Energy and Environmental Profile of the U.S. Petroleum Refining Industry

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Prepared by

ENERGETICS
Incorporated
Columbia, Maryland

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Table of Contents

Foreword ii

1. Overview 1

2. The Integrated Petroleum Refinery 29

3. Crude Oil Distillation 39

4. Cracking and Coking Processes 49

5. Catalytic Reforming 69

6. Alkylation 75

7. Hydrotreatment 83

8. Additives and Blending Components 89

9. Lubricating Oil Manufacture 97

10. Supporting Processes: Sulfur Management, Chemical Treatment,
Water Treatment and Process Heating 103

Bibliography 117

FOREWORD

In 1996, the U.S. Department of Energy's Office of Industrial Technologies (DOE/OIT) began work on a series of reports in support of DOE/OIT's Industries of the Future strategy. Under this industry-led strategy, DOE/OIT works with U.S. industry to develop technology partnerships and support collaborative R&D projects that enhance energy efficiency, competitiveness and environmental performance. To date these industries include agriculture, aluminum, chemicals, forest products, glass, metalcasting, mining, petroleum refining, and steel.

Though the profiles are intended primarily to better inform collaborative industry-DOE R&D planning, they provide a valuable resource that can also be widely used by many others who are not directly involved in these efforts. Through these profiles, research managers, policymakers, industry analysts and others can gain a general perspective of energy use and environmental impacts in industry. The profiles do not attempt to recreate sources that already exist; rather, they provide a "snap-shot" of the industry and an excellent source of references on the topic.

The primary advantage of the profiles is that they synthesize into a single document information that is available in many different forms and sources. Aggregated data for the entire industry as well as data at the process level is presented according to the major unit operations of each industry. Data is obtained from the most currently available published sources, industry experts, and government reports. Prior to publication, profiles are reviewed by those working in the industry, trade associations, and experts in government and the national laboratories.

To date, energy and environmental profiles have been published for the aluminum, steel, and petroleum refining industries. Development of profiles for the glass, metalcasting, forest products, and chemical industries is currently underway, and similar reports are planned for the remaining industries.

1

Overview

1.1 Petroleum Refining: An Essential and Volatile Industry

Petroleum is the single largest source of energy for the United States. When measured in British thermal units, the Nation uses two times more petroleum than either coal or natural gas, and four times more petroleum than nuclear power, hydroelectricity, and other renewable energy sources. On average, every citizen in the U.S. consumes about 20 pounds of petroleum per day. This primary dependence on petroleum for energy has been a reality for decades, with petroleum's share of the domestic energy mix peaking at 49 percent in 1977 [DOE 1993].

Before petroleum can be used it must be "refined" into products with the desired properties. **Petroleum refineries** use various physical and chemical methods to convert crude oil into a large array of useful petroleum products. While the United States is one of the world's largest producers of crude oil, the Nation relies heavily on imports to meet demand for petroleum products for consumers and industry. This reliance on international ties to petroleum trade has led to numerous upheavals in the industry over the last three decades.

Geopolitical Disruptions and Volatile World Oil Prices Have Dramatically Impacted U.S. Refiners

In 1973, Arab nations angry at the U.S. for its support of Israel in the 1973 Arab-Israeli war, disrupted supplies of crude oil, increasing petroleum prices and motivating refineries to import crude oil from any available source. The embargo created sudden price hikes and short-term shortages in refined petroleum products. When the embargo was lifted 6 months later, world crude oil prices had tripled and OPEC (Organization of Petroleum Exporting Countries) was in control of the world oil market. Numerous efforts were subsequently undertaken to conserve energy and switch from petroleum to less costly alternative fuels. Electric utilities began to displace distillate and residual fuel oil in favor of coal and natural gas for power production.

In 1973 the Emergency Petroleum Allocation Act established a two-tiered pricing system to ensure distribution of products and establish equitable prices in the oil industry. "Old oil" (from facilities producing at less than 1972 production levels) was subject to a price ceiling, while "new oil" could be sold at market prices. Problems with this system led to additional legislation (e.g., the Buy-Sell Program, the Supplier-Purchaser Rule, and the Crude Oil Entitlements Program).

Subsidies under the Crude Oil Entitlement Program favored production from smaller refineries. The small refinery bias increased the profitability of operating small, inefficient refineries, and construction of these facilities boomed. Most of the new capacity was in the form of unsophisticated hydro-skimming plants with less than 30,000 barrels per day of crude distillation capacity. Between 1973 and 1981, the number of operable refineries in the U.S. rose from 281 to a record high of 324. Crude oil distillation capacity grew dramatically, from 13.7 million barrels per day at the beginning of 1973 to 18.6 million barrels per day in 1981 [DOE 1993]

Further upheavals between 1979 and 1981 followed the Iranian revolution, which again disrupted supplies of crude oil in world markets, including U.S. refiners. Imports of crude oil into the U.S. were at a record high prior to this period. The resulting efforts to supply consumers around the world pushed world oil prices to unprecedented levels. The world price of crude rose from about $14 per barrel in 1979 to more than $35 per barrel in 1981. Over the next two years upward pressure on oil prices eased and by 1983 prices had stabilized at around $29 per barrel.

As a result of the higher oil prices of the early 1970s and early 1980s, U.S. consumption of petroleum products decreased and increased focus was put on energy conservation and fuel switching. Other fuels began to replace petroleum in many applications, and industrial processes as well as motors and appliances became more efficient. Use of petroleum fuels for electricity generation dropped significantly. The end result was a large impact on U.S. petroleum demand, which dropped in 1983 to its lowest level since 1971. World demand also began to decrease.

Full decontrol of prices and supplies in the industry occurred in 1981. For the first time since the early 1970s market forces determined prices, which rose to market-clearing levels. Many small refineries and more inefficient plants could not compete and began to shut down. Between 1981 and 1985 the number of refineries in the U.S. dropped from 324 to 223.

The industry was shaken again by the collapse of crude oil prices in 1986. The collapse was primarily the result of the return to a free market and a true equilibrium of supply and demand forces (increased production in a market with weakening demand). OPEC had significantly cut output in the early 1980s to defend its official price, with Saudi Arabia as swing producer taking most of the production cuts. In late 1985 Saudi Arabia abandoned its role as swing producer and increased production to capture greater market share. Saudi Arabia also offered a netback pricing concept which tied crude oil prices to the value of refined products and guaranteed specific margins to refiners. In response, other OPEC members also increased production and offered netback pricing arrangements to maintain market share and offset declining revenues. The result was a glut of crude oil in world markets, which caused prices to fall and contributed to an increase in economic growth.

The collapse of crude oil prices in 1986 reversed the increase in domestic production seen since the early 1970s. Many high cost wells became unprofitable in 1986 and were shut down. After world oil prices fell by more than 50 percent,

Major Events Impacting Petroleum Refining Over Three Decades

1970	Clean Air Act Amendments of 1970
1973	Arab Oil Embargo
1973	Emergency Petroleum Allocation Act
1975	Energy Policy and Conservation Act
1976	Resource Conservation and Recovery Act
1977	Airline Deregulation Act
1977	Department of Energy Organization Act
1978	Powerplant and Industrial Fuel Use Act
1978	Iranian Revolution
1980	Comprehensive Environmental Response, Compensation & Liability Act (CERCLA)
1981	Petroleum Price/Allocation Decontrol
1985	Clean Water Act
1986	Crude Oil Price Collapse
1986	Emergency Planning & Right to Know Act
1989	Reid Vapor Pressure Regulations
1990	Clean Air Act Amendments of 1990
1990	Persian Gulf Crisis of 1990-1991
1990	Oil Pollution Liability & Compensation Act
1992	Reid Vapor Pressure Regulations
1992	Energy Policy Act
1995	Reformulated Gasoline

domestic drilling fell dramatically, and has continued to decline ever since. A number of the temporary conservation measures instituted during earlier oil disruptions were discontinued, and major investments in energy conservation have slowly declined. The net result of the decline in production was an increase in crude oil imports which continued steadily until 1990 when it reached 60 percent. Although imports have decreased, they remain high [DOE 1997d].

The demand for energy products other than petroleum has slowly increased over the last two decades. From a share of 49 percent of total U.S. energy consumption in 1977, petroleum's share decreased to 41 percent in 1992, and is currently at 40 percent (1996) [DOE 1997b].

The number of refineries continues to slowly decline, with those remaining operating at higher capacity and with greater efficiency. For U.S. refiners the 1990s have been characterized by low product margins and low profitability. Cash operating margins are low, as is return on equity (about 5%). Part of the reason is the cost of regulation. U.S. refineries spent about $30 billion during the 1990s to comply with government mandates (largely environmental) [OGJ 1998a]. In some cases it has been more economical to shut down facilities rather than continue to operate. Although capital costs for environmental compliance for refiners are fairly steady now, they increased by almost 400 percent between 1988 and 1992 [DOC 1997].

Refineries also have to deal with the economic impacts of low crude prices, crude quality variability, low marketing and transport profit margins, and consequently the need for increased flexibility, increased throughputs, higher conversions, greater process efficiency, operating cost reductions, and greater reliability. In general, persistently low profits have prompted domestic refiners to pursue greater value from their existing fixed assets while reducing operating costs and improving efficiency. Petroleum products are also the most heavily taxed commodity in the market. Taxes on gasoline sales, for example, can represent as much as 20 percent of market price.

U.S. Petroleum Refining Is a Major Force in Domestic and World Markets

Most refineries are concentrated on the West and Gulf coasts, primarily because of access to major sea transportation and shipping routes. Figure 1-1 shows the geographic distribution of petroleum refineries among the states. The U.S. petroleum refining industry has been described as "a relatively small number of large facilities." The majority of oil distillation capacity is currently centered in large, integrated companies with multiple refining facilities. About 25 percent of all facilities are small operations producing fewer than 50,000 barrels per day, representing about 5 percent of the total output of petroleum products annually [NPRA 1997].

Beginning with crude oil distillation, refineries use a series of processes to produce many different petroleum products, most of which are used as fuels. After distillation the resulting intermediate refinery streams are subject to further processing in "downstream" units. Table 1-1 provides data on the distillation and downstream charge capacity of U.S. refineries over the last 10 years. Table 1-2 shows the relative mix of products from downstream processing over the last decade, based on the production capacity of U.S. operable refineries. On a weight basis, the petroleum refining industry handles the largest flow of products of any manufacturing industry in the United States.

In 1996 the average hourly wage for production workers in the petroleum refining industry was $22.4 per hour, the highest wage paid to production workers in the nation. By comparison, the next most highly paid workers (transportation equipment) received an average wage about 17 percent lower (about $18.5 per hour), and chemical industry production workers received average wages over 23 percent lower ($17.2 per hour).

According to the Department of Commerce, 43,400 production workers were responsible for refinery shipments with a value of $158 billion in 1996 [DOC 1998]. This represents a very high annual value-of-shipments per worker ($3.6 million) compared to other industrial sectors. The

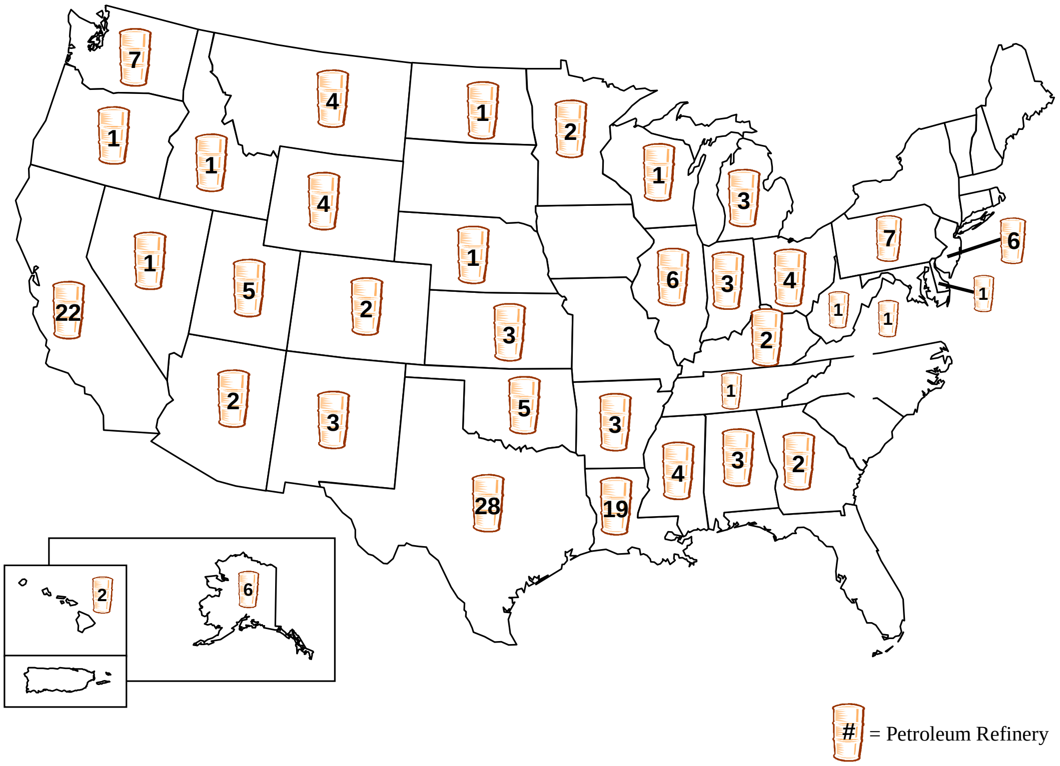

Figure 1-1. Geographic Distribution of Petroleum Refineries in the United States [Source: OGJ 1998a]]

chemical industry, for example, employed about 476,800 production workers to manufacture shipments valued at over $367 billion in 1996, a value-of-shipments per worker of $770,620 [DOC 1998].

In the world refining industry, the U.S. is the largest, most sophisticated producer of refined petroleum products, followed closely by Western Europe and the Far East (see Table 1-3). In 1995 U.S. refinery production represented about 23 percent of world production. The U.S. has the largest refining capacity in the world, with 163 operating refineries and 16.3 million barrels per day of crude distillation capacity at the end of 1997 [OGJ 1997i].

Capacity Utilization Has Increased While the Number of Refineries Declines

Since 1990 the number of U.S. refineries has declined from 205 to the current number of 163 (as of January 1998). New capacity has been in the form of downstream processing units, particularly "bottom of the barrel" processing. This is due in large part to the steadily decreasing quality of crude oils, which are heavier and contain more contaminants than in previous years, and the need to respond to environmental regulations [DOE 1997d, OGJ 1997i].

The utilization of existing capacity has been increasing steadily since 1981, from a low of about 65 percent to the rate of over 95 percent in some months in 1997 (see Figure 1-2). Increasing capacity utilization is the result of refiners meeting increasing oil demand with little or no change in plant capacity.

Substantial Changes in Technology Have Improved the Performance of Refinery Processes and Products

There have been a number of technology-driven changes in the U.S. refining industry that have improved the performance of refinery processes. The development of multi-functional catalytic cracking catalysts, for example, has provided higher product yields, better product selectivity, and reduced air emissions, while exhibiting longer catalyst life.

Some technological changes have been driven by the need to respond to changing consumer requirements and environmental regulations governing refined products. Examples are the need to produce new lubricating oils that are suitable for higher performance combustion engines, and the production of gasoline that meets demands for reduced auto emissions.

Table 1-1. Distillation and Downstream Charge Capacity (Thousand Barrels per Stream Day)

Year	Atmospheric Crude oil Distillation	Vacuum Distillation	Thermal Cracking	Catalytic Cracking		Catalytic Hydrocracking	Catalytic Reforming	Catalytic Hydrotreating	Fuels Solvent De-asphalting
				Fresh	Recycle				
Jan 1, 1987	16,460	6,935	1,928	5,251	466	1,189	3,805	9,083	230
Jan 1, 1988	16,825	7,198	2,080	5,424	381	1,202	3,891	9,170	240
Jan 1, 1989	16,568	7,225	2,073	5,324	326	1,238	3,911	9,440	245
Jan 1, 1990	16,507	7,245	2,108	5,441	314	1,282	3,896	9,537	279
Jan 1, 1991	16,557	7,276	2,158	5,559	304	1,308	3,926	9,676	271
Jan 1, 1992	16,633	7,172	2,100	5,608	280	1,363	3,907	9,644	276
Jan 1, 1993	15,935	6,892	2,082	5,540	244	1,397	3,728	9,677	269
Jan 1, 1994	15,904	6,892	2,107	5,586	191	1,376	3,875	10,616	261
Jan 1, 1995	16,326	7,248	2,123	5,583	169	1,386	3,867	10,916	251
Jan 1, 1997	16,287	7,349	2,050	5,595	155	1,388	3,727	11,041	275

Source: *Petroleum Supply Annual 1996, Volume 1*. U.S. Department of Energy, June 1997.
Note: There are 355 stream days/calendar year

Table 1-2. Capacity for Selected Refinery Unit Products (Thousand Barrels per Stream Day)

Year	Alkylates	Aromatics	Asphalt and Road Oil	Isomers	Lubricants	Marketable Petroleum Coke	Hydrogen (MMcfd)	Sulfur (short tons/day)
Jan 1, 1987	974	287	788	326	250	364	2,569	23,806
Jan 1, 1988	993	289	788	465	232	368	2,418	27,639
Jan 1, 1989	1,015	290	823	469	230	333	2,501	28,369
Jan 1, 1990	1,030	290	844	456	232	341	2,607	24,202
Jan 1, 1991	1,077	292	866	490	229	367	2,527	23,875
Jan 1, 1992	1,095	290	812	494	217	356	2,644	23,811
Jan 1, 1993	1,083	286	814	499	217	393	2,674	25,940
Jan 1, 1994	1,086	278	793	499	213	410	2,940	24,554
Jan 1, 1995	1,105	285	846	502	217	427	3,139	24,885
Jan 1, 1997	1,120	288	872	577	244	458	3,052	26,466

Source: *Petroleum Supply Annual 1996, Volume 1*. U.S. Department of Energy, June 1997.

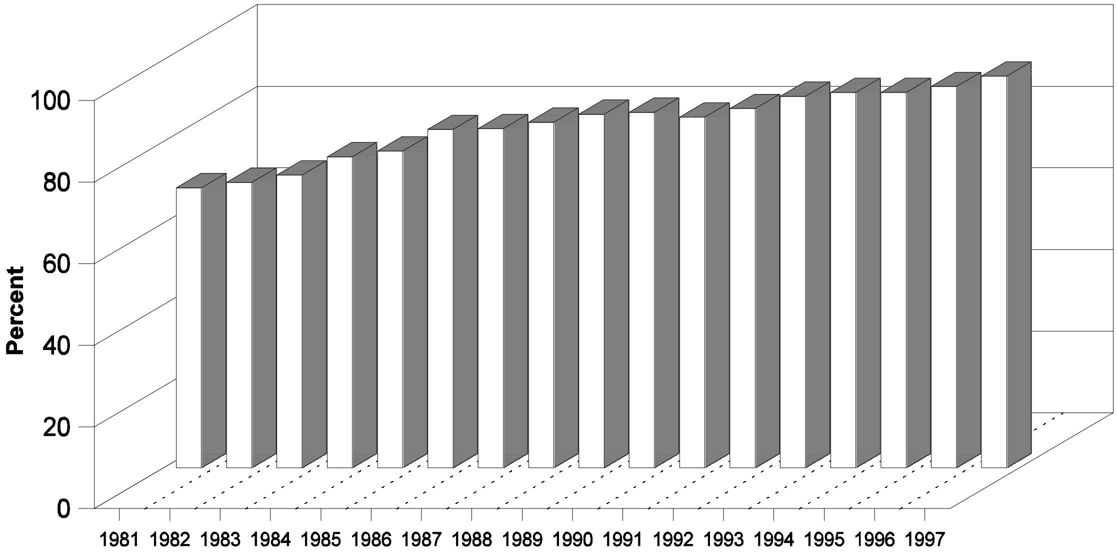

Figure 1-2. Domestic Refinery Capacity Utilization, 1981-1997 [DOE 1997d]

Table 1-3. World Output of Refined Petroleum Products - 1995		
Country/Continent	**Production (thousand barrels per day)**	**Percentage (%) of World Production**
North America		
Canada	1,800	2.6
Mexico	1,856	2.7
United States	16,124	23.4
Central and South America	4,808	7.0
Western Europe	14,273	20.7
Eastern Europe and Former U.S.S.R.	6,569	9.5
Middle East	5,343	7.7
Africa	2,746	4.0
Far East and Oceania	15,406	22.4
WORLD TOTAL	68,925	100.0

Source: U.S. Department of Energy, Energy Information Administration, International Energy Group, January 1998.

1.2 Market Trends and Statistics

About 50 percent of Crude Oil and Petroleum Inputs to Refineries are Imported

The supply of refined petroleum products has increased by more than 3 million barrels per day since 1970 (see Table 1-4). In 1996, over 18 million barrels per day of refined petroleum products were supplied by U.S. refiners. U.S. refiners rely on both domestic and foreign producers for crude oil inputs, as well as some unfinished feedstocks (primarily motor and aviation gasoline blending components) and refined products. Historical trends over the last ten years indicate imports of crude have been rising steadily (see Figure 1-3).

Net imports of crude and products are estimated to have averaged a record high of 10 million barrels per day in 1997, up over 500,000 barrels per day from the year before. Some of the increase can be attributed to the need to rebuild industry stocks of crude oil. Imports of products declined last year, although tight refining capacity (high utilization rates) had been expected to result in much higher imports of products. Refiners have been able to add refining capacity and keep pace with demand. As long as capacity remains sufficient to meet demand, refiners will import crude oil rather than refined products [OGJ 1998a].

Projections indicate that although distillation capacity will increase to some degree at existing U.S. refineries, U.S. petroleum imports could continue to rise if oil prices remain low [DOE 1996]. More important, increases in the level of imports will be affected by domestic production, which is declining. The import situation will be exacerbated by increasing environmental restraints and costs, which greatly inhibit the construction of new facilities to expand the Nation's distillation capacity [OGJ 1997h].

Table 1-4. Overview of Petroleum Supply (million barrels per day)

Year	Domestic Crude Oil and Plant Liquids Production and Stocks	Foreign Trade				Refined Petroleum Products Supplied
		Crude Oil Imports	Petroleum Product Imports	Total Imports	Total Exports	
1970	11.65	1.32	2.1	3.42	0.26	14.7
1975	10.52	4.1	1.95	6.06	0.21	16.32
1980	10.85	5.26	1.65	6.91	0.54	17.06
1985	11.34	3.2	1.87	5.07	0.78	15.73
1990	9.93	5.89	2.12	8.02	0.86	16.99
1991	10.08	5.78	1.84	7.63	1.00	16.71
1992	10.03	6.08	1.80	7.89	0.95	17.03
1993	9.77	6.79	1.83	8.62	1.00	17.24
1994	9.68	7.06	1.93	9.00	0.94	17.72
1995	9.59	7.23	1.61	8.83	0.95	17.72
1996	9.67	7.48	1.92	9.40	0.98	18.23

Source: *Annual Energy Review 1996.* U.S. Department of Energy, Energy Information Administration, July 1997.

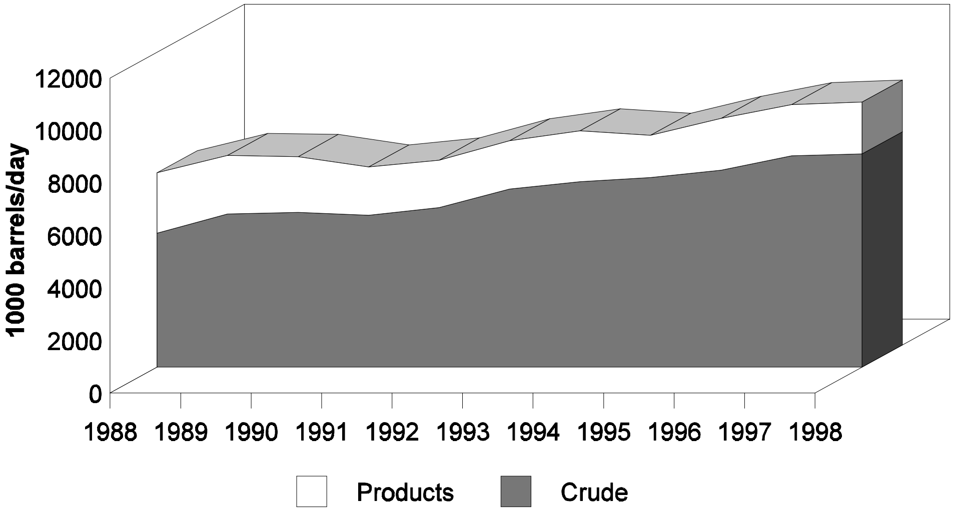

Figure 1-3. Imports of Crude and Petroleum Products [OGJ 1998b]

However, imports of refined products also depend on competition in the marketplace between domestic and foreign refiners, not just capacity.

Exports of refinery products include fuel oils (distillate and residual) and petroleum coke, which represents the largest share (about 59 percent of total exports). Petroleum coke is exported mostly to Japan, where it is used as a fuel. In this country petroleum coke is used as a fuel, as a feedstock in production of carbon black, and in the production of anodes for metals manufacture.

About 90 Percent of Refinery Products are Fuels

The crude oil that enters a petroleum refinery will be physically, thermally, and chemically separated into its major distillation fractions, which are further converted into finished petroleum products in one of three categories. About 90 percent of the oil is converted to **fuel products**. Fuels include gasoline, distillate fuel oil (diesel fuel, home heating oil, industrial fuel); jet fuels (kerosene and naphtha types); residual fuel oil (bunker fuel, boiler fuel); liquefied petroleum gases (propane, ethane, butane); coke; and kerosene.

Another category of petroleum products includes the **nonfuel products,** represented by asphalt and road oil, lubricants, naphtha solvents, waxes, nonfuel coke, and miscellaneous products. The third and smallest category includes **petrochemicals and petrochemical feedstocks** such as naphtha, ethane, propane, butane, ethylene, propylene, butylene, benzene, toluene, xylene, and others.

The annual supply of refined products to consumers is derived from a combination of a small amount of field production (natural gas liquids, hydrocarbon liquids, blending components), products generated at refineries, imported refined products, and stocks on hand. Refinery production is dominated by production of gasoline at over 46 percent (see Figure 1-4). Distillate and residual fuels comprise the next largest share, with about 25 percent of refinery production. Trends in the quantity of petroleum products (refinery output plus field production plus stocks, including imports) over the last five years are shown in Table 1-5 [OGJ 1998a].

The principal classes of refining products, along with their typical boiling ranges and uses are shown in Table 1-6.

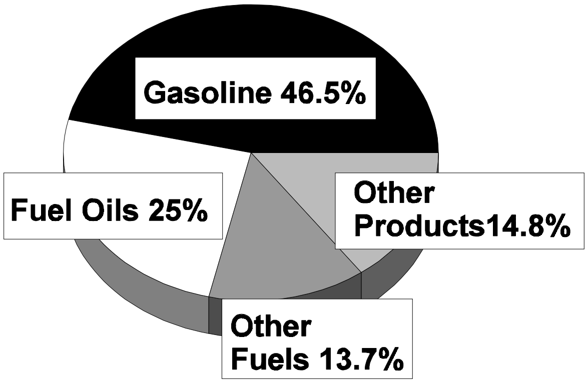

Figure 1-4. Refinery Outputs 1996 [DOE 1997a]

Table 1-5. Supply of U.S. Refined Products (Million barrels)

	1997	1996	1995	1994	1993
Natural Gas Liquids and LRG	101.6	92.6	101.2	108.0	117.1
Finished Products					
Gasoline	210.2	197.6	204.8	217.4	228.4
Special Naphthas	2.11	1.9	2.0	2.2	2.5
Kerosine	6.3	7.0	7.2	8.0	4.1
Distillate Fuel	134.8	126.7	130.2	145.2	140.9
Residual Fuel	41.8	45.9	37.2	41.9	44.2
Kerosine jet fuel	39.8	39.8	39.5	45.6	38.0
Naphtha jet fuel	1.7	0.08	0.60	1.2	2.4
Unfinished Oils	88.7	87.9	86.5	91.3	88.4
Other refined products[a]	60.1	58.4	59.8	63.0	58.9
TOTAL	**687.0**	**657.7**	**667.9**	**723.9**	**724.8**

a lubricants, waxes, petroleum coke, asphalt/road oil, miscellaneous products.

Source: *Petroleum Supply Annual, 1996.* U.S. Department of Energy, Energy Information Administration, June 1997. Table 3.

Table 1-6. Major Petroleum Products		
Product	**Boiling Range (ºF)**	**Uses**
Low Octane Gasoline	30 - 400	gasoline, solvents
High Octane Gasoline	30 - 400	high octane gasoline
Liquid Petroleum Gas	- 259 - +31	fuel gas, bottled gas, petrochemical feedstock
Diesel Fuels	350 - 700	fuel for diesel engines
Jet Fuel	150 - 550 (military) 350 - 550 (commercial)	gas turbine (jet) engines
Distillate Fuel Oil	350 - 700	residential and commercial heating
Residual Fuel Oil	500 - 1200	electrical generation, large steam plants, marine fuel
Lubricating Oils	1200+	automobile, aircraft, marine engines; refrigeration, electrical transformers, heavy machinery lubrication
Asphalt	nonvolatile	coatings, paving
Coke	nonvolatile	fuel, electrode manufacture

Within product categories there may be a variety of products with different specifications. For example, there are over 1000 different lubricating oils produced, and probably as many as 40 different types of gasoline.

1.3 Energy and Materials Consumption

Petroleum Refineries Use By-Products to Meet Process Energy Needs

Petroleum refining is the most energy-intensive manufacturing industry in the United States, and accounted for about 7 percent of total U.S. energy consumption in 1994 [DOE 1997b, DOE 1998][1]. According to the most recent Manufacturing Energy Consumption Survey (MECs) conducted by the Energy Information Administration at the U.S. Department of Energy, the U.S. petroleum refining industry consumed 6.263 quads (quadrillion Btu, or 10^{15} Btu) of energy in 1994 (excluding electricity generating and transmission losses incurred by the generating utility) (see Table 1-7) [[DOE 1997b].

In a more recent survey conducted by EIA for the *Petroleum Supply Annual*, data was collected concerning volumes of fuel used at refineries for processing, as well as all non-processing losses of crude oil and petroleum products (e.g., from spills, fire losses, contamination). The total energy used for heat and power from this survey for 1996 is 3,258 trillion Btus, as shown in Table 1-8. This is somewhat lower than the value for energy consumed shown in Table 1-7 (3,984 trillion Btus). The discrepancy between the two EIA surveys is attributed to the different years data was collected, as well as some differences in collection and estimation methods.

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[1] *Based on energy use from MECs survey for 1994, and total energy used in the residential, industrial, transportation, and utility sectors in 1994.*

As can be seen in Table 1-8, the industry uses a diversity of fuel sources (e.g., natural gas, crude oil and derivatives, electricity, coal). The industry relies heavily on refining process by-products as energy sources. These include refinery gas (sometimes referred to as "still" gas, a component of crude oil and product of distillation, cracking and other refinery processes), petroleum coke[2], and other oil-based by-products. In 1996, about 2.08 quadrillion Btus, or about 65 percent of the energy consumed by the industry for power and heat, was provided by fuels that are by-products of the refining process [DOE 1997b]. The purchased fuel sources that supply the remainder of the energy needed by the refining industry include natural gas (25 percent), electricity (10 percent), purchased steam (1 percent), and small quantities of coal [DOE 1997b].

Energy accounting for the petroleum refining industry is unique compared with other industries, because most of the products manufactured are energy products. To avoid double-counting, the energy value of the crude oil and any petroleum *feedstock that is used to produce another energy product* (e.g., gasoline, kerosene, fuel oil, refinery gas) *is not included* here to avoid double-counting in energy end-use. Consumption of these products is counted as energy use under the other sectors of the economy where it is consumed (e.g., transportation, buildings). It is only considered here if the energy source is used in the refinery as a fuel for heat and power, or as a feedstock if it is used to produce a *non-energy product* (e.g, petrochemical feedstock, lubricating oils, asphalt). Table 1-7 illustrates that about 38 percent of the total energy used is in the form of petroleum feedstocks used to produce non-energy products.

Net energy use as well as total primary energy use are shown in Table 1-7. Net energy use represents the amount of energy used for heat and power, plus the energy value of petroleum feedstocks used for non-energy products (as discussed above). This includes electricity purchased from the grid, as well as electricity that is generated on-site through power generation or cogeneration facilities. Total primary energy use includes the losses incurred by utilities in generating electricity through turbine inefficiency and in transmission of energy in power lines (assumes an electricity conversion of 10,500 Btu/kilo-watt hours). Energy losses in generation and transmission of electricity are included to illustrate the total energy consumption represented by the purchase of electricity.

Energy expenditures represent a significant portion of manufacturing costs for petroleum refiners. In 1996 the industry spent approximately $4 billion on energy (fuels and purchased electricity) [DOC 1998].

From 1974 to 1988, the industry reduced its energy consumption by 30 percent, partially the result of conservation initiatives instituted in response to disruptions in oil supply and the high cost of petroleum. Other factors contributing to reductions in energy use include downsizing and consolidation of capacity, shut downs of older, smaller, inefficient facilities, and continuing improvements in technology.

Over the last decade, while technology continued to improve incrementally, energy intensity has remained fairly constant. In the current period of low energy prices, high environmental costs, and low margins for refiners, improvements in efficiency may receive increased attention as refiners struggle to increase profitability and reduce the costs of doing business. One motivation is that the cost of energy for heat and power represents a dominating factor in refinery production-- as much as 40 percent of variable annual operating costs [Robertson 1998].

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[2] *Mostly catalytic coke from catalytic crackers. Coke from coking units is marketable coke and is mostly sold to off-site users for electricity generation and anode manufacture.*

Table 1-7. Petroleum Refining (SIC 2911) Energy Use, 1985, 1988, 1991, and 1994 MECS Estimates (Trillion Btu)

Year	Fuels	Purchased Electricity	Net Energy for Heat and Power	Feedstocks[a]	Total Net Energy Use	Electricity Losses[b]	TOTAL PRIMARY ENERGY
1985	2,461	109	2,570	2,449	5,019	226	5,245
1988	2,951	101	2,895	3,258	6,310	210	6,520
1991	2,794	99	2,893	2,869	5,762	206	5,968
1994	3,870	114	3,984	2,393	6,263	237	6,500

Source: *Manufacturing Energy Consumption Surveys, 1985, 1988, 1991, 1994.* U.S. Department of Energy, Energy Information Administration. Publication dates 1988, 1991, 1994, 1997 respectively.

a Petroleum feedstock used to produce non-energy products only (e.g., petrochemicals, lubricating oils, asphalt)

b Electricity losses incurred during the generation, transmission, and distribution of electricity are based on a conversion factor of 10,500 Btu/kilowatt-hour.

Table 1-8. Petroleum Refining (SIC 2911) Energy Consumed[a] - 1996 (Trillion Btu)

Energy Source	Quantity	% of Total
Crude Oil	0.01	<1
Liquified Petroleum Gases	26.7	1
Distillate Fuel Oil	4.3	<1
Residual Fuel Oil	54.9	2
Refinery Gas	1,435	44
Marketable Petroleum Coke	19.5	<1
Catalyst Petroleum Coke	504.5	16
Natural Gas	797.6	25
Coal	3.1	<1
Purchased Electricity (including losses)	337	10
Purchased Steam	40.1	1
Other Products[b]	35.7	1
TOTAL	3258.4	100.0

Source: *Petroleum Supply Annual, 1996.* U.S. Department of Energy, June 1997. Table 47.

a For heat and power.

b Other products include miscellaneous petroleum products such as motor gasoline, unfinished oils, pentanes plus, hydrogen, oxygenates, asphalt, gasoline blending components, lubricants, wax, and jet fuel

1.4 Environmental Overview

Both the Manufacture and Use of Refined Petroleum Products Impact the Environment

Petroleum products are critical to the economy and supply about 40 percent of the total energy used by the U.S. and practically all the energy consumed by transportation. As these fuels are burned in cars, trucks, industrial heaters, utility boilers, and residential heating systems, they create various air emissions.

In addition, the manufacturing processes used to produce these critical petroleum products also generate a variety of air emissions and other residuals. Some of these are also hazardous and/or toxic chemicals.

The environmental impacts of petroleum refining and the use of refined products have resulted in a number of environmental laws and regulations. Some of the most significant statutes are those that focus on altering the formulation of products (mostly fuels) to reduce air emissions generated by their use . These often require substantial changes in refinery processes along with large capital investments. A number of Federal and state regulations also focus on reducing refinery process emissions to air, land, and water. The combination of regulations to reformulate fuels and those aimed at reducing emissions from refinery operations make petroleum refining one of the most heavily regulated industries in the United States [EPA 1995a]. A summary of legislative and regulatory control programs affecting the refining industry is shown in Table 1-9.

Refiners Have Significantly Improved Environmental Performance

Like most U.S. manufacturing industries, the petroleum refining industry has been challenged with improving environmental performance and complying with a substantial array of environmental, health and safety regulations. Petroleum refiners spent about $5.5 billion in 1995 on environmental compliance [API 1997b]. About 40 percent of this was for capital expenditures; the remainder was for operation and maintenance of equipment for environmental control and abatement.

The refining industry participates in a number of public and private initiatives aimed at improving environmental performance. The STEP initiative (Strategies for Today's Environmental Partnership), for example, is a collective environmental strategy supported by the membership of the American Petroleum Institute (API) to improve environmental, health and safety performance [API 1997a]. The National Petroleum Refiners Association sponsors a similar program, Building Environmental Stewardship Tools (BEST) to bring some of the same principles to refineries that are not members of API. Some refineries also participate in a number of private initiatives such as the Global Environmental Management Initiative, the Petroleum Environmental Research Forum, and various API-sponsored research and survey activities [EPA 1995a].

Many refineries also participated in the Environmental Protection Agency's 33/50 program to reduce air toxics. In 1995 about 30 percent of U.S. refineries participated in this program, which is significantly higher than the average for other industries (about 14 percent). A few refineries are also actively involved with other government environmental initiatives such as the Common Sense Initiative and the Green Lights Program.

Refineries have also been working to increase recycling, reduce pollution and decrease releases of toxic chemicals. Approximately 40 percent of refineries conduct pollution prevention activities at their facilities [EPA 1995a]. In 1995 refineries recycled about 54 percent of their residuals compared with 22 percent in 1987. In addition, total releases of toxic chemicals from refineries (counting only those included in the Toxic Release Inventory since 1988) have declined by 26 percent since 1988 [API 1997a].

