, and then recovering the products. The reactor conditions are set to give favorable reaction rates and equilibria with a minimum amount of side reactions. Separation of the unreacted normal paraffins from the isoparaffin product can be accomplished using distillation or solid adsorbent systems.

The effect of temperature is very important in isomerization processes. In general, equilibrium concentrations of the isoparaffins are increased by reducing the reaction temperature.[19,20]

This effect is illustrated in Table F4-58 which shows the equilibrium composition of several n-paraffin-isoparaffin mixtures as a function of temperature.

The catalysts used for isomerization are of three general types. The first group consists of aluminum chloride promoted with hydrochloric acid. The reaction may be conducted in the vapor phase over a solid catalyst bed, or in the liquid phase with the catalyst dissolved in a solvent such as antimony trichloride.

The second group of catalysts contain a metal such as platinum on a silica-alumina or zeolite base. With these catalysts, the reaction occurs in the vapor phase in packed-bed reactors. These dual functional catalysts are noncorrosive and

TABLE F4-58. THERMODYNAMIC EQUILIBRIA OF BUTANE, PENTANE, AND HEXANE MIXTURES

Compound,	Temperature		
Vol. %	212°F	570°F	800°F
n-butane	35	52	-
Isobutane	65	48	-
	100	100	
n-pentane	16	∿38	-
Isopentane	84	∿62	-
	100	100	
n-hexane	9	14	∿21
2-methylpentane	28	38	∿40
3-methylpentane	13	19	∿20
2,2-dimethylbutane	39	20	∿10
2,3-dimethylbutane	11	9	∿ 9
	100	100	100

Source: Reference 1, 20

easy to handle. However, operating temperatures are higher resulting in a less favorable equilibrium.[19]

The third group of catalysts are the low temperature, dual-functional hydroisomerization catalysts. These catalysts are essentially a hybrid of the first two groups, and are the most recent types to be developed. These "third generation" catalysts are prepared by treating a platinum-alumina composite with a polyhalide such as carbon tetrachloride, chloroform, aluminum chloride, etc. These catalysts permit operations in the range of 200-400°F, temperatures which promote higher equilibrium concentrations of the isoparaffin.[19,20]

Figure F4-22 shows a flow diagram for a typical solid-bed butane isomerization unit. Butane feed is first charged to a deisobutanizer where isobutane is removed as the overhead product. The normal butane stream from the bottom of the deisobutanizer is mixed with hydrogen to suppress the polymerization of small amounts of olefins formed during the isomerization reaction. Hydrogen consumption, however, is quite low.[2] The mixture is sent to a fired heater, and the vaporized feed is charged to the reactor. In the reactor, the n-butane is converted to a near equilibrium mixture of normal and isobutane. The conversion to isobutane is maximized by operating at low temperatures. In addition, trace amounts of organic chlorides are added to the reactor feed to promote the reaction. The reactor effluent is cooled and sent to a separator where recycle hydrogen is recovered. The mixture is stabilized to remove traces of light gases and sent to the deisobutanizer for separation of the isobutane product. Unconverted n-butane plus n-butane from the fresh feed are returned to the system.

As mentioned previously, butane isomerization is a means of providing isobutane feed for alkylation. These two units can be designed to use common distillation equipment with a considerable reduction in cost.

The design of C_5-C_6 fixed bed reactor isomerization units is similar to that of C_4 isomerization units; however, several differences are noted. First, the feed is usually hydrotreated and dried with molecular sieves to protect catalyst activity. In addition, a guard or lead isomerization reactor may be used to saturate aromatics and olefins present in the feed.

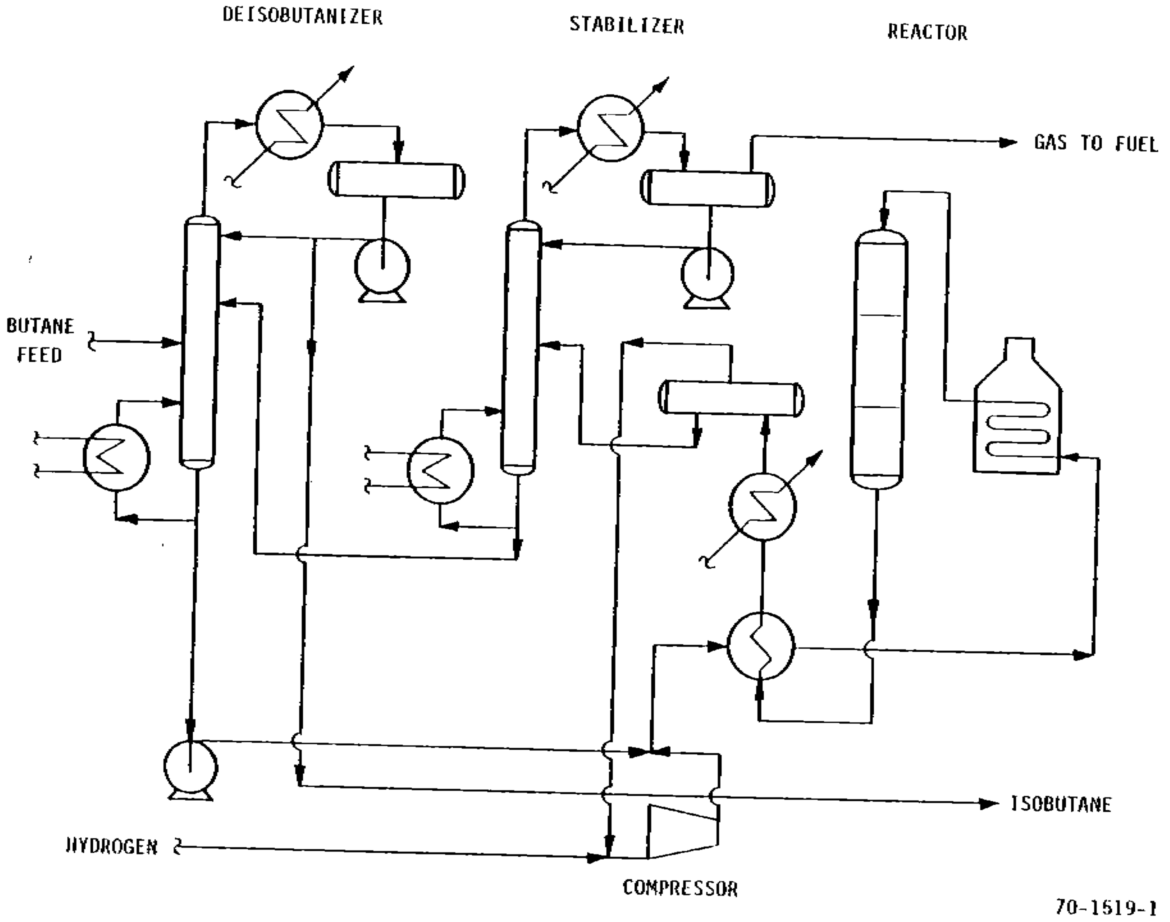


Figure F4-22. Process flow diagram - butane isomerization.

Source: Reference 18, p. 66.

A flow diagram for the n-butane liquid phase isomerization process is given in Figure F4-23. This process is based on the use of liquid aluminum chloride, promoted with hydrogen chloride, as the catalyst. The n-butane feed is passed through a feed drier, a heater, and a catalyst scrubber tower to the reactor. A small sidestream of catalyst from the reactor is also charged to the catalyst scrubber column. The active catalyst components are extracted with the fresh feed and returned to the reactor. A fluid inactive aluminum chloride-hydrocarbon complex, which forms as a result of side reactions, flows to the bottom of this column and is drained off. Hydrogen chloride recycle and makeup streams are added to the butane feed. This mixture is sent to the reactor where it is contacted with the aluminum chloride catalyst, which may be in the form of a complex or dissolved in a solvent such as molten antimony trichloride. After the hydrocarbon and the catalyst phases separate in the upper section of the reactor, the hydrocarbon phase is sent to the catalyst removal column for removal of the dissolved catalyst by distillation. The recovered catalyst is sent back to the reactor while the hydrocarbons are sent to an HCl stripper where acid gas is removed and recycled to the reactor. The mixed butanes from the HCl stripper are caustic washed and separated into normal and isobutane product streams.[1]

The flow plan for the liquid phase isomerization of C_5-C_6 fractions is similar to that for C_4 isomerization. However, a hydrogen system is added to suppress disproportioning reactions.

Operating conditions and utility information for the isomerization process are given in Table F4-59.

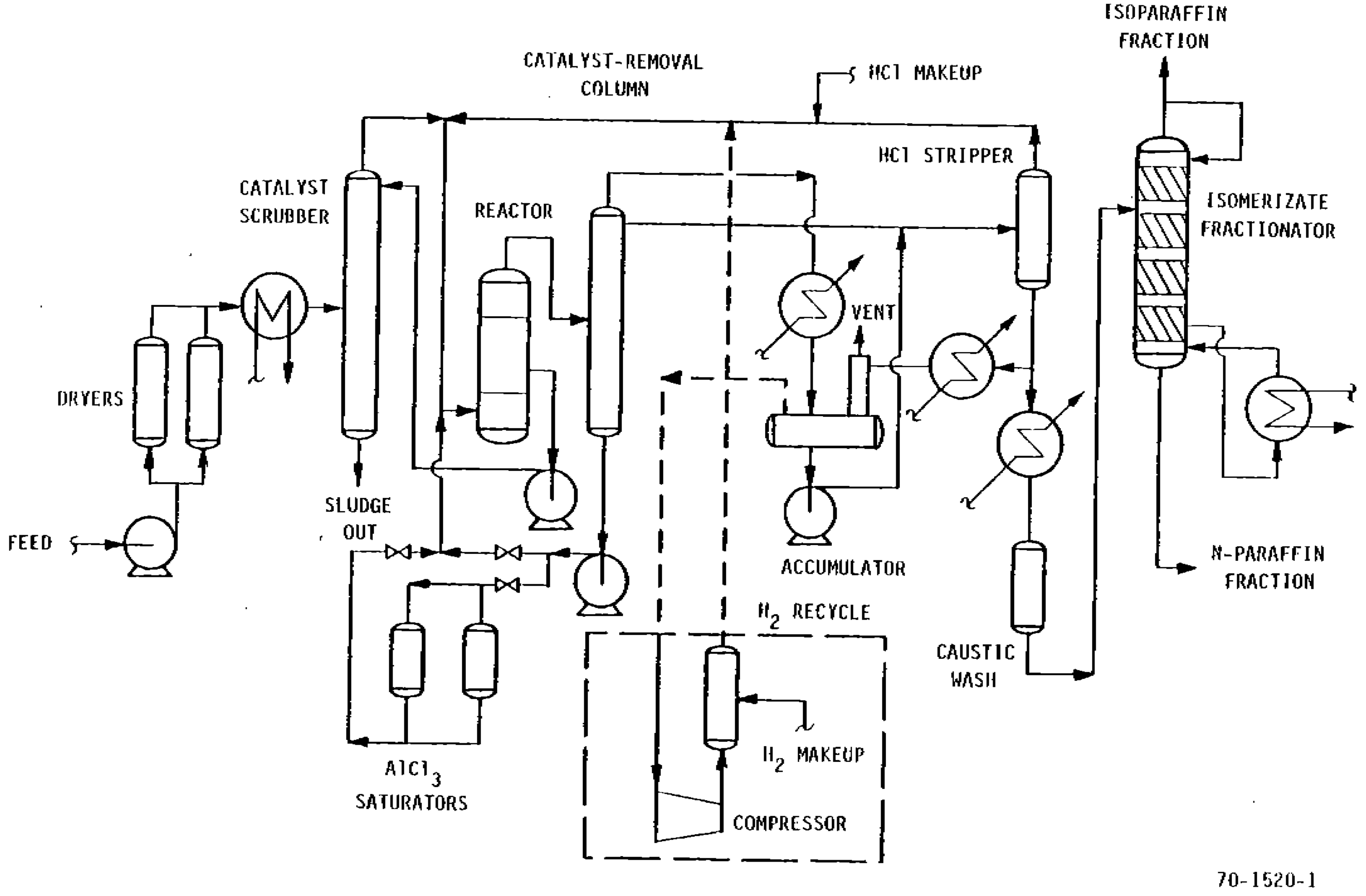


Figure F4-23. Process flow diagram - liquid phase isomerization.

Source: Reference 18

Process Heaters--Emission factors for various pollutants from process heater are given in Table F4-62. A typical hydrodealkylation process will require one process heater. It is used to preheat the feed prior to its entry into the reactor. In addition, a process heater may be used as a reboiler for the main fractionation column, particularly when processing heavier aromatic feeds.

Total emissions for the hydrodealkylation heater are also given in Table F4-62. These figures are given as pounds of pollutant per thousand barrels of feed using a heat input of 290,000 Btu per barrel of fresh feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical hydrodealkylation unit are given in Table F4-63. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained elsewhere in this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and

TABLE F4-60. TYPICAL EMISSIONS FROM ISOMERIZATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	0.71
- Residual oil		
Grade 4	7	2.5
Grade 5	10	3.6
Grade 6	10(S)+3	3.6(S)+1.1
Sulfur Dioxide[c]		
- Distillate oil	142(S)	50.7(S)
- Residual oil	157(S)	56.1(S)
Sulfur Trioxide[c]	2(S)	0.71(S)
Carbon Monoxide[d]	5	1.8
Hydrocarbons (as CH_4)[d]	1	0.36
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	7.9
- Residual oil[e]	$22+400(N)^2$	$7.9+143(N)^2$
Gas Fired Heaters		
Particulates	5-15	0.24-0.71
Sulfur Oxides (as SO_2)[f]	0.6	0.029
Carbon Monoxide	17	0.81
Hydrocarbons (as CH_4)	3	0.14
Nitrogen Oxides (as NO_2)	120-230	5.71-11.0

[a] Source: Reference 11

[b] Based on a heat input of 50,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

Total emissions from the isomerization unit heater are also given in Table F4-60. These figures are given as pounds of pollutant per thousand barrels of feed using a heat input of 50,000 Btu per barrel feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, cpmpressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical butane isomerization unit are given in Table F4-61. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[10]

The methods used to develop estimates for the number of each source type have been previously described in Section 4.1.1.3 of this Appendix.

TABLE F4-61. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL BUTANE ISOMERIZATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	238	0.059	14.0
	Light Liquid (VP > 0.1 psia @ 100°F)	310	0.024	7.44
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0	0.0005	0.0
	Hydrogen Service	102	0.018	1.84
	Total	650[a]		23.3
Open-End (Sample) Valves	All	-	0.005	-
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	10(14)	0.25	3.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	0(0)	0.046	0.0
	Total	10(14)[a]		3.50
Drains	All	26[a]	0.070	1.82
Flanges & Fittings	All	2321[a]	0.00056	1.30
Relief Valves	All	6[a]	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	1.4	0.0
	Hydrogen	2(4)	0.11	0.44
	Total	2(4)[a]		0.44
				31.5

[a] Estimated

The source counts listed in Table F4-61 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. The source counts given in Table F4-61 are not necessarily representative of all or even the majority of isomerization units.

