

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



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Prepared for
U.S. Department of Energy
Industrial Technologies Program



Acknowledgements

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Table of Contents

Acknowledgements	2
Table of Contents	3
1 Overview	5
1.1 Petroleum Refining: An Essential and Volatile Industry	5
1.2 Market Trends and Economic Statistics	9
1.3 Energy and Materials Consumption	19
1.4 Environmental Overview	22
2 The Integrated Petroleum Refinery	39
2.1 Overview	39
2.2 Energy Overview	42
2.3 Environmental Overview	43
3 Separations: Atmospheric and Vacuum Distillation	48
3.1 Distillation Process Overview	48
3.2 Energy Requirements	53
3.3 Air Emissions	54
3.4 Effluents	54
3.5 Waste, Residuals and By-products	56
4 Cracking and Coking Processes	57
4.1 Cracking and Coking Process Overview	57
4.2 Energy Requirements	67
4.3 Air Emissions	70
4.4 Effluents	71
4.5 Waste, Residuals and By-products	73
5 Catalytic Reforming	74
5.1 Catalytic Reforming Process Overview	74
5.2 Energy Requirements	76
5.3 Air Emissions	77
5.4 Effluents	78
5.5 Waste, Residuals and By-products	78
6 Alkylation	117
6.1 Alkylation Overview	117
6.2 Energy Requirements	121
6.3 Air Emissions	122
6.4 Effluents	123
6.5 Waste, Residuals and By-products	123
7 Hydrotreatment	117
7.1 Hydrotreatment Overview	117
7.2 Energy Requirements	119
7.3 Air Emissions	120
7.4 Effluents	120
7.5 Waste, Residuals and By-products	121
8 Additives & Blending Components	117
8.1 Additives and Blending Components Overview	117
8.2 Energy Requirements	123
8.3 Air Emissions	126

8.4	Effluents	127
8.5	Hazardous and Toxic Residuals	127
9	Lubricating Oil Manufacture.....	117
9.1	Lubricating Oil Manufacture Process Overview.....	117
9.2	Energy Requirements	126
9.3	Air Emissions	127
9.4	Effluents	127
10	Supporting Processes: Sulfur Management, Chemical Treatment, Water Treatment, & Process Heating.....	128
10.1	Overview of Auxiliary Processes.....	128
10.2	Energy Requirements	137
10.3	Air Emissions	137
10.4	Effluents	139
10.5	Waste, Residuals and By-products.....	139
	BIBLIOGRAPHY	141

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 (Btu), the Nation relies on petroleum two times more than either coal or natural gas, and four times more than nuclear power, hydroelectricity, and other renewable energy sources. On average, every U.S. citizen consumes about 20 pounds of petroleum per day. This primary dependence on petroleum for energy has been a reality for decades, and despite the influx of potential alternative fuels, is predicted to continue well into the future [DOE 2006c].

Before petroleum can be used it must be “refined” into products with the desired properties. This occurs in **petroleum refineries**, where various physical and chemical methods are used to convert crude oil into a large array of useful petroleum products. Petroleum refineries are considered to be part of the U.S. manufacturing sector and are an essential component of the economy. In addition to the millions of Americans who depend on petroleum fuels to enable them to get to work and have a decent quality of life, there are also nearly 2 million jobs associated with the infrastructure for production, refining, and distribution of petroleum fuels [Vision 2020].

Petroleum Refining

The U.S. Petroleum Refining Industry

- *Produces fuels to power land, air and sea transport and heat homes and businesses*
- *Provides petrochemical building blocks for plastics and other consumer products*
- *Manufactures products for use in buildings and infrastructure, such as asphalt and roofing materials*

Over the last three decades, petroleum and refined petroleum products have become one of the most traded commodities in the world. The petroleum industry in general has a volatile history, and trading of crude oil continues to be a subject of controversy and uncertainty in global markets. The results of uncertainty are felt throughout the petroleum refining industry, impacting profitability, capacity utilization, and the price and supply of refined products.

Geopolitical Disruptions have Dramatically Impacted U.S. Refiners for Three Decades

Despite being one of the world’s largest producers of petroleum, the United States relies heavily on imports to meet consumer and industrial demand for petroleum products. This reliance on international trade has led to numerous upheavals in the petroleum industry over the last three decades.

In 1973, Arab nations angry about the United States’ 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 a spike in prices and short-term shortages in refined petroleum products. When the embargo was lifted 6 months later, world crude oil prices had tripled and the Organization of Petroleum Exporting Countries (OPEC) was in control of the world oil market.

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, such as 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. This 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 a crude

distillation capacity of less than 30,000 barrels per day. Between 1973 and 1981, the number of operable refineries in the United States rose from 281 to a record high of 324 and 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 United States were at a record high prior to this period. The resulting efforts to supply consumers around the world pushed 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.

The spike in oil prices in the early 1970s and higher oil prices of the early 1980s decreased U.S. consumption of petroleum products and increased the focus on energy conservation and fuel switching. Efforts to improve energy efficiency and switch from petroleum to less costly fuels were undertaken, and electric utilities displaced significant amounts of distillate and residual fuel oil with coal and natural gas for power generation. Other fuels began to replace petroleum in industrial processes, and motors and appliances became more efficient. As a result, in 1983 the U.S. demand for petroleum dropped to its lowest level since 1971.

Major Domestic and World Events Impacting Petroleum Refining Over Three Decades

1970	<i>Clean Air Act Amendments of 1970</i>
1973	<i>Arab Oil Embargo</i>
1973	<i>Emergency Petroleum Allocation Act</i>
1975	<i>Energy Policy and Conservation Act</i>
1976	<i>Resource Conservation and Recovery Act</i>
1977	<i>Airline Deregulation Act</i>
1977	<i>Department of Energy Organization Act</i>
1978	<i>Powerplant and Industrial Fuel Use Act</i>
1978	<i>Iranian Revolution</i>
1980	<i>Comprehensive Environmental Response, Compensation & Liability Act (CERCLA)</i>
1981	<i>Petroleum price/allocation decontrol</i>
1985	<i>Clean Water Act</i>
1986	<i>Collapse of crude oil price</i>
1986	<i>Emergency Planning & Right to Know Act</i>
1989	<i>Reid Vapor Pressure Regulations</i>
1990	<i>Clean Air Act Amendments of 1990</i>
1991	<i>Persian Gulf Crisis of 1990-1991</i>
1990	<i>Oil Pollution Liability & Compensation Act</i>
1992	<i>Reid Vapor Pressure Regulations</i>
1992	<i>Energy Policy Act</i>
1995	<i>Reformulated Gasoline</i>
2001	<i>9/11 Attacks</i>
2003	<i>Iraq War</i>
2005	<i>EPA Act 2005</i>
2005	<i>Hurricane Katrina</i>
2005	<i>Record crude oil prices</i>
2006	<i>Ethanol Fuel Mandates</i>
2006	<i>Continued Middle Eastern Conflict</i>

Full decontrol of prices and supplies in the industry in 1981 meant that for the first time since the early 1970s market forces determined prices, which rose to market-clearing levels. Small refineries and less efficient plants could not compete and began to shut down. Between 1981 and 1985 the number of refineries in the United States dropped from 324 to 223.

The industry was shaken again by the collapse of crude oil prices in 1986, primarily the result of free market forces and a true equilibrium of supply and demand (i.e., increased production in a market with weakening demand). In late 1985 Saudi Arabia, having increased production to capture greater market share, offered netback pricing which tied crude oil prices to the value of refined products and guaranteed specific margins to refiners. Other OPEC members subsequently increased production and offered similar pricing arrangements to maintain market share and offset declining revenues. The resulting glut of

crude oil in world markets caused prices to begin to fall.

The 1986 collapse of crude oil prices reversed the increase in domestic production that had begun in the early 1970s, and many high cost wells became unprofitable and were shut down. After world oil prices fell by more than 50 percent, 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 declined. Declining production resulted in an increase in crude oil imports. U.S. crude oil imports have continued to increase, from 32% of total supply in 1986, to 54% in 1996, and now 66% in 2006 [DOE 2006d].

Between 1990 and 2003, world spot prices for a barrel of oil ranged from as low as \$10 a barrel to nearly \$30 a barrel [DOE 2006e]. During that period a number of political and military events occurred in the Middle East and Asia that could potentially impact oil supply and price (Taiwan Strait Crisis, 1996; Operation Desert Strike, 1996; Operation Desert Fox, 1998; others). In 1991, the Persian Gulf War, precipitated by the invasion of Kuwait by Iraq, began a long period of uncertainty and unrest in the Middle East that would be further complicated by the fear of weapons of mass destruction and the increased influence of radical terrorist organizations. As a result, the period from the start of the Gulf War through the terrorist attack of September 11, 2001 was a period of relative volatility for the U.S. oil industry in terms of price and supply.

A pattern in oil futures trading emerged: prior to a crisis, oil futures costs would escalate due to the uncertainty of the future availability of oil (“war premium” added to oil costs); following the military response or political intervention, fears of future uncertainty would be somewhat alleviated and prices would stabilize, sometimes within relatively short periods of time. This pattern continued through the 2003 Iraq war: oil markets prior to the 2003 conflict were generally strong; in February 2003, fears that a conflict in Iraq could damage oil fields and supply in some Arabian Gulf states pushed prices to nearly \$40 per barrel. With the impending war just days or hours away, optimism about a quick resolution to the conflict led traders to go short, expecting prices to fall following the onset of war. Expectation of increasing exports from Venezuela fueled optimism, and prices dropped dramatically to \$22-\$28 per barrel within a very short time. A similar drop (by one-third, or about \$10 per barrel) was experienced on January 17, 1991, the start of the Gulf War [CCC 2003].

While oil production in Iraq is still below pre-war levels, it has been improving steadily. The Iraq conflict and events that could impact world oil prices are monitored by the U.S. Department of Energy, and more details can be found in their country analysis for the Middle East [DOE 2006g]. Continued tensions in other Middle East countries, including the recent conflict between Israel and Lebanon, have increased fears that other countries in the region will be drawn into a war and supply shortages will result. Iran, for example, has indicated it would use an export supply cut-off similar to that of 1979 during the Iranian Revolution if threatened [AP 2006, MSNBC 2006, MEES 2006]. In today’s complex global oil market, however, geopolitics is only one of many factors impacting oil price volatility.

Increasing World Demand, Tight Capacity, Natural Disasters, and Speculation are all Contributing to Record High Oil Prices

World oil spot prices have risen to record highs in the last decade, from \$16.63 per barrel in 1995 to \$49.87 per barrel in 2005. The average spot price in 2006 was \$60.32 per barrel, and the average 2007 spot price through October 2007 has increased to over \$65 per barrel. Oil producing countries around the world are generating record revenues and quarterly profits, contributing to higher rates of economic growth. The low profit margins of the 1990s are history for most petroleum producers and refiners. A number of factors not related to geopolitical issues are contributing to the unprecedented rise in prices.

World demand for petroleum products continues to climb, especially in developing countries. Historically, high prices reduce demand; however, if the increase in oil prices is gradual and predicted, demand reduction may not occur. High oil prices may also not lead to reduced demand if government expenditures rise at the same time to encourage economic growth. In the last three years, the increase in government expenditures in OECD countries was unprecedented, especially in the United States, and as a result our economy, as well as the economies of India, China, and others, continues to grow at high rates despite the burden of high energy prices [MEES 2006, DOE 2006f]. Low interest rates also contribute to economic growth and countering the impacts of high oil prices.

Many oil-producing countries are now operating with limited **spare capacity** for both oil production and refined products. With the exception of Saudi Arabia, OPEC producers are producing at the limits of capacity. When OPEC countries do not have excess marketable production capacity, they are much more limited in their ability to influence oil prices. The inability to increase production to meet rising demand is increasingly adding premiums to the price of oil.

Natural disasters such as hurricanes, earthquakes and tornados can have an impact on oil prices as well as refinery operations. This is particularly true for operations in the Gulf of Mexico region, which accounts for nearly 30 percent of U.S. offshore oil production and almost 50 percent of U.S. refinery capacity. Also, about 24 percent of the crude oil imported into the U.S. enters the country through Gulf Coast ports. In 2005, Hurricane Katrina shut down the equivalent of 30 percent of Gulf oil production, after which spot prices for oil worldwide rose to nearly \$60 per barrel. Refineries operating along the Texas and Louisiana coastline were also significantly impacted. The widespread devastation of Katrina has escalated trading uncertainties, particularly during hurricane season [DOE 2005a].

Hedge funds and other speculators are significant players in the oil market worldwide and could be impacting prices, though the exact degree of impact is uncertain. The rapid run-up in crude oil prices over the past several years (see Figure 1-1) has been partially attributed to the increased investment in energy markets worldwide. The International Monetary Fund reported that over the past three years approximately \$100-\$120 billion has been invested in energy commodity markets worldwide and about \$60 billion has been invested in oil futures on the New York Mercantile Exchange (NYMEX) [Senate 2006]. Oil futures prices have traded for over \$90 per barrel in 2007. It has been estimated that price speculation has bumped crude oil prices up by about \$20 per barrel [NW 2006, CNN 2006, Senate 2006].

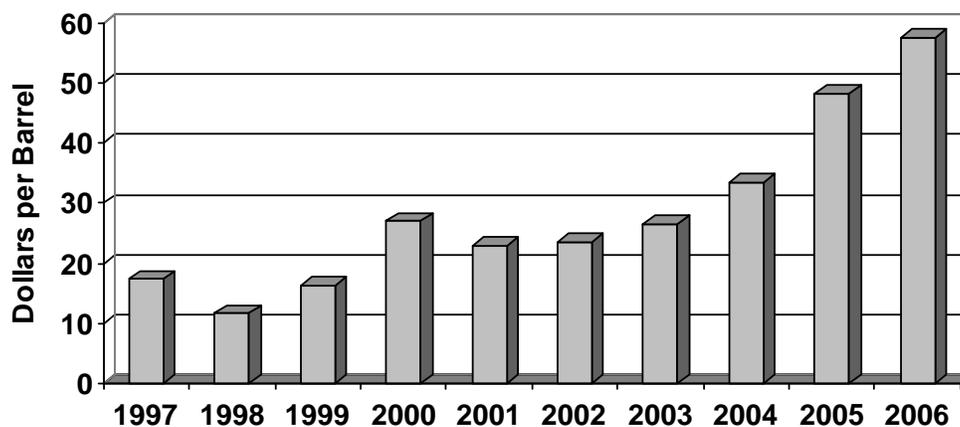


Figure 1-1. Median U.S. Crude Oil Spot Price, by Estimated Import Volume [DOE 2006f]

Terrorism and Energy Security Create New Challenges for Today's Petroleum Refiners

Since the 1990s, refineries have been dealing with the economic realities of crude quality variability and the need for increased flexibility, greater throughput, higher conversion, greater process efficiency, reduced operating costs, and greater reliability. During the 1990s and into the new century, persistently low profits prompted domestic refiners to pursue greater value from their existing fixed assets while reducing operating costs and improving efficiency. Today, refiners are enjoying higher profit margins but also face increasing costs of safeguarding facilities, workers, nearby communities, and neighbors from the threat of terrorism. Refiners and petrochemical manufacturers have been voluntarily spending billions to improve plant security [HP 2006c, NPRA 2006a], though despite industry efforts, many of the investments have been made by the largest producers and not necessarily the most vulnerable sites.

In early 2006, chemical facility security legislation was introduced into the U.S. House of Representatives (House) and U.S. Senate (Senate) that would have given the U.S. Department of Homeland Security (DHS) the authority to tell facility owners and operators, including those of petroleum facilities, which processes and technologies could and could not be used [NPR 2006a]. While the legislation did not pass, in October 2006 DHS was authorized as part of its Fiscal Year (FY) 2007 budget appropriations to regulate chemical facility security for three years and establish risk-based standards and regulations for chemical facilities, including refineries [NPR 2006a]. The chemical security program would require facilities to conduct security vulnerability assessments, develop facility security plans, and submit these to DHS for approval.

Although the refining and petrochemical industries support establishing plant security standards, the general consensus is that the federal government should build upon the strong public-private partnership that currently exists between industry and DHS. Legislation such as that introduced in 2006 could create an adversarial relationship and slow efforts to maintain and expand facility security [NPR 2006a]. To date, industry has taken the lead and collaborated with DHS and other federal agencies to develop guidelines for improving security within plants and at offshore operations [API 2006f]. Although the creation and enforcement of uniform security procedures will likely be a long process, the American Petroleum Institute, National Petrochemical and Refiners Association, and member companies are dedicated to working with the federal government to ensure the safety and security of the Nation's energy supply.

1.2 Market Trends and Economic Statistics

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

The United States is one of the largest, most sophisticated producers of refined petroleum products in the world, along with Western Europe and Asia (see Table 1-1). In 2003, U.S. refinery production accounted for about 23 percent of world production. However, over the last decade Asia and Oceania supplanted the United States with the largest refining capacity worldwide by increasing production capacity by 4.4 million barrels per day since 1995 (a nearly 30% increase). At the end of 2005, there were 142 operating refineries in the United States with 17.3 million barrels per day of crude distillation capacity [DOE 2006a].

Petroleum refining provides the U.S. market with many high-paying jobs. According to the U.S. Department of Commerce, 40,647 production workers were employed by the refining industry in 2004 [DOC 2004], and the average hourly wage for production workers in petroleum refining was \$31.8 per hour, the highest wage paid to production workers in the nation. By comparison, the next most highly

paid workers (transportation equipment and chemicals manufacture) received an average wage of about \$23 per hour). In addition to the workers employed directly by refineries, there are an estimated nearly 2 million workers employed in distributing petroleum products nationwide [Vision 2020]. Despite the high wages of refinery employees, oil companies are facing a serious technical human resource shortage that could interfere with future capital investment programs [HP 2006b]. In the near term, companies are bringing more engineers out of retirement. Long-term efforts to make the petroleum industry more attractive to young engineers include summer internships, scholarships, and company-university research programs.

Table 1-1. World Output of Refined Petroleum Products—2003		
Country/Continent	Production (thousand barrels per day)	Percentage (%) of World Production
North America		
Canada	2,154	2.8
Mexico	1,410	1.8
United States	17,794	22.8
Central and South America	5,945	7.6
Europe	16,278	20.8
Eurasia	5,608	7.2
Middle East	6,379	8.2
Africa	2,709	3.4
Asia and Oceania	19,803	25.4
WORLD TOTAL	78,080	100.0

Source: U.S. Department of Energy, Energy Information Administration, *International Energy Annual 2004*.

Petroleum products also provide a significant contribution to the gross domestic product (GDP). In 2004, the value of shipments from petroleum refineries totaled about \$300 billion (including lube oil manufacture). Petroleum products are the most heavily taxed commodity in the market; taxes on gasoline sales, for example, can represent as much as 20 percent of market price [DOE 2006q]. In addition to federal taxes, individual states, counties, and cities may also levy sales and other taxes on gasoline. Despite what appears to be a large tax bite, gasoline taxes in the United States are considerably lower than in other developed countries such as the United Kingdom, where taxes account for approximately 60 percent of the pump price [CPC 2006].

The United States of America is the world's largest energy producer, consumer, and net importer. In 2006 the US consumed 20.6 million barrels of crude oil per day, almost three times more than second largest crude oil consumer, China (7.3 million barrels per day)[DOE 2006g]. The US economy is heavily impacted by variations in crude oil price. Maintaining sufficient domestic refining capacity is a critical factor in predicting the value of crude oil in the US. The trend towards increased imports of finished petroleum product is considered by many to have a detrimental effect on our economy. Gasoline imports have doubled since 2000, from 527 thousand barrels per day in 2000 to 1137 thousand barrels per day in 2006 [DOE 2006d].

More than 60 Percent of Crude Oil and Petroleum Inputs to Refineries are Imported

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. The supply of refined petroleum products has increased by more than 3 million barrels per day in the decade since 1995 (see Table 1-2), to over 20 million barrels per day in 2004. Imports have continued to increase, averaging over 66 percent of total volume during the first six of months of 2006 [DOE 2006d].

Table 1-2. Overview of Petroleum Supply (million barrels per day)						
Year	Domestic Crude Oil and Plant Liquids Production and Stocks	Foreign Trade				Refined Petroleum Products Supplied (% Imports)
		Crude Oil Imports	Petroleum Product Imports	Total Imports	Total Exports	
1995	9.59	7.23	1.61	8.83	0.95	17.72 (49.8)
1996	9.67	7.48	1.92	9.40	0.98	18.23 (51.6)
1997	9.61	8.23	1.94	10.17	0.90	18.62 (54.6)
1998	9.39	8.71	2.00	10.71	0.84	18.92 (56.6)
1999	9.18	8.73	2.12	10.85	0.82	19.52 (55.6)
2000	9.21	9.07	2.39	11.46	0.99	19.70 (58.2)
2001	9.07	9.33	2.54	11.87	0.95	19.65 (60.4)
2002	9.11	9.14	2.39	11.53	0.98	19.76 (58.4)
2003	8.85	9.67	2.60	12.27	1.01	20.03 (61.3)
2004	8.88	10.04	2.86	12.90	1.02	20.52 (62.9)

Source: *Annual Energy Review 2004*. U.S. Department of Energy, Energy Information Administration, August 2005.

Imports of crude have steadily risen over the last ten years (see Figure 1-2), and net imports of crude and petroleum products reached an estimated record high average of 10 million barrels per day in 2004, up over 600,000 barrels per day compared with 2003. Some of the increase can be attributed to the need to rebuild industry stocks of crude oil, and the demand for gasoline and other products outstripping domestic production and tight refining capacity (high utilization rates) have also resulted in much higher imports of products. The import situation is exacerbated by increasing environmental restraints and costs, which greatly inhibit the construction of new facilities to expand the Nation's distillation capacity [HP 2005e].

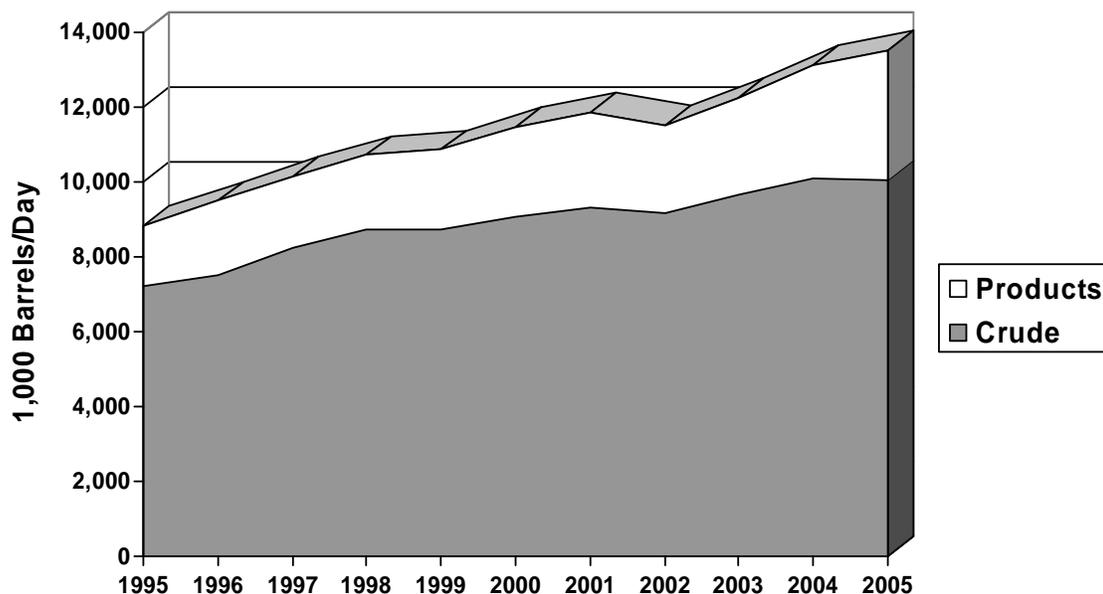


Figure 1-2. Imports of Crude and Petroleum Products [DOE 2006k]

However, imports of refined products also depend on competition in the marketplace between domestic and foreign refiners, and petroleum demand has grown rapidly in Eastern Europe and Asia. While it might be expected that increased competition from these markets would have a detrimental

effect on U.S. prices and imports, these nations are adopting the same quality standards as the developed world, which may have the opposite effect and lead to a larger supply of products by encouraging refineries worldwide to become more sophisticated and able to provide products suitable for the U.S. market [DOE 2006c].

The United States relies on crude oil and petroleum product imports from many countries. Imports from the Organization of Petroleum Exporting Countries (OPEC) (primarily Saudi Arabia, Nigeria, and Venezuela) have declined over the last decade from approximately 48 percent to around 41 percent of U.S. imports (See Table 1-3). Mexico, Canada, and other countries comprise the remainder of imports.

Exports of refinery products include fuel oils (distillate and residual), finished motor gasoline, and petroleum coke, which represents the largest share (about 30 percent of total exports). In 2005, crude oil and refined product exports totaled 425 million barrels and three countries—Mexico (23 percent), Canada (15 percent), and Japan (5 percent)—represented the largest shares [DOE 2006p].

Table 1-3. U.S. Crude Oil and Petroleum Products Imports (Thousand Barrels per Day)				
Year	Persian Gulf ^a	OPEC	Non-OPEC	Total (% OPEC)
1995	1,573	4,231	4,604	8,835 (48%)
1996	1,604	4,211	5,267	9,478 (44%)
1997	1,755	4,569	5,593	10,162 (45%)
1998	2,136	4,905	5,803	10,708 (46%)
1999	2,464	4,953	5,899	10,852 (46%)
2000	2,488	5,203	6,257	11,459 (45%)
2001	2,761	5,528	6,343	11,871 (47%)
2002	2,269	4,605	6,925	11,530 (40%)
2003	2,501	5,162	7,103	12,264 (42%)
2004	2,493	5,701	7,444	13,145 (43%)
2005	2,298	5,508	8,019	13,527 (41%)

^a A subcategory of OPEC countries composed of Iran, Iraq, Kuwait, Qatar, Saudi Arabia, and United Arab Emirates
Source: U.S. Department of Energy, Energy Information Administration, *Petroleum Navigator: U.S. Imports by Country of Origin*, Updated 12 June 2006, <http://www.eia.doe.gov>.

Fuels Account for Approximately 90 Percent of Refinery Products

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 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. The second category of petroleum products is comprised of **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 1-3). Distillate and residual fuels comprise the next largest share, with about 25 percent of refinery production.

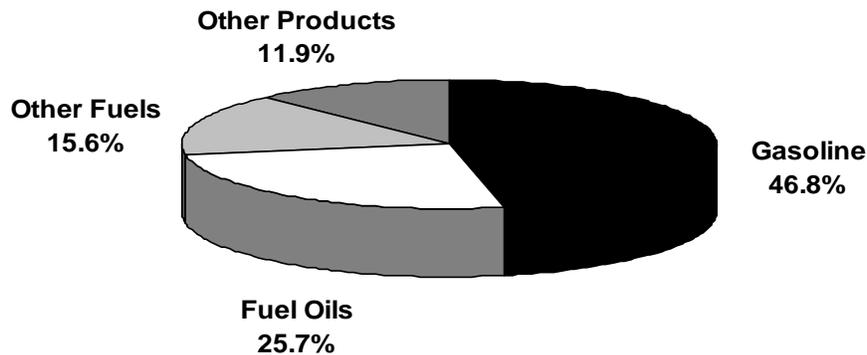


Figure 1-3. Refinery Outputs 2005 [DOE 2006m]

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 1-4 [DOE 2002, DOE 2003c, DOE 2004, DOE 2005c, DOE 2006m].

Table 1-4. Supply of U.S. Refined Products (Million barrels)					
	2005	2004	2003	2002	2001
Natural Gas Liquids and LRG	117.4	111.1	100.9	113.3	128.3
Finished Products					
Gasoline	209.7	219.0	208.1	210.6	211.5
Special Naphthas	1.5	1.8	2.1	2.0	2.0
Kerosene	5.1	4.9	5.6	5.5	5.4
Distillate Fuel	136.0	126.3	136.5	134.1	144.5
Residual Fuel	37.4	42.4	37.8	31.3	41.0
Kerosene Jet Fuel	41.7	40.1	38.8	39.1	41.9
Naphtha Jet Fuel	0.0	0.0	0.02	0.06	82.0
Unfinished Oils	85.7	81.4	75.9	75.8	87.7
Other Refined Products ^a	54.9	56.5	55.3	59.4	61.8
TOTAL	689.4	683.5	661.0	671.2	806.1

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

Sources: DOE 2002, DOE 2003c, DOE 2004, DOE 2005c, DOE 2006m.

The principal classes of refining products along with their typical boiling ranges and uses are shown in Table 1-5. Within each product category 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.

Table 1-5. Major Petroleum Products		
Product	Boiling Range (°F)	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

U.S. Petroleum Refining Capacity Is Located in Coastal Regions

Most refineries are concentrated on the West and Gulf coasts, primarily because of access to major sea transportation and shipping routes. Figure 1-4 shows the geographic distribution of operating petroleum refineries (as of January 1, 2006) 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 30 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 [DOE 2006a].

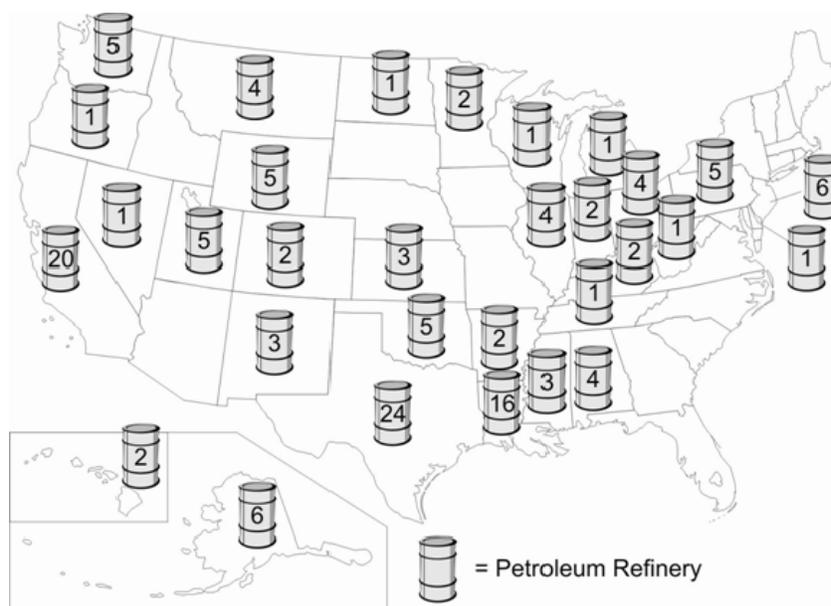


Figure 1-4. Petroleum Refineries Operating in the United States
[Source: DOE 2006a]

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 1-6 provides data on

the distillation and downstream charge capacity of U.S. refineries over the last 10 years. Table 1-7 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.