Table 1-9. Federal Requirements Affecting the Refining Industry

Requirement	Provisions That Affect Petroleum Refining
Clean Air Act of 1970 (CAA) and regulations	National Ambient Air Quality Standards (NAAQS) for six constituents; new more stringent standards for ozone under NAAQS (more than doubles non-attainment areas); new standards under NAAQS that require control of particulate matter of 2.5 microns or smaller; lead-free gasoline; low-sulfur fuel; reformulated gasoline; hazardous air pollutants; visibility requirements; New Source Performance Standards
Clean Air Act Amendments of 1990 (CAAA) and regulations thereunder	Oxygenated Fuels Program for "nonattainment areas"; low-sulfur highway diesel fuel; Reformulated Fuels Program; Leaded Gasoline Removal Program; Reid Vapor Pressure regulations to reduce VOCs and other ozone precursors; New Source Review for new or expanded facilities or process modifications; National Emission Standards for Hazardous Air Pollutants; Risk Management Plans; National Ambient Air Quality Standards
Resource Conservation and Recovery Act (RCRA)	Standards and regulations for handling and disposing of solid and hazardous wastes
Clean Water Act (CWA)	Regulates discharges and spills to surface waters; wetlands
Safe Drinking Water Act (SDWA)	Regulates disposal of wastewater in underground injection wells
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)	"Superfund"; liability for CERCLA hazardous substances could apply to wastes generated during refining; includes past releases; exempts petroleum and crude oil; provides for natural resource damages
Emergency Planning and Community Right-to-Know (EPCRA)	Requires annual reporting on the releases and transfers of listed toxic chemicals (§313); reporting presence of "extremely hazardous substances" in excess of threshold planning quantities (§302); reporting certain releases of CERCLA hazardous substances and EPCRA extremely hazardous substances (§304); presence of hazardous chemicals over specified thresholds, to state and local governments and local fire departments, to help local government to respond in case of spills or accidental releases (§§311-312)
1990 Oil Pollution Act and Spill Prevention Control and Countermeasure Plans	Liability against facilities that discharge oil to navigable waters or pose a threat of doing so
OSHA Health Standards and Process Safety Management Rules	Limits benzene and other chemical exposures in the workplace; safety plans required in all refineries
Toxic Substances Control Act (TSCA)	Collection of data on chemicals for risk evaluation, mitigation and control; can ban chemicals that pose unreasonable risks
Energy Policy Act of 1992	Use of alternative fuels for transportation; efficiency standards for new federal buildings, buildings with federally backed mortgages, and commercial and industrial equipment; R&D programs for technologies; will reduce demand for petroleum products

Sources: *Cumulative Impact of Environmental Regulations on the U.S. Petroleum Refining, Transportation and Marketing Industires*, American Petroleum Institute, October 1997.
Sector Notebook: Profile of the Petroleum Refining Industry, U.S. Environmental Protection Agency, September 1995.

Refinery Air Emission Sources Include Fuel Combustion, Leaks, and Manufacturing Processes

Air emissions are generated from several sources within the petroleum refinery, including:

- **combustion emissions** associated with the burning of fuels in the refinery, including fuels used in the generation of electricity,
- **equipment leak emissions** (**fugitive emissions)** released through leaking valves, pumps, or other process devices,
- **process vent emissions (point source emissions)** released from process vents during manufacturing (e.g., venting, chemical reactions),
- **storage tank emissions** released when product is transferred to and from storage tanks, and
- **wastewater system emissions** from tanks, ponds and sewer system drains.

Combustion emissions for the refining industry can be calculated based on the energy consumption by fuel type shown in Table 1-8. These emissions are shown in Table 1-10 for 1996. Table 1-11 lists the emissions factors used for this calculation. Combustion emissions are typically controlled through a wide variety of measures, depending on the fuel being combusted (see Section 10, Process Heaters, for more information).

Equipment leak emissions (fugitive emissions) could occur throughout the refinery, and are primarily composed of volatile compounds such as ammonia, benzene, toluene, propylene, xylene, and others. Sources for these emissions include leaking valves, pumps, seals, pressure relief valves, piping joints, and numerous similar sources. The emissions from any single leak are small. However, the sum of all fugitive leaks at a refinery can be substantial. A number of published studies are available that provide data on estimating fugitive emissions from leaking equipment in refineries. The *Air Toxics Multi-year Study -- Study of Refinery Fugitive Emissions from Equipment Leaks* -- provides updated emission correlation equations for connectors, open-ended lines, pump seals, and valves [API 1994a]. A more recent study provides correlations for emissions from refinery process drains [API 1996a].

Process vent emissions (often referred to as point source emissions) typically include emissions generated during the refining process itself. Gas streams from all refinery processes contain varying amounts of refinery fuel gas, hydrogen sulfide and ammonia. These streams are passed through gas treatment and sulfur recovery units to remove sulfur and recycle the fuel gas. Sulfur recovery may generate emissions of hydrogen sulfide, sulfur dioxides, and nitrogen oxides.

The periodic regeneration of catalysts may also generate some emissions, including relatively high levels of carbon monoxide, particulates, and volatile organic compounds. For the catalytic cracking unit, these streams can be processed by burning carbon monoxide and volatiles as fuel for a boiler. The gases are then passed through an electrostatic precipitator or cyclone separator to remove particulates.

Storage tanks used to store crude oil and intermediate process feeds also account for emissions of volatile organic compounds. **Storage tank emissions** are released when crude and products are transferred to and from storage tanks.

Wastewater emissions represent a considerable source of air emissions from refineries. Releases to the air from wastewater treatment systems usually occur as fugitive emissions from numerous tanks, treatment ponds and sewer system drains. Emissions also arise in the treatment of oil/water separators used to treat oily water from crude desalting and other refinery processes, and from cooling water towers (note: cooling water is not necessarily a waste water -- most is recycled over and over). Typical constituents of wastewater emissions include hydrogen sulfide, ammonia, and light hydrocarbons. Table 1-12 provides fugitive emission factors for cooling towers and oil/water separators.

Some of the emissions that arise from leaking equipment and process vents are **air toxics and hazardous air pollutants** (HAPs). Releases of these compounds are reported annually to the EPA. The most current data available are shown in Table 1-13. Topping the list are toluene, ammonia, methanol, hexane, and propylene.

The Clean Air Act Continues to Have the Greatest Impact on the Petroleum Refining Industry

The **Clean Air Act** (CAA) of 1970 and its Amendments in 1977 and 1990 (CAAA) have had a significant impact on the petroleum refining industry, both in terms of refining processes as well as the formulation of refined products.
The 1970 CAA authorized the EPA to establish the National Ambient Air Quality Standards (NAAQS) for sulfur dioxide, nitrogen oxides, carbon monoxide, ozone, non-methane hydrocarbons, opacity, and total suspended particulates in ambient air. Regulatory actions under the CAA required reductions of lead in gasoline in the early 1970s and elimination of lead in gasoline in the mid-1980s. To meet the lead reduction requirement, refineries incorporated considerable changes in processing (more downstream conversion units, catalytic processes, octane boosting additives) to make up for the

Table 1-10. Estimated Combustion-Related Air Emissions for Petroleum Refining[a] (million lbs/year)

Year	SO_x	NO_x	CO	Particulates	VOCs
1996	2001	1,063	313	557	18

a Calculations of combustion emissions based on energy use data by fuel type as shown in Table 1-7. Emission factors are shown in Table 1-10. Electricity use includes losses during generation and transmission (conversion factor of 10,500 Btu/kWh).

Table 1-11. Combustion Emission Factors By Fuel Type (lbs/million Btu)

Fuel Type	SO_x	NO_x	CO	Particulates	VOCs[a]
Distillate Fuel	0.160	0.140	0.0361	0.010	0.002
Residual Fuel	1.700	0.370	0.0334	0.080	0.009
Other Oils	1.700	0.370	0.0334	0.080	0.009
Natural Gas	0.000	0.140	0.0351	0.003	0.006
Refinery Gas	0.000	0.140	0.0340	0.003	0.006
LPG	0.000	0.208	0.0351	0.007	0.006
Propane	0.000	0.208	0.0351	0.003	0.006
Steam Coal	2.500	0.950	0.3044	0.720	0.005
Petroleum Coke	2.500	0.950	0.3044	0.720	0.005
Electricity	1.450	0.550	0.1760	0.400	0.004

Sources: Particulates, SOx, NOx, VOCs - Compilation of Air Pollution Emission Factors, Vol 1, Stationary Point and Area Sources, Supplement A (October 1986) and Supplement B (September 1988), and 1995 updates. U.S. EPA. CO_2 - Emissions of Greenhouse Gases in the United States, 1987-1992, and 1995, U.S. Department of Energy.

a volatile organic compounds

Table 1-12. Fugitive Emission Factors for Petroleum Refineries

Emission Source	Emission Factor Units	Emission Factors: Uncontrolled Emissions	Emission Factors: Controlled Emissions	Applicable Control Technology
Cooling towers	lb/10^6 gal cooling water	6	0.7	Minimization of hydrocarbon leaks into cooling water system; monitoring of cooling water for hydrocarbons
Oil/water separators	lb/10^3 gal waste water	5	0.2	Covered separators and/or vapor recovery systems

Source: *AP 42, Chapter 5, Petroleum Industry*, Environmental Protection Agency, January 1995. [Based on limited data]

Table 1-13. Major Air Toxics from Petroleum Refining 1996

Compound	Total Air Emissions (million pounds)
Toluene	7.1
Ammonia	6.8
Methanol	5.2
n-Hexane	4.9
Propylene	4.3
Methyl Ethyl Ketone	4.3
Xylene (mixed isomers)	3.9
Benzene	2.7
Methyl tert-butyl ether	2.3
Ethylene	1.9
Hydrochloric acid	1.4
Cyclohexane	1.2
Ethylbenzene	0.9
1,2,4-Trimethylbenzene	0.7

Source: *1996 Toxic Release Inventory,* U.S. Environmental Protection Agency 1998.

properties lost as a result of reducing lead anti-knock additives. The 1970 Act also called for limits on sulfur in residual and distillate fuel oils used by electric utilities and industrial plants, motivating the development of desulfurization processing units [EPA 1995a].

The 1990 Amendments increased the stringency of the 1970 Act in response to a growing number of non-attainment areas (geographic regions not in compliance with National Ambient Air Quality Standards). In addition to increased regulation of air emissions, the CAAA called for reformulation of motor fuels to reduce emissions from mobile sources. The **Oxygenated Fuels Program** under the CAAA required that all gasoline sold in 39 carbon monoxide non-attainment areas have a minimum of 2.7 percent oxygen (by weight) for at least four winter months, by November 1992.

The response of U.S. refineries to this mandate was to increase domestic capacity for oxygenates. Oxygenates (e.g., ethanol, methyl tertiary butyl ether and other ethers) are added to fuels to boost octane. Oxygenates reduce carbon monoxide because they are already partially oxidized. Capacity for oxygenates also increased at non-refinery stand-alone facilities that produce ethanol from grain, MTBE from oil field butane streams, and methanol from natural gas (an increase in total domestic capacity of 59 percent occurred from 1991 to 1993).

The **Reformulated Gasoline Program** required the use of regulated gasoline formula by January 1, 1995 in nine U.S. metropolitan areas with the worst ground level ozone problems. Other metropolitan areas with serious ozone problems have opted to join the program. The requirements for reformulated gasoline are a minimum oxygen content of two percent by weight, a maximum benzene content of one percent by volume, and no lead or manganese. In addition, baseline tailpipe requirements were established for nitrogen oxides, volatile organic compounds, and toxic air emissions. By 1998, this program calls for a new “complex” formula that provides more flexibility for refiners to comply.

Compliance with reformulation rules has been a significant challenge for refiners and has required a number of process changes. Gasoline formulations have been changed to reduce aromatic and VOC emissions. In some cases this has resulted in less use of catalytic reforming units. If production of aromatics is curtailed by shutting down reformers, there is a reduction in hydrogen produced and greater demand may be placed on other options for hydrogen production (hydrogen plant, coke gasification and others). Hydrotreater units will also be utilized more to meet lower sulfur requirements, which will increase refinery energy consumption. However, the complex formula is heavily dependent on gasoline sulfur and olefins content.

Refiners must also comply with tighter **Reid Vapor Pressure** (RVP) regulations, first established by EPA in 1989 and now in effect under the VOC standards of the 1990 CAAA. Early standards were met by reducing the amount of butane (a high octane, high vapor pressure component) blended into gasoline. To compensate for the decrease in octane that accompanied the drop in vapor pressure, refiners increased the use of catalytic cracking and alkylation units. New standards are now being met by further increases in downstream processing and the addition of high-octane, lower RVP components. In some cases production of these new blending components has required large capital investments and increased operating costs [EPA 1995a].

Under Title III of the 1990 CAAA, the EPA is required to develop **National Emission Standards for Hazardous Air Pollutants (NESHAPs)**, including benzene and twenty other chemicals emitted at petroleum refineries. During the first phase of rule-making, EPA is developing maximum achievable control technology (MACT) standards for all new and existing sources. Under phase one, EPA promulgated MACT standards for some sources at petroleum refineries in August 1995 (Refinery MACT I rule). EPA will promulgate MACT standards for the remaining refinery sources by April 1999 (Refinery MACT II rule). The second phase is expected to be implemented in 2000 and will assess whether the remaining risk (after MACT standards have been implemented) is acceptable.

The MACT rule-making requires that refineries install control equipment on certain process vents that reduces hazardous air pollutants (HAPs) by 98 percent. In addition, storage tanks must be retrofitted with an internal or external floating roof or an external control device (e.g., flare, vapor recovery unit). HAPs in wastewater are regulated under the ruling, and must meet threshold levels or be reduced to acceptable levels using steam stripping, biotreatment, or other recovery technologies. Refiners must also implement leak detection and repair programs. Compliance with refinery MACT I is required by August 1998 (except for storage tanks — these must be retrofitted at next cleaning or by 2005).

Refineries that have marine terminals are also subject to a MACT ruling aimed at preventing releases when marine vessels are loaded and unloaded. The rule requires that certain vapors be recovered (e.g., via condenser) or burned using a flare. Refineries with marine terminals must implement modifications by August 1999.

The economic impact of the MACT rules is expected to be substantial. EPA has estimated the capital investment associated with compliance with Refinery MACT to be about $213 million. In addition, annual operating and monitoring costs are estimated to be about $79 million [API 1997b]. Capital costs for marine terminal modifications at refineries are estimated by EPA to be between $66.5 million and $110 million, with annual costs of $15-25 million [API 1997b].

The refining industry is also affected by changes in **national ambient air quality standards (NAAQS).** In July 1997, the EPA adopted a new 8-hour standard for ozone of 0.08 parts per million (ppm). Under this standard, areas would be in non-attainment when the 4th highest daily maximum 8-hour concentration averaged over three years is above 0.08 ppm. This more stringent standard could more than double the number of non-attainment areas. Refineries in existing and new non-attainment areas will have to install technology to reduce emissions of both NOx and volatile organic compounds (VOCs). Most refineries will also need to implement more stringent leak detection programs [API 1997b]. Also, more refineries may opt into RFG or established state fuel programs.

The current NAAQS for particulate matter was also revised by the EPA in July 1997 to include control of small particulates (particles of 2.5 microns or smaller). Although it is uncertain how extensively refineries will be affected by this new ruling, refineries are likely to be significantly affected by both facility emission control requirements and additional fuel requirements. Many will probably have to install wet gas scrubbers on fluid catalytic cracking units, which is the best available control technology for controlling particulates at this level [API 1997b].

The economic cost to refineries to comply with new NAAQS for ozone and particulates will be considerable. Capital investments for new control technologies are estimated at nearly $3.1 billion, with associated annual costs of $561 million (in 1995 dollars) [API 1997b]. {Note: As this report went to press, legal challenges to the ozone and particulate matter NAAQS are pending.}

Effluents Are Regulated Under the Clean Water Act and Safe Drinking Water Act

Processing of crude oil requires large volumes of **water**, a large portion of which is continually recycled, but much of which is moderately or highly contaminated, requiring primary and secondary and sometimes tertiary treatment. The amount of water used by a refinery can vary significantly, depending on process configuration, refinery complexity, capability for recycle, degree of sewer segregation, and local rainfall.

In 1992, the total amount of water used in refineries was estimated by one source to average from 65-90 gallons of water per barrel of crude oil processed, a substantial decrease from the 2,000 gallons per day reported in 1975 [OGJ 1992a]. The amount discharged (via National Pollutant Discharge Elimination System permit or to public water treatment facilities) is estimated to be in the range of 20-40 gallons per barrel of crude. More information on the discharge of process wastewaters can be found in Section 2 and in individual process sections.

Refineries produce four types of wastewater: surface water runoff, cooling water, process water, and sanitary wastewater. Wastewaters are treated in water treatment facilities and then discharged to public water treatment plants or surface waters (permitted under the National Pollutant Discharge Elimination System).

When refinery wastewaters are released to surface waters, they are regulated under the **Clean Water Act** (CWA). Effluent limitation guidelines for refinery wastewaters are listed under 40 CFR Part 419 for point source categories. Limits are placed on the quantities of suspended solids, oil, grease, phenolic compounds, ammonia, sulfides, and chromium that may be present in the wastewater [BNA 1992, EPA 1995a][3].

Refineries that use underground injection wells for the disposal of wastewater are regulated through the underground injection control program of the **Safe Drinking Water Act**. This program seeks to protect usable aquifers from contaminants that migrate from injection wells.

Surface water runoff is generated intermittently and may contain constituents from spills to the surface, leaks in equipment, and materials in drains. Crude and product storage tank roof drains are also a source of surface water.

Refineries also use large volumes of **cooling water** which normally does not come into contact with oil streams and contains less contaminants than process wastewater. Almost all cooling water is recycled over and over with a bleed or blowdown stream to control the amount of contaminants and solids in the water. Cooling towers are used within the recycle loop to cool the water with ambient air. Cooling water may contain chemical additives used to prevent scaling and biological growth in heat exchanger pipes (e.g., phosphates, anti-fouling biocides) [EPA 1995a]. "Once through" cooling water is used once and then discharged directly into the wastewater treatment plant. Chemical additives are rarely used in once-through cooling water.

Process wastewater that has been contaminated by direct contact with oil accounts for a significant portion of total refinery wastewater. This wastewater arises from crude oil desalting, steam stripping, fractionator reflux drum drains, and other sources. Treatment of oil-contaminated wastewater usually involves separation of oil, water and solids by various physical and/or chemical means. Many of these are sour water streams and are also subjected to treatment to remove hydrogen sulfide and ammonia (see Section 10, Supporting Processes, for more discussion on wastewater treatment).

Refineries Recycle Over Half of Their Residuals

Both hazardous and non-hazardous wastes and other residuals are produced, recycled, treated, and disposed of during refinery operations. The method of disposal of these residuals depends upon the nature of the residual and applicable regulations. Residuals are generated from many refining processes, from the handling of the petroleum products through wastewater treatment. A summary of the generation of residual streams from refineries is shown in Table 1-14. Table 1-15 illustrates how refineries manage these residuals. Overall, refineries recycle about 54 percent of the residuals produced, according to 1995 data. Further, the trend towards increased recycling continued in 1996, which saw about 60 percent recycling of residuals produced [API 1997c].

Most refinery residuals are in the form of sludges, spent caustics, spent process catalysts, filter clay, and incinerator ash. Most of these are **non-hazardous residuals**, and are incinerated, land-filled, or regenerated to provide products that can be sold off-site or returned for re-use at a refinery [EPA 1995a]. For example, in 1995, nearly 89 percent of all spent caustics was recycled, primarily through reclamation and regeneration procedures. Residuals sold off-site include spent caustic, spent sulfuric acid, sulfur, acetic acid, phosphoric acid, and recovered metals. Metals from catalysts (contained in the catalyst or deposited there during processing from the crude oil) are often recovered off-site by third-party facilities.

Residuals generated by refineries that are classified as hazardous wastes are regulated under the Resource Conservation and Recovery Act (RCRA). Listed hazardous wastes include oily sludges, slop oil emulsion solids, dissolved air flotation floats, leaded tank bottom corrosion solids and wastes from the cleaning of heat exchanger bundles (see Table 1-16). In addition, in August 1998, EPA listed as hazardous wastes: refinery crude oil storage tank sludge; clarified slurry oil tank sludge; spent hydrotreating catalyst; and spent hydrocracking catalyst. Other refinery residuals that could be regulated under RCRA "characteristic tests" include laboratory residuals,

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[3] *The use of chromates as a cooling water additive is no longer permitted under NESHAP rules.*

residual paint materials, and residuals containing benzene [BNA 1995, EPA 1995a, OGJ 1990].

Under the current "mixture and derived-from" rules, wastes that result from mixing listed hazardous with non-hazardous wastes, and wastes that result from treating listed hazardous wastes are classified as hazardous under RCRA. Industry has argued that many of these are low-risk wastes that, under current regulations, must undergo expensive treatment although they pose little health or environmental risk.

The EPA is working on new rules that could provide a common sense guide to determine when hazardous wastes no longer requires costly treatment. The planned Hazardous Waste Identification Rule (HWIR) is based on a conservative risk-assessment model and is intended to set risk-based exit levels for many hazardous wastes. EPA was recently granted a four-year extension to reconsider the methodology behind the HWIR and make a final ruling [HP 1997].

Refineries also use large quantities of chemicals during the processing of crude oil, many of which are **toxic chemicals**. Toxic chemicals are monitored through the Toxic Release Inventory (TRI), instituted under the Emergency Planning and Community Right-to-Know Act (EPCRA) [EPA 1995a]. Under the TRI, companies are asked to report on how they manage toxic chemicals, including transfers, treatment and disposal, recycling, energy recovery, and releases to land, air or water.

In 1995, petroleum refineries managed about 1.3 billion pounds of TRI chemicals. Of these, 38 percent were burned to provide process energy, and 20 percent were recycled. Another 36 percent was treated to reduce volume and/or toxicity prior to disposal. The remaining 6 percent -- about 60 million pounds -- entered the environment as air emissions (see Table 1-13).

Table 1-14. Selected Residual Generation Estimates for U.S. Petroleum Refining (1000 wet tons)

RESIDUAL	1995	1994	1991	1989	1987
Spent Caustics	988	1379	909	716	675
Biomass	582	773	855	642	757
Contaminated soils/solids	525	661	809	512	165
DAF float	164	355	406	496	652
Pond sediments	65	143	372	313	337
API separator sludge (K051)	37	101	210	419	400
FCC catalyst or equivalent	173	286	204	182	173
Primary sludges (F037, F038)	128	328	307	--	--
Slop oil emulsion solids	225	49	165	272	208
Hydroprocessing catalysts	63	53	32	36	40
Other spent catalysts	15	18	23	33	33
Tank bottoms	83	87	--	--	--
TOTAL	3048	4233	4292*	3621*	3440*

* Total does not include data for primary sludges and/or tank bottoms.

Source: *Management of Residual Materials: 1995 -- Petroleum Refining Performance*, API Publication Number 339, June 1997, and *The Generation and Management of Residual Materials: 1991 -- Petroleum Refining Performance*, API Publication Number 329, May 1994. American Petroleum Institute.

Table 1-15. Management of Refinery Residuals in 1995 (1000 wet tons)

RESIDUAL	Recycle	Treatment	Disposal
Spent Caustics	876	99	13
Biomass	113	306	162
Contaminated soils/solids	11	163	351
DAF float (K048)	137	23	4
Pond sediments	3	7	55
API separator sludge (K051)	23	11	3
FCC catalyst or equivalent	70	20	83
Primary sludges (F037, F038)	94	32	3
Slop oil emulsion solids (K049)	222	3	1
Hydroprocessing catalysts	50	1	12
Other spent catalysts	4	1	11
Tank bottoms	28	12	43
TOTAL	1631	678	741

Source: *Management of Residual Materials: 1995 -- Petroleum Refining Performance*, API Publication Number 339, June 1997.

Top chemicals (by weight) released from refineries include ammonia, toluene, xylenes, propylene, n-hexane, methyl ethyl ketone, nitrate compounds, ethylene, benzene and methyl tert-butyl ether (MTBE) (see Table 1-17) [API 1997a].

Environmental Costs and Changes in Legislation Will Continue to Impact U.S. Refineries

The cost of complying with environmental regulations will continue to have a significant impact on refineries. Increasingly higher costs could cause the closure of some moderately-complex refineries, resulting in increased imports of refined products from off-shore, low-complexity producers during periods of high demand. The shut-down of domestic capacity could increase price volatility, resulting in refining margins that change dramatically with small changes in supply and demand. To compete in this volatile market, refineries will have to develop innovative ways to improve financial performance and still comply with environmental regulations [NPRA 1995].

Continuing changes in legislation and increased stringency of current regulations will put further economic pressure on refiners. Many refiners charge that the high cost of environmental compliance is a major impediment in continuing to operate. Huge expenditures needed to meet the requirements of the Clean Air Act, for example, are often cited as one reason for continuing low profitability and margins in the refining industry. EPA's proposed new rules for ozone and particulates, which have generated considerable industry opposition, could potentially cost the U.S. industrial sector $90 to $150 billion (in 1990 dollars) [OGJ 1997d, OGJ 1997e].

Finally, continuing implementation of the Clean Air Act Amendments of 1990 will steadily increase the cost of environmental compliance for refiners. In general, the fuel reformulation program and proposed changes will continue to have a large impact. As regions opt-in or out of fuel reformulation programs, the demand for high-priced oxygenates could shift considerably, resulting in fluctuations in pricing for gasoline.

Table 1-16. Hazardous Wastes Associated with Petroleum Refining

EPA Waste Classification	Summary Description	Hazardous Constituents
D002	Spent sulfuric acid (from alkylation process)	Sulfuric acid
D003	Sulfur (on spent catalyst surfaces)	Sulfur
D007	Non-specific residuals containing chromium	Chromium
D008	Non-specific residuals containing lead	Lead
D018	Non-specific residuals containing benzene	Benzene
F037	Petroleum refinery primary oil/water/solids separation sludge from gravitational separation of process waters and oily cooling waters	Benzene, benzo(a)pyrene, chrysene, lead, chromium
F038	Petroleum refinery secondary (emulsified) oil/water/solids separation sludge from physical and/or chemical separation of process wastewaters and oily cooling waters	Benzene, benzo(a)pyrene, chrysene, lead, chromium
K048	Dissolved air flotation (DAF) float	Hexavalent chromium, lead
K049	Slop oil emulsion solids	Hexavalent chromium, lead
K050	Heat exchanger bundle cleaning sludge	Hexavalent chromium
K051	API separator sludge	Hexavalent chromium, lead
K052	Leaded tank bottom corrosion solids	Lead
K169	Crude oil storage tank sediment from petroleum refining operations	Benzene
K170	Clarified slurry oil tank sediment and/or in-line filter/ separation solids from petroleum refining operations	Benzene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, 3-methylcholanthrene, 7,12-dimethylbenz(a)anthracene
K171	Spent hydrotreating catalyst from petroleum refining (does not include inert support media)	Benzene, arsenic
K172	Spent hydrorefining catalyst from petroleum refining	Benzene, arsenic

Sources: Bureau of National Affairs, Hazardous Waste Criteria, 161:2217 (S-1006), 1995.
Federal Register/Vol. 63, No. 151, Table 302.4, List of Hazardous Substances and Reportable Quantities, 8/6/98

EPA recently proposed procedural changes designed to ensure a smooth transition into the program's second phase, which will begin in 2000 and will require refiners to meet additional reductions in nitrogen oxides, volatile organics, and toxic emissions over 1990 baseline levels. Under new procedural changes, states that opt-in to the program in 2000, for example, will not be able to opt-out until December 2003. This will guarantee use of the reformulated fuel for a full four years and allow refiners to better gauge the market in advance [OGJ 1996d, OGJ 1997b].

Health and safety issues have also arisen concerning the use of methyl tertiary butyl ether (MTBE), the most widely used oxygenate. California recently considered banning the use of MTBE in reformulated fuels sold in California

Table 1-17. Top 15 Toxic Chemical Releases from Petroleum Refineries (million lbs/yr)

TOXIC CHEMICAL	1996	1995
Nitrate compounds	9.3	4.5
Ammonia	9.0	11.2
Toluene	7.7	9.3
Methanol	5.4	1.3
n-Hexane	5.1	5.8
Propylene	4.3	6.4
Methyl Ethyl Ketone	4.3	5.3
Xylene (mixed isomers)	4.1	6.5
Benzene	3.0	3.4
Methyl tert-butyl ether	2.6	2.8
Ethylene	2.0	3.3
Hydrochloric Acid	1.4	N/a*
Cyclohexane	1.3	1.9
Ethylbenzene	1.0	1.1
1,2,4-trimethylbenzene	0.7	0.9
Other chemicals	7.7	9.0
Total	68.9	75.4

* Hydrochloric acid was not among the top fifteen in 1995.
Source: *1996 and 1995 Toxic Release Inventory,* U.S. Environmental Protection Agency 1997 and 1998.

[OGJ 1997c]. This legislation was defeated in 1997, and California is currently studying the relative benefits and impacts of MTBE use.

Global Climate Change Concerns and Reducing Emissions of Greenhouse Gases May be a Future Challenge

Global climate change refers to the myriad of environmental problems that are believed by some to be caused, in part, by the reaction of the world's climate (temperature, rainfall, cloud cover) to rapidly increasing human activities such as the combustion of fossil fuels, pollutant emissions to air and water, changes in the Earth's reflectivity (albedo) due to deforestation, and emissions of ozone-depleting chemicals.

Greenhouse gases refers to gases that trap heat in the atmosphere. In particular, they are transparent to solar radiation that enters the Earth's atmosphere, but strongly absorb the infrared thermal radiation emitted by the Earth. The most common man-made and natural sources of greenhouse gases are shown in Table 1-18. The natural greenhouse effect is what permits life to exist on earth. Without greenhouse gases in the atmosphere, ambient temperatures would be much

Table 1-18. Sources of Greenhouse Gases				
Greenhouse Gas	**Anthropogenic Sources**	**Global Emissions of Anthropogenic Sources (MMTCE)**	**Natural Sources**	**Global Natural Emissions (MMTCE)**
Carbon dioxide (CO_2)	Combustion of fossil fuels; calcination of limestone, soda ash manufacture and use; aluminum production.	7,100	Biological processes	150,000
Nitrous oxide (NO, NO_2)	Combustion of fossil fuels; nitrogen fertilizers, manufacture of adipic and nitric acid.	4-8	Biogenic processes in soil; lightning.	6-12
Methane (CH_4)	Coal mining; oil refining; gas drilling and transmission; chemical, iron and steel production.	300-450	Aerobic decay of vegetation; termites (tropics); ruminant animals; rice fields.	110-210
Chlorofluorocarbons (CFC-11, CFC-12, CFC-113)	Release of engineered chemical refrigerants and solvents	0.2 (U.S. only)	No natural source.	—

colder -- below the freezing temperature for water -- and the earth would be incapable of sustaining life.

The Earth's climate system adapts relatively well to small and slow changes in atmospheric greenhouse gas concentration. However, rapid changes in anthropogenic (man-made) greenhouse gases may constitute a major force for climate change. An increase in the average temperature of the earth could have serious implications for global climates. Larger environmental disruptions may result from climatic disequilibrium caused by a combination of climate change forces, i.e., increasing greenhouse gases, albedo changes, and stratospheric ozone depletion. When climate forces are disrupted, global weather patterns become less predictible and can result in an increase in hurricanes, flooding, and tornados. As greenhouse gases increase, the rate of change in global climate patterns may accelerate and limit the ability of ecosystems to adapt to these changes.

There is little doubt among the scientific community that global warming and other changes in global climates could have significant impacts on the world as we know it. However, there is no scientific consensus that global warming is actually occurring at the present time. NASA satellite data do not show net warming over the past 18 years, and actually indicate a slight cooling trend since the early 1900s. Surface temperature readings, however, show an increase of 1 Celsius degree over the past century, with most of the warming occurring before 1940 and before the large majority of man-made emissions.

Such uncertainties in the available data have resulted in considerable disagreement in the scientific community over the extent and potential of global warming, if any. A recent report of the Intergovernmental Panel on Climate Change noted that the ability to quantify the human influence on global climate is limited by estimates of natural variability and uncertainties in key factors. Scientists do agree that the issue requires extensive research, along with a long-term assessment of the impact of the increase.

Refineries produce greenhouse gases through the combustion of fuels in process heating systems (carbon dioxide). Methane is also emitted along with other volatile hydrocarbons through fugitive emissions from refining equipment, storage tanks, and gas flaring systems. Methane leaks from equipment when methane and oil are separated during refining processes. When oil is transferred to storage tanks at the refinery, methane is also emitted as vapors are displaced. During flaring of gases, unburned methane may also be emitted.

Chlorinated compounds (e.g., refrigerants, solvents) are also emitted from refineries as fugitive emissions and from point sources in small quantities. Although these compounds are suspected of impacting the global climate, their actual effects have not been quantified. They are also suspected to contribute to ozone depletion in the upper atmosphere.

An estimate of greenhouse gas emissions from the combustion of fossil fuels in petroleum refineries is shown in Table 1-19. These emissions were calculated based on energy consumption as reported for 1996 [Petroleum Supply Annual 1996] and using carbon coefficient factors developed for individual fuel types.

The amount of carbon released when fossil fuels are burned is dependent on the carbon content, density, and gross heat of combustion for the particular fuel. For example, the carbon coefficient for refinery gas was estimated by assuming that the gas consists of a mix of hydrocarbons (principally methane, ethane, ethylene, normal butane, butylene, propane, and propylene) plus hydrogen. The carbon coefficients and energy consumption data used in this study are shown in Table 1-19. A detailed explanation of how carbon coefficients were derived can be found in *Emissions of Greenhouse Gases in the United States, 1987-1992* [DOE 1994].

Refinergy Emissions of Non-CO2 Greenhouse Gases

Methane (1995)
- Fugitive Emissions 0.082 million metric tons
- Storage Tanks 0.002 million metric tons
- Gas Flaring 0.002 million metric tons

Chlorinated Compounds (1993)
- Trichloroethane 75 metric tons
- CFC12 89 metric tons
- Carbon tetrachloride 9 metric tons

Sources: Methane - DOE 1996b; chlorinated compounds - EPA Toxic Release Inventory.

The Union of Concerned Scientists (UCS) is urging world leaders and the current U.S. administration to take immediate action and sign a global warming treaty. At an international summit in Kyoto, Japan in late 1997, world leaders met to discuss and formulate an international agreement to reduce the generation of greenhouse gases. The resulting Kyoto Protocol calls for a significant reduction in greenhouse gases for the United States and European Nations by the year 2010. The United States has not yet signed the agreement.

The Kyoto Protocol could have dramatic impacts on consumer prices and economic growth. Many industries are concerned that the economic impacts of such a treaty, as well as the scientific basis for it, are not well understood, and are opposed to the U.S. signing the agreement.

Summary of the Kyoto Protocol

- U.S. to reduce greenhouse gas emissions to 7% below 1990 levels by 2010
- European Nations to reduce greenhouse gas emissions by 8% below 1990 levels by 2010
- No commitments from developing nations to reduce greenhouse gas emissions, and no agreement on a voluntary process for reducing/limiting their emissions
- Emissions trading for Annex I parties only (main sellers would be Russia and Ukraine)
- Joint Implementation linked to Clean Development Mechanism (a UN body that will certify projects)

Table 19. Carbon Emissions from Combustion of Fossil Fuels in Petroleum Refineries - 1996

Fuel Type	Carbon Coefficient (lbs CO_2/million Btu)	1996 Energy Use in Petroleum Refining (Trillion Btu)	Carbon Emissions (MMTCE)	CO_2 Emissions (1000 tons)
Crude Oil	163.9	0.01	0.000203	0.8195
LPG	138.6	26.7	0.458103	1850.31
Distillate Fuel	161.2	4.3	0.085807	346.58
Residuel Fuel	173.6	54.9	1.179807	4765.32
Refinery Gas	141.5	1,435	25.13605	101526.25
Petroleum/ Catalyst Coke	224.98	524.0	14.59365	58944.76
Natural Gas	116.9	797.6	11.53	46570.00
Coal	207.5	3.1	0.079	319.10
Purchased Electricity	133.4	337.0	5.57	22497.9
Purchased Steam	207.5	40.1	1.03	4160.375
Unfinished Oils	163.3	35.7	0.7207	2914.905
TOTALS		3258.41	60.39	243896.3195

Note: MMTCE indicates million metric tons of carbon equivalents.

A recent study indicates that the economic cost to the U.S. of implementing the treaty would be high, and that mandatory emissions goals could result in a loss of gross domestic product of $227 billion (1992 dollars) in 2010 alone (holding emissions to 1990 levels) [WEFA 1997]. According to the study, implementing the protocol would also mean sharply higher prices for energy, which could give developing nations (those not required to reduce emissions) a competitive advantage over the U.S. and other developed countries. The study also indicates that energy-producing states would suffer the most economic disruption.

As the issue is debated, petroleum industry leaders are addressing the issue head on. The American Petroleum Institute (API) acknowledges that climate change is a legitimate concern, but advocates a “go slow” approach to the climate change issue that includes voluntary reduction actions and the development of cost-effective long-term strategies for greenhouse gas reduction. According to API President Red Cavaney, “Business and industry leaders have repeatedly conveyed to the administration our willingness to promote expansion of the President’s voluntary greenhouse gas emissions reductions programs, to support greater investment in research programs aimed at reducing the range of scientific uncertainties, and to support increased research and development of new technologies. “ [API 1998a].

Along with other industry groups, API has expressed its concern over the potentially high economic impacts of implementing the Kyoto Protocol, and does not believe the Protocol targets can be met through employing new technologies, reducing the carbon intensity of energy, or reducing energy use while achieving the administration’s economic objectives [API 1998b]. API continues to work with the Global Climate Coalition to maintain strong opposition to the agreement [API 1998].

2

The Integrated Petroleum Refinery

2.1 The Integrated Refinery Overview

Refineries Upgrade Crude Oil to Useful Products

Petroleum refineries extract and upgrade the valuable components of crude oil to produce a variety of marketable petroleum products that are vital to everyday life. Today's modern refinery is a complex facility where a wide diversity of technologies is used to obtain the maximum value from a barrel of crude while maintaining the flexibility to meet continually changing consumer demands.

The type of crude oil a refinery can process depends on the processing units operated (complexity) as well as the desired product slate. Complex refineries have a variety of processing and treatment options and thus have more flexibility in selecting crude oil inputs. For example, a refinery with greater ability to desulfurize feedstocks will have more input flexibility. Refinery complexity can also change in response to the availability of certain types of crude oil (e.g., sour versus sweet).

Refinery Complexity — the weighted average of the complexity factors for the process units that comprise a refinery. Complexity factors are the ratios of the costs of various process operations to the cost of crude distillation and desalting, plus 50 percent for some of the auxiliaries needed in any refinery.

While many relatively simple refineries still operate in the United States, most fall into the complex category. This level of complexity is necessary for domestic refiners to effectively respond to changes in product supply and demand by shifting the product slate. For example, refineries may produce more gasoline during the spring and summer months when demand for this product is high, than they do during the winter when demand for heating oils is high.

Refining Processes Distill, Crack, and Rearrange Hydrocarbon Molecules

Refinery operations essentially fall into five categories: topping, or separation of hydrocarbons; thermal and catalytic cracking of hydrocarbons; combination/rearrangement of hydrocarbons; treating and blending of products; and specialty product manufacture. The major processes that fall within each of these categories are shown in Table 2-1. The overall refinery flow diagram is shown in Figure 2-1 [DOE 1991].

Topping or separation processes involve separating crude oil into different hydrocarbon groups, or fractions. The most common means of doing this in refineries is distillation. Solvent deasphalting is an efficient process for separating crude oils to produce conversion unit feedstocks.