4.5.4 Hydrodealkylation

Aromatic hydrocarbons, required in the production of plastics, fibers, rubber, detergents, insecticides, etc., are produced within the refinery from certain petroleum fractions. This source of aromatics was established in the early 1950's as a result of:[23]

- The development and rapid growth of the catalytic reforming process,
- The development of improved separation processes for isolating high purity aromatics, and
- The insufficiency of other sources of aromatics (such as coal tar by-products) to meet rising demand.

The single ring aromatics produced in catalytic reforming include benzene, toluene, and xylenes. Of these, the demand for toluene and m-xylene is low. However, considerable quantities of these hydrocarbons are produced during the reforming process. A similar situation exists for double ring aromatics as the demand for naphthalene exceeds that for the alkyl-naphthalenes. Hence, processes have been developed to convert low value aromatics into higher value products. One such process is hydrodealkylation.

4.5.4.1 Process Description--

The hydrodealkylation process serves to remove alkyl groups from aromatic rings at elevated temperatures in the presence of hydrogen. Toluene and xylene are converted to benzene while alkyl-naphthalenes are converted to naphthalene.

A number of commercial hydrodealkylation processes have been developed. The reaction can be conducted either by using a catalyst at pressures of 280-850 psig and temperatures of 1020-1170°F, or thermally, in the absence of a catalyst at 1200-1440°F in the same pressure range.[2,3]

At present, 11 hydrodealkylation units are in operation with a total installed capacity of 29,340 bbl/day.[3] Most of these units appear to be producing benzene from feed obtained from BTX operations.

4.5.4.2 Process Technology--

A simplified flow diagram for the combined hydrodealkylation of single and double ring aromatics is given in Figure F4-24. Fresh feed and unconverted recycle materials are mixed with hydrogen, preheated, and charged to the reactor. The hydrogen, often from a reformer, may range in purity from 25-95 percent. A hydrogen purification unit can be installed to reduce hydrogen consumption.

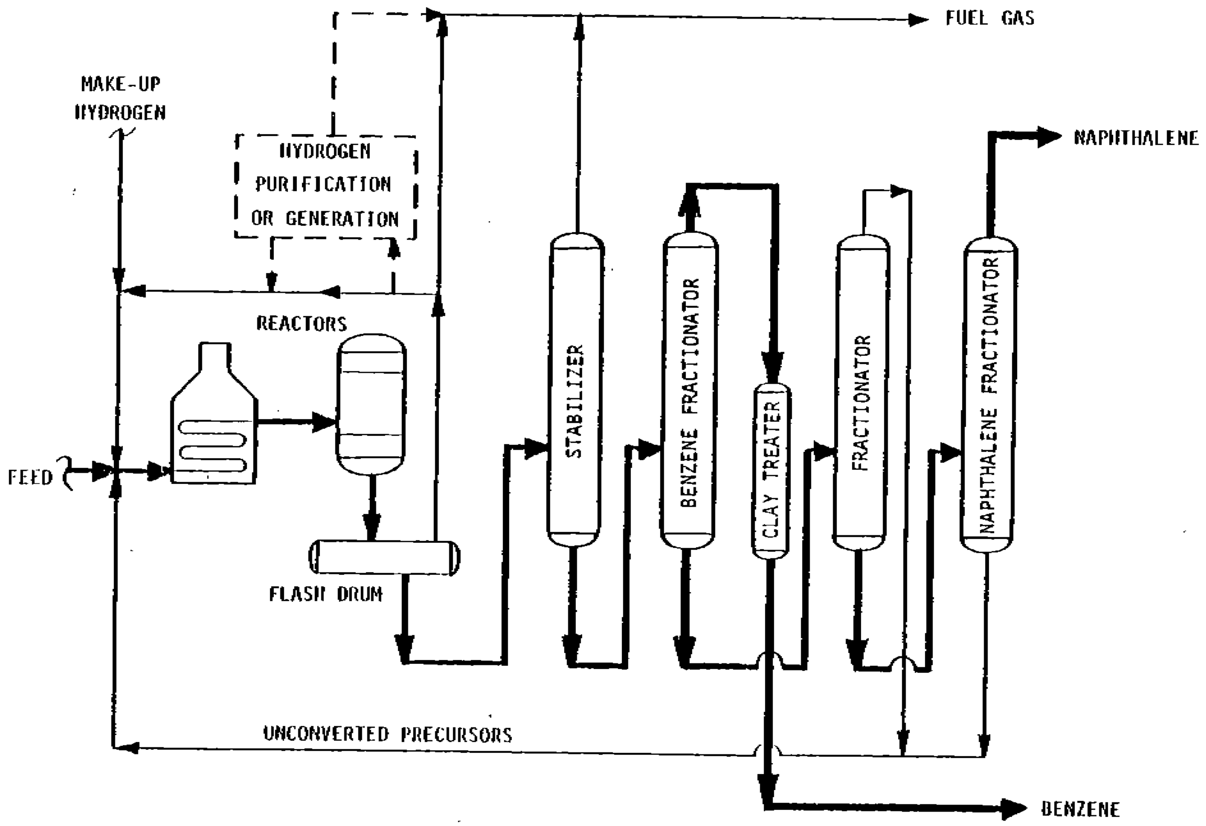


Figure F4-24. Process flow diagram - hydrodealkylation.

Source: Reference 23

At reactor conditions, alkyl groups are removed from the aromatic base with the liberation of light gases. Non-aromatic hydrocarbons may be cracked to lighter hydrocarbons. In addition, sulfur in the feed, if any, is converted to H_2S, leaving the products essentially sulfur free.[24]

The reactor products discharge into a high pressure separator where hydrogen and most of the light hydrocarbons (C_1-C_5) are removed. Liquid from the separator is stabilized and fractionated into benzene, naphthalene, and an unconverted recycle stream.

A variety of feedstocks may be used provided that the aromatics concentration is sufficiently high. Typical feeds for benzene production are toluene and/or xylene. Xylene feeds, however, are less economical than toluene as a larger portion of the feed is converted to gaseous products. Hydrogen consumption is also increased with xylene feeds.[23]

Feeds for the production of naphthalene include heavy reformate, catalytic cracker cycle oils, and other heavy aromatic feeds. To avoid excessive hydrogen consumption, the aromatic components in these streams must be concentrated by distillation, solvent extraction, or other separation processes.

4.5.4.3 Process Emissions--

Emission sources from hydrodealkylation processes include:

- Process heater flue gas, and
- Fugitive emissions.

Process Heaters--Emission factors for various pollutants from process heater are given in Table F4-62. A typical hydrodealkylation process will require one process heater. It is used to preheat the feed prior to its entry into the reactor. In addition, a process heater may be used as a reboiler for the main fractionation column, particularly when processing heavier aromatic feeds.

Total emissions for the hydrodealkylation heater are also given in Table F4-62. These figures are given as pounds of pollutant per thousand barrels of feed using a heat input of 290,000 Btu per barrel of fresh feed.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical hydrodealkylation unit are given in Table F4-63. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained elsewhere in this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and

TABLE F4-62. TYPICAL EMISSIONS FROM HYDRODEALKYLATION UNIT PROCESS HEATERS

	EPA Emission Factor[a] (lb/10^3 gal-oil fired) (lb/10^6 scf-gas fired)	Total Emissions[b] (lb/10^3 bbl of fresh feed)
Oil Fired Heaters		
Particulates		
- Distillate oil	2	4.1
- Residual oil		
Grade 4	7	15
Grade 5	10	21
Grade 6	10(S)+3	21(S)+6.2
Sulfur Dioxide[c]		
- Distillate oil	142(S)	294(S)
- Residual oil	157(S)	325(S)
Sulfur Trioxide[c]	2(S)	4.1(S)
Carbon Monoxide[d]	5	10
Hydrocarbons (as CH_4)[d]	1	2.1
Nitrogen Oxides (as NO_2)		
- Distillate oil	22	46
- Residual oil[e]	$22+400(N)^2$	$46+829(N)^2$
Gas Fired Heaters		
Particulates	5-15	1.4-4.1
Sulfur Oxides (as SO_2)[f]	0.6	0.17
Carbon Monoxide	17	4.7
Hydrocarbons (as CH_4)	3	0.83
Nitrogen Oxides (as NO_2)	120-230	33.1-63.5

[a] Source: Reference 11

[b] Based on a heat input of 290,000 Btu/bbl of fresh feed with the following fuel heating values: Oil - 140,000 Btu/gal; Gas - 1050 Btu/scf.

[c] S = wt % sulfur in the oil

[d] Improper combustion may cause a significant increase in emissions

[e] Use this emission factor for residual oils with less than 0.5% ($N<.5$) nitrogen content. For oil with higher nitrogen content ($N>0.5$), use emission factor of 120 lb/10^3 gal

[f] Based on sulfur content of 2000 gr/10^6 scf

TABLE F4-63. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDRODEALKYLATION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit		Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
		Counts or Estimates From Radian Study	Counts or Estimates From PES Study[c]		
Valves	Gas/Vapor	179	116	0.059	6.84 - 10.6
	Light Liquid (VP > 0.1 psia @ 100°F)	391	352	0.024	8.45 - 9.38
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	43	0	0.0005	0.0 - 0.022
	Hydrogen Service	77	100	0.018	1.39 - 1.80
	Total	690[b]	568[b]		16.7 - 21.8
Open-End (Sample) Valves	All	-	10[a]	0.005	0.05
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	13(18)	6(8)	0.25	2.00 - 4.50
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	1(2)	0(0)	0.046	0.0 - 0.092
	Total	14(20)[b]	6(8)[a]		2.00 - 4.59
Drains	All	36[b]	-	0.070	2.52
Flanges & Fittings	All	2463[b]	1880[b]	0.00056	1.05 - 1.38
Relief Valves	All	6[b]	-	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	1.4	0.0
	Hydrogen	3(6)	2(4)	0.11	0.44 - 0.66
	Total	3(6)	2(4)[a]		0.44 - 0.66
					23.9 - 32.1

[a] Counted from Flow Diagrams

[b] Estimated

[c] Reference 10

- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[10]

The methods used to develop estimates for each source type have been previously discussed in Section 4.1.1.3 of this Appendix.

The source counts listed in Table F4-63 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process types, and processing flexibility. Thus, the source counts given in Table F4-62 may not be representative of all or even the majority of hydrodealkylation units.

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4.6 GAS PROCESSING

Gas processing recovers various hydrocarbons as pure products or as mixtures of specified compositions. The products of gas processing may be fuel gas, methane, ethane, propane, propylene, normal and isobutane, butylenes, normal and isopentane, amylene, and/or a light naphtha. These products may be used in other refinery processes, used as gasoline blending components, or sold.

The feed to gas processing units is from crude distillation, catalytic reforming, catalytic cracking, hydrocracking, thermal cracking, and to a lesser extent, hydrodesulfurization. Many refineries "spike" the crude with natural gas liquids to increase the yield of gaseous products. Major units include acid gas removal, dehydration, and separation.

4.6.1 Gas Treating/Cleaning

4.6.1.1 Acid Gas Removal--

The acid gas removal unit removes hydrogen sulfide from hydrocarbon gases, usually by absorption in an aqueous, regenerative sorbent. CO_2 and/or mercaptans may also be removed, depending on the process used.

A number of acid gas removal processes are available, distinguished primarily by the regenerative sorbent used. Amine-based sorbents are most commonly used.

The feed to a typical unit is contacted with the sorbent, such as diethanolamine, in an absorption column to selectively absorb H_2S from the hydrocarbon gases. Hydrogen sulfide is then removed from the sorbent in a regeneration step. The products are a sweet hydrocarbon gas and a concentrated hydrogen sulfide stream. The hydrogen sulfide stream is normally routed to a sulfur plant for recovery of its sulfur content. Alternatively, the sulfide gas may be flared to produce the less toxic sulfur oxides.

Acidic gases can also be absorbed into an aqueous caustic soda solution. In this case, the spent absorbent is periodically dumped.

Process Conditions--A typical absorber operates at a pressure of about 150 psi and a temperature of about 100°F. Pressure and temperature may, in some instances, be significantly higher.

Emissions--If a regenerative sorbent system is used in conjunction with a sulfur recovery unit, only fugitive emissions are produced. If the hydrogen sulfide stream is flared, sulfur oxide emissions are produced. If caustic soda is used, a liquid waste stream of the spent absorbent is produced.

4.6.1.2 Sulfur Recovery--(See Section 4.7.5)

4.6.1.3 Dehydration--

Dehydration removes water from the gas after the acid gas removal step. The required content is specified as the dew point, the temperature at which the water begins to condense.

Excess water may be removed by refrigeration, absorption, or adsorption. Refrigeration processes decrease the temto below the required dew point; condensed moisture is collected for disposal.

Absorption processes allow the moist gas to flow over a hygroscopic material such as di- or triethylene glycol. Two to five kilograms of glycol are circulated per kilogram of water to be removed.

Solid dissicants such as silica gel or alumina are used in adsorption processes. When the last traces of water, higher hydrocarbons, dissolved elemental sulfur, and residual sulfur compounds must be removed, a molecular sieve bed may be used. Beds are regenerated with hot gas.

Process Conditions-- Temperature and pressure are interdependent in condensation processes. For example, if the required dew point is 50°F at 135 psig and the best available cooling is 80°F, the pressure will be 460 psig.

For absorption processes using di- or triethylene glycol, absorption temperatures must be kept below the glycol's decomposition temperature (327°F for DEG, 405°F for TEG). Dew point depressions of 40° to 50°F can be obtained by using DEG at atmospheric pressure and reboiler temperatures of 290° to 320°F. Temperatures in the regenerator, where water is separated from the glycol, usually range from 375° to 400°F. The pH is controlled at 6.0 to 7.5: a low pH accelerates decomposition of the glycol.

Regeneration temperatures for solid dessicants are 480° to 500°F.

Utilities--A glycol absorption process requires about 0.1 percent of the fuel produced.

Emissions--An estimated 0.1 gallon of triethylene glycol per 10 ft^3 of gas processed is emitted by a glycol absorption unit in vented water vapor. Water contaminated with glycol may be vented as steam or it may be disposed of as a liquid.

4.6.2 Product Separation/LPG Production

Refinery gas is sometimes used without separation into its dry gas and liquid components, especially if it is to be used as fuel gas. However, the gas is often separated into its components in a gas separation plant. This separation is usually accomplished by contacting the gas with an absorber oil. Refrigerated absorption, refrigeration, or adsorption may be used when a separate methane stream is desired.

In the oil absorption process, the gas is contacted with an absorber oil in a packed or bubble tray column. Propane and heavier hydrocarbons are absorbed by the oil while most of the methane and ethane pass through the absorber. The enriched absorber oil is then taken to a stripper where the absorbed propane and heavier compounds are stripped from the oil. If the feed is refrigerated to a -40°F dew point before entering the unit, all hydrocarbons except methane are absorbed.