Year	Atmospheric Crude oil Distillation	Vacuum Distillation	Thermal Crack- ing	Catalytic Cracking		Catalytic Hydro- cracking	Catalytic Reform- ing	Catalytic Hydro- treating	Fuels Solvent De-asphalting
				Fresh	Recycle				
1995	16,326	7,248	2,123	5,583	169	1,386	3,867	10,916	251
1997	16,287	7,349	2,050	5,595	155	1,388	3,727	11,041	275
1999	17,155	7,538	2,046	5,920	153	1,552	3,779	11,461	319
2000	17,393	7,617	2,163	5,949	99	1,576	3,770	11,440	351
2001	17,511	7,798	2,277	5,983	86	1,615	3,797	11,673	350
2002	17,676	7,779	2,329	5,989	80	1,633	3,753	11,845	362
2003	17,675	7,788	2,377	6,052	79	1,644	3,777	11,987	350
2004	17,815	7,964	2,435	6,098	87	1,602	3,812	13,501	366
2005	18,031	8,120	2,491	6,151	87	1,624	3,836	14,087	384
2006	18,308	8,398	2,540	6,188	87	1,637	3,859	14,808	386

Source: *Refinery Capacity 2006*. U.S. Department of Energy, June 2006.

Year	Alkylates	Aromatics	Asphalt & Road Oil	Isomers	Lubricants	Marketable Petroleum Coke	Hydrogen (MMcfd)	Sulfur (short tons/day)
1995	1,105	285	846	502	217	427	3,139	24,885
1997	1,120	288	872	577	244	458	3,052	26,466
1999	1,172	302	846	667	233	441	3,104	26,423
2000	1,185	315	886	643	218	464	3,143	26,645
2001	1,191	318	900	654	214	538	3,230	27,446
2002	1,181	313	917	658	218	548	3,244	29,107
2003	1,191	316	873	679	216	646	3,265	29,766
2004	1,205	322	887	688	210	672	3,258	30,606
2005	1,229	318	881	703	217	696	2,965	31,004
2006	1,238	319	893	708	220	709	2,823	32,421

Source: *Refinery Capacity 2006*. U.S. Department of Energy, June 2006.

Capacity Utilization Has Increased While the Number of Refineries Declines

Since 1990 the number of U.S. refineries has declined from 205 to 142 (as of January 2006). The utilization of existing capacity has been increasing steadily since 1981, from a low rate of about 65 percent to over 95 percent in 1997 and now hovers between 90 and 93 percent (see Figure 1-5). Increasing capacity utilization is the result of refiners meeting increasing oil demand with little or no change in plant capacity. Environmental rules have shut down new refinery construction over the past two decades and refiners have refrained from making substantial investments until firm rules and policies have been passed [HP 2005e, RAND 2003].

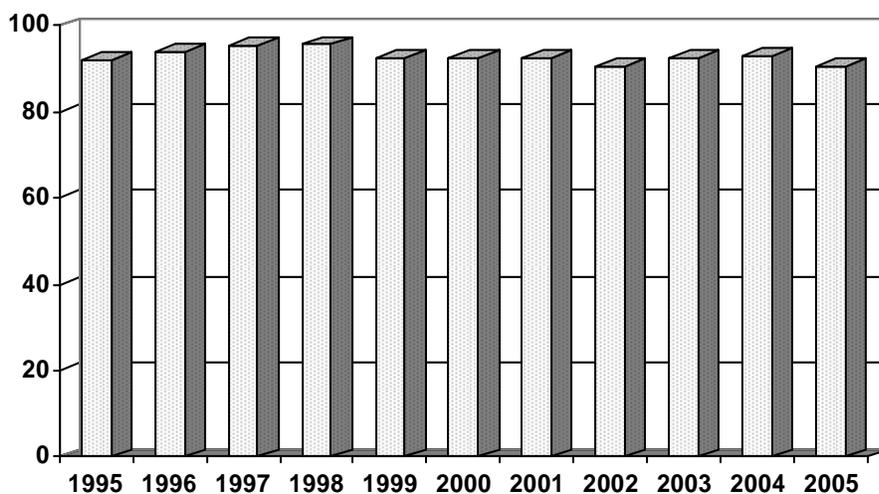


Figure 1-5. Domestic Refinery Capacity Utilization, 1995-2005 [DOE 2006b]

Capital spending, which has been in the range of \$3 billion to \$4 billion annually between 1997 and 2000, has increased to \$6 billion to \$7 billion in the past three years [HP 2006c]. Past investments have been directed at environmental, clean fuels and low-cost incremental expansions (known as “capacity creep”) such as removing physical bottlenecks, applying advanced catalysts, and introducing other productivity enhancements [RAND 2003]. These low-cost capacity expansions, along with more intensive use of existing capacity through lengthened run times between overhauls and increased imports, have helped refineries keep up with product demand. However, larger investments in capacity expansions will be the focus in the future. Expenditures are projected to be between \$8 billion and \$9 billion per year. Table 1-8 shows refinery expansion plans for North American refineries through 2012.

New capacity will be 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, [HP 2005e].

Most domestic oil refineries were designed twenty or more years ago to process primarily light sweet crude oil. Many of these refineries are limited in their capability to process increasingly heavier crudes. Refiners around the world are investing in increased capacity to refine heavier, high-sulfur oils to meet rising demand. Sour, or high-sulfur, crude often sells at a discount to sweet crude because it is heavier and yields less light fuel such as gasoline. Any crude oil purchase cost savings are outweighed by the increased investment and operating costs, including energy use, for added downstream processing capacity in units such as cokers, hydrocrackers, and visbreakers.

Company – Location	Added Capacity (Mbpd)
Coffeyville	15
ConocoPhillips—Various	230
Flint Hills—Rosemount	50
Frontier—El Dorado	11
Holly—Artesia	10
Marathon—Detroit	26
Marathon—Garyville	180
Motiva—Port Arthur	325
Sinclair—Sinclair	13
Sinclair—Tulsa	17
Sunoco—Various	100
Valero—Various	406
Wynnewood	20
Arizona	150 ^a
Total	1,553

a New refinery.
Mbpd Million barrels per day.
Source: HP 2006c

Crude oils are categorized and priced based on several quantitative measures of quality, including sulfur content, corrosivity (total acid number), density, and residue fraction (crude oil fraction with a

boiling temperature of 975°F or greater) [HP 2005f, DOE 2006c]. Sour crude oils are typically 0.7 weight percent sulfur but can contain as much as 5 weight percent sulfur [HP 2005e]. These crude oils are discounted to compensate for the lower yield of hydrocarbon fuel. Figure 1-6 shows that the average sulfur content of crude oil input into U.S. refineries has been slowly increasing over the past two decades.

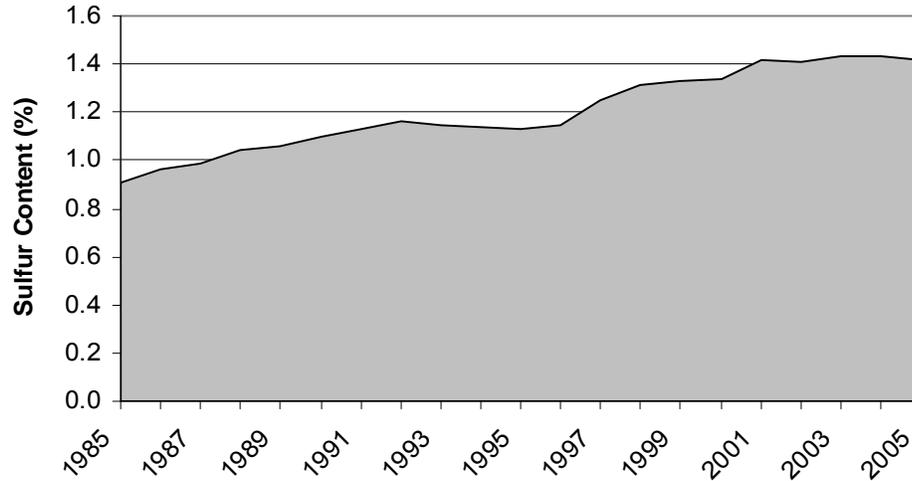


Figure 1-6. Weighted Average Sulfur Content of Crude Oil Input to U.S. Refineries [DOE 2006o]

Corrosivity, or the total acid number (TAN), is measured as the number of milligrams of potassium hydroxide required to neutralize the acid in one gram of oil. Crude oils with TANs greater than one are considered very corrosive and require special measures, such as the addition of basic compounds, to neutralize the acid. Some refiners instead choose to upgrade all of their piping and process equipment materials to stainless steel. While in 1990 there were no high-TAN crude oils processed in the United States, they now account for about 2 percent of the crude oil slate and are projected to increase to 5 percent or more by 2020 [DOE 2006c].

Crude oil density is measured using a specific gravity scale developed by the American Petroleum Institute (API) (see Figure 1-7). In general, high API gravity degree (lighter) oils have a greater value and lower API gravity (heavier) oils have lower value, although this only applies to oils with API gravities up to 45 degrees. Beyond 45 degrees, the hydrocarbon chains become shorter and less valuable to a refinery [DOE 2006n]. Over the past two decades, the average API gravity of crude oil inputs has decreased from 32.5 to 30.2 degrees (see Figure 1-8) [DOE 2006o]. This trend is expected to continue as light oil production declines in the North Sea, Australia, and Canada and is replaced by heavy and medium crude production in Mexico, Russia, and countries in South America and Africa [OGJ 2006c].

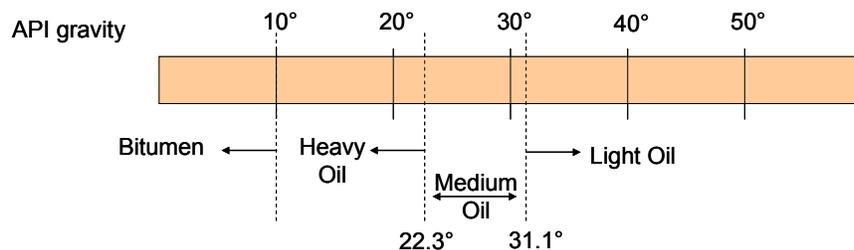


Figure 1-7. Crude Oil Grades and API Gravity [CFE 2006]

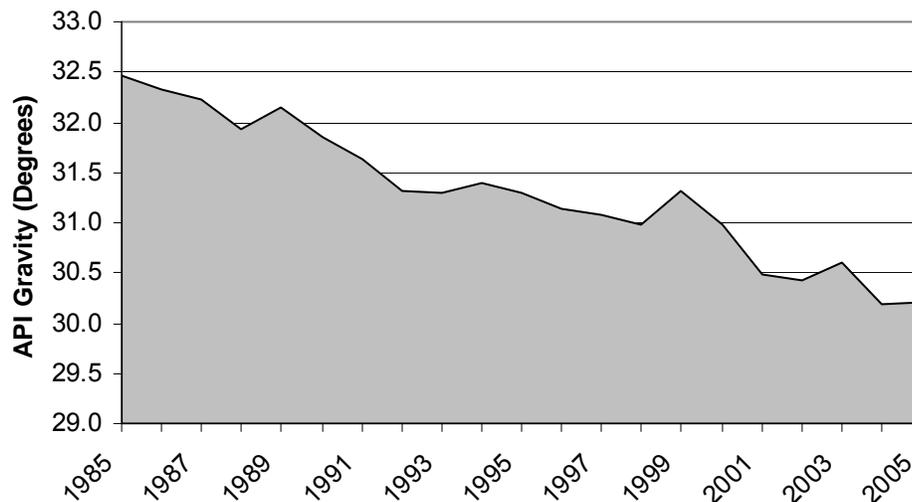


Figure 1-8. Weighted Average API Gravity of Crude Oil Inputs to U.S. Refineries
[DOE 2006o]

The impact of environmental compliance on refining profitability has been substantial. U.S. refining capital expenditures for pollution abatement increased from slightly over 10 percent shortly before the Clean Air Act Amendments of 1990 to over 40 percent in 1995. Environmental operating costs are the out-of-pocket expenses for prevention, control, abatement, or elimination of environmental pollution. For refiners the compliance costs also include Clean Air Act motor fuel standards, and reformulated gasoline and low-sulfur diesel requirements. After many years of operating under minimal or non-existent profit margins, refinery profitability has been on the rise since the mid 1990's. The increase in refining profitability since 1995 is partly attributable to reduced operating costs, including environmental costs. Apart from energy costs, refiners reduced overall operating costs by 20% between 1995 and 2001. Environmental costs decreased by 30 percent and energy costs increased by 49% over this same period [DOE 2003].

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

A number of technology-driven changes in the U.S. refining industry have improved the performance of refinery processes. The development of multi-functional catalytic cracking catalysts, for example, has provided higher product yields, improved feedstock flexibility, better product selectivity, and reduced air emissions while exhibiting longer catalyst life. Although many innovations have occurred in catalyst materials, substrate materials and structures, and catalysis modeling and application, catalyst developers and suppliers feel that there is still room for improvement.

Some technological changes have been driven by the need to respond to changing consumer needs and environmental regulations. Examples include the need to produce new lubricating oils that are suitable for higher performance combustion engines and the production of gasoline and diesel that meet demands for reduced vehicle emissions. Advanced process monitoring and controls have enabled refiners to meet the more stringent product quality specifications in a more reliable manner.

Maintenance and reliability have improved as refiners have adopted more efficient maintenance schedules and protocols. Rather than using standard rules of thumb when evaluating equipment performance and life, operators are using new sensor, control, and imaging technologies to monitor and address problems before breakdowns occur (e.g., x-ray and mass spectroscopy to inspect

equipment for wear) [RAND 2003]. Risk analysis tools are being applied to specific pieces of equipment such as pumps and valves, and utilizing operating histories of similar components to determine the likelihood of failure. Improvements in maintenance and reliability are valued not only for boosting productivity, but also for their impact on corporate environment, health, and safety policies; business risk-management strategies; and public perception of the company or facility.

Long-Term Trends in Technologies and Operations

With the changing slate of oil feedstock, there is a great incentive to retrofit older processing units to handle heavy, sour crude oil. Promising technologies for processing heavier crude oils include resid hydrocracking, which can be used to supplement residue coking, and high-pressure gasoil hydrocracking for gasoils that contain refractory and high nitrogen containing materials [HP 2005f]. Solvent deasphalting reduces the carbon content of residue, reduces coking expansion needs, and can be used as feedstock for gasification. Gasification is attractive because it destroys unwanted residue material and generates hydrogen, steam, and power [HP 2005f]. Hydrogen demand is expected to increase significantly with the need for ultra-low sulfur fuels that require additional hydrotreatment.

New oxidative, biocatalytic, adsorption, and membrane technologies are in the development and demonstration phase and may help address the demand for ultra-low sulfur fuels. Advancements in process monitoring and measurement technologies are enabling improved separation technologies (e.g., “flooded tower” or liquid continuous distillation), and are expected to drive the technology development process [RAND 2003].

1.3 Energy and Materials Consumption

Petroleum Refineries Use By-Products to Meet Process Energy Needs

Petroleum refining is the second most energy-intensive manufacturing industry in the United States, and accounted for about 7 percent of total U.S. energy consumption in 2002 [DOE 2005d, DOE 2006h].¹ According to the most recent Manufacturing Energy Consumption Survey (MECS) conducted by the Energy Information Administration (EIA) of the U.S. Department of Energy (DOE), the U.S. petroleum refining industry consumed 6.391 quads (quadrillion Btu, or 10^{15} Btu) of energy in 2002 (excluding electricity generating and transmission losses incurred by the generating utility) [DOE 2002b].

Table 1-9 illustrates net energy use as well as total primary energy. 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 generated on-site (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/kilowatt-hours). Energy losses in generation and transmission of electricity are included to illustrate the total energy consumption represented by the purchase of electricity.

¹ Based on energy use from MECS for 2002, and total energy used in the residential, industrial, transportation, and utility sectors in 2002.

Table 1-9. Petroleum Refining (SIC 2911, NAICS 324110) Energy Use, 1985, 1988, 1994, 1998, and 2002 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
1998	3,359	118	3,477	3,730	7,207	245	7,452
2002	2,965	121	3,086	3,307	6,393	251	6,644

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.

Sources: DOE 2005d, DOE 2001b, DOE 1997, DOE 1994, DOE 1991, DOE 1988.

Energy accounting for the petroleum refining industry is unique compared with other industries, because most of the products manufactured are energy products. As such, products are 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, and asphalt). To avoid double-counting in energy end-use, 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; consumption of these products is counted as energy use under the other sectors of the economy where it is consumed (e.g., transportation, buildings). As seen in Table 1-9, about 52 percent of the total energy used is in the form of petroleum feedstocks used to produce non-energy products. Table 1-10 breaks down refinery process energy consumption by fuel source.

Table 1-10. Petroleum Refining (SIC 2911, NAICS 324110) Energy Use by Fuel Type, 1994, 1998, and 2002 MECS Estimates (Trillion Btu)

Year	Net Electricity	Residual Fuel Oil	Distillate Fuel Oil	Natural Gas	LPG and NGL	Coal	Coke and Breeze	Other ^a	Total Net Energy Use	Electricity Losses ^b	TOTAL PRIMARY ENERGY
1994	114	68	7	756	W	W	0	2,161	3,153	237	3,390
1998	118	70	4	948	33	*	0	2,304	3,477	245	3,722
2002	121	21	5	821	20	1	0	2,097	3,086	251	3,337

a Includes net steam (the sum of purchases, generation from renewables, and net transfers), and other energy that was used to produce heat and power.

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

* Estimate less than 0.5.

W Withheld to avoid disclosing data for individual establishments.

Sources: DOE 2005d, DOE 2001b, DOE 1997.

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 2005 is 3,187 trillion Btu, as shown in Table 1-11. This is somewhat higher than the value for 2002 energy consumption shown in Tables 1-9 and 1-10 (3,086 trillion Btu). The discrepancy between the two EIA surveys is attributed not only to the different years data was collected, but also differences in collection and estimation methods.

Table 1-11. Petroleum Refining (NAICS 324110) Energy Consumed^a—2005 (Trillion Btu)		
Energy Source	Quantity	% of Total
Crude Oil	0.0	0
Liquified Petroleum Gases	16.0	<1
Distillate Fuel Oil	4.4	<1
Residual Fuel Oil	13.9	<1
Refinery Gas	1,435.5	45
Marketable Petroleum Coke	13.5	<1
Catalyst Petroleum Coke	526.5	17
Natural Gas	701.4	22
Coal	0.9	<1
Purchased Electricity (including losses)	384.2	12
Purchased Steam	70.0	2
Other Products ^b	20.3	1
TOTAL	3,186.5	100.0

a For heat and power.

b Other products include pentanes plus, other hydrocarbons, oxygenates, hydrogen, unfinished oils, gasoline, special naphthas, jet fuel, lubricants, asphalt and road oil, and other miscellaneous products.

Source: DOE 2006a

As can be seen in Table 1-11, the industry uses a diversity of fuel sources and 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 coke², and other oil-based by-products. In 2005, about 2.03 quadrillion Btu, or about 64 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 2006a]. The purchased fuel sources that supply the remainder of the energy needed by the refining industry include natural gas (22 percent), electricity (12 percent), purchased steam (2 percent), and small quantities of coal [DOE 2006a].

Energy expenditures represent a significant portion of manufacturing costs for petroleum refiners. In 2005 the industry spent approximately \$11.2 billion on energy (fuels and purchased electricity) [DOC 2006]. 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. Despite the current high margins for refiners, high energy prices, high environmental costs, and the focus on national energy security are driving refiners to continue improving energy efficiency. One motivation is that the cost of energy for heat and power represents a dominating factor in refinery production—as much as 50 percent of variable annual operating costs (excluding depreciation) [LBNL 2005]. As Figure 1-9 shows, although refiners have reduced energy (fuels, steam, and electricity) purchases and relied more on on-site energy sources, energy expenditures have drastically increased due to the significant increase in energy costs since 2001.

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.

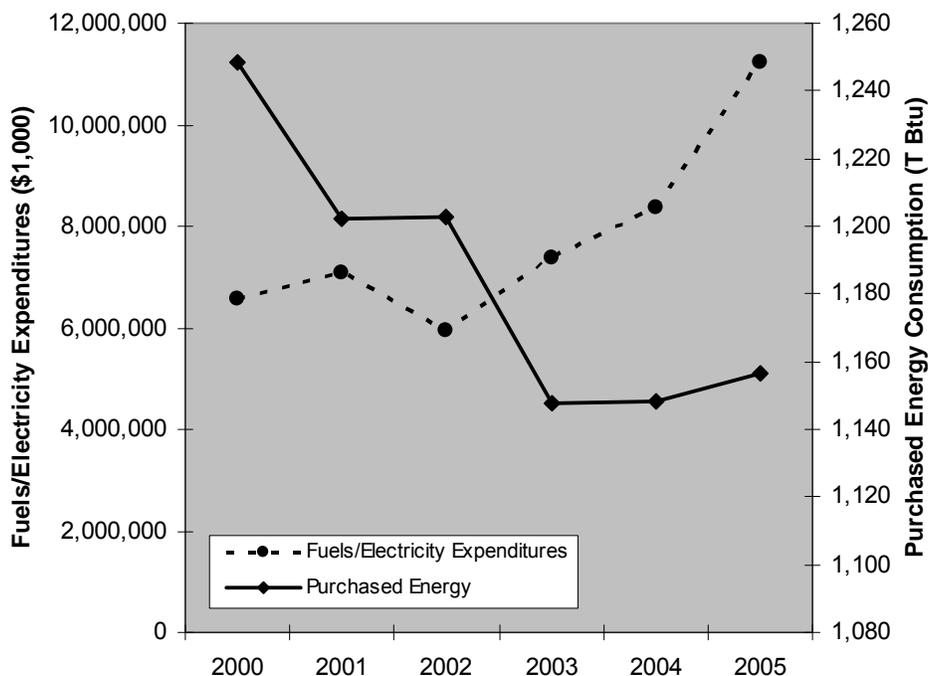


Figure 1-9. Recent Trends in Purchased Energy Consumption and Expenditures [DOE 2006a, DOE 2005c, DOE 2004, DOE 2003c, DOE 2002, DOE 2001c, DOC 2006, DOC 2003]

Member refineries of API and NPRA have committed to improving energy efficiency by 10 percent by 2012 as part of API’s Climate Action Challenge program, which is aimed at reducing greenhouse gas emissions [API 2006g].

1.4 Environmental Overview

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

Petroleum products are critical to the economy, supplying about 40 percent of the total energy used by the U.S. and practically all the energy consumed by transportation [DOE 2006h]. 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 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 1-12.

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. The industry spent about \$10.3 billion in 2004 on environmental compliance, an increase of approximately 2.4 percent from 2003 expenditures [API 2006a], and participates in a number of public and private initiatives aimed at improving environmental performance.

In 2003, American Petroleum Institute (API) members established the API Climate Challenge Programs to develop rigorous, industry-wide tools and procedures for estimating and tracking emissions and to reduce emissions through increased energy efficiency, use of alternative energy, and development of new technologies for the elimination or sequestration of emissions. As part of the Climate Challenge, member refiners have committed to improving their energy efficiency by 10 percent between 2002 and 2012 [API 2005]. API and its members have established clean water committees that collaborate with industry, governmental, and other groups to address a broad range of water quality issues, including biomonitoring research, production effluent guidelines, and soil/groundwater research, and emergency preparedness and response [API 2006b]. Many API member companies also partner with local communities, academic institutions, government agencies, and non-governmental organizations in efforts to protect wildlife, rehabilitate habitats, support environmental education, and fund research conversation studies [API 2006c].

Refineries have also been working to increase recycling, reduce pollution and decrease releases of toxic chemicals. Many refineries participated in the Environmental Protection Agency's 33/50 Program to reduce air toxics by 33 percent in 1992 and 50 percent in 1995, as measured against a 1998 baseline. The 33/50 Program met its ultimate goal (50 percent reduction) a year early and refineries have continued efforts to reduce toxic emissions [EPA 1999]. U.S. refineries have steadily increased the amount of residual wastes that are recycled from 26 percent in 1985 to 62 percent in 1997 [API 2006d]. In addition, total releases of toxic chemicals from refineries (counting only those included in the Toxic Release Inventory since 1988) have declined by 73 percent since 1988 [EPA 2006a].

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

Requirement	Provisions That Affect Petroleum Refining
Emergency Planning and Community Right-to-Know Act (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
Energy Policy Act of 2005	Provides incentives for the use of alternative motor vehicles and fuels for transportation; Renewable fuels standard (RFS) mandates that renewable fuels comprise a specified volume of the U.S. transportation fuel market; restriction on the use of MTBE as a fuel oxygenate; 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
U.S. Navy Memorandum, January 18, 2005	Requires all U.S. Navy and Marine non-tactical diesel vehicles to operate on a blend of 20% biodiesel fuel (B20); will reduce demand for petroleum diesel
State Ethanol Mandates	Five states (Minnesota, Missouri, Montana, Hawaii, and Washington) have passed renewable fuel standards mandating that gasoline and diesel fuel sold in the state must contain specified amounts of ethanol and biodiesel, respectively; specified amounts range from 2-10% ethanol and 2-20% biodiesel; will reduce demand for petroleum products.
State Methyl Tertiary Butyl Ether (MTBE) Legislation	Twenty-five states enacted legislation limiting MTBE as a fuel oxygenate; will reduce demand for petroleum products and may create tightness in gasoline supply due to production, distribution, and storage of critical blendstocks

Sources: *Cumulative Impact of Environmental Regulations on the U.S. Petroleum Refining, Transportation and Marketing Industries*, American Petroleum Institute, October 1997.
Sector Notebook: Profile of the Petroleum Refining Industry, U.S. Environmental Protection Agency, September 1995.
Energy Policy Act of 2005, H.R.6, June 28, 2005, <http://thomas.loc.gov>.
 "Legislative Actions: State," Renewable Fuels Association, Updated March 2006, Accessed 3 August 2006, <http://www.ethanolrfa.org/policy/actions/state/>
 "News Release: NPRA Submits Statements to Senate on the Impact of Reduced MTBE Use in Gasoline," National Petroleum Refiners Association, Accessed 28 July 2006, <http://www.npra.org>.
 "Facility Security," National Petroleum Refiners Association, Accessed 28 July 2006, <http://www.npra.org>.
 "U.S. Navy Calls for Broad Use of Biodiesel at Navy and Marine Facilities," National Biodiesel Board press release, March 11, 2005, <http://www.biodiesel.org>.
 "Senate Bill Report ESHB 2738," Senate Committee on Water, Energy & Environment, State of Washington, 22 February 2006, <http://www.leg.wa.gov/pub/billinfo/2005-06/Pdf/Bill%20Reports/Senate/2738-S.SBR.pdf>.

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

Air emissions are generated from several sources within the petroleum refinery, including combustion, equipment leaks, process venting, storage tanks, and wastewater systems.

Emissions that arise from leaking equipment and process vents include **air toxics and hazardous air pollutants** (HAPs). Releases of these compounds are reported annually to the U.S. Environmental Protection Agency (EPA). The most current data available are shown in Table 1-13. Topping the list are ammonia, sulfuric acid, n-hexane, toluene, and propylene.

Compound	Total Air Emissions (million pounds)
Ammonia	11.9
Sulfuric Acid	10.7
n-Hexane	4.6
Toluene	4.4
Propylene	3.0
Xylene (Mixed Isomers)	2.6
Benzene	2.0
Formaldehyde	2.0
Hydrochloric Acid	1.6
Ethylene	1.3
Methanol	1.1
Carbonyl Sulfide	1.0
Methyl Tertiary Butyl Ether	0.9
Cyclohexane	0.8

Source: 2004 Toxic Release Inventory, U.S. Environmental Protection Agency, updated 9 June 2006, <http://www.epa.gov/triexplorer/>.

Combustion emissions are associated with the burning of fuels in the refinery, including fuels used in the generation of electricity. These emissions can be calculated based on the energy consumption by fuel type, as shown in Table 1-14, and emission factors used for this calculation are illustrated in Table 1-15. 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).

SOx	NOx	CO	Particulates	VOCs
5,457	2,187	129	1,563	16

^a Calculations of combustion emissions based on energy use data by fuel type as shown in Table 1-11. Electricity use includes losses during generation and transmission (conversion factor of 10,500 Btu/kWh).

Fuel Type	SOx	NOx	CO	Particulates	VOCs ^a
Distillate Fuel	0.160	0.140	0.0360	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	0.0817	0.003	0.006
Refinery Gas	0.000	0.140	0.0817	0.003	0.006
LPG	0.000	0.208	0.0817	0.007	0.006
Coal	2.500	0.950	0.0243	0.720	0.005
Petroleum Coke	2.500	0.950	0.0243	0.720	0.005
Electricity	1.450	0.550	0.0702	0.400	0.004

^a Volatile organic compounds

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.

Equipment leak emissions (fugitive emissions) are released through leaking valves, pumps, seals, pressure relief valves, piping joints, or other process devices, and may occur throughout the refinery.

Such emissions are primarily composed of volatile compounds such as ammonia, benzene, toluene, propylene, xylene, and others. While the emissions from any single leak are small, 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) are the result of venting during manufacturing (e.g., venting, chemical reactions) and 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 tank emissions are released when crude and products such as intermediate process feeds are transferred to and from storage tanks. These emissions are largely volatile organic compounds (VOCs).

Wastewater emissions, 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 1-16 provides fugitive emission factors for cooling towers and oil/water separators.

Emission Source	Emission Factor Units	Emission Factors		Applicable Control Technologies
		Uncontrolled Emissions	Controlled Emissions	
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

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 and 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 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 carbon monoxide non-attainment areas have a minimum of 2.7 percent oxygen (by weight) for at least four winter months, by November 1992. U.S. refineries responded to this mandate by increasing domestic capacity for oxygenates. Oxygenates (e.g., ethanol, methyl tertiary butyl ether and other ethers) are added to fuels to boost octane, and reduce carbon monoxide because they are already partially oxidized. Production of methyl tertiary butyl ether (MTBE) increased from 49.4 million barrels per year in 1993 to a high of 94.8 million barrels per year in 1999 [DOE 2006i]. Since 1992, the number of areas participating in the Oxygenated Fuels Program has been reduced from thirty-nine in 1992 to twelve in 2005 [EPA 2005].

The **Reformulated Gasoline Program** was also established under the CAAA requiring the use of regulated gasoline formula by January 1, 1995 in nine U.S. metropolitan areas with the worst ground level ozone problems, though other metropolitan areas with serious ozone problems have opted to join the program. The requirements for reformulated gasoline (RFG) include 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, VOCs, and toxic air emissions. In 2005, the Reformulated Gasoline Program was amended by the Energy Policy Act to remove the RFG oxygen content requirement and revise the commingling prohibition to address non-oxygenated reformulated gasoline [EPA 2006b].