Thermal and catalytic cracking of hydrocarbons involves "cracking" or breaking down large, heavy hydrocarbon molecules into smaller hydrocarbon molecules. Cracking can be achieved either through the application of heat or through the use of catalysts. Cracking operations include delayed and fluid coking, visbreaking, catalytic cracking, and catalytic hydrocracking.

Combination of hydrocarbons involves linking two or more hydrocarbon molecules together to form a larger molecule (e.g., converting gases to liquids). Alkylation and polymerization are refinery processes that combine smaller molecules to produce high octane gasoline blending stock.

Rearrangement of hydrocarbons alters the original structure of the molecule, producing a new molecule with different characteristics (but the same number of carbon atoms). Catalytic reforming and isomerization are commonly used techniques for hydrocarbon rearrangement.

Treating operations involve processing of petroleum products to remove some of the sulfur, nitrogen, heavy metals, and other impurities. **Blending** is the last phase of the refining process and is used to obtain the final product. A variety of processes are also employed to produce specialty products such as lubricating oils, grease, wax, and asphalt.

Table 2-1. Major Petroleum Refining Processes

Category	Major Process
Topping (Separation of Crude Oil)	Atmospheric Distillation Vacuum Distillation Solvent Deasphalting
Thermal and Catalytic Cracking	Delayed Coking Fluid Coking/Flexicoking Visbreaking Catalytic Cracking Catalytic Hydrocracking
Combination/Rearrangement of Hydrocarbons	Alkylation Catalytic Reforming Polymerization Isomerization Ethers Manufacture
Treating	Catalytic Hydrotreating/Hydroprocessing Sweetening/Sulfur Removal Gas Treatment
Specialty Product Manufacture	Lube Oil Grease Asphalt

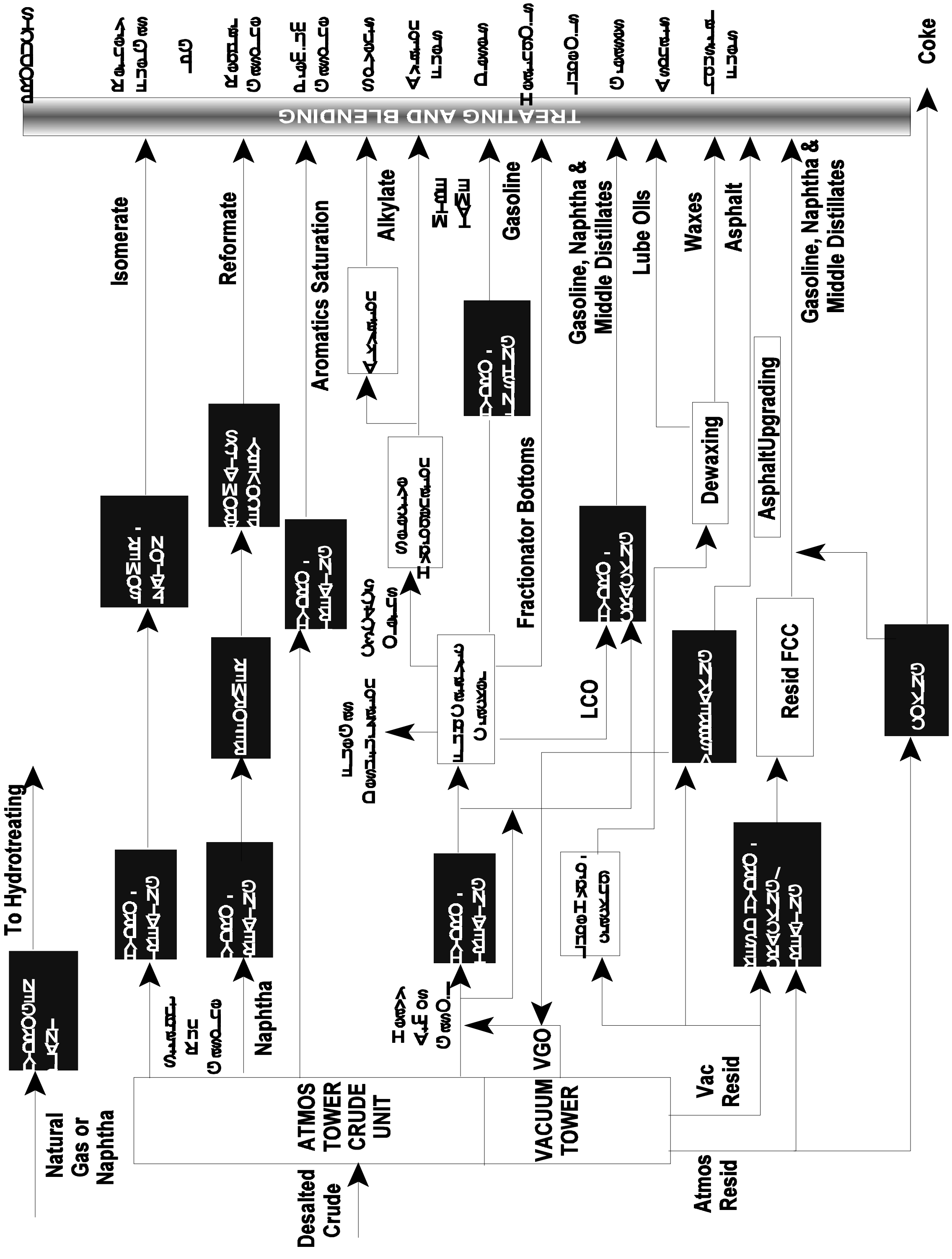

Figure 2-1. Typical Refinery Flow Diagram

2.2 Energy Overview

Distillation and Hydrotreating Consume the Most Energy in the Refinery

Petroleum refining processes are very energy-intensive, often requiring large amounts of power and process heat. Table 2-2 provides estimates of process energy use and the contribution to overall refinery energy use, based on average values for a number of technologies currently in use. The total shown in Table 2-2 differs somewhat from total process energy use for refining in 1994 shown in Table 1-6 because average values were used to calculate total consumption, based on capacity utilization of 93 percent. As can be seen from the ranges of specific energy use in Table 2-2, actual energy consumption can vary considerably between various technologies in use. In addition, capacity utilization varies monthly, and over the last year has ranged from as low as 90 percent to over 96 percent. A number of supporting processes that consume energy were also not included in this table (e.g., hydrogen production, sulfur recovery and management, cooling towers, water treatment).

Excluding lubricating oil manufacture (which is only done at some refineries), the most energy intensive refining processes are ethers manufacture, alkylation, and C4 (butylene) isomerization [most isobutylene is produced as by-product, not through a process dedicated to that purpose].

Overall refinery energy consumption is dominated by a few processes that, while not the most energy intensive, have the greatest throughput. Atmospheric and vacuum distillation, for example, account for 35-40 percent of total process energy consumption. This large share of energy consumption results because every barrel of crude oil entering the refinery must be subjected to an initial separation by distillation. Hydrotreating, which is used to remove sulfur, nitrogen, and metal contaminants from petroleum feed, also accounts for a large portion of energy use (nearly 19 percent). Hydrotreating is used to treat feedstocks for a number of refinery processes to improve catalyst life and enhance product quality.

Lubricating oil manufacture is accomplished by a series of energy-intensive processes (deasphalting, solvent extraction, dewaxing), all requiring energy-intensive solvent recovery processes. The combined energy consumption for all the processes required for lubricating oil manufacture is over 1.5 million Btu per barrel of feed processed. Despite the relatively low throughput to lubricating oil manufacture, it still accounts for about 4 percent of overall refining energy consumption.

2.3 Environmental Overview

Refinery Processes Generate Emissions to Air, Water, and Land

During the refining of crude oil into various petroleum products, petroleum refineries use and generate an enormous amount of chemicals, some of which are present in air emissions, wastewater, or solid wastes. Emissions are also created through the combustion of fuels, and as by-products of chemical reactions occurring when petroleum fractions are upgraded.

Tables 2-3 through 2-7 summarize the various air emissions, effluents, residuals and wastes (hazardous, non-hazardous, and toxic) generated by refineries through various processes [EPA 1995a, HP 1996, Meyers 1997].

A large source of **air emissions** is process heaters and boilers (CO, SOx, NOx). In addition, some processes create considerable amounts of particulates and other emissions from catalyst regeneration or decoking processes. Volatile chemicals and hydrocarbons are also released from equipment leaks, storage tanks, and wastewaters.

Table 2-2. Estimated Energy Use by Refining Process

Process	Specific Energy Use[a] (10^3 Btu/bbl)	Average Use[b] (10^3 Btu/bbl)	Capacity (10^6 bbl/cday)[c]	Annual Energy Use (10^{12} Btu/year)
Atmospheric Distillation[d]	82 - 186	113.8	15.45	641.6
Vacuum Distillation	51 - 113	91.5	7.15	238.8
Visbreaking[e]				
- Coil	136	136	0.0215	1.07
- Soaker	25 - 95	63	0.0436	1.00
Delayed Coking	114 - 230	166	1.671	114.6
Fluid Coking (net)	258	258	0.075	7.1
Flexicoking (net)	167	167	0.112	6.7
Fluid Catalytic Cracking	50 - 163	100	5.2	190.6
Catalytic Hydrocracking	159 - 321	240	1.3	109.7
Catalytic Hydrotreating	61 - 164	120	10.7	468.3
Catalytic Reforming	213 - 342	284	3.6	376.3
Alkylation				
- Sulfuric Acid	330 - 340	335	0.44	53.3
- Hydrofluoric Acid	401	401	0.66	95.5
Ethers Production	295 - 564	403	0.18	33.4
Isomerization				
- Isobutane	359	359	0.098	13.0
- Isopentane/Isohexane	102 - 236	175	0.42	27
- Isobutylene	476	476	n/a	n/a
Lube Oil Manufacture	1,506	1506	0.20	109.5
TOTAL[F]	**-**	**-**	**-**	**2487.5**

a Gross energy use, which includes losses incurred during the generation and transmission of electricity (electricity conversion factor of 10,500 Btu/kWh). Does not include hydrogen or oxygen consumption.
b Average energy use based on estimated utility requirements for a range of technologies. See individual chapters for additional details.
c bbls/cday = barrels per calender day (365 days per year).
d Includes energy consumed for desalting of crude.
e Assumes 33 percent of capacity is coil type, and 67 percent is soaker type visbreakers.
f Does not include hydrogen production processes, sulfur recovery and management processes, operation of cooling towers, and other supporting processes.
n/a indicates data is not available.

Sources: See individual chapters for each process for a detailed source listing.

Table 2-3. Summary of Emissions, Effluents, Residuals and Waste Streams for Topping/Separation Processes

Process	Air Emissions	Process Wastewater	Waste, Residuals or By-Products
Crude Oil Desalting	Largest source - heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)	Largest source - hot salty process water (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids) Water flow - 2.1 gal/bbl of oil	Crude oil/desalter sludge (iron rust, clay, sand, water, emulsified oil and wax, heavy metals)
Crude Distillation (atmospheric and vacuum	Largest source - heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)and steam injector emissions (hydrocarbons)	Largest source - oily sour water from the fractionators (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol) Water flow - 26.0 gal/bbl oil	Little or no residual, wastes or byproducts

Table 2-8 summarizes the available process air emission factors (non-combustion) for individual refining processes. Combustion emission factors for process heaters and boilers are provided in Section 10, Supporting Processes. More information on emissions for specific processes, as well as how these emissions are controlled, can be found in the individual chapters describing these processes.

Process wastewater is also a significant effluent from a number of refinery processes. Atmospheric and vacuum distillation create the largest volumes of process wastewater, about 26 gallons per barrel of oil processed. Fluid catalytic cracking and catalytic reforming also generate considerable amounts of wastewater (15 and 6 gallons per barrel of feed, respectively).

A large portion of wastewater from these three processes is contaminated with oil and other impurities and must be subjected to primary, secondary and sometimes tertiary water treatment processes, some of which also create hazardous waste. More information about wastewater treatment can be found in Section 10, Supporting Processes.

An estimate of the amount of wastewater released by an integrated petroleum refinery can be obtained from the effluent limitations given by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419, which was originally promulgated in 1974. Table 2-9 shows the limitations for average daily values for 30 consecutive days using best practicable control technology (BPT) currently available [BNA 1992]. The limitations shown in Table 2-9 are for a refinery with the following operations: topping (crude distillation), cracking and coking processes, lubricating oil manufacture, and petrochemical feedstock production units (e.g., isomerization and others).

Wastes, residuals and by-products are produced by a number of processes. Residuals produced during refining can be but are not necessarily wastes. They can be recycled or regenerated, and in many cases do not become part of the waste stream but are useful products. For example, processes utilizing caustics for neutralization of acidic gases or solvent (e.g., alkylation, sweetening/chemical treating, lubricating oil manufacture) create the largest source of residuals in the form of spent caustic solutions. However, nearly all of these caustics are recycled.

The treatment of oily wastewater from distillation, catalytic reforming and other processes generates the next largest source of residuals in the form of biomass sludges from biological treatment and pond sediments. Water treatment of oily wastewater also produces a number of sludges associated with oil-water separation processes. Such sludges are often recycled in the refining process and are not considered wastes.

Catalytic processes (fluid catalytic cracking, catalytic hydrocracking, hydrotreating, isomerization, ethers manufacture) also create some residuals in the form of spent catalysts and catalyst fines or particulates. The latter are sometimes separated from exiting gases by electrostatic precipitators or filters. These are collected and disposed of in landfills or may be recovered by off-site facilities. Individual sections on catalytic processes provide more detail about catalytic residuals and their disposition.

Table 2-4. Summary of Emissions, Effluents, Residuals and Waste Streams for Thermal and Catalytic Cracking Processes

Process	Air Emissions	Process Wastewater	Waste, Residuals or By-Products
Visbreaking	Largest source -fugitive emissions from process vents	Largest source - sour wastewater from the fractionator (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids) Water flow - 2.0 gal/bbl feed	Little or no residuals, waste or byproducts generated
Coking	Largest source - heater stack gas (CO, SOx, NOx, hydrocarbons and particulates). Particulate emissions from decoking can also be considerable.	Largest source - coke-laden water from decoking operations in delayed cokers (hydrogen sulfide, ammonia, suspended solids) [Fluid coking produces little or no effluents)) Water flow - 1.0 gal/bbl feed	Coke dust (carbon particles and hydrocarbons) may not be a waste; coke fines may be a product.
Fluid Catalytic Cracking	Largest sources - catalyst regeneration and CO boilers (hydrocarbons, CO, NOx, SOx and particulates)	Largest source - sour wastewater from the fractionator/gas concentration units and steam strippers (high levels of oil, suspended solids, phenols, cyanides, H_2S, $NH_{3)}$). Water Flow - 15 gal/bbl feed	Spent catalysts (metals from crude oil and hydrocarbons), spent catalyst fines from electrostatic precipitators (aluminum silicate and metals).
Catalytic Hydrocracking	Largest sources - heater stack gas (CO, SOx, NOx, hydrocarbons and particulates).	Largest source - sour wastewater from the fractionator and hydrogen separator (suspended solids, H_2S). Water Flow - 2 gal/bbl feed	Spent catalysts (metals from crude oil, and hydrocarbons).

Table 2-5. Summary of Emissions, Effluents, Residuals and Waste Streams for Combination/Rearrangement Processes

Process	Air Emissions	Process Wastewater	Waste, Residuals or By-Products
Alkylation	Process vents, fugitive emissions	Wastewater from water-wash of reactor hydrocarbon products (suspended solids, dissolved solids, hydrogen sulfide) and spent sulfuric acid Water flow - ~2.6 gal/bbl feed Spent Sulfuric Acid - 13-30 lbs/bbl alkylate	Neutralized alkylation sludge (sulfuric acid, hydrocarbons)
Catalytic Reforming	Heater stack gas (CO, SOx, NOx), hydrocarbons and particulates), fugitive emissions, and catalyst regeneration	Process wastewater (high levels of oil, suspended solids, low hydrogen sulfide) Water flow - 6.0 gal/bbl feed	Spent catalyst and hydrogen gas Hydrogen Gas production: 1100 - 1700 scf/bbl:
Isomerization	Boiler/heater stack gas (CO, SOx, NOx, hydrocarbons and particulates), HCl (possible in fuel gas), vents and fugitive emissions (hydrocarbons)	Sour water (low hydrogen sulfide, ammonia), chloride salts, and caustic wash water	Calcium chloride sludge from neutralized HCl gas
Ethers Manufacture	Boiler stack gas (CO, SOx, NOx, hydrocarbons and particulates)	Pretreatment wash-water (nitrogen contaminants); cooling and alcohol wash water are recycled	Spent catalysts

Table 2-6. Summary of Emissions, Effluents, Residuals, By-Products and Waste Streams for Treatment Processes

Process	Air Emissions	Process Wastewater	Waste, Residuals or By-Products
Catalytic Hydrotreating	Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)	Sour wastewater from the fractionator and hydrogen separator (suspended solids, H_2S, NH_3, phenols) Water Flow - 1 gal/bbl feed	Spent catalyst fines (aluminum silicate and metals)
Sweetening/ Merox Process	Vents and fugitive emissions	Little or no wastewater generated	Spent caustic solution, residual oil-disulfide mixture
Sulfur Removal/ Claus Process	Process tail gas (NOx, SOx, hydrogen sulfide), fugitive emissions	Process wastewater (hydrogen sulfide, ammonia)	Hazardous air emissions - hydrogen sulfide, carbonyl sulfide (COS) and carbon disulfide (CS2); fugitive solvent emissions may be toxic (e.g., diethanolamine)

Table 2-7. Summary of Emissions, Effluents, Residuals, By-Products and Waste Streams for Specialty Products Manufacture

Process	Air Emissions	Process Wastewater	Waste, Residuals or By-Products
Lubricating Oil Manufacture (deasphalting, solvent extraction, dewaxing)	Heater stack gas (CO, NOx, SOx, hydrocarbons, particulates), fugitive propane, and fugitive solvents	Steam stripping wastewater (oil and solvents), solvent recovery wastewater (oil and propane)	Little or no residuals, wastes or by-products Fugitive solvent emissions may be toxic (toluene, methly ethyl ketone, methyl isobutyl ketone)

Table 2-8. Air Emission Factors for Petroleum Refining Processes (lbs/1000 barrels of fresh feed)

Process	SO_x	NO_x	CO	Total Hydro-carbons	Alde-hydes	Ammonia	Partic-ulates
Fluid Catalytic Cracking Units							
- Uncontrolled	493	71	13,700	220	19	54	242
- Electrostatic Precipitator and CO Boiler	493	71	Neg	Neg	Neg	Neg	45
Moving Bed Catalytic Crackers	60	5	3,800	87	12	6	17
Fluid Cokers							
- Uncontrolled	ND	ND	ND	ND	ND	ND	523
- Electrostatic Precipitator and CO Boiler	ND	ND	Neg	Neg	Neg	Neg	6.8
Vacuum Distillation Column Condensers							
- Uncontrolled	Neg	Neg	Neg	50	Neg	Neg	Neg
- Controlled (vented to heater or incinerator)	Neg	Neg	Neg		Neg	Neg	Neg
Claus Plant and Tail Gas Treatment							
- SCOT Absorber and Incinerator	5.66	Neg	Neg	Neg	Neg	Neg	Neg
- Incinerator Exhaust Stack (2 catalytic stages)	85.9	Neg	Neg	Neg	Neg	Neg	Neg
Blowdown Systems							
- Uncontrolled	Neg	Neg	Neg	580	Neg	Neg	Neg
- Vapor Recovery System and Flaring	26.9	18.9	Neg	0.8	Neg	Neg	Neg

. Source: *AP 42, Chapter 5, Petroleum Refining.* U.S. Environmental Protection Agency, January 1995.

Table 2-9. Effluent Limitations for an Integrated Refinery[a]
Average of Daily Values for 30 Consecutive Days
(lbs/1000 bbl of crude oil)

Constituent	BPT Limitation [d]
Total Suspended Solids	8.4
Oil and Grease	3.2
Phenolic Compounds	0.068
Ammonia (as Nitrogen)	3.8
Sulfide	0.056
Total Chromium	0.17
Hexavalent Chromium	0.011
[b]BOD5	10.2
[c]COD	70.0

[a] Combined limits for a refinery including topping, cracking and coking, lubricating oil manufacturing, and petrochemical operations.

[b] Biochemical oxygen demand (BOD); the five (5) subscript indicates an incubation period of 5 days.

[c] Chemical oxygen demand (COD) is a relative measure of environmental damage from wastewater based on oxygen demand. It is equal to the number of milligrams of oxygen which a liter of sample will absorb from a hot, acidic solution of potassium dichromate.

[d] BPT as defined by EPA is the “best practicable control technology currently available.”

3

Crude Oil Distillation

3.1 Distillation Process Overview

Distillation Separates Crude Oil into Boiling Fractions

Crude oil is composed of many different hydrocarbon compounds that boil at characteristic boiling points ranging from 90°F to over 800°F [Gary 1994, Humphrey 1991]. Separating crude oil into its various boiling fractions is one of the first and most critical operations in the refinery, and is commonly accomplished through **fractional distillation.** As the boiling points of different hydrocarbons are reached, the vapors condense and are collected in streams called "fractions". Lighter fractions are collected through atmospheric distillation; heavier fractions have very high boiling points and must be collected in a vacuum tower at lower pressure so they do not decompose.

In 1997, approximately 14.3 million barrels of crude oil per day will be fed to atmospheric crude distillation units in domestic refineries. With the current U.S. refining capacity of 15.4 million barrels per day, this represents a capacity utilization rate of about 93 percent. Vacuum distillation capacity is projected to be about 6.9 million barrels per day in 1997, less than half the capacity of atmospheric distillation [OGJ 1997, Leger 1997].

Boiling Ranges of Crude Fractions

Fraction	ASTM Boiling Range °F
Light Straight-Run Gasoline	90 -220
Naphtha	180-400
Kerosene	330-540
Light Gas Oil	420-640
Atmospheric Gas Oil	520-830
Heavy Residue	650+
Vacuum Gas Oil	750+
Vacuum Reduced Crude	1000+

Desalting Prepares the Crude Oil for Atmospheric Distillation

Prior to distillation, crude oil is often **desalted** to remove corrosive salts as well as metals and other suspended solids which can deactivate

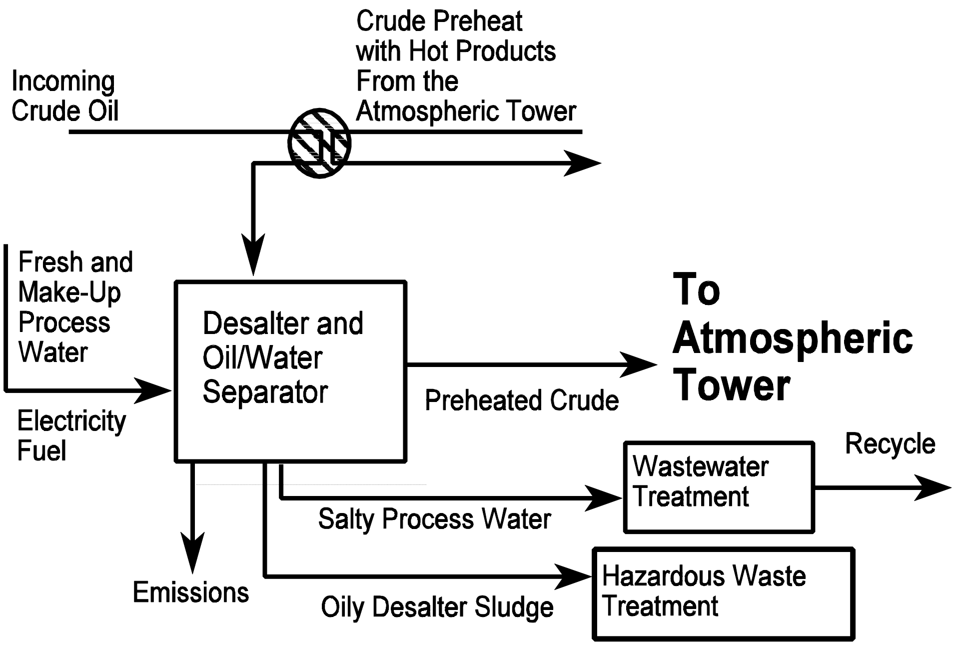

Figure 3-1. Crude Oil Desalting Flow Diagram [HP 1993a, EPA 1995a, ANL 1981]

Key Energy and Environmental Facts - Desalting			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross: 540 Btu/bbl of oil* *Net - 203 Btu/bbl of oil*	*No significant air emissions.*	*Hot salty process water (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids)* *Water flow - 1.2-4.0 gal/bbl of oil*	*Crude oil/desalter sludge (iron rust, clay, sand, water, emulsified oil and wax, heavy metals)*

catalysts in downstream processing units. The desalting process involves mixing preheated crude oil with water (about 3 to 10 percent water by volume of crude) to extract the salts (see Figure 3-1). The resulting dispersed mixture of crude and water is separated by exposure of the mixture to an electric field to coalesce the polar salt water droplets. Demulsifier chemicals are sometimes added to assist in breaking the emulsion. The water used to strip salts often comes from other processes in the refinery (e.g., stripped sour water[1], boiler feedwater) [EPA 1995, HP 1993a, OGJ 1992a].

After desalting the crude is usually heated further (to about 550°F) using process-to-process heat exchangers (heat exchange with other hot process fluids) to reduce fuel consumption in the crude furnace.

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[1] *Sour water contains dissolved hydrogen sulfide, other sulfur compounds and ammonia which are stripped in a tower with gas or steam before discharge to the water treatment plant.*

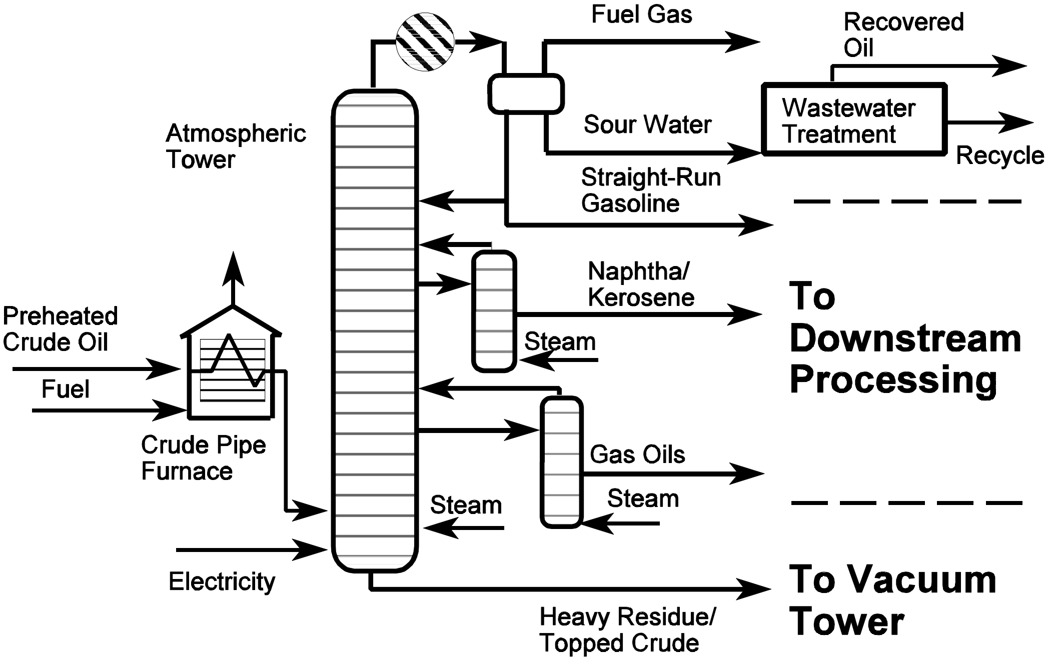

Figure 3-2. Atmospheric Distillation Flow Diagram
[HP 1993a, EPA 1995a, ANL 1981]

Key Energy and Environmental Facts - Atmospheric Distillation			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross: 113.8 10^3 Btu/bbl oil* *Net - 109.4 10^3 Btu/bbl oil*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)*	*Oily sour water from the fractionators (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol)*	*Little or no residual waste or byproducts*

Desalting creates an oily desalter sludge that may be a hazardous waste and a high temperature salt waterwaste stream (treated along with other refinery wastewaters). In some cases it is possible to recycle the desalter effluent water back into the desalting process, depending upon the type of crude being processed (up to 50 percent recycle has been reported) [OGJ 1992a].

All Incoming Crude Passes Through the Atmospheric Distillation Column

Atmospheric distillation is used to separate the desalted crude oil into specific hydrocarbon groups, or "fractions" with similar boiling points. The term "atmospheric" refers to the pressure at which the column is operated. Boiling ranges of fractions produced in atmospheric distillation go up to about 700°F.

In this process, preheated crude from the desalter is first heated to about 700°F in a tubular pipe-still furnace (see Figure 3-2). Many different configurations can be used for the tubular furnace, but most use hot furnace flue gases to preheat pipes, which reduces energy requirements as well as the amount of time the crude must spend at extremely high temperatures.

Feed flow to the furnace is split into several passes to assure even heat distribution. To assure equal flow through each pass a control valve is adjusted by input from a flow meter. Flow to these control valves must be single phase (all liquid) to assure proper operation of the valves. This limits the temperature to which heat may be recovered in the feed prior to the furnace.

After heating in the furnace a foaming stream of petroleum enters the atmospheric distillation column, which is a vertical cylindrical tower that can be as large as 13 feet in diameter and over 80 feet high, operating just above atmospheric pressure.

The tower contains anywhere from 30 to 50 horizontal fractionation trays, each corresponding to a different temperature. There are perforations in the trays to allow the hot vapor rising to pass through and contact the condensed liquid that is held on each tray. The most volatile components on the trays are vaporized; the least volatile are absorbed and remain with the liquid on the tray. Going up the column the trays are cooler and contain a more volatile mix than the trays below. The lower-boiling fractions condense and are collected toward the top of the column; heavier fractions collect toward the bottom. The heavy bottoms contact a stream of steam which removes (strips) any light components and produces a heavy liquid residue which is sometimes sent to a vacuum distillation column for further separation.

At least two low-boiling point side-streams from the atmospheric column are sent to smaller stripping towers with 4 to 10 trays, where steam is injected under the bottom tray. The steam is used to strip out the most volatile components from the heavier components, which are the desired products. The steam and volatiles are then fed back to the atmospheric tower.

Atmospheric distillation produces gasoline, naphtha, kerosene, gas oils, and heavy crude residue. Products of atmospheric distillation are often referred to as straight-run liquids (e.g., straight-run gasoline), and are further processed to make final products or blended with products from downstream processes. Atmospheric columns also produce a light non-condensable fuel gas composed mostly of methane and ethane that is often referred to as still gas or refinery gas. This gas also contains hydrogen sulfide and ammonia[2] and must be treated before it can be used as a fuel in process heaters. Sour water is also produced from the side fractionators and must be separated from the condensed hydrocarbon liquids so that it can be reused as process water. Oil can be recovered in this process by skimming with internal baffles, and is pumped to recovered oil storage. [Process Description: Gary 1994, EPA 1995a, DOE 1991, DOE 1990, ANL 1981]

Heavier Crude Fractions Must be Separated by Vacuum Distillation

Heavy crude residue (often called topped crude or bottoms) from the atmospheric column is further separated using a lower-pressure distillation process. At atmospheric pressure the fractions contained in the residue boil at temperatures of 750°F or greater, but cannot be heated to their boiling point because many of the components decompose at that temperature. Excessive heat also puts a greater strain on the equipment and can lead to the formation of coke deposits, which must be physically removed. **Vacuum distillation** is essentially a means to lower the boiling points of the fractions and permit separation at lower temperatures, without decomposition and excessive coke formation.

The vacuum tower is typically a packed column of up to 45 feet in diameter (see Figure 3-3). The pressure in the vacuum tower is reduced and maintained using mechanical pumps, steam ejectors, and surface condensers. Superheated steam is also injected at the base to further reduce the partial pressure (and boiling points of the fractions) and facilitate vaporization and separation.

The product of the vacuum distillation column is a vacuum gas oil (top of the column), a heavy pitch bottom residue, and an intermediate oil product that can be used for lubricating oil or as feed to the catalytic cracker downstream. Side

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[2] *The mixture of these two gases is often called sour or acid gas.*

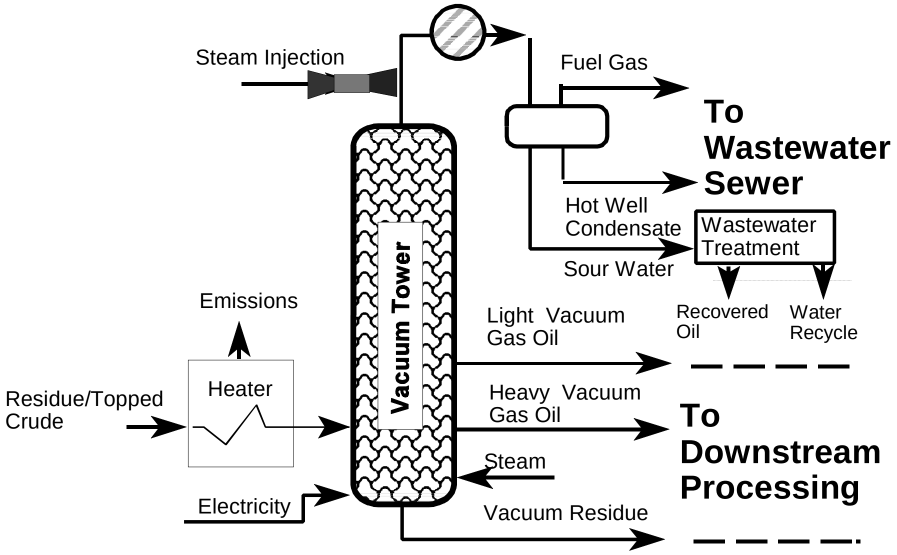

Figure 3-3. Vacuum Distillation Flow Diagram [HP 1993a, EPA 1995a, ANL 1981]

Key Energy and Environmental Facts - Vacuum Distillation			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross: 92.3 10^3 Btu/bbl oil* *Net - 89.9 10^3 Btu/bbl oil*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulate) and steam injector emissions (hydrocarbons)*	*Oily sour water from the fractionators (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol)*	*Little or no residual waste or byproducts*

streams can also be sent to steam stripping units to increase yields of selected fractions and meet flash point specifications. Vacuum bottoms can be used as fuel, or can be further processed in coking units where they can be converted to gasoline components, petroleum coke, and refinery gases.

Sour water is separated from condensed hydrocarbon liquids and may be reused. Oil can be recovered and pumped to storage tanks. Non-condensable vapors are compressed and exit as fuel gas for use elsewhere in the refinery. [Process Description: Gary 1994, EPA 1995a, DOE 1991, ANL 1981]

3.2 Summary of Inputs/Outputs

The following is a summary of the inputs and outputs of the entire crude distillation process, including desalting, atmospheric and vacuum distillation processes.

Inputs:	Outputs:.
Crude Oil	Straight-Run Gasoline
Process Water	Naphtha
Steam	Kerosene
Fuel (Gas/Oil)	Atmospheric Gas Oils
Electricity	Heavy Residue
	Vacuum Gas Oils
	Vacuum Residue
	Fuel Gas
	Process Wastewater
	Desalter Sludge

3.3 Energy Requirements

The **process energy** used in atmospheric distillation (including desalting) and vacuum distillation is shown in Tables 3-1 and 3-2 [HP 1993a, EI 90, ANL 81]. The energy content of the crude oil feedstock is not considered here, as it is used to make energy products that are combusted for heat and power in other industries(e.g., transportation, buildings, petrochemicals) or used to make materials (e.g., plastics in the petrochemical industry). Process

Table 3-1. Estimated Energy Use in Atmospheric Distillation[a]- 1996

Energy Source[b]	Specific Energy Use[g] (10^3 Btu/bbl of oil)	Total Industry Use[f] (10^{12} Btu/yr)
Natural Gas	29.3	165.2
Refinery Gas	52.6	296.6
Electricity[c]	7.0	39.5
Coke	19.3	108.8
Oils[d]	3.5	19.7
Other[e]	2.1	11.8
TOTAL	**113.8**	**641.6**

a Includes energy used for desalting
b Fuel mix for fossil fuels (not electricity) based on typical use at refineries
c Includes losses incurred during the generation and transmission of electricity
d Includes crude oil, distillate and residual fuel oil
e Includes liquefied petroleum gases, coal, and purchased steam
f Based on input to crude stills for 1996 (15.45 x 10^6 bbls/cday (93 percent capacity) [DOE 1997a].
g Based on estimated utility requirements for several licensed technologies [ANL 1981, HP 1996, SFA 1990].

Table 3-2. Estimated Energy Use in Vacuum Distillation - 1996

Energy Source[a]	Specific Energy Use[f] (10^3 Btu/bbl of oil)	Total Industry Use[e] (10^{12} Btu/yr)
Natural Gas	24.1	62.9
Refinery Gas	43.2	112.7
Electricity[b]	3.6	9.4
Coke	15.9	41.5
Oils[c]	2.9	7.6
Other[d]	1.8	4.7
TOTAL	**91.5**	**238.8**

a Fuel mix for fossil fuels (not electricity) based on typical use at refineries
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, coal, and purchased steam
e Based on estimated vacuum distillation capacity of 7.15 x 10^6 bbl/cday (93 percent capacity) [DOE 1997a]
f Based on estimated utility requirements for several licensed technologies [ANL 1981, HP 1996, SFA 1990]

energy does include, however, any energy by-products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas). The majority of the process energy input to distillation is in the form of fuels used in process heaters and in boilers to produce steam. While some of these fuels are purchased (e.g., natural gas), most are produced on-site (refinery gas, coke, oils) through refinery processes. Refinery gas is the most prevalent of these and accounts for over 50 percent of fuel inputs for process heat. Refinery fuel gas (sometimes referred to as still gas) is generally any mixture of gases produced in the refinery by distillation, cracking, reforming, and other downstream processes. The main constituents of refinery gas are methane, ethane, ethylene, butane, butylene, propane, and other light hydrocarbons.

Electricity is used mostly to power pumps, compressors, and other auxiliary equipment. Some electricity is also used in the desalting process in electrostatic precipitators to separate oil and water.

Atmospheric and vacuum distillation are very energy-intensive processes. Their combined estimated consumption is about 800 trillion Btus/year, which represents about 40 percent of all process energy used in the refinery complex.

3.4 Air Emissions

Crude Distillation Creates Emissions through Fuel Combustion and System Leaks

Air emissions from crude distillation include emissions from the combustion of fuels in process heaters and boilers, fugitive emissions of volatile constituents in the crude oil and fractions, and emissions from process vents. Table 3-3 lists emission factors for major air emissions from vacuum distillation column condensers. Emission factors for process heaters and boilers are shown in Chapter 10.

The primary source of emissions is combustion of fuels in the crude pre-heat furnace and in boilers that produce steam for process heat and stripping. When operating in an optimum condition and burning cleaner fuels (e.g., natural gas, refinery gas), these heating units create relatively low emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbons. If fired with lower grade fuels (e.g., refinery fuel pitch, coke) or operated inefficiently (incomplete combustion), heaters can be a significant source of emissions.