In the refrigeration process, the gas is first dried with molecular sieve beds to a dew point of -150°F or less. It is then cooled in a heat exchanger to -25°F. Condensed hydrocarbons are removed in a gas-liquid separator. The gas from this separator is passed through a second separator at -135°F. Liquids from the separators are fed to a series of distillation columns where methane, ethane, propane, butane, and other products are recovered.

An activated carbon bed adsorbs all hydrocarbons except methane. The bed is regenerated with heat and steam; the resulting hydrocarbon vapor is condensed and the water separated. The resulting hydrocarbon product is then fractionated into its various components.

Process Conditions--Pressure in an oil absorber may be as high as 400 psi, but is usually lower. Inlet gas and oil temperatures are 90° to 100°F.

Emissions--Fugitive emissions from leaking pumps, valves, compressors, and other fittings are the only emissions from product separation.

4.6.3 References for Section 4.6

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4.7 OTHER PROCESSES

4.7.1 Asphalt Processing/Production

Asphalt is produced as the bottoms from vacuum distillation, as discussed in Section 4.1.2. Any lube oil present can be removed by deasphalting, as described in Section 4.7.2.

4.7.1.1 Process Description--

Asphalt blowing oxidizes the asphalt to increase its melting temperature and hardness. Both batch and continuous processes are employed. Fresh feed and recycle are heated to approximately 500°F and charged to a vertical vessel. Pressurized, preheated air (390-590°F) is charged into the bottom of the vessel through a sparger. The reaction is exothermic and quench steam is sometimes required for temperature control. Excess air is minimized to avoid combustion of exhaust fumes. In some cases, ferric chloride or phosphorus pentoxide are used as catalysts to increase the reaction rate and impart special characteristics to the asphalt. Utilities required for asphalt blowing include 5,000 to 10,000 Btu/bbl heat required for heating the asphalt to the reaction temperature and one kWh/bbl for air compression.

4.7.1.2 Atmospheric Emissions--

The quantity of hydrocarbon emissions from asphalt-blowing units should be relatively small since the asphalt is distilled at high temperatures before reaching the air-blowing process. Available data indicate that uncontrolled emissions amount to 60 pounds per ton of asphalt.[1] The operating conditions are favorable for the production of extremely undesirable polynuclear aromatics.

In some refineries, air-blown brightening units have been replaced by vessels packed with solid absorbents. These vessels have no hydrocarbon emissions other than fugitive emissions.

4.7.2 Lube Oil Processing/Production

Lube oil stock is produced as the 700° to 1000°F fraction of the residium from vacuum distillation. For better control of lube oil processing, the vacuum distillation unit is usually built as part of the lube oil plant.[2] Operation of the vacuum distillation unit is discussed in Section 4.1.2.

Procedures for processing the lube oil stock into specific products vary greatly with the individual refinery. It is not possible to present any one flow scheme as representative of the industry. Processing procedures can, however, be categorized into four groups: deasphalting, treating, dewaxing, and finishing.

Each of these processes is closed to the atmosphere. Except for hydrotreating, there are no emissions other than fugitive emissions from valves, flanges, etc., and emissions from process heaters. Because of the low volatility of the charge stock, fugitive emissions of the material are expected to be generally low. However, more volatile materials may be used in certain treating operations and fugitive emissions of these materials can be significant. With hydrotreating, there are emissions, particularly CO, associated with the periodic regeneration of the catalyst.

4.7.2.1 Deasphalting--

A very heavy oil (brightstock) can be produced from vacuum residues by extraction with propane. The process, called propane deasphalting, is particularly effective because propane is a very selective solvent. At temperatures from 104°F to 140°F, paraffins are quite soluble in propane, but high molecular weight asphaltic and resinous compounds precipitate. The extract phase contains about 15-20 weight percent oil dissolved in propane. The raffinate is a colloid or emulsion of precipitated asphalt material in propane.

The major equipment for the above process includes a heat exchanging system, an extractor, and a propane recovery system. Propane recovery is usually in two stages. The first stage is operated at an elevated pressure; and recovered propane is condensed by air or water cooling. In the second stage, the propane is stripped at atmospheric pressure. The stripping steam is then condensed and the propane vapor compressed and condensed. A relatively large amount of propane is required for the production of commercial quantities of lube oil.

In special cases, propane can be used to separate a lighter oil fraction (SAE50), brightstock, and hard asphalt. The fractionating property of propane is used for this separation. For this fractionation, a propane deasphalting unit consists of two units in series. The raffinate from the first unit, along with more solvent, is sent to the second unit which operates at a lower temperature. The second unit splits the raffinate into a heavy oil and hard asphalt.

Old propane deasphalting units used a mixer-settler system for contacting the vacuum residue with the propane, but, because of the high viscosity of the residue, the contact was poor. A counter-current tower with perforated baffles is now widely used for this purpose. A rotating disc contactor has also been used successfully, but it has a relatively complicated mechanical seal on the rotating shaft.

4.7.2.2 Treating--

There are several treating processes used to improve the characteristics of the lube oil. Of particular interest are the viscosity index, the color, and the carbon residue content. The two most popular treating methods are phenol extraction and furfural treating; the choice between these two is often one of solvent availability. Hydrotreating has also been used.

Phenol Extraction--Aromatic and naphthenic hydrocarbons are particularly soluble in phenol. Because of this, a relatively low solvent to oil ratio is required. In fact, some hydrocarbons dissolve in phenol so readily that water must be injected to control this solubility. The degree of extraction and the selectivity of the process are controlled by several variables: solvent to oil ratio, extraction temperature, temperature gradient, and water injection rate.

In the process, oil is extracted with phenol in a counter-current extractor; water is injected into the extract phase as it leaves the extraction zone. Hydrocarbons which separate from the extract upon addition of water are returned to the extraction zone. This intensive mass transfer operation results in a sharp separation of the extract products from the raffinate.

Hydrocarbons are less soluble in phenol at lower temperatures; therefore reducing the temperature of the extract phase as it leaves the extraction zone has a similar effect to that of adding water. In this case, the extraction tower is operated with a temperature gradient. Phenol entering the counter-current extractor is at a higher temperature than the oil, therefore the raffinate phase leaving the extraction has a higher temperature than the extract.

Water is partly miscible with phenol and also forms an azeotrope with the phenol, therefore it must be removed in a drier as a vapor phase phenol-water azeotrope. The phenol is then absorbed in the oil entering the process.

A phenol extraction unit consists of an extraction stage and a phenol recovery section. The phenol recovery section includes flash towers and vacuum steam strippers.

The counter-current packed tower or a tray tower has been used for phenol extraction since the process was first used for the treatment of lube oil. Modern units use either rotating disc contactors or Podbielniak extractors.

The Podbielniak extractor is a horizontal centrifuge in which counter-current flow is accomplished by centrifugal force. The extractor is highly efficient and has a much smaller volume than does an extraction tower. The small volume makes possible quick changes in feedstock necessitated by market demands. This extractor is, however, a very complicated piece of equipment. Scale and dirt in the feedstock can cause vibration if unevenly distributed across the cross-section of the rotating drum.

The rotating disc contactor (RDC) consists of a series of compartments formed by stator rings and rotating discs. The heavy phase falls onto the rotating disc and is thrown tangentially against the incoming light phase. An RDC may be one third the height of a packed tower with equal extractive ability. The smaller volume of the RDC makes possible quick change-overs of feedstock.

Furfural Treating--Furfural treating is similar to phenol extraction. Two main differences are that (1) a larger solvent to oil ratio is required and (2) there is no need for water injection to reduce the solubility of certain hydrocarbons.

Furfural can be easily oxidized to organic acids which are extremely corrosive, therefore some furfural treating units have been designed with charge stock deaerators to keep air out of the system. Extraction was originally accomplished in packed towers, but since the 1950's the rotating disc contactor has become popular.

Hydrotreating-- Hydrotreating is used for viscosity index improvement, desulfurization, denitrogenation, demetallization, removal of gum forming compounds, and color improvement.

The oil feed is mixed with make-up and recycle hydrogen and charged to a fixed catalyst bed reactor. Reactor effluent flows through high and low pressure separators for removal of hydrogen for recycle and light ends, respectively. The product is then steam stripped to remove any remaining impurities.

The feed to a hydrotreating unit can be either solvent refined lube oils and waxes or raw distillates and deasphalted oils. Hydrogen requirements vary from 100 to 200 cubic feet H_2 per barrel of oil. The catalyst generally has a cobalt or nickel-molybdenum base.

The reactor operates at 600 to 750°F and 500 to 700 psi. Utilities for the treatment of one barrel of oil are 2-5 kwh electricity, 15 to 30 lb steam, and 35,000 to 140,000 Btu heater fuel.

Other Treating Processes--Treatment of lube oil with sulfuric acid is a simple matter of contacting the oil with the acid and then separating the resulting acid sludge from the refined oil by clay filtration. This process was once used more extensively, but is seldom used now because of operating difficulties and sludge disposal problems.

Duo-sol, a process using propane and cresilic acid for simultaneous deasphalting and treating, was once used for about 20 percent of the lube oil produced. It is seldom used now because of increased quality requirements for lube oil products.

Other solvents which have been suggested for lube oil treating are liquid SO_2, a liquid SO_2/benzene mixture, a mixture of cresols, a mixture of phenol and cresols, nitrobenzene, aniline, and dichloroethylether. Some of these have been used in commercial plants.

4.7.2.3 Dewaxing--

Dewaxing is the most difficult part of lube oil manufacture. The dewaxing process removes wax from lube oils to improve the low temperature fluidity characteristics of the oil. The oil is contacted with solvent and chilled, causing the wax to precipitate. The precipitated wax is separated from the mixture by filtration or centrifuging. The dewaxed oil and solvent are separated by distillation and steam stripping. Solvent is recycled. The wax, usually containing at least 10 percent oil, is solvent treated again under different conditions to obtain a deoiled wax product of the desired specifications. Refrigeration and filtration are used to recover the wax and solvent.

The most widely used solvent for oil dewaxing and wax deoiling is methyl ethyl ketone (MEK) or a mixture of MEK and toluene or benzene. Both operations are frequently combined in one unit using a MEK solvent. Other solvents used in oil dewaxing and wax deoiling are methyl butyl ketone, either alone or mixed with toluene or benzene, and propane, acetone, and chlorinated hydrocarbons.

Oil dewaxing and wax deoiling processes are major energy consumers because of refrigeration and filtration requirements. Two to ten kwh of electricity and 100-400 pounds of steam are required per barrel of oil.

4.7.2.4 Finishing--

The color of a product can be quickly deteriorated by the presence of traces of resinous materials and chemically active compounds. There are several finishing methods for removing these compounds.

The compounds can be absorbed by contacting the oil with various types of mineral clays, activated earth, or artificial absorbents. The oil is either mixed with the absorbent or percolated through a long column packed with the absorbent. Absorption occurs at high temperatures, about 600°F. The absorbent is then removed from the oil by filtration. Clay absorption is no longer used in large-scale lube oil manufacture because of problems with disposal of the spent absorbent.

Hydrotreating is also used for finishing lube oils (hydrofinishing). Hydrofinishing effectively removes nitrogen compounds which cause the oil to darken and to be unstable. Removel of nitrogen compounds usually requires considerably higher pressures than do middle distillate desulfurizers, therefore the sulfur content of the oil is also reduced. Hydrofinishing also removes oxygen very efficiently.

In hydrofinishing, the charge stock is combined with hydrogen gas, heated in a furnace, and passed through a hydrofinishing reactor. The reactor effluent is cooled and the liquid and vapor phases are separated. The vapor phase is recycled. The liquid is sent to a stripper where H_2S, NH_3 and light hydrocarbons are removed.

4.7.3 Blending Operations

Refinery blending operations involve the mixing of various components to achieve a product of desired characteristics. The most common blending operation in petroleum refining is the final step in gasoline manufacturing. Gasoline components such as catalytic gasoline, reformate, alkylate, isomerate, butane, lead, and dye are mixed in proportions required to meet gasoline-marketing specifications.

4.7.3.1 Process Description and Technology--

There are two methods of blending: batch and in-line. Batch blending is accomplished in a blending tank (or tanks) into which each component is added individually. Mixing is continued until a homogeneous mixture of the desired properties is produced. The final blend is routed to storage tanks to await transfer out of the refinery or pumped directly to transportation facilities.

Agitation in the blending tank is accomplished either by an external circulation loop (or loops) or by internal impellers powered by external motors. The impeller shafts are sealed in the same ways as are rotating pump shafts. A special case is the blending of butane into gasoline, wherein liquid butane is sometimes charged through a sparger ring in the bottom of the blending tank.

In-line blending can be either partial or continuous. Partial in-line blending involves simultaneous combination of stock components in a mixing manifold. Final additions and adjustments are made downstream or in a storage tank.

Continuous in-line blending involves continuous and simultaneous blending of all stock components and additives in a mixing manifold. Each component stream is controlled automatically by a feedback control loop; the entire control system is often under computer guidance. There is no blending tank, and storage capacity is often minimized by direct discharge of blended products to transportation facilities or pipeline.

4.7.3.2 Atmospheric Emissions--

Agitation in batch blending operations increases the evaporation of lighter components. Thus, fugitive losses from batch blending tanks are generally greater than those from similar quiescent storage tanks. Emissions from in-line blending are limited to fugitive leaks from valves, flanges, and other process equipment.

Control technology for batch blending operations includes floating roofs on blending tanks and replacement of batch operations by in-line blenders. Hydrocarbon leaks from in-line blending systems can be reduced by proper inspection and maintenance of valve stem seals, flange gaskets, and pump seals.

4.7.4 Hydrogen Production

Hydrogen is a by-product of several refining processes. However, a refinery with a large distillate hydrotreater or gas oil hydrocracker requires additional high purity hydrogen. It is estimated that by 1980, slightly less than 40 percent of the hydrogen used in refineries will be manufactured.[3]

A steam-hydrocarbon reforming process is commonly used for hydrogen production. However, the light hydrocarbons used as fuel for this process are more economically used in other processes such as alkylation and catalytic reforming. Therefore, steam-hydrocarbon reforming will probably be replaced by partial oxidation of heavy oils. The choice between the two processes will depend on the cost and availability of raw materials.[4] Both processes are described here.

4.7.4.1 Steam-Hydrocarbon Reforming--

Process Technology--Either a light natural gas-type product or a heavier hydrocarbon mixture such as naphtha can be used as feedstock for the steam-hydrocarbon reforming process. The feedstock is first desulfurized to prevent catalyst deactivation. Desulfurization may be accomplished by adsorption on activated carbon at ambient temperatures, high temperature reaction with zinc oxide, or catalytic hydrogeneration followed by reaction with zinc oxide.

After desulfurization, the feedstock and superheated steam are catalytically reacted in a high temperature reactor (reformer) at about 1400 to 1600°F. A nickel catalyst is used for the light hydrocarbon feedstock; a special catalyst is used for the heavier hydrocarbons.[5]

The reformed gas contains hydrogen, carbon monoxide, carbon dioxide and excess steam. After the gas is cooled, the carbon monoxide is reacted with steam in a shift converter to produce carbon dioxide and more hydrogen. An iron catalyst is used.