The **Tier 2 Vehicle and Gasoline Sulfur Program** and the **Highway Diesel Rule** and **Nonroad Diesel Rule** were finalized in 1999, 2001 and 2004, respectively, to implement more stringent standards for gasoline and diesel engines and fuels (see Table 1-17) [EPA 2006d, EPA 1999b, EPA 2000]. Tier 2 standards are designed to further reduce the emissions most responsible for vehicle impacts on ozone and particulate matter levels: nitrogen oxides and non-methane organic gases (NMOG; e.g., hydrocarbons and VOCs). Reduced sulfur content will enable current and improved vehicle emission control technologies to operate more effectively and longer and directly reduce sulfur emissions.

Compliance with reformulation rules has been a significant challenge for refiners and has required a number of process changes. Gasoline and diesel formulations have been changed to reduce aromatic, VOC, sulfur, nitrogen oxide (NO_x), and particulate matter emissions [EPA 2005, EPA 2006b, EPA 2006d, EPA 1999b, EPA 2000]. Coupled with the trend towards refining heavier crude oils which contain more sulfur and other contaminants, refiners have had to implement additional hydrotreating steps to reduce contaminants [HP 2005b, HP 2005c]. As a result of the additional processing, refinery energy consumption and costs are increasing [OGJ 2005a].

Refiners must also comply with **Reid Vapor Pressure (RVP)** regulations, first established by EPA in 1989 and now in effect under the VOC standards of the 1990 CAAA. Phase I standards (1989-1991) 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. Phase II standards (1992 and later) require that gasoline RVP not exceed 9.0 or 7.8 pounds per square inch (psi) depending on the state and month [EPA 2006c]. Refiners have met the requirements through 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].

Table 1-17. Current Vehicle and Fuel Standards			
Regulation	Entities Affected	Emissions Standards^d	Implementation Date
Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulfur Control Requirements	Manufacturers of passenger cars, light trucks (includes light LDTs ^a rated at less than 6,000 lbs GVW ^b , heavy LDTs rated at more than 6000 lbs GVW), larger passenger vehicles (medium-duty passenger vehicles (MDPV): includes SUVs ^c and passenger vans between 8,500 and 10,000 lbs GVW)	<u>Final Standards</u> Average NOx levels of 0.07 grams per mile (g/mi) 0.09 g/mi NMOG 0.018 g/mi Formaldehyde <u>Phase-In Standards^f</u> Passenger cars, light LDTs: 0.30 g/mi average NOx Heavy LDTs and MDPVs: 0.20 g/mi average NOx (vehicles not covered by the phase-in will have a cap of 0.60 g/mi NOx for heavy LDTs and 0.09 g/mi NOx for MDPVs)	New passenger cars and light LDTs: beginning 2004, fully phased in by 2007 Heavy LDTs and MDPVs: phase in beginning 2008, full compliance in 2009
	Refiners and importers of gasoline	<u>Gasoline Sulfur Standard^e</u> Corporate Average: 120 ppm Cap: 300 ppm Individual Refineries Average: 30ppm Cap: 80 ppm	2004 2006
Highway Diesel and Nonroad Diesel Rules	Manufacturers of highway and nonroad diesel engines	<u>Particulate Matter (PM)</u> New heavy-duty diesel engine particulate matter (PM) standard: 0.01 grams per brake-horsepower-hour (g/bhp-hr) <u>NOx and Non-Methane Hydrocarbons (NMHC)</u> NOx: 0.20 g/bhp-hr NMHC: 0.14 g/bhp-hr	2007 model year Phased in between 2007 and 2010 using a percent-of-sales basis: 50% from 2007-2009 and 100% in 2010
	Refiners and distributors of diesel fuels	<u>Sulfur Content Requirement</u> 15 ppm	Refinery production by June 1, 2006 Fuel terminal availability as of July 15, 2006 Retail station and fleet availability by September 1, 2006.

^a Light-duty vehicle

^b Gross vehicle weight

^c Sport utility vehicle

^d Average emissions of a company's production must meet the target emission levels.

^e Temporary, less stringent standards will apply to refineries who produce fuel for use in the Geographic Phase-In Area through 2006 and a few small refineries through 2007.

^f An optional program for interim standards for passenger vehicles exists.

Until recently, the most common oxygenate and low-RVP additive used to meet RFG and RVP requirements has been MTBE, followed by ethanol. Between 1993 and 1999, MTBE production nearly doubled from 49.4 to 94.3 million barrels per year, while ethanol production increased from 28.6 to 35 million gallons per year [DOE 2006i, RFA 2006]. However, discovery of MTBE in California drinking wells in the mid-1990s sparked controversy over the continued use of MTBE as an oxygenate [LLNL 2006]. Since then, twenty-five states have enacted legislation mandating the

reduction or elimination of MTBE in fuel supplies and refiners have begun replacing MTBE with ethanol in those markets. Consumption of MTBE has declined from its high of 94.8 million barrels in 1999 to 393.4 million barrels in 2005 [DOE 2006i].

Ethanol consumption has continued to increase as, in addition to MTBE phase-outs, federal and state governments have established renewable fuels standards mandating that gasoline supplies contain renewable fuels such as ethanol. The **Energy Policy Act of 2005** created a national **Renewable Fuels Standard** (RFS) which established a baseline for renewable fuel (e.g., ethanol, biodiesel) use of 4 billion gallons per year in 2006. This increases annually to 7.5 billion gallons in 2012. The majority of the renewable fuels is likely to be ethanol and would require a doubling of the domestic ethanol industry over the next six years [EPACT 2005, RFA 2006]. In addition, five states have passed RFS mandating that all gasoline and diesel sold in the state contain specific amounts of ethanol and biodiesel (2-10% ethanol, 2-20% biodiesel), respectively [NBB 2005, WA 2006, RFA 2006b].

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. EPA has developed maximum achievable control technology (MACT) standards for all new and existing stationary (major and area) sources. MACT standards are reviewed every eight years to see if new technology is available, and to evaluate whether there is any remaining residual risk and implement additional controls, if necessary. Area sources emit less than 10 tons per year (tpy) of any single HAP or 25 tpy of any combination of HAPs while major sources exceed these limits. EPA is expected to set Generally Achievable Control Technology (GACT) standards for area sources such as gasoline distribution facilities and oil and natural gas production sites [API 2006e].

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 was required by August 1998 (except for storage tanks—these were to 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. These modifications were to be implemented by August 1999. Table 1-18 lists the MACT rules the petroleum refining industry is subject to [API 2006e].

Table 1-18. MACT Rules Affecting U.S. Petroleum Refining Industry		
Source Category	Final Rule Date	Federal Register Citation
Hazardous Organic NESHAP	4/24/1994	59FR19402
Gasoline Distribution (Stage 1)	12/14/1994	59FR64303
Marine Vessel Loading Operations	9/19/1995	60FR48388
Petroleum Refineries I	8/18/1995	60FR43244
Petroleum Refineries II	4/11/2002	67FR17761
Site Remediation	10/8/2003	68FR58171
Organic Liquids Distribution	2/3/2004	69FR5038
Reciprocating Internal Combustion Engines	6/15/2004	69FR33473
Industrial, Commercial, and Institutional Boilers and Process Heaters	9/13/2004	69FR55217
Combustion Turbines	3/5/2004	69FR10511

Source: API 2006e

In 2000, the EPA established the Petroleum Refinery Initiative to address the most significant CAA and CAAA compliance concerns affecting the petroleum refining industry. As of March 2006, 17 global refinery settlements have been reached with refiners representing nearly 77 percent of domestic refining capacity and negotiations are ongoing with nine other refiners (11 percent of domestic capacity) [EPA 2006h].

The refining industry is also affected by changes in **National Ambient Air Quality Standards** (NAAQS). The NAAQS limit the amount of six principle pollutants, or “criteria” pollutants, which are considered harmful to public health and the environment: carbon monoxide, lead, nitrogen dioxide, particulate matter (PM₁₀ and PM_{2.5}), ozone, and sulfur oxides (Table 1-19). Primary standards protect public health, including the health of “sensitive” populations such as asthmatics and the elderly, while secondary standards protect public welfare by protecting against decreased visibility, and damage to animals, crops, vegetation, and buildings [EPA 2006e].

A few of the criteria pollutants are also regulated by the **1999 Regional Haze Rule** which requires emissions controls known as best available retrofit technology (BART) for industrial facilities emitting air pollutants that reduce visibility. The BART requirements apply to facilities built between 1962 and 1977 that have the potential to emit more than 250 tons a year of visibility-impairing pollutants, including fine particulate matter (PM_{2.5}) and compounds that contribute to PM_{2.5} formation, such as nitrogen oxides, sulfur dioxides, some volatile organic compounds, and ammonia [EPA 2006f, EPA 2006g]. Many of these facilities—utility and industrial boilers and large industrial plants such as pulp mills, refineries, and smelters—have not been regulated by federal pollution control measures for these pollutants in the past. The **Clean Air Visibility Rule**, passed in 2005, amends the Regional Haze Rule and provides BART guidelines to help states determine which facilities must install controls and the type of controls the facilities must use [EPA 2006g].

Pollutant	Primary Standards	Averaging Times	Secondary Standards
Carbon Monoxide (CO)	9 ppm (10 mg/m ³)	8-hour ^a	None
	35 ppm (40 mg/m ³)	1-hour ^a	None
Lead	1.5 µg/m ³	Quarterly average	Same as Primary
Nitrogen Dioxide (NO ₂)	0.053 ppm (100 µg/m ³)	Annual (arithmetic mean)	Same as Primary
Particulate Matter (PM ₁₀) ^b	150 µg/m ³	24-hour ^a	Same as Primary
Particulate Matter (PM _{2.5}) ^c	15.0 µg/m ³	Annual arithmetic mean ^d	Same as Primary
	35 µg/m ³	24-hour ^e	Same as Primary
Ozone	0.08 ppm	8-hour ^f	Same as Primary
	0.12 ppm	1-hour ^g	Same as Primary
Sulfur Oxides	0.03 ppm	Annual arithmetic mean	None
	0.14 ppm	24-hour ^a	None
	None	3-hour ^a	0.5 ppb (1300 µg/m ³)

^a Not to be exceeded more than once per year.

^b Particles with an aerodynamic diameter less than or equal to 10 µm.

^c Particles with an aerodynamic diameter less than or equal to 2.5 µm.

^d To attain this standard, the 3-year average of the weighted annual mean PM_{2.5} concentrations from single or multiple community-oriented monitors must not exceed 15.0 µg/m³.

^e To attain this standard, the 3-year average of the 98th percentile of 24-hour concentrations of each population-oriented monitor within an area must not exceed 35 µg/m³.

^f To attain this standard, the 3-year average of the fourth highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area of each year must not exceed 0.08 ppm.

^g The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is less than or equal to 1. As of June 15, 2005, EPA revoked the 1-hour ozone standard in all areas except the fourteen 8-hour ozone non attainment Early Action Compact (EAC) areas.

Source: EPA 2006e

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. Much of this water 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 average amount of water used in refineries was estimated between 65 and 90 gallons per barrel of crude oil processed [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 to 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 [NARA 2006, 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 use large volumes of cooling water, which normally does not come into contact with oil streams and contains fewer 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) [HP 2005d]. “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

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

the generation of residual streams from refineries is shown in Table 1-20. Table 1-21 illustrates how refineries manage these residuals. Overall, refineries recycle about 62 percent of the residuals produced, according to 1997 data, an increase of 36 percent from 1985 [API 2006d].

Residual	1995	1994	1991	1989	1987
Spent Caustics	988	1,379	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	3,048	4,233	4,292^a	3,621^a	3,440^b

^a Current data is unavailable.

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

Sources: *Management of Residual Materials: 1995 – Petroleum Refining Performance*, American Petroleum Institute, API Publication Number 339, June 1997.

The Generation and Management of Residual Materials: 1991 – Petroleum Refining Performance, American Petroleum Institute, API Publication Number 329, May 1994

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	1,631	678	741

^a Current data is unavailable.

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

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 were 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 1-22). 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, residual paint materials, and residuals containing benzene [NARA 2006b, EPA 1995a, OGI 1990].

Table 1-22. 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. NARA 2006b.

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.

In 1998, EPA promulgated a final rule to provide a common sense guide to determine when hazardous wastes no longer require costly treatment. The 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. Under the HWIR, nine petroleum refining wastes are considered hazardous and are subject to the stipulations of the Resource Conservation and Recovery Act with respect to treatment, storage, and disposal: dissolve air flotation (DAF) float (K048), slop oil emulsion solids (K049), heat exchanger bundle cleaning sludge (K050), API separator sludge (K051), leaded tank bottom corrosion solids (K052), crude oil storage tank sediment from petroleum refining operations (K169), clarified slurry oil storage tank sediment and/or in-line filter/separation solids from petroleum refining operations (K170), spent hydrotreating catalyst from petroleum refining (does not include inert support material) (K171), and spent hydrotreating catalysts (K172) [EPA 1998, NARA 2006b].

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 2004, petroleum refineries managed about 82 million pounds of TRI chemicals. Of these, 65 percent entered the environment as air emissions (see Table 1-13); 24 percent was released through surface water discharges to streams, rivers, lakes, oceans, and other bodies of water; approximately 7 percent was disposed of in underground injection wells (Classes I-V), landfills, and other land disposal sites; and 4 percent—about 3 million pounds—was put into storage or stabilized/solidified [EPA 2006]. Table 1-23 outlines the top chemicals (by weight) released from refineries [EPA 2006].

Table 1-23. Top Toxic Chemical Releases from Petroleum Refineries (million lbs/yr)		
Toxic Chemical	2004	2003
Nitrate compounds	17.0	15.1
Ammonia	14.3	10.9
Sulfuric acid	10.8	10.9
Toluene	4.8	4.4
n-Hexane	4.6	4.1
Propylene	3.1	3.0
Xylene (mixed isomers)	2.7	2.7
Benzene	2.2	2.2
Formaldehyde	2.0	0.1*
Zinc compounds	1.6	1.4
Hydrochloric acid	1.6	1.5
Methanol	1.5	1.5
Ethylene glycol	1.4	0.2*
Ethylene	1.3	1.2
Sodium nitrite	1.0	0.1*
Methyl tert-butyl ether	1.0*	1.2
Cyclohexane	0.8*	1.1
Carbonyl sulfide	1.0*	1.0
Other chemicals	9.3	8.6
Total	82.0	71.2

* This chemical was not among the top fifteen for this year.

Source: 2004 Toxic Release Inventory, U.S. Environmental Protection Agency, updated 9 June 2006, <http://www.epa.gov/triexplorer/>.

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

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. EPA's new rules for ultra low sulfur gasoline and diesel were estimated to cost \$2.2 billion and \$2.5 billion in 2004 and 2005, respectively, but could be as high as \$13 billion [DOE 2001]. The increasingly high costs of complying with environmental regulations could force the closure of some moderately-complex refineries, resulting in increased imports of refined products as off-shore, low-complexity producers step up to meet 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 [HP 2002].

Continuing implementation of the Clean Air Act Amendments of 1990 and subsequent rules affecting alternative fuel use (e.g., Energy Policy Act of 2005) 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.

The increased demand for ethanol as a fuel component could affect the production, distribution, and storage of gasoline due to the different properties of ethanol. Since ethanol has a higher oxygen content than MTBE, less ethanol (approximately half the volume of MTBE) must be blended with gasoline to achieve the 2 percent oxygen requirement [DOE 2003, OGJ 2006b]. Ethanol is also more volatile than MTBE and requires high-quality blendstock to ensure the final product meets emissions standards, placing additional burden on the refining industry [DOE 2006j, OGJ 2006b]. In order to maintain a stable fuel supply, refiners will need to increase production capacity to counter the net loss of gasoline supply that results from the replacement of MTBE with ethanol. The need for high-quality blendstock and MTBE-free product could also potentially reduce the import supply.

Fuel distributors will be affected by the increased use of ethanol due to its affinity for water. If a gasoline-ethanol blend interacts with water, the ethanol will separate from the gasoline and mix with the water. Since the petroleum distribution and storage system contains water, ethanol must be transported and stored separately until the last step in the distribution chain. New infrastructure will be required for both ethanol delivery and fuel blending [DOE 2003, DOE 2006j].

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. The Earth's climate system adapts relatively well to small and slow changes in atmospheric concentration of greenhouse gases—gases that trap heat in the atmosphere. These gases are transparent to solar radiation that enters the Earth's atmosphere, but strongly absorb the infrared thermal radiation emitted by the Earth. The natural greenhouse effect is what permits life to exist on earth. Without greenhouse gases in the atmosphere, ambient temperatures would be much colder—below the freezing temperature for water—and the earth would be incapable of sustaining life.

However, rapid changes in anthropogenic (man-made) greenhouse gases may constitute a major force for climate change; the most common man-made and natural sources of greenhouse gases are shown in Table 1-24. 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 predictable 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.

Greenhouse Gas	Anthropogenic Sources	U.S. Emissions of Anthropogenic Sources (MMTCE)	Natural Sources	U.S. Natural Emissions (MMTCE)
Carbon dioxide (CO ₂)	Combustion of fossil fuels; calcination of limestone, soda ash manufacture and use; aluminum production.	1,634	Biological processes	NA
Nitrous oxide (N ₂ O)	Combustion of fossil fuels; nitrogen fertilizers, manufacture of adipic and nitric acid.	106	Biogenic processes in soil; lightning.	NA
Methane (CH ₄)	Coal mining; oil refining; gas drilling and transmission; chemical, iron and steel production.	152	Aerobic decay of vegetation; termites (tropics); ruminant animals.	NA
Hydrofluorocarbons, Perfluorocarbons, Sulfur Hexafluoride	Release of engineered chemical refrigerants and solvents	0.3	No natural source.	—

NA Not available
Source: EPA 2006i

While there is little doubt among the scientific community that global warming and other changes in global climates could significantly impact the world as we know it, there is no scientific consensus that global warming is currently occurring. 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 do show an increase of one 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 available data have resulted in considerable disagreement in the scientific community over the extent and potential of global warming. 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. An estimate of greenhouse gas emissions from the combustion of fossil fuels in petroleum refineries is shown in Table 1-25. These emissions were calculated based on energy consumption as reported for 2002 and using carbon coefficient factors developed for individual fuel types.

Refinery Emissions of Non-CO₂ Greenhouse Gases
<i>Methane (2004)</i>
- Vented Emissions 0.142 MMTCE
- Combustion Emissions 0.011 MMTCE
- Fugitive Emissions 0.010 MMTCE
<i>Chlorinated Compounds (2004)</i>
- Chlorotrifluoromethane 16 metric tons
- Carbon tetrachloride 1 metric ton
Sources: EPA 2006, EPA 2006i

Greenhouse gas emissions also stem from a number of other sources. Methane leaks from equipment when methane and oil are separated during refining processes and is emitted when oil is transferred to storage tanks at the refinery (as vapors are displaced), during flaring of gases (unburned methane may be emitted), and along with other volatile hydrocarbons through fugitive emissions from refining equipment, storage tanks, and gas flaring systems. Chlorinated compounds (e.g., refrigerants, solvents) are emitted as fugitive emissions and from point sources in small quantities. While these compounds are suspected of impacting the global climate, their actual effects have not been quantified. They are also suspected of contributing to ozone depletion in the upper atmosphere.

Fuel Type	Carbon Coefficient (lbs CO₂/Million Btu)	2002 Energy Use in Petroleum Refining (Trillion Btu)	Carbon Emissions (MMTCE)	CO₂ Emissions (1000 tons)
Net Electricity	135.2	121	2.024	8179
Residual Fuel Oil	173.7	21	0.451	1824
Distillate Fuel Oil	161.3	5	0.100	403
Natural Gas	117.0	821	11.880	48,015
LPG and NGL	137.3	20	0.340	1,373
Coal	208.1	1	0.026	104
Other ^{a,b}	208.1	2,097	53.977	218,160
TOTALS		3,086	68.797	278,059

Note: MMTCE indicates million metric tons of carbon equivalents.

^a Includes net steam (the sum of purchases, generation from renewables, and net transfers), and other energy used to produce heat and power.

^b Assumes that this is primarily purchased steam. Emissions are approximated by coal.

Sources: DOE 2005b, DOE 2003b.

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. The carbon coefficients and energy consumption data used in this study are shown in Table 1-25. A detailed explanation of how carbon coefficients were derived can be found in *Emissions of Greenhouse Gases in the United States, 2002* [DOE 2003b].

In 1994, the United Nations Framework Convention on Climate Change (UNFCCC) was created to consider the issue of global warming. The Kyoto Protocol, which shares the same objective, principles, and institutions as the Convention, was introduced in 1997 to strengthen the Convention by committing Annex I Parties to individual, legally-binding targets to limit or reduce their greenhouse gas emissions [UNFCCC 2006]. Of the 189 countries that are members of the UNFCCC, 165 have ratified the Kyoto Protocol. The individual targets for Annex I Parties add up to a total cut in greenhouse gas emissions of at least 5 percent from 1990 levels in the commitment period 2008-2012.

Summary of the Kyoto Protocol

- *Annex I Parties to reduce greenhouse gas emissions to 5% below 1990 levels by 2012*
- *No commitments from developing nations to reduce greenhouse gas emissions, and no agreement on a voluntary process for reducing/limiting their emissions*
- *Countries may partially meet their targets by increasing “sinks”—forests, which remove carbon dioxide from the atmosphere—in their own territories or in other countries. They can also pay for foreign projects that result in greenhouse gas reductions.*
- *Emissions trading for Annex I parties only (main sellers would be Russia and Ukraine)*
- *The Marrakesh Accords, adopted in 2001, provide instructions on how to “operate” the Protocol*

Although the United States helped shape the Kyoto Protocol during the 1990s, in 2001 the United States renounced the Protocol on the grounds that it would hurt the economy and is ineffective and discriminatory. To meet the Kyoto targets, the United States would have reduce coal consumption by 18 to 77 percent and replace the lost energy through increased in natural gas and renewable fuel consumption [HP 2005g]. U.S. energy prices would increase dramatically by 17 to 83 percent in constant 1996 dollars. Also, large, rapidly industrializing countries escape the limits and may thereby gain an economic advantage over the United States and other developed countries [WP 2005]. While developed countries currently produce a majority of carbon dioxide (CO₂) due to higher energy consumption to sustain their economics, developing countries would be allowed to continue using less efficient energy production and produce significant amounts of CO₂ (see Figure 1-10) [HP 2005g].

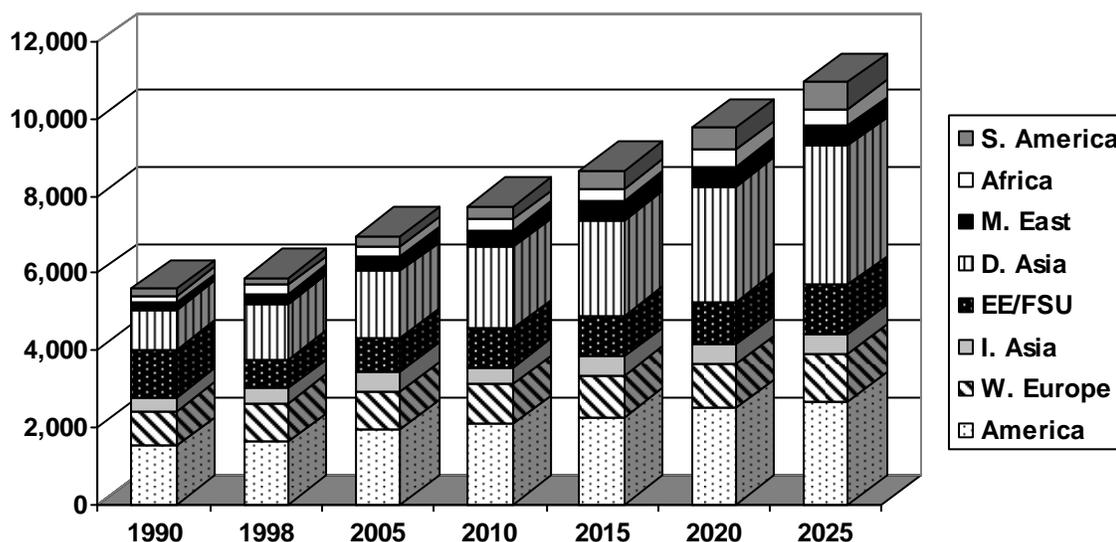


Figure 1-10. Forecast CO₂ Emissions by Geographical Region, 1990-2025 [HP 2005g]⁴

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. In 2003, API members established the API Climate Change Challenge Programs to increase industry efforts in addressing the climate change issue [API 2005]. Member companies are collaborating with government, academic research groups, and others to reduce emissions by:

- Increasing energy efficiency and promoting alternative energy use
- Establishing standardized, industry-wide tools and procedures for estimating and tracking emissions
- Helping develop new technologies that can eliminate or sequester emissions.

As part of the Climate Change Challenge Programs, API and its refiner members have set a goal to improve their energy efficiency by 10 percent between 2002 and 2012, and are thus far on track to meet the goal [API 2005].

⁴ Abbreviated categories are as follows: South America, Middle East, Developing Asia, Eastern Europe and Former Soviet Union, Industrialized Asia, and Western Europe.

2 The Integrated Petroleum Refinery

2.1 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 utilizing diverse technologies 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).

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 is high than they do during the winter when demand for heating oils is high.

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.

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].

Table 2-1. Major Petroleum Refining Processes		
Category	Major Process	Description
Topping (separation of crude oil)	<ul style="list-style-type: none"> • Atmospheric Distillation • Vacuum Distillation • Solvent Deasphalting 	Separating crude oil into different hydrocarbon groups, or fractions. The most common means 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	<ul style="list-style-type: none"> • Delayed Coking • Fluid Coking/ Flexicoking • Visbreaking • Catalytic Cracking • Catalytic Hydrocracking 	“Cracking” or breaking down large, heavy hydrocarbon molecules into smaller hydrocarbon molecules can be achieved either through the application of heat or through the use of catalysts.

Table 2-1. Major Petroleum Refining Processes		
Category	Major Process	Description
Combination/ Rearrangement of Hydrocarbons	<ul style="list-style-type: none"> Alkylation Polymerization Catalytic Reforming Isomerization Ethers Manufacture 	<p>Combination of hydrocarbons involves linking two or more hydrocarbon molecules together to form a larger molecule (e.g., converting gases to liquids).</p> <p>Alkylation and polymerization combine smaller molecules to produce high octane gasoline blending stock.</p> <p>Rearrangement of hydrocarbons alters the original structure of the molecule, producing a new molecule with different characteristics (but the same number of carbon atoms).</p> <p>Catalytic reforming and isomerization are commonly used techniques for hydrocarbon rearrangement.</p>
Treating	<ul style="list-style-type: none"> Catalytic Hydrotreating/ Hydroprocessing Sweetening/Sulfur Removal Gas Treatment 	Processing of petroleum products to remove some of the sulfur, nitrogen, heavy metals, and other impurities.
Blending and Specialty Product Manufacture	<ul style="list-style-type: none"> Lube Oil Grease Asphalt 	<p>Blending is the last phase of the refining process and is used to obtain the final product.</p> <p>A variety of processes are employed to produce specialty products such as lubricating oils, grease, wax, and asphalt.</p>

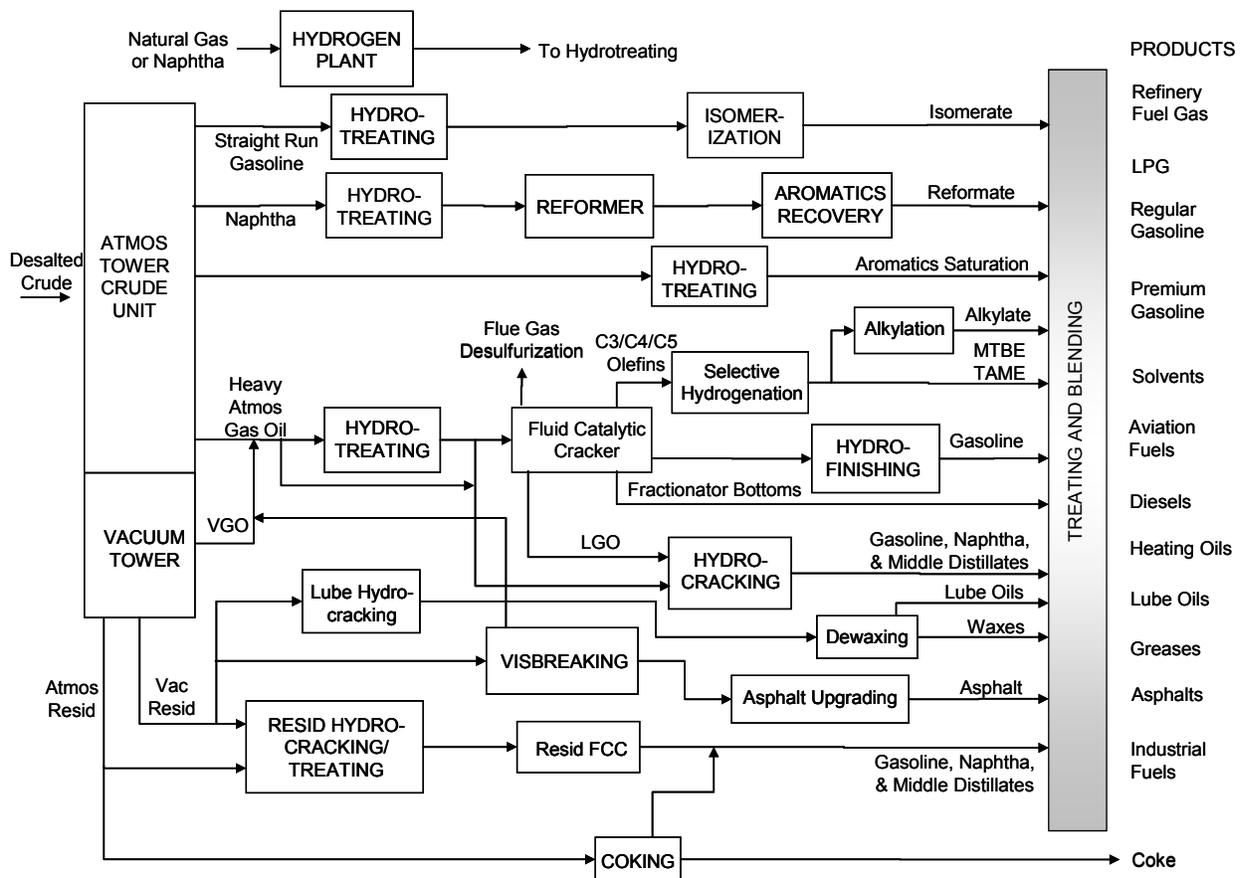


Figure 2-1. Typical Refinery Flow Diagram

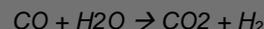
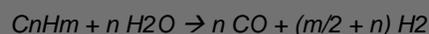
Refineries are Improving Hydrogen Management and Expanding Production

Declining fuel quality and the push for clean fuels have increased the importance of hydrogen production to refinery operations. The primary sources of hydrogen in a refinery are catalytic reformers, hydrogen plants, and purchased hydrogen. As the need for hydrogen grows, refiners are exploring ways to revamp and debottleneck existing hydrogen plants, better manage the hydrogen network, and integrate hydrogen production with other utilities (steam, electricity). Outsourcing hydrogen production is a viable alternative to onsite production, enabling refinery operational flexibility. Additionally, by eliminating the large capital investment required for significant hydrogen plant capacity expansion, bringing in hydrogen from outside the refinery can improve the facility's return on capital employed (ROCE), an important financial measure.