Equipment Leak Emissions Can be Substantial

Fugitive emissions of volatile hydrocarbons arise from leaks in valves, pumps, flanges, and other similar sources where crude and its fractions flow through the system. While individual leaks may be minor, the combination of fugitive emissions from various sources can be substantial. In 1996, over 52 million pounds of toxic fugitive emissions were reportedly released by U.S. refineries [EPA 1998]. Those potentially released during crude distillation include ammonia, benzene, toluene, and xylenes, among others. These emissions are controlled primarily through leak detection and repair programs and occasionally through the use of special leak resistant equipment.

Both atmospheric and vacuum distillation produce refinery fuel gas streams containing a mixture of light hydrocarbons, hydrogen sulfide and ammonia. These streams are processed through gas treatment and sulfur recovery units to recover fuel gas and sulfur. Sulfur recovery creates emissions of ammonia, H_2S, SO_x, and NO_x (see Section 10, Supporting Processes).

3.5 Effluents

Large Volumes of Process Water are Required for Crude Distillation

Crude distillation generates considerable wastewater. The process water used in distillation often comes in direct contact with oil, and can be highly contaminated.

The desalting process produces a high temperature salt water waste stream which is usually treated along with other process wastewaters from the refinery. Typical wastewater flow from the desalter is about 2.1 gallons per barrel of oil processed. The primary polluting constituents in desalter wastewater include hydrogen sulfide, ammonia, phenol, high levels of suspended solids, and dissolved solids, with a high biochemical oxygen demand (BOD)[3].

Both atmospheric and vacuum distillation produce an oily sour wastewater (condensed steam containing hydrogen sulfide and ammonia) from side stripping fractionators and reflux drums. Many refineries now use vacuum pumps and surface condensers in place of barometric condensers to eliminate the generation of the wastewater stream and reduce energy consumption. Reboiled side stripping towers rather than open steam stripping can also be utilized on the atmospheric tower to reduce the quantity of sour water condensate.

Typical constituents of sour wastewater streams from crude distillation include hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, and phenol, characterized by a high pH. Combined flows from atmospheric and vacuum distillation are about 26.0 gallons per barrel of oil, and represent one of the largest sources of wastewater in the refinery [EPA 1995a, HP 1993a].

An estimate of the amount of pollutants generated from crude distillation processes can be obtained from the effluent limitations given by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419, which was originally promulgated in 1974. Table 3-4 shows the limitations for average daily values for 30 consecutive days using best practicable control technology (BPT) currently available and the best available technology economically available (BAT) [BNA 1992].

As indicated in Table 3-4, the limitations shown are for the subset of refinery processes that includes desalting, atmospheric and vacuum distillation (Subpart A refineries). Later in this report BPT limitations will be given for other subsets of the refinery (thermal cracking processes, etc.). However, Subpart A and other Subpart refineries can also have hydrotreating, alkylation and isomerizatiaon processes, and still be captured under the stated guidelines. In other words, BPT guidelines are calculated based on a subset of refinery processes, and other refinery processes may be present in the BPT subcategories, although they are not specifically identified. The result is that effluent guidelines are useful but limited for predicting individual process-related effluent constituents.

Wastewater Treatment Permits Recovery of Oil and Water

Wastewater from crude distillation is contaminated by oil and is usually treated by both primary and secondary processes involving chemical and physical separation of oil and water. In addition, sour wastewater from crude distillation must be treated prior to the primary process by stripping in a tower with gas or steam. After the stripping process, which removes hydrogen sulfide, other organic sulfur compounds, and ammonia, the wastewater can be discharged to the wastewater treatment plant for primary treatment. A more detailed discussion of wastewater treatment is provided in Section 10.

Usable oil is recovered from the wastewater treatment process, and may be directly reused or sent to oil storage tanks for reuse in the refinery. In addition, an oily sludge is often produced that must be dewatered and may be treated as a hazardous waste under some circumstances (see Section 10) [EPA 1995a]. If the oily sludge is recycled in the refining process, it is not a hazardous waste. In some cases, even when it is not recycled, it may not be a hazardous waste.

3.6 Waste, Residuals and Byproducts

Desalting and Water Treatment Processes May Create Hazardous Sludges

The EPA classifies a number of residuals from the petroleum refining industry as hazardous waste under Title 40 Code of Federal Regulations (CFR), Part 261, Section 32. These include some wastes associated with wastewater treatment processes, which are discussed in more detail in Chapter 10 under water treatment processes.

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[3] *A measure of potential environmental damage from wastewater. It is equal to the amount of dissolved oxygen which is consumed by a sample incubated for a specified length of time at 20°C. A high BOD can deplete oxygen in receiving waters and kill aerobic organisms [Bailey 1986].*

The desalting process used to wash crude oil prior to atmospheric distillation produces an oily sludge (desalter mud) that may or may not be a hazardous waste (under hazardous waste category F037). Primary components of the sludge include iron rust, clay, sand, water, emulsified oil and wax, and metals.

Table 3-3. Emission Factors for Vacuum Distillation Column Condensers (lbs/barrel of vacuum feed)

Source	Particulates	SO_x	CO	Total Hydrocarbons	NO_x
Vacuum Distillation Condenser Column	--	--	--	50	--

Source *AP 42, Chapter 5, Petroleum Refining*, Environmental Protection Agency, January 1995.

Table 3-4. Crude Distillation Effluent Limitations[a] - Average of Daily Values for 30 Consecutive Days (lbs/1000 bbl of crude oil)

Constituent	BPT Limitation [d]
Total Suspended Solids	3.6
Oil and Grease	1.3
Phenolic Compounds	0.027
Ammonia (as Nitrogen)	0.45
Sulfide	0.024
Total Chromium	0.071
Hexavalent Chromium	0.071
[b]BOD5	4.25
[c]COD	21.3

a Combined limits for desalting, atmospheric, and vacuum distillation
b The five (5) subscript indicates an incubation period of 5 days.
c Chemical oxygen demand (COD) is a relative measure of environmental damage from wastewater based on oxygen demand. It is equal to the number of milligrams of oxygen which a liter of sample will absorb from a hot, acidic solution of potassium dichromate.
d BPT as defined by EPA is the “best practicable control technology currently available.”

Sour Water from Crude Distillation Is Responsible for Some Toxic Releases

Crude distillation is also responsible for some of the toxic releases reported by the refining industry, notably ammonia. Ammonia is a component of the sour water generated in the vacuum distillation unit and from side steam strippers or fractionators. Releases of ammonia from refineries ranked second in 1996 (over 9 million pounds released that year)[EPA 1998]. About 60 percent of ammonia releases from refining occur as the result of treated wastewater discharges (to surface waters and through underground injection).

A Number of Options Can Reduce Sludge Generation

Refineries are exploring a number of ways to reduce sludge generation from desalting and treatment of sour waters from distillation. One of these is to minimize the amount of solids present in the crude oil leaving the desalter. This can be accomplished by maximizing solids removal during desalting through techniques such as using lower shear mixing devices or lower water pressure to avoid turbulence in the desalter

Another option is to improve the recovery of oil from oily sludges, which make up a large portion of the residuals generated indirectly from the crude distillation process. This would involve increasing the use of mechanical oil separators such as belt filter presses, recessed chamber pressure filters, rotary vacuum filters, scroll and disc centrifuges, and other devices.

4

Cracking and Coking Processes

4.1 Cracking and Coking Process Overview

Cracking and Coking Increase the Yield of Gasoline and Other Light Fuels

Crude oil distillation produces a relatively small amount of fuel that is in the gasoline boiling range (from 10 to 25 percent, depending on the quality of the crude).   To increase the yield of gasoline and other light fuels refineries employ various thermal and catalytic "cracking" processes, often referred to as "bottom-of-the-barrel" processes. These processes break or "crack" large, heavy hydrocarbon molecules into smaller hydrocarbon molecules in the range of gasoline and other premium fuels. Thermal processes (e.g., visbreaking, delayed and fluid coking) achieve cracking by the application of heat. Catalytic processes (e,.g., fluid catalytic cracking, deep catalytic cracking, moving bed catalytic cracking, hydrocracking) also employ heat but utilize a catalyst to accelerate the cracking process.

The quality of products from catalytic processes is generally better than those from thermal cracking processes. The principal feedstocks for these processes are heavy products from the atmospheric and vacuum distillation columns (e.g., topped crude, vacuum residual).

In 1997, approximately 1.8 million barrels per day of heavy oil feedstocks (about 10 percent of the crude run) were input to thermal cracking and coking units in domestic refineries. Input to catalytic cracking and hydrocracking units was about 6.5 million barrels per day in 1997 (including both fresh and recycled feeds). These inputs are based on a 93 percent overall average refinery capacity utilization as reported in the first quarter of 1997 [OGJ 1997, EIA 1997, Leger 1997]. The major feedstocks for these processes are heavy gas oils from the atmospheric and vacuum distillation columns, and deasphalting oil from solvent deasphalters.

4.1.1 Visbreaking

Visbreaking Uses Heat and Pressure to "Crack" Heavy Feedstocks

Visbreaking is a non-catalytic thermal process used to convert large hydrocarbon molecules in heavy feedstocks to lighter products such as fuel gas, gasoline, naphtha, and gas oil. There are a number of configurations of differing complexity used for visbreaking, depending upon the desired product slate and refinery requirements. In general the visbreaking process involves heating the heavy feed in a furnace and then passing the heated feed through a pressurized soaking zone, which completes the desired cracking (see Figure 4-1).

Two types of heating and soaking designs are commercially available -- coil and soaker. The coil type achieves cracking of the feed within a dedicated soaking coil located in the furnace. The soaker design achieves some cracking within the heater, but then passes the feed to a separate reaction vessel or soaker where the effluent is held for a period of time while cracking is achieved. The advantage of the short-residence-time coil design is better control of the material being heated and easier decoking of the heater tubes. The long- residence-time soaker design operates with lower fuel costs, but decoking is more difficult and creates a coke-laden wastewater that must be handled, filtered, and recycled.

The product stream exiting from the heating/soaking unit is quenched with a cooler recycle stream (gas oil or fractionator bottoms) to stop the cracking reaction. The vapor-liquid product is then transferred to a fractionating column to be separated into gasoline, naphtha, gas oil, visbroken resid (tar), and fuel gas. Steam stripping is used to increase recovery of gas oil. A vacuum flasher is sometimes added to increase yields by converting the visbroken resid to vacuum gas oils. In cases where maximum production of lighter products is desired, vacuum gas oil from the vacuum flasher is fed to a thermal cracker which cracks the gas oil and returns it to the fractionator where it is added to the primary product stream.

Important variables in visbreaking include temperature, pressure, and residence time. Any one of these can be varied (within limits) to alter the product slate. For example, raising the visbreaker heater outlet temperature can increase yields of distillates and gaseous hydrocarbons. Typical cracking temperatures in the visbreaking heater can range from 700°F to as much as 1000°F. Pressures vary from 50 to 250 psig. Gasoline from visbreaking, often called VIS gasoline, is usually blended into the naptha stream from the atmospheric column and subsequently subjected to downstream processing before entering the gasoline pool. Gas oils and naphtha from visbreaking are also blended with similar streams from the atmospheric column and subjected to downstream processing. Part of the heavy residue is recycled to provide cooling to stop the cracking reactions; the remaining residue is blended into residual fuel or used as feed for downstream catalytic crackers.

Like many other refinery processes, visbreaking also produces a light sour fuel gas that must be treated before it can be used as a fuel. Sour water is also produced from the fractionators and is treated in a similar fashion to other sour waters produced throughout the refinery. [Process Description: Meyers 1997, HP 1996, EPA 1995a, EPA 1995b]

4.1.2 Coking Processes

Coking Converts Low Value Oils to Higher Value Gasoline, Gas Oils and Marketable Coke

Like visbreaking**, coking** is a thermal non-catalytic cracking process. Residual fuel oil from the vacuum distillation column is a typical feedstock for coking processes in refineries; the resulting product slate includes gasoline, gas oils, fuel gas, and petroleum coke. The petroleum coke contains most of the feed sulfur and nitrogen as well as essentially all the metals and ash.

Petroleum coke is a marketable product that can be used on-site as a fuel, or marketed externally as a fuel or for electrode manufacture, depending on the quality. Sponge coke, a substance that resembles coal, can be used as a fuel by electric utilities or in cement kilns. It is generally blended with bituminous coal or used in combination with oil or gas. Low-sulfur, low-metals sponge coke can also be used to

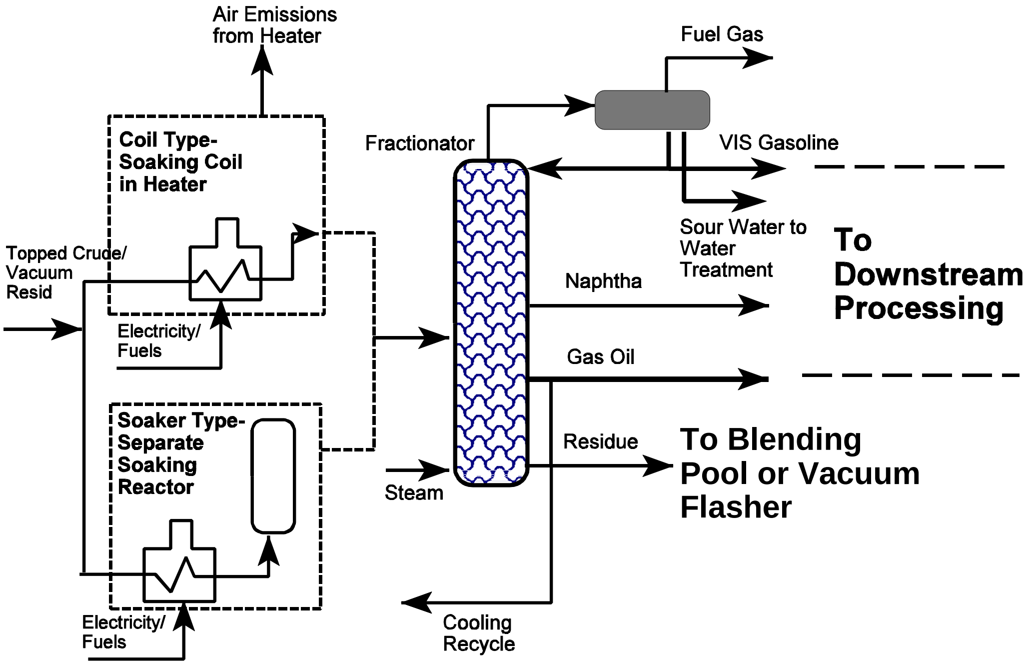

Figure 4-1. Visbreaking Flow Diagram [Meyers 1997, HP 1996, EPA 1995a]

Key Energy and Environmental Facts - Visbreaking

Energy	*Emissions*	*Effluents*	*Waste, Residuals or Byproducts*
Energy use: *Coil Type -* *Gross: 136 10^3 Btu/bbl feed* *Net: 130 10^3 Btu/bbl feed* *Soaker Type-* *Gross: 63 10^3 Btu/bbl feed* *Net: 58 10^3 Btu/bbl feed*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)*	*Sour wastewater from the fractionator (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids)* *Water flow - 2.0 gal/bbl feed*	*Little or no residual waste or byproducts generated*

manufacture anodes for the aluminum industry. Needle coke is a higher grade coke that is preferred for the production of graphite electrodes for electric-arc furnaces in the steel industry and for production of phosphorus, titanium dioxide, and calcium carbide.

Low-sulfur petroleum coke (less than 2.5 percent) can be used in ferrous metallurgy in a blend with coking coals, as in steel making. Most coke can also be used as a gasification feed to produce low-Btu gas or syngas, and this alternative has received increasing interest over the last few years as the quality of crude has declined [EI 1996, OGJ 1996a, OGJ 1996b].

Since anode-grade coke production requires sweeter crudes as refinery feedstocks, the trend of the industry has been to produce fuel-grade coke. The majority of coke currently produced in refineries (more than 65%) is fuel-grade sponge coke. Purge coke from fluid coking operations can also be used to fuel cement kilns or in conventional boilers to produce steam.

4.1.2.1. Delayed Coking

The most commonly used coking processes are delayed coking and fluid coking. **Delayed coking** produces either sponge or needle coke, depending upon the feed used. Heavy residues (e.g., vacuum residual, sometimes atomospheric residual) are commonly used in delayed coking to produce regular-grade coke, often referred to as sponge coke. However, vacuum residuals are not suitable for the production of needle coke, which requires a highly aromatic, low-sulfur, low-metal content feed. Typically this translates into a feed with an aromatics content of greater than 60 liquid volume percent, with a sulfur content less than 1 percent, and a Conradson carbon residue (CCR) of less than 10 percent.

The CCR, determined by the Conradson carbon test (ASTM D 189), is a measure of the carbon residue formed after evaporation and pyrolysis of a petroleum product, and is a direct indication of the carbon content. The higher the CCR, the more coke is produced. However, since delayed coking is employed to maximize production of clean liquids and minimize the production of coke, a high CCR makes this more difficult to achieve. The current trend toward decreasing crude quality is exacerbating the problem of high CCR for many refiners who must sometimes process feedstocks to the delayed coker with CCR values as high as 20 to 30 percent. Residue hydrodesulfurization is sometimes used upstream of the delayed coker when the feedstock is very heavy or of poor quality to reduce CCR as well as metals and sulfur impurities.

Delayed coking is a semibatch process (see Figure 4-2). A feed stream of heavy residues is introduced to a fractionating tower as a quench for hot lighter materials. The bottoms are further heated to about 900 to 1000°F in a furnace, and then fed to an insulated coke drum, where thermal cracking coke formation occurs to produce coke and lighter reaction products. Conversion to coke takes place only in the coke drum, where the hot products are held for a period of time.

After the coke drum is filled the feed is alternated to a parallel empty coke drum. Hot vapors produced in the coke drums are fed back to the fractionator where they can be drawn off and treated as sour gases or used as intermediate products. Vapor and liquid streams from the fractionator overhead drum may be processed further in a vapor recovery unit. A heavy gas oil pumparound stream is often used to remove heat from the fractionating tower, and can be used to reboil the towers in the vapor-recovery plant, to preheat the feed, or to generate steam for other uses.

Steam is injected into the full coke drum to remove hydrocarbon vapors, and water is injected to cool the coke so that it can be removed (decoking). A widespread practice in the industry is quench-cycle coking. Following the coking (heating) cycle, the coke is then cooled by means of quenching with water that is injected into the coke drum. At the beginning of the "quench cycle," some facilities also inject oil-bearing residuals along with the quench water. This process allows for recovery of the hydrocarbons in these residuals for use as fuels, either through vaporization, or secondarily, through incorporation of hydrocarbons into the coke product itself. In fact, EPA finalized a rule that would exclude residuals re-inserted into the coker (or other process units) from the RCRA definition of solid waste in June 1998.

A coke-drum blowdown system is used to recover hydrocarbon and steam vapors generated during the quenching and steaming process, and is designed to minimize air pollution during this operation. Decoking is accomplished by cutting the coke from the drum with high pressure water jets. Typical coke drum schedules consist of 24 hours of coking and 24 hours of decoking.

During the decoking operation, coke and drilling water fall from the bottom of the coke drum, requiring a coke dewatering and handling system. This usually consists of a loading system (direct railcar loading, pad loading, pit loading) and dewatering bins.

The excess moisture and volatile matter is removed from the "green" coke by calcining in a rotary kiln or rotary hearth. The coke is first crushed and then fed to the kiln or hearth by continuous feeders. Process heat is supplied to the kiln through a burner and by the heat of combustion of the volatile materials in the coke.

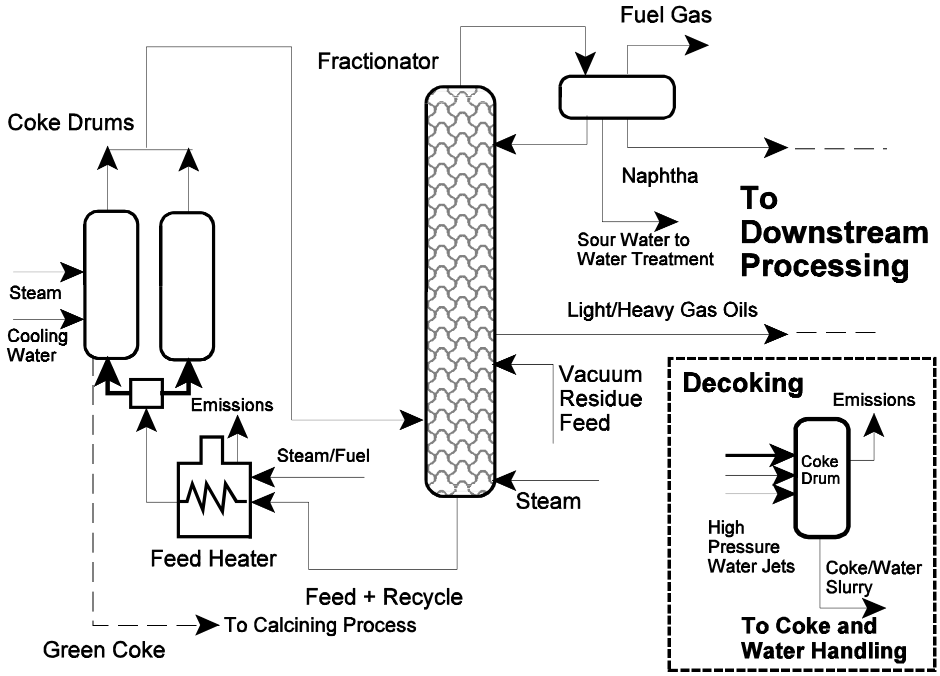

Figure 4-2. Delayed Coking Flow Diagram [HP 1996, Meyers 1997, EPA 1995a]

Key Energy and Environmental Facts - Delayed Coking			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross: 166 10^3 Btu/bbl feed* *Net: 144 10^3 Btu/bbl feed*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates). Particulate emissions from decoking can also be considerable.*	*Coke-laden water from decoking operations (hydrogen sulfide, ammonia, suspended solids)* *Water flow - 1.0 gal/bbl*	*Coke dust (carbon particles and hydrocarbons)*

Important variables in delayed coking include temperature, pressure, and recycle ratio. Temperature is used to control the volatile combustible material content and hardness of the coke product. Too low temperatures create pitch or soft coke; too high temperatures create coke that is too hard and difficult to remove from the drum. Typical operating temperatures range from 900 to 1100°F.

Pressure affects the amount of heavy hydrocarbons that are retained in the drum. When sponge coke is the product, delayed cokers are often designed with marginally lower operating pressures to produce the most liquid product possible. In this case pressures can be as low as 15 lb/in^2 (gage). For needle coke production (a higher valued coke product), pressures as high as 150 lb/in^2 (gage) may be required. Recycle ratio has the same general effect as pressure, and is used primarily to control production of liquid products. [Process Description: ANL 1981, EPA 1995a, HP 1996, Meyers 1997]

4.1.2.2 Fluid Coking

Unlike delayed coking, **fluid coking** is a continuous process (see Figure 4-3). In this process heavy feedstocks (typically vacuum residue) are injected into a reactor where they are thermally cracked to yield coke and a variety of lighter products. Light products from the reactor are quenched, where entrained coke fines are

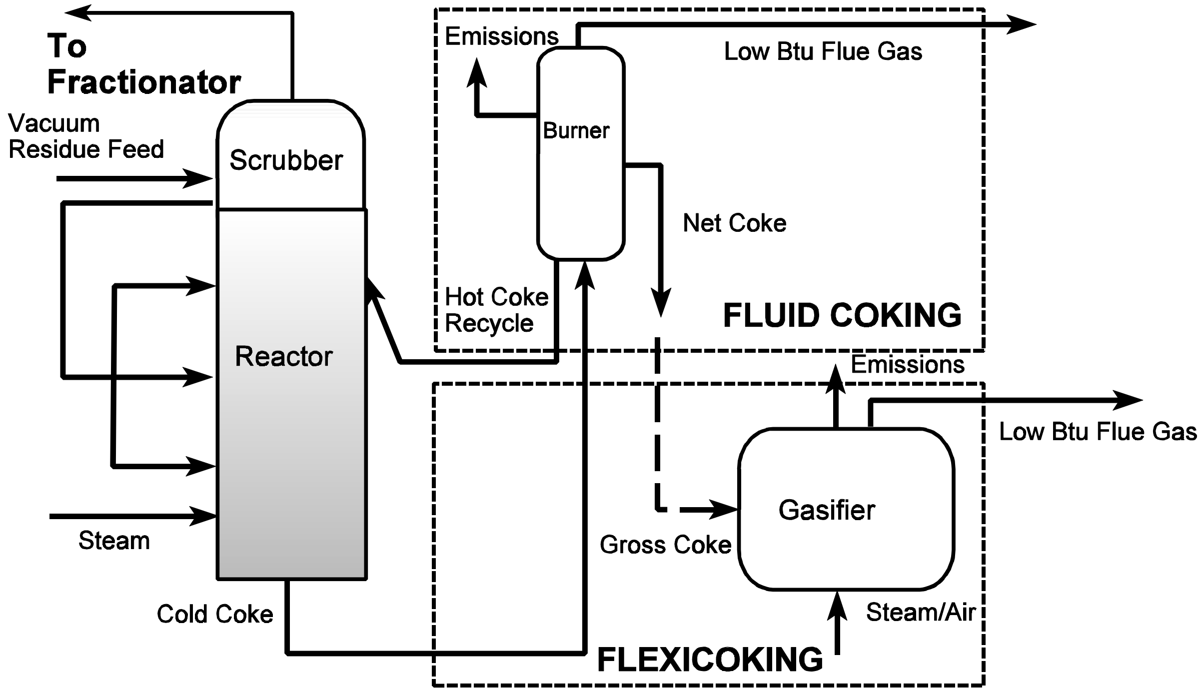

Figure 4-3. Fluid Coking/Flexicoking Flow Diagram [EPA 1995b, HP 1996]

Key Energy and Environmental Facts - Fluid Coking/Flexicoking			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Fluid Coking -* *Gross: 258 10^3 Btu/bbl of feed* *Net: 45 10^3 Btu/bbl of feed* *Flexicoking -* *Gross: 167 10^3 Btu/bbl of feed* *Net: (46 10^3) Btu/bbl of feed* *Flexicoking is a net energy producer.*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates).*	*No significant effluents.*	*Small amounts of coke dust and particulate matter.*

removed, and then fractionated. Volatiles in the coke are then removed by passage of the coke through a heater. The volatiles removed in this process are treated to remove fines and sulfur to yield a low-Btu fuel gas (20 to 40 Btu/scf). Roughly 15 to 25 percent of the coke is burned with air to fill process heat requirements, which eliminates the need for an external fuel supply. The use of fluid coking has diminished as the popularity of Flexicoking has increased. No purely fluid cokers have been built since the late 1970s [SFA 1993]

In **Flexicoking**[1] units, the devolatilized coke is sent to a gasifier where 95 to 97 percent is gasified at high temperature with steam and air or oxygen. The gaseous products and coke from the gasifier are returned to the heater to supply process heat. [Process Description: EPA 1995b, HP 1996]

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[1] *Tradename for process developed by Exxon Research and Engineering.*

4.1.3 Catalytic Cracking

Catalytic Cracking Produces Higher Yields of Gasoline than Thermal Cracking

Catalytic cracking is similar to thermal cracking except that the cracking reaction occurs in the presence of a catalyst. Catalysts used in catalytic cracking usually consist of mixtures of crystalline synthetic silica-alumina (referred to as zeolites) and amorphous synthetic silica-alumina. Feedstocks for catalytic cracking are usually light and heavy gas oils produced from atmospheric or vacuum distillation, coking, and deasphalting operations. Relative to thermal cracking, the product slate favors the production of gasoline, less heavy fuel oils, and light gases, making it a more prevalent (and profitable) option than thermal cracking processes. From 50 to 60 percent of the output of a catalytic cracker is high octane gasoline blending stock. Gasoline from catalytic crackers contain olefins and more i-paraffins and aromatics than straight-run gasoline, and these components contribute to its high octane.

The catalytic cracker is often central to the operation of the refinery because of its adaptability to changing feedstocks and product demands, and because of the high margins between feedstock and product. In 1996, total charge capacity for catalytic crackers was over 24 percent of crude oil refining capacity in U.S. refineries [DOE 1997].

Catalytic crackers have historically been operated to produce maximum yields of gasoline and distillates. With the recent requirements for reformulated gasolines, catalytic crackers have been increasingly changed to operate in a mode to produce higher yields of olefins. Light iso-olefins from catalytic cracking units (e.g., isobutylene, isoamylene) are a necessary feedstock for production of reformulated gasoline blending components like methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME).

A number of catalytic cracking designs are available, including fluidized-bed, fixed-bed, and moving-bed reactors. The most prevalent are fluidized-bed, representing about 98 percent of catalytic cracking capacity. A relatively new adaptation of the conventional fluidized-bed called deep catalytic cracking is currently being licensed for use in the United States.

4.1.3.1 Fluid Catalytic Cracking

Fluidized-bed catalytic cracking, often called **fluid catalytic cracking (FCC),** is the most widely used catalytic cracking process. The process is named after the behavior of the finely powdered catalyst, which takes on the properties of a fluid when mixed with the vaporized feed.

The design of FCC units has evolved significantly since its early development in the 1930s. Although some of the very earliest FCC units are still operating, most current designs take advantage of the reactions occurring within the dilute phase of the riser, or feed line, through which both the catalyst and heavy feeds are sent to the reactor. Designs have also evolved to enable the FCC to handle increasingly poor quality feedstocks with higher percentages of sulfur, metals, and carbon residue, as well as higher boiling feedstocks which contain these substances.

There are a number of licensors of this technology offering a variety of configurations, but general operation is very similar. The heart of an FCC system is the reactor-regenerator section (see Figure 4-4). In this section, fresh feed and sometimes recycled oil are introduced into the feed line or riser together with hot regenerated catalyst (from 1100°F to 1300°F). The hot catalyst vaporizes the feed and the vapors carry the catalyst upward through the riser. The charge may be heated by heat exchange or, in some cases, by a fired heater. Catalytic cracking is typically performed at temperatures ranging from 900°F to 1000°F and pressures of 1.5 to 3 atmospheres.

Most of the cracking reactions take place in the riser as the catalyst and oil mixture flow upward into the reactor. At the top of the reactor, most of the cracking reactions have been completed, and the fluidized catalyst particles and cracked hydrocarbon vapors are mechanically separated using cyclones. The cracked vapors are fed to a main fractionation tower where gasoline and light olefins are taken overhead and routed to a gas concentration unit. Light cycle oil, recovered

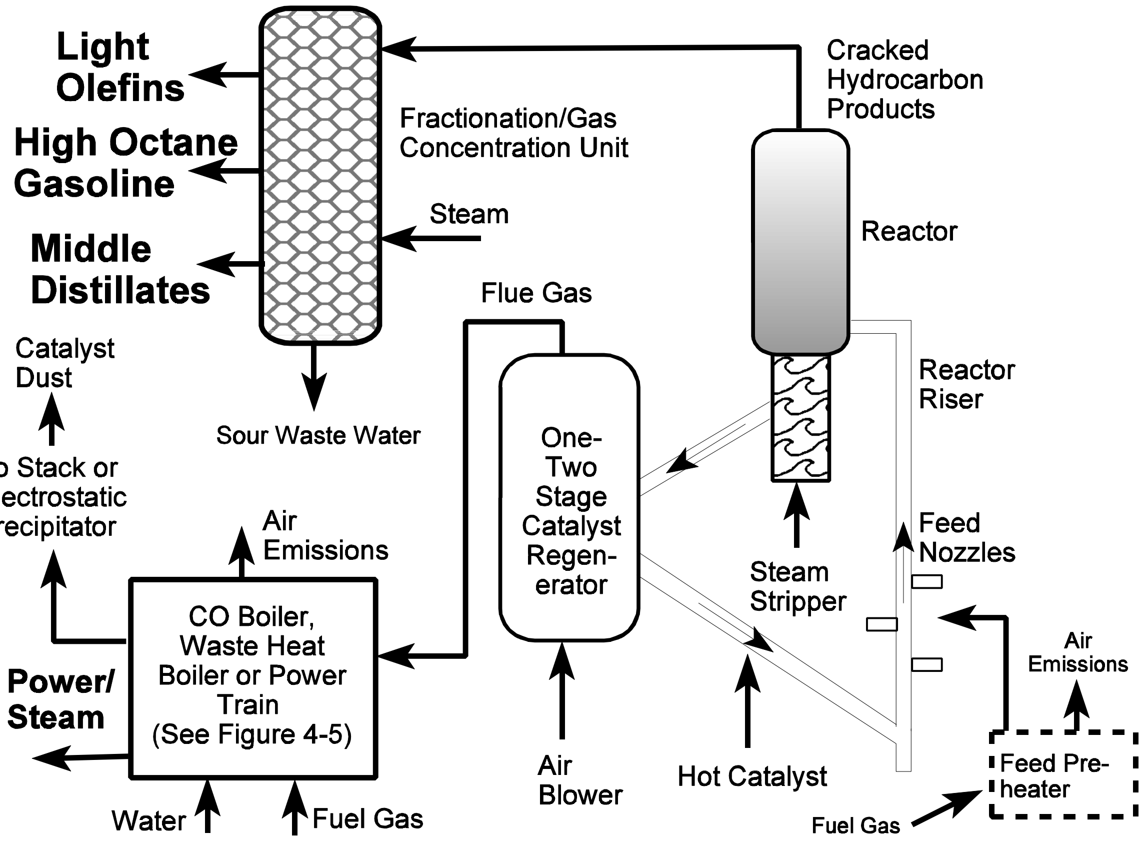

Figure 4-4. Fluid Catalytic Cracking Flow Diagram
[HP 1996, HP 1994, Meyers 1997, OGJ 1990]

Key Energy and Environmental Facts - Fluid Catalytic Cracking			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy Use: *Gross: 100 10^3 Btu/bbl of feed* *Net: 81 10^3 Btu/bbl of feed* *Fluid catalytic crackers are usually operated as net energy producers.* *Range of Steam Production:* *16 - 177 10^3 Btu/bbl of feed*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates), and catalyst regeneration (CO, NOx, SOx and particulates).*	*Sour waste water from the fractionator/gas concentration units and steam strippers (high levels of oil, suspended solids, phenols, cyanides, H_2S, NH_3).* *Water Flow - 15 gal/bbl*	*Spent catalysts (metals from crude oil and hydrocarbons), spent catalyst fines from electrostatic precipitators (aluminum silicate and metals).*

as a sidecut, is stripped of light ends and stored. Column bottoms are called slurry oil because they contain some catalyst fines. Removal of these fines results in clarified oil. The gas concentration section is usually an assembly of absorbers and fractionators that separate the main fractionator overhead into gasoline and other light products. Olefinic products from other processes (e.g., coking) are also often routed through the FCC gas concentration unit.

The spent catalyst falls to the bottom of the reactor, and oil remaining on the catalyst surface is removed by stripping with steam. The spent catalyst is then sent to a separate system for regeneration, where coke that has collected on the catalyst surface is burned off. Fresh regenerated catalyst is added from a storage hopper to maintain an appropriate volume of active catalyst in the system at all times.

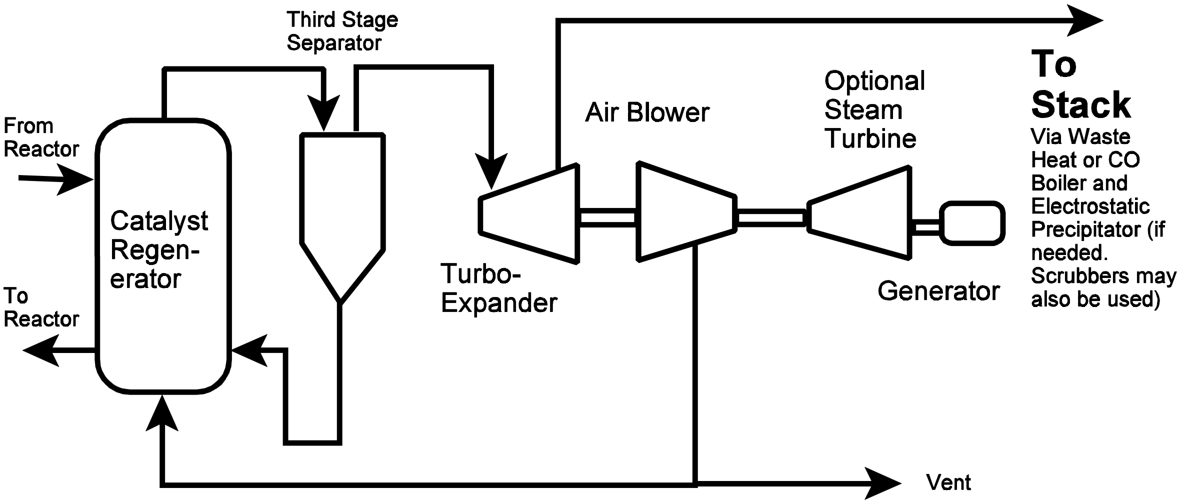

Figure 4-5. Typical Turboexpander Power Train for an FCC Unit

Regeneration of the catalyst must be continuously performed to maintain catalytic activity and prolong catalyst life. The regenerator serves two functions — it burns the coke, which imparts heat to the catalyst that is used to meet the thermal requirements of the cracking reaction. Coke deposition is a function of the percentage conversion of the feed to cracked products, as well as the CCR (Conradson carbon residue) and metals content of the feed. Table 4-1 shows typical coke deposition and associated heating values in catalytic cracking processes [ANL 1981].

Table 4-1. Coke Deposition and Heating Value in Catalytic Cracking

55% Conversion of Feed		
° API	**Wt% Coke**	**Heating Value (10^6 Btu/bbl feed)**
19	9.6	0.37
23	6.6	0.25
85% Conversion of Feed		
19	14.7	0.57
23	10.6	0.40

The regeneration process generates hot flue gas with large embodied energy (enthalpy) due to heat energy and pressure. To enhance the cost- and energy-efficiency of the plant, many refiners utilize the enthalpy of the hot flue gas to drive a gas expander turbine, which generates power for the air blower required for the catalyst regenerator (see Figure 4-5). If the system is large enough, a steam turbine can be integrated to allow the export of electricity. This power can be used on-site for other power requirements or sold to the local grid.

The regenerator may be operated to achieve complete or partial combustion of CO to CO_2, or the CO may be converted to CO_2 in a relatively complex external CO boiler. If CO is converted internally, the sensible heat of the flue gas can be recovered in a much more compact, simpler waste heat boiler or flue gas cooler. High pressure steam is produced in the CO boiler; super-heated medium pressure steam is recovered from waste heat boilers. Flue gas exiting the waste heat recovery system or CO boiler then passes to the stack, where a SO_x scrubbing unit or electrostatic precipitator may be installed, depending on environmental requirements.

The operation of an FCC is affected by six important independent operating variables:

- riser (feed line) temperature;
- feed preheat temperatures;
- fresh feed rate;
- catalyst make-up rate;
- recycle rates; and
- gasoline endpoint.