The carbon dioxide and hydrogen-rich gas is then cooled and scrubbed to remove practically all of the carbon dioxide. Carbon dioxide may be removed by one of several methods, depending on the cost of utilities. Two such methods are monoethanolamine (MEA) scrubbing and the more thermally efficient Benfield activated hot carbonate process. The remaining carbon dioxide and carbon monoxide are removed by heating the gas and passing it through a nickel base methanation catalyst. Here the carbon dioxide and carbon monoxide react with hydrogen to form methane. Typically, about 280,000 SCF of natural gas or 60 barrels of naphtha are required for the production of one million SCF of hydrogen. A flow diagram of the steam-hydrocarbon reforming process is given in Figure F4-25.

Major equipment for the process includes the reformer and the shift converter. The reformer consists of catalyst-filled tubes. The converter has two catalyst beds, the first containing a high temperature catalyst and the second a low temperature catalyst. The gas is cooled between beds.

Emissions--Emissions from steam-hydrocarbon reforming hydrogen units include:

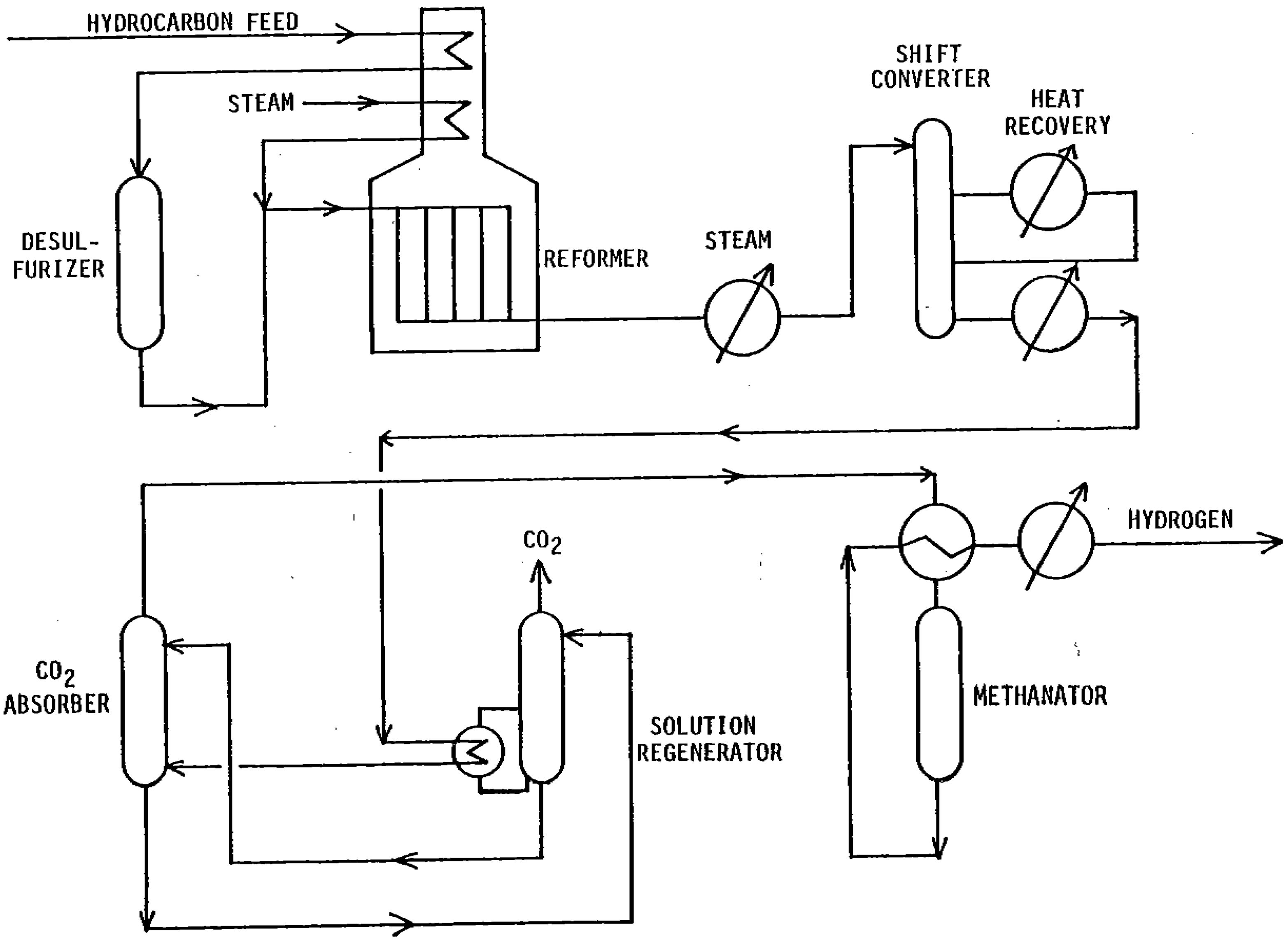

Figure F4-25. Hydrogen production by steam reforming.

- Emissions of process heater flue gas, and
- Fugitive emissions.

Emissions of various pollutants from process heaters are discussed in Section 4.1.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, relief valves, and drains. Hydrocarbon emission rates for each individual source are quite low. However, total fugitive emissions are significant because of the large number of such sources within the refinery.

Total estimated fugitive non-methane hydrocarbon emissions from a typical hydrogen production unit are given in Table F4-64. The listed emission factors were determined as a part of this program. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category, are contained in Appendices B and C of this report.

Estimates for the number of sources within each source category were developed from:

- Actual field source counts conducted during the course of this program, and
- Counts contained in The Development of Petroleum Refinery Plot Plans, EPA publication number 450/3-78-025.[7]

The methods used to develop estimates for each source type are discussed in Section 4.1.1.3 of this Appendix.

TABLE F4-64. ESTIMATED FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A TYPICAL HYDROGEN PRODUCTION UNIT

Emissions Source Type	Process Stream Service Classification	Number of Sources in Process Unit: Counts or Estimates From Radian Study	Number of Sources in Process Unit: Counts or Estimates From PES Study[d]	Source Emission Factor, lb/hr	Estimated Total Emissions, lb/hr
Valves	Gas/Vapor	19	244	0.059	1.12 - 14.4
	Light Liquid (VP > 0.1 psia @ 100°F)	93	2101	0.024	2.23 - 50.4
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	62	0	0.0005	0.0 - 0.031
	Hydrogen Service	8	122	0.018	0.14 - 2.20
	Total	182[a]	2467[c]		3.49 - 67.0
Open-End (Sample) Valves	All	--	46[b]	0.005	0.23
Pumps (Pump Seals)	Light Liquid (VP > 0.1 psia @ 100°F)	3(4)	2(3)	0.25	0.75 - 1.0
	Heavy Liquid (VP ≤ 0.1 psia @ 100°F)	2(3)	0(0)	0.46	0.0 - 0.138
	Total	5(7)[a]	2(3)[b]		0.75 - 1.14
Drains	All	17[c]	--	0.070	1.19
Flanges & Fittings	All	635[a]	8225[c]	0.00056	0.36 - 4.61
Relief Valves	All	6[c]	--	0.19	1.14
Compressors (Compressor Seals)	Hydrocarbon	0(0)	0(0)	0.4	0.0
	Hydrogen	3(6)	3(6)	0.11	0.66
	Total	3(6)[c]	3(6)[b]		0.66
					7.82 - 75.6

[a] Physically Counted

[b] Counted From Flow Diagrams

[c] Estimated

[d] Reference 18

The source counts given in Table F4-64 refer to those sources located within the battery limits of the process. That is, equipment located in tankage or transfer lines is not included in these source counts.

The number of sources per unit depends on a variety of factors including processing complexity, process type, and processing flexibility. Hence, the number of sources shown in Table F4-64 are not necessarily representative of all or even the majority of hydrogen production units.

The estimated composition of fugitive non-methane hydrocarbon emissions from a steam reformer hydrogen unit utilizing naphtha as the feedstock is given in Table F4-65. These estimates indicate the types of hydrocarbons contributed by sources on a number of streams within the process unit. Additional information on these estimates may be found in Section 2.4 of Appendix D.

4.7.4.2 Partial Oxidation (Texaco Synthesis Gas Generation Process)--

Process Technology-- Large quantities of hydrogen can be produced economically from high sulfur residual petroleum stocks by the partial oxidation process. The hydrogen can be generated at any selected pressure up to 160 atmospheres. The use of fuel-fired heaters is minimized; the hydrogen sulfide produced can be recovered in the sulfur recovery unit.[6]

The residual fuel oil is first partially combusted with oxygen in the presence of steam. The combustion is exothermic and non-catalytic. The synthesis gas produced by the combustion is composed primarily of hydrogen and carbon monoxide, with small

TABLE F4-65. ESTIMATED COMPOSITION OF FUGITIVE NON-METHANE HYDROCARBON EMISSIONS FROM A HYDROGEN PRODUCTION UNIT UTILIZING NAPHTHA AS A FEEDSTOCK

	Streams				
	Fuel Gas	Straight Run Naphtha	LPG	H_2 Recycle Gas	Totals
Estimated percentage of emissions attributed to each stream - wt %	38	19	19	24	100%
Weighted contribution of each component to unit emissions ppmw					
Benzene	0	48	0	0	48
Toluene	0	498	0	0	490
Ethylbenzene	0	169	0	0	169
Xylenes	0	308	0	0	308
Other Alkylbenzenes	0	3150	0	0	3150
Naphthalene	0	278	0	0	278
Anthracene	0	1	0	0	1
Biphenyl	0	119	0	0	119
Other Polynuclear Aromatics	0	2847	0	0	2847
n-Hexane	0	7379	0	0	7379
Other Alkanes	349600	94926	190000	156000	790526
Olefin	22800	0	0	0	22800
Cycloalhanes	0	80277	0	0	80277
Hydrogen	7600	0	0	84000	91600
					1,000,000

amounts of carbon dioxide and minor quantities of hydrogen sulfide, methane, nitrogen, argon, carbonyl sulfide, and soot.

The majority of the soot in the synthesis gas is removed in a water quench tower. A selected soot level is maintained in the circulating water system by withdrawing a portion of the water and contacting it with naphtha. The carbon is transferred to the naphtha phase; the water and naphtha are separated in a decanter and the water returned to the circulating system. The naphtha-carbon mixture is then mixed with a portion of the residual oil feed to the generator. The naphtha is recovered by distillation and the soot is transferred to the generator feed.

The gas product from the combustion chamber exits at about 2000 to 2800°F. It is cooled with hot water and simultaneously saturated with steam. This steam-saturated gas stream is fed to a shift converter where the carbon monoxide is catalytically converted to carbon dioxide and additional hydrogen.

Gas from the shift converter is primarily hydrogen and carbon dioxide with lesser amounts of carbon monoxide, methane, hydrogen sulfide, argon, and nitrogen. The Rectisol process, which uses methane at temperatures of -50 to -60°F, effectively separates a pure carbon dioxide stream with less than 1 to 5 ppm hydrogen sulfide and a 30 to 40 percent hydrogen sulfide stream which is sent to the sulfur recovery unit. The remaining hydrogen is more than 95 to 98 percent pure. Removal of carbon monoxide, perhaps with copper liquor, raises the purity of the hydrogen to 97 to 99 percent.

A flow diagram of the partial oxidation process is given as Figure F4-26. Fuel and utility requirements for the

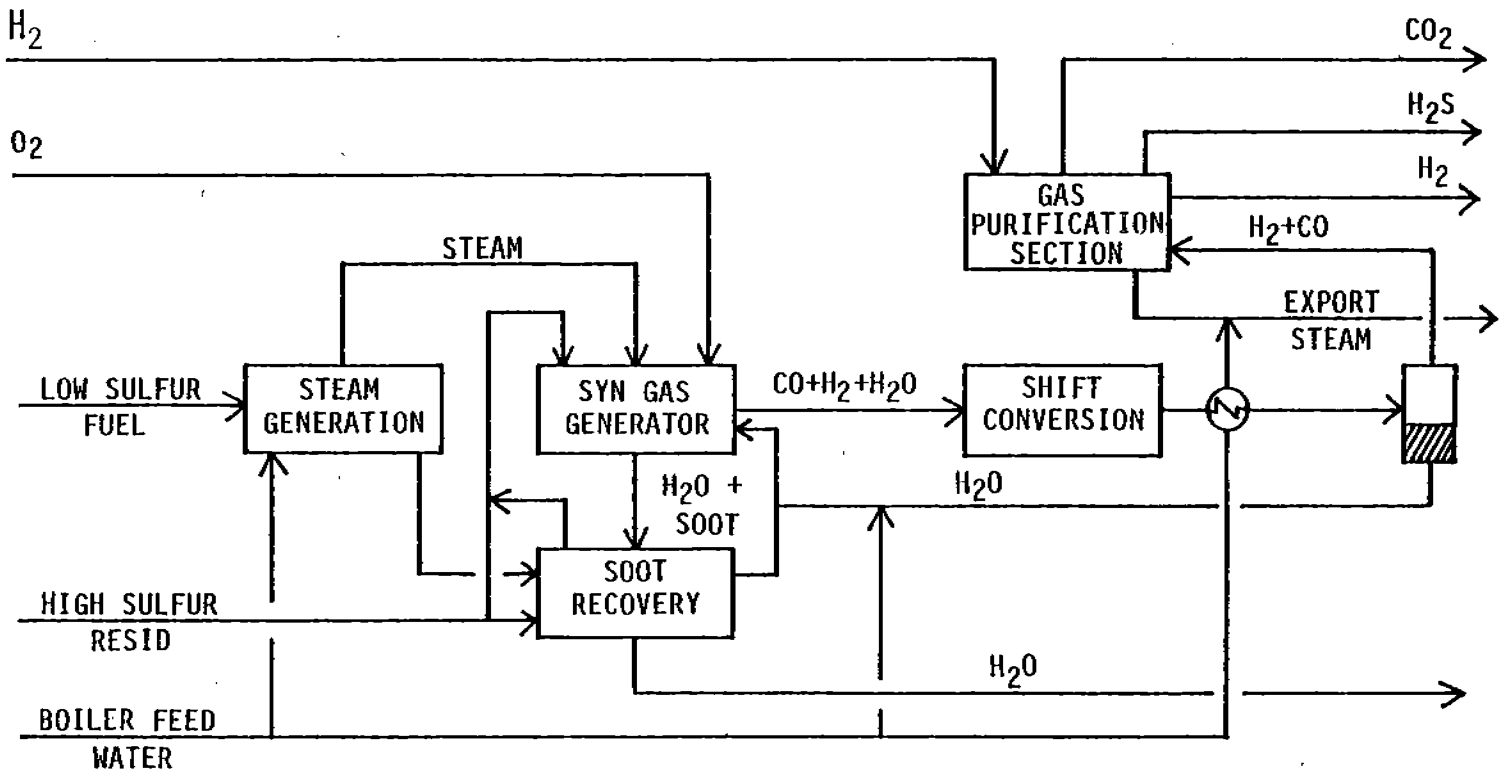

Figure F4-26. Hydrogen production by partial oxidation.

production of one million SCF 100 percent hydrogen are given as Table F4-66.