Steam methane reforming (SMR) is the most common hydrogen production process, accounting for over 95 percent of on-purpose hydrogen. Methane (natural gas) and other light hydrocarbons are reacted with steam over a nickel catalyst to generate hydrogen and carbon monoxide (CO), also known as synthesis (syn) gas. This reaction is endothermic, and excess natural gas is fed with the natural gas feedstock and combusted to generate heat to drive the reforming reaction. Additional hydrogen is generated using the water-gas shift reaction in which CO reacts with steam to form hydrogen and carbon dioxide (CO₂). Steam is generated as a by-product of SMR.

Alternatives to SMR include partial oxidation (gasification) and autothermal reforming (ATR) which is a combination of partial oxidation and steam reforming. Partial oxidation can process any hydrocarbon feedstock (e.g., coke, coal), but the high pressure and pure oxygen requirements make it expensive for hydrogen production. ATR is not widely used for hydrogen production because the synthesis gas hydrogen-to-carbon monoxide ratio is more suitable for petrochemical feedstocks, it requires a low-cost supply of oxygen, and produces a large quantity of excess steam.

Steam Methane Reforming Reactions



The gas streams exiting the water-gas shift reactor are purified before the hydrogen is used throughout the refinery. In some applications, 95 volume percent hydrogen content is sufficient, but for catalytic processes, a higher purity hydrogen stream is necessary (99 volume percent or higher, carbon oxide content less than 10 parts per million volume, ppmv). The three most commonly used processes for hydrogen purification are pressure swing adsorption (PSA), membrane separation, and cryogenic separation (cold box). Selection of the hydrogen purification technology depends on several factors, including the purity required, the pressure drop between feed gas and hydrogen, possibility of by-product recovery, the difference in value of the recovered hydrogen and the value of the feed gas as a fuel, and capacity. [Process Technology Description: HP 2006a, HP 2005k, HP 2005l, HP 2003c]

Petrochemical Feedstocks are an Important Secondary Product of Petroleum Refining

Several chemicals, including propylene and benzene, are produced during petroleum refining processes. These chemicals are recovered for use as feedstock for the petrochemical industry which converts the compounds to a myriad of products, including polymers for film, fiber, and rubber applications. More information on the petrochemical markets, manufacturing processes, and energy and environmental inputs and outputs are available in the U.S. Department of Energy's *Energy and Environmental Profile of the U.S. Chemical Industry*.

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 process energy use shown differs somewhat from total process energy use for refining shown in Table 1-9 because of the different data years (2002 versus 2005) and because average values were used to calculate total consumption based on 2005 capacity utilization of 90.4 percent (average values include losses incurred during electricity generation and transmission and exclude hydrogen/oxygen consumption and by-product production).

Table 2-2. Estimated Energy Use by Refining Process				
Process	Specific Energy Use^a (10³ Btu/bbl)	Average Use^b (10³ Btu/bbl)	Capacity (10⁶ bbl/cday)^c	Annual Energy Use (10¹² Btu/year)
Atmospheric Distillation ^d	82 - 186	114	15.86	658.8
Vacuum Distillation	51 - 113	92	7.14	238.5
Fluid Catalytic Cracking ^e	209	209	5.48	417.5
Catalytic Hydrocracking	159-321	168	1.43	87.5
Delayed Coking	114 - 230	166	2.03	122.9
Fluid Coking	258	258	0.07	6.7
Flexicoking	167	167	0.11	6.6
Visbreaking ^f				
- Coil	136	136	0.0052	0.29
- Soaker	25 - 95	63	0.0106	0.24
Catalytic Reforming	213 - 342	269	3.4	331.1
Alkylation				
- Sulfuric Acid	330 - 340	335	0.43	52.9
- Hydrofluoric Acid	255	255	0.65	60.3
Catalytic Hydrotreating	61 - 164	88	13.7	442.0
Ethers Production	295 - 564	403	0.10	16.2
Isomerization				
- Isobutane	359	359	0.20	26.2
- Isopentane/Isohexane	102 - 236	175	0.42	26.9
- Isobutylene	476	476	n/a	n/a
Lube Oil Manufacture	1,506	1,506	0.17	92.2
Hydrogen Production	63 - 158 ^g	111 ^g	7.17 ^h	290.5 ^g
TOTALⁱ	-	-	-	2877.3

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 or production (by-product).

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 calendar day (365 days per year). Includes the 2005 capacity factor of 90.4 percent.

d Includes energy consumed for desalting of crude.

e Includes energy from coke combustion that is used to drive the cracking reaction.

f Assumes 33 percent of capacity is coil type, and 67 percent is soaker type visbreakers.

g Includes both natural gas consumed as feedstock and fuel and electricity used in steam methane reforming [HP 2006a, DOE 2005e]. Values are in 10³ Btu/kg H₂.

h Onsite (captive), on-purpose production only. Value is in 10⁶ kg H₂/cday [CMR 2003].

i Does not include sulfur recovery and management processes, operation of cooling towers, and other supporting processes. The production energy of ethanol, a fuel additive, is not included here because ethanol production is classified under a separate NAICS (NAICS 325193, Ethyl Alcohol Manufacturing).

n/a indicates data is not available.

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

As can be seen from the ranges of specific energy use in Table 2-2, actual energy consumption can vary considerably between technologies in use. In addition, capacity utilization varies monthly, and over the last year has ranged from as low as 85 percent to 93 percent. A number of supporting processes that consume energy were also not included in this table (e.g., 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 30-40 percent of total process energy consumption. This large share of energy consumption is the result of every barrel of crude oil entering the refinery being 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 (over 15 percent) as does fluid catalytic cracking (nearly 15 percent). Hydrotreating is used to treat feedstocks for a number of refinery processes to improve catalyst life and enhance product quality. Fluid catalytic cracking breaks down larger and heavier hydrocarbon molecules into lighter molecules and is used to increase the yield of gasoline from crude oil.

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 over 3 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.

Process heaters and boilers are a large source of **air emissions**. In addition to CO, SO_x, and NO_x, 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.

Process wastewater is a significant effluent from a number of refinery processes. Atmospheric distillation 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.

Wastes, residuals and by-products are produced by a number of processes during refining can be but are not necessarily wastes. Many can be recycled or regenerated and 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 residuals in the form of spent caustic solutions. However, nearly all of these caustics are recycled.

Catalytic processes (fluid catalytic cracking, catalytic hydrocracking, hydrotreating, isomerization, ethers manufacture) also create 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.

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.

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, HP 2006a, Meyers 2004].

Table 2-3. Summary of Emissions, Effluents, Residuals and Waste Streams for Topping/Separation Processes			
Process	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Crude Oil Desalting	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates)	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)	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates) and steam injector emissions (hydrocarbons)	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 by-products

Table 2-4. Summary of Emissions, Effluents, Residuals and Waste Streams for Thermal and Catalytic Cracking Processes			
Process	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Visbreaking	Fugitive emissions from process vents	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 by-products generated
Coking	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates) Particulate emissions from decoking can also be considerable	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	Catalyst regeneration and CO boilers (hydrocarbons, CO, NO _x , SO _x and particulates)	Sour wastewater from the fractionator/gas concentration units and steam strippers (high levels of oil, suspended solids, phenols, cyanides, H ₂ S, 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	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates)	Sour wastewater from the fractionator and hydrogen separator (suspended solids, H ₂ S). 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	Largest Sources of Air Emissions	Largest Sources of 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), 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, SO _x , NO _x), 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, SO _x , NO _x , 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, SO _x , NO _x , 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	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Catalytic Hydrotreating	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates)	Sour wastewater from the fractionator and hydrogen separator (suspended solids, H ₂ S, 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 (NO _x , SO _x , hydrogen sulfide), fugitive emissions	Process wastewater (hydrogen sulfide, ammonia)	Hazardous air emissions - hydrogen sulfide, carbonyl sulfide (COS) and carbon disulfide (CS ₂); 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	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Lubricating Oil Manufacture (deasphalting, solvent extraction, dewaxing)	Heater stack gas (CO, NO _x , SO _x , 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, methyl ethyl ketone, methyl isobutyl ketone)

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.

Table 2-9 shows the limitations for average daily values for 30 consecutive days using best practicable control technology (BPT) currently available [NARA 2006]. The limitations 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).

Table 2-8. Air Emission Factors for Petroleum Refining Processes (lbs/1000 barrels of fresh feed)							
Process	SOx	NOx	CO	Hydrocarbons	Aldehydes	Ammonia	Particulates
Fluid Catalytic Cracking Units							
- Uncontrolled	493	71	13,700	220	19	54	242
- Electrostatic Precipator 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 Precipator 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

Neg negligible

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^b
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
^c BOD ₅	10.2
^d COD	70.0

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

b BPT as defined by EPA is the "best practicable control technology currently available."

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

d 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.

3 Separations: Atmospheric and Vacuum 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 2006, approximately 16.1 million barrels of crude oil per day were fed to atmospheric crude distillation units in domestic refineries. With the current U.S. refining capacity of 17.8 million barrels per day, this represents a capacity utilization rate of about 90 percent. Vacuum distillation capacity was projected to be about 8.2 million barrels per day in 2006, less than half the capacity of atmospheric distillation [DOE 2006a, DOE 2006b, OGJ 2006a].

<i>Fraction</i>	<i>ASTM Boiling Range, °F</i>
Light Straight-Run Gasoline	90-220
Naphtha	108-400
Kerosene	330-540
Light Gas Oil	420-640
Atmospheric Gas Oil	520-830
Heavy Residue	650+
Vacuum Gas Oil	750+

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 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 and Table 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 water¹, 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. Desalting creates an oily desalter sludge that may be a hazardous waste and a high temperature salt wastewater 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].

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.

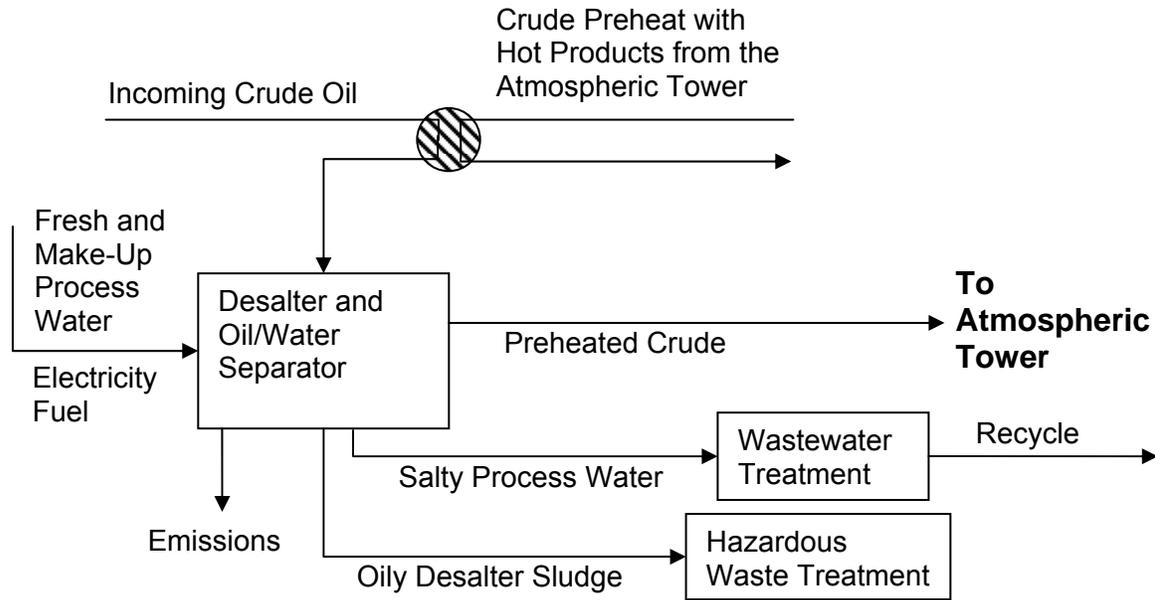


Figure 3-1. Crude Oil Desalting Flow Diagram [HP 1993a, EPA 1995a, ANL 1981]

Table 3-1. Key Energy and Environmental Facts—Desalting			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 203 Btu/bbl of oil Total: 540 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)

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, about 700°F. The term “atmospheric” refers to the pressure at which the column is operated. 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 and Table 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, limiting 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.

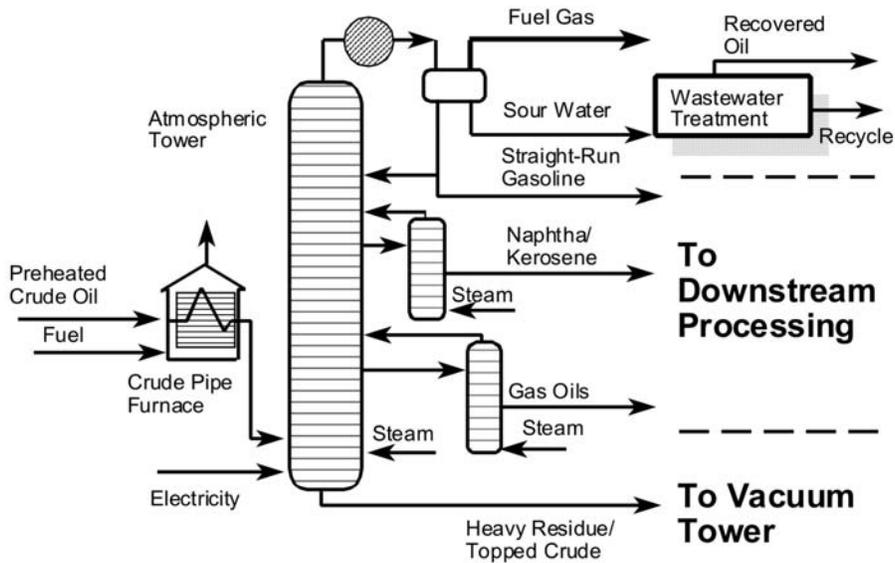


Figure 3-2. Atmospheric Distillation Flow Diagram
 [HP 1993a, EPA 1995a, ANL 1981]

Table 3-2. Key Energy and Environmental Facts—Atmospheric Distillation			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 109.1 x 103 Btu/bbl oil Total: 113.8 x 103 Btu/bbl oil	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates)	Oily sour water from the fractionators (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol)	Little or no residual waste or by-products

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 and the least volatile are absorbed and remain with the liquid on the tray. The higher column the trays are progressively 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 ammonia² and must be treated before it can be used as a fuel in process heaters.

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

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]

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.

Heavier Crude Fractions Must Be Separated by Vacuum Distillation

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 and Table 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.

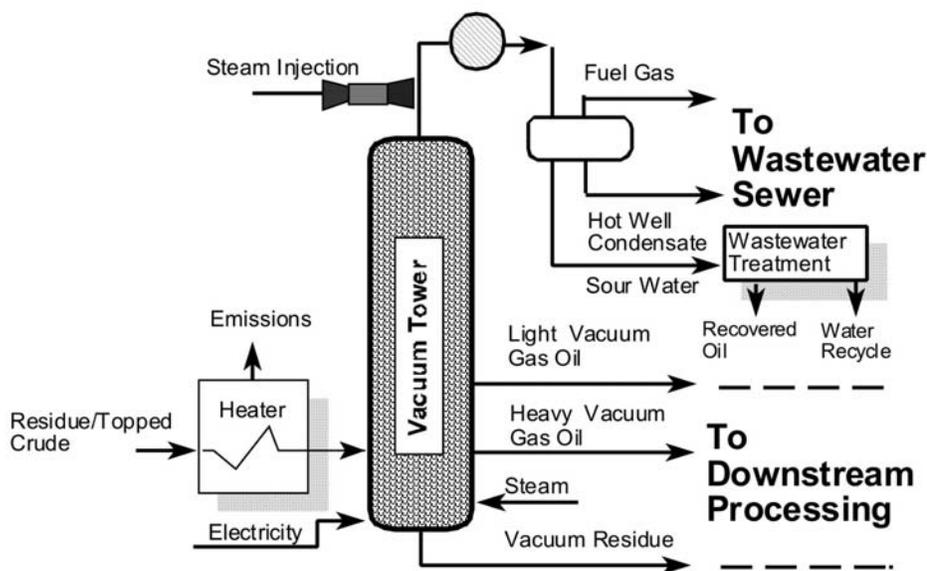


Figure 3-3. Vacuum Distillation Flow Diagram [HP 1993a, EPA 1995a, ANL 1981]

Table 3-3. Key Energy and Environmental Facts—Vacuum Distillation			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 89.1 x 10 ³ Btu/bbl oil Total: 91.5 x 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 by-products

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 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]

Table 3-4 summarizes the input and output streams for crude distillation processes, including desalting, atmospheric distillation and vacuum distillation.

Table 3-4. Summary of Inputs/Outputs for Crude Distillation Process (includes desalting, atmospheric distillation and vacuum distillation)			
Inputs		Outputs	
Crude Oil		Straight Run Gasoline	Vacuum Gas Oils
Process Water		Naphtha	Vacuum Residue
Steam		Kerosene	Fuel Gas
Fuel (Gas Oil)		Atmospheric Gas Oils	Process Wastewater
Electricity		Heavy Residue	Desalter Sludge

New Technologies Save Energy and Reduce Costs

Crude oil distillation is one of the most energy intensive petroleum refining processes. Heat integration via the crude preheat train (CPT) enables the use of product streams exiting the distillation tower to preheat crude feed entering the tower. However, fouling of the CPT heat exchangers can significantly reduce the heat transfer efficiency and increase the pressure drop. This leads to higher fuel input to the atmospheric tower furnace, a greater pumping load, and therefore increased operating costs and carbon emissions [87f, Smaili 2002, Yeap 2005, Wilson 2002, Bories 2004, Master 2003]. It is estimated that heat exchanger fouling costs U.S. refiners more than \$2 billion annually [IHS 2000]. Advances in heat exchanger configuration and improved fouling modeling are helping to reduce fouling in the CPT and other heat exchanger networks [Master 2003, Wilson 2002].

Desalter performance is another area of concern as poor performance can lead to corrosion, fouling, and increased VOCs in the brine wastewater [Fransen 2004, Kremer 2004]. When stable emulsions form, an organic (oil) and aqueous (water) layer builds resulting in oil residual in the brine stream, water residual in the crude oil stream, and less efficient removal of salt and metal contaminants. Improved desalter control systems allow operators to monitor the desalter and prevent upsets (e.g., electrical grid overload) due to the formation of stable emulsions [Fransen 2004]. New additives such as dispersants and demulsifiers are enabling refiners to process heavier crudes and crudes with higher contaminant contents while countering the increased fouling propensity of these crude oils [Lindemuth 2001, Kremer 2004]. Removal of contaminants such as calcium naphthenate, iron compounds, nickel, and vanadium also helps reduce the formation of stable emulsions and FCC catalyst poisoning.

Other separation technologies that may lead to significant energy savings but require greater capital investment include column add-ons such as vapor compression pumps, and advanced membranes.

3.2 Energy Requirements

Atmospheric distillation and vacuum distillation are very energy-intensive processes, accounting for approximately 900 trillion Btus/year, or about 30 percent of total process energy used in a refinery complex. The **process energy** used in atmospheric distillation (including desalting) and vacuum distillation is shown in Tables 3-5 and 3-6 [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 energy does include 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.

Table 3-5. Estimated Energy Use in Atmospheric Distillation^a—2005		
Energy Source	Specific Energy Use^b (10³ Btu/bbl of oil)	Total Industry Use^c (10¹² Btu/yr)
Electricity^d	2.3	13.3
Energy for Steam/Process Heat^e		
Natural Gas	29.3	169.6
Refinery Gas	52.6	304.5
Coke	19.3	111.7
Oils ^f	3.5	20.3
Other ^g	2.1	12.2
NET PROCESS ENERGY	109.1	631.6
Electricity Losses	4.7	27.2
TOTAL PROCESS ENERGY	113.8	658.8

- a Includes energy used for desalting.
- b Based on estimated utility requirements for several licensed technologies [ANL 1981, HP 2006a, SFA 1990].
- c Based on input to crude stills for 2005 (15.86 x 10⁶ bbls/cday assuming 90.4 percent capacity and 355 stream days per calendar year) [DOE 2006a, DOE 2006b].
- d Does not include losses incurred during the generation and transmission of electricity.
- e Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005.
- f Includes crude oil, distillate and residual fuel oil.
- g Includes liquefied petroleum gases, coal, and purchased steam.

Table 3-6. Estimated Energy Use in Vacuum Distillation—2005		
Energy Source^a	Specific Energy Use^b (10³ Btu/bbl of oil)	Total Industry Use^c (10¹² Btu/yr)
Electricity^d	1.2	3.1
Energy for Steam/Process Heat		
Natural Gas	24.1	62.8
Refinery Gas	43.2	112.6
Coke	15.9	41.4
Oils ^c	2.9	7.6
Other ^d	1.8	4.7
NET PROCESS ENERGY	89.1	232.2
Electricity Losses	2.4	6.3
TOTAL PROCESS ENERGY	91.5	238.5

- a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005.
- b Based on estimated utility requirements for several licensed technologies [ANL 1981, HP 2006a, SFA 1990].
- c Based on estimated vacuum distillation capacity of 7.14 x 10⁶ bbl/cday (assuming 90.4 percent capacity and 355 stream days per calendar year) [DOE 2006a, DOE 2006b].
- d Does not include losses incurred during the generation and transmission of electricity.
- e Includes crude oil, distillate and residual fuel oil.
- f Includes liquefied petroleum gases, coal, and purchased steam.

3.3 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 3-7 lists emission factors for major air emissions from vacuum distillation column condensers. Emission factors for process heaters and boilers are discussed in Section 10.

Table 3-7. Emission Factors for Vacuum Distillation Column Condensers (lbs/barrel of vacuum feed)					
Source	Particulates	SOx	CO	Total Hydrocarbons	NOx
Vacuum Distillation Condenser Column	--	--	--	50	--

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

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 SOx, NOx, 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 2004, 13.8 million pounds of toxic fugitive emissions were reportedly released by U.S. refineries [EPA 2006]. However, this represents a 73% reduction in toxic fugitive emissions since 1996 [EPA 1998, EPA 2006].

Fugitive emissions 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.

Atmospheric distillation and vacuum distillation both 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, H₂S, SOx, and NOx (see Section 10, Supporting Processes).

3.4 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. 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].

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 distillation 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.

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 3-8 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) [NARA 2005].

Constituent	BPT Limitation^b
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	0.0044
BOD ₅ ^c	4.25
COD ^d	21.3

a Combined limits for desalting, atmospheric, and vacuum distillation

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

c The five (5) subscript indicates an incubation period of 5 days.

d 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.

Source: NARA 2005

The limitations for the subset of refinery processes illustrated in Table 3-8 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 isomerization processes, and still be captured under the stated guidelines. 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

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^oC. A high BOD can deplete oxygen in receiving waters and kill aerobic organisms [Bailey 1986].

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. Usable oil is also recovered from the wastewater treatment process and may be directly reused or sent to oil storage tanks for reuse in the refinery. A more detailed discussion of wastewater treatment is provided in Section 10.

3.5 Waste, Residuals and By-products

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, including some wastes associated with wastewater treatment processes, which are discussed in more detail in Section 10.

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.

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 fourth in 2004 (14.3 million pounds released that year) [EPA 2006]. About 16 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 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. Catalytic cracking processes, including fluid catalytic cracking (FCC), moving bed catalytic cracking and hydrocracking, employ a catalytic agent to accelerate the cracking process. Moving bed units are less common today as fluidized bed units have taken over the field. Thermal cracking processes (e.g., visbreaking, delayed coking, and fluid coking) break down, rearrange, or combine hydrocarbon molecules with the application of heat and pressure. The quality of products from catalytic processes is generally better than those from thermal cracking due to the higher octane value.

The principal feedstocks for catalytic cracking processes are heavy products from the atmospheric and vacuum distillation columns (e.g., vacuum residual). As of January 2006, domestic refineries processed approximately 6.3 million barrels per day of heavy oil feedstock in catalytic cracking units; this value includes 6.2 million barrels of fresh feed and 0.1 million barrels of recycled feed. Input to hydrocracking units was about 1.6 million barrels per day, comprising distillate, gas oil, and residual hydrocracking. Thermal cracking units processed approximately 2.5 million barrels per day, with 2.3 million barrels input to delayed coking units and the remainder to fluid coking, visbreaking and other gas oil cracking. U.S. refinery production capacity for cracking and coking processes is shown in Table 4-1. Overall average refinery capacity utilization in 2004 was 93 percent, based on gross input to distillation units for 149 operable domestic refineries. [DOE 2006a, DOE 2006h]

Catalytic Cracking		Catalytic Hydrocracking			Thermal Cracking			
Fresh	Recycled	Distillate	Gas Oil	Residual	Delayed Coking	Fluid Coking	Visbreaking	Other/ Gas Oil
6,187,883	87,240	516,600	920,200	200,400	2,305,510	205,400	18,000	10,600

Source: DOE 2006a

Fluid Catalytic Cracking Is the Most Widely Used Refinery Conversion Process

Catalytic cracking is the process of breaking down larger, heavier, and more complex hydrocarbon molecules into simpler and lighter molecules through the application of heat and the use of a catalytic agent. Cracking, and all of the other processes identified in Table 4-1, seeks to increase the yield of gasoline from crude oil. The 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. 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. Gasoline from catalytic crackers contains olefins and more i-paraffins

and aromatics than straight-run gasoline, and these components contribute to its high octane—between 50 and 60 percent of the output of a catalytic cracker is high octane gasoline blending stock..

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 2004, the total charge capacity for catalytic crackers was over 38% of the refinery capacity in the U.S., based on gross input to distillation units [DOE 2006h]. The most prevalent catalytic cracking process design is the fluidized-bed reactor, representing about 98 percent of catalytic cracking capacity.

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.

Though a number of licensors offer a variety of configurations of this technology, general operation remains very similar. The heart of an FCC system is the reactor-regenerator section (see Figure 4-1 and Table 4-2). 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.

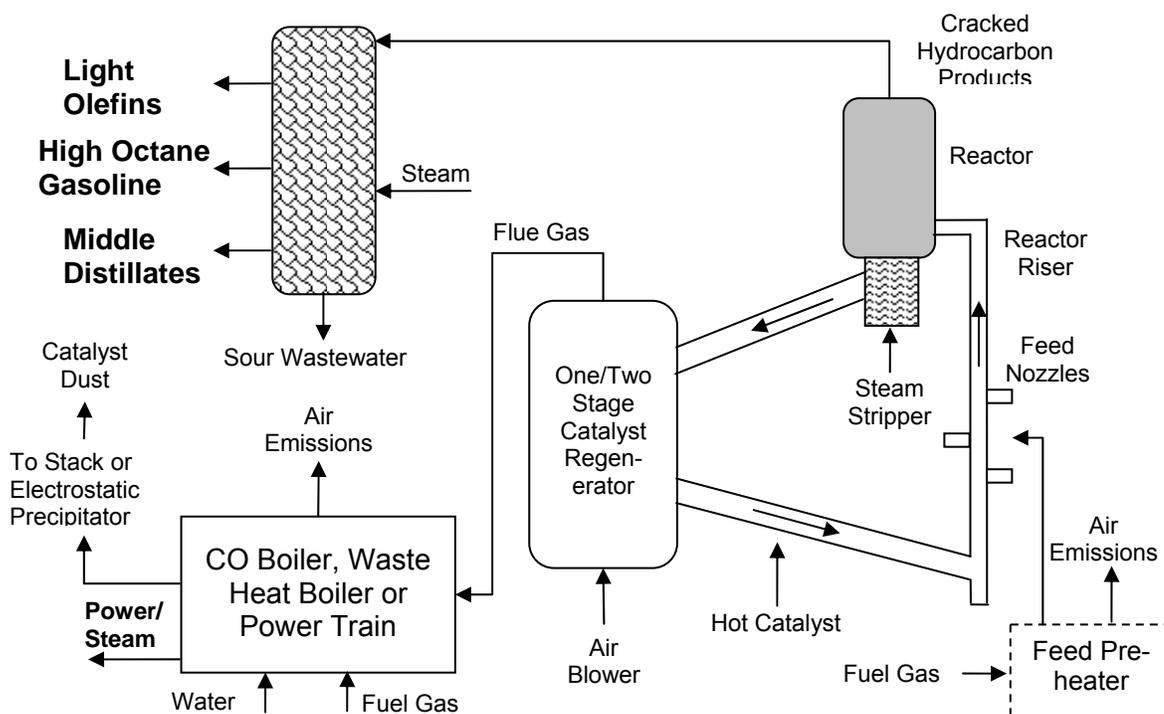


Figure 4-1. Fluid Catalytic Cracking Flow Diagram
[HP 2006a, Meyers 2004, HP 1994, OGJ 1990]

Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 74.5 x 10 ³ Btu/bbl of oil Total: 208.7 x 10 ³ Btu/bbl of oil	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 ₂ S, 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)

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 olefins⁵ are taken overhead and routed to a gas concentration unit. Light cycle oil, recovered 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. 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 then imparts heat to the catalyst, and helps 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 4-3 shows typical coke deposition and associated heating values in catalytic cracking processes [ANL 1981].

55% Conversion of Feed			85% Conversion of Feed		
° API	Wt% Coke	Heating Value (10⁶ Btu/bbl feed)	° API	Wt% Coke	Heating Value (10⁶ Btu/bbl feed)
19	9.6	0.37	19	14.7	0.57
23	6.6	0.25	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 4-2). 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.

⁵ Olefin is a common name for alkenes, or compounds containing carbon-carbon double bonds.