These can be manipulated in a number of ways to change the quantity and quality of the product yield. For example, increased riser temperature (and associated hot catalyst circulation) will increase conversion of desirable products and improve octane. However, beyond a certain temperature, gasoline yield will be adversely affected. The manipulation of these variables is highly dependent on the outcome desired by the individual refinery and specific FCC configuration in use. [Process Description: EPA 1995a, HP 1996, HP 1994, HP 1990, Meyers 1997]

4.1.3.2 Deep Catalytic Cracking

Deep catalytic cracking is a process developed by the Research Institute of Petroleum Processing (RIPP) and Sinopec International, both located in China, and recently licensed for use in the United States by an American equipment manufacturer [HP 1996, Meyers 1997, NPRA 1994, NPRA 1990]. The process favors the production of light olefins (e.g., propylene, isobutylene, isoamylene) which are used for the production of reformulated gasoline blending components. Growing demand for these components has forced many refineries to increasingly operate their fluid catalytic crackers in a maximum olefin mode (rather than a maximum gasoline mode), which increases operating severity and places a considerable strain on the FCC unit. Along with increased demand for oxygenated fuel blending components, refineries are facing increased demand for propylene for the production of polypropylene products (half of the propylene used by the chemical industry is supplied by refineries).

The DCC provides a process for generating light olefins to help meet the growing demand. The technology can be integrated into an existing refinery or petrochemical facility, and is suitable for incorporation either as a retrofit or in a grassroots plant.

DCC is very similar to the FCC process, in that it is a fluidized catalytic process for cracking a variety of feedstocks to light olefins. It employs a traditional reactor/regenerator unit with catalysts having physical properties similar to the FCC catalyst. However, innovations in catalyst development, selection of process variables, and operating severity enable the DCC to significantly increase production of olefins.

When operated in a maximum propylene mode (Type I), the DCC employs both catalytic riser and fluidized bed cracking at severe reactor conditions. When in maximum isoolefin mode, the DCC utilizes riser cracking much like an FCC unit. The DCC also requires higher catalyst/oil ratios and steam injection rates than the FCC. A comparison of DCC operating conditions with typical FCC conditions is shown in Table 4-2. A comparison of yields is shown in Table 4-3. Table 4-3 illustrates the higher production of lighter components achieved with the DCC. Coke production is also much higher than seen in the FCC, primarily due to the higher heat of reaction required for the conversion of the feed to lighter products, which requires a higher reactor temperature.

4.1.4 Catalytic Hydrocracking

Catalytic Hydrocracking Uses Hydrogen and a Catalyst to Produce Gasoline and Other Fuels

Like catalytic cracking, **hydrocracking** is used to produce blending stocks for gasoline and other fuels from heavy feedstocks. The introduction of hydrogen in addition to a catalyst allows the cracking reaction to proceed at lower temperatures than in catalytic cracking, although pressures are much higher (1200 - 2000 psig). The hydrogen reacts with the cracked products, which suppresses the formation of heavier compounds and increases the yield. Hydrocracking gasoline is not olefinic, but blends well with FCC gasoline and increases octane. In general, hydrocracking is more effective in converting gas oils to lighter products, but it is more expensive to operate.

Feedstocks to hydrocrackers are often very similar to those of the fluid catalytic cracker such as heavy gas oils, FCC cycle oils, deasphalted oil, and visbreaker or coker gas oils. Products also vary greatly, depending on the specific hydrocracker configuration and operating parameters, which are tailored to individual refinery requirements. In general

Table 4-2. DCC and FCC Operating Conditions

Parameter	DCC Type I (Maximum Propylene)	DCC Type II (Maximum Isoolefins)	FCC
Temperatures			
Reactor °F	~1035	~1000	~985
Regenerator °F	~1265	~1265	~1293
Reactor Pressure (lbs/in^2 gage)	9.9-14.2	14.2-19.9	19.9-29.9
Reaction Time/seconds	2 sec + 2-8 weight hourly space velocity in reactor bed	2 (riser)	2 (riser)
Catalyst/Oil Ratio	9-15	7-11	5-8
Steam Injection, wt% Feed	20-30	10-15	2-7

Source: **Handbook of Petroleum Processes**, 2nd Edition, Robert A. Meyers Editor, McGraw-Hill 1997.

Table 4-3. DCC and FCC Yields (wt% of feed)

Component	DCC Type I (Maximum Propylene)	DCC Type II (Maximum Isoolefins)	FCC
Hydrogen	0.3	-	0.1
Dry Gas (C_1-C_2)	12.6	5.6	3.8
LPG (C_3-C_4)	42.3	34.5	27.5
Naphtha (C_5 + naphtha)	20.2	39.0	47.9
Cycle/Slurry Oils	15.2	15.6	14.6
Coke	9.4	4.3	6.1
Light Olefins			
C_2	5.7	2.26	0.9
C_3	20.4	14.3	8.2
C_4	15.2	22.7	13.1

Source: **Handbook of Petroleum Processes**, 2nd Edition, Robert A. Meyers Editor, McGraw-Hill 1997.

products can include gasoline, jet fuel, kerosine, diesel fuel, high quality FCC feed, low-sulfur fuel oil or blending stocks, or lubricating oils.

Hydrocracking typically involves a reactor section, gas separator, scrubber for sulfur removal, and product fractionator (see Figure 4-6). Once-through and recycle options are available to provide operating flexibility and economy.

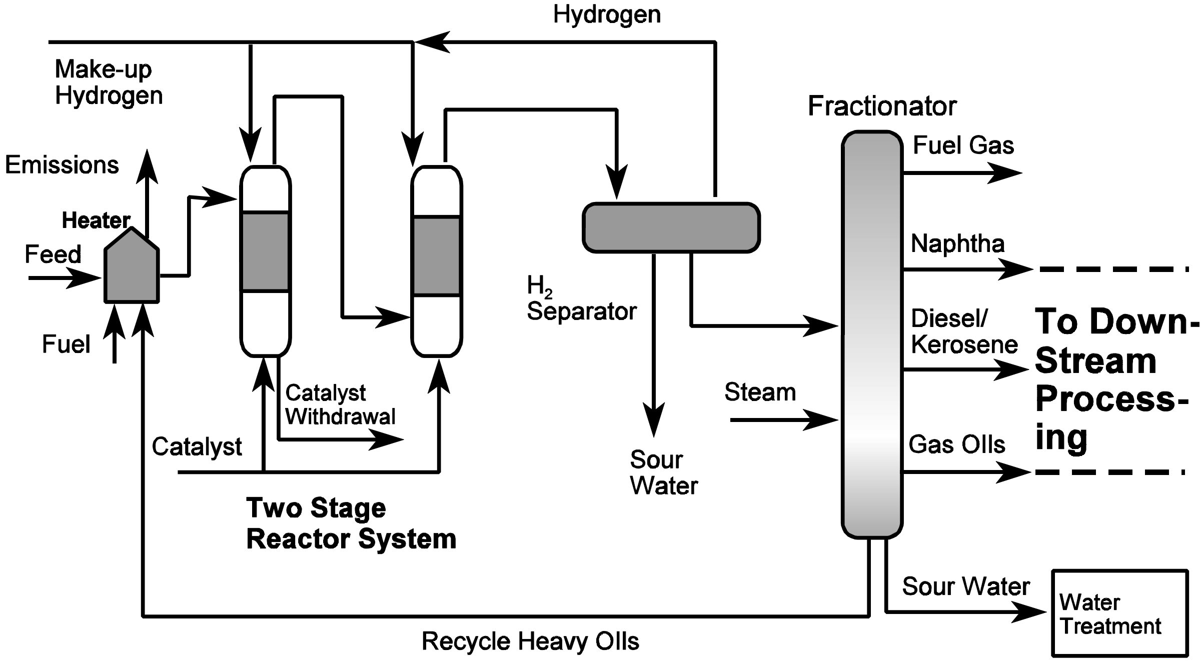

Figure 4-6. Catalytic Hydrocracking Flow Diagram
[EPA 1995a, HP 1996, Meyers 1997]

Key Energy and Environmental Facts - Catalytic Hydrocracking			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy Use: *Gross: 240 10^3 Btu/bbl of feed* *Net: 198 10^3 Btu/bbl of feed* *Hydrogen Consumption:* *343 - 857 10^3 Btu/bbl of feed* *(1000 - 2500 scf/bbl)*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates).*	*Sour waste water from the fractionator and hydrogen separator (suspended solids, H_2S).* *Water Flow - 2 gal/bbl*	*Spent catalyst fines (metals from crude oil, and hydrocarbons).*

The reactor section contains a catalyst bed where sometimes both hydrotreating (amorphous type) and hydrocracking (zeolites) catalysts can be employed, depending on the desired product slate. Catalyst beds can be one, two or three stage, of fixed-bed or ebullated-bed type, and some employ on-stream catalyst addition and withdrawal to maintain catalytic activity.

Water has a detrimental effect on some hydrocracking catalysts and is often removed by passing the feed stream through a silica gel or molecular sieve dryer prior to entering the reactor. Sulfur and nitrogen impurities can also cause deactivation of the catalyst. During the hydrocracking process, heavy compounds containing sulfur and nitrogen are also cracked, releasing these impurities to where they could potentially create fouling of the catalyst. For this reason the feedstock is often hydrotreated (see Chapter 7, Hydrotreatment) to remove impurities before entering the hydrocracker unit [Process Description: EPA 1995a, Meyers 1997, HP 1996].

4.2 Summary of Inputs/Outputs

The following is a summary of the inputs and outputs of cracking and coking processes, often termed the "bottom of the barrel" processing units.

Inputs:	Outputs:
Heavy oil feedstocks	High Octane Gasoline
Hydrogen	Diesel Fuel
Fuel Gas	Naphtha
Process Water	Middle Distillates
Steam	Heavy Oils/Residuum
Electricity	Marketable Coke
Catalysts	Fuel Gas
	Hydrogen Sulfide
	Process Wastewater
	Sour Water
	Catalyst Fines
	Spent Catalyst

4.3 Energy Requirements

The process energy used in various cracking and coking processes is shown in Tables 4-4 through 4-8 [ANL 1981, HP 1996, Meyers 1997]. The energy content (i.e., feedstock energy) of the feedstock is not considered here, as it is used to make an energy product that is combusted for heat and power in other industries (e.g., transportation, buildings, petrochemicals). Process energy does include, however, any energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

The majority of the process energy input to thermal cracking and coking processes is in the form of fuels used in process heaters and in boilers to produce steam. Refinery gas produced on-site is the most prevalent fuel and accounts for 50 percent of fuel inputs for process heat.

Electricity is used primarily to power compressors, pumps, air blowers, filtering systems, conveyers, grinders, and other auxiliary equipment. Electricity typically accounts for about 10 to 20 percent of overall energy consumption in coking and cracking.

All thermal cracking processes take advantage of process steams to provide heating and/or cooling where possible. These processes also produce low-Btu refinery gas that is used for process heat both in thermal cracking and throughout the refinery. Some coking processes also take advantage of the heat and the energy value of the petroleum coke produced by the process to help meet process heat requirements. In fluid coking, about 15 to 20 percent of the coke produced is burned to provide all the process heat needed for the process. The remaining coke is withdrawn as a product. In this process hot coke is also circulated back to the reactor to supply the heat needed to maintain the desired coking temperatures. In Flexicoking, about 95 to 97 percent of the gross coke product from the reactor is gasified with steam and air to produce a low-Btu fuel gas which powers the process [HP 1996].

Most of the energy required for catalytic cracking is for steam stripping, feed preheaters, and electricity for air blowing through the regenerator. Fluid catalytic cracking is usually a net energy producer -- the process generates large quantities of hot flue gas that can be recovered in a waste heat or CO boiler to provide steam and/or power for the regenerator air blowing system. Energy generated through the burning of coke in the regenerator also imparts heat to the catalyst, eliminating the need for external heating sources. Table 4-7 provides an indication of the average amount of energy (in terms of steam production) that can be exported by an FCC unit.

Unlike fluid catalytic cracking, catalytic hydrocracking is not a net energy producer and uses large quantities of hydrogen in addition to fuel gas and steam , although both are steam exporters (see Table 4-8).

Table 4-4. Estimated Energy Use in Visbreaking- 1996

Energy Source[a]	Specific Energy Use (10^3 Btu/bbl of feed)	Total Industry Use[b] (10^{12} Btu/yr)
Natural Gas	18.3	0.44
Refinery Gas	42.0	1.00
Electricity[b]	7.6	0.18
Coke	13.5	0.32
Oils[c]	4.0	0.09
Other[d]	1.6	0.04
TOTAL	**87**	**2.07**

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Based on visbreaking capacity at U.S. refineries on January 1, 1997 (65,359 bbls/cday), operating at 93% capacity. Assumes 33% of the market is coil type, and 67% is soaker type visbreakers. [DOE 1997, Meyers 1997]

Table 4-5. Estimated Energy Use in Delayed Coking - 1996

Energy Source[a]	Specific Energy Use (10^3 Btu/bbl of oil)	Total Industry Use[e] (10^{12} Btu/yr)
Natural Gas	35.1	21.4
Refinery Gas	63.1	38.5
Electricity[b]	38.2	23.3
Coke	23.3	14.2
Oils[c]	4.2	2.6
Other[d]	2.4	14.6
TOTAL	**166.3**	**114.6**

a Fuel mix for fossil fuels (not electricity) based on typical use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Based on delayed coking capacity at U.S. refineries on January 1, 1997, operating at 93% capacity (1,671,612 bbls/cday). [DOE 1997]

Table 4-6. Estimated Energy Use in Fluid/ Flexicoking - 1996		
Energy Source	**Specific Energy Use (10^3 Btu/bbl of oil)**	**Total Industry Use[b] (10^{12} Btu/yr)**
Electricity[a]	315.0/ 315.0	8.56/ 12.84
Steam Used, 125 psig	165.0/ 27.5	4.5/ 1.1
Steam Exported, 600 psig	(222.0)/ (176.0)	6.0/ 7.2
TOTAL	**258/ 166.5**	**7.1/ 6.74**

a Includes losses incurred during the generation and transmission of electricity
b Based on fluid coking capacity at U.S. refineries on January 1, 1997, operating at 93% capacity (186,448 bbls/cday)[DOE 1997]. Assumes 60 percent Flexicoking, 40 percent fluid coking [SFA 1993].

Table 4-7. Estimated Energy Use in Fluid Catalytic Cracking- 1996		
Energy Source	**Specific Energy[e] (10^3 Btu/bbl of oil)**	**Total Industry Use[f] (10^{12} Btu/yr)**
Natural Gas	17.0	32.3
Refinery Gas	30.5	57.9
Electricity[a]	38.4	72.9
Coke	11.2	21.3
Oils[b]	2.1	4.0
Other[c]	1.2	2.3
TOTAL	**100.4**	**190.6**
Net Steam Exported[d] (mostly at 600 psig)	(97.7)	(185.5)

a Includes losses incurred during the generation and transmission of electricity
b Includes crude oil, distillate and residual fuel oil
c Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
d Assumes various degrees of steam production (CO/waste heat boiler), but not energy recovery through a turboexpander
e Average values based on estimated utility requirements for various licensed technologies, including ABB Lummus FCC, MW Kellogg Orthoflow, Exxon Flexicracking, UOP FCC and others [ANL 1981, HP 1996, Meyers 1997]. Fuel mix for fossil fuels (not electricity) is based on typical use at refineries in 1996 [DOE 1997a]. A true energy balance is not shown here. In practice, the energy content of the hot circulating catalyst and the heat of combustion of the coke burned off the catalyst in the regenerator are important elements in the energy balance, as well as fired heaters used to preheat the feed (if any). Steam production also varies considerably between configurations. Net export of power (power generated in excess of that needed to power the air blower and other equipment) is not shown, although this could be considerable for large systems (20 MW and higher) if a steam turbine is included in the configuration (see inset previous page).
f Based on catalytic cracking capacity (fresh and recycled feed) at U.S. refineries on January 1, 1997, operating at 93% capacity (5,200,668 bbls/cday). [DOE 1997a]

Table 4-8. Estimated Energy Use in Catalytic Hydrocracking- 1996

Energy Source	Specific Energy[e] (10^3 Btu/bbl of oil)	Total Industry Use[f] (10^{12} Btu/yr)
Natural Gas	32.9	15.1
Refinery Gas	59.0	27.0
Electricity[a]	119.6	54.8
Coke	21.7	9.9
Oils[b]	4.0	1.8
Other[c]	2.4	1.1
TOTAL	**239.6**	**109.7**
Hydrogen Consumed[d]	602.0	275.9
Net Steam Exported (mostly at 600 psig)	(71.8)	(32.9)

a Includes losses incurred during the generation and transmission of electricity

b Includes crude oil, distillate and residual fuel oil

c Includes liquefied petroleum gases, miscellaneous oils, and purchased steam

d Hydrogen demand ranges from 1000-2500 scf/bbl of feed. Hydrogen is a by-product of catalytic reforming, and is also produced on-demand through various means. Hydrogen recycle is incorporated in the process.

e Source: Average values based on estimated utility requirements for various licensed technologies, including ABB Lummus LC-Fining, Chevron Isocracking, IFP Hydrocracking, UOP Unicracking, IFP H-Oil, M.W. Kellogg MAK Hydrocracking, and VEBA OEL Technologie/Automatisiering GmbH [HP 1996, Meyers 1997].

f Based on hydrocracking capacity at U.S. refineries on January 1, 1997, operating at 93% capacity (1,255,500 bbls/cday) [DOE 1997a].

4.4 Air Emissions

Thermal Cracking Generates Emissions Through Fuel Combustion and Decoking Processes

Air emissions from thermal cracking include emissions from the combustion of fuels in process heaters and boilers, equipment leaks of volatile constituents, and emissions that arise from the removal of coke from coke drums (decoking).

Equipment leaks of volatile hydrocarbons from valves, pumps, tanks, flanges, and other similar sources can be significant and are dependent upon the equipment type and configuration, operating conditions, and general maintenance practices. Propylene is one of the light gases produced during thermal cracking and coking, and is usually used as a feedstock for downstream processing. However, it is highly volatile and soluble in water, making releases to air and water potentially significant. Fugitive emissions throughout the refinery are controlled through good operating practices and leak detection programs.

Hydrocarbon emissions are also released during the cooling and venting of the coke drums prior to decoking. Particulate emissions from decoking (in delayed coking processes) are potentially significant, although very limited data is available on actual releases. These occur during the removal of coke from the coke drum, as well as subsequent storage and handling operations. Data available for fluid coking, from which the lowest coke emissions would be released, indicates that about 523 lbs of particulates are emitted for every 1000 barrels of feed (0.523 lb/bbl) [EPA 1995b].

Catalytic Cracking Is One of the Largest Sources of Air Emission in Refineries

Air emissions are released in process heater flue gas, as fugitive emissions from leaking valves and pipes, and during regeneration of the cracking catalyst. If not controlled, catalytic cracking is one of the most substantial sources of carbon monoxide and particulate emissions in the refinery. Emission factors for fluid catalytic cracking are shown in Table 4-10. These do not include emissions from the combustion of fuels in process heaters, which are evaluated separately. In non-attainment areas where carbon monoxide and particulates are above NAAQS levels, CO boilers and particulate controls are employed. Carbon monoxide produced during regeneration of the catalyst is converted to carbon dioxide either in the regenerator or further downstream in a carbon monoxide waste heat boiler (CO boiler). As can be seen in Table 4-10, catalytic crackers are also significant sources of SO_x and NO_x. The NO_x produced by catalytic crackers is expected to be a major target of emissions reduction in the future.

Fluid catalytic crackers also produce a significant amount of **fine catalyst dust** which results from the constant movement of catalyst grains against each other. This dust consists primarily of alumina and small amounts of nickel and vanadium, and is generally carried along with the carbon monoxide stream to the CO boiler. The dust is separated from the carbon dioxide stream exiting the boiler through the use of cyclones, flue gas scrubbing or electrostatic precipitators, and may be disposed of at an off-site facility [EPA 1995a, EPA 1995b].

Catalytic hydrocracking generates air emissions through process heater flue gas, vents, and fugitive emissions. Unlike fluid catalytic cracking catalysts, hydrocracking catalysts are usually regenerated off-site after months or years of operations, and little or no emissions or dust are generated from the catalyst regeneration process.

4.5 Effluents

Thermal Cracking Produces Small Quantities of Wastewater

Thermal cracking and coking processes produce a relatively small amount of sour wastewater from steam strippers and fractionators. Wastewater is also generated during coke removal and cooling operations and from the steam injection process to cut coke from the coke drums. Combined wastewater flows from thermal cracking and coking processes are about 3.0 gallons per barrel of process feed.

Catalytic Cracking Produces Large Volumes of Wastewater and Spent Catalysts

Catalytic cracking (primarily fluid catalytic cracking) generates considerable sour wastewater from fractionators used for product separation, from steam strippers used to strip oil from catalysts, and in some cases from scrubber water

.

Like most separation processes in the refinery, the process water used in fractionators often comes in direct contact with oil, and can have a high oil content (much of that oil can be recovered through wastewater oil recovery processes). The steam stripping process used to purge and regenerate catalysts can also contain metal impurities (e.g., chromium, lead) from the feed in addition to oil and other contaminants.

The main constituents of sour water from catalytic cracking include high levels of oil, suspended solids, phenols, cyanides, hydrogen sulfate, and ammonia. Typical wastewater flow from catalytic cracking is about 15.0 gallons per barrel of feed processed (more than one-third of a gallon of waste water for every gallon of feed processed), and represents the second largest source of wastewater in the refinery [EPA 1995a].

Hydrocracking Produces Less Sour Wastewater Than Catalytic Cracking

Hydrocracking, like catalytic cracking, produces sour wastewater at the fractionator,

Table 4-10. Emission Factors for Catalytic Cracking (lbs/barrel of feed processed)							
Source (uncontrolled)	**Particu-lates**	**SO_x**	**CO**	**Total Hydro-carbons**	**NO_2**	**Aldehydes**	**Ammonia**
Fluid Catalytic Cracker (FCC)	93-340	100-525	13,700	220	37-145	19	54

Source: AP-42, *Background Chapter 5.1, Petroleum Refining*, U.S. Environmental Protection Agency, January 1995.

Table 4-11. Effluent Limitations for Cracking/Coking[a] - Average of Daily Values for 30 Consecutive Days (lbs/1000 bbl of crude oil)

Pollutant	BPT Limitation
Total Suspended Solids	4.4
Oil and Grease	1.6
Phenolic Compounds	0.036
Ammonia (Nitrogen)	3.0
Sulfide	0.029
Total Chromium	0.088
Hexavalent Chromium	0.0056
[b]BOD_5	5.5
[c]COD	38.4

[a] Combined limits for topping (desalting, atmospheric, and vacuum distillation) and cracking and coking (visbreaking, thermal cracking, FCC, moving bed catalytic cracking, hydrocracking, delayed coking, fluid coking, and hydrotreating).

[b] The five (5) subscript indicates an incubation period of 5 days.

[c] Chemical oxygen demand (COD) is a relative measure of environmental damage from wastewater based on oxygen demand. It is equal to the number of milligrams of oxygen which a liter of sample will absorb from a hot, acidic solution of potassium dichromate.

but in much lower quantities. However, if the hydrocracking feedstocks are hydrotreated prior to processing to remove impurities, relatively low levels of hydrogen sulfide and ammonia will be present. Typical wastewater flow for catalytic hydrocracking is about 2.0 gallons per barrel of feed. Both wastewater streams contain some hydrogen sulfide, suspended solids, ammonia, and phenols. Limitations for wastewater effluents are set by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419. Table 4-11 shows the limitations for average daily values for 30 consecutive days using best practicable control technology (BPT) currently available for a refinery utilizing cracking and coking in addition to topping processes [BNA 1992].

Sour Wastewater is Treated Along with Other Refinery Wastewater

Wastewater from cracking and coking is usually treated along with other refinery sour wastewaters from distillation and reforming processes, using both primary and secondary processes (see Section 10 for a full discussion).

These processes include processing in a separator (API separator, corrugated plate interceptor) which creates a sludge. Physical or chemical methods are then used to separate the remaining emulsified oils from the wastewater. Treated wastewater may be discharged to public wastewater treatment, to a refinery secondary treatment plant for ultimate discharge to public wastewater treatment, or may be recycled and used as process water. The separation process permits recovery of usable oil, and also creates a sludge that may be recycled or treated as a hazardous waste [EPA 1995a].

4.6 Waste, Residuals and Byproducts

Spent Catalysts From Catalytic Cracking Are Sent Off-site

Catalytic cracking generates significant quantities of spent process catalysts (containing metals from crude oils and hydrocarbons) that are often sent off-site for disposal or recovery or recycling. Management options can include land-filling, treatment, or separation and recovery of the metals. Metals deposited on catalysts are often recovered by third-party recovery facilities. Spent catalyst fines (containing aluminum silicate and metals) from electro-static precipitators are also sent off-site for disposal and/or recovery options.

In addition, oily sludges from the wastewater treatment facility that result from treating sour wastewaters may be hazardous wastes (unless they are recycled in the refining process). These include API separator sludge, primary treatment sludge, sludges from various gravitational separation units, and float from dissolved air flotation units. See Section 10, Supporting Processes, for more information on wastewater treatment.

Propylene, another source of toxic releases from refineries, is produced as a light end during cracking and coking processes. It is volatile as well as soluble in water, which increases its potential for release to both air and water during processing. Propylene was ranked sixth in the list of toxic chemicals released from refineries in 1996 (over 4.3 million pounds)[EPA 1998].

Sour Water and Gas from Fractionators and Steam Strippers Are Responsible for Some Toxic Releases

Cracking and coking processes all include some form of fractionation or steam stripping as part of the process configuration. These units all produce sour waters and sour gases containing some hydrogen sulfide and ammonia. Like crude oil distillation, some of the toxic releases reported by the refining industry are generated through sour water and gases, notably ammonia. Gaseous ammonia often leaves fractionating and treating processes in the sour gas along with hydrogen sulfide and fuel gases. Releases of ammonia ranked second in the list of toxic chemicals released from refineries in 1996 (over 9 million pounds released that year)[EPA 1993].

A significant portion of toxic chemicals released from refining are metal compounds, many of which are present in spent catalyst sludge and catalyst fines generated from catalytic cracking and hydrocracking. These include metals such as nickel, cobalt, molybdenum, and others [EPA 1993].

5

Catalytic Reforming

5.1 Catalytic Reforming Process Overview

Catalytic Reforming Increases Octane Rating and Produces Aromatics

Catalytic reforming is employed to increase the octane rating of naphthas and heavy straight-run gasoline produced by atmospheric crude oil distillation. It also produces substantial yields of aromatic hydrocarbons used as petrochemical feedstocks and generates hydrogen gas for use in many other refinery processes (e.g., hydrocracking, hydrotreating). Catalytic reforming also produces light gases and liquified petroleum gas (LPG).

In 1997, catalytic reformers produced approximately 3.4 million barrels of high octane product. This production is based on a 93 percent overall average refinery capacity as reported in the first quarter of 1997 [OCJ 1997, DOE 1997a].

Four Major Chemical Reactions Occur During Catalytic Reforming

Rather than combining or breaking down molecules to obtain the desired product, catalytic reforming essentially restructures hydrocarbon molecules that are the right size but have the wrong molecular configuration, or structure. There are four major types of reactions which occur during reforming processes, as shown in Figures 5-1 through 5-4:

- Dehydrogenation of napthenes to aromatics
- Isomerization of paraffins and naphthenes
- Dehydrocyclization of paraffins to aromatics
- Hydrocracking

Dehydrogenation of naphthenes is a principal reaction in catalytic reforming and occurs quickly, producing hydrogen gas and aromatic compounds. Isomerization must take place before dehydrogenation to the aromatic state can occur, and also occurs rapidly. Dehydrocyclization is the most difficult reaction to catalyze, and consists of the molecular rearrangement of a paraffin to a naphthene. All three of the above reactions are endothermic (energy absorbing) and produce hydrogen gas that can be used in other refinery processes. Dehydrogenation in particular is highly endothermic, requiring the hydrocarbon stream to be heated between each catalyst bed.

During hydrocracking (an exothermic reaction), paraffin compounds are cracked out of the gasoline boiling range and aromatics become concentrated in the product, increasing octane.

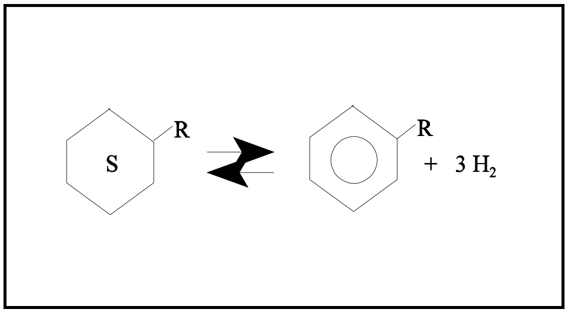

Figure 5-1. Dehydrogenation of Naphthenes to Aromatics

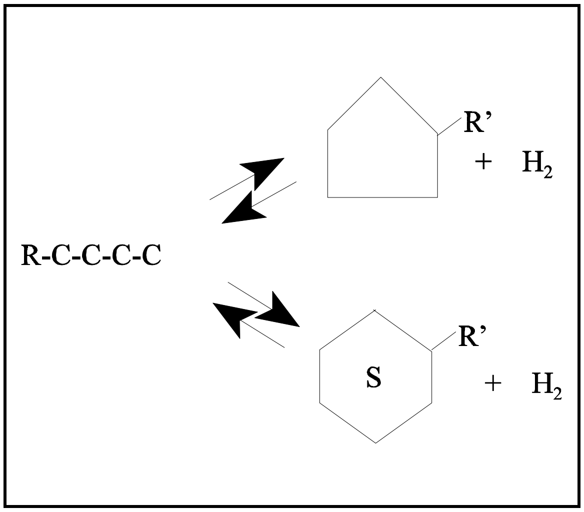

Figure 5-2. Dehydrocyclization of Paraffins to Aromatics

Catalytic reforming reactions are promoted by the presence of a metal catalyst. Catalysts are typically platinum deposited on alumina, or bimetallic catalysts such as platinum-rhenium on alumina. Some multi-metallic catalysts have also been introduced. Bimetallic catalysts provide results comparable to platinum-alumina catalysts with a lower hydrogen-to-feed ratio and a lower pressure.

Reforming catalysts must be protected from lead, arsenic, copper, ammonia, organic nitrogen, and sulfur. These undesirable elements tend to concentrate in heavier oil fractions and are often removed by hydrotreating prior to reforming (see Section 7).

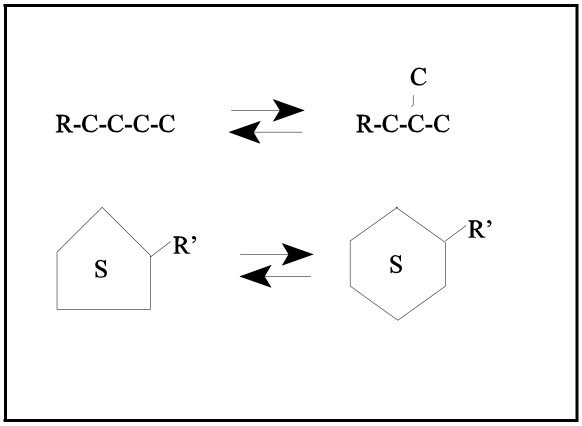

Figure 5-3. Isomerization

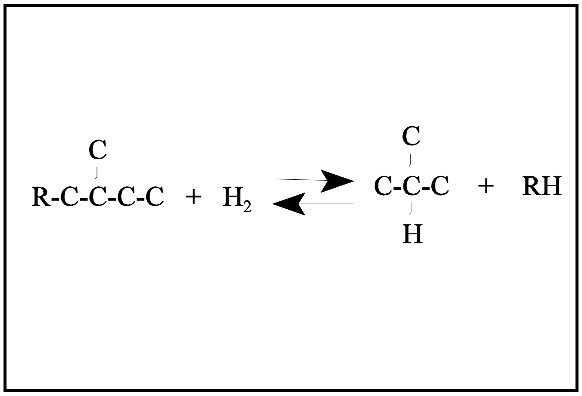

Figure 5-4. Hydrocracking

Catalytic Reformers Utilize Multiple Reactor Beds

Catalytic reformers utilize fixed-bed or moving-bed processes in a series of three-six reactors to allow separation of the primarily endothermic reactions (see Figure 5-5). Interstage heaters are installed between reactors to maintain the required temperature of the hydrocarbon feed stream.

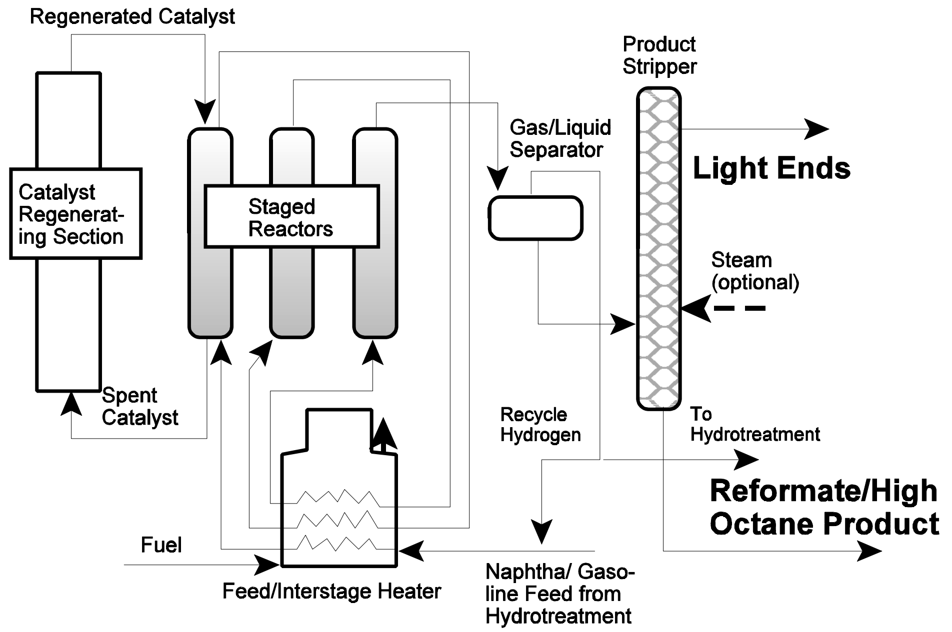

Figure 5-5. Catalytic Reforming Flow Diagram (continuous)
[EPA 1995a, HP 1996, Meyers 1997]

Key Energy and Environmental Facts - Catalytic Reforming			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross:* *284 10^3 Btu/bbl* *Net:* *250 10^3 Btu/bbl*	*Fugitive emissions (benzene, toluene, xylene) and particulates from catalyst regeneration*	*Process waste water (high levels of oil, suspended solids, low hydrogen sulfide)* *Water flow - 6.0 gal/bbl*	*Spent catalyst and hydrogen gas* *Hydrogen Gas production:* *1100 - 1700 scf/bbl:*

Feed to the reformer (naptha, a light petroleum fraction) is mixed with recycled hydrogen gas, raised to the reaction temperature (900 - 1020°F) by heat exchange and a fired heater, and is then charged to the reactor section. After proceeding through the series of reactors, effluent is cooled by air or water cooling. Gas and liquid products are then separated. Some of the gas from the separator is recycled back to the reactor section; net hydrogen produced is used elsewhere in the refinery complex (e.g., hydrocracking, hydrotreating). The liquid effluent is then pumped to a stabilizer system where light, volatile hydrocarbons (methane, ethane, propane and butane) are fractionated off. Aromatic components are left in the stabilizer bottoms as reformate. The primary product stream (80-90 percent) is a high-quality gasoline blending component (RON of 100 or better, MON of 90 or better)[1].

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[1] *RON (research octane number) is determined in a standard engine running at low speed. MON (motor octane number) is a rating obtained in a test engine.*

Catalytic reforming processes can be continuous (e.g., cyclic) or semi-regenerative. In continuous processes, the catalysts can be regenerated one reactor at a time without disruption in operation. During semi-regenerative reforming, regeneration of catalysts in all the reactors is conducted simultaneously after some period of time while the process is shut-down. The continuous process can be operated at lower pressures and can produce higher octane products. Stripping steam may be required to remove the light volatile hydrocarbons in the product stripper, but it is not standard practice for cycle and semi-regenerative reformer strippers. Sufficient light volatile hydrocarbons are usually present to provide adequate stripping vapors for removal. [Process Description: EPA 1995a, HP 1996, Meyers 1997]

5.2 Summary of Inputs/Outputs

The following is a summary of the inputs and outputs for catalytic reforming:

Inputs:	Outputs:.
Straight-Run Gasoline	High Octane Gasoline/
Naphtha	Blending Stock
Hydrogen	Hydrogen
Catalyst	LPG
Cooling Water	Fuel Gas
Electricity	Aromatics
Fuel Gas	
Steam	

5.3 Energy Requirements

The process energy used for catalytic reforming is shown in Table 5-1 [HP 1996, Meyers 1997]. The energy content (i.e., feedstock energy) of the feedstock is not considered here, as it is used to make an energy product that is combusted for heat and power in other industries (e.g., transportation, buildings, petrochemicals). Process energy does include, however, any energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

The majority of the process energy input to reforming is in the form of fuels used in process heaters for feed or interstage heating and catalyst regeneration. Electricity is used to power compressors in the separator, pumps, and other auxiliary equipment.

The mode of catalyst regeneration also influences the energy-intensity of catalytic reforming processes. Continuous regeneration processes are more complex and require as much as 24 times the electricity needed for semi-regenerative processes, and about 25 percent more fired fuels (based on barrel of feed input).

5.4 Air Emissions

Process Heaters and Fugitive Emissions Are Sources of Air Pollutants from Catalytic Reforming

Emissions from catalytic reforming include fugitive emissions of volatile constituents in the feed, and emissions from process heaters and boilers. As with all process heaters in the refinery, combustion of fossil fuels produces emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbons.

Toluene, xylene, and benzene are toxic aromatic chemicals that are produced during the catalytic reforming process and used as feedstocks in chemical manufacturing. Due to their highly volatile nature, fugitive emissions of these chemicals are a source of their release to the environment during the reforming process. Point air sources may also arise during the process of separating these chemicals.

In a continuous reformer, some particulate and dust matter can be generated as the catalyst moves from reactor to reactor, and is subject to attrition. However, due to catalyst design little attrition occurs, and the only outlet to the atmophere is the regeneration vent, which is most often scrubbed with a caustic to prevent emission of hydrochloric acid (this also removes particulates).

Table 5-1. Estimated Energy Use in Catalytic Reforming- 1996		
Energy Source[a]	**Specific Energy Use[e] (10^3 Btu/bbl of feed)**	**Total Industry Use[f] (10^{12} Btu/yr)**
Natural Gas	69.6	92.1
Refinery Gas	125.0	165.4
Electricity[b]	30.3	40.1
Coke	46.0	60.9
Oils[c]	8.4	11.1
Other[d]	5.1	6.7
TOTAL	**284.4**	**376.3**
Hydrogen Produced	(479.2)	(634.2)
Steam Produced	(15.4)	(20.4)

[a] Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996

[b] Includes losses incurred during the generation and transmission of electricity

[c] Includes crude oil, distillate and residual fuel oil

[d] Includes liquefied petroleum gases, miscellaneous oils, and purchased steam

[e] Source: Average values based on estimated utility requirements for various licensed technologies, including IFP Octanizing, UOP Semi-regenerative Platforming, UOP Continuous Catalyst, Regenerative Platforming, and Howe-Baker Reforming [HP 1996, Meyers 1997].