TABLE F4-66. UTILITY REQUIREMENTS FOR THE PRODUCTION OF 1,000,000 SCF 100 PERCENT H_2

Electric Power, kwh	1,700
Cooling Water, Gal	90,000
Deionized Water, Gal	450
Boiler Feed Water, Gal	10,350
Low Sulfur Fuel, Bbl	0.8

Emissions--No specific information was available on emissions from the partial oxidation method. It is assumed that the only emissions are those from process heaters and the fugitive emissions from valves, flanges, etc. Emissions from process heaters are discussed in Section 4.1.

4.7.5 Sulfur Recovery

A sulfur recovery plant convents hydrogen sulfide to elemental sulfur. The Claus process is the accepted method for sulfur recovery in the refining industry; it is assumed to be used by all major refiners.

Process Technology--Process types and process flow diagrams for the Claus process are given in Section 3.2.1.3 of Appendix E. Raw materials for the unit include H_2S from the acid gas removal plant and H_2S from sour water stripper systems. The amount of sulfur reaching the sulfur recovery unit varies with the percent sulfur in the crude and the extent of desulfurization. Typically, 60 percent of the sulfur in the crude reaches the sulfur recovery plant.

A Claus plant operates at about 473°F and one to two atmospheres. About 19 Btu of heat are required per pound of sulfur produced. However, about four pounds of steam per pound of sulfur are produced in a waste heat boiler. This steam can provide from five to thirty percent of the total refining steam requirements.

The major equipment for a Claus plant consists of a combustor and from two to four reactors, depending on the conversion desired and the acid gas concentration. Each reactor has an effluent condenser where elemental sulfur is recovered.

Emissions--Process emissions from Claus plants are discussed in Section 3.2.1.3 of Appendix E. A 100,000 bpd refinery with a one percent sulfur crude and a 95 percent efficient sulfur plant will produce 5 to 6 tons/day of sulfur emissions. Possible sulfur emissions are SO_2, H_2S, COS, CS_2, and mercaptans.

It is estimated that there are 200 valves, 800 flanges, 9 pump seals, 20 drains, and 4 relief valves on a typical Claus unit. These are the sources of the fugitive emissions of various sulfur compounds from the Claus unit. However, sulfur recovery units sampled during this program were found to be leaking hydrocarbons at rates considerably lower than other refinery process units.

4.7.6 References for Section 4.7

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6. Schlinger, W. G. and W. L. Slater. Partial Oxidation - A Minimum Pollution Route for Hydrogen Manufacture. 16(2), Texaco, Inc., ACS, Div. Petrol. Chem., Montebello, CA, 1971.

7. Environmental Protection Agency. Development of Petroleum Plot Plans. EPA-450/3-78-025. Research Triangle Park, NC, 1978.

4.8 WASTE TREATMENT

4.8.1 Blowdown/Flare Systems

Blowdown/flare systems are items common to all crude oil refineries. These systems are present for reasons including:

- The collection and destruction of small quantities of waste gas produced during normal operations,
- The collection and destruction of large waste gas flows during unit upsets, shutdowns, fires, or other emergency situations, and
- The prevention of the above gas streams from venting directly to the atmosphere where they might cause safety problems, contribute to air pollution, or produce a fire or explosion hazard.

4.8.1.1 Process Description--

A blowdown or pressure-relieving system consists of relief valves, safety valves, manual bypass valves, blowdown headers, knockout vessels, and holding tanks. A blowdown-recovery system may also include compressors and vapor surge vessels. In either case, a flare is used for final disposal of non-condensible combustible gases.

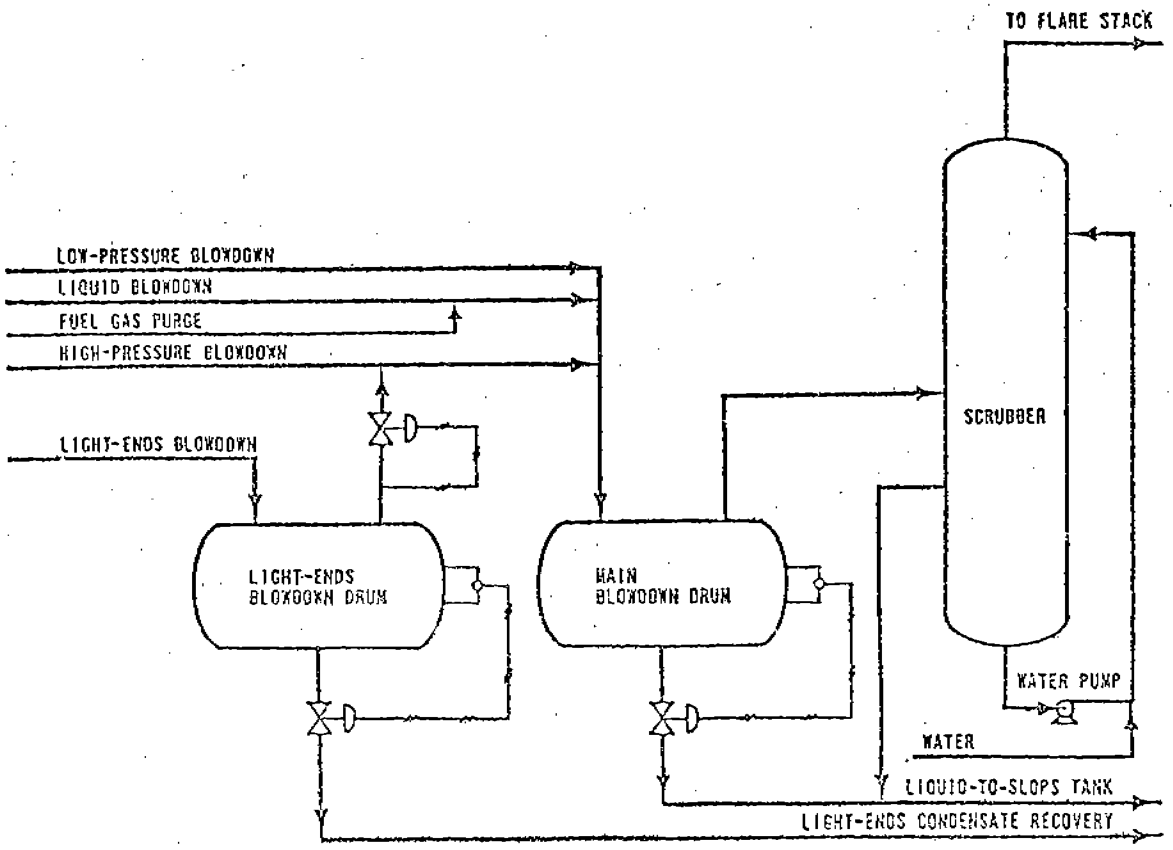
An example of a typical refinery blowdown system is shown in Figure F4-27. For reasons of safety and economy, vessels and equipment relieving to the blowdown system are usually segregated according to their operating pressure. That is, there is a high-pressure blowdown system for equipment operating, for example, above 100 psig, and a low-pressure system for vessels and equipment operating below 100 psig. In addition, separate collection systems are provided for liquids and for a fuel gas purge stream.

The above streams enter the main blowdown drum. Liquid from this drum is sent to a slops tank while the vapor is sent to a direct-contact type condenser to permit recovery of as much hydrocarbon liquid as possible. The resulting light vapor stream is sent to a flare for disposal by burning.

Butane and propane are usually discharged to a separate blowdown drum. This drum is often operated above atmospheric pressure to increase liquid recovery. Liquids from this drum are recovered while the vapors are combined with the high pressure blowdown.[1]

4.8.1.2 Process Technology--

Key elements common to all types of blowdown systems include pressure relief devices such as safety valves, relief valves, and rupture discs, and a flare system for the ultimate disposal of the final waste gas stream. The various types of pressure relief devices and flare equipment are briefly discussed below.



Source: Reference 1

Figure F4-27. Typical refinery blowdown system.

Pressure Relief Devices--Common pressure relief devices include pressure-relief valves and rupture disks. Pressure relief valve is a generic term applying to relief valves, safety valves and safety-relief valves.

A relief valve is an automatic pressure-relieving device actuated by the static pressure upstream of the valve. The valve opens in proportion to the increase in pressure over the opening pressure. It is used primarily for liquid service.

A safety valve is an automatic pressure-relieving device actuated by the static pressure upstream of the valve and characterized by rapid full opening or pop action. It is used for gas or vapor service. (In the petroleum industry it is used normally for steam or air.)

A safety-relief valve is an automatic pressure-relieving device suitable for use as either a safety or relief valve, depending on application. (In the petroleum industry it is normally used in gas and vapor service or for liquid.)

A rupture disk consists of a thin metal diaphragm held between flanges. A rupture disk is sometimes put upstream of a pressure relief valve to prevent hydrocarbon losses from leaking pressure relief valve seals.

Flares--Flares are used for the disposal of waste gases by combustion. This includes the combustion of large surges of gas during an emergency as well as the disposal of smaller quantities of excess gas produced in more or less constant amounts. There are, in general, three types of flare systems: burning pits, elevated flares, and ground level flares.

Burning pits are generally reserved for burning large quantities of gases produced during emergencies. Ordinarily, the main gas header to the flare system has a water seal bypass to the burning pit. Excessive pressure in the header blows the water seal and permits vapors and gases to vent to the burning pit.

A typical burning pit is merely an excavation from 4-6 feet deep and from 30-40 feet square, with a burner wall of brick along one side. The burners are mounted in the wall and directed at an angle toward the bottom of the pit. Burning pits are no longer common in U.S. refineries.

An elevated flare consists of a stack, the supporting structure, the burner tip, and auxiliaries, such as a liquid trap, seal, pilot burner and igniter. The elevated flare allows gases to be burned safely at high elevations and is the most common type of flare currently in use.

Ground flares are similar to elevated flares. However, they must be installed in a larger open area than elevated flares for safety and fire protection.[2]

<u>Smokeless Operation</u>--Smoke is a result of incomplete combustion and smoke emissions from flares are avoided whenever possible. Smokeless operation is achieved by following basic combustion principles:

- Sufficient heat values to maintain critical combustion temperatures,
- Adequate supply of combustion air, and

- Adequate turbulence to promote mixing of air and fuel.

Adequate turbulence is usually induced by injecting steam into the combustion zone. A variety of methods for mixing steam with air and fuel are available, and all result in increased velocity and turbulence in the combustion zone. The use of steam can result in additional benefits:

- Steam reacts with the fuel to form oxygenated compounds that burn readily at relatively low temperatures. Water-gas reactions also occur, with the same end result.

- Steam reduces the partial pressure of the fuel and retards polymerization. Polymerized hydrocarbons are heavier and more difficult to burn.

Materials other than steam have been used to some extent to promote smokeless operation; the most common being air and water. Mechanical air blowing would be ideal for promoting combustion. However, it is generally uneconomical because the equipment necessary to provide high air flow rate is quite costly.

Inspiration of air by water has proven successful, particularly for ground flares. Pumping costs, however, prohibit the use of water inspiration in elevated flares. Water is not quite as effective as steam, however, for controlling smoke when high flare rates, olefins, or wet gases are involved.

4.8.1.3 Atmospheric Emissions--

Emissions sources from blowdown/flare systems include:

- Combustion products from flares, and
- Fugitive emissions

Emissions from Flares--In general, emissions of carbon monoxide and hydrocarbons from flares are higher than those from process heaters or boilers. Factors which may account for less effective combustion for flares include:

- Variable firing rates which make control of steam and combustion air flow rates difficult.
- Variable heat values for fuel which may also contain significant quantities of olefins or aromatics, and
- Relatively low combustion temperatures with short residence times compared to process heaters and boilers.

EPA emission factors for smokeless flares are listed in Table F4-67. The emissions listed here are given as pounds of pollutant per thousand barrels of refinery capacity.

Fugitive Emissions--Fugitive emissions can occur from a variety of sources including valves, pumps, compressors, flanges and other fittings, pressure relief valves, and drains.

TABLE F4-67. EMISSIONS FROM SMOKELESS FLARES

Component	EPA Emission Factors[a,b] (lb/10^3 Bbl total refinery capacity)
Particulates	Negligible
SO_x[c]	26.9
CO	4.3
Hydrocarbons[d]	0.8
NO_x	18.9
NH_3	Negligible
Aldehydes	Negligible

[a] Source: Reference 3

[b] These emission factors have been given an emission factor rating of "C."

[c] Varies with fuel sulfur content

[d] Methane content of hydrocarbon emissions was unavailable

Hydrocarbon emission rates for each source are quite low. However, total fugitive emissions are significant because of the large numbers of such sources within the refinery.

The emission factors developed during this program for each of the above sources are listed in Table F4-68. Additional information on these emission factors, including a complete discussion on their derivation and the confidence intervals for each source category are contained in Appendices B and C of this report. No attempt has been made here to determine total fugitive emissions from blowdown systems because of wide variations in the type of waste gas processing employed by refiners.

TABLE F4-68. FUGITIVE EMISSION FACTORS FOR VARIOUS REFINERY FITTINGS

Source	Emission Factor lb/hr/Source
Valves	
Gas-vapor service	0.059
Light liquid (VP > 0.1 psia @ 100°F)	0.024
Heavy liquid (VP ≤ 0.1 psia @ 100°F)	0.0005
Hydrogen service	0.018
Open-ended (sample	0.005
Pumps seals	
Light liquid (VP > 0.1 psia @ 100°F)	0.25
Heavy liquid (VP ≤ 0.1 psia @ 100°F)	0.046
Compressor seals	
Hydrocarbon service	1.4
Hydrogen service	0.11
Drains	0.07
Flanges and fittings	0.00056
Relief valves	0.19

4.8.2 Wastewater Systems

Tremendous quantities of water are utilized by the refining industry to cool various process streams, to produce steam, to be used directly in processing, and to meet a variety of additional needs. In general, a substantial quantity of this water is reused prior to discharge. The amount of water required for makeup ranges from less than one barrel to nearly 20 barrels per barrel of crude oil capacity, depending on factors including the age of the refinery and the degree to which the water is processed for reuse.

The largest amount of water used within the refinery is for cooling. In spite of efforts to prevent cooling water from coming in contact with process streams, this water usually contains some contaminants. Contaminants enter the cooling water via a variety of mechanisms--for example, leaks in heat exchanger tubes or other process equipment.

Water used directly in processing accounts for a much smaller portion of the total water requirements than cooling water. However, this water is almost always laden with contaminants due to direct contact with oil. Examples of process water uses include desalting of crude oil, steam stripping operations, tank drawoff, and pump gland cooling water. Although oil free, other water streams such as boiler blowdown and water from sanitary sources also require treatment for contaminant removal.

The purpose of the wastewater treating system is to remove contaminants and provide effluent water of a quality sufficient to meet state and federal standards. These standards cover a variety of contaminants and can require the use of sophisticated treatment techniques.