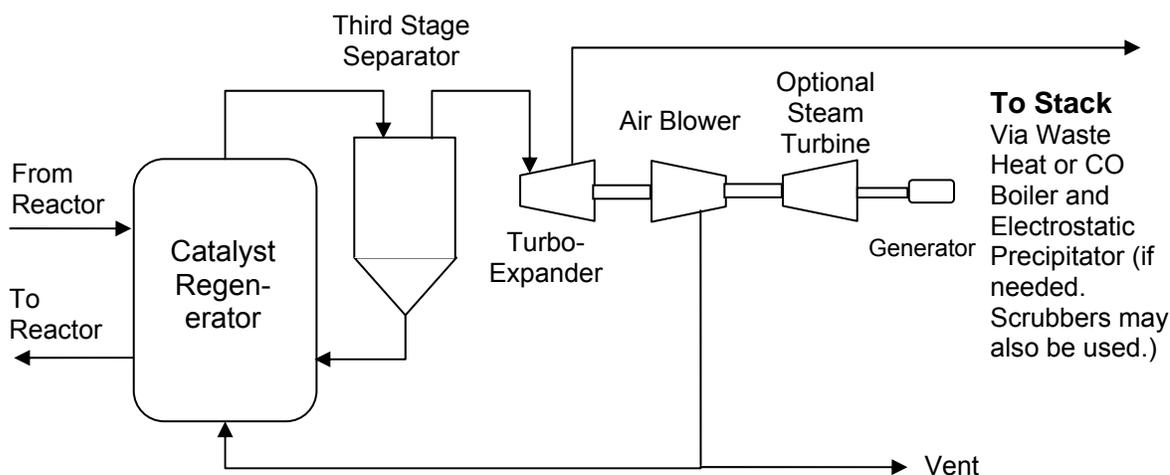


Figure 4-2. Typical Turboexpander Power Train for an FCC Unit

The regenerator may be operated to achieve complete or partial combustion of CO to CO₂, or the CO may be converted to CO₂ 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 equipment is often installed to minimize regulated emissions such as SO_x and NO_x and remove remaining coke particulates.

FCC operation is affected by six important independent operating variables:

- Riser (feed line) temperature
- Feed preheat temperatures
- Fresh feed rate
- Catalyst make-up rate
- Recycle rates
- 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: HP 2006A, Meyers 2004, EPA 1995a]

Recent improvements in pretreatment, feed distribution, riser and stripper design, and catalyst selection have improved FCC yield, product selectivity, and emissions control. A common objective in many of these technology improvement areas is to lower the delta coke (weight percentage of coke on catalyst per pass through the regenerator) to achieve better yields and higher throughput. [UOP 2004c]

Catalytic crackers have historically been operated to produce maximum yields of gasoline and distillates. As demand for reformulated gasoline has increased, catalytic crackers have been increasingly changed to operate in a mode to produce higher yields of olefins. Olefins are useful for

production of clean fuels such as alkylates or as octane-enhancers such as ethers. Although high-octane gasoline is the main product from catalytic cracking, the process is increasingly being considered for the production of light olefin petrochemical feedstocks such as ethylene, propylene, and butylene which may be more profitable to produce. Fluidized-bed catalytic cracking technologies that have recently been developed to increase light olefin yield include: Deep Catalytic Cracking (DCC), Selective Component Cracking (SCC), Catalytic Pyrolysis Process (CPP), Ultimate Catalytic Cracking (UCC), and High Severity (HS) FCC. [Ng 2006, HP 2006a, Letsch 2002]

Catalytic Hydrocracking Uses Hydrogen and a Catalyst to Produce Fuels

Like catalytic cracking, **hydrocracking** is used to produce blending stocks for gasoline and other fuels from heavy feedstocks (see Figure 4-3 and Table 4-4). 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.

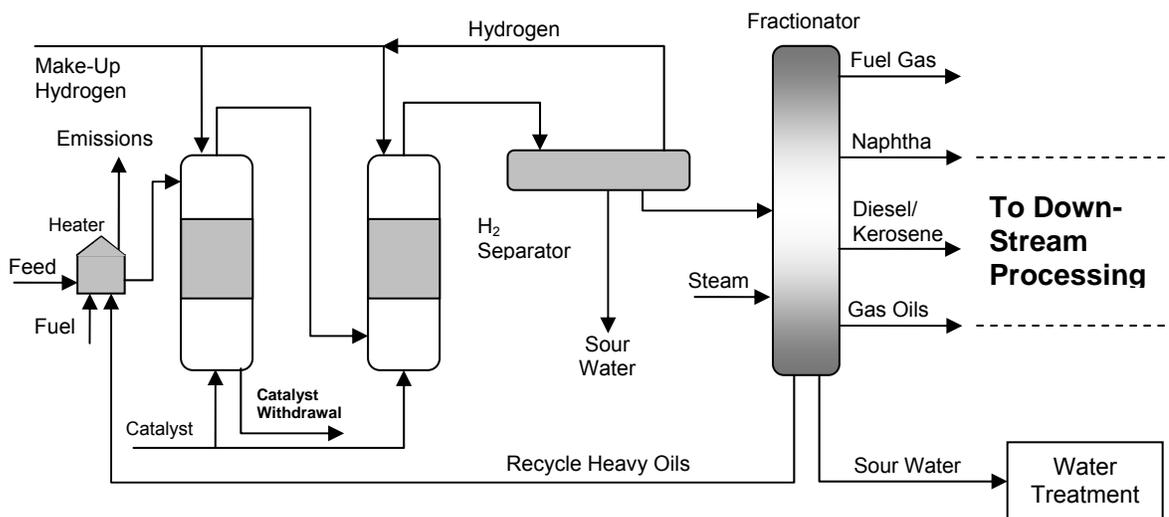


Figure 4-3. Catalytic Hydrocracking Flow Diagram [HP 2006a, Meyers 2004, EPA 1995a]

Table 4-4. Key Energy and Environmental Facts—Catalytic Hydrocracking			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 158.9 x 10 ³ Btu/bbl of oil* Total: 529.3 x 10 ³ Btu/bbl of oil	Heater stack gas (CO, SO _x , NO _x , hydrocarbons and particulates)	Sour waste water from the fractionator and hydrogen separator (suspended solids, H ₂ S) Water Flow = 2 gal/bbl	Spent catalyst fines (metals from crude oil, and hydrocarbons)

* Includes 361.5 x 10³ Btu/bbl to produce the required hydrogen (1500 scf/bbl)

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. These products can include gasoline, jet fuel, kerosene, 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. Once-through and recycle options are available to provide operating flexibility and economy. 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: Meyers 2004, HP 2006a, EPA 1995a].

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

A number of processes fall into the category of thermal cracking, including fluid coking, visbreaking, and delayed coking, the most common of these non-catalytic conversion processes. Residual fuel oil from the vacuum distillation column is a typical feedstock for coking and visbreaking; the resulting product slate includes gasoline, gas oils, fuel gas, and petroleum coke. The majority of coke currently produced in refineries (more than 65%) is fuel-grade sponge coke.

- Petroleum coke can be used on-site as a fuel or, depending on the quality, be marketed externally as a fuel or for electrode manufacture.
- Sponge coke, a substance that resembles coal and is generally blended with bituminous coal or used in combination with oil or gas, can be used as a fuel by electric utilities or in cement kilns.
- Purge coke from fluid coking operations can also be used to fuel cement kilns or in conventional boilers to produce steam. Low-sulfur, low-metals sponge coke can also be used to 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. Since anode-grade coke production requires sweeter refinery feedstocks, the trend of the industry has been to produce fuel-grade coke.

Interest in coke gasification has increased significantly in recent years. What was previously thought of as a poor quality and low value waste stream is increasingly being considered as an important feedstock for hydrogen and Fischer-Tropsch blending fuel production and power and steam generation. Rising and fluctuating natural gas costs and increased demand for hydrogen to produce cleaner fuels has opened the door to producing hydrogen via gasification of petroleum coke, which in some cases may be more cost effective than methane steam reforming. Available technologies, such as the integrated gasification combined cycle plant, may provide refineries with a new means for reliable steam and electric power, a source for increasing hydrogen needs, and elimination of coke disposal costs [Marano 2003, Gray 2000].

The Most Commonly Used Coking Processes Are Delayed Coking and Fluid Coking

Depending on the feed used, **delayed coking** produces sponge or needle coke. Heavy residues (e.g., vacuum residual, sometimes atmospheric residual) are commonly used 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. This typically

translates into a feed with an aromatics content of greater than 60 liquid volume percent, a sulfur content of 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 hydrosulfurization is sometimes used upstream of the delayed coker to reduce CCR as well as metals and sulfur impurities when the feedstock is very heavy or of poor quality.

Delayed coking is a semibatch process (see Figure 4-4 and Table 4-5). 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.

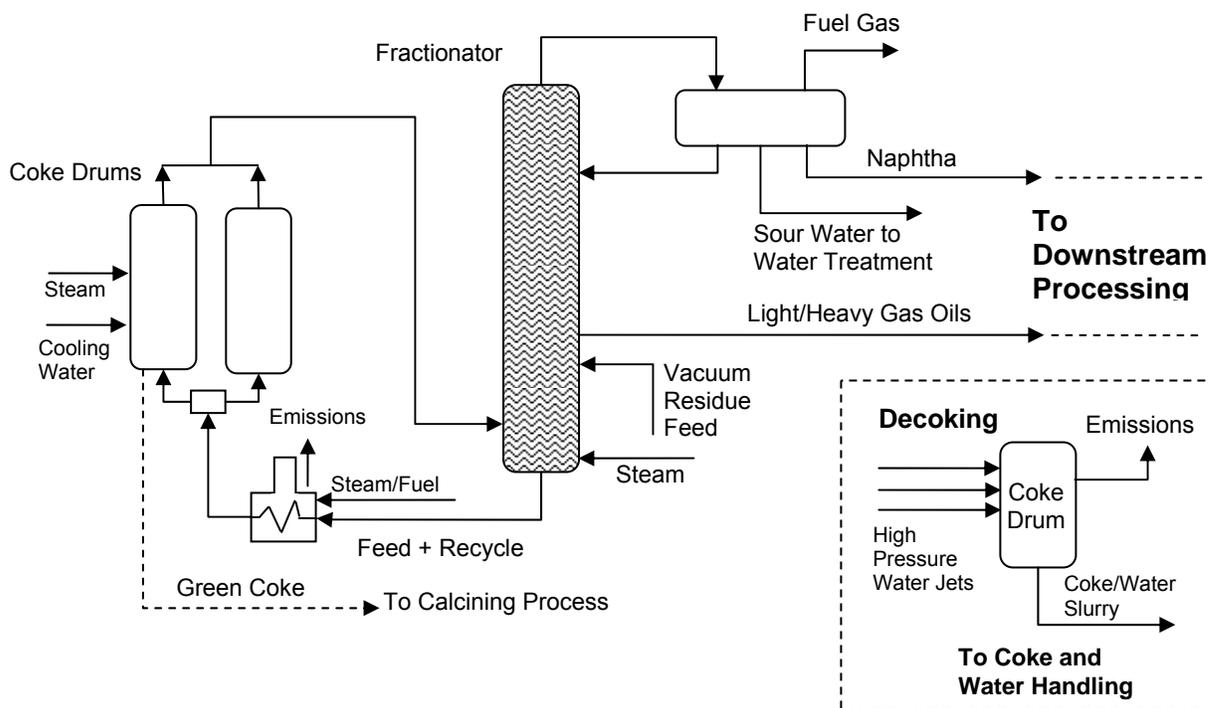


Figure 4-4. Delayed Coking Flow Diagram [HP 2006a, Meyers 2004, EPA 1995a]

Table 4-5. Key Energy and Environmental Facts—Delayed Coking			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 140.5×10^3 Btu/bbl of oil Total: 166.3×10^3 Btu/bbl of oil	Heater stack gas (CO, SO _x , NO _x , 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)

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, preheat the feed, or 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 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 recovers hydrocarbon and steam vapors generated during the quenching and steaming process, and is designed to minimize air pollution. Decoking then uses high pressure water jets to cut the coke from the drum. 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. Typical coke drum schedules consist of 24 hours of coking and 24 hours of decoking.

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. Typical operating temperatures range from 900 to 1100°F—too low temperatures create pitch or soft coke, too high temperatures create coke that is too hard and difficult to remove from the drum. 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/in² (gage). For needle coke production (a higher valued coke product), pressures as high as 150 lb/in² (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: HP 2006a, Meyers 2004, EPA 1995a, ANL 1981].

Unlike delayed coking, **fluid coking** is a continuous process (see Figure 4-5 and Table 4-6) in which 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 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**¹ has increased; no purely fluid cokers have been built since the late 1970s [SFA 1993]. In Flexicoking units, the devolatilized

¹ Tradename for process developed by Exxon Research and Engineering.

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: HP 2006a, EPA 1995b]

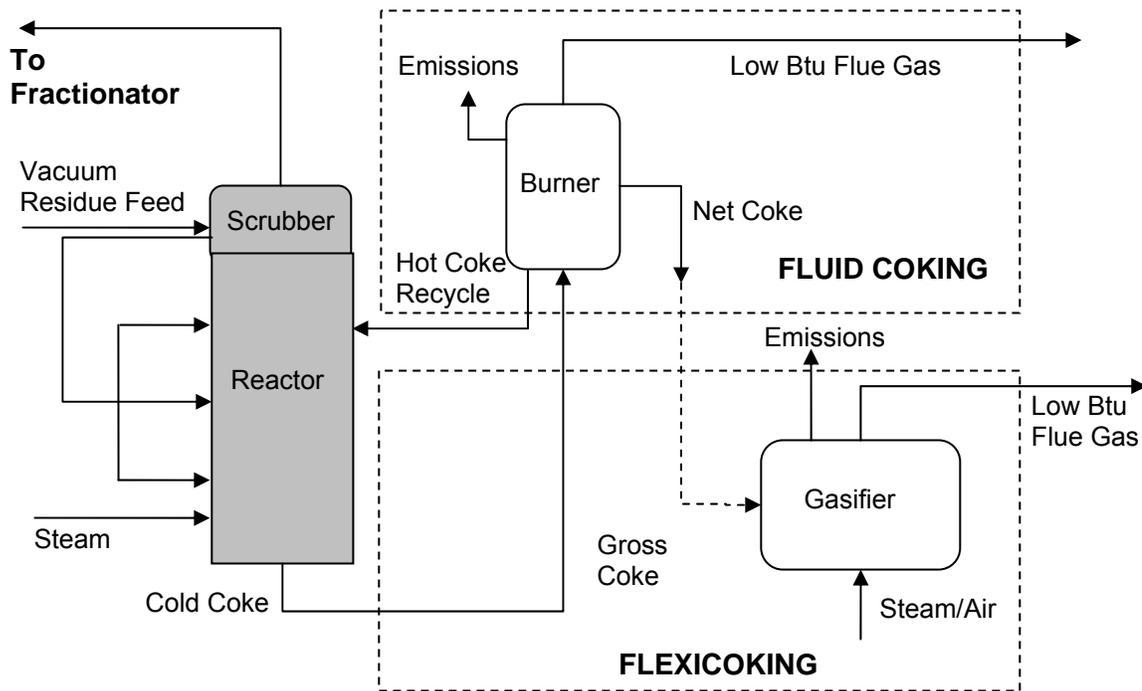


Figure 4-5. Fluid Coking/Flexicoking Flow Diagram [HP 2006a, EPA 1995b]

Table 4-6. Key Energy and Environmental Facts—Fluid Coking/Flexicoking			
Energy	Emissions	Effluents	Waste, Residuals or By-products
<u>Fluid Coking</u> Net: 267.4 x 103 Btu/bbl of oil Total: 258.0 x 103 Btu/bbl of oil	Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)	No significant effluents	Small amounts of coke dust and particulate matter
<u>Flexicoking</u> Net: 129.9 x 103 Btu/bbl of oil Total: 166.5 x 103 Btu/bbl of oil			

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 4-6 and Table 4-7).

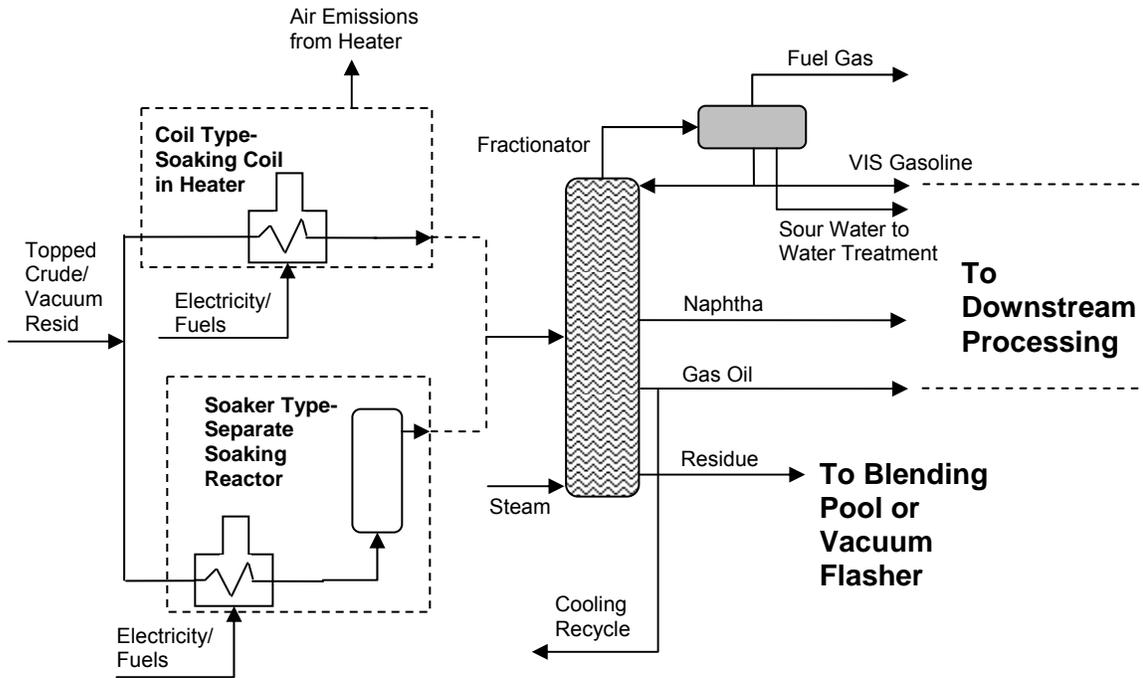


Figure 4-6 Visbreaking Flow Diagram [Meyers 2004, HP 2006a, EPA 1995a]

Table 4-7. Key Energy and Environmental Facts—Visbreaking			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
<u>Coil Type</u> Net: 130×10^3 Btu/bbl of oil Total: 136×10^3 Btu/bbl of oil	Heater stack gas (CO, SO _x , NO _x , 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 by-products generated
<u>Soaker Type</u> Net: 58×10^3 Btu/bbl of oil Total: 63×10^3 Btu/bbl of oil			

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 naphtha 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 2004, HP 2006a, EPA 1995a, EPA 1995b]

Table 4-8 summarizes the input and output streams for cracking and coking processes.

Table 4-8. Summary of Inputs and Outputs of Cracking and Coking Processes		
Inputs:	Outputs:	
Heavy oil feedstocks	High Octane Gasoline	Fuel Gas
Hydrogen	Diesel Fuel	Hydrogen Sulfide
Fuel Gas	Naphtha	Process Wastewater
Process Water	Middle Distillates	Sour Water
Steam	Heavy Oils/Residuum	Catalysts Fines
Electricity	Marketable Coke	Spent Catalysts
Catalysts		

4.2 Energy Requirements

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

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 2006a].

Most of the energy required for catalytic cracking is for steam stripping, feed preheaters, and electricity for air blowing through the regenerator. Most units follow a heat balance design, where the heat produced by burning the coke off the catalyst during regeneration supplies the heat consumed during the endothermic cracking reactions, often eliminating the need for external heating sources. From a utility perspective, some units are net energy producers given the large quantities of hot flue gas produced in the regenerator that can be recovered in a waste heat or CO boiler to provide steam and/or power for the regenerator air blowing system.

Tables 4-9 through 4-13 illustrate the process energy used in various cracking and coking processes [HP 2006a, Meyers 2004, ANL 1981]. The energy content of the feedstock (i.e., feedstock energy) is not considered, 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, however, include any energy products manufactured by the refinery that are used on-site (e.g., refinery fuel gas).

Table 4-9 provides an indication of the average energy use by an FCC unit. The Total Process Energy value accounts for energy exported in the form of steam production and energy consumed by burning coke off the catalyst. Energy produced by combustion of coke in a typical FCC unit is estimated by catalyst manufacturer, GRACE Davison, in their *Guide to Fluid Catalytic Cracking*.

Unlike fluid catalytic cracking, catalytic hydrocracking uses large quantities of hydrogen in addition to fuel gas and steam. Table 4-10 provides the estimated energy use in catalytic hydrocracking. Energy exported in the form of steam production and energy required to produce the required hydrogen are accounted for in the Total Process Energy value. Energy use for hydrogen demand is estimated assuming the majority of hydrogen is produced onsite via methane steam reforming.

Table 4-9. Estimated Energy Use in Fluid Catalytic Cracking—2005		
Energy Source	Specific Energy Use^a (10³ Btu/bbl of oil)	Total Industry Use^b (10¹² Btu/yr)
Electricity ^c	12.5	25.0
Energy for Steam/Process Heat ^d		
Natural Gas	17.0	34.0
Refinery Gas	30.5	61.0
Coke	11.2	22.4
Oils ^e	2.1	4.2
Other ^f	1.2	2.5
NET PROCESS ENERGY	74.5	149.1
Electricity Losses	25.9	51.8
Energy Export ^g	(97.7)	(195.4)
Combustion of Coke (ΔH_c) ^h	206	412.0
TOTAL PROCESS ENERGY	208.7	417.5

a Average values based on estimated utility requirements for various licensed technologies, including ABB Lummus

FCC, MW Kellogg Orthoflow, Exxon Flexicracking, UOP FCC and others [HP 2006a, Meyers 2004, ANL 1981].

b Based on catalytic cracking fresh feed capacity at U.S. refineries on January 1, 2005 (6,067,096 bbls/cday) operating at 90.4% capacity and assuming 355 stream days per calendar year [DOE 2006a, DOE 2006b].

c Does not include losses incurred during the generation and transmission of electricity.

d Fuel mix for fossil fuels (not electricity) based on typical use at refineries in 2005.

e Includes crude oil, distillate and residual fuel oil.

f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

g Assumes various degrees of steam production (CO/waste heat boiler), but not energy recovery through a turboexpander.

h Based on Walden Oil example energy produced by the combustion of coke [Davison 1993].

Energy Source	Specific Energy Use^a (10³ Btu/bbl of oil)	Total Industry Use^b (10¹² Btu/yr)
Electricity ^c	38.9	20.3
Energy for Steam/Process Heat ^d		
Natural Gas	32.9	17.1
Refinery Gas	59.0	30.7
Coke	21.7	11.3
Oils ^e	4.0	2.1
Other ^f	2.4	1.3
NET PROCESS ENERGY	158.9	82.8
Electricity Losses	80.7	42.1
Energy Export ^g	(71.8)	(37.4)
Hydrogen Demand ^h	361.5	188.4
TOTAL PROCESS ENERGY	529.3	275.9

a 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/Automatisierung GmbH [HP 2006a, Meyers 2004].

b Based on catalytic hydrocracking fresh feed capacity at U.S. refineries on January 1, 2005 (1,579,507 bbls/cday) operating at 90.4% capacity and assuming 355 stream days per calendar year [DOE 2006a, DOE 2006b].

c Does not include losses incurred during the generation and transmission of electricity.

d Fuel mix for fossil fuels (not electricity) based on typical use at refineries in 2005.

e Includes crude oil, distillate and residual fuel oil.

f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

g Assumes various degrees of steam production, mostly 600 psig.

h Hydrogen demand ranges from 1000-3000 scf/bbl of feed. It is assumed that on average, 1500 scf of hydrogen is supplied via steam reforming of methane – power and fuel energy use for methane steam reforming is approximately 241 Btu/scf [Gary 1984].

Energy Source	Specific Energy Use (10³ Btu/bbl of oil)	Total Industry Use^a (10¹² Btu/yr)
Electricity ^b	12.4	9.1
Energy for Steam/Process Heat ^c		
Natural Gas	35.1	25.9
Refinery Gas	63.1	46.6
Coke	23.3	17.3
Oils ^d	4.2	3.1
Other ^e	2.4	1.8
NET PROCESS ENERGY	140.5	103.8
Electricity Losses	25.8	19.1
TOTAL PROCESS ENERGY	166.3	122.9

a Based on delayed coking charge capacity at U.S. refineries on January 1, 2006 (2,242,345 bbls/cday) operating at 90.4% capacity and assuming 355 stream days per calendar year [DOE 2006a, DOE 2006b].

b Does not include losses incurred during the generation and transmission of electricity.

c Fuel mix for fossil fuels (not electricity) based on typical use at refineries in 2005.

d Includes crude oil, distillate and residual fuel oil.

e Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

Energy Source	Specific Energy Use (10 ³ Btu/bbl of oil)	Total Industry Use ^a (10 ¹² Btu/yr)
Electricity ^b	102.4/102.4	2.7/4.1
Steam	165.0/27.5	4.3/1.1
NET PROCESS ENERGY	267.4/129.9	7.0/5.2
Electricity Losses	212.6/212.6	5.6/8.4
Energy Export ^c	(222.0/176.0)	(5.9/7.0)
TOTAL PROCESS ENERGY	258.0/166.5	6.7/6.6

a Based on fluid coking charge capacity at U.S. refineries on January 1, 2006 (199,773 bbls/cday) operating at 90.4% capacity and assuming 355 stream days per calendar year [DOE 2006a, DOE 2006b]. Assumes 60 percent Flexicoking, 40 percent fluid coking [SFA 1993].

b Does not include losses incurred during the generation and transmission of electricity.

c Assumes various degrees of steam production, mostly 600 psig

Energy Source	Specific Energy Use (10 ³ Btu/bbl of oil)	Total Industry Use ^a (10 ¹² Btu/yr)
Electricity ^b	2.5	0.01
Energy for Steam/Process Heat ^c		
Natural Gas	18.3	0.11
Refinery Gas	42.0	0.24
Coke	13.5	0.08
Oils ^d	4.0	0.02
Other ^e	1.6	0.01
NET PROCESS ENERGY	81.9	0.47
Electricity Losses	5.1	0.03
TOTAL PROCESS ENERGY	87.0	0.50

a Based on visbreaking charge capacity at U.S. refineries on January 1, 2006 (17,507 bbls/cday) operating at 90.4% capacity and assuming 355 stream days per calendar year [DOE 2006a, DOE 2006b]. Assumes 33% of the market is coil type, and 67% is soaker type visbreakers. [Meyers 2004]

b Does not include losses incurred during the generation and transmission of electricity.

c Fuel mix for fossil fuels (not electricity) based on typical use at refineries in 2005.

d Includes crude oil, distillate and residual fuel oil.

e Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

4.3 Air Emissions

Air emissions from **thermal cracking** originate in the combustion of fuels in process heaters and boilers, equipment leaks of volatile constituents, and emissions that arise from 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 released during the cooling and venting of coke drums prior to decoking. Particulate emissions from decoking (in delayed coking processes) are potentially

significant, although very limited data is available. 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, potentially one of the most substantial sources of carbon monoxide and particulate emissions, releases emissions in process heater flue gas, as fugitive emissions from leaking valves and pipes, and during regeneration of the cracking catalyst. 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). Emission factors for fluid catalytic cracking are shown in Table 4-14, not including emissions from the combustion of fuels in process heaters, which are evaluated separately. As can be seen, catalytic crackers are significant sources of SOx and NOx. New technologies are being employed to comply with current EPA and state regulations, including wet gas scrubbers, selective catalytic reduction, and selective non-catalytic reduction.

Source (uncontrolled)	Particulates	SOx	CO	Total Hydrocarbons	NO2	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.

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.

4.4 Effluents

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 (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. The process water used in fractionators, like most separation processes in the refinery, 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, like catalytic cracking, produces sour wastewater at the fractionator, 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 4-15 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 [NARA 2006].

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

Source: NARA 2006

- 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.

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].

4.5 Waste, Residuals and By-products

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, 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.

Oily sludges that result from wastewater treatment facility of 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.

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 2004 (over 3 million pounds) [EPA 2006].

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

Cracking and coking processes include some form of fractionation or steam stripping as part of the process configuration. These units 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 2004 (over 14 million pounds released) [EPA 2006].

A small portion (approximately 2 percent) of toxic chemicals released from refining is 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 zinc, vanadium, nickel and others [EPA 2006].

5 Catalytic Reforming

5.1 Catalytic Reforming Process Overview

Catalytic Reforming Increases Octane Rating and Produces Aromatics

Catalytic reforming increases 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, generates hydrogen gas for use in many other refinery processes (e.g., hydrocracking, hydrotreating), and produces light gases and liquified petroleum gas (LPG). In 2005, catalytic reformers produced approximately 3.7 million barrels of high octane product. This production is based on a 90 percent overall average refinery capacity [OGJ 2006a, DOE 2006a, DOE 2006b].

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. Four major types of reactions occur during reforming processes:

- **Dehydrogenation of naphthenes** occurs quickly, producing hydrogen gas and aromatic compounds (see Figure 5-1).
- **Isomerization** also occurs rapidly and must take place before dehydrogenation to the aromatic state can occur (see Figure 5-2).
- **De-hydrocyclization** is the most difficult reaction to catalyze, and consists of the molecular rearrangement of a paraffin to a naphthene (see Figure 5-3).
- During **hydrocracking**, paraffin compounds are cracked out of the gasoline boiling range and aromatics become concentrated in the product, increasing octane (see Figure 5-4).

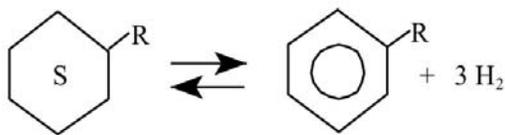


Figure 5-1. Dehydrogenation of Naphthenes to Aromatics

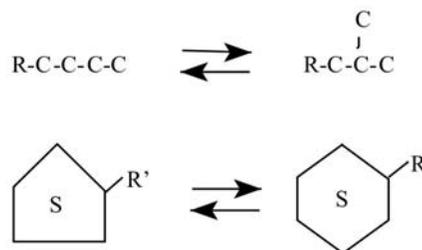


Figure 5-2. Isomerization

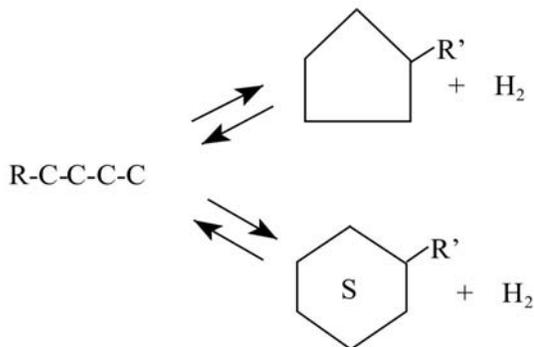


Figure 5-3. Dehydrocyclization of Paraffins to Naphthenes

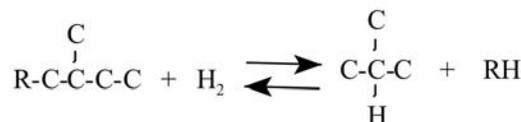


Figure 5-4. Hydrocracking

The first 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. Hydrocracking is exothermic.

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).

Catalytic Reformers Utilize Multiple Reactor Beds

Catalytic reformers utilize fixed-bed or moving-bed processes in a series of three to six reactors to allow separation of the primarily endothermic reactions (see Figure 5-5 and Table 5-1). Interstage heaters are installed between reactors to maintain the required temperature of the hydrocarbon feed stream.