[f] Based on catalytic reforming capacity at U.S. refineries on January 1, 1997, operating at 93% capacity (3,624,404 bbls/cday) [DOE 1997a].

5.5 Effluents

Catalytic Reforming is the Third Largest Source of Process Wastewater

Catalytic reforming is the third largest generator of wastewater in the refinery (primarily process and cooling water). Typical water flow for catalytic reforming is about 6 gallons per barrel of product [EPA 1995a]. These wastewaters are treated along with other refinery process wastewater.

Limitations for wastewater effluents are set by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419. Table 6-3 in Section 6, Alkylation, shows combined limitations (catalytic reforming and alkylation) for average daily values for 30 consecutive days using the best available technology economically available (BAT) [BNA 1992].

5.6 Waste, Residuals and Byproducts

Spent reforming catalysts are rarely, if ever, disposed of as a hazardous waste. The precious metals (usually platinum) contained in the catalysts are recovered from the spent catalyst, while the remainder of the catalyst can often be used as a feedstock in other processes.

6

Alkylation

6.1 Alkylation Overview

Alkylation is an important process used in refineries to upgrade light olefins to high-value gasoline components. Alkylation is used to combine small hydrocarbon molecules into larger molecules to produce a higher octane product for blending with gasoline. The principal feedstocks for alkylation come from the light ends (gases) produced in catalytic crackers, visbreakers and cokers. The high octane of alkylation products (typically around 92-96 research octane number, or RON), their low vapor pressure, and lack of olefins or aromatics make alkylates one of the best gasoline blending components produced in the refinery. In addition, the ability to upgrade light olefins and isobutane from lower-valued liquefied petroleum gas to the higher gasoline product value makes it a popular process alternative for refineries with catalytic crackers.

Typical Primary Alkylation Reactions

$$C_4H_{10} \quad + \quad C_4H_8 \quad \xrightarrow{H_2S0_4 \text{ or HF}} \quad 2,2,4$$

trimethylpentane Isobutane Butylene
"Isooctane"

$$C_4H_{10} \quad + \quad C_3H_6 \quad \xrightarrow{\text{HF or } H_2S0_4} \quad \text{2,3 dimethylpentane}$$

Isobutane Propylene

In 1997, an estimated 1.0 million barrels per day of alkylates were produced in domestic refineries. This estimate is based on a 93 percent overall average refinery capacity utilization as reported in the first quarter of 1997 [OGJ 1997, DOE 1997a].

Alkylation Uses an Acid Catalyst to Combine Small Hydrocarbon Molecules

Alkylation is essentially the reverse of cracking or coking processes — it selectively combines small hydrocarbon molecules (rather than "cracking" large hydrocarbon molecules) to form a high octane gasoline blending stock. During alkylation, light olefins[1] (e.g., propylene,

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[1] *Olefin is a common name for alkenes, or compounds containing carbon-carbon double bonds.*

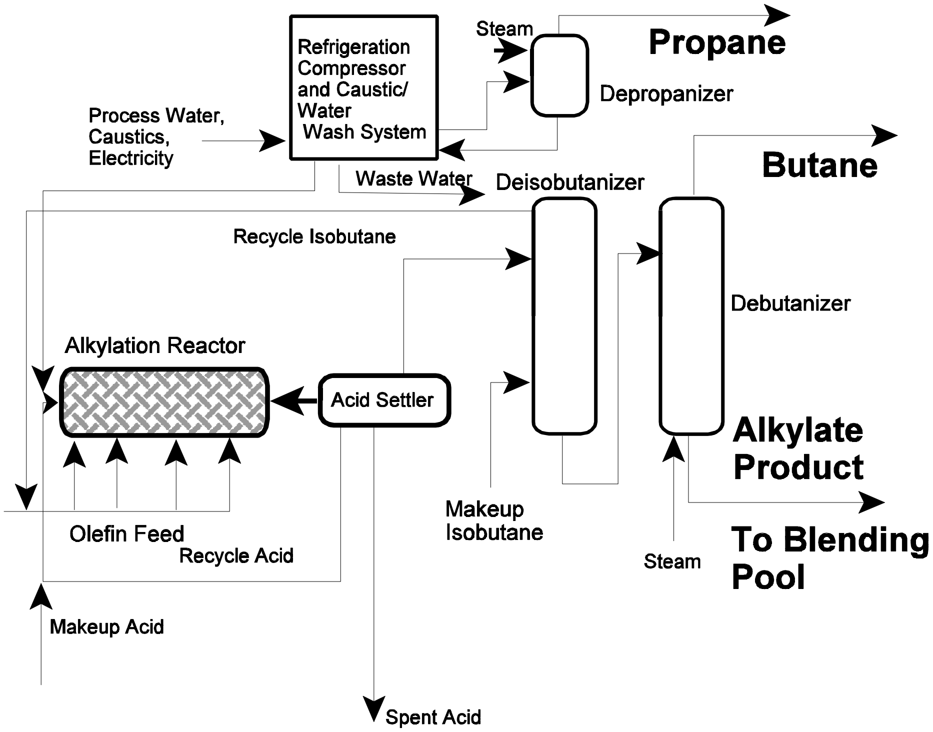

Figure 6-1. Sulfuric Acid-Based Alkylation Flow Diagram
[Meyers 1997, HP 1996]

Key Energy and Environmental Facts - Sulfuric-Acid Based Alkylation			
issn	***E***	***elffE Energy***	***bkseRW Byproducts***
Energy use: *Sulfuric Acid Catalyst - Gross:* *335 10^3 Btu/bbl feed* *Net:* *250 10^3 Btu/bbl feed*	*No significant emissions.*	*Wastewater from water-wash of reactor hydrocarbon products (suspended solids, dissolved solids, hydrogen sulfide) and spent sulfuric acid* *Water flow - ~2.6 gal/bbl feed* *Spent Sulfuric Acid - 13-30 lbs/bbl alkylate*	*Neutralized alkylation sludge (sulfuric acid, hydrocarbons)*

butylene) are combined with an isoparaffin[2] (e.g., isobutane) in the presence of a strong acid (e.g. sulfuric acid or hydrofluoric acid) to produce high octane alkylate (see inset). The primary reaction also competes with a number of side reactions (e.g., polymerization, hydrogen transfer, cracking).

The feedstocks for alkylation include light olefins (propylene, butylene, amylene, pentylene, pentenes) which are combined with isobutane to produce an alkylate with low Reid vapor pressure and high octane.

Alkylation processes are based on either a sulfuric acid or hydrofluoric acid catalyst, with quite different configurations. **Sulfuric acid-based alkylation** processes (see Figure 6-1) typically utilize a refrigeration cycle to effect the reaction and/or product separation. In the

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[2] *Paraffin is another name for alkanes, or compounds with single carbon-carbon bonds, so named for their low affinity or reactivity toward many chemical reagents (Latin:* ***parum affinis****, or low affinity).*

configuration shown in Figure 6-1, olefin feed and recycled isobutane are introduced into a stirred, autorefrigerated reactor, where mixers provide contact between reactants and the acid catalyst. The olefin and isobutane react quickly in the presence of the sulfuric acid and produce heat along with alkylate. The heat is removed by vaporization of some of the isobutane from the reaction mixture. Vapors leaving the reactor are routed to the refrigeration section where they are compressed, condensed, and returned to the reactor. A depropanizer is included in the configuration to remove any propane introduced to the alkylation unit along with the feed or created during alkylation. The reactor product is sent to a settler where hydrocarbons are separated from the acid, which is then recycled back to the reactor. The hydrocarbon product is caustic- and water-washed to remove any acidic components, including SO_2. The hydrocarbons are further processed in a deisobutanizer and a debutanizer to produce the desired high octane alkylate.

Material Inputs for Sulfuric Acid Alkylation*

Isobutane (pure)	1.2 bbl/bbl butylene feed
Sulfuric Acid	19 lbs/bbl alkylate
Caustics (NaOH)	0.1 lbs/bbl alkylate

* based on Exxon's Autorefrigeration Process

The concentration of sulfuric acid is a key operating parameter for the refrigerated sulfuric acid process. When the sulfuric acid concentration becomes less than around 88 percent, a portion of the acid must be removed and replaced with stronger acid. The acid that is removed must be regenerated in a sulfuric acid plant that is usually located off-site. Generation of spent sulfuric acid is substantial (about 13-30 lbs per barrel of alkylate produced).

Feed impurities can also affect the amount of sulfuric acid required for the process. Many of these impurities form acid-soluble compounds that will increase acid make-up requirements, since they must be purged along with the spent acid. Mercaptan sulfur, a common feed impurity, is one example — roughly 40 pounds of additional make-up acid are needed for each pound of mercaptan that enters along with the feed. For this reason, caustic treating facilities are used in the refinery to remove sulfur from the olefin feed (see Section 10, Gas Treatment and Sulfur Recovery).

Butadiene, which tends to polymerize and form acid-soluble oils, is another feed impurity that will increase acid make-up requirements. For every pound of butadiene in the feed, about 10 pounds of additional make-up catalyst will be required. [Process Description: HP 1996, Meyers 1997, EPA 1995a].

In the **hydrofluoric acid-based alkylation** process (see Figure 6-2), the olefin feed is dried first using a desiccant-drying system to minimize acid catalyst consumption and promote the quality of the alkylate. As with sulfuric-acid based alkylation, sulfur compounds may also be removed from the feed prior to alkylation. The dried olefin and isobutane feed is then charged to a reactor-heat exchanged system, where the heat of reaction is removed by heat exchange with a large volume of coolant. The effluent from the reactor then enters a settler, where the acid is separated out and returned to the reactor.

Material Inputs for HF Acid Alkylation*

Isobutane (pure)	1.2 bbl/bbl butylene feed
Hydrofluoric Acid	0.3 lbs/bbl alkylate (net)

When the propane or normal butane from the HF reactor will be used as liquified petroleum gas (LPG), it is defluorinated over alumina to prevent corrosion of burners. Defluorination is also performed when the butane is to be used as feedstock for an isomerization unit.

The hydrocarbon product, which contains some dissolved hydrofluoric acid (HF acid), is then preheated and sent to an isostripper where product alkylate is recovered from the bottom of the column. Unreacted isobutane is recovered and recycled back to the reactor. The isostripper

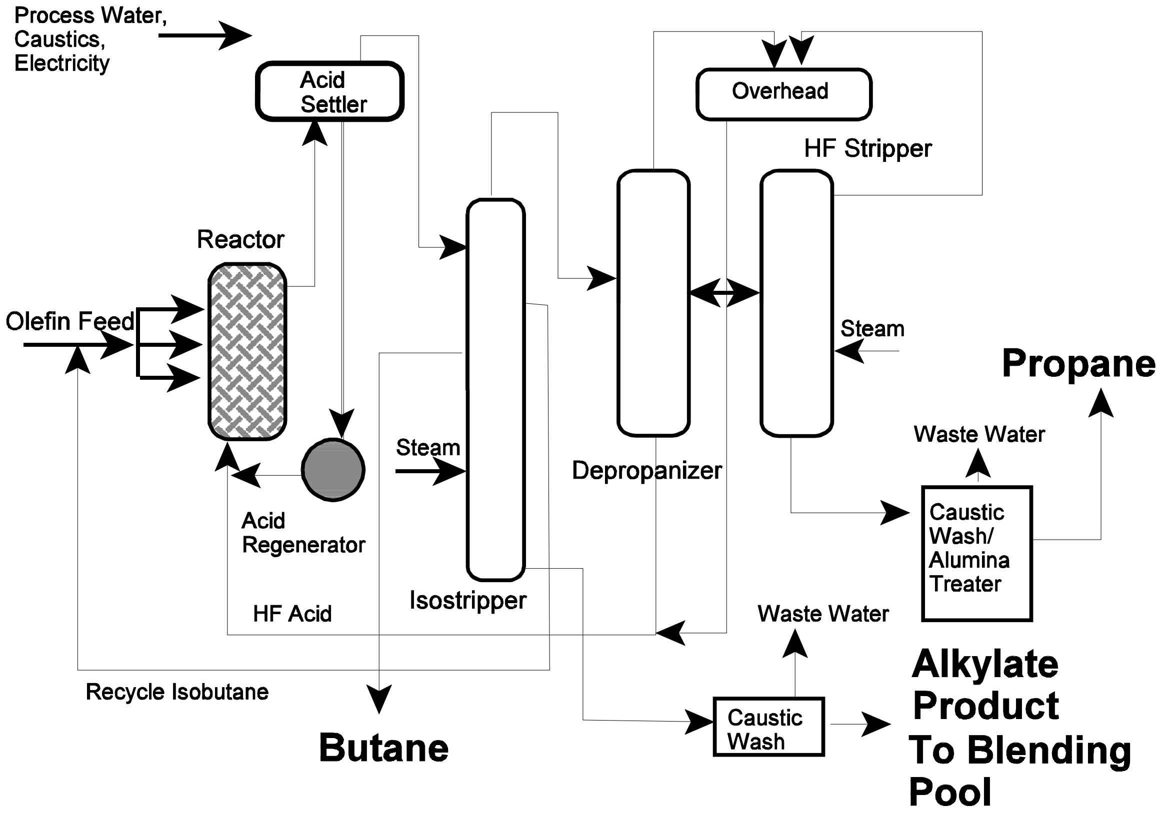

Figure 6-2. Hydrofluoric Acid-Based Alkylation Flow Diagram
[Meyers 1997, HP 1996]

Key Energy and Environmental Facts - Hydrofluoric-Acid Based Alkylation

Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross: 401* 10^3 *Btu/bbl feed* *Net: 391* 10^3 *Btu/bbl feed*	*No significant emissions.*	*Wash water (suspended solids, dissolved solids, hydrogen sulfide)*	*Neutralized alkylation sludge (calcium fluoride, un-reacted lime, hydrocarbons) and product-treating residual solids (alumina)*

overhead contains HF acid and a portion of the overhead is sent to an HF stripper to recover acid and isobutane. A portion of the isostripper overhead is depropanized and the propane product scrubbed of acid in the HF stripper.

Acid regeneration is accomplished in an acid regenerator or through an internal regeneration method. Net consumption of HF acid is about 0.3 lbs per barrel of alkylate produced. The use of HF acid requires specialized engineering design, operator training, and safety precautions to protect operators from accidental contact with HF acid, a very hazardous and toxic substance.

Auxiliary neutralizing and scrubber equipment is often incorporated to ensure that all materials leaving the process are free of acid. Neutralization systems typically utilize a scrubber and potassium hydroxide mixing and regeneration tanks to remove any HF acid that might be present. In most cases, all acid vents and relief valves are piped to this section. After gases are neutralized they are vented to the refinery flare system. Neutralized HF acid eventually leaves the unit as an alkali metal fluoride, usually calcium fluoride. This is accomplished by treating the effluent containing HF acid with a lime solution or slurry.

The environmental hazards associated with HF acid have prompted a number of companies to pursue the development of additives that modify some of the hazardous properties of this acid [OGJ 1994, Meyers 1997]. [Process Description: Meyers 1997, HP 1996, EPA 1995a]

6.2 Summary of Inputs/Outputs

The following is a summary of the inputs and outputs for alkylation processes:

Inputs:	Outputs:.
Paraffins	High Octane Blending Stock
- isobutane	(alkylate)
- butane	Butane
- propane	Propane
- pentane	Wastewater
Olefins	Neutralized Acid Sludge
- isobutylene	Spent Caustic
- butylene	
- butenes	
- propylene	
Acid Catalysts	
- Sulfuric	
- Hydrofluoric	
Caustic	
- Potassium Hydroxide	
- Sodium Hydroxide	
Electricity	
Fuel Gas	
Steam	
Cooling/Process Water	

6.3 Energy Requirements

The process energy used for alkylation processes is shown in Tables 6-1 and 6-2 [ANL 1981, HP 1996, Meyers 1997]. The energy content (i.e., feedstock energy) of the feedstock is not considered here, as it is used to make an energy product that is combusted for heat and power in other industries (e.g., transportation, buildings, petrochemicals). Process energy does include, however, any energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

The majority of the process energy input to alkylation is in the form of fuels used in boilers to produce steam. Steam is used in stripping units that depropanize and debutanize the products of the alkylation reaction.

Electricity is used primarily to power refrigeration compressors, pumps, mixers, filtering systems, and other auxiliary equipment. Electricity typically accounts for about 10 percent of overall fuel consumption (gross basis) in alkylation.

6.4 Air Emissions

Process Vents and Fugitive Emissions Are Sources of Air Pollutants from Alkylation

Emissions from alkylation include fugitive emissions of volatile constituents in the feed, and emissions that arise from process vents during processing. These can take the form of acidic hydrocarbon gases, non-acidic hydrocarbon gases, and fumes that may have a strong odor (from sulfinated organic compounds and organic acids, even at low concentrations).

To prevent harm to personnel and the environment from accidental releases of HF acid, refineries install a variety of mitigation and control technologies (e.g., acid inventory reduction, HF-detection systems, isolation valves, rapid acid transfer systems, and water spray systems). When necessary, strong odors are controlled by scrubbing or incineration systems. Risk Management Plans (RMPs) and Process System Safety Plans are also prepared and followed to protect workers and the environment from releases of this acutely toxic substance.

In HF acid alkylation processes, **acidic hydrocarbon gases** can originate anywhere HF acid is present (e.g., during a unit upset, unit shutdown, or maintenance). HF acid alkylation units are designed to pipe these gases from acid vents and valves to a separate closed-relief system where the acid is neutralized. The

Table 6-1. Estimated Energy Use in Sulfuric Acid Alkylation- 1996

Energy Source[a]	Specific Energy Use[e] (10^3 Btu/bbl of feed)	Total Industry Use[f] (10^{12} Btu/yr)
Natural Gas	57.3	9.1
Refinery Gas	102.8	16.4
Electricity[b]	126.0	20.0
Coke	37.8	6
Oils[c]	6.9	1.1
Other[d]	4.2	0.67
TOTAL	**335.0**	**53.3**

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Average value based on estimated utilities for various licensed technologies, including Exxon Autorefrigeration Alkylation and Stratco Effluent Refrigeration Alkylation [HP 1996].
f Based on alkylation production capacity at U.S. refineries on January 1, 1997 , operating at 93% capacity (~440,000 bbls/cday). Assumes 40% of the market is sulfuric acid-based alkylation. [DOE 1997a, OGJ 1996c]

Table 6-2. Estimated Energy Use in Hydrofluoric Acid Alkylation- 1996

Energy Source[a]	Specific Energy Use[e] (10^3 Btu/bbl of feed)	Total Industry Use[f] (10^{12} Btu/yr)
Natural Gas	65.7	15.8
Refinery Gas	118.0	28.4
Electricity[b]	15.1	3.6
Coke	43.4	10.5
Oils[c]	7.9	1.9
Other[d]	4.7	1.1
TOTAL	**254.8**	**61.3**

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Average based on estimated utilities for various licensed technologies [ANL 1981].
f Based on alkylation capacity at U.S. refineries on January 1, 1997, operating at 93% capacity (~ 660,000 bbls/cday). Assumes 60% of the market is HF acid alkylation [DOE 1997a, OGJ 1996c].

neutralization system consists of a relief-gasscrubber, a potassium hydroxide (KOH) mixing tank, neutralization drum, circulating pumps, and a KOH-regeneration tank. The acid-free gases are then routed to the refinery flare gas system where they are disposed of through burning.

Non-acidic hydrocarbon gases originate from process vents and relief valves and are discharged directly into the refinery flare gas system [Meyers 1997]. **Strong odors** can originate from the neutralizing basin. To prevent these fumes from discharging into the environment, the neutralizing basins are tightly covered and equipped with a gas scrubbing system to remove odors, using either water or activated charcoal as the scrubbing agent [EPA 1995a, Meyers 1997]. Another source of emissions is combustion of fuels in process boilers to produce steam for strippers. As with all process heaters in the refinery, these boilers produce significant emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbons.

6.5 Effluents

Alkylation generates relatively low volumes of wastewater, primarily from water washing of the liquid reactor products. Wastewater is also generated from steam strippers, depropanizers and debutanizers, and can be contaminated with oil and other impurities. Typical water flow (not including cooling water) for alkylation is about 2-3 gallons per barrel of alkylate [Meyers 1996]. These wastewaters are treated along with other refinery process wastewater (see Section 10 for more details on wastewater treatment).

Limitations for wastewater are set by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419. Table 6-3 shows limitations for average daily values for 30 consecutive days using the best available technology economically available (BAT) [BNA 1992].

Liquid process waters (hydrocarbons and acid) originate from minor undesirable side reactions and from feed contaminants, and usually exit as a bottoms stream from the acid regeneration column. The bottoms is an acid-water mixture which is sent to the neutralizing drum. The acid in this liquid eventually ends up as insoluble calcium fluoride [Meyers 1997].

6.6 Waste, Residuals and Byproducts

Sulfuric acid alkylation generates considerable quantities of spent acid that must be removed and regenerated (about 13-30 lbs per barrel of alkylate produced). Nearly all the spent acid generated at refineries is regenerated and recycled [API 1997b]. Although technology for on-site regeneration of spent sulfuric acid is available, this challenging task is usually performed off-site by the supplier of the acid. However, in countries where sulfuric acid production capacity is limited (e.g., Japan) acid regeneration is often done on-site. The development of internal acid regeneration for HF units has virtually eliminated the need for external regeneration, although most operations retain one for start-ups or during periods of high feed contamination [Meyers 1997].

Neutralization Sludge Can Be Used by Steel Mills or Recycled for Other Uses

Both sulfuric acid and HF acid alkylation generate **neutralization sludge** from treatment of acid-laden streams with caustics in neutralization or wash systems. Sludge from HF alkylation neutralization systems consists largely of calcium fluoride and unreacted lime, and is usually trucked off-site and disposed of in a landfill. It can also be directed to steel manufacturing facilities, where the calcium fluoride can be used as a neutral flux to lower the slag-melting temperature and improve slag fluidity. Calcium fluoride can also be routed back to an HF acid manufacturer. A basic step in HF manufacture is the reaction of sulfuric acid with fluorspar (calcium fluoride) to produce hydrogen fluoride and calcium sulfate.

Spent alumina is also generated by the defluorination of some HF acid alkylation products over alumina. It is disposed of or sent to the alumina supplier for recovery. Other solid residuals from HF acid alkylation include any porous materials (e.g., wood, wiping cloths, pipe coverings, packings) that may have come in contact with HF acid. These are generated during maintenance or normal operation, and are disposed of by burning. For this reason wood staging materials are kept to a minimum.

Table 6-3. Effluent Limitations for Alkylation/Reforming[a] -Average of Daily Values for 30 Consecutive Days (lbs/1000 bbl of crude oil)

Pollutant	BAT Limitation
Phenolic Compounds	0.032
Total Chromium	0.037
Hexavalent Chromium	0.0031

[a] Combined limits for sulfuric acid alkylation and catalytic reforming.

7 Hydrotreatment

7.1 Hydrotreatment Overview

Hydrotreatment Removes Undesirable Impurities from Petroleum Products

Hydrotreating (often referred to as **hydrodesulfurization,** and **hydroprocessing)** is used to remove impurities (e.g., sulfur, nitrogen, oxygen, and halides) from petroleum fractions. Hydrotreating further "upgrades" heavy feeds by converting olefins and diolefins to paraffins, which reduces gum formation in fuels. Hydroprocessing also cracks heavier products to lighter, more saleable products.

The severity of the hydrotreating process determines the final result. Mild hydrotreating, for example, is employed to remove sulfur and saturate olefins. More severe hydrotreating removes nitrogen, additional sulfur, and saturates aromatic rings. Common hydrotreatment reactions are shown in Figure 7-1.

Hydrotreating and hydroprocessing units are usually placed upstream of units where catalyst deactivation may occur from feed impurities (e.g., fluid catalytic crackers, hydrocrackers, catalytic reforming units).

Hydrotreatment improves the economics of downstream conversion processes considerably by lowering sulfur content and eliminating or reducing the need for costly flue gas desulfurization facilities. Addition of hydrogen to the feed by the hydrotreater also improves product yields and quality in downstream units.

In 1997, an estimated 10.0 million barrels of feed per day were charged to hydrotreatment units in domestic refineries. This figure is based on a 93 percent overall average refinery capacity utilization as reported in the first quarter of 1997 [OGJ 1997, DOE 1997a].

Hydrotreating Employs Catalysts that Selectively Remove Impurities

The hydrotreatment process (see Figure 7-2) is similar in many ways to hydrocracking, except that the catalyst employed is selective for the removal of sulfur and nitrogen compounds (hydrodesulfurization and denitrification reactions) as well as metals and other impurities. Hydrotreatment catalysts commonly contain cobalt or molybdenum oxides on alumina, and less often nickel and tungsten [OGJ 1995b].

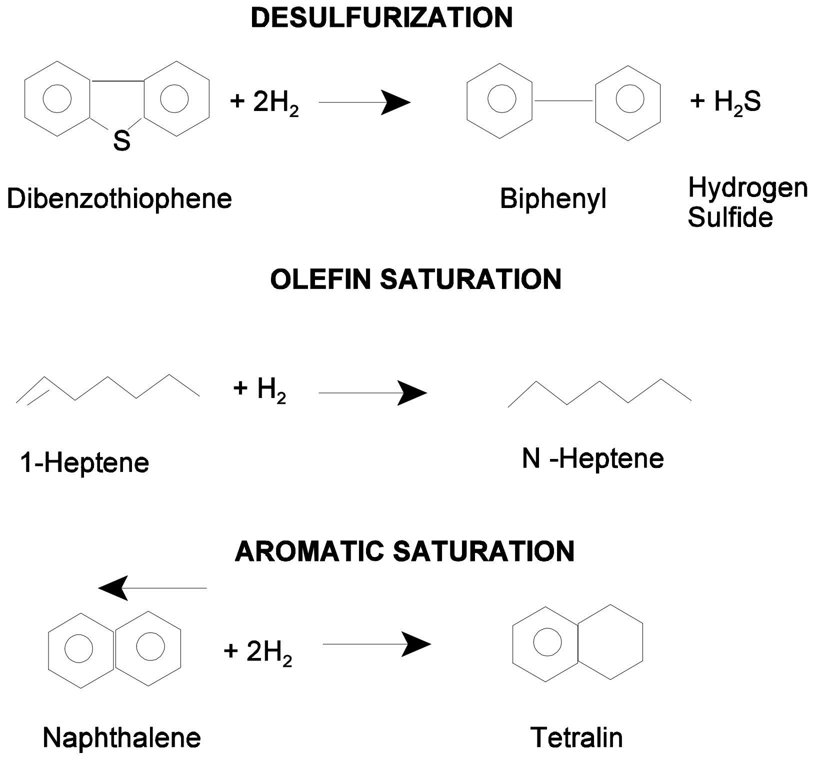

Figure 7-1. Typical Hytrotreatment Reactions [Meyers 1997]

Most configurations employ a single or multi-stage reactor system with a fixed catalyst bed operating under high pressure and with the addition of hydrogen. Like catalytic hydrocracking, hydrogen for the process is provided from catalytic reforming byproduct hydrogen and on-site production of hydrogen.

After the feed passes through the reactor, cracked products are separated in a hydrogen separator and then sent to a fractionator or steam stripper.

A variety of separation configurations can be employed, including high- and low-pressure separators in series, sulfur gas scrubbers/absorption units, and so on, in conjunction with steam strippers, fractionating sections, or other similar units. The ultimate objective is to produce a treated liquid product stream that is suitable for downstream processing. Hydrotreaters can also produce finished products (e.g., middle distillates, diesel). The actual product slate can vary considerably depending on catalysts and operating conditions employed, as well as the entering feed.

In addition to liquid products, the hydrotreater produces a stream of light fuel gases, hydrogen sulfide, and ammonia. Hydrogen is recycled back to the reactor. The off-gas from hydrotreatment is rich in hydrogen sulfide and light fuel gases, and is usually sent to a sour gas treatment unit and sulfur recovery unit.

The temperature at the inlet of the reactor is gradually increased over time to compensate for catalyst deactivation. The entire system must be designed to operate at the high end of run temperatures, as well as start of run conditions. Catalyst regeneration is done after months or years of operation, and is usually performed at an off-site facility. Valuable metals (if any) from spent catalysts are also recovered off-site. Description: EPA 1995a, HP 1996, Meyers 1997].

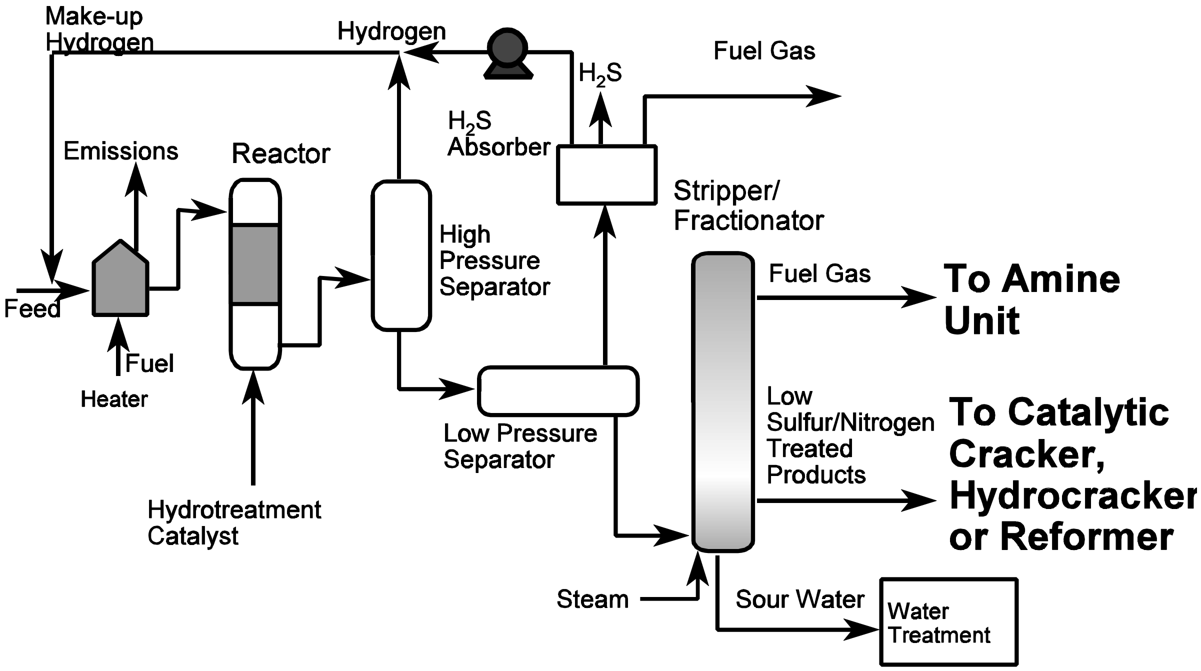

Figure 7-2. Catalytic Hydrotreatment Flow Diagram
[EPA 1995a, HP 1996, Meyers 1997]

Key Energy and Environmental Facts - Catalytic Hydrotreating			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy Use: *Gross:* *120 10^3 Btu/bbl of feed* *Net:* *76 10^3 Btu/bbl of feed* *Note: Energy use depends on feed type and amount of sulfur and other impurities:*	*Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates).*	*Sour waste water from the fractionator and hydrogen separator (suspended solids, H_2S, NH_3, phenols).* *Water Flow - 1 gal/bbl*	*Spent catalyst fines (aluminum silicate and metals).*

7.2 Summary of Inputs/Outputs

The following is a summary of the inputs and outputs for hydrotreating:

Inputs:	Outputs:.
Atmospheric Resid	Diesel/Middle Distillates
Distillates	Low Sulfur/Nitrogen Products
Vacuum Resid	Light Ends
Vacuum Gas Oils	

Inputs:	Outputs:.
Hydrogen	Fuel Gas
Fuel Gas	Sour Water
Process Water	Catalyst Fines
Steam	Spent Catalyst
Electricity	Hydrogen Sulfide
Catalysts	

7.3 Energy Requirements

The process energy used in various hydrotreating processes is shown in Table 7-1 [HP 1996, Meyers 1997]. The energy content (i.e., feedstock energy) of the feedstock is not considered here, as it is used to make an energy product that is combusted for heat and power in other industries (e.g., transportation, buildings, petrochemicals). Process energy does include, however, any energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

The majority of the process energy input to hydrotreating is in the form of fuels used in process heaters and in boilers to produce steam. Electricity is used primarily to power compressors, pumps, air blowers, filtering systems, and other auxiliary equipment. Electricity typically accounts for about 48 percent of overall energy consumption (including losses from generation and transmission) in hydrotreating.

Catalytic hydrotreating is also one of the more energy intensive refinery processes. Because it is used to pretreat a relatively large share of inputs to downstream refinery processes, catalytic hydrotreating accounts for more annual energy consumption than atmospheric distillation of crude.

7.4 Air Emissions

Hydrotreating Produces Air Emissions from Process Heaters and Fugitive Emissions

Hydrotreating generates air emissions through process heater flue gas, vents, and fugitive emissions. Unlike fluid catalytic cracking catalysts, hydrotreating catalysts are usually regenerated off-site after months or years of operations, and little or no emissions or dust are generated from the catalyst regeneration process at the refinery. Section 10 provides air emissions factors for emissions from process heaters and boilers used throughout the refinery.

The off-gas stream from hydrotreating is usually very rich in hydrogen sulfide and light fuel gas. This gas is usually sent to a sour gas treatment and sulfur recovery unit along with other refinery sour gases (see Section 10 for more details on sulfur management).

Fugitive air emissions of volatile components released during hydrotreating may also be toxic components. These include toluene, benzene, xylenes, and other volatiles that are reported as toxic chemical releases under the Toxics Release Inventory [EPA 1998]. Although there are no estimates as to the amount of these constituents released during hydrotreating, refinery-wide releases are substantial.

Table 7-1 Estimated Energy Use in Catalytic Hydrotreating- 1996

Energy Source	Specific Energy[e] (10^3 Btu/bbl of oil)	Total Industry Use[f] (10^{12} Btu/yr)
Natural Gas	17.0	66.6
Refinery Gas	30.6	119.9
Electricity[a]	57.3	224.6
Coke	11.3	44.3
Oils[b]	2.1	8.2
Other[c]	1.2	4.7
TOTAL	**119.5**	**468.3**
Hydrogen Consumed[d]	223.0	874.0
Net Steam Exported	(31.1)	(121.9)

a Includes losses incurred during the generation and transmission of electricity
b Includes crude oil, distillate and residual fuel oil
c Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
d Hydrogen demand ranges from 1000-2500 scf/bbl of feed. Hydrogen is a by-product of catalytic reforming, and is also produced on-demand through various means. Hydrogen recycle is incorporated in the process.
e Source: Average values based on estimated utility requirements for various licensed technologies, including IFP Hyvahl, Chevron RDS/VRDS, Exxon DODD, Howe-Baker Hydrotreating, and UOP Unionfining [HP 1996, Meyers 1997].
f Based on hydrotreating capacity at U.S. refineries on January 1, 1997 (10,738,264 bbls/cday), operating at 93% capacity. [DOE 1997a]

7.5 Effluents

Hydrotreating Produces Wastewater and Spent Catalysts

Catalytic hydrotreating generates sour wastewater from fractionators used for product separation. Like most separation processes in the refinery, the process water used in fractionators often comes in direct contact with oil, and can be highly contaminated. It also contains hydrogen sulfide and ammonia and must be treated along with other refinery sour waters. In hydrotreating, sour wastewater from fractionators is produced at the rate of about 1.0 gallon per barrel of feed.

7.6 Waste, Residuals or Byproducts

Hazardous Wastes May Result from Treating Oily Hydrotreating Wastewaters

Oily sludges from the wastewater treatment facility that result from treating oily and/or sour wastewaters from hydrotreating and other refinery processes may be hazardous wastes, depending on how they are managed. These include API separator sludge, primary treatment sludge, sludges from various gravitational separation units, and float from dissolved air flotation units . See Section 10 for more details on wastewater treatment.

Hydrotreating also produces some residuals in the form of spent catalyst fines, usually consisting of aluminum silicate and some metals (e.g., cobalt, molybdenum, nickel, tungsten). Spent hydrotreating catalyst is now listed as a hazardous waste (K171)(except for most support material.) Hazardous constituents of this waste include benzene and arsenia. The support material for these catalysts is usually an inert ceramic (e.g., alumina).

8

Additives and Blending Components

8.1 Additives and Blending Components Overview

Ethers Dominate the Additives Market

A variety of chemical compounds are added to gasoline and other transportation fuels to improve performance or to comply with federal and state environmental regulations. After passage of the 1970 Clean Air Act and the subsequent phase-out of lead additives, **alcohols and ethers** were added to gasoline to increase octane levels and reduce the generation of carbon monoxide.

More recently, the Clean Air Act Amendments of 1990 have called for minimum and maximum amounts of chemically combined oxygen in motor fuels and upper limits on Reid vapor pressure to promote cleaner-burning fuels. Additive compounds that increase the amount of chemically combined oxygen in fuels are called **oxygenates**. These include alcohols (methanol and ethanol) and a variety of ethers. **Ethers** are more effective in meeting new fuel requirements since they are less soluble in water (and produce less chemically-combined oxygen), have a lower blending vapor pressure, and impart high octane properties to the fuel. As a consequence, alcohols are being supplanted by the use of ethers which are better able to meet the new oxygen requirements as well as vapor pressure limits.

During the 1990s, the market for oxygenates (especially ethers) has been the fastest growing portion of the gasoline pool,

EPA Interpretive Rules for Oxygenates [EPA 1991]

Fuel Ethanol: Blends of up to 10% by volume (the “gasohol waiver”).

Methanol: Blends of methanol up to 0.3% by volume, exclusive of other oxygenates. Blends of methanol and gasoline-grade butyl alcohol (GTBA) such that total oxygen does not exceed 3.5% by weight. Blends of up to 5.0% by volume methanol with a minimum of 2.5% co-solvent alcohols having a carbon number of 4 or less. Total oxygen cannot exceed 3.7% by weight.

Methyl Tertiary Butyl Ether (MTBE): Blends of up to 15% by volume. Blends with MTBE cannot be used as base gasolines for other oxygenated blends.

primarily due to environmental concerns and consumer demands for high performance fuels. The introduction of midgrade and high-grade premium gasolines, and newer, more sophisticated automotive engines, have both contributed to an increasing demand for higher-quality gasoline and the need to improve octane in the gasoline pool through additives [Meyers 1997, EPA 1995a, DOE 1997a].

Ethers used as additives include methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), and diisopropyl ether (DIPE). The most commonly used is MTBE, although significant quantities of alcohol are also still in use (see Table 8-1) [DOE 1997a].

Table 8-1. Inputs of Oxygenates, 1996

Oxygenate	Input (Million Barrels)	%of Total
Fuel Ethanol	11.2	12
Methanol	0.13	<1
MTBE	79.4	84
Other Oxygenates	3.4	4
TOTAL	94.1	100

Many refineries produce their own MTBE and other ethers; smaller refineries usually purchase these additives from chemical manufacturers or larger refineries.