4.8.2.1 Characteristics of Receiving Waters--

Before beginning a discussion of specific refinery wastewater treatment processes, a summary of the effect of various wastes on water quality is in order. These effects, summarized from the API manual on the disposal of liquid refinery wastes, are discussed under the following headings:[2]

- pH, acidity, and alkalinity,
- Dissolved oxygen and oxygen demand,

- Hardness and salinity,
- Toxicity, taste, and odor,
- Color, turbidity, and suspended matter,
- Oil,
- Temperature.

pH, Acidity, and Alkalinity--The pH value of natural waters is an approximate measure of acidity or alkalinity in the water. High or low pH values, caused by the discharge of refinery waste streams containing strong acids or bases, can result in a variety of adverse affects.

One important consideration is the buffer effect, or resistance to change in the pH value upon the addition of acidic or basic wastes. This buffer effect stems from the presence of weak acids or bases and various salts. For example, many natural waters contain carbonic acid (a weak acid formed by absorption of carbon dioxide), and salts such as sodium or calcium carbonates and bicarbonates. Moderate amounts of strong acids or bases can be added to such waters with only small changes in the pH value. In the absence of such buffering agents, however, even small additions of strong acid or base can cause a marked change in the pH value. Thus, when evaluating the effects of acidic or basic waste streams, both the quantity of the waste and the characteristics of the receiving water must be evaluated.

Low pH values, caused by the addition of untreated acidic waste, may result in effects ranging from increased corrosion rates to damage of aquatic life. The first effect of adding strong acid to natural waters is to convert the bicarbonates to the salts of the acid added. Carbon dioxide is liberated during this process. With the continued introduction of strong acid, the pH value continues to decrease slowly until a pH of approximately 4.3 is obtained. At this point, all the bicarbonate has been destroyed and continued introduction of acid causes the pH to drop sharply.

Acidic waters tend to promote corrosion of steel, concrete, and similar structures. The carbon dioxide produced is itself a corrosive agent and can adversely affect steel, concrete, and even wooden structures. Highly acidic water is harmful to many lower forms of life. For example, most bacteria can not survive at pH values less than 4.5. And, many plankton are destroyed by a pH value lower than 6.5. These organisms are essential in the "self purification" processes that normally oxidize and destroy organic pollution. In addition, the absence of these organisms tends to break the chain of food supply.

Fish are affected by acidity in a number of ways. One effect is that acidic water interferes with the ability of fish to extract dissolved oxygen from the water. An additional effect is noted in waters where carbon dioxide, produced by the addition of acidic waste, remains dissolved in the water at high concentrations. As a result of metabolic processes, fish produce carbon dioxide which must be eliminated against the partial pressure of carbon dioxide in the surrounding water. If this partial pressure becomes too high, as it may from the discharge of acidic waste, carbon dioxide will not be eliminated fast enough. The carbon dioxide will accumulate in the tissues, halting metabolism, and the fish will die.

Highly alkaline wastes, such as caustic from certain treating processes, can have adverse affects on aquatic life when discharged to receiving waters. The initial effect is a rise in the pH value of the receiving water. The extent of the rise for a given quantity of alkaline waste depends on the buffer action of the natural waters, a situation similar to that described for the addition of acidic wastes.

Most aquatic life, particularly minute plants, can not survive when the pH exceeds 9.0. The destruction of minute plants interrupts the food chain, affecting all forms of aquatic life. Fish can survive relatively wide ranges in pH. However, hydroxide ions, present in highly alkaline waters, can attack the membranes of the gills.

Dissolved Oxygen and Oxygen Demand--Dissolved oxygen is necessary for the maintenance of fish life. Generally, oxygen is present in natural waters at concentrations around 7-9 mg per liter by weight. This oxygen occurs as a result of absorption of oxygen from the air, and by photosynthesis. When oxygen is present, an aerobic condition exists and the aquatic life oxidizes organic matter to carbon dioxide and water. In the absence of oxygen, an anaerobic, or septic, condition exists. This results in the breakdown of organic matter to methane and various sulfur and nitrogen compounds which are odorous to human beings and toxic to aquatic life. Also, anaerobic waters are corrosive, of poor appearance, and unsuitable for many uses.

Many substances present in refinery wastes exert a demand on the dissolved oxygen content of the water. That is, they tend to react with dissolved oxygen and remove it from the water. Oxygen demand can be classified as chemical oxygen demand (COD), biological oxygen demand (BOD), and immediate oxygen demand (IOD).

Chemical oxygen demand is defined as the amount of oxygen required to oxidize components in the wastewater by chemical reaction. Several methods have been developed to measure this characteristic. Biological oxygen demand is defined as the amount of oxygen required to oxidize the components of the wastewater biologically, as determined by an empirical standard procedure. Immediate oxygen demand refers to materials which react quickly with dissolved oxygen. This characteristic is also determined by standard procedures.

Many pollution regulations specify limits on the discharge of materials which exhibit oxygen demand to prevent low dissolved oxygen conditions from developing.

Hardness and Salinity--Hardness in fresh water is due to the presence of dissolved salts. Carbonate or temporary hardness arises from calcium and magnesium carbonate or bicarbonates. Noncarbonate or permanent hardness is caused mainly by calcium and magnesium sulfates and chlorides. Refinery wastes contain these and other ions in amounts depending on the quality of the refinery raw water and the type of water treatment used.

The effect of increasing the hardness of fresh waters is to lessen their value for steam generation and other industrial uses. The cost of treatment for domestic users is also increased.

Aquatic life can tolerate increased hardness unless the concentration of ions is unusually high. Under this circumstance, the water balance within living cells can be disrupted by osmotic effects.

The discharge of salt (sodium chloride) contained in refinery wastewaters must be carefully monitored. The introduction of large quantities of salt into fresh waters can damage fish life. Conversely, the introduction of fresh water into the ocean or its bays can have an adverse effect on marine life.

Toxicity, Taste, and Odor--Certain refinery wastes can contain materials toxic to aquatic life. Such materials as sulfides, ammonia, or phenolics can be directly toxic, through either internal or external mechanisms, or toxic by indirect means. The latter group would include the toxic effects of acids, bases, excessive dissolved solids, and materials which exhibit oxygen demand.

The toxicity of a particular compound is usually a function of concentration and time of exposure. A compound which is harmless at low concentrations may become lethal at higher concentrations. Some compounds may accumulate in the tissues and prove lethal at a later time or cause changes in metabolism, reproduction, or other vital functions. Other factors affecting toxicity include the characteristics of the water and the tolerance or immunity developed by various forms of aquatic life.

Materials such as hydrocarbons, sulfur compounds, phenolics, and nitrogen compounds can impart objectionable taste and odor to potable waters, even at low concentration levels.

Complete removal of tastes and odors produced by some compounds is extremely difficult and treatment can even accentuate the problem. For example, if chlorine is used to sterilize water which contains phenolics, chlorophenolics may be formed. The taste and odor of chlorophenols is even more offensive than phenolics alone.

Color, Turbidity, and Suspended Matter--The color, turbidity, and suspended matter contents of water are properties which may be significantly affected by refinery wastes. The presence of certain solutes and suspended matter can cause coloration of the water. Strongly colored water can limit the penetration of light to the first few feet below the surface. Thus, photosynthesis, which is an important source of dissolved oxygen, is reduced.

Turbidity is caused by finely divided particles which form colloidal suspensions that do not settle. Turbidity adversely affects recreational uses and the aesthetic qualities of the receiving water.

As coarser suspended matter settles, it can drag small plants and animals with it causing the formation of a sludgy mat on the bottom of the lake or stream. This mat contains organic matter and bacteria which create a heavy oxygen demand.

There are a variety of sources of suspended solids in refinery wastewaters. These include finely divided carbon, coke, catalyst fines, clay, silt, cinders, emulsions, and flocculent matter.

Oil--Oil discharged with refinery wastewaters is nearly always objectionable from a recreational and aesthetic viewpoint. Even low concentrations of oil can cause unpleasant taste and odor problems. Floating oil can coat the feathers of water fowl, the gills of fish, and adhere to the surface of smaller organisms. In addition, heavy oil films interfere with aeration and photosynthesis. Water soluble components can exert toxic action on fish and other organisms.

Temperature--The discharge of warm wastewater causes the temperature of the receiving waters to increase. An increase in temperature causes the solubility of oxygen to decrease. Also, reaction rates increase resulting in increased oxygen consumption. Metabolic functions such as respiration and food consumption are accelerated. In addition, the toxic effect of some pollutants increases.

Aquatic organisms are sensitive to temperature and can exist only within a limited temperature range. Changes in water temperature can drastically affect the biological makeup of the receiving waters.

4.8.2.2 Wastewater Treatment Technology--

A variety of potential pollutants is contained in refinery waste streams. As indicated in Table F4-69, nearly every operation produces waste materials in varying amounts and forms. Some of these materials are:

- Oil
- Dissolved solids

TABLE F4-69. TYPICAL WASTE STREAM CHARACTERISTICS OF VARIOUS PROCESS OPERATIONS

Process Unit	Flow Gal/Bbl	pH	BOD lb/Bbl	COD lb/Bbl	Oil lb/Bbl	H_2S lb/Bbl	NH_3 lb/Bbl	TDS lb/Bbl
Crude Desalting	2.1	6.7-9.1	.003	.032	.012	.008	.009	.250
Crude Fractionation	26.0	8.6	.0002	.005	.017	.001	-	.035
Catalytic Cracking	15.0	8.3-9.7	.015	.018	.100	.036	.040	.090
Thermal Cracking	2.0	6.4	.001	.003	.001	.001	-	-
Hydrocracking	2.0	7.3	.002	.045	-	.002	-	.002
Hydrotreating	1.0	9.0	.010	.050	-	.002	.030	.035
Delayed Coking	1.0	8.8-9.1	-	.032	.006	-	-	.030
Reforming	6.0	7.6	-	.040	.050	.001	-	.125
Sour Condensates	3.0	4.5-9.5	.100	.200	.100	1.00	0.75	-
Alkylation	60.0	8.1-12.	.001	.010	-	.010	0	.300

Source: Reference 4

- Suspended solids
- Hydrogen sulfide
- Acids
- Bases
- Soluble organics
- Phenolics
- Metallic ions
- Ammonia

These materials may be contained in a number of waste streams including:[5]

- Oily wastewaters
- Chemical wastewaters
- Boiler blowdown
- Cooling water
- Cooling tower blowdown
- Stripping steam condensates
- Spent catalysts

- Spent regenerants
- Storm and surface runoff
- Sanitary sewage

The methods used in refinery wastewater treatment can be classified as follows:

- In-plant or pretreatment
- End of pipe treatment

In-plant or pre-treatment involves the use of procedures which can (1) reduce the amount of pollutants sent to the wastewater system, (2) reduce the amount of water discharged to the receiving waters, and (3) make subsequent end of pipe treatment more efficient.

End of plant treatment processes can be further classified as either primary, intermediate, secondary, or tertiary processes, depending on their function in the treatment scheme.

In-plant or Pretreatment Technology--A variety of procedures are available which can reduce the waste load charged to water treatment facilities. One such procedure is the use of sour water stripping. Certain water streams, particularly sour water condensate from stripping operations, contain high concentrations of hydrogen sulfide and ammonia. These components, which are toxic, odorous, and exhibit high oxygen demand, result from desulfurization, denitrification, and hydrotreating operations.

Hydrogen sulfide and ammonia are often removed via steam stripping before this water is sent to the wastewater system. Processes are available which can recover essentially pure sulfur and ammonia.

Some sour water condensates, particularly those from cracking or coking operations, contain high concentrations of water soluble phenol. High concentrations or surges of phenol can kill bacteria used in subsequent water treatment processes. To avoid this problem, these condensates are often used as raw desalter water. A portion of the phenol in the wastewater is absorbed by the crude oil thereby reducing the amount of phenol reaching the wastewater system.[4]

Other methods of reducing wasteloads to the wastewater system include limiting waste production at the source. Techniques which limit contact between water and oil such as replacing barometric condensers with surface condensers have been used. Additional techniques include the installation of initial treatment facilities for removal of a particular pollutant at the pollution source.[9]

Another technique for improving wastewater quality is to reduce the amount of water which requires treating. A considerable amount of effort has been directed toward developing methods to recirculate certain water streams rather than discharging them to receiving waters. These techniques include the installation of air coolers and cooling towers, the elimination of once-through cooling, chemical treatment to prevent scaling, corrosion, and biological (algae growth), and a variety of others. These procedures have greatly reduced the quantity of fresh makeup water required to process each barrel of crude oil. Additional benefits include a reduction in thermal water pollution.[6]

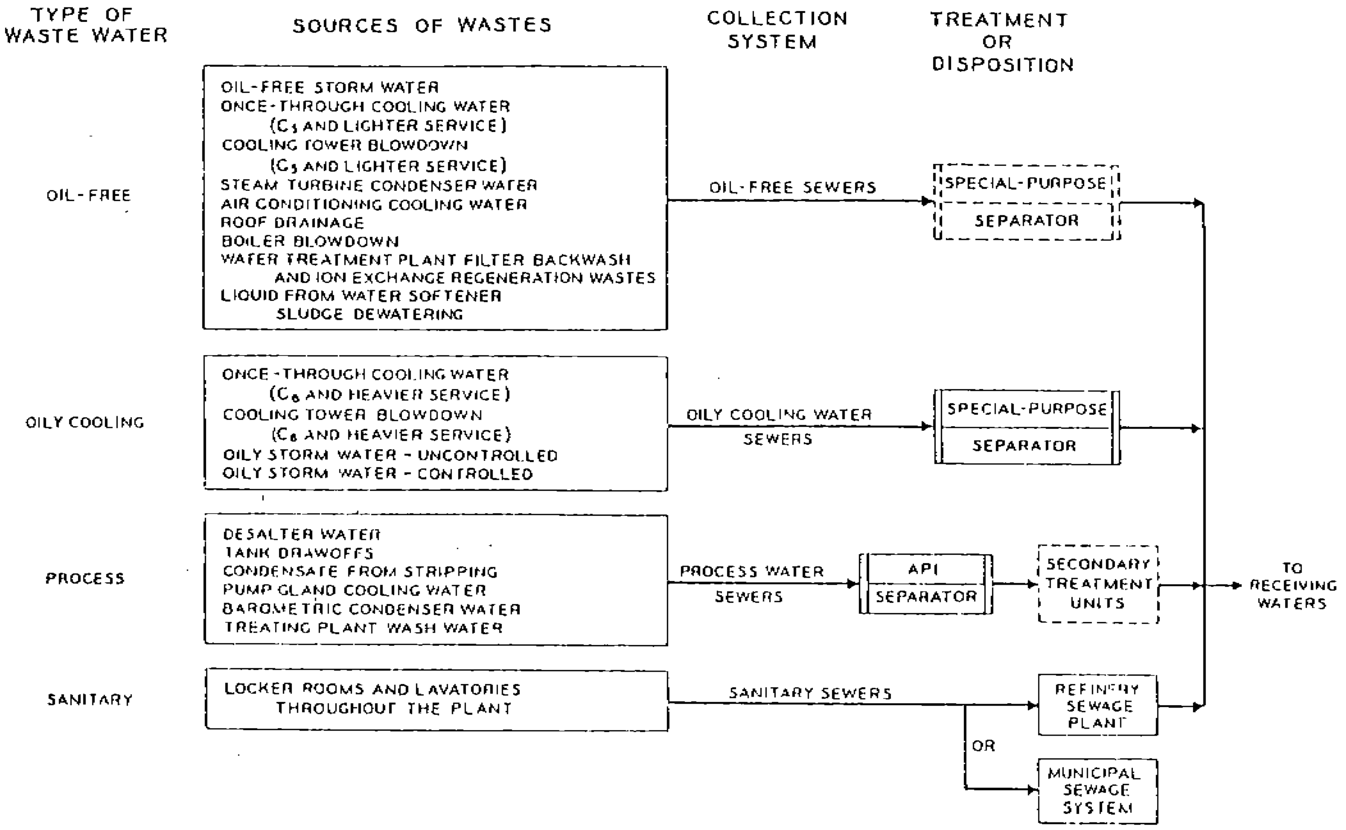
There are a number of pretreatment techniques available to help improve the efficiency of end of pipe water treatment processes. The most important technique is stream segregation. It has long been recognized that water treatment operations could be made more efficient by treating certain streams separately from the others. An example of such a stream segregation scheme is given in Figure F4-28.