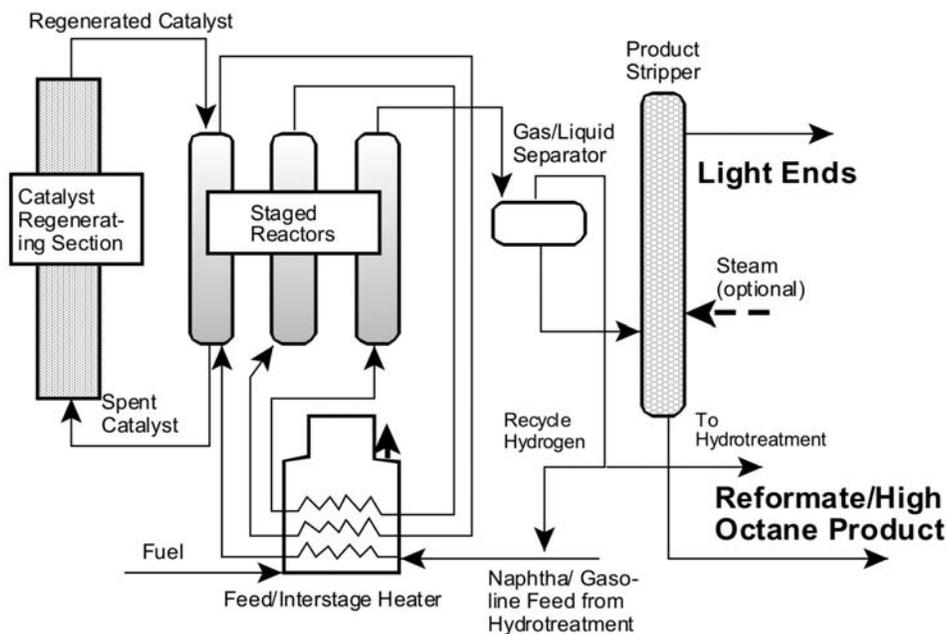


Figure 5-5. Catalytic Reforming Flow Diagram (continued)
[EPA 1995a, HP 2006a, Meyers 2004]

Table 5.1. Key Energy and Environmental Facts—Catalytic Reforming			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 263.9×10^3 Btu/bbl Total: -210.2×10^3 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 to 1700 scf/bbl:

Feed to the reformer (naphtha, 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).

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 2006a, Meyers 2004]

Developments in Catalytic Reforming Technologies Are Proving Beneficial

As operating costs soar due to stringent environmental regulations and fuel requirements, refiners are investing in new catalysts as they can have a significant impact on product yield and refinery profitability. New catalysts (e.g., sulfated zirconia, novel metal oxide) with higher activities, robustness, and tolerance of feedstock contaminants are entering the market [Weyda 2003, SB 2004, Kane 2004, UOP 2004a, UOP 2004b]. Increased tolerance to contaminants such as sulfur and water can help reduce operating costs by eliminating the need for the expensive pretreatment of feedstocks. Additionally, the new catalysts generate more hydrogen and can help refiners meet the increasing demand for hydrogen that is due to new fuel requirements and the movement towards processing heavier and sour crude oils.

Table 5-2 summarizes the input and output streams for catalytic reforming processes.

Table 5-2. Summary of Inputs and Outputs of Catalytic Reforming			
Inputs:		Outputs:	
Straight Run Gasoline	Cooling Water	High Octane	LPG
Naphtha	Electricity	Gasoline/Blending Stock	Fuel Gas
Hydrogen	Fuel Gas	Hydrogen	Aromatics
Catalyst	Steam		

5.2 Energy Requirements

The majority of the process energy input to catalytic 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 process energy shown in Table 5-3 [HP 2006a, Meyers 2004] does not consider the energy content (i.e., feedstock energy) of the feedstock, 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).

Table 5-3. Estimated Energy Use in Catalytic Reforming—2005		
Energy Source^a	Specific Energy Use^b (10³ Btu/bbl of feed)	Total Industry Use^c (10¹² Btu/yr)
Electricity ^d	9.8	12.1
Energy for Steam/Process Heat		
Natural Gas	69.6	85.7
Refinery Gas	125.0	153.9
Coke	46.0	56.6
Oils ^e	8.4	10.3
Other ^f	5.1	6.3
NET PROCESS ENERGY	263.9	324.9
Electricity Losses	20.5	25.2
Hydrogen Produced	(479.2)	(589.9)
Steam Produced	(15.4)	(19.0)
TOTAL PROCESS ENERGY	(210.2)	(258.8)

- a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005.
b 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 2006a, Meyers 1997, Meyers 2004].
c Based on catalytic reforming capacity at U.S. refineries on January 1, 2006 (3,730,427 bbls/cday, assumes 355 stream days per calendar year) operating at 90.4% capacity [DOE 2006a, DOE 2006b].
d Does not include losses incurred during the generation and transmission of electricity.
e Includes crude oil, distillate and residual fuel oil.
f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

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).

5.3 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.

The toxic aromatic chemicals toluene, xylene, and benzene 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 may be released 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 atmosphere is the regeneration vent, which is most often scrubbed with a caustic to prevent emission of hydrochloric acid (this also removes particulates).

5.4 Effluents

Catalytic Reforming is the Third Largest Source of Process Wastewater

The naphtha dehydrogenation process on the feed to the catalytic reformer is the third largest generator of wastewater in the refinery. Typical water flow for naphtha dehydrogenation is about 6 gallons per barrel of product [EPA 1995a]. This wastewater is 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 6-6 in Section 6 shows combined limitations (catalytic reforming and alkylation) for average daily values for 30 consecutive days using the best available technology economically available (BAT) [NARA 2006].

5.5 Waste, Residuals and By-products

Hydrogen gas is a valuable by-product of catalytic reforming. Hydrogen recovery from catalytic reforming is often not enough to meet total refinery requirements. As crude quality has declined and refiners are processing heavier sour crudes, the overall hydrogen to carbon ratio is also decreasing. Hydrogen content is an important factor in crude value. The lower quality crude will most likely result in declining naphtha yield and hence lower hydrogen production. Declining in-plant hydrogen production volumes leads to increased hydrogen demand, necessitating the manufacture of additional hydrogen or obtaining a supply from external sources. [Gary 2007].

Spent reforming catalysts are not disposed of as a hazardous waste. The precious metals (usually platinum) contained in the catalysts are recovered from the spent catalyst.

6 Alkylation

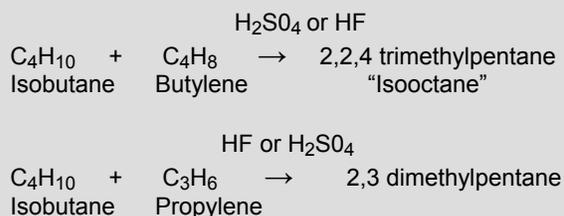
6.1 Alkylation Overview

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), 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. In 2005, an estimated 1.1 million barrels per day of alkylates were produced in domestic refineries. This estimate is based on a 90 percent overall average refinery capacity utilization [OGJ 2006a, DOE 2006a].

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 olefins⁶ (e.g., propylene, butylene) are combined with an isoparaffin⁷ (e.g., isobutane) in the presence of a strong acid (e.g. sulfuric acid or hydrofluoric acid) to produce high octane alkylate. 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.

Typical Primary Alkylation Reactions



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 and Table 6-1) typically utilize a refrigeration cycle to effect the reaction and/or product separation. In the 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

Material Inputs for Sulfuric Acid Alkylation*

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

⁶ Alkenes, or compounds containing carbon-carbon double bonds.

⁷ 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).

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 SO₂. The hydrocarbons are further processed in a deisobutanizer and a debutanizer to produce the desired high octane alkylate.

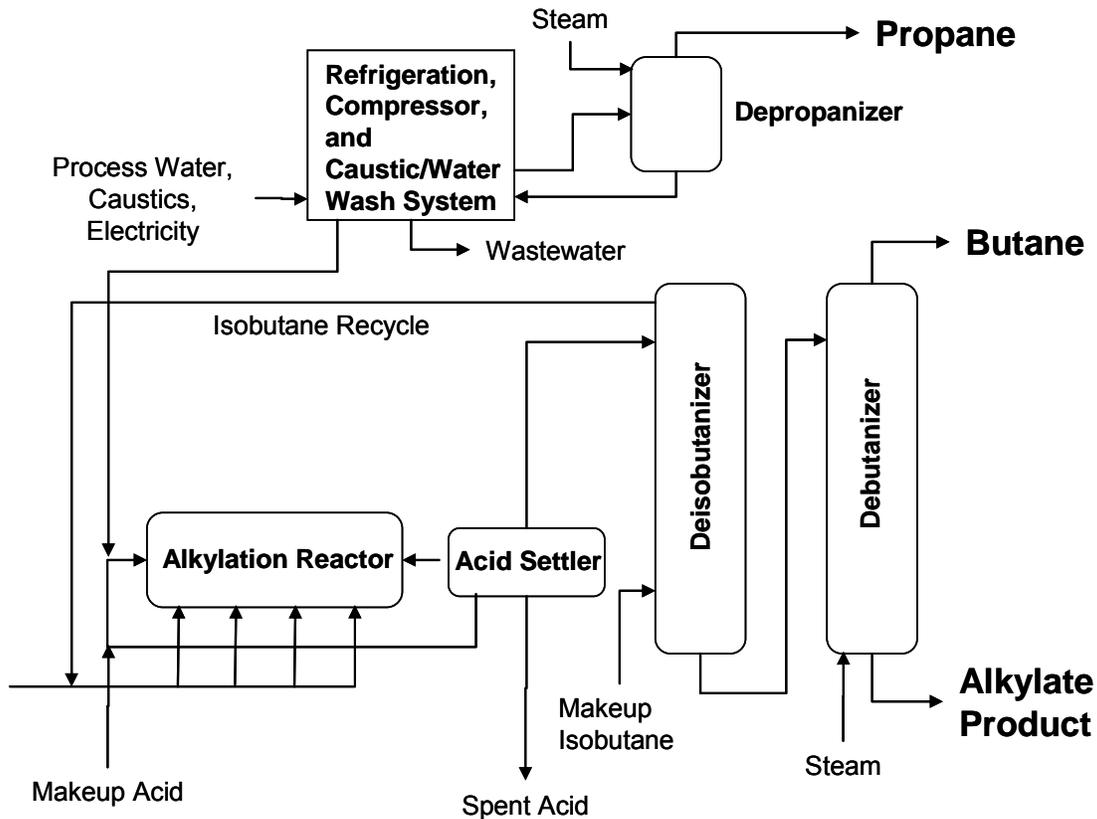


Figure 6-1. Sulfuric Acid-Based Alkylation Flow Diagram
[Meyers 2004, HP 2006a]

6.1 Key Energy and Environmental Facts—Sulfuric-Acid Based Alkylation			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Sulfuric Acid Catalyst Net: 250×10^3 Btu/bbl feed Total: 335×10^3 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)

The concentration of sulfuric acid is a key operating parameter for the refrigerated sulfuric acid process. When the sulfuric acid concentration falls below about 88 percent, a portion of the acid must be removed and replaced with stronger acid, while the acid that is removed must be regenerated in a sulfuric acid plant (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. Caustic treating facilities are used to remove sulfur from the olefin feed (see Section 10). 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 2006a, Meyers 2004, EPA 1995a].

In the **hydrofluoric acid-based alkylation** process (see Figure 6-2 and Table 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*	
<i>Isobutane (pure)</i>	<i>1.2 bbl/bbl butylene feed</i>
<i>Hydrofluoric Acid</i>	<i>0.3 lbs/bbl alkylate (net)</i>
* based on UOP's HF Alkylation Process	

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 (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 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.

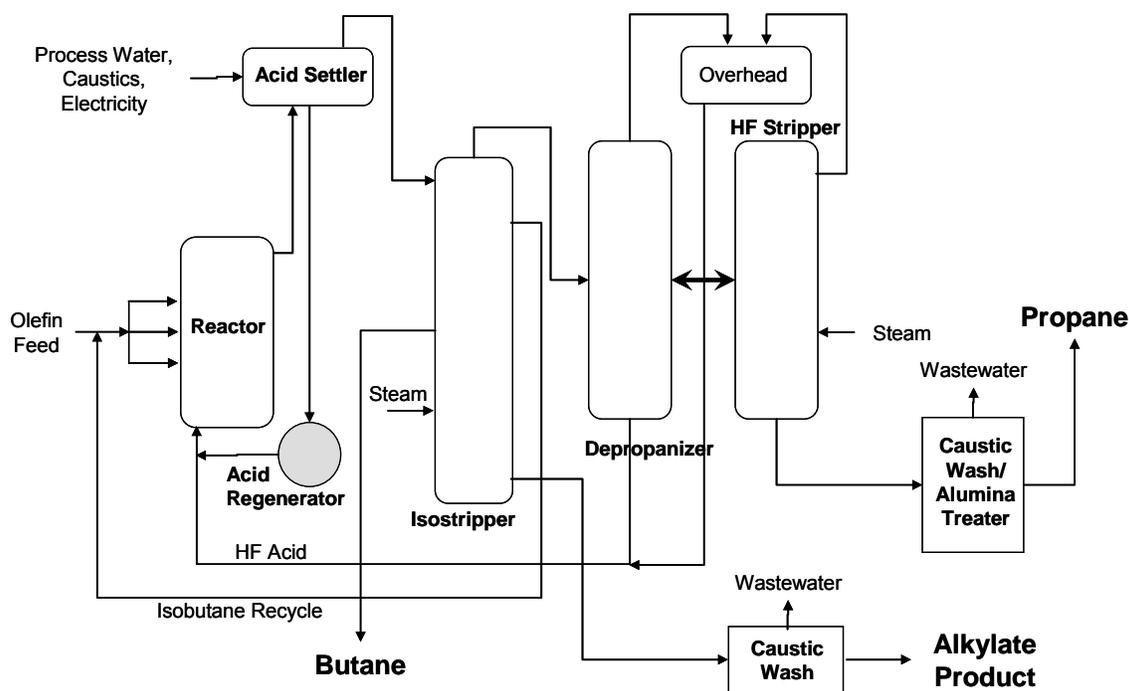


Figure 6-2. Hydrofluoric Acid-Based Alkylation Flow Diagram
[Meyers 2004, HP 2006a]

6.2 Key Energy and Environmental Facts—Hydrofluoric-Acid Based Alkylation			
Energy	Emissions	Effluents	Waste, Residuals or By-products
Net: 245 x 10 ³ Btu/bbl feed Total: 255 x 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)

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 2004]. [Process Description: Meyers 2004, HP 2006a, EPA 1995a]

Emerging Technologies Enable Safer and More Environmentally-Friendly Alkylation

Demand for alkylate is increasing with the introduction of clean fuels legislation and phase-out of MTBE. The low vapor pressure and high octane content of alkylate make it a key blending component to meet federal Reid vapor pressure and octane standards. As refiners are faced with the prospect of pushing alkylation units to maximum capacity, HF alkylation units are emerging as the best choice for these expansion efforts. HF alkylation has several clear advantages over sulfuric acid alkylation, including lower expansion costs, greater maximum capacity increase, and operation costs that remain controllable [Nowak 2003, HP 2005a]. Improved acid mitigation systems are reducing the safety and environmental hazards associated with HF acid catalysis [Nowak 2003, HP 2004].

Hydrofluoric and sulfuric acids are hazardous materials to work with. HF acid is particularly dangerous, in that if liquid HF is sprayed into the atmosphere a vapor cloud can be formed that is difficult to disperse. This vapor cloud could be carried into a populated area and lead to fatalities. New methods have been recently developed to minimize the formation of a HF vapor cloud; these methods include using additives that prevent the formation of a vapor cloud and equipment design changes to significantly reduce the amount of HF in the unit and to provide emergency dumping of the acid in the system to underground storage tanks (e.g., water curtain) [Gary 2007].

New alkylation technologies utilizing solid acid catalyst, such as zeolite or phosphoric acid, are now available. The catalyst systems eliminate the risks and costs of liquid acid catalysis (e.g., corrosion issues, expensive materials of construction), reduce sensitivity to changes in olefin composition of feedstocks, and eliminate by-product (acid soluble oils) production [van Rooijen 2005, HP 2004].

Table 6-3 summarizes the input and output streams for alkylation processes.

Inputs		Outputs	
<u>Paraffins</u>	<u>Olefins</u>	<u>Caustic</u>	Wastewater
Isobutane	Isobutylene	Potassium Hydroxide	Neutralized Acid Sludge
Butane	Butylene	Sodium Hydroxide	Spent Caustic
Propane	Butenes	Electricity	High Octane Blending
Pentane	Propylene	Fuel Gas	Stock (alkylate)
<u>Acid Catalysts</u>		Steam	Butane
Sulfuric		Cooling/Process Water	Propane
Hydrofluoric			

6.2 Energy Requirements

The majority of the process energy input to alkylation is in the form of fuels used in boilers to produce steam. The process energy shown in Tables 6-4 and 6-5 [ANL 1981, HP 2006a, Meyers 2004] does not consider the energy content of the feedstock (i.e., feedstock energy), 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, however, include energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

Energy Source ^a	Specific Energy Use ^b (10 ³ Btu/bbl of feed)	Total Industry Use ^c (10 ¹² Btu/yr)
Electricity ^d	40.9	6.5
Energy for Steam/Process Heat		
Natural Gas	57.3	9.0
Refinery Gas	102.8	16.2
Coke	37.8	6.0
Oils ^e	6.9	1.1
Other ^f	4.2	0.7
NET PROCESS ENERGY	249.9	39.5
Electricity Losses	85.1	13.4
TOTAL PROCESS ENERGY	335.0	52.9

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005.

b Average value based on estimated utilities for various licensed technologies, including Exxon Autorefrigeration Alkylation and Stratco Effluent Refrigeration Alkylation [HP 2006a, Meyers 2004].

c Based on alkylation production capacity at U.S. refineries on January 1, 2005 (1,195,148 bbls/cday, assuming 355 stream days per calendar year) operating at 90.4% capacity. Assumes 40% of the market is sulfuric acid-based alkylation. [DOE 2006a, DOE 2006b, OGJ 1996c].

d Does not include losses incurred during the generation and transmission of electricity

e Includes crude oil, distillate and residual fuel oil

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

Table 6-5. Estimated Energy Use in Hydrofluoric Acid Alkylation—2005		
Energy Source^a	Specific Energy Use^b (10³ Btu/bbl of feed)	Total Industry Use^c (10¹² Btu/yr)
Electricity ^d	4.9	1.2
Energy for Steam/Process Heat		
Natural Gas	65.7	15.5
Refinery Gas	118.0	27.9
Coke	43.4	10.3
Oils ^e	7.9	1.9
Other ^f	4.7	1.1
NET PROCESS ENERGY	244.6	57.9
Electricity Losses	10.2	2.4
TOTAL PROCESS ENERGY	254.8	60.3

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005.

b Average based on estimated utilities for various licensed technologies [ANL 1981].

c Based on alkylation production capacity at U.S. refineries on January 1, 2005 (1,195,148 bbls/cday, assuming 355 stream days per calendar year) operating at 90.4% capacity. Assumes 60% of the market is HF acid alkylation [DOE 2006a, DOE 2006b, OGJ 1996c].

d Does not include losses incurred during the generation and transmission of electricity.

e Includes crude oil, distillate and residual fuel oil.

f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

Steam is used in stripping units that depropanize and debutanize the products of the alkylation reaction. Electricity accounts for about 10 percent of overall fuel consumption (gross basis) in alkylation, powering refrigeration compressors, pumps, mixers, filtering systems, and other auxiliary equipment.

6.3 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). Combustion of fuels in process boilers to produce steam for strippers is an additional source of emission, and as with all process heaters in the refinery, these boilers produce significant emissions of SO_x, NO_x, CO, particulates, and volatile hydrocarbons.

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.

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 neutralization system consists of a relief-gas scrubber, 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 2004].

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 2004].

6.4 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 2004]. 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 6-6 shows limitations for average daily values for 30 consecutive days using the best available technology economically available (BAT) [NARA 2006].

Table 6-6. 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.

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 stream 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 2004].

6.5 Waste, Residuals and By-products

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], and while the 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 2004].

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, which is then 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.

Process energy does, however, include energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas). Steam is used in stripping units that depropanize and debutanize the products of the alkylation reaction. Electricity accounts for about 10 percent of overall fuel consumption (gross basis) in alkylation, powering refrigeration compressors, pumps, mixers, filtering systems, and other auxiliary equipment.

7 Hydrotreatment

7.1 Hydrotreatment Overview

Hydrotreatment Removes Undesirable Impurities from Petroleum Products

Hydrotreating, often referred to **hydroprocessing**, is used to remove impurities (e.g., sulfur, nitrogen, oxygen, halides, and trace metals) from petroleum fractions. When the process is employed specifically for sulfur removal, it is usually called **hydrodesulfurization**. 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 saturates aromatic rings and removes nitrogen and additional sulfur. Common hydrotreatment reactions are shown in Figure 7-1.

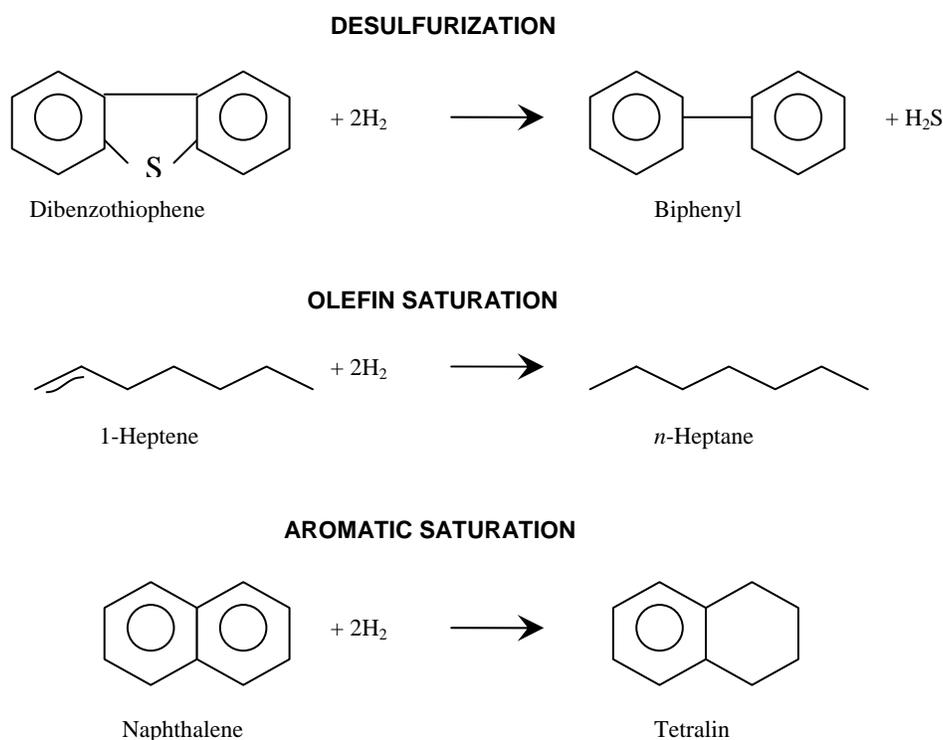


Figure 7-1. Typical Hydrotreatment Reactions [Meyers 2004]

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 2005, an estimated 12.3 million barrels of feed per day were charged to hydrotreatment units in domestic refineries. This estimate is based on a 90 percent overall average refinery capacity utilization [OGJ 2006a, DOE 2006a].

Hydrotreating Employs Catalysts that Selectively Remove Impurities

The hydrotreatment process (see Figure 7-2 and Table 7-1) 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 include cobalt-molybdenum, nickel-molybdenum, nickel-tungsten, or a combination of the three [HP 2006a].

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). 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 by-product 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: [HP 2006a, Meyers 2004].

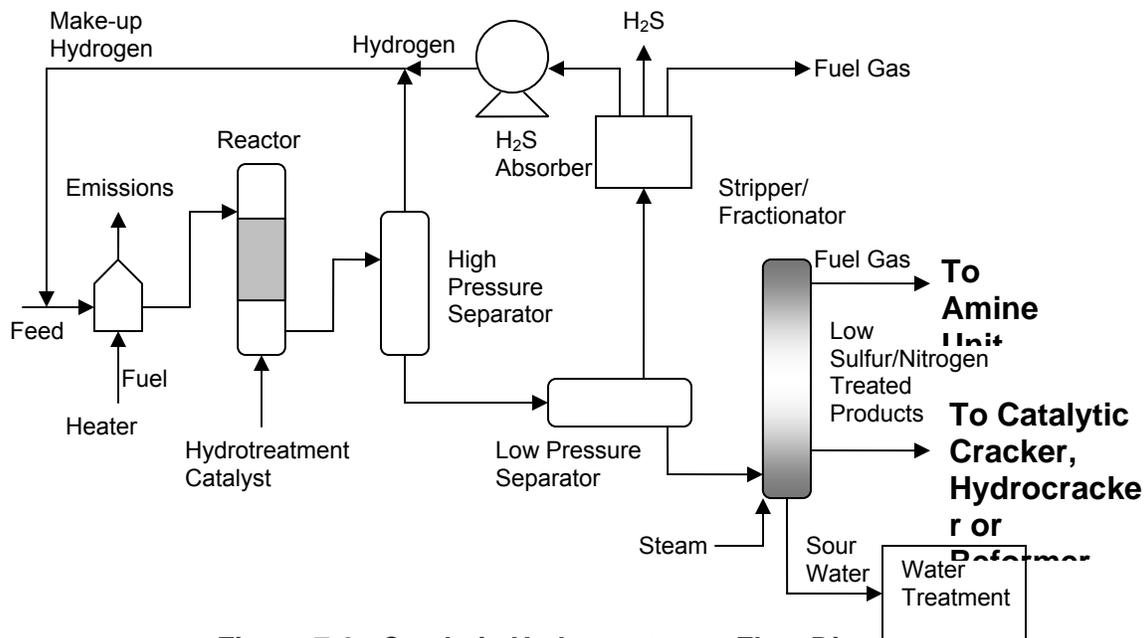


Figure 7-2. Catalytic Hydrotreatment Flow Diagram
[EPA 1995a, HP 2006a, Meyers 2004]

Energy	Emissions	Effluents	Waste, Residuals or By-products
Net: 81 x 10 ³ Btu/bbl Total: 311 x 10 ³ Btu/bbl	Heater stack gas (CO, SO _x , NO _x , hydrocarbons, and particulates).	Sour waste water from the fractionator and hydrogen separator (suspended solids, H ₂ S, NH ₃ , phenols). Water flow = 1.0 gal/bbl	Spent catalyst fines (aluminum silicate and metals).

Developments in Hydrotreating Technologies Can Enhance Product Yield

Transition to ultra-low-sulfur gasoline (ULSG) and ultra-low-sulfur diesel (ULSD) has prompted a variety of studies and the development of techniques that can cost-effectively enhance product yield. Experiments have found that employing the most highly-active catalysts, optimizing refinery configuration, and improving fractionation will allow many refiners to economically increase their ULSD yields and hydrotreater run lengths by segregating the easy and difficult-to-treat sulfur species [HP 2006d, OGJ 2006d, Golden 2006, UOP 2006]. Severe hydrotreating of fluid catalytic cracking (FCC) feedstreams to low sulfur and low aromatics levels can yield clean, direct blending streams for gasoline and diesel [HP 2005b]. In regards to low-severity hydrotreating, experiments are being conducted to produce liquid fuels from biomass [PNNL 2006].

Table 7-2 summarizes the input and output streams for hydrotreating processes.

Inputs		Outputs	
Atmospheric Resid	Fuel Gas	Diesel/Middles	Sour Water
Distillates	Process Water	Distillates	Catalyst Fines
Vacuum Resid	Steam	Low Sulfur/Nitrogen	Spent Catalysts
Vacuum Gas Oils	Electricity	Products	Hydrogen Sulfide
Hydrogen	Catalysts	Light Ends	
		Fuel Gas	

7.2 Energy Requirements

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.

The process energy used in various hydrotreating processes is shown in Table 7-3 [HP 2006a, Meyers 1997, Meyers 2004]. The energy content of the feedstock (i.e., feedstock energy) 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).

Table 7-3. Estimated Energy Use in Hydrotreatment—2005		
Energy Source^a	Specific Energy Use^b (10³ Btu/bbl of feed)	Total Industry Use^c (10¹² Btu/yr)
Electricity ^d	18.6	93.0
Energy for Steam/Process Heat		
Natural Gas	17.0	85.0
Refinery Gas	30.6	153.0
Coke	11.3	56.5
Oils ^e	2.1	10.5
Other ^f	1.2	6.0
NET PROCESS ENERGY	80.8	404.0
Electricity Losses	38.7	193.5
Hydrogen Consumed	223.0	1,115.2
Net Steam Exported	(31.1)	(155.5)
TOTAL PROCESS ENERGY	311.4	1,557.2

a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005.

b 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 2006a, Meyers 1997, Meyers 2004].

c Based on catalytic hydrotreatment/desulfurization capacity at U.S. refineries on January 1, 2006 (13,701,236 bbls/cday, assuming 355 stream days per calendar year), operating at 90.4% capacity [DOE 2006a, DOE 2006b].

d Does not include losses incurred during the generation and transmission of electricity.

e Includes crude oil, distillate and residual fuel oil.

f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

7.3 Air 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.

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 have toxic components. These include toluene, benzene, xylenes, and other volatiles that are reported as toxic chemical releases under the Toxics Release Inventory [EPA 2006]. There are no estimates as to the amount of these constituents released during hydrotreating.

7.4 Effluents

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.

7.5 Waste, Residuals and By-products

Oily sludge 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, sludge 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 & Blending Components

8.1 Additives and Blending Components Overview

Regulation Affects 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.

The Clean Air Act Amendments of 1990 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 which increase the amount of chemically combined oxygen in fuels are called **oxygenates**. These include alcohols (methanol and ethanol) and a variety of ethers, such as methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), tertiary amyl methyl ether (TAME), and diisopropyl ether (DIPE). During the early 1990s, the market for oxygenates (especially ethers) had been the fastest growing portion of the gasoline pool, primarily due to environmental concerns and consumer demands for high performance fuels. The introduction of mid-grade and high-grade premium gasolines, and newer, more sophisticated automotive engines, have both contributed to increased demand for higher-quality gasoline and the need to improve octane in the gasoline pool through additives [Meyers 2004, EPA 1995a].

Until recently, MTBE had been the most common oxygenate additive used to meet fuel requirements, followed by ethanol. However, discovery of MTBE in California drinking wells in the mid-1990s sparked controversy over the continued use of MTBE as an oxygenate [LLNL 2006]. Since then, twenty-five states have enacted legislation mandating the reduction or elimination of MTBE in fuel supplies and refiners have begun replacing MTBE with ethanol in those markets. Furthermore, the Energy Policy Act of 2005 removed the requirement to use oxygenates in reformulated gasoline (RFG). Removal of the oxygenate mandate in the US has enabled refiners to produce RFG without oxygenates while, at the same time, specifying that US gasoline must increase its content of domestically produced ethanol. Coupled with the establishment of federal and state renewable fuels standards requiring the increased use of renewable fuels such as ethanol, MTBE has become unattractive as a US gasoline-blending additive [OGJ 2006e, DOE 2006j, EPA 2006j].