Isomers Are High Octane Blending Components

Isomerization, which alters the arrangement of a molecule without adding or removing anything, is used in refineries to produce compounds with high octane (e.g., isopentane, isohexane) for **blending** into to the gasoline pool. Isomerization is also used to produce isobutane, an important feedstock for alkylation (see Section 6).

In 1997, approximately 562 thousand barrels of feed per day were charged to isomerization units in domestic refineries. This figure is based on a 93 percent overall average refinery capacity utilization as reported in the first quarter of 1997 [OGJ 1997, DOE 1997a].

8.1.1 Production of Ethers

Acidic Ion Exchange Resins Catalyze the Ether Production Process

MTBE, ETBE, and TAME are all produced by the reaction of an isoolefin with alcohol in the presence of a solid acidic catalyst, typically a sulfonic ion-exchange resin. The reaction proceeds in the liquid phase under relatively mild operating conditions. A small amount of excess alcohol is used to prevent olefin dimerization, an exothermic reaction that can increase the temperature of the resin bed and create irreversible catalyst fouling.

Etherification Reactions

$CH_2{=}C(CH_3)_2 + CH_3OH \rightarrow (CH_3)_3\text{-}C\text{-}O\text{-}CH_3$

Isobutylene Methanol MTBE

$CH_2{=}C(CH_3)_2 + CH_3CH_2OH \rightarrow (CH_3)_3\text{-}C\text{-}O\text{-}CH_2CH_3$

Isobutylene Ethanol ETBE

$CH_3CH{=}C(CH_3)_2 + CH_3OH \rightarrow CH_3CH_2(CH_3)_2\text{-}C\text{-}O\text{-}CH_3$

Isoamylene Methanol TAME

A typical process configuration for tertiary ethers is shown in Figure 8-1. Diisopropyl ether (DIPE) is also produced in a similar catalytic process from propylene, isopropyl alcohol, and water. The hydrocarbon feed (isobutylene or isoamylene) is first water-washed to remove nitrogen compounds if necessary, and is charged to the reactor section along with fresh and recycled alcohol (methanol or ethanol). Two fixed-bed adiabatic reactors are commonly used in series, with most of the reaction to ethers occurring in the first reactor. Cooling between reactors is used to maximize the approach to equilibrium in the second reactor.

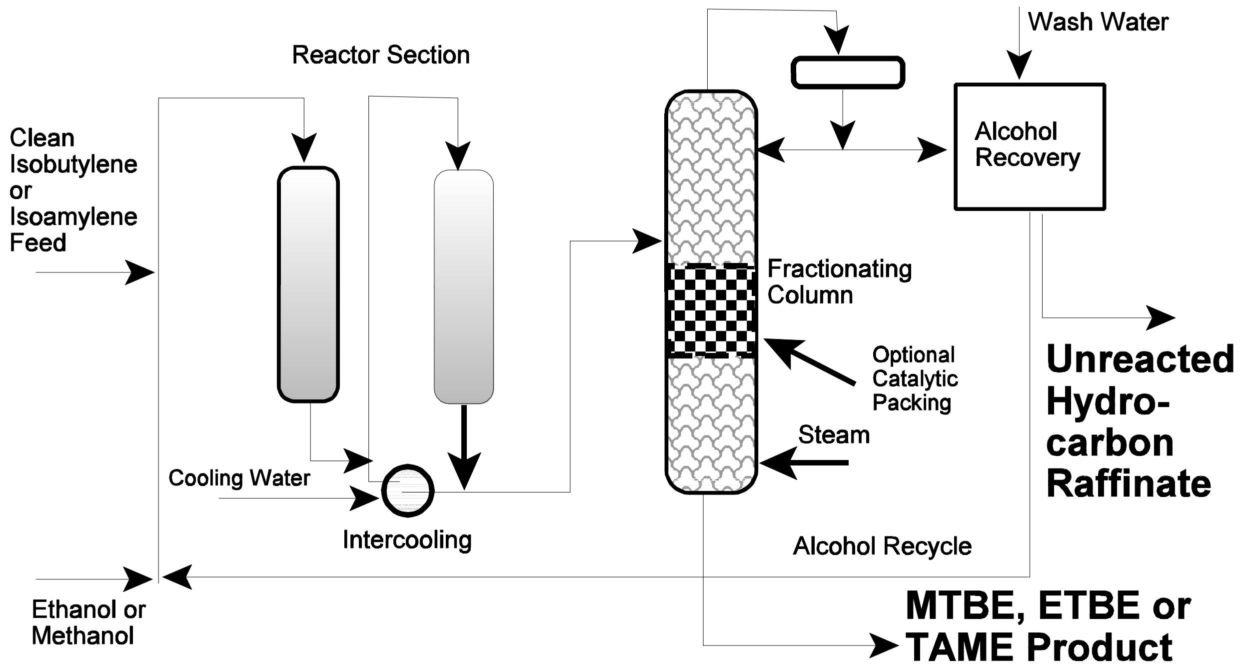

Figure 8-1. Ethers Manufacture Flow Diagram [HP 1996, Meyers 1997]

Key Energy and Environmental Facts - Ethers Manufacture

Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross:* *403 10^3 Btu/bbl feed* *Net:* *383 10^3 Btu/bbl feed*	*Boiler stack gas (CO, SOx, NOx, hydrocarbons and particulates)*	*Pretreatment wash-water (nitrogen contaminants); cooling and alcohol wash water are recycled*	*Spent catalysts (acidic ion-exchange resins)*

The products from the reactor section are sent to a fractionation column where high-purity ethers are recovered from the column bottoms. Unreacted hydrocarbons and alcohol are taken from the column top and water- washed to remove excess alcohol, which is recycled. Water from this step is also recycled back to the wash system.

Figure 8-1 illustrates a simple single stage system, although two stage systems are often employed. A two stage system comprises two reactor-fractionation column combinations placed in series.

New designs utilize a catalytic packing in the fractionating column (catalytic distillation) to increase conversion of unreacted isoolefins to ethers. Yields as high as 97 to greater than 99 percent have been reported for processes utilizing catalytic distillation. [Process Description: HP 1996, Meyers 1997]

8.1.2 Isomerization

Isomerization Is Catalyzed by Zeolites or Noble Metal Catalysts

Isomerization typically involves the conversion of paraffins (e.g., butane, pentane, hexane) to isoparaffins, which have a much higher octane. Isoparaffins are produced through a series of rearrangement and hydrogenation reactions over a zeolitic or

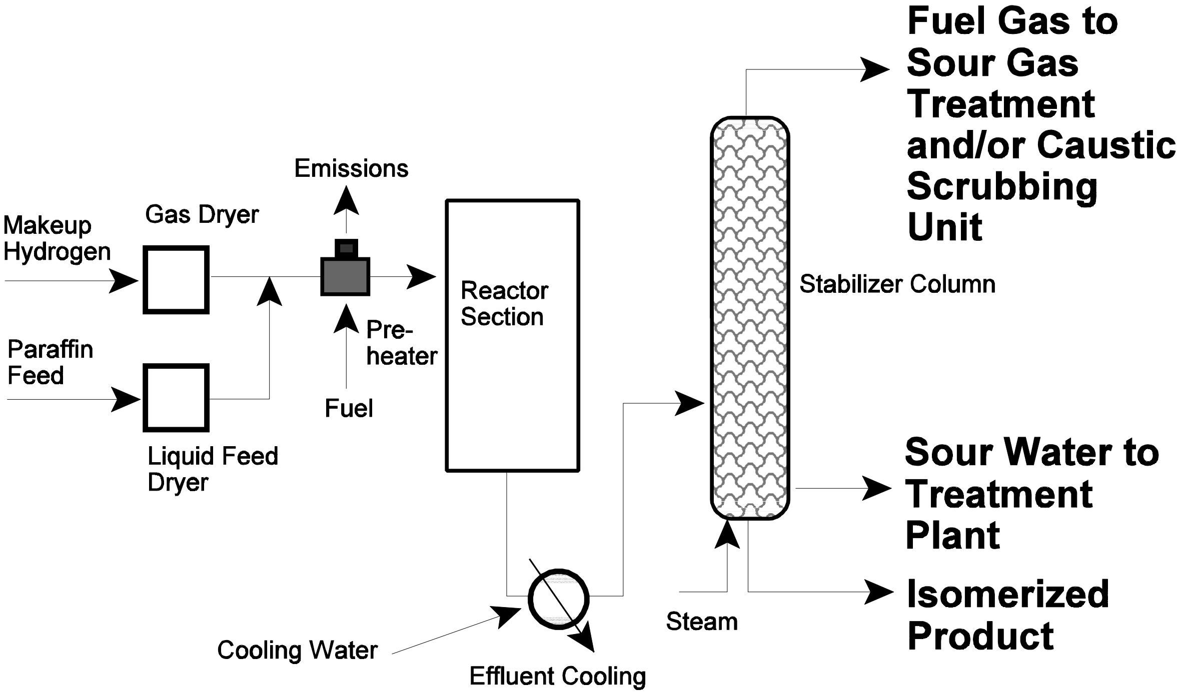

Figure 8-2. Isomerization Flow Diagram [HP 1996, Meyers 1997]

Key Energy and Environmental Facts - Isomer Manufacture			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Isobutane- Gross: 359 10^3 Btu/bbl feed Net: 337 10^3 Btu/bbl feed Isopentane/Isohexane- Gross: 175 10^3 Btu/bbl feed Net: 163 10^3 Btu/bbl feed Isobutylene- Gross: 476 10^3 Btu/bbl feed Net: 453 10^3 Btu/bbl feed	*Boiler/heater stack gas (CO, SOx, NOx, hydrocarbons and particulates), HCl (possible in fuel gas), vents and fugitive emissions (hydrocarbons)*	*Sour water (low hydrogen sulfide, ammonia), chloride salts, and caustic wash water*	*Calcium chloride sludge from neutralized HCl gas*

noble metal catalyst (e.g., platinum on an alumina support). The reaction is sometimes promoted by the use of organic chlorides or a chlorided alumina catalyst.

A typical isomerization flow diagram is shown in Figure 8-2. A feed stream containing concentrated levels of the paraffin (e.g., butane, or a mix of hexane and pentane) is directed to the reactor section where it is combined with hydrogen gas, heated, and sent to a reactor or series of reactors. The product from the reactor is cooled and sent to a stabilizer where the isomerized product is separated from other light products. Where organic chloride has been added to reactor feed to maintain catalyst activity, the overhead vapors from the stabilizer must be scrubbed with caustic to remove corrosive hydrogen chloride. The stabilized isomerate, which contains some normal paraffins along with the isoparaffins, is then sent to the gasoline blending pool.

In some cases the normal and isoparaffins from the stabilizer are separated by fractionation or molecular sieve separation to recycle the normal paraffins and low octane byproducts (e.g., methylpentanes).

Water, other oxygen-containing compounds, and nitrogen compounds can irreversibly poison isomerization catalysts that utilize organic chlorides. Molecular sieve drying is employed to clean and pretreat both the gas and hydrocarbon feed. Sulfur can also temporarily inhibit catalyst activity, and if present in high enough levels, the feed may be hydrotreated or treated with a caustic extraction process prior to isomerization. Feeds taken from hydrofluoric acid- based alkylation units also contain fluorides, which can degrade the molecular sieve drying system. These are removed by passing the feed over a hot bed of alumina.

Both types of catalysts require an atmosphere of hydrogen to minimize coke deposits on the catalyst. Overall, however, consumption of hydrogen is negligible. Isomerization catalysts lose their activity over time and must be replaced every two to three years or longer. Spent catalyst is shipped off-site, and the platinum in the catalyst is recovered at an off-site facility. [Process Description: EPA 1995a, HP 1996, Meyers 1997]

Isobutylene Is an Important Feedstock for Ethers Production

Isobutylene, which is used as a feed for the production of both MTBE and ETBE, is produced by the isomerization of normal butenes in the presence of a zeolite-based catalyst. The process is relatively similar to that used for other isomerization processes, and utilizes the raffinate (unreacted hydrocarbon stream) from MTBE units as a feedstock. The hydrocarbon feed does not require pretreatment or the addition or steam or diluents, and catalytic activation agents are normally not needed to promote the reaction.

Isobutylene is more commonly obtained from a number of refinery sources, including light naphtha from FCC units, and as a by-product from steam cracking of naphtha during ethylene production. Isobutylene can also be obtained from the conversion of tertiary butyl alcohol recovered as a by-product in the manufacture of propylene oxides. [Process Description: [EPA 1995a, HP 1996]

8.2 Summary of Inputs and Outputs

The following is a summary of the inputs and outputs for **tertiary ethers** production:

Inputs:	Outputs:
Isoolefins	Tertiary Ether
- isobutylene	- MTBE
- isoamylene	- ETBE
Alcohols	- TAME
- ethanol	Hydrocarbon Raffinate
- methanol	Spent Catalyst
Fuel Gas	Alcohol for Recycle
Process Water	
Steam	
Electricity	
Catalysts	

The following is a summary of the inputs and outputs for **isomerization**:

Inputs:	Outputs:
Paraffins	Isomers
- butane	- isobutane
- pentane	- isopentane
- hexane	- isohexane
Hydrogen	Fuel Gas
Process Water	Sour Water
Caustic	Calcium Chloride Sludge
Steam	
Fuel Gas	
Electricity	
Catalysts	

8.3 Energy Requirements

The process energy used in various etherification and isomerization processes is shown in Tables 8-1 to 8-4 [HP 1996, Meyers 1997]. The energy content (i.e., feedstock energy) of the feedstock is not considered here, as it is used to make an energy product that is combusted for heat and power in other industries (e.g., transportation, buildings, petrochemicals). Process energy does include, however, any energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

The majority of the process energy input to ether manufacture and isomerization is in the form of fuels used in process heaters and in boilers to produce steam. Electricity is used primarily to power compressors and pumps for water cooling systems. Cooling of reactor streams requires considerable amounts of process water in addition to electricity. Electricity typically accounts for about 8 percent of overall energy consumption (including losses from generation and transmission).

Ether production is one of the most energy-intensive processes in the refinery. However, because throughput to ether production is small compared with total refinery input, it does not account for a large share of overall refinery energy consumption. Isomerization of butane to isobutane is also very energy-intensive but again does not contribute very much to total refinery energy consumption because of low throughput.

Estimated energy consumption for the production of isobutylene in reactors dedicated to that purpose is shown in Table 8-4. The total specific energy consumption of 476 thousand Btus per barrel of product is the highest for any refinery process. However, most isobutylene is not obtained from dedicated reactors but is recovered as a byproduct from other refinery processing units. No estimates were available on the amount of isobutylene currently produced in this way in domestic refineries.

8.4 Air Emissions

Etherification and Isomerization Produce Air Emissions from Process Heaters and Fugitive Emissions

Both ethers manufacture and isomerization processes generate air emissions through process heater flue gas, vents, and equipment leaks. Emission factors for process heaters can be found in Section 10.

Catalysts are either ion exchange resins (which do not produce dust) or are noble metal catalysts that are regenerated off-site after months or years of operations. Subsequently little or no emissions or dust are generated from the regeneration of these catalysts at the refinery.

Light fuel gases stripped from the product stream leaving the isomerization reactor must be sent to the sour gas treatment facility to remove hydrogen sulfide and ammonia. For processes that utilize chloride catalyst activation agents, HCl may be present in the light fuel gases and must be neutralized by caustic treatment [EPA 1995a].

8.5 Effluents

Isomerization Produces Sour Water and Caustic Wastewater

The ether manufacturing process utilizes a water wash to extract methanol or ethanol from the reactor effluent stream. After the alcohol is separated this water is recycled back to the system and is not released.

In those cases where chloride catalyst activation agents are added, a caustic wash is used to neutralize any entrained HCl. This process generates a caustic wash water that must be treated before being released. This process also produces a calcium chloride neutralization sludge that must be disposed of off-site.

8.6 Hazardous and Toxic Residuals

Additives May Be Reported as Toxic Chemical Releases

Gasoline blending additives (e.g., methanol, ethanol, MTBE) are reported as toxic releases from refineries because of their high volatility. Most are released as fugitive emissions and from processing vents. Over 5.4 million pounds of methanol were reported as a toxic release in 1996. Releases of MTBE were also significant (about 2.6 million pounds).

Table 8-1. Estimated Energy Use in Ethers Manufacture - 1996		
Energy Source[a]	**Specific Energy Use[e] (10^3 Btu/bbl of feed)**	**Total Industry Use[f] (10^{12} Btu/yr)**
Natural Gas	102.2	6.6
Refinery Gas	183.4	11.9
Electricity[b]	30.5	2.0
Coke	67.5	4.4
Oils[c]	12.3	8.0
Other[d]	7.5	0.5
TOTAL	**403.4**	**33.4**

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Source: Average values based on estimated utility requirements for various licensed technologies, including UOP/HULs Ethermax, UOP Oxpro, and Snamprogetti Ethers [HP 1996, Meyers 1997].
f Based on total refinery production of MTBE and other oxygenates(ETBE, TAME) in 1996 (177,400 bbls/cday) [DOE 1997a].

Table 8-2. Estimated Energy Use in Isobutane Manufacture - 1996		
Energy Source[a]	**Specific Energy Use[e] (10^3 Btu/bbl of feed)**	**Total Industry Use[f] (10^{12} Btu/yr)**
Natural Gas	89.5	3.2
Refinery Gas	160.7	5.8
Electricity[b]	32.6	1.2
Coke	59.1	2.2
Oils[c]	10.8	0.4
Other[d]	6.5	0.2
TOTAL	**359.3**	**13.0**

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Source: Butamer® process (UOP) [HP 1996, Meyers 97]
f Based on isobutane capacity in U.S. refineries on January 1, 1997(98,170 bbls/cday) operating at 93% capacity [DOE 1997a].

Table 8-3. Estimated Energy Use in Isopentane and Isohexane Manufacture - 1996		
Energy Source[a]	**Specific Energy Use[e] (10^3 Btu/bbl of feed)**	**Total Industry Use[f] (10^{12} Btu/yr)**
Natural Gas	43.1	6.7
Refinery Gas	77.4	12.0
Electricity[b]	17.9	2.8
Coke	28.5	4.4
Oils[c]	5.1	0.8
Other[d]	3.1	0.5
TOTAL	**175.1**	**27.2**

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Source: Average values based on estimated utility requirements for various licensed technologies,including UOP Penex, UOP Once-Through Zeolitic, and IFP IPSorb.
f Based on isopentane and isohexane capacity in U.S. refineries on January 1, 1997(424,080 bbls/cday) operating at 93% capacity [DOE 1997a].

Table 8-4. Estimated Energy Use in Isobutylene Manufacture	
Energy Source[a]	**Specific Energy Use[e] (10^3 Btu/bbl of feed)**
Natural Gas	121.1
Refinery Gas	217.5
Electricity[b]	33.6
Coke	80.0
Oils[c]	14.6
Other[d]	8.8
TOTAL	**475.6**

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Average values based on estimated utility requirements for CDTECH ISOMPLUS [HP 1996].

9

Lubricating Oil Manufacture

9.1 Lubricating Oil Manufacture Process Overview

Refineries Use Petroleum Distillation Intermediates to Manufacture Lubricants, Waxes, and Petrolatum

Lubricants are substances used to reduce friction between bearing surfaces or as process materials that are incorporated in the manufacture of other products. Base stocks for petroleum lubricants can be produced from distillates or residues, and finished lubricants may also contain other compounds added to impart or improve certain properties.

Lubricating oils are produced from feeds that have already gone through atmospheric and vacuum distillation processes to remove volatile components. The feed must also undergo further separation and treatment processes to make it suitable for use as a high quality lubricant. **Solvent extraction**, **hydrogen treatment, deasphalting, and dewaxing** processes rid the feed of undesirable components such as aromatics, cycloalkanes, straight chain paraffins (waxes), and asphalt-like compounds. Remaining are the most desirable lubricating oil compounds, i.e., those with one or two aromatic or cycloalkane rings and long side chains.

A typical refinery flow scheme incorporating the manufacture of lube oils, waxes, and petrolatum is shown in Figure 9-1. In this configuration, distillates and heavy oils from the vacuum distillation column are sent to solvent extraction where multi-ring aromatics are removed. Raffinate from this process is treated with hydrogen and then charged to a dewaxing unit to remove paraffins. Deasphalting removes heavy asphalt compounds from the vacuum tower bottoms before they are charged to solvent extraction, producing an asphalt byproduct.

Hydrogen treatment is used to treat the raffinate stream before dewaxing to remove unstable gum-forming compounds or colored materials. The finished lubricating oil is blended with additives to improve the viscosity and/or increase oxidation resistance. If desired, thickeners can be added to lubricating oils to produce greases.

In 1996, domestic refineries produced over 63 million barrels of lubricants. This production represents about 73 percent of operable capacity (production capacity is about 86 million barrels) [DOE 1997a].

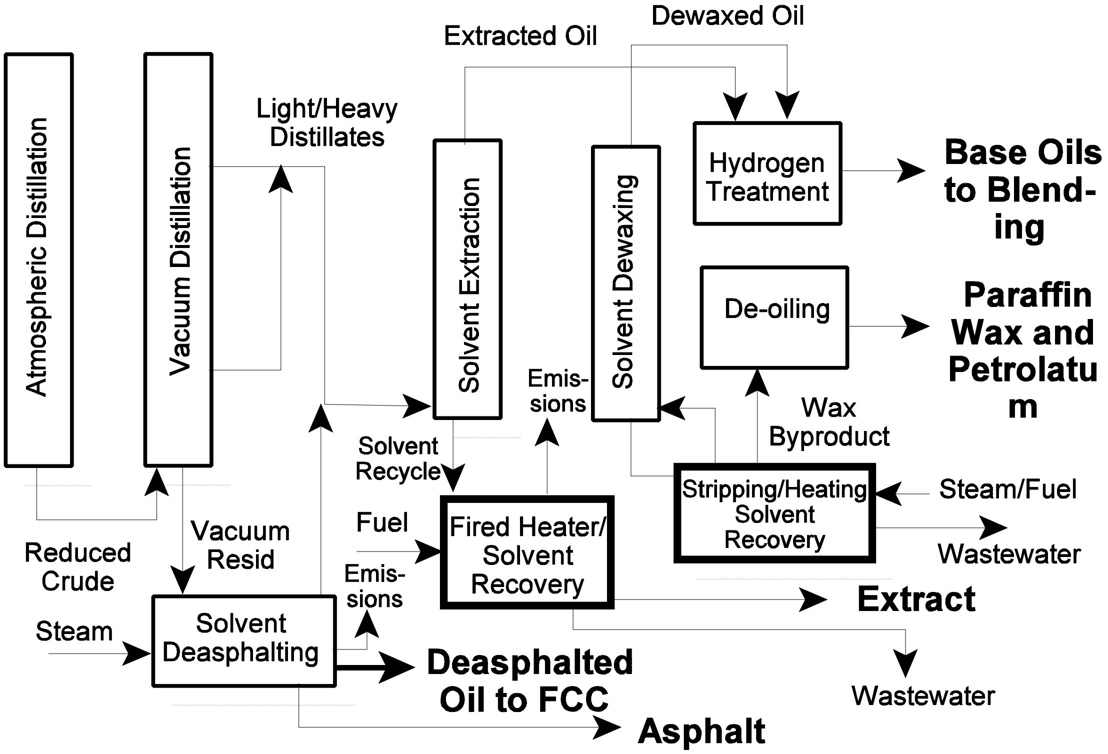

Figure 9-1. Typical Refinery Scheme for Lubricating Oil Manufacture
[ANL 81, EPA 1995a, HP 1996, Meyers 1997]

Key Energy and Environmental Facts - Lube Oil and Wax Manufacture			
Energy	***Emissions***	***Effluents***	***Waste, Residuals or Byproducts***
Energy use: *Gross:* *1506 10^3 Btu/bbl feed* *Net:* *1379 10^3 Btu/bbl feed*	*Heater stack gas (CO, NOx, Sox, hydrocarbons, particulates), fugitive propane, and fugitive solvents*	*Steam stripping wastewater (oil and solvents), solvent recovery wastewater (oil and propane)*	*Little or no residual wastes* *Fugitive solvent emissions may be toxic (toluene, methly ethyl ketone, methyl isobutyl ketone)*

Solvent Extraction Removes Undesirable Aromatics from Lube Oil Feedstocks

Solvent extraction is based on large differences in solubility in a given solvent exhibited by various compounds. In lubricating oil manufacture, solvent extraction is used to separate multiple-ring aromatics without side chains from the feed. These compounds have poor stability and poor viscosity-temperature characteristics, making them unsuitable for lubrication. Aromatics also tend to oxidize and produce sludge-forming compounds.

During the solvent extraction process, feed enters the bottom of a tower or rotating disk contactor and flows against a countercurrent of solvent, which dissolves the undesirable compounds. Typical solvents for removing aromatics include NMP (trade name) and phenol. NMP is the most commonly used solvent. The solvent to feed ratio is typically 2 to 1.

Raffinate containing the lube stock is removed from the top of the extracting tower, and must be stripped to remove any residual solvent. Solvent and extract are removed from the bottom and are separated in a solvent recovery step. The solvent is recycled, and the extract can be sold as a byproduct for use in the manufacture of plastics, rubber, or ink. Alternately, extracts can be sent to catalytic cracking or coking. The same solvent may be reused up to fifteen times per day. Steam stripping and solvent recovery require extensive equipment configurations and are typically the most capital- and energy-intensive portion of the extraction process. [Process Description: EPA 1995a, ANL 81]

Dewaxing Removes Straight-Chain Paraffins (Waxes)

Wax is removed from lubricating oil stocks by **solvent dewaxing** to help ensure that the lubricating oil will have the proper viscosity at low ambient temperatures. Both solvent dewaxing and catalytic dewaxing processes are in use, with solvent dewaxing being the more prevalent.

During solvent dewaxing, the lube stock is diluted with chilled solvent, which lowers the viscosity to allow filtration at reduced temperatures, and is then chilled until the wax crystallizes out and can be filtered off on rotating suction drums. The wax by-product is cut off the drums with knives, re-dissolved in solvent, and chilled to obtain the final product. The product wax can be used as a feedstock for the catalytic cracker or can be de-oiled and sold as an industrial wax.

Solvents typically used for dewaxing include propane and mixtures of methyl ethyl ketone (MEK) mixed with methyl isobutyl ketone (MIBK) or MEK with toluene. The most widely used solvent mixture is that of MEK with up to 70 percent toluene added. Solvent-to-charge ratios range widely, from about 1.5-5 to 1.

When propane is used as the solvent, it also functions as the refrigerant medium. The extraction temperature for propane dewaxing is about 130^{o}F, and pressure is reduced until about 50 percent of the solvent has exaporated, which reduces the temperature to about 40^{o}F.

Solvent is stripped from the oil product through a solvent recovery system that includes heating, then two-stage flashing, followed by steam stripping. As in solvent extraction, solvent recovery from dewaxing is capital- and energy intensive.

Catalytic dewaxing (selective hydrocracking) utilizes non-noble-metal zeolite catalysts to selectively crack the wax paraffins in the feedstock. The feed is first hydrotreated to remove sulfur, nitrogen and other contaminants. After hydrotreatment the effluent is cooled and charged to the dewaxing reactor where the feed flows over the zeolite catalyst. Cold, hydrogen-rich gas is injected into both reactors to maintain temperature.

Effluent from the second reactor is cooled and flashed into a hot high-pressure separator, where liquid products are separated from hydrogen-rich vapors. The separator liquid fraction is then charged to a fractionator for final product separation, and the vapors are sent to a cold high-pressure separator. [Process Description: ANL 1981, EPA 1995a, Meyers 1997]

Deasphalting Removes Asphaltenes to Produce Lube Oil Stocks, FCC Feed and Asphalt

The heavy intermediate product stream from the vacuum distillation column contains asphaltenes (asphalt-like materials) that must be removed before the stream can enter the solvent extraction unit. Processes in use for **deasphalting** are based on solvents such as propane (the most common), butane, or pentane, and utilize tower or rotating disk contactor solvent extraction or supercritical fluid extraction technology.

In **tower or rotating disk deasphalting**, liquid solvent along with feed enters the bottom of a packed or baffled extraction tower or rotating disk contactor. The oil, which is more soluble in the propane, dissolves and flows to the top of the unit. Asphaltenes and resins flow to the bottom of the unit where they are removed as a mixture that contains some propane. The tower method requires four to eight volumes of propane for each volume of oil feedstock.

Propane is recovered from both streams through two-stage flash systems followed by stripping with steam. The propane is compressed and removed by cooling at high pressure in the first stage and at low pressure in the second stage. Deasphalted oil is used as feed for fluid catalytic crackers. The asphalt product is blended with other refinery asphalt or fuel oil streams or used as a fuel for cokers. [Process Description: ANL 1981, EPA 1995a, HP 1996, Meyers 1997]

In **supercritical fluid extraction** processes, resid is charged to a mixer where it is mixed with solvent before entering an asphaltene separator. Countercurrent solvent flow extracts lighter components while asphaltenes are rejected as bottoms, along with a small amount of solvent. An intermediate resin product is retrieved from the solvent solution overhead and is subsequently stripped of solvent. The overhead is heated so that the solvent exists as a supercritical fluid in which the oil is virtually insoluble.

Recovered solvent is cooled by heat exchange and recycled back to the extraction system. Deasphalted oil is stripped of dissolved solvent using steam stripping. This solvent is also recovered and returned to the system. Operating conditions are modified depending on the desired product quality and yields.

A wide range of solvents can be used for supercritical fluid extraction, from propane to hexane, with propane being the most common. [Process Description: Meyers 1997]

Hydrocracking Can Be A Source of High Quality Lube Stocks

Hydrocrackers remove heavy aromatics effectively to produce highly paraffinic lube base stocks, and can also be easily adapted to meet other processing objectives in the refinery. When demand for lube oils is low, for example, refiners can use the hydrocracker to produce fuels and premium feed for the fluid catalytic cracker. By-products from hydrocracking also include high quality transportation fuels, whereas solvent refining produces a highly aromatic extract which can only be used in fuel oil or as feed for the fluid catalytic cracker. Use of hydrocracking for lube oil production is, however, highly dependent on the individual refinery’s needs and desired product slate.

9-2. Summary of Inputs/Outputs

The following is a summary of the inputs and outputs for lubricating oil manufacture:

Inputs:	Outputs:
Vacuum Residue	Lube Oils
Distillates	Paraffin Wax
Solvent	Petrolatum/Grease
Fuel	Sour Water
Electricity	Wastewater
Steam	Solvent
Cooling Water	
Hydrogen	

9-3. Energy Requirements

Lubricating oil manufacture is the most energy intensive process in a refinery. The combination of solvent extraction, dewaxing, deasphalting, and associated solvent recovery processes consume thirteen times as much energy per barrel of feed as atmospheric distillation of crude. However, while lube oil manufacture tops the list of energy intensive processes, the throughput is small compared with total refinery input. The result is a relatively small contribution to overall refinery energy consumption.

Process energy requirements by fuel type for all the processes associated with lubricating oil manufacture are shown in Table 9-1. The energy content (i.e., feedstock energy) of the feedstock used to make non-energy products (lube oils, grease, wax) is not shown here because it varies considerably based on the individual refinery’s desired product slate. Process energy includes any energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

The majority of the process energy input to lube oil manufacture is in the form of fuels used in process heaters and in boilers to produce steam. Electricity is used primarily to power compressors and pumps for water cooling of effluent streams, filters, mixers, and other auxiliary equipment. Electricity typically accounts for about 13 percent of overall energy consumption (including losses from generation and transmission).

Table 9-1. Estimated Energy Use in Lubricating Oil Manufacture - 1996[e]

Energy Source	Specific Energy Use (10^3 Btu/bbl of feed)					Total Industry Use[f] (10^{12} Btu/yr)
	Solvent Deasphalting	Solvent Dewaxing	Solvent Extraction	Solvent Recovery[a]	TOTAL	
Natural Gas	40.0	21.1	125.2	174.9	361.2	26.3
Refinery Gas	71.9	37.9	224.6	314.0	648.4	47.1
Electricity[b]	19.3	51.5	21.0	96.6	188.4	13.7
Coke	26.4	13.9	82.6	115.6	238.5	17.3
Oils[c]	4.8	2.6	15.1	21.1	43.6	3.2
Other[d]	2.9	1.5	9.1	12.8	26.3	1.9
TOTAL	**165.3**	**128.5**	**477.6**	**735.0**	**1506.4**	**109.5**

a Based on single effect evaporative solvent recovery. Double-effect and triple-effect can use upwards of 50% less steam.
b Includes losses incurred during the generation and transmission of electricity
c Includes crude oil, distillate and residual fuel oil
d Includes liquefied petroleum gases, miscellaneous oils, and purchased steam
e Average values based on estimated utility requirements for various licensed technologies, as follows: solvent deasphalting - IFP Solvahl process, Foster Wheeler LEDA process, MW Kellog ROSE supercritical fluid technology; solvent dewaxing - UOP catalytic dewaxing; solvent extraction - East coast refinery, generic operating experience [HP 1996, Meyers 1997, ORNL 1980]. Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 1996 [DOE 1997a].
f Based on lubricating oil production capacity in U.S. refineries on January 1, 1997 operating at 84% capacity (199,186 bbls/cday)[DOE 1997a]

Solvent separation and recovery processes are necessary at all stages of lube oil manufacture and account for the greatest energy consumption. In solvent extraction, heat for stripping the raffinate is typically supplied by heat exchangers and steam. The extract and solvent stream, however, may be heated in a direct-fired heater. In both dewaxing and deasphalting operations, solvent recovery requires heating and two-stage flashing in addition to steam stripping.

9.4 Air Emissions

Lube Oil Manufacture Results in Equipment Leaks and Process Vent Emissions

The manufacture of lube oils generates air emissions through process heater flue gas and equipment leaks. Heater stack gases produce emissions of CO, SOx, NOx, hydrocarbons and particulates. Equipment leaks are usually comprised of volatile solvents emitted during extraction processes as well as solvent recovery operations (e.g., propane, methyl ethyl ketone) [EPA 1995a].

Solvents are Released as Fugitive Air Emissions During Lube Oil Manufacture

Solvents, released from equipment leaks and process vents, are a source of toxic air releases from lube oil manufacture. Volatile solvents such as toluene, methyl ethyl ketone (MEK), and methyl isobutyl ketone, which are used in dewaxing, can be released to both air and water during processing. Reported toxic releases of these solvents from refineries are significant (over 4.3 million pounds released in 1996, mostly MEK) [EPA 1998]. Losses from non-volatile lubes and waxes are negligible.

9.5 Effluents

Lube Oil Wastewater Contains Oil and Solvents

Solvent extraction generates sour wastewater from steam strippers used for product separation and solvent recovery systems. The sour water

contains hydrogen sulfide and ammonia in addition to oil and solvents, and must be treated along with other refinery sour waters before reuse or release to public water treatment works.
The solvent recovery stage in both dewaxing and deasphalting also results in a solvent contaminated water stream which is typically sent to the wastewater treatment plant.

An estimate of the amount of pollutants generated from lube oil manufacture can be obtained from the effluent limitations given by the U.S. Environmental Protection Agency (EPA) in 40 CFR, Part 419, which was originally promulgated in 1974. Table 9-2 shows limitations for average values for 30 consecutive days using the best available technology economically available (BAT) [BNA 1992].

Table 9-2. Lube Oil Manufacture Limitations - Average of Daily Values for 30 Consecutive Days (lbs/1000 bbl of crude oil)

Pollutant	BAT Limitation
Phenolic Compounds	0.257
Total Chromium	0.297
Hexavalent Chromium	0.0248

10

Supporting Processes: Sulfur Management, Chemical Treatment, Water Treatment and Process Heating

10.1 Overview Of Auxiliary Processes

Sulfur Management Enables Compliance with Environmental Regulations

During processing, much of the sulfur and nitrogen contained in crude oil are converted primarily to hydrogen sulfide (H_2S) and ammonia (NH_3). Organic sulfur (COS and CS_2) and mercaptans are produced in lesser amounts (mercaptans are mostly converted to H_2S). These compounds are present in off-gases or fuel gases that are produced by many refinery processes, and in the sour water that results from stripping of both liquid and gaseous hydrocarbon products. Sour water can also contain phenols, cyanide, CO_2, salts and acids.

Management of sulfur compounds created by refining processes is a critical part of today's modern refinery. Increasingly stringent environmental standards on emissions of sulfur (as well as nitrogen) compounds, along with low sulfur regulations for fuel products, have mandated the development and implementation of more effective sulfur management techniques. The situation has been exacerabated by the decreasing quality and increasing sulfur content of crude oil.

Sulfur management usually consists of:

- amine treating and regeneration units to remove H_2S and other sulfur-containing compounds from off-gases and fuel gas and/or LPG;
- sour water strippers;
- Claus sulfur units to recover elemental sulfur from acid gases from amine units and water strippers; and
- tail gas clean-up units to boost sulfur recovery to over 99 percent.

A typical complete sulfur management system is shown in Figure 10-1.

In the amine treatment unit, H_2S and other sulfur-containing compounds in fuel gases (primarily ethane and methane) are dissolved in an amine solvent (e.g., diethanolamine (DEA), monoethanol amine (MEA), methyl diethanol amine (MDEA)). {Note: Dry adsorbents such as molecular sieves,activated carbon, iron sponge, and zinc oxide can also be used for this purpose.}

DEA or another amine solvent is first charged to an absorption tower where the sour gases (e.g., recycle gas, fuel gas, or liquified petroleum gas (LPG)) are contacted and hydrogen sulfide is dissolved and removed. The clean recycle or fuel gas is removed for use as a fuel in process

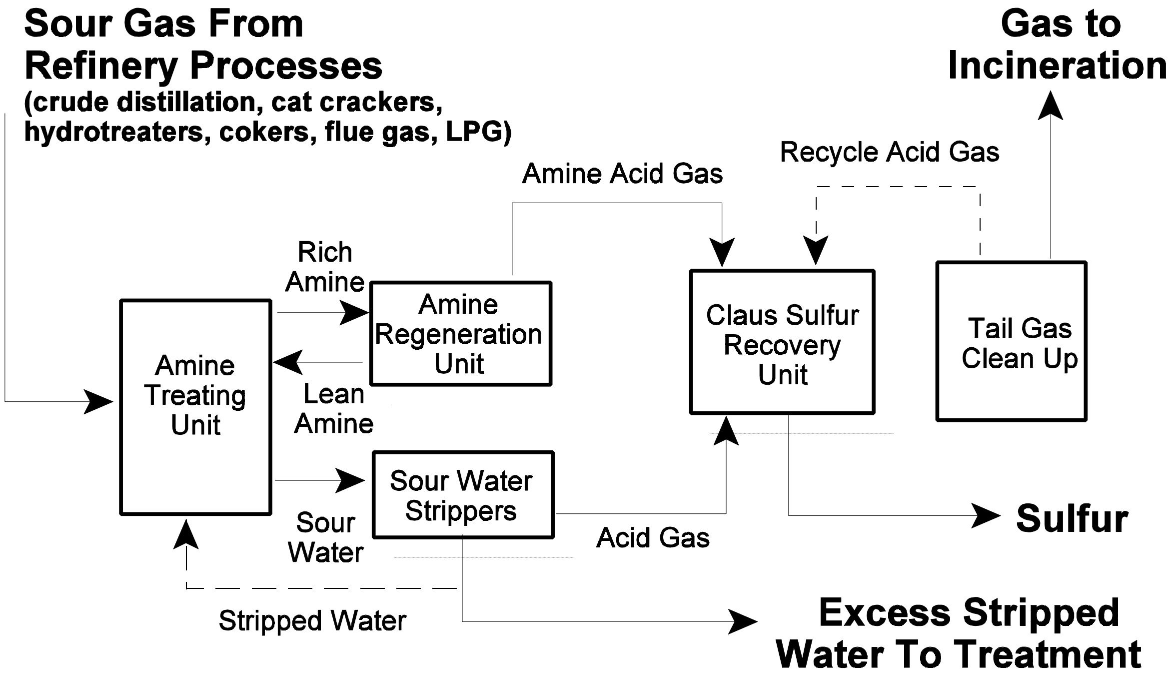

Figure 10-1. Typical Sulfur Management Flow Schematic
[EPA 1995a, Meyers 1997]

furnaces and in other refinery operations. LPG must be subjected to further treatment to remove mercaptans and any residual H_2S. The amine-hydrogen sulfide solution is sent to the **amine regeneration unit**. There the amine-hydrogen sulfide solution is heated and subjected to steam stripping to remove the hydrogen sulfide. The lean amine stream is then filtered, cooled and returned to the absorption tower. The acid gas containing hydrogen sulfide is sent on to the sulfur removal unit.