By segregating waters which require only minimal treatment from those which require substantial treatment, the size of treatment facilities can be reduced. Most newer refineries use a segregated sewer system similar to that of Figure F4-28. Older refineries, however, were not built with such systems and the cost of conversion can be prohibitive. Most older refineries do, however, segregate sanitary wastes.

Additional pretreatment schemes include pre-aeration of the wastewater to meet immediate oxygen demand and equalization or surge ponds to smooth variations in water or waste flow.

<u>End of Pipe Treatment</u>--End of pipe treatment consists of processes designed to produce an effluent water stream of sufficient quality to meet state and federal pollution regulations. In general, each refinery will have its own particular water processing scheme based on the type of refinery, the water use pattern, and the final effluent purity requirements.

The processes used to meet water quality standards are often classified as shown in Table F4-70. The utilization of these processes by refiners is indicated in Table F4-71.



Source: Reference 2

Figure F4-28. Example of refinery stream segregation.

TABLE F4-70. CLASSIFICATION OF REFINERY WASTEWATER TREATMENT PROCESSES

Treatment	Objectives	Processes
Pre- or Inplant Treatment	Removal of Phenolics, $S^=$, NH_3, RSH, Acid Sludge, Oil Water Reuse and Equalization	Unit Separators Steam Stripping Air Oxidation Neutralization Surge Ponds
Primary Treatment	Free Oil and Suspended Solids Removal	API Separators Parallel Plate Separators
Intermediate Treatment	Emulsified Oil, Suspended Solids, and Colloidal Solids Removal	Dissolved Air Flotation Coagulation-Flotation Coagulation-Precipitation Filtration Equalization
Secondary Treatment	Dissolved Organics Removal Reduction in BOD and COD	Activated Sludge Trickling Filters Aerated Lagoons Oxidation Ponds Rotating Biological Discs
Tertiary Treatment	Variable Objectives	Filtration Air Flotation Coagulation Activated Carbon

TABLE F4-71. REFINERY UTILIZATION OF WASTEWATER TREATMENT PROCESSES

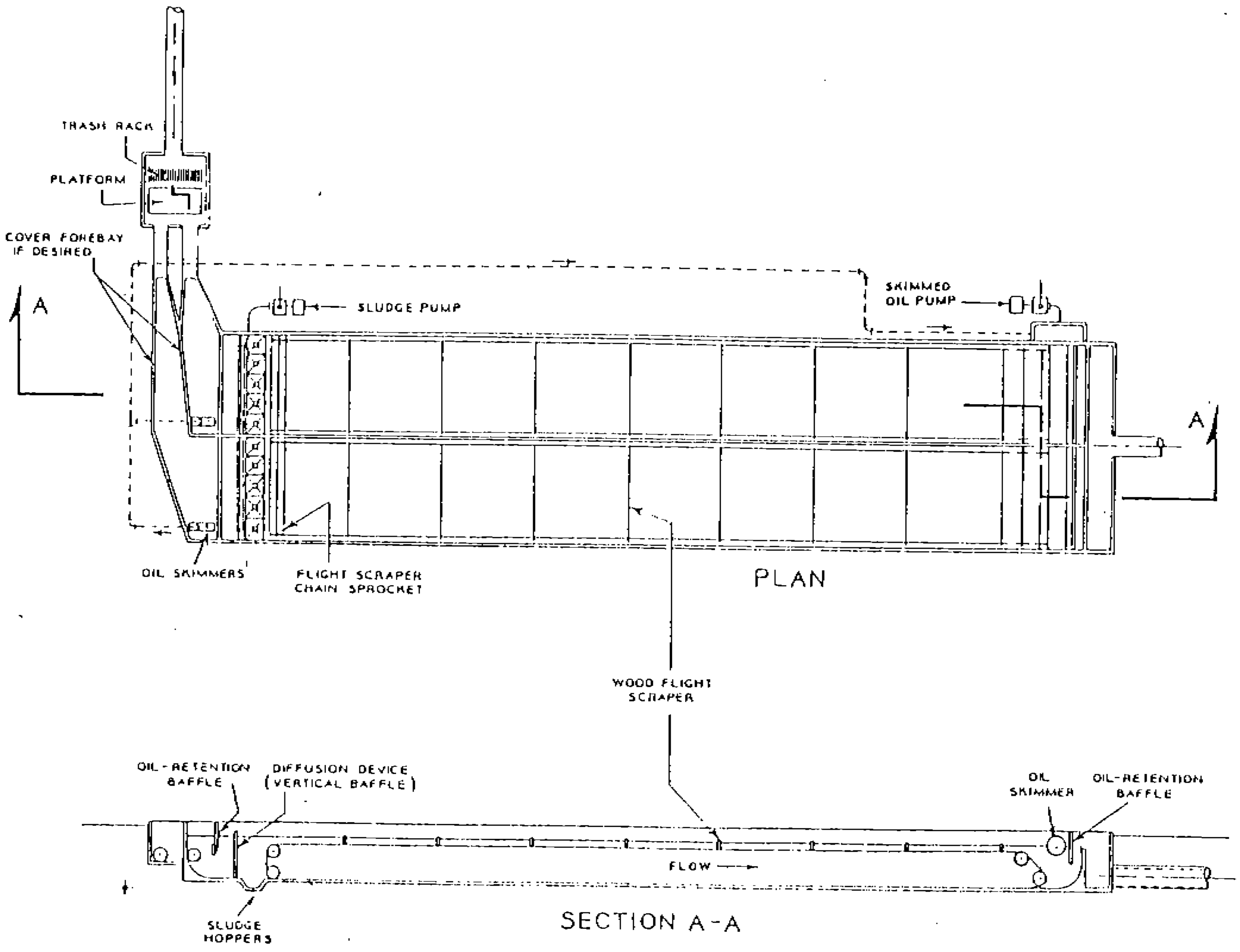
	Crude Capacity (BPCD)	% of US Capacity
Primary treatment only	3446000	33.0
Intermediate treatment	1171000	11.2
Biological treatment	4433000	42.4
	9050000	86.6

Source: Reference 8

Primary treatment - Primary treatment processes include API separators and parallel plate separators. The purpose of these units is to remove floating oil and suspended solids from the wastewater. All refineries use some sort of primary separation device and it is often the only treatment required.

A. API Separators--API separators have been used in petroleum refining operations for over 30 years. Oily water enters one end of a rectangular channel, flows through the length of the channel, and discharges at the other end. A sufficient residence time is provided to allow oil droplets to float and coalesce at the surface of the wastewater. An oil skimmer is provided near the end of the separator to collect floating oil.

Floating oil is advanced toward the skimmer by an oil and sludge moving device. These devices consist of a series of moving flights which span the width of the separator. As the flights move over the surface of the separator, floating oil is advanced toward the skimmer. The flights return to the inlet of the separator on the bottom of the channel. Solids which have settled out of the water are thus scraped along the channel bottom to a sludge collecting hopper. Both the skimmed oil and the settled sludge are collected and treated for disposal or reuse. The water stream is either discharged to receiving waters or routed to additional treating facilities. A schematic diagram of a typical API separator is given in Figure F4-29.



Source: Reference 2

Figure F4-29. Schematic diagram of a typical API separator.

B. Parallel-Plate Separators--The parallel plate separator is a relatively recent development which functions by reducing the distance oil droplets must travel before being collected and coalesced. The separator consists of a number of parallel plates set at an angle and approximately 4 inches apart. The oil droplets coalesce on the underside of the plates and creep up to the surface of the water. Conversely, solids accumulate on the top of the plates and travel to the bottom of the separator. Parallel plate separators have the advantage of occupying less area than API separators.[10] Typical efficiencies for various oil-water separators are given in Table F4-72.

Intermediate treatment - API and parallel plate separators are unable to remove materials which neither float nor settle within the residence time provided. Thus, materials such as emulsions and suspended or colloidal solids must be removed by other methods.

Biological and physical-chemical treatment processes require that the influent to the treatment system be of some minimum quality. For this reason, additional oil and suspended solids removal may be required after gravity separation. Such treatment can be provided by processes such as:

- Dissolved air flotation,
- Induced air flotation,

TABLE F4-72. TYPICAL EFFICIENCIES OF OIL SEPARATION UNITS

Oil Content		Oil Removed (%)	Type	COD Removed (%)	SS Removed (%)
Influent (mg/1)	Effluent (mg/1)				
300	40	87	Parallel Plate	-	-
220	49	78	API	45	-
108	20	82	Circular	-	-
108	50	54	Circular	16	-
98	44	55	API	-	-
100	40	60	API	-	-
42	20	52	API	-	-
2,000	746	63	API	22	33
1,250	170	87	API	-	68
1,400	270	81	API	-	35

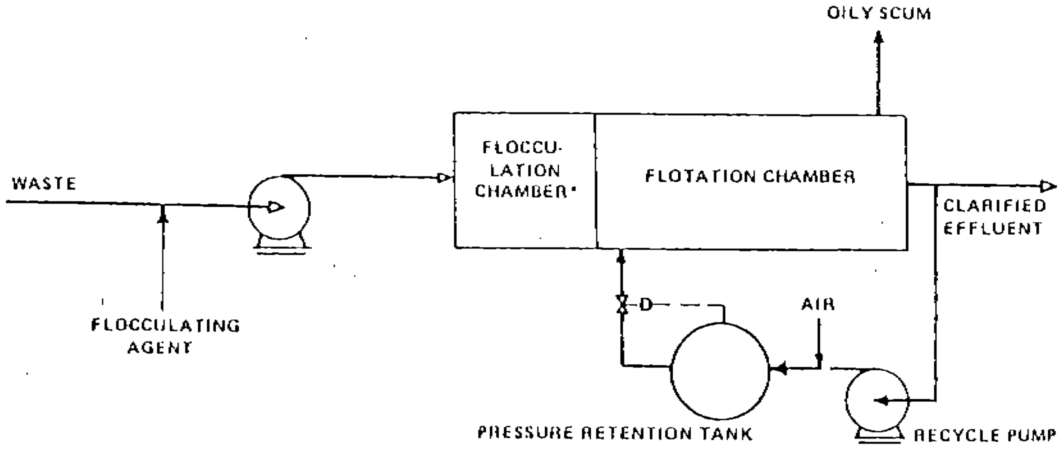
Source: Reference 10

- Chemical coagulation and sedimentation, and
- Filtration.

Dissolved air flotation (DAF) is used for separating suspended and colloidal materials from water, including suspended solids and insoluble oily wastes. The DAF unit separates oily wastes and suspended solids from water by introducing many tiny air bubbles into the water. These bubbles attach themselves onto oil globules and suspended solids that are dispersed through the waste stream. The buoyancy of the resultant oil globule/air bubble complex is substantially increased. These complexes, therefore, rise through the wastewater and collect on the water's surface where they can be removed by surface skimming devices.

In many cases, removal of emulsified oils is enhanced by adding flocculating agents to the wastewater. These materials improve oil and solids removal by improving floc formation which results in more efficient and rapid solids flotation.[11]

The most common flow scheme for this type of operation is diagrammed in Figure F4-30. In this example, wastewater, combined with a flocculation agent, is charged to a flocculation chamber. From there, the water-floc mixture flows to the flotation chamber. Tiny air bubbles are introduced to the flotation chamber by dissolving air in a recycled portion of the clarified effluent. This water is mixed with air at pressures about 40 psig. This water is then sent to the flotation chamber where, under reduced



Source: Reference 8

Figure F4-30. Recycle-flow pressurization scheme for a dissolved air flotation unit.

pressure, the dissolved air emerges in the form of small bubbles.[8]

In addition to removing oil emulsions and suspended solids, dissolved air flotation can also result in a reduction in the oxygen demand of the water.

Induced air flotation (IAF) systems operate using the same principles as the pressurized DAF units. The gas, however, is self-induced by a rotor-disperser mechanism. The rotor forces the liquid through the disperser openings, thereby creating a negative pressure that pulls the gas downward into the liquid. IAF oil removal efficiencies are usually comparable to the DAF systems.[12]

Coagulation and precipitation have been applied to refinery wastewaters for removal of suspended and colloidal pollutants. The conventional coagulation system utilizes a rapid mix tank followed first by slow agitation of the mixture in a flocculation chamber to promote floc particle growth and then sedimentation by gravity. The applicability of this process is determined on a case-by-case basis. The significant parameters in this process include pH, flocculation time and chemical selection.[7]

Filtration is another candidate process for the removal of oil and solids in refinery wastewater prior to biological treatment. Several types of filtration devices have been proposed for removing free and emulsified oil from refinery wastewaters. These filters range from units with simple sand media to those containing special media which exhibit a specific affinity for oil. The wastewater may flow up through a graded sand media which serves as a filtering and coalescing section. Thus, even small particles are separated and retained on the media. Regeneration of the filter beds is accomplished by backwashing the filter pad to remove the solids and remaining oil.

Equalization of wastewaters discharged from refinery processing units as an intermediate step in the treatment system has been found to greatly improve treatment results. Biological processes as well as physical-chemical systems operate more efficiently if the composition and flow of the wastewater feed is relatively constant. Periodic and unpredictable large discharges can occur in any refinery. Requirements of the NPDES require a fairly consistent effluent discharge.[11]

Secondary treatment - Petroleum refineries have wastewater streams containing dissolved organics. Removal of these organics is required before reuse or discharge of these streams. Processes for removal of dissolved organics are generally classified as physical, biological, or chemical treatment. Wastewaters from the petroleum refining industry are generally biologically treated after secondary deoiling. Physical and chemical treatment are considered advanced treatment processes that follow biological treatment.

All of the biological methods for treating organic wastes in water involve oxidative decomposition by microorganisms. The biological wastewater treatment methods used by the refining industry include:

- Activated sludge,
- Trickling filters,
- Aerated lagoons,
- Oxidation ponds, and
- Rotating biological discs.