With the additives industry currently in transition, Table 8-1 depicts the working storage capacity of oxygenate additives at the beginning of 2006 [DOE 2006a]. Ethanol began replacing MTBE in RFG starting in early 2006. According to the Energy Policy Act of 2005, the use of MTBE as an oxygenate will be allowed in certain circumstances until 2009 [OGJ 2006e, EPACK 2005]. A recent shortfall in ethanol supply has brought increased attention to other potential bio-derived fuel additives.

Oxygenate	Input (Thousand Barrels)	Percent of Total
Fuel Ethanol	468	12
MTBE	3,156	79
Other Oxygenates	351	9
TOTAL	3,975	100

2007 EPA registered bio-derived gasoline additives: [EPA 2007]
methanol, mixed alcohols (Ecalene), and ethyl tertiary butyl ether (ETBE).
EPA registered diesel additive:
biodiesel

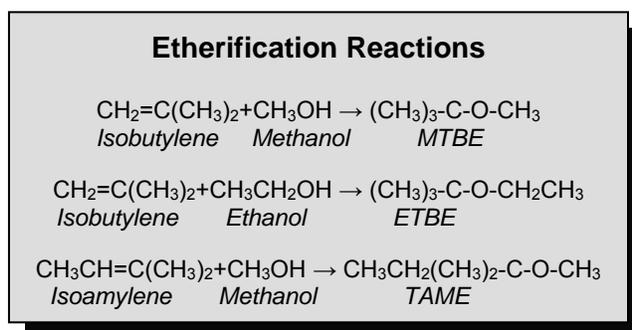
Many studies are underway to compare the performance of various emerging biofuels, including important characteristics such as feedstock availability, life cycle energy requirement, emissions impact, driving performance, and infrastructure and automobile compatibility. Biofuels have taken the spotlight in recent years as the government has laid out increasingly aggressive goals for moving biomass derived fuels into the marketplace to increase the nation's energy independence and reduce transportation sector greenhouse gas emissions.

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 the gasoline pool. Isomerization is also used to produce isobutane, an important feedstock for alkylation (see Section 6). In 2005, approximately 615 thousand barrels of feed per day were charged to isomerization units in domestic refineries. This figure is based on a 90 percent overall average refinery capacity utilization [OGJ 2006a, DOE 2006a].

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.



A typical process configuration for tertiary ethers is shown in Figure 8-1 and key energy and environmental facts for ethers manufacturing are presented in Table 8-2. 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. 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.

While Figure 8-1 illustrates a simple single stage system, two stage systems are often employed. A two stage system comprises two reactor-fractionation column combinations placed in series. Catalytic packing in the fractionating column (catalytic distillation) increases conversion of unreacted isoolefins to ethers. Yields as high as 97 to 99 percent have been reported for processes utilizing catalytic distillation. [Process Description: HP 1996, HP 2006a, Meyers 2004]

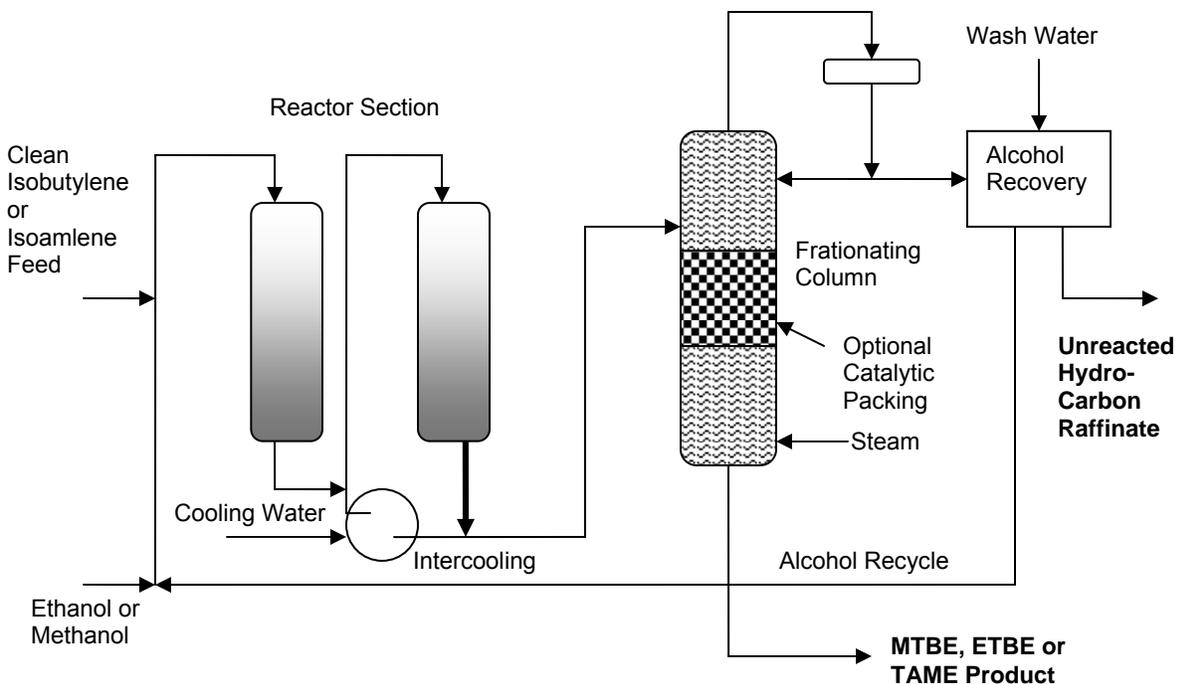


Figure 8-1. Ethers Manufacture Flow Diagram [HP 2006a, Meyers 2004]

Table 8-2. Key Energy and Environmental Facts—Ethers Manufacture			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: 383×10^3 Btu/bbl Total: 403×10^3 Btu/bbl	Boiler stack gas (CO, SO _x , NO _x , hydrocarbons, and particulates)	Pretreatment wash-water (nitrogen contaminants); cooling and alcohol wash water are recycled	Spent catalysts (acidic ion-exchange resins)

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 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, and key isomer manufacture energy and environmental facts are presented in Table 8-3. 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 by-products (e.g., methylpentanes).

Water, other oxygen-containing compounds, and nitrogen compounds can irreversibly poison isomerization catalysts that utilize organic chlorides, so 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 2006a, Meyers 2004]

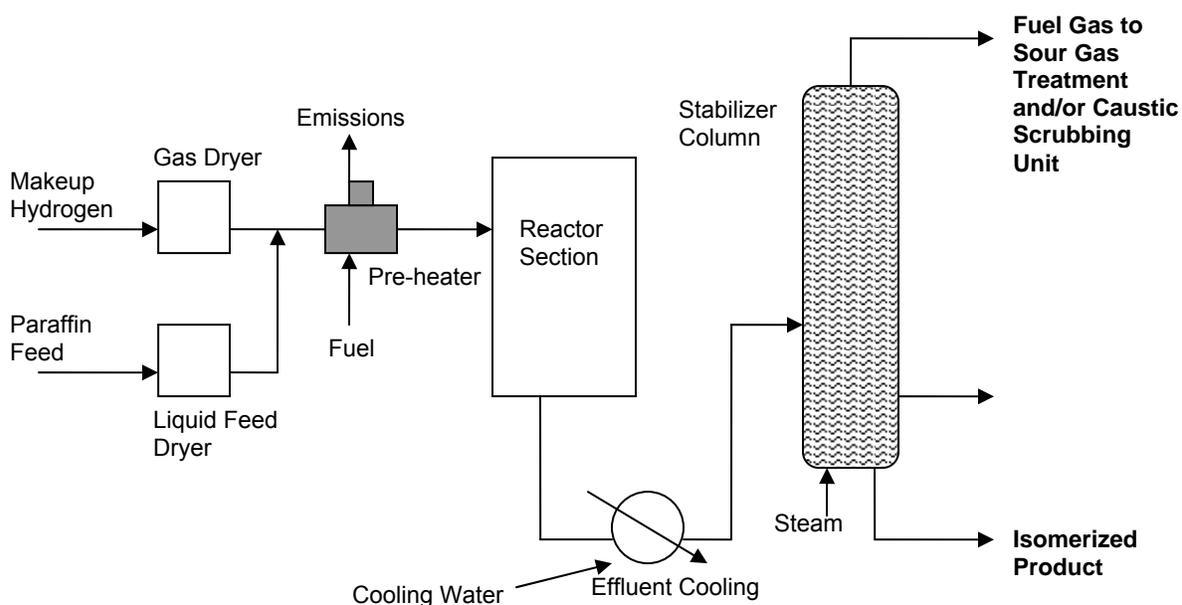


Figure 8-2. Isomerization Flow Diagram
[HP 2006a, Meyers 2004]

Table 8-3. Key Energy and Environmental Facts—Isomer Manufacture			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
<u>Isobutane</u> Net: 337×10^3 Btu/bbl Total: 359×10^3 Btu/bbl	Boiler/heater stack gas (CO, SO _x , NO _x , 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
<u>Isopentane/Isohexane</u> Net: 163×10^3 Btu/bbl Total: 175×10^3 Btu/bbl			
<u>Isobutylene</u> Net: 453×10^3 Btu/bbl Total: 476×10^3 Btu/bbl			

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 of 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 2006a]

Fuel Component Ethanol is Produced from Corn Grain

Ethanol as a blending component is primarily produced through the dry milling of corn grain; wet mills primarily focus on the manufacture on a range of other products that include high fructose corn syrup, starch, food and food additives, and vitamins. In 2005, dry mills accounted for 79 percent of ethanol production versus 21 percent from wet mills, up from 75 percent dry mill and 25 percent wet mill ethanol production in 2004, and 67 percent dry mill and 33 percent wet mill ethanol production in 2003.

As the market share of dry mill ethanol is expected to continue to grow, and the ethanol facilities under construction use the dry mill process, only dry milling will be described in depth here. A wet milling process description is available from the Renewable Fuels Association, and energy consumption for both processes is provided here for comparison. A typical depiction of the dry mill process is shown in Figure 8-3, with description of key energy and environmental facts in Table 8-4 [RFA 2006, RFA 2005, RFA 2004, USDA 2004].

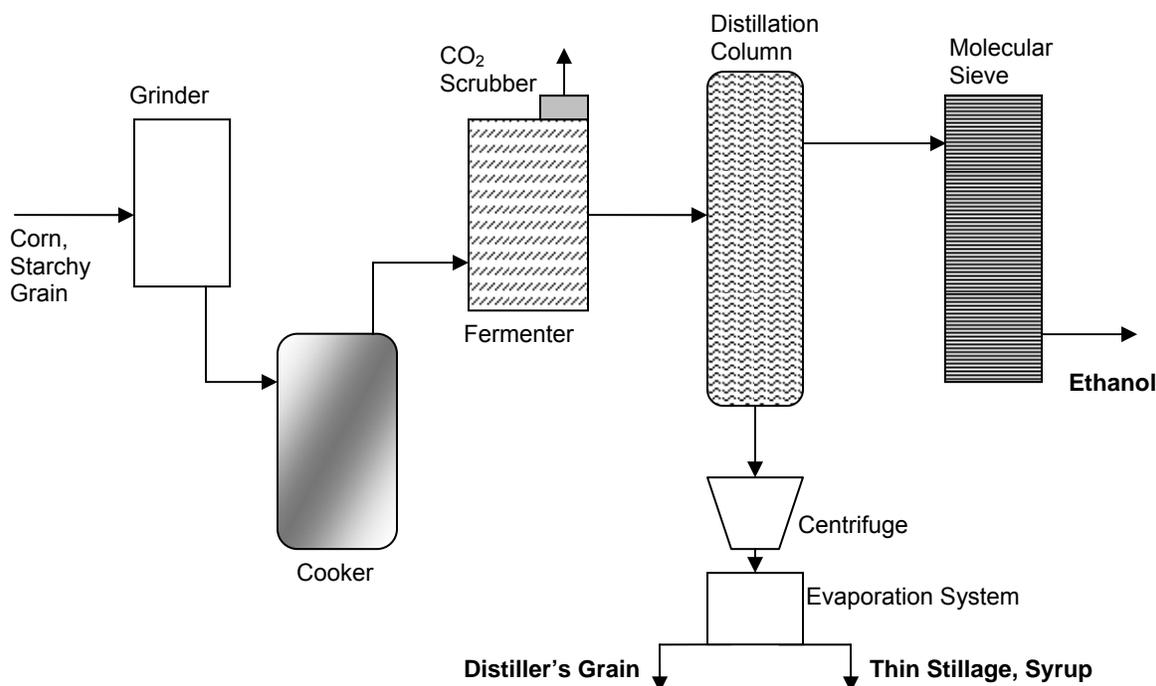


Figure 8-3. Dry Mill Ethanol Manufacture Flow Diagram
[RFA 2006c, MPCA 2002]

Table 8-4. Key Energy and Environmental Facts—Ethanol Manufacture			
Energy Use	Emissions	Effluents	Waste, Residuals or By-products
<u>Dry Mill</u> Net: 38.4 x 10 ³ Btu/gal Total: 47.1 x 10 ³ Btu/gal	Boiler/heater stack gas (CO, NOx, and particulates), VOCs from fermentation, distillation, and drying	Wastewater	Dry milling: distiller's grain (livestock feed component), thin stillage/syrup (livestock feed component), CO ₂ for sale
<u>Wet Mill</u> Net: 49.2 x 10 ³ Btu/gal Total: 52.3 x 10 ³ Btu/gal			Wet milling: many co-products, including sweeteners (high fructose corn syrup), corn oil, and starch.

The production of ethanol begins with the grinding of an entire corn kernel or other starchy grain into flour, or “meal,” and processing it without separating out the various component parts of the grain. The meal is slurried with water to form a “mash.” Enzymes are added to the mash to convert the starch to dextrose, and ammonia is added for pH control and as a nutrient to yeast.

The mash is processed in a high-temperature cooker to reduce bacteria levels ahead of fermentation, and then cooled and transferred to fermenters, where yeast is added to begin the conversion of sugar to ethanol. During the 40-50 hour fermentation process, the mash is agitated and kept cool to facilitate the activity of the yeast. After fermentation, the resulting “beer” is transferred to distillation columns where the ethanol is separated from the remaining stillage. The ethanol is concentrated to 190 proof using conventional distillation and then is dehydrated to approximately 200 proof in a molecular sieve system. The product is ready for shipment to gasoline terminals and retailers upon blending the anhydrous ethanol with about 5% denaturant (such as natural gasoline) to render it undrinkable.

The leftover stillage passes to a centrifuge that separates coarse grain from soluble material. Solubles are concentrated by evaporation to make “syrup” which can be sold on its own or mixed back with coarse grain to form “distiller’s grain,” a high quality, nutritious livestock feed. The CO₂ released during fermentation is captured and sold for use in carbonating beverages and manufacturing of dry ice. [Process Description: RFA 2006c, MPCA 2002]

Transitioning to Greater Ethanol Demand

Ethanol production in 2006 reached a record high of an estimated 4.9 billion gallons, and has become a blending component in more than 46% of the nation’s gasoline. A variety of investments need to address the increased demand of ethanol with the phase-out of MTBE and resolve issues surrounding infrastructure for its distribution and storage due to its volatile and hygroscopic nature. Currently, operating refineries have the capacity to produce more than 5.4 billion gallons annually. Ethanol producers assert that with improvements in manufacturing and scale economies, tripling the size of an ethanol plant can cut unit cost by 40%. Planned construction and expansion looks to add more than 6 billion gallons of new capacity by the middle of 2009 [RFA 2007, OGJ 2006e, OGJ 2006f, DOE 2006j].

Tables 8-5, 8-6, and 8-7 summarize the input and output streams for ethers, isomerization, and dry mill ethanol manufacturing processes.

Table 8-5. Summary of Inputs and Outputs for Tertiary Ethers Production			
Inputs:		Outputs:	
Isoolefins	Fuel Gas	Tertiary Ether	
Isobutylene	Process Water	Methyl Tertiary Butyl Ether	
Isoamylene	Steam	Ethyl Tertiary Butyl Ether	
Alcohols	Electricity	Tertiary Amyl Methyl Ether	
Ethanol	Catalysts	Hydrocarbon Raffinate	
Methanol		Spent Catalyst	
		Alcohol for Recycle	

Table 8-6. Summary of Inputs and Outputs for Isomerization			
Inputs:		Outputs:	
Paraffins	Water	Isomers	Fuel Gas
Butane	Caustic	Isobutane	Sour Water
Pentane	Steam	Isopentane	Calcium Chloride
Hexane	Fuel Gas	Isohexane	Sludge
Hydrogen	Electricity		
Process	Catalysts		

Table 8-7. Summary of Inputs and Outputs for Dry Mill Ethanol Production			
Inputs:		Outputs:	
Corn Kernel/Starchy Grain	Yeast	Ethanol	CO ₂
Water	Denaturant	Thin Stillage, Syrup	Fuel Gas
Enzymes	Gasoline	Distiller's Grain	Wastewater
Ammonia	Fuel Gas	(Livestock Feed)	
	Electricity		

8.2 Energy Requirements

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. Though ether production is one of the most energy-intensive processes in the refinery, because throughput is small compared to 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. Electricity is used primarily to power compressors and pumps for water cooling systems, typically accounting for 8 percent of overall energy consumption (including losses from generation and transmission). Cooling of reactor streams requires considerable amounts of process water in addition to electricity.

The process energy used in etherification and isomerization processes is shown in Tables 8-8 to 8-11 [HP 1996, HP 2006a, Meyers 2004]. The energy content of the feedstock (i.e., feedstock energy) 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 any energy products manufactured by the refinery that are used on-site for this purpose (e.g., refinery fuel gas).

Table 8-8. Estimated Energy Use in Ethers Manufacture—2005		
Energy Source^a	Specific Energy Use^b (10³ Btu/bbl of feed)	Total Industry Use^c (10¹² Btu/yr)
Electricity ^d	9.9	0.4
Energy for Steam/Process Heat		
Natural Gas	102.2	4.1
Refinery Gas	183.4	7.4
Coke	67.5	2.7
Oils ^e	12.3	0.5
Other ^f	7.5	0.3
NET PROCESS ENERGY	382.8	15.4
Electricity Losses	20.6	0.8
TOTAL PROCESS ENERGY	403.4	16.2

- a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005
- b Source: Average values based on estimated utility requirements for various licensed technologies, including UOP/HULS Ethermax, UOP Oxpro, and Snamprogetti Ethers [HP 2006a, Meyers 2004].
- c Based on total refinery production of MTBE and other oxygenates (ETBE, TAME, etc.) in 2005 (110,743 bbls/cday), calculated as net refinery inputs minus imports plus exports [DOE 2006m].
- d Does not include losses incurred during the generation and transmission of electricity
- e Includes crude oil, distillate and residual fuel oil
- f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam

Table 8-9. Estimated Energy Use in Isobutane Manufacture—2005		
Energy Source^a	Specific Energy Use^b (10³ Btu/bbl of feed)	Total Industry Use^c (10¹² Btu/yr)
Electricity ^d	10.6	0.8
Energy for Steam/Process Heat		
Natural Gas	89.5	6.5
Refinery Gas	160.7	11.7
Coke	59.1	4.3
Oils ^e	10.8	0.8
Other ^f	6.5	0.5
NET PROCESS ENERGY	337.2	24.6
Electricity Losses	22.0	1.6
TOTAL PROCESS ENERGY	359.2	26.2

- a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005
- b Source: Butamer® process (UOP) [HP 2006a, Meyers 2004].
- c Based on isobutane capacity in U.S. refineries on January 1, 2005 (220,147 bbls/cday, assumes 355 stream days per calendar year) operating at 90.4% capacity [DOE 2006a, DOE 2006b].
- d Does not include losses incurred during the generation and transmission of electricity
- e Includes crude oil, distillate and residual fuel oil
- f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam

Table 8-10. Estimated Energy Use in Isopentane and Isohexane Manufacture—2005

Energy Source ^a	Specific Energy Use ^b (10 ³ Btu/bbl of feed)	Total Industry Use ^c (10 ¹² Btu/yr)
Electricity ^d	5.8	0.9
Energy for Steam/Process Heat		
Natural Gas	43.1	6.6
Refinery Gas	77.4	11.8
Coke	28.5	4.4
Oils ^e	5.1	0.8
Other ^f	3.1	0.5
NET PROCESS ENERGY	163.0	25.0
Electricity Losses	12.1	1.9
TOTAL PROCESS ENERGY	175.1	26.9

- a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005
- b Source: Average values based on estimated utility requirements for various licensed technologies, including UOP Penex, UOP Once-Through Zeolitic, and IFP IPSorb [HP 2006a, Meyers 2004].
- c Based on isopentane and isohexane capacity in U.S. refineries on January 1, 2005 (463,779 bbls/cday, assumes 355 stream days per calendar year) operating at 90.4% capacity [DOE 2006a, DOE 2006b].
- d Does not include losses incurred during the generation and transmission of electricity
- e Includes crude oil, distillate and residual fuel oil
- f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam

Estimated energy consumption for the production of isobutylene in reactors dedicated to that purpose is shown in Table 8-11. The total specific energy consumption of 476 thousand Btu 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 by-product from other refinery processing units. No estimates were available on the amount of isobutylene currently produced in this way in domestic refineries.

Table 8-11. Estimated Energy Use in Isobutylene Manufacture—2005

Energy Source ^a	Specific Energy Use ^b (10 ³ Btu/bbl of feed)
Electricity ^c	10.9
Energy for Steam/Process Heat	
Natural Gas	121.1
Refinery Gas	217.5
Coke	80.0
Oils ^d	14.6
Other ^e	8.8
NET PROCESS ENERGY	452.9
Electricity Losses	22.7
TOTAL PROCESS ENERGY	475.6

- a Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005
- b Average values based on estimated utility requirements for CDTECH ISOMPLUS [HP 1996].
- c Does not include losses incurred during the generation and transmission of electricity
- d Includes crude oil, distillate and residual fuel oil
- e Includes liquefied petroleum gases, miscellaneous oils, and purchased steam

Process energy values for the conversion of corn to ethanol are depicted in Table 8-12. On the average, dry mill ethanol plants used 1.09 kWh of electricity and about 35,000 Btu of thermal energy (lower heat value, LHV) per gallon of ethanol. When energy losses to produce electricity and natural gas were taken into account, the average dry mill ethanol plant consumed about 47,000 Btu of primary energy per gallon of ethanol produced [USDA 2004]. Ethanol produced through wet milling consumes 11 percent more energy per gallon of ethanol.

Energy Source	Specific Energy Use^a (10³ Btu/gallon)	Total Industry Use^b (10¹² Btu/yr)
Electricity ^c	3.7/na ^d	11.7/na ^d
Energy for Steam/Process Heat ^e	34.7/49.2	109.7/41.3
NET PROCESS ENERGY	38.4/49.2	121.4/41.3
Energy Losses ^f	8.7/3.1	27.5/2.6
TOTAL PROCESS ENERGY	47.1/52.3	148.9/43.9

na Not available

a Average values based on estimated utility requirements in a U.S. survey conducted in 2001 by BBI International. Does not include by-product or co-product energy credits [USDA 2004].

b Based on 2005 total ethanol production of 4 billion gallons with 2005 production capacity composed of 79 percent dry mill and 21 percent wet mill ethanol [RFA 2006].

c Does not include losses incurred during the generation and transmission of electricity

d Wet mills generate electricity onsite and the coal and natural gas used for onsite electricity generation are rolled up in the energy for steam/process heat [USDA 2004].

e Dry mills use natural gas to produce steam; wet mills use natural gas or coal for steam and electricity generation [USDA 2004].

f Accounts for average electricity losses incurred during the generation and transmission of electricity (dry milling) and losses incurred during natural gas and coal production (wet milling) [USDA 2004].

8.3 Air Emissions

Additive Production Generates Air Emissions from Process Heaters and Fugitive Emissions

Isomerization processes and ethers and ethanol manufacture 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, hydrochloric acid (HCl) may be present in the light fuel gases and must be neutralized by caustic treatment [EPA 1995a].

During fermentation, distillation, and drying in the ethanol production process, VOCs such as acetaldehyde, acrolein, ethanol, formaldehyde, 2-furaldehyde, methanol, acetic acid and lactic acid are released [MPCA 2002].

8.4 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 caustic wash water that must be treated before being released, and also produces a calcium chloride neutralization sludge that must be disposed of off-site.

8.5 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 1.5 million pounds of methanol were reported as a toxic release in 2004. Releases of MTBE were also significant (about 1.0 million pounds).

9 Lubricating Oil Manufacture

9.1 Lubricating Oil Manufacture Process Overview

Lubricants are 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. What remain 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. Table 9-1 describes key energy and environmental facts for lube oil and wax manufacturing. 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 by-product. 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.

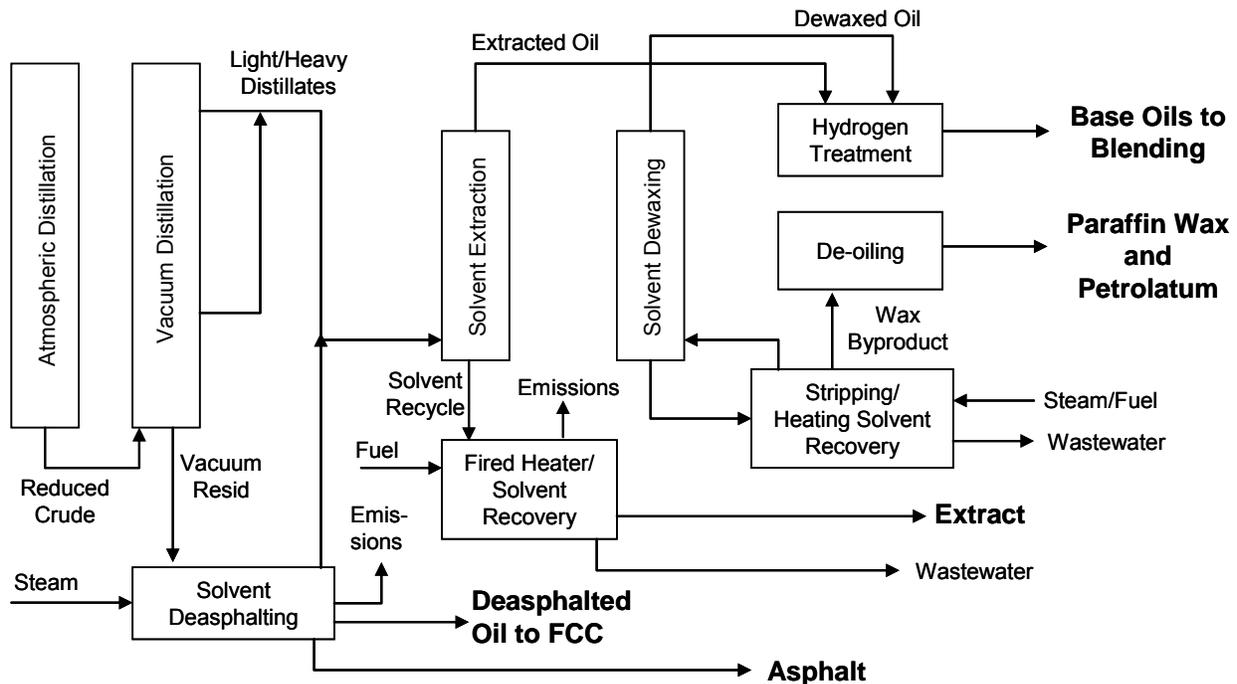


Figure 9-1. Typical Refinery Scheme for Lubricating Oil Manufacture

Energy Use	Emissions	Effluents	Waste, Residuals or By-products
Net: $1,379 \times 10^3$ Btu/bbl feed Total: $1,506 \times 10^3$ 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, methyl ethyl ketone, methyl isobutyl ketone)

In 2005, domestic refineries produced over 61 million barrels of lubricants. This production represents about 83 percent of operable capacity (production capacity is about 74 million barrels) [DOE 2006a, DOE 2006m].

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 (N-methyl-2-pyrrolidone) 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 by-product 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 portions of the extraction process. [Process Description: EPA 1995a, ANL 1981, HP 2006a] In some instances refiners are required to reprocess used lube oil which can be very inefficient.

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 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 130oF, and pressure is reduced until about 50 percent of the solvent has evaporated, which reduces the temperature to about 40°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 2004, HP 2006a]

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 2006a, Meyers 2004]

In **supercritical fluid extraction** processes, resid is charged to a mixer where it is mixed with solvent before entering an asphaltene separator. 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 2004]. 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.

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 needs and desired product slate of an individual refinery.

New Technologies Offer Energy and Cost Savings, and Environmental Benefits

Lubricant production is one of the most energy-intensive processes in the refinery. Higher energy costs, increasingly stringent environmental regulations, and tightening capacity are leading refiners to adopt a variety of advanced technologies. Process modeling (e.g., neural networks) and improved process monitoring and controls are helping to optimize processes such as solvent extraction, resulting in higher yields, increased energy efficiency, reduced air emissions, and cost savings [HP 1998, RAND 2003].

Innovative separation processes utilizing membrane technology are being used to improve solvent recovery in the dewaxing process. Refiners benefit from reduced energy consumption, lower solvent (VOC) emissions, and increased production capacity (due to debottlenecking of filtration in the solvent dewaxing unit) [EM 2007, Gould 2001]. Processing additives (i.e. dewaxing aids) also increase the processing rate and enhance oil-wax separation efficiency, leading to increased production of high quality lube oil and debottlenecking of the rotary drum filters and solvent recovery system [RohMax 2007].

In the future, use of alternative feedstocks, such as gas-to-liquid (GTL) streams and biobased oils as lubricating oil base stock, may challenge refiners for their market share due to their unique properties. GTL streams are highly paraffinic and biobased oils offer enhanced environmental performance. GTL facilities are predicted to produce 30,000 to 50,000 barrels per day (10 to 17 million barrels per year) of lubricant base oils by 2010 to 2012, and several manufacturers market plant oil-based products [HP 2005h, OGJ 2003a, USB 2006].

Table 9-2 summarizes the input and output streams for lube oil manufacturing processes.

Table 9-2. Summary of Inputs and Outputs for Lubricating Oil Manufacture			
Inputs		Outputs	
Vacuum Residue	Electricity	Lube Oils	Sour Water
Distillates	Steam	Paraffin Wax	Wastewater
Solvent	Cooling Water	Petrolatum/Grease	Solvent
Fuel	Hydrogen		

9.2 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 the 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.

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 12 percent of overall energy consumption (including losses from generation and transmission).

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.

Process energy requirements by fuel type for all the processes associated with lubricating oil manufacture are shown in Table 9-3. The energy content of the feedstock (i.e., feedstock energy) 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).