Sour water strippers can be designed to remove H_2S and NH_3 as well as phenols and other contaminants. In a typical sour water stripper system, sour water passes through a flash/separation drum and/or tank to flash (evaporate) off the dissolved gases and separate hydrocarbon oils and solids. The feed to the stripper is often preheated by heat exchange with the hot bottoms water from the stripper. Steam injection or reboiler steam is used to provide steam for stripping.

The H_2S and NH_3 vapors are subjected to cooling, water is condensed out, and the resulting acid gas is then sent to the sulfur removal unit. The stripped water can be recycled to process units as injection wash water, if it is non-phenolic. Stripped water from phenolic sour water strippers is corrosive and may poison catalysts, thus reuse is limited. Most refineries try to recycle as much stripped water as possible by re-using it for crude desalting, as makeup water for coker units, as wash water for hydrotreaters, and sometimes as cooling tower makeup water.

Acid gases from both amine treating units and sour water strippers must be further treated to remove sulfur. **Sulfur removal** typically consists of a combination of processes -- one to treat the initial acid gas and achieve most of the sulfur recovery (90-98 percent), and another to treat the tail gas from the first unit and remove as much of the remaining sulfur as possible.

The **Claus process** is the first stage in the sulfur recovery process, and is comprised of multistage catalytic oxidation of hydrogen sulfide preceded by an initial thermal conversion step (see Figure 10-2). The process achieves sulfur removal through the reaction of hydrogen sulfide with oxygen to form sulfur dioxide during combustion, and the subsequent reaction of hydrogen sulfide with sulfur dioxide (the Claus reaction). Many other side reactions also occur in the furnace.

A number of variations of the process are in use, with the main differences based on mole percent of hydrogen sulfide and heat integration within the unit. These include the straight-through process, the split flow process, split flow with preheating, and the sulfur recycle process.

When high concentrations of hydrogen sulfide are present in the feed (greater than 50 mole percent), the straight-through process is used. At mole percents between 20 and 50 percent the split flow process is employed. When the feed contains less than 20 mole percent and the flame is not self-sustaining at ambient temperatures, the split flow scheme is supplemented with feed preheat. The sulfur recycle process is typically only employed when the mole percent of hydrogen sulfide in the feed is less than 10 percent and a self-sustaining flame occurs.

The first step in the Claus process is partial combustion of the hydrogen sulfide-rich acid gas stream in a thermal reaction furnace using enough air to combust about one-third the hydogen sulfide and all the hydrocarbons and ammonia. Enriched air or oxygen can also be used to significantly enhance the capacity of the Claus unit. This is often done in operations utilizing multiple Claus units, so that additional capacity can be utilized when one of the units is shut down for repairs or maintenance.

The thermal furnace normally operates at temperatures ranging from 1800 to 2800^{o}F, with pressures of 10 psi or less. Hot waste gases from the furnaces are quenched in a waste heat boiler to provide high to medium pressure steam, permitting recovery of about 80 percent of the heat released from burning the hydrogen sulfide.

Claus Process Reactions

$2H_2S$	+	$3O_2$	→	$2SO_2$	+	$2H_2O$	+	Heat
Hydrogen Sulfide		Oxygen		Sulfur Dioxide		Water Vapor		

$2H_2S$	+	SO_2	→	$3S$	+	$2H_2O$	+	Heat (Claus Reaction)
Hydrogen Sulfide		Sulfur Dioxide		Sulfur		Water Vapor		

CO_2	+	H_2S	→	COS	+	H_2O
Carbon Dioxide		Hydrogen Sulfide		Carbonyl Sulfide		Water Vapor

COS	+	H_2S	→	CS_2	+	H_2O
Carbonyl Sulfide		Hydrogen Sulfide		Carbon Disulfide		Water Vapor

$2COS$	→	CO_2	+	CS_2
Carbonyl Sulfide		Carbon Dioxide		Carbon Disulfide

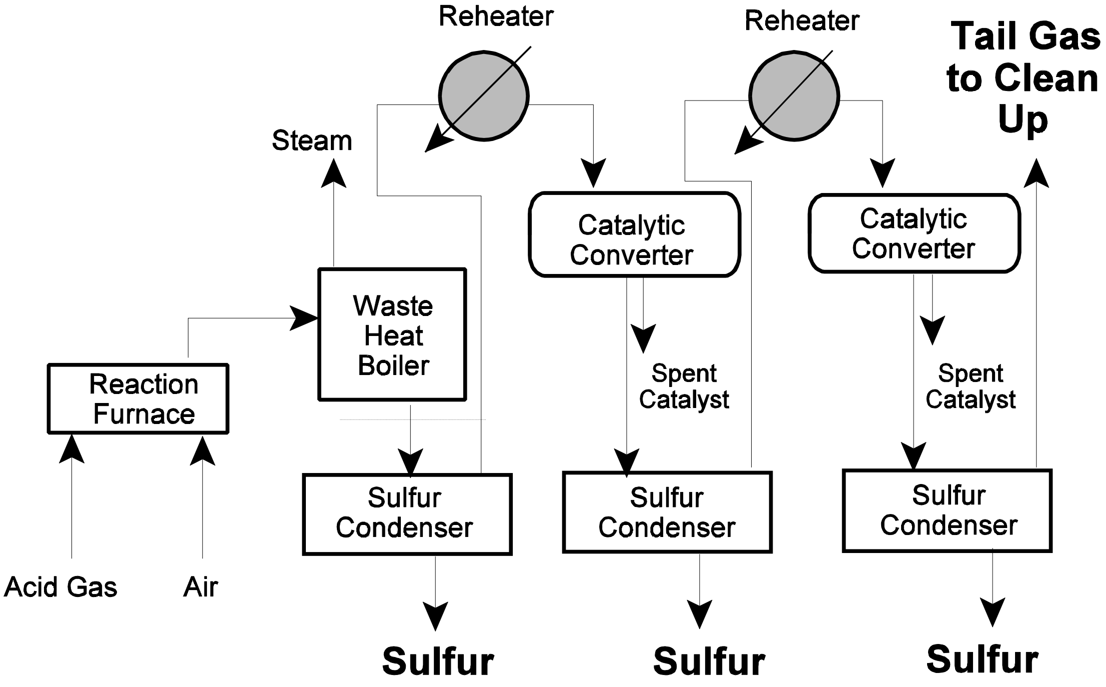

Figure 10-2. Claus Process Flow Schematic
[EPA 1997, Meyers 1997]

Key Energy and Environmental Facts - Claus Process			
Energy	***Emissions***	***Effluents***	***Wastes, Residuals, or Byproducts***
Energy use: *Electricity only-* *Gross:* *388.5* 10^3 *Btu/bbl feed* *Net:* *126.2* 10^3 *Btu/bbl feed*	*Process tail gas (NOx, SOx, hydrogen sulfide), fugitive emissions* *Hazardous air pollutants - hydrogen sulfide, carbonyl sulfide (COS) and carbon disulfide (CS2)* *Fugitive solvent emissions may be toxic (e.g., diethanolamine)*	*Little or no wastewater.*	*Spent catalysts*

About 60 percent of the sulfur is recovered in this thermal recovery section. The rest is recovered from a catalytic conversion process, which is often accomplished in two or three stages. Most plants are now built with two catalytic stages, although some regional air emission requirements may necessitate the addition of a third stage. Each catalytic stage utilizes a gas reheater, a catalytic reactor chamber, and a condenser. During the catalytic stage, the sulfur dioxide resulting from the initial combustion stage is reacted with the remaining unburned hydrogen sulfide over a bauxite or alumina catalyst to produce molten elemental sulfur. The molten sulfur is cooled in a waste heat boiler and thermal sulfur condensor. Liquid sulfur from the sulfur condenser passes into a covered pit from which it is pumped to trucks or rail cars for shipment to end-users. Total sulfur removal from the incoming gas stream ranges from 92 to over 99 percent.

Overall requirements for sulfur emissions at most refineries in the United States (New Source Performance Standards) are 250 to 300 parts per million in tail gas, depending on whether the tail gas process is based on oxidation or reduction. To achieve this level of sulfur removal, tail gas from the Claus unit is usually subjected to further treatment to destroy or recover residual sulfur pollutants. Emissions in this tail gas can be reduced in a number of ways, including **enhanced Claus conversion** at lower temperatures, and **gas scrubbing**.

Enhanced Claus conversion can be achieved by extending the Claus reaction into a lower temperature liquid phase. Processes currently in use for this purpose include the BSR Selectox, Sulfreen, Cold Bed Absorption, Maxisulf, and IFP-1 processes. These processes are all based on the enhancement of the Claus conversion at cooler temperatures. When installed downstream of a two- or three-stage Claus unit these processes can increase sulfur recovery to 99 percent or greater.

A scrubber can also be added to remove residual sulfur. The **Wellman-Lord oxidation** process has been successfully applied in U.S. refineries for this purpose. This process uses a wet, generative process involving sodium sulfite to reduce stack gas sulfur dioxide concentration to less than 250 parts per million volume (ppmv), and can achieve upwards of 99 percent sulfur removal.

Reduction scrubbing processes include the SCOT (Shell Claus Offgas Treatment) and Beavon processes. The **Beavon process** is based on absorption of hydrogen sulfide in a quinone solution. In this process the dissolved hydrogen sulfide is oxidized to form a mixture of elemental sulfur and hydro-quinone.

The sulfur is removed by filtering or centrifuge and the quinone is recovered and recycled. This process also removes sulfur dioxide, carbonyl sulfide, and carbon disulfide (in small amounts) that have not been removed by the Claus process. A cobalt molybdate catalyst is used to first convert these compounds to hydrogen sulfide prior to entering the Beaven unit.

The **SCOT process** (Shell Claus Offgas Treatment) uses a cobalt-molybdenum catalyst in the presence of a reducing gas to convert virtually all the sulfur compounds in the Claus unit tail gas (COS, SO_2, CS_2, sulfur vapor) to hydrogen sulfide. The reducing gas (H_2, CO), generated by combustion of fuel gas with steam, also heats the tail gas. The reactor products are cooled and contacted with amine (usually di-isopropanolamine (DIPA)) to remove all but trace amounts of hydrogen sulfide.

Hydrogen sulfide is stripped out of the amine stream with steam and directed to the Claus unit. The lean amine is then filtered, cooled and reused [Process Description - Sulfur Management: CHEMB 1993, EPA 1995a, EPA 1997, Meyers 1997, Sulphur 1994]

Chemical Treatment Removes or Alters Undesirable Compounds in Petroleum Fractions

After processing many petroleum product streams still contain sulfur, nitrogen, or oxygen compounds that impart undesirable properties. **Chemical treatment** is used to remove or alter these compounds and achieve the desired product quality.

Chemical treatment can be accomplished by extraction or oxidation (referred to as "sweetening") processes. Extraction removes sulfur from light petroleum fractions (e.g., propane, propylene, butane, butylene). Oxidation is used for sweetening gasoline and distillates.

Both extraction and sweetening can be accomplished using a **Merox process** (see Figure 10-3). Merox treatment improves odor as well as the response of gasoline stocks to oxidation inhibitors added to prevent gum formation during storage.

Both Merox extraction and oxidation are based on the ability of an organometallic catalyst to accelerate the oxidation of mercaptans to organic disulfides at or near ambient temperature and pressure, in an alkaline environment.

Merox extraction is commonly used to remove mercaptans (organic sulfur compounds) from light fractions. Hydrogen sulfide that is present in these fractions is removed prior to Merox extraction by amine treating and caustic prewashing. After hydrogen sulfide removal the

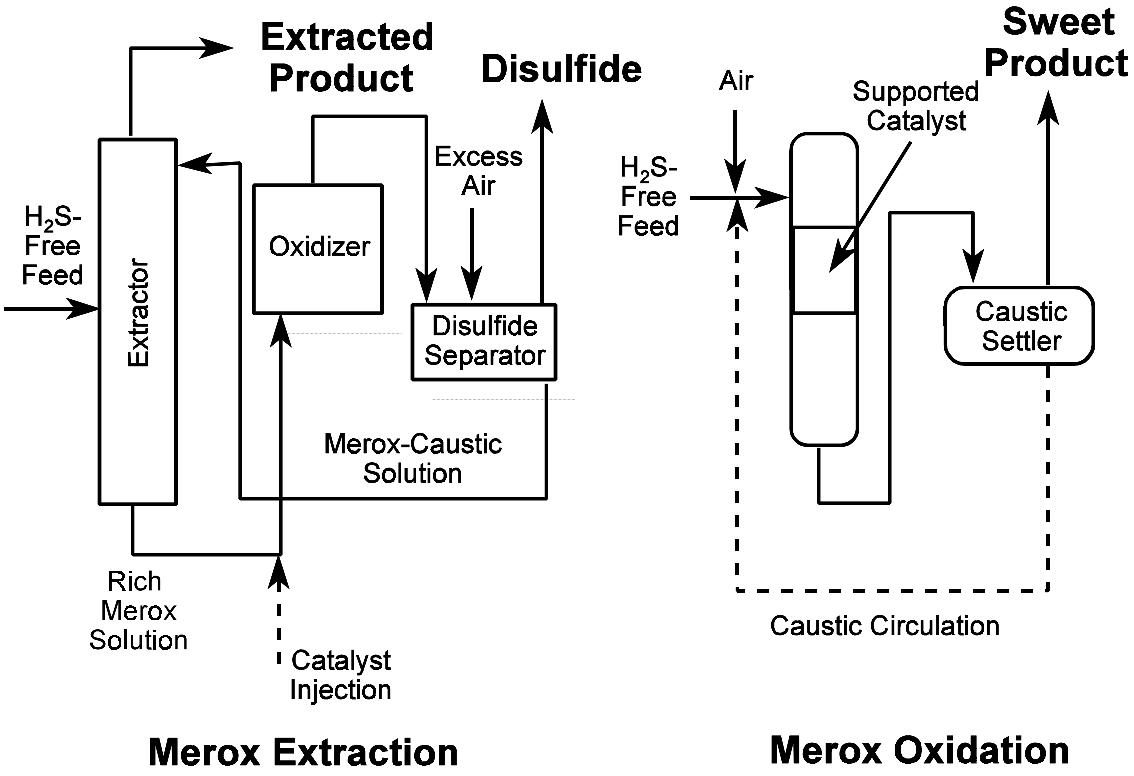

Figure 10-3. Merox Process Flow Schematic
[EPA 1997, Meyers 1997]

Key Energy and Environmental Facts - Merox Process			
Energy	***Emissions***	***Effluents***	***Wastes, Residuals, or Byproducts***
Energy use: *Not available*	*Vents and fugitive emissions (hydrogen disulfide)*	*Little or no wastewater generated*	*Spent caustic solution, waste oil-disulfide mixture*

light fractions are passed through the trays of an extraction tower. Caustic solution flows down through the extraction tower and absorbs mercaptans from the feed stream. The mercaptan-rich caustic is then regenerated by oxidizing the mercaptans to disulfide in the presence of an aqueous Merox catalyst. The lean caustic is then recirculated for re-use in the extraction tower. The disulfide is not soluble in the caustic and is separated out.

A considerable amount of the disulfides can be further treated and sent to the Claus plant as hydrogen sulfide. For example, the waste oil containing disulfides can be sent to a hydrodesulfurization unit where the sulfur can be reduced to hydrogen sulfide and then sent to the Claus plant.

Highly selective catalysts are essential for promoting the mercaptan conversion to disulfides. These proprietary catalysts are typically water soluble and are sometimes supplemented by activity promoters. A small amount of Merox catalyst is added periodically to maintain activity.

Merox oxidation utilizes a solid catalyst bed to remove mercaptans from liquid feeds and convert them directly to disulfides. The process can proceed in four ways:

- Fixed-bed processing where caustic solution is circulated intermittently
- Fixed-bed processing using continuous injection of weak caustic solution
- Caustic-free Merox using highly active catalysts in the presence of a weak base (ammonia) to produce alkalinity
- Liquid-liquid Merox where feed, air and aqueous caustic soda are simultaneously contacted in a mixing device

In all of the above except the last, the hydrocarbon stream passes through a catalyst bed and the mercaptans are oxidized to disulfide. Caustic may or may not be regenerated. The disulfide remains with the liquid hydrocarbon product, since it does not possess the characteristically unpleasant odor of mercaptans (hence the nickname, "sweetening").

The caustic-free Merox process is the latest development in this technology, and is preferable because it eliminates the purchase of caustics and costs associated with handling and disposal of spent caustics. [Process Description: EPA 1995a, Meyers 1997, OGJ 1995a]

Large Volumes of Process Water Pass Through Wastewater Treatment

Processing of crude oil requires large volumes of water, a large portion of which is continually recycled, but some of which is moderately or highly contaminated, requiring primary and secondary and sometimes tertiary treatment. Large volumes are lost as cooling tower evaporation. Total refinery flow of water currently averages from 65-90 gallons of water per barrel of crude oil processed, a substantial decrease from the 2,000 gallons per day reported in 1975 [OGJ 1992a]. Wastewaters consist of cooling water, process water, sanitary sewage treatment, and storm water.

Wastewater from various refining processes is treated by both primary and secondary processes (see Figure 10-4). In the primary process, oil, water and solids are separated in two stages. First, wastewater moves slowly through some type of separator (API separator, corrugated plate interceptor) where free oil floats to the surface and solids settle to the bottom, where they are scraped off and sent to a sludge collector. Physical or chemical methods are then used to separate the remaining emulsified oils from the wastewater. Settling tanks or dissolved air flotation (DAF) are common physical separation methods. Chemical methods employ polymers to coagulate impurities into a froth that is skimmed off the top.

Sour wastewater from distillation units and fractionators must be treated prior to the primary process by stripping in a tower with gas or steam (sour water strippers are described on page 100). After the stripping process, which removes hydrogen sulfide, other organic sulfur compounds, and ammonia, the wastewater can be discharged to the wastewater treatment plant for primary treatment (e.g., air floatation).

After primary treatment, wastewater can be discharged to a publicly owned water treatment works (POTWs) for secondary treatment or to an on-site secondary treatment plant for ultimate discharge to surface waters under a National Pollution Discharge Elimination System (NPDES) permit. A few facilities may use underground injection of wastewater streams.

Optimization of water re-use is a major consideration in the operation of most refineries. Treated wastewater can be recycled in many cases and used as process water for desalting or other refinery processes. Sour water that has been steam stripped can be used to provide make-up water for the desalter and other processes.

Usable oil is recovered during the wastewater treatment process, and is then reused or sent to oil storage tanks for reuse in the refinery as a fuel or feedstock.

In most cases a secondary treatment process is necessary for direct discharge to a surface water. This often consists of biological treatment with microorganisms which consume dissolved oil and other organic components. Air is usually added to facilitate the bio-consumption. This secondary treatment process produces a biomass sludge that must can be treated aerobically prior to dewatering. It is disposed of as a non-hazardous waste. Other secondary treatment processes include dissolved air flotation, coagulation, and settling ponds [EPA 1995a].

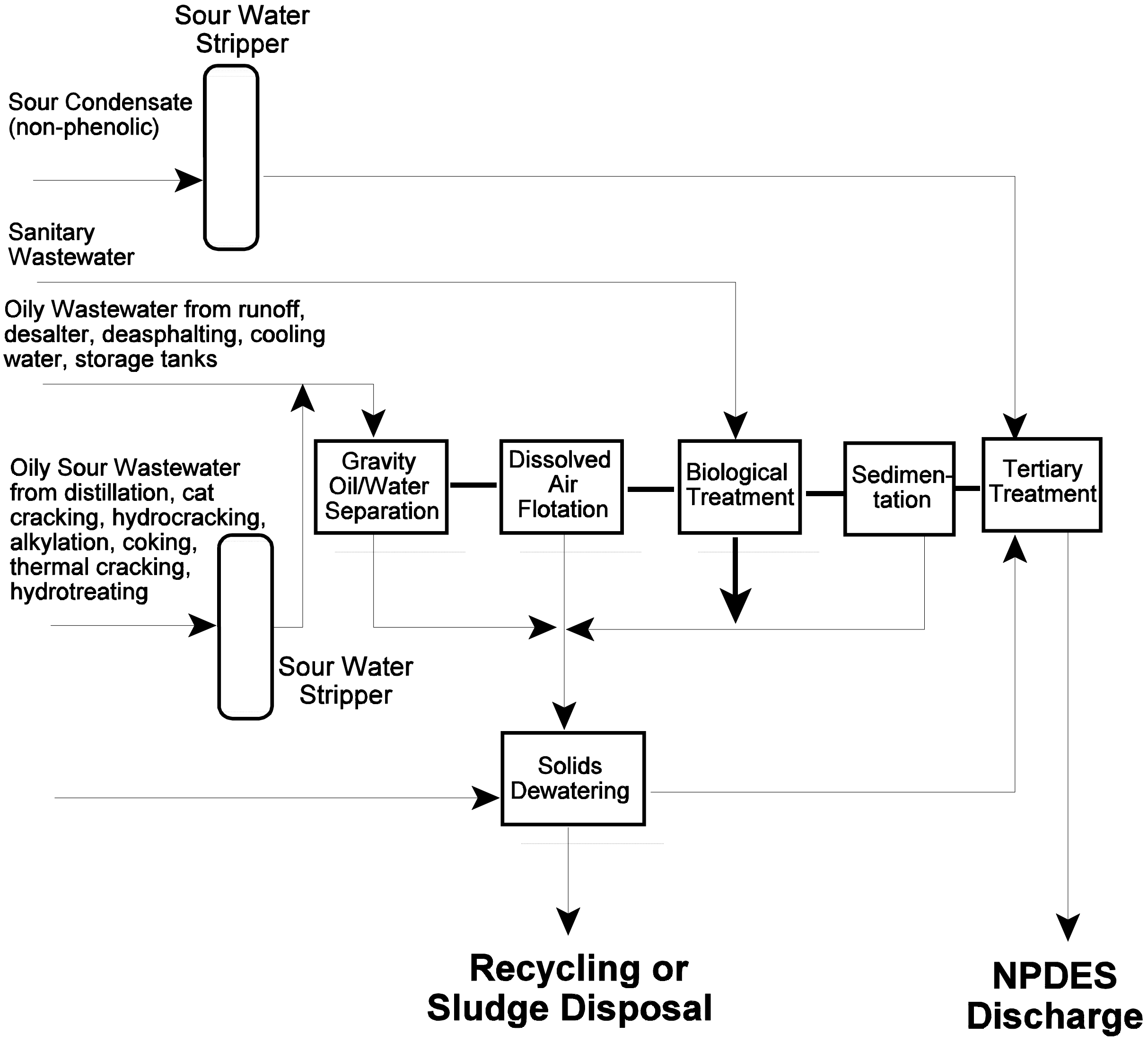

Figure 10-4. Refinery Wastewater Treatment Flow Schematic
[EPA 1995a]

Key Energy and Environmental Facts - Merox Process			
Energy	***Emissions***	***Effluents***	***Wastes, Residuals, or /Byproducts***
Energy use: *Not available*	*Fugitive emissions (hydrogen disulfide, ammonia, and hydrocarbons)*	*Not applicable*	*API separator sludge (phenols, metals and oil), chemical precipitation sludge (chemical coagulants, oil), DAF floats, biological sludges (suspended solids, metals, oils), spent lime*

Some refineries must also employ "polishing" to meet discharge limitations. Polishing involves filtering with activated carbon, anthracite coal, or sand or placement in quiescent tertiary tanks or ponds to remove any residual impurities (e.g., biomass, silt, trace metals, inorganic chemicals, and organic chemicals). Many refineries try to segregate storm water from process waters to minimize the quantity of water that requires treating.

As part of the Clean Air Act Amendments of 1990, refineries must also comply with National Emission Standards for Hazardous Air Pollutants (NESHAPS) for benzene emissions (40 CFR 61.340). Systems to control benzene emissions (benzene strippers, closed drain systems) are required for all refineries whose wastewater system contains more than a threshold amount of benzene (all large refineries).

Process Heaters Are Integrated into Every Refinery Process

Process heat from **direct-fired heaters** and **boiler steam** are necessary for nearly every process in the refinery. Steam, for example, is used for stripping petroleum fractions, among other uses. Most of the energy consumed in a refinery is used in heaters and boilers.

An integral utilities plant usually supplies the steam necessary for most refinery processes. In most cases the steam is used primarily for heating and boiling hydrocarbon streams. When used for this purpose the steam heats the petroleum indirectly and is then returned to the boiler.

In direct contact operations, the steam is used as a stripping medium or process fluid. In some applications steam may be used in vacuum ejectors to produce a vacuum.

Process heaters are used extensively throughout the refinery to supply heat to raise the temperature of feed streams to a level necessary for chemical reaction or distillation. Maximum fluid temperatures reached by process heaters are about 950°F. Air preheaters are heat exchangers that recover heat in the flue gas by heating up combustion air. They are usually applied on large heaters in areas where NOx emissions are not a severe problem. Heaters with air preheaters produce much more NOx than do heaters that use air at ambient temperatures. Steam convection section can sometimes be used to duplicate the high efficiency obtained from a heater with an air preheater.

Furnaces are also used in some cases for the incineration of effluent streams containing air pollutants, toxic chemicals, or hazardous wastes. In these specialized waste destruction furnaces, temperatures can be much higher. Excess heat from these furnaces is often recovered through heat exchange.

Boilers and process heaters exist in a wide variety of designs, and a discussion of the many possible configurations is outside the scope of this report. However, typical emission factors for these units are provided in Section 10-4.

10.2. Summary of Inputs/Outputs

The following is a summary of the inputs and outputs for various auxiliary refinery processes, including sulfur management, chemical treatment, and process heaters.

Sulfur Management

Inputs:	Outputs:
Fuel Gas/LPG	Clean Fuel Gas/LPG
Recycle Gas	Elemental Sulfur
Sour Water	Recycle Water
Amine	Recycle Acid Gas
Catalyst	Treated Tail Gas
Steam	Wastewater
Cooling Water	
Electricity	

Chemical Treatment

Inputs:	Outputs:
Sour Petroleum	Mercaptan-Free Product
Catalyst	Spent Caustic
Caustic	Caustic Wastewater
Ammonia	Ammoniated Wastewater
Cooling Water	
Air/Oxygen	
Filter Materials	
Electricity	

Water Treatment

Inputs:	Outputs:
Sour Water	Treated Water
Contaminated Water	Sulfur Compounds
Ferric or Al Oxide	Oil
Biological Agents	Hazardous Sludge
Electricity	Biomass or other Non-Hazardous Sludge

Process Heating

Inputs:	Outputs:
Fuels	Steam
Boiler Feedwater	Electricity
Cooling Water	Process Heat
	Wastewater
	Recycle Cooling Water

10.3 Energy Requirements

Energy requirements for sulfur management systems are highly dependent upon the nature and volume of feed that will be treated, and specific energy data on a per barrel basis are limited. Energy requirements for chemical treatment and water treatment also vary considerably depending upon the contaminants present and volume of feed or wastewater treated. General specific energy intensities per barrel of feed or gallon of water treated were not available.

Energy requirements for a Claus process by fuel type are shown in Table 10-1. Energy is consumed primarily in the furnace. Electricity is used to power pumps, compressors, and filtering systems.

Energy requirements for process heaters also vary considerably depending upon the fuel consumed, the age, type and efficiency of the system, auxiliary systems, heat exchange systems, and numerous other variables. Energy consumption in process heating equipment is itself a vast topic and will not be considered here.

10.4 Air Emissions

Sulfur Dioxide Is the Primary Air Emission from Sulfur Management Systems

Sulfur dioxide is the primary air emission from Claus sulfur recovery systems (excluding those in heater stack gases). Controls for these emissions include tail gas treatment processes (SCOT and Beavon) followed by incineration, or stand-alone incineration. Air emissions may also include releases from process vents and equipment leaks. Existing New Source Performance Standards (NSPS) limit sulfur emissions from Claus sulfur recovery plants of greater than 20.32 metric tons (22.4 tons) per day capacity to 0.025 percent 250 ppmv). This is comparable to the 99.9 percent level of sulfur removal achieved by oxidation or reduction control systems, followed by incineration.

Incineration oxidizes sulfur compounds, such as hydrogen sulfide, carbon disulfide, and carbonyl sulfide to form sulfur dioxide. It does not reduce the total amount of sulfur compound emissions, but does convert hydrogen sulfide into less toxic sulfur dioxide. The SCOT and Beavon processes permit recovery of additional sulfur and less production of sulfur dioxide (which is regulated under the Clean Air Act). Table 10-2 illustrates sulfur dioxide emission factors for various control options. More information is available describing the various options in the original AP 42 Background Document from the EPA [EPA 1997].

Air emissions from chemical treatment include equipment leaks and process vents on separators which may contain disulfides [EPA 1995a]. Some toxic and hazardous compounds may also be emitted as fugitive emissions during gas treatment, sulfur recovery, and chemical treatment processes. Hydrogen sulfide, carbonyl sulfide (COS) and carbon disulfide (CS_2). Toxic air emissions may include diethanolamine and other amines from amine treatment units.

Wastewater treatment plants are also a considerable source of air emissions. These emissions, which consist mostly of ammonia, hydrogen sulfide, and various hydrocarbons, arise from numerous tanks, ponds and sewer system drains throughout the water treatment plant.

Control of emissions from water treatment systems includes covering areas where emissions are greatest (oil-water separators, settling basins) and removing dissolved gases from water streams with sour water strippers and phenol recovery units before contact with the atmosphere.

Table 10-3 provides emissions factors for fugitive emissions from oil-water separators used in water treatment facilities. A more detailed discussion of water treatment emissions and their estimation can be found in AP-42, Chapter 4, Waste Water Collection, Treatment and Storage, available from the U.S. Environmental Protection Agency.

Atmospheric emissions from cooling towers are comprised of fugitive volatile hydrocarbons and gases stripped from the cooling water as the air and water come in contact. Leaking heat exchangers are typical sources for these emissions. Dissolved gases such as hydrogen sulfide and ammonia may also be present. Control of these emissions is accomplished by proper maintenance of heat exchangers and condensers. Table 10-3 provides emission factors for emissions from cooling water towers for both controlled and uncontrolled sources.

Emissions from furnaces used for process heat or steam raising include sulfur oxides (SOx), nitrogen oxides (NOx), CO, particulates, and hydrocarbon emissions. If combustion is not complete, or if heaters are fired with refinery pitch or heavy residuals, emissions can be substantial. Emission factors for combustion of fuels are shown in Table 1-11.

Table 10-1. Estimated Electricity Use in Claus Sulfur Recovery Units

Gross Energy Use[a] (103 Btu/ton of sulfur in feed[b])	Net Energy Use (103 Btu/ton of sulfur in feed)
388.5	126.2

[a] Includes losses incurred during the generation and transmission of electricity

[b] Short tons of sulfur; assumes sulfur recovery of 99.7 percent [Sulphur 1994].

Table 10-2. Sulfur Dioxide Emission Factors for Claus Units

Control Equipment	Emission Factor (lbs SO_2/tons sulfur produced)
SCOT Absorber and Incinerator Exhaust Stack	5.66
Incinerator Exhaust Stack (Claus Plant with Two Catalytic Conversion Stages)	85.9

Source: *Background Report, AP-42 Section 5.18, Sulfur Recovery*. Prepared for U.S. Environmental Protection Agency by Pacific Environmental Services, Inc., Research Triangle Park, NC. October 14, 1997.

Table 10-3. Fugitive Emission Factors for Petroleum Refineries				
Emission Source	**Emission Factor Units**	**Emission Factors**		**Applicable Control Technology**
		Uncontrolled	**Controlled**	
Cooling Towers	lb/10^6 gal cooling water	6	0.7	Minimization of hydrocarbon leaks into cooling water system; monitoring of cooling water for hydrocarbons
Oil/water Separators	lb/10^3 gal wastewater	5	0.2	Covered separators and/or vapor recovery systems

Source: *AP 42, Chapter 5, Petroleum Industry*, Environmental Protection Agency, January 1995. [Based on limited data]

Control systems for industrial boilers and process heaters depend on the primary fuel used. Those systems burning cleaner fuels like refinery gas, natural gas, and LPG are concerned more with control of NOx than other emissions. The most prevalent NOx control techniques applied are low NOx burners and flue gas recirculation. Post-combustion techniques for control of NOx include selective noncatalytic reduction and selective catalytic reduction [EPA 1996].

In boilers combusting fuel oils or refinery oil byproducts (heavy resids, coke, refinery pitch), a variety of control techniques may be employed, depending on the fuel type. Particulates are typically controlled by post combustion techniques (e.g., mechanical collectors, electrostatic precipitators). Sulfur oxides are also controlled by post combustion methods, primarily flue gas desulfurization with an alkaline reagent. Control of nitrogen oxides is achieved through the use of low excess air, biased-burner firing, flue gas recirculation, overfire air, and low NOx burners. Post-combustion controls are similar to those used for natural gas [EPA 1996b].

Considerable amounts of organic compounds, including volatile organics, semi-volatile organics, and condensible organics are emitted by boilers utilizing fuel oils, although these comprise a very small share of refinery boilers. The source of these compounds is unburned hydrocarbons, emitted as aliphatic, oxygenated and low molecular weight aromatic compounds which exist in the vapor phase at flue gas temperatures. Emissions include alkanes, alkenes, aldehydes, carboxylic acids, and substituted benzenes (e.g., benzene, toluene, xylene, and ethyl benzene). Formaldehyde and polycyclic organics can be emitted in the condensed or vapor phase [EPA 1996b].

Trace metals are emitted from the combustion of oils, many of which may be hazardous air pollutants under Title III of the 1990 Clean Air Act Amendments. The quantity of trace metals emitted depends on combustion temperature, fuel feed mechanisms, and the composition of the fuel, and emission factors can vary widely. A good discussion of these metals and their emission factors can be found in *AP-42, Chapter 1-3, Fuel Oil Combustion*, available from the Environmental Protection Agency [EPA 1996].

10.5 Effluents

Effluents Include Oily Wastewater from Cleaning of Heat Exchangers

Gas treatment and sulfur recovery generate some process wastewater containing hydrogen sulfide, ammonia and amines. Little or no wastewater is generated from chemical treatment. Caustic wash water used in these systems is typically recycled.

Cleaning of heat exchangers used throughout the refinery to heat or cool process streams generates some residuals. Heat exchangers consist of bundles of pipes, tubes, plate coils, or steam coils enclosing heating or cooling water, steam or oil to transfer heat indirectly to process streams. These bundles are cleaned on a regular basis to remove scales, sludge, and oily residues. The cleaning process generates an oily wastewater that is sent to water treatment for oil separation.

10.6 Waste, Residuals and Byproducts

Spent Caustic Solution, Trace Metals, and Wastewater Treatment Sludge May be Hazardous

Gas treatment and sulfur recovery processes produce spent catalysts that may or may not be hazardous, depending on catalyst type. The Merox extraction process generates a waste oily disulfide stream. Sulfur in this stream is often converted to hydrogen dissulfide which is then sent to the Claus plant. Spent caustic is also generated as a byproduct of the Merox process.

Since chromium has been almost eliminated as a cooling water additive, sludges generated from the cleaning of heat exchanger tubes no longer account for a significant portion of hazardous wastes from refineries. Heat exchanger bundle cleaning sludge was reported to be about 1000 wet tons in 1991 [API 1991].

The EPA classifies a number of residuals from the petroleum refining industry as hazardous waste under Title 40 Code of Federal Regulations (CFR) Part 261.32. However, most of these residuals, and several others, are not considered hazardous waste if they are recycled in the refining process. Several of these residuals are associated with wastewater treatment processes, and are summarized in Table 10-4 [BNA 1992]. These include API separator sludge, primary treatment sludge, sludges from various gravitational separation units, and float from dissolved air flotation units.

Table 10-4. Hazardous Wastes Associated with Sludge/Water Treatment Processes

EPA Waste Classification	Summary Description	Hazardous Constituents
F037	Petroleum refinery primary oil/water/solids separation sludge - Any sludge generated from the gravitational separation of oil/water/solids during the storage or treatment of process wastewaters and oily cooling waters from petroleum refineries	Benzene, benzo(a)pyrene, chrysene, lead, chromium
F038	Petroleum refinery secondary (emulsified) oil/water/solids separation sludge from physical and/or chemical separation of process wastewaters and oily cooling waters	Benzene, benzo(a)pyrene, chrysene, lead, chromium
K048	Dissolved air flotation float	Hexavalent chromium, lead
K049	Slop oil emulsion solids	Hexavalent chromium, lead
K051	API separator sludge	Hexavalent chromium, lead

Source: Bureau of National Affairs, Hazardous Waste Criteria, 161:2217 (S-1006), 1995. Federal Register Vol. 63, Number 151, August 6,1998.

Table 10-5. Waste Generation Associated with Water Treatment at U.S. Refineries (1000 wet tons)

Effluent/Waste Stream	1995	1994	1991	1989
Biomass	582	773	855	642
Contaminated soils/solids	525	661	809	512
DAF Float (K048)	164	355	406	496
Pond Sediments	65	143	372	313
API Separator Sludge (K051)	37	101	210	419
Primary sludges (F038 and F037)	128	328	307	--

Source: Management of Residual Materials: 1995 - Petroleum Refining Performance, API Publication 339, June 1997 and The Generation and Management of Residual Materials: 1991 -- Petroleum Refining Performance, API Publication 329, May 1994. American Petroleum Institute.

Management of those residuals that are not recycled may be accomplished by incineration, chemical fixation, neutralization and other treatment methods. Table 10-5 illustrates trends in generation of wastes from water treatment over the last decade.

Water treatment is also responsible for some of the toxic releases reported by the refining industry, notably ammonia. Ammonia is a component of the sour water generated in the water distillation unit and from side steam strippers or fractionators. Ammonia ranks second on the list of toxic chemicals released from refineries in 1996 [EPA 1998]. About 60 percent of ammonia releases from refining occur as the result of treated wastewater discharges (to surface waters and through underground injection) [EPA 1995b].

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