The processes used in each refinery are determined by the flow and contaminant characteristics of the waste stream to be treated. As refineries expand or process configurations change, additional units are built in series or parallel to accommodate the effluent treatment requirements.

A. Activated Sludge--Activated sludge processes are used extensively for removing biodegradable organic contaminants. A high quality effluent is usually obtainable from a properly designed and operated activated sludge system.

This process is carried out in a reaction tank containing a high concentration of microorganisms. Oxygen is supplied to the wastewater in the reaction tank either by mechanical aerators or a diffused-air system. Microorganisms remove the organic materials by biochemical synthesis and oxidation reactions, converting it to CO_2, water, and new cell material. The biological solids must be removed for disposal.

The main components of the process are the aeration (reaction) vessel and the clarification tank. Sludge removed from the clarification tank is recycled to the aeration vessel to maintain the required concentration of microorganisms. A portion of the sludge must be discarded and requires disposal.[11]

B. Trickling Filters--A trickling filter consists of a large, open-topped vessel containing a packed medium that provides a growth site for biological microorganisms. The soluble organic pollutants are consumed by the organisms, and converted to CO_2, water, and new protoplasm. In general, the filter media is corrugated plastic sheets (polystyrene and PVC) welded or bonded together in predetermined configuration. Rock, tile, coal or slag can also be used; however, problems such as plugging, resistance to air flow, and low loadings make these materials less satisfactory. The air flow through a trickling filter is generally down and is generally cool.

C. Aerated Lagoons--An aerated lagoon is a lagoon constructed to a depth of about 10 feet with oxygen supplied by artificial means. The oxygen requirements of the system are usually satisfied with the use of mechanical aeration. This treatment method involves biological oxidation in which microorganisms convert dissolved or suspended organic contaminants to stable organic compounds, CO_2, and water. This wastewater treatment method has been primarily adopted in warm climates and is best used as polishing process after recovery of organics such as phenol.

The common classes of aeration equipment most often considered are: diffused aeration systems, submerged turbine aerators, and high- and low-speed surface aerators. In addition, gravity aerators and spray aerators are available.

D. Oxidation Ponds--The depth of the ponds is normally limited to three to four feet to assure an adequate supply of oxygen so that aerobic conditions are maintained without mechanical mixing. Aeration is achieved by oxygen transfer at the surface and by the photosynthetic action of algae present in the pond. Microorganisms then cause aerobic degradation of organic contaminants in the wastewater.

E. Rotating Biological Discs--A rotating biological disc system is a mechanical process that brings wastewater, air, and microorganisms together for biological oxidation. This process consists of a series of closely spaced discs (10-12 feet in diameter) which are mounted on a horizontal shaft and rotated with about one-half of the surface immersed in the wastewater. The process has been used in Europe for several years. The discs are typically constructed of light-weight plastic. When the process is placed in operation, the microbes in the wastewater begin to adhere to the rotating surfaces and grow there until the entire surface area is covered with a 1/16-1/8 inch layer of biological growth. As the discs rotate, they carry a film of wastewater into the air where it trickles down the surface of the discs, absorbing oxygen. Upon completion of a rotation, the aerated and partially treated wastewater is mixed with the balance of the wastewater. This adds to the dissolved oxygen content and reduces the concentration of organic matter in the tank. BOD removal and oxidation of ammonia nitrogen is inversely proportional to the hydraulic loading on the disc units.[11]

Tertiary treatment - Some refineries provide additional treatment downstream of the biological treatment units. This polishing treatment may be required by changes in refinery effluent water quality or effluent regulations which force refiners to install equipment to remove contaminants remaining after biological treatment. Facilities commonly utilized by the refining industry to polish final effluent streams include various units for the reduction of suspended solids and carbon adsorption units for organic pollutants removal.

A. Suspended Solids Reduction--Effluent quality can be improved by further suspended solids reduction after biological treatment. Suspended solids removal processes include filtration, air flotation, chemical coagulation with gravity precipitation, and polishing ponds. Filtration and air flotation have been applied to biologically treated refinery wastewaters. The primary objective of these processes is suspended solids removal; however, a natural and corresponding reduction in organic parameters such as BOD, COD, TOC, and oil may occur. The magnitude of organic parameter reduction varies among refinery effluents.

B. Carbon Adsorption Organics Removal--The activated carbon adsorption process has not been used widely for refinery wastewater treatment, yet preliminary pilot work and limited experience indicate selected applicability. Carbon absorption systems will remove non-biodegradable and toxic organics which may be present in the wastewater after biological treatment.

4.8.2.3 Atmospheric Emissions from Wastewater Treatment Units--

Hydrocarbons are released to the air as fugitive emissions from all of the above named operations. The extent of these emissions is a function of the amount of hydrocarbon entering the unit, the volatility of that hydrocarbon, the type of control built into or onto the unit, and other factors. Thus, the greatest opportunity for emission should be at the front end of a wastewater system, i.e., sewers, open ditches, holding ponds occurring prior to the API separator, and the API separator itself. Since the API separator removes most of the hydrocarbons with the skimmed oil, units following it in the system should release substantially lower quantities of fugitive hydrocarbons.

Typical controls available to the industry include: operating a sealed sewer system with the hydrocarbon vapors being flushed to a heater or flare; using fixed or floating roofs on the API separator and in some cases venting the hydrocarbon vapors to a heater or flare; eliminating all ditches and holding ponds prior to the API separator; and using covered DAF units.

The quantity and character of emissions are subject to between-refinery variations due to the type of crude being processed, the process units and product slate of a refinery, the type of wastewater system, the presence or absence of various emission controls within the wastewater system, and the refinery maintenance practices. The quantity and character of emissions also vary within a refinery due to upsets, spills, and turnarounds, storm runoff if sewers are not segregated, malfunctioning controls in the wastewater system and changes in ambient temperatures, wind direction and velocity. Several other less common factors also affect emissions such as the presence of emulsions, malfunctioning of the wastewater unit, improper bacterial growth, etc.

The current hydrocarbon emission factors listed by the EPA for API separators are given in Table F4-73. Research is now underway by EPA to update these figures.

4.8.3 Sludge and Solids Treatment/Disposal

A variety of types of solid waste are generated by petroleum refineries. Many of the solid wastes contain toxic hydrocarbons or metallic compounds, which must be handled carefully to protect human health and avoid environmental damage.

Refinery solid waste streams may be classified in two main groups: those wastes that are generated intermittently and those that are generated continuously.[13] Intermittent wastes include process vessel sludges, scale and other deposits removed during turnarounds; storage tank sediments; and product treatment wastes, e.g., spent filter clay or catalyst.

Continuous wastes are those requiring relatively continuous (at less than two-week intervals) disposal. Typical

TABLE F4-73. API SEPARATOR HYDROCARBON EMISSION FACTORS[a,b,c]

	Emissions	
	lb/10^3 Gal Wastewater	lb/10^3 Bbl Refinery feed
API separators (uncontrolled)	5	200
API separators (controlled by fixed or floating roof or vapor recovery system)	0.2	10

[a] Source: Reference 3

[b] These emission factors have been given an emission factor rating of "D."

[c] Less than 1 percent of total emissions are methane.

continuous wastes include coker wastes; spent catalysts and catalyst fines from fluid catalytic cracking units; spent and spilled grease and wax wastes from lube oil plants; waste biological sludges and other oily sludges from wastewater treatment facilities.

In the past, the majority of refinery solid waste was either sent to landfills or ponds on-site, or partially dewatered and hauled to an off-site landfill or dump. Although landfills are still a common solid waste disposal method, increasingly stringent environmental regulations have forced refiners to consider other disposal options, such as incineration, chemical fixation, or a combination of methods.

The remainder of this section discusses the sources and characteristics of typical refinery solid wastes, and the options available for treatment and disposal of these wastes.

4.8.3.1 Sources and Composition of Refinery Solid Waste--

Refinery solid waste is generated both from process-related sources and from effluent treatment units. A list of wastes from both sources is characterized in Table F4-74. Brief descriptions of each waste type are given in the following paragraphs.

Storage tank bottoms accumulate in storage tanks and are removed when tanks are periodically cleaned. Crude storage tank bottoms consist of a mixture of iron rust, clay, sand, water, and emulsified oil and wax. Product tank bottoms vary in composition depending on the product stored. Bottoms from leaded product storage tanks contain small amounts of tetraethyl or tetramethyl lead, other heavy metals, and phenols.

Neutralized alkylation sludge is produced by both sulfuric acid- and hydrofluoric acid-based alkylation processes. The sludge from sulfuric acid processes contains sulfuric acid, polymerized hydrocarbons, and storage tank scale. Spent hydrofluoric acid is neutralized with lime to produce an insoluble calcium fluoride sludge.

Filter clays are used in removing color bodies, chemical treatment residues, and trace moisture from gasoline, kerosene, jet fuel, light fuel oil, and lube oil streams. Spent filter clay forms a sludge or cake which contains traces of oil and heavy metals.

Catalyst fines are continuously generated by fluid catalytic cracking units and collected by electrostatic precipitators. The fines, which are generated continuously, contain aluminum silicate particles onto which heavy metals (e.g., vanadium and nickel) are adsorbed.

TABLE F4-74. SOURCES AND CHARACTERISTICS OF REFINERY SOLID WASTES

Description	Source	Characteristics
Process Solids		
Crude oil sediment and water	Crude oil storage, desalter	Iron rust, iron sulfides, clay, sand, water and oil
Catalyst fines and spent catalyst	Fluid catalytic crackers, catalytic reformers, hydrotreating/hydrorefining processes	Inert solids, catalyst particles (miscellaneous heavy metals), carbon
Coke fines	Coker	Carbon particles, hydrocarbons
Spent sludges	HF alkylation units	Calcium fluoride, bauxite
Spent clay	Lube oil treatment units	Clay, acid sludges, oil
Tank bottoms	Storage tanks	Oil, water, solids
Effluent Treatment Solids		
API separator sludge and slop oil emulsion solids	API separator	Oil, sands, and miscellaneous process solids
Chemical precipitation sludge	Chemical wastewater treatment processes	Aluminum or ferric hydroxides, calcium carbonate
Scums or froth	Air flotation	Oil, solids, flocculants
Waste biological sludges	Biological treatment	Water, inerts, biological solids

Source: Reference 15

Spent catalysts result from a number of refinery process units which use a fixed-bed catalyst: catalytic reforming, hydrodesulfurization, hydrotreating, hydrocracking, and others. Spend catalysts contain a number of heavy metals, plus organic contaminants absorbed from process feedstocks.

API separator sludge and slop oil emulsion solids are non-recycled components from API separators. Slop oil emulsion solids contain water, oil, and suspended particulate matter. Separator sludge contains a mixture of all sewered wastes, including tank bottoms, desalter waste and oil. The sludge usually contains high concentrations of phenols and heavy metals.

Chemical precipitation sludge is generated at some refineries which chemically treat aqueous waste streams. Chemical coagulants are added to the streams to form a gelatinous precipitate in which oil and solids are trapped.

Waste biological sludge contains oil, suspended solids, and organic cell material generated in secondary biological wastewater treatment. Some heavy metals may also be present.

4.8.3.2 Treatment and Disposal of Refinery Solid Wastes--

Both process and effluent treatment solid wastes have historically been sent directly to landfills or open pits for disposal. Oily wastes, although sometimes incinerated, have usually been sent to an oily waste disposal pit.

However, promulgation of more stringent solid waste disposal regulations has forced refiners to consider methods of waste disposal which minimize or prevent discharge of waste-contaminated materials into the environment. Landfills, although still a viable means of waste disposal, are being redesigned to contain wastes so that no hazardous or toxic materials enter the air, ground, or surface waters. Other treatment methods, such as incineration or chemical fixation, are being considered for use in conjunction with landfilling. Some states permit landfarming, in which small amounts of oily sludge are distributed in topsoil. These methods are described in the remainder of this section.

Landfilling is the most often-used solid waste disposal method. However, landfill design criteria are currently undergoing change. Regulations proposed under the Resource Conservation and Recovery Act (1978) require that landfills be designed and constructed so that no direct contact exists between the landfill and surface or groundwater.[15] These regulations generally prohibit landfilling of ignitable, reactive, or volatile wastes, and bulk liquids, semi-solids, and sludges. Landfills must be lined with either a natural impermeable material or one of several artificial liner systems.[15] The proposed regulations require that groundwater and leachate monitoring systems be maintained around the landfill.[15]

Landfilling is currently the typical disposal method for most of the solid wastes listed in Table F4-74. However, existing landfills are probably inadequate for disposal of most oily refinery waste, since leaching of toxic organics and heavy metals is a strong possibility.

Landfarming is used in some areas for the disposal of refinery solid wastes. This method uses soil bacteria to biodegrade organic materials in solid wastes. Sludge biodegradation rate is dependent on its oil content and depth of plowing.[16]

No long-term data exist as to the adequacy of landfarming as a refinery sludge disposal method. Little is known about the nature of its degradation products or about the percolation and leaching of heavy metals or toxic organic compounds into ground or surface waters.[16]

Incineration is a relatively expensive means of solid waste treatment. Pollution controls may be required on some incinerators, and additional fuel may be necessary to incinerate low heat content materials. Additionally, a pretreatment dewatering step is usually required to decrease the water content of the solid waste.[17]

Several types of incinerators may be used to combust solid waste: box furnaces, vortex incinerators, rotating hearth incinerators, rotary kiln incinerators, and fluidized bed incinerators.[17,18] Supplemental fuel requirements for each type of incinerator have not been reported in the literature. However, one source reported that sludge having a heating value of 57,000 Btu/gallon is adequate for supporting combustion in a fluidized bed incinerator.[18]

Although incineration reduces sludge volume, incinerated ash must still be disposed. Disposal is usually to a landfill, where design and operating constraints discussed previously for raw sludge may also apply.

Chemical fixation is a solid waste treatment method in which polyvalent metal ions and waste hydrocarbons are chemically bound in a cross-linked, polymeric matrix.[22] In the second phase of the process, the polymeric material reacts with soluble silicates in the reactor to form an insoluble solid. The resulting solid is usually landfilled.

Results of tests conducted under a variety of simulated landfill conditions have indicated that little leaching of heavy metals and organic compounds results from chemically-fixed waste.[13]

4.8.4 References for Section 4.8

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SECTION 5

CONVERSION FACTORS

To Convert From	To	Multiply By
Btu	kcal	0.252
bbl	ℓ	159.0
gal	ℓ	3.785
ton	kg	907.2
lbs	kg	0.454
cm	in	0.394
ft^3	m^3	0.0283
psi	kg/cm^2	14.223
g/gal	g/ℓ	0.264
Btu/bbl	kcal/ℓ	0.0016
kWh/bbl	kWh/ℓ	0.0063
lb/bbl	kg/ℓ	0.0285
lb/10^6 Btu	g/Mcal	18.0
grain/ft^3	g/m^3	2.29
gal/10^{6}ft^3	ℓ/10^{6}m^3	133.7
gpm	m^3/hr	0.227
lb/1000 gal	mg/ℓ	119.8