Table 9-3. Estimated Energy Use in Lubricating Oil Manufacture—2005^a						
Energy Source	Specific Energy Use (10³ Btu/bbl of feed)					Total Industry Use^c (10¹² Btu/yr)
	Solvent Deasphalting	Solvent Dewaxing	Solvent Extraction	Solvent Recovery^b	TOTAL	
Electricity ^d	6.3	16.7	6.8	31.4	61.2	3.7
Energy for Steam/Process Heat						
Natural Gas	40.0	21.1	125.2	174.9	361.2	22.1
Refinery Gas	71.9	37.9	224.6	314.0	648.4	39.7
Coke	26.4	13.9	82.6	115.6	238.5	14.6
Oils ^e	4.8	2.6	15.1	21.1	43.6	2.7
Other ^f	2.9	1.5	9.1	12.8	26.3	1.6
NET PROCESS ENERGY	152.3	93.7	463.4	669.8	1,379.2	84.4
Electricity Losses	13.0	34.8	14.2	65.2	127.2	7.8
TOTAL PROCESS ENERGY	165.3	128.5	477.6	735.0	1,506.4	92.2

- a 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 2006a, Meyers 2004, ORNL 1980]. Fuel mix for fossil fuels (not electricity) based on typical process heating use at refineries in 2005 [DOE 2006a].
- b Based on single effect evaporative solvent recovery. Double-effect and triple-effect can use upwards of 50% less steam.
- c Based on 2005 U.S. lubricating oil production of 61,238,000 bbl [DOE 2006m].
- d Does not include losses incurred during the generation and transmission of electricity.
- e Includes crude oil, distillate and residual fuel oil.
- f Includes liquefied petroleum gases, miscellaneous oils, and purchased steam.

9.3 Air Emissions

The manufacture of lube oils generates air emissions through process heater flue gas and equipment leaks. Heater stack gases produce CO, SO_x, NO_x, hydrocarbon and particulate emissions. 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]. Volatile solvents such as toluene, methyl ethyl ketone (MEK), and methyl isobutyl ketone, which are used in dewaxing, can be released during processing. Reported toxic releases of these solvents from refineries are significant (4.8 million pounds of toluene were released in 2004) [EPA 2006]. Non-volatile lube and wax losses are negligible.

9.4 Effluents

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 9-4 shows limitations for average values for 30 consecutive days using the best available technology economically available (BAT) [NARA 2006].

Table 9-4. 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, & Process Heating

10.1 Overview of Auxiliary Processes

Sulfur Management Enables Compliance with Environmental Regulations

Much of the sulfur and nitrogen contained in crude oil are converted to hydrogen sulfide (H_2S) and ammonia (NH_3) during processing. Organic sulfur (COS and CS_2) and mercaptans, present in off-gases or fuel gases produced by many refinery processes and in the sour water that results from stripping of both liquid and gaseous hydrocarbon products, are produced in lesser amounts (mercaptans are mostly converted to H_2S). 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 a 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 exacerbated by the decreasing quality and increasing sulfur content of crude oil. Additionally, the handling of solid sulfur waste is becoming increasingly difficult. Refineries in many Western states have been unable to sell or dispose of elemental sulfur waste; the chemical industry market for purchasing sulfur product is insufficient considering the growing supply.

A typical complete sulfur management system is shown in Figure 10-1. 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
- Tail gas clean-up units to boost sulfur recovery to over 99 percent

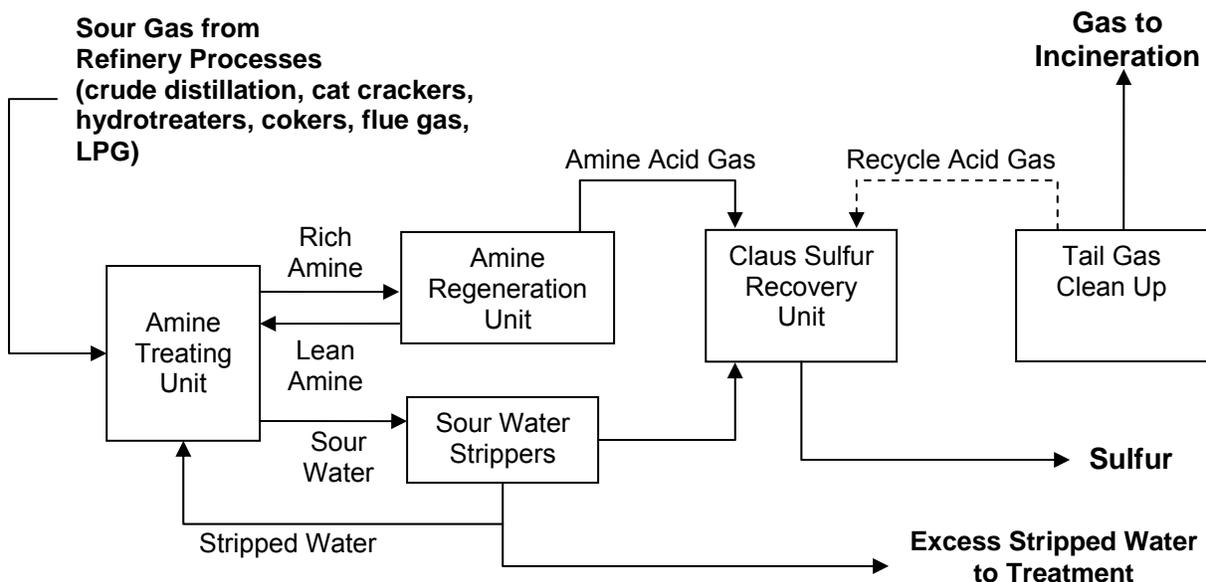


Figure 10-1. Typical Sulfur Management Flow Schematic
 [EPA 1995a, Meyers 2004]

In the **amine treatment** unit, H₂S 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 liquefied 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 furnaces and in other refinery operations. LPG must be subjected to further treatment to remove mercaptans and any residual H₂S. 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 H₂S and NH₃ 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 H₂S and NH₃ 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 removes sulfur 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.

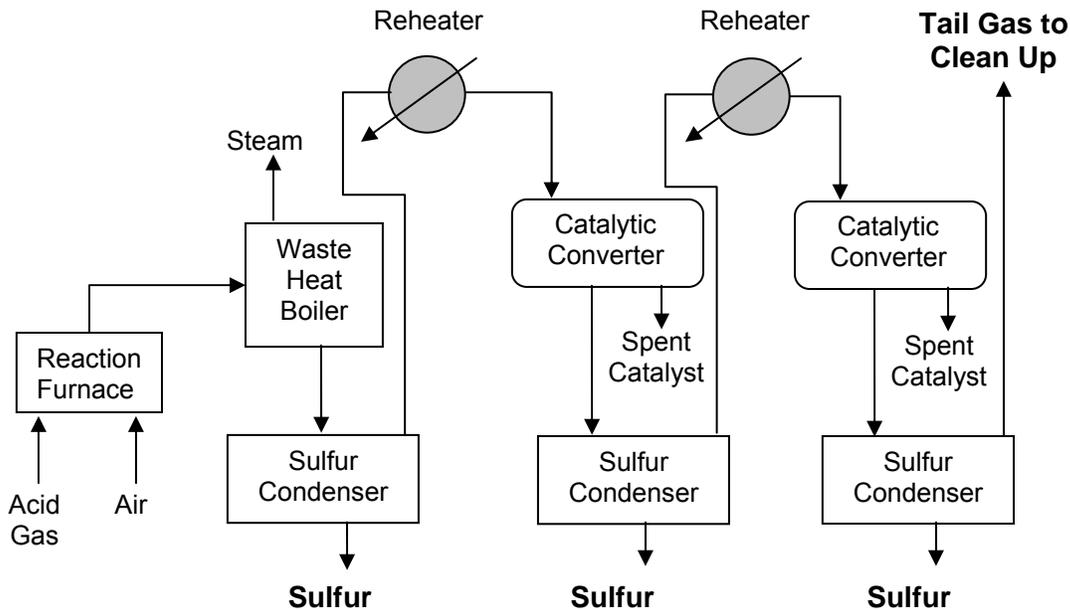
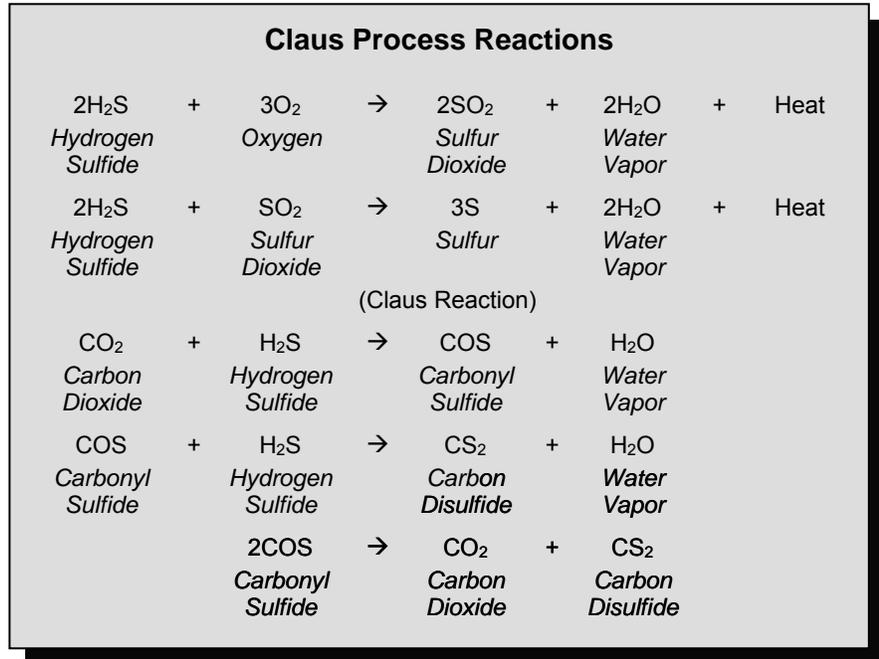


Figure 10-2. Claus Process Flow Schematic
[EPA 1997, Meyers 2004]

Table 10-1. Key Energy and Environmental Facts—Claus Process

Energy Use	Emissions	Effluents	Wastes, Residuals, or By-products
<u>Electricity only</u> Net: 126.2×10^3 Btu/ton sulfur in feed Total: 388.5×10^3 Btu/ton sulfur in feed	Process tail gas (NO _x , SO _x , hydrogen sulfide) Hazardous air pollutants - hydrogen sulfide, carbonyl sulfide, and carbon disulfide Fugitive emissions (solvent emissions may be toxic, e.g., diethanolamine)	Little or no wastewater	Spent catalysts

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—the straight-through process is used when high concentrations of hydrogen sulfide are present in the feed (greater than 50 mole percent); the split flow process is employed at concentrations between 20 and 50 percent; and 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 hydrogen 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 1800 to 2800°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. 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 condenser. 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 U.S. refineries (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 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 Adsorption, and Maxisulf 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.

Liquid redox processing can achieve removal efficiencies exceeding 99.9 percent. There are two approaches to coupling a liquid redox process to a Claus unit: 1) cool the tail gas prior to the liquid redox unit; and 2) convert all of the SO₂, CS₂, and COS in the tail gas to H₂S using a hydrogenation/hydrolysis reactor, cool the reactor exit gas, and then send it to a liquid redox unit. Both approaches offer comparable removal efficiencies and 100 percent turndown; selection of the approach depends on the amount of SO₂ in the tail gas. Solid elemental sulfur is generated by the liquid redox unit.

Residual sulfur can also be removed with a scrubbing process. The **Wellman-Lord oxidation** 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.

The Beavon process is based on absorption of hydrogen sulfide in a quinone solution; 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 Beavon 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, SO₂, CS₂, sulfur vapor) to hydrogen sulfide. The reducing gas (H₂, CO), generated by combustion of fuel gas with steam, also heats the tail gas. The reactor products are cooled and contacted with amine (usually diisopropanolamine (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, HP 2006e, HP 2005j, HP 2003a, Meyers 2004, Sulphur 1994, WP 2000]

The amount of sulfur compounds in off-gas, fuel gas, and other streams, and the number of streams that must be treated are increasing due to the increasing sulfur content of crude oil and the ultra-low sulfur fuel requirements. To boost sulfur recovery unit (SRU) capacity while continuing to comply with emission standards, refiners are increasing Claus ratios of H₂S/SO₂ (from the typical 2:1 ratio to 4:1) and implementing improved liquid redox technology [HP 2005i, HP 2005j, HP 2001, HP 2003a, HP 2003b]. Increased H₂S/SO₂ ratios enable higher plant operating flexibility and processing capacity without capital investment. Liquid redox technology can be used to process many gas streams (e.g., fuel gas, amine acid gas, sour-water stripper gas), thereby relieving some of the Claus unit load, as well as processing the Claus tail gas.

Although liquid redox is a commercially-proven technology, recent advances in liquid redox technology have resolved operational challenges such as high catalysts costs, plugging, foaming, and ability to treat high-pressure gas. An improved mass transfer device in the oxidizer is in the demonstration phase and offers reductions in equipment size and capital costs.

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** removes or alters these compounds to achieve the desired product quality through 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 and Table 10-2).

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, HP 2006a, Meyers 2004, OGJ 1995a]. Merox treatment improves odor as well as the response of gasoline stocks to oxidation inhibitors added to prevent gum formation during storage.

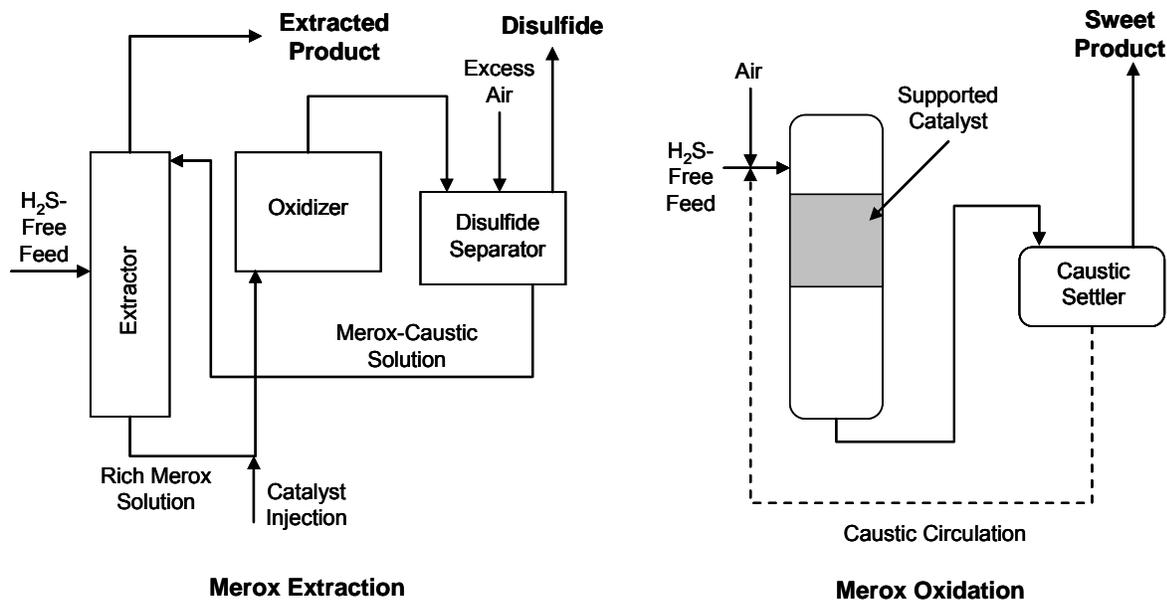


Figure 10-3. Merox Process Flow Schematic
[EPA 1997, Meyers 2004]

Table 10-2. Key Energy and Environmental Facts—Merox Process			
Energy Use	Emissions	Effluents	Wastes, Residuals, or By-products
Not available	Vents and fugitive emissions (hydrogen disulfide)	Little or no wastewater generated	Spent caustic solution, waste oil-disulfide mixture

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 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 hydro-desulfurization 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 the first three of the above, 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").

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; some of which is moderately or highly contaminated, requiring primary and secondary and sometimes tertiary treatment; and some of which is lost as cooling tower evaporation. Total refinery flow of water currently averages 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 earlier in this section). After the stripping process removes hydrogen sulfide, other organic sulfur compounds, and ammonia, the wastewater can be discharged to a 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. In many cases treated wastewater can be recycled 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.

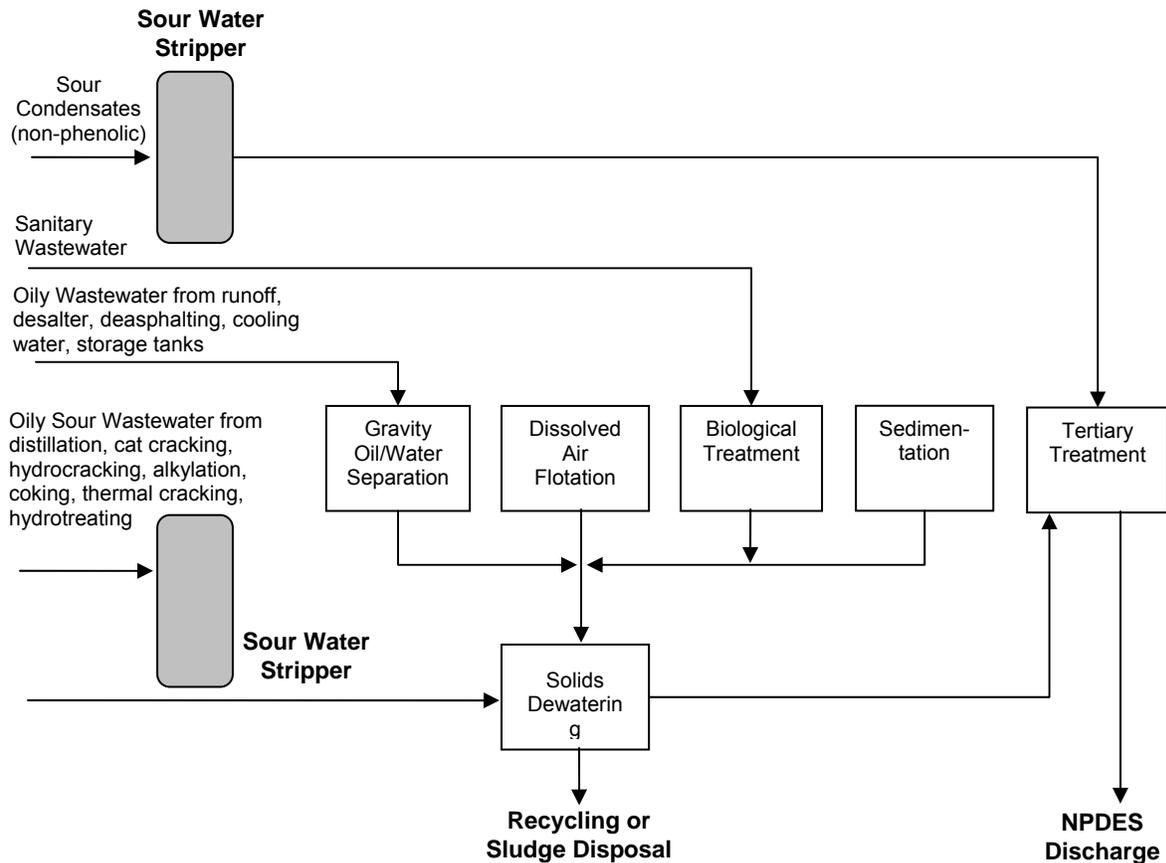


Figure 10-4. Refinery Wastewater Treatment Flow Schematic [EPA 1995a]

Table 10-3. Key Energy and Environmental Facts—Wastewater Process			
Energy Use	Emissions	Effluents	Wastes, Residuals, or /By-products
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

In most cases a secondary treatment process is necessary for direct discharge to 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 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].

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** is necessary for nearly every process in the refinery, and as such most of the energy consumed in a refinery is used in heaters and boilers.

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 reach 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.

Steam, often supplied by an integral utilities plant, is used for a variety of applications throughout the refinery. In most cases the steam is used for heating and boiling hydrocarbon streams, heating the petroleum indirectly and is then returning 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.

Furnaces are also used 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. Typical emission factors for these units are provided in Section 10-3.

The following tables (10-4 through 10-7) provide a summary of the inputs and outputs for the various auxiliary refinery processes, including sulfur management, chemical treatment, and process heaters.

Table 10-4. Summary of Inputs and Outputs for Sulfur Management			
Inputs		Outputs	
Fuel Gas/LPG	Catalyst	Clean Fuel Gas/LPG	Recycle Acid Gas
Recycle Gas	Steam	Elemental Sulfur	Treated Tail Gas
Sour Water	Cooling Water	Recycle Water	Wastewater
Amine	Electricity		

Table 10-5. Summary of Inputs and Outputs for Chemical Treatment			
Inputs		Outputs	
Sour Petroleum	Cooling Water	Mercaptan-Free Product	
Catalyst	Air/Oxygen	Spent Caustic	
Caustic	Filter Materials	Caustic Wastewater	
Ammonia	Electricity	Ammoniated Wastewater	

Table 10-6. Summary of Inputs and Outputs for Water Treatment			
Inputs:		Outputs:	
Sour Water	Biological Agents	Treated Water	Hazardous Sludge
Contaminated Water	Electricity	Sulfur Compounds	Biomass or other Non-Hazardous Sludge
Ferric or Al Oxide		Oil	

Table 10-7. Summary of Inputs and Outputs for Process Heating			
Inputs:		Outputs:	
Fuels		Steam	Wastewater
Boiler Feedwater		Electricity	Recycle Cooling Water
Cooling Water		Process Heat	

10.2 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 a Claus process by fuel type are shown in Table 10-8. Energy is consumed primarily in the furnace, and electricity is used to power pumps, compressors, and filtering systems.

Table 10-8. Estimated Electricity Use in Claus Sulfur Recovery Units	
Energy Source	Specific Energy Use (10³ Btu/ton of sulfur in feed^a)
Electricity (Net)	126.2
Electricity Losses ^b	262.3
TOTAL ELECTRICITY	388.5

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

^b Includes losses incurred during the generation and transmission of electricity

Energy requirements for chemical treatment and water treatment vary considerably depending upon the contaminants present and volume of feed or wastewater treated. Energy intensities per barrel of feed or gallon of water treated were not available.

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.

10.3 Air Emissions

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 10-9 illustrates sulfur dioxide emission factors; more information is available describing the various options in the original AP 42 Background Document from the EPA [EPA 1997].

Control Equipment	Emission Factor (lbs SO₂/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

Chemical treatment air emissions 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. Examples of hazardous air pollutants (HAPs) include carbonyl sulfide (COS) and carbon disulfide (CS₂). 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 10-10 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 10-10 provides emission factors for cooling water towers for both controlled and uncontrolled sources.

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]

Emissions from furnaces used for process heat or raising steam include sulfur oxides (SO_x), nitrogen oxides (NO_x), 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 1-15.

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 NO_x than other emissions. The most prevalent NO_x control techniques applied are low NO_x burners and flue gas recirculation. Post-combustion techniques for control of NO_x include selective noncatalytic reduction and selective catalytic reduction [EPA 1996].

In boilers combusting fuel oils or refinery oil by-products (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 NO_x 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].

10.4 Effluents

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.

10.5 Waste, Residuals and By-products

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 disulfide which is then sent to the Claus plant. Spent

caustic is also generated as a by-product 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 10-11 [BNA 1992]. These include API separator sludge, primary treatment sludge, sludges from various gravitational separation units, and float from dissolved air flotation units. Management of residuals that are not recycled may be accomplished by incineration, chemical fixation, neutralization and other treatment methods. Table 10-12 illustrates trends in generation of wastes from water treatment over the last decade.

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.

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.

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	--

a Current data is unavailable.

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 2004 [EPA 2006]. 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].

BIBLIOGRAPHY

- ANL 1981 L.L. Gaines and A.M. Wolsky, “Energy and Materials Flows in Petroleum Refining”, Argonne National Laboratory (ANL/CNSV-10), February 1981.
- AP 2006 Gillian Wong. “Oil Prices Rise Toward \$78 a Barrel.” Associated Press. July 16, 2006.
- API 1997a *5th Annual Report: Petroleum Industry Environmental Performance*, American Petroleum Institute, May 1997.
- API 1997b *Cumulative Impact of Environmental Regulations on the U.S. Petroleum Refining, Transportation and Marketing Industries*, American Petroleum Institute, October 1997.
- API 1997c *Management of Residual Materials: 1995: Petroleum Refining Performance*, API Publication 339, June 1997.
- API 1996a *Estimation of Fugitive Emissions from Petroleum Refinery Process Drains, Phase I Report*, API Publication 4639. April 1996.
- API 1994 *Air Toxics Multi-Year Study: Study of Refinery Fugitive Emissions from Equipment Leaks*, API Publication 4612. April 1994.
- API 1991 *The Generation and Management of Residual Materials: 1991; Petroleum Refining Performance*, API Publication Number 329, May 1994.
- API 2005 “Climate Challenge: A Progress Report,” American Petroleum Institute, 2005, <http://www.api.org>.
- API 2006a “Environmental Record of Performance – 2006,” American Petroleum Institute, updated 12 September 2006, <http://www.api.org/ehs/performance/index.cfm>.
- API 2006b “Clean Water Committees,” American Petroleum Institute, updated 15 September 2006, <http://www.api.org>.
- API 2006c “Environmental Examples,” American Petroleum Institute, updated 12 September 2006, <http://www.api.org>.
- API 2006d “Waste Prevention,” American Petroleum Institute, updated 12 September 2006, <http://www.api.org>.
- API 2006e “Air Toxics,” American Petroleum Institute, updated 18 September 2006, <http://www.api.org>.
- API 2006f “Industry Security: Vigilance and Protection,” American Petroleum Institute, Accessed 14 July 2006, <http://www.api.org>.
- API 2006g “Energy Efficiency and Recycling,” American Petroleum Institute, Updated 14 September 2006, <http://new.api.org/ehs/conservation/index.cfm>.

- Bailey 1986 J. E. Bailey and D. F. Ollis, *Biochemical Engineering Fundamentals*, 2nd Edition, McGraw-Hill, Inc. 1986.
- BNA 1995 *Hazardous Waste Criteria*, 40 CFR 261.31(a), and Part 261, Appendix VII, Bureau of National Affairs, 1995.
- BNA 1992 *EPA Effluent Guidelines for Petroleum and Petroleum Refining*, 40 CFR Part 419, Bureau of National Affairs, 1992.
- Bories 2004 Bories, M., Patureaux, T., "Preheat Train Crude Distillation Fouling Propensity Evaluation by the Ebert and Panchal Model," *Proceedings of the 2003 ECI Conference on Heat Exchanger Fouling and Cleaning: Fundamentals and Applications*, Paper 27, 2004.
- CCC 2003 Robert Looney. "Oil Prices and the Iraq War: Market Interpretations of Military Developments." Strategic Insight. Center for Contemporary Conflict, Naval Postgraduate School. April 2003. www.ccc.nps.navy.mil
- CFE 2006 "What is oil?," Canadian Centre for Energy Information, updated 12 November 2006, <http://www.centreforenergy.com>.
- CHEMB 1993 T. Wett, "Pushing the Sulfur Recovery Envelope," *Chemical Business*, Vol. 15, No. 11, pg. 13(3), November 1993
- CMR 2003 "Chemical Profile: Hydrogen," *Chemical Market Reporter*, 24 February 2003, p.43.
- CNN 2006 Cantrell, A., "The blame game: hedge funds and oil," CNNMoney.com, 26 April 2006, http://money.cnn.com/2006/04/26/markets/hedge_oil/.
- CPC 2006 "Energy Answers: Gasoline," ConocoPhillips Company, Updated 22 December 2006, http://www.conocophillips.com/newsroom/other_resources/energyanswers/gasoline.htm.
- Davison 1993 GRACE Davison, "Guide to Fluid Catalytic Cracking, Part One," W.R. Grace & Company, 1993.
- DOC 2006 *Annual Survey of Manufactures, Statistics for Industry Groups and Industries: 2005*. U.S. Department of Commerce. 2006.
- DOC 2004 *Annual Survey of Manufactures 2004*. U.S. Department of Commerce. 2005.
- DOC 2003 *Annual Survey of Manufactures, Statistics for Industry Groups and Industries: 2001*. U.S. Department of Commerce. 2003.
- DOC 1998 U.S. Department of Commerce (DOC). *1996 Annual Survey of Manufactures, Statistics for Industry Groups and Industries*. M96(AS)-1. February 1998.
- DOC 1997 *Draft Industry Summaries, Chapter 4, Petroleum Refining*, for forthcoming *1998 Industrial Outlook*, U.S. Department of Commerce, November 1997 www.doc.gov
- DOC 1993 U.S. Congress, Office of Technology Assessment (U.S. Congress, OTA). *Industrial Energy Efficiency*. Washington, D.C. OTA-E-560, August 1993.

- DOE 2003 *The Impact of Environmental Compliance Costs on U.S. Refining Profitability*, U.S. Department of Energy, Energy Information Administration, May 2003.
- DOE 2006a U.S. Department of Energy (DOE). 2006. *Refinery Capacity 2006*. Energy Information Administration, June 2006.
- DOE 2006b “U.S. Percent Utilization of Refinery Operable Capacity (Percent),” U.S. Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 12 June 2006, http://tonto.eia.doe.gov/dnav/pet/pet_sum_top.asp.
- DOE 2006c *Annual Energy Outlook 2006*. U.S. Department of Energy, Energy Information Administration.
- DOE 2006d “U.S. Crude Oil Supply and Disposition,” and “Weekly Imports & Exports.” U.S. Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 25 August 2006 and 7 September 2006, respectively. <http://tonto.eia.doe.gov/dnav/pet/>
- DOE 2006e “All Countries Spot Price FOB Weighted by Estimated Export Volume (dollars per barrel),” Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 7 September 2006. <http://tonto.eia.doe.gov/dnav/pet/>
- DOE 2006f Cushing, Ok Crude Oil Future Contract 4 (Dollars per Barrel), Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 7 September 2006. <http://tonto.eia.doe.gov/dnav/pet/hist/rclc4d.htm>
- DOE 2006g *Country Analysis Briefs*. U.S. Department of Energy, Energy Information Administration. 2006. <http://www.eia.doe.gov/emeu/cabs>
- DOE 2006h *Annual Energy Review 2005*. U.S. Department of Energy, Energy Information Administration, July 2006, DOE/EIA-0384(2005).
- DOE 2006i “U.S. Oxygenates MTBE Inputs into Refineries,” Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 28 July 2006. <http://tonto.eia.doe.gov/dnav/pet/>.
- DOE 2006j “Eliminating MTBE in Gasoline in 2006,” U.S. Department of Energy, Energy Information Administration, 22 February 2006, http://www.eia.doe.gov/pub/oil_gas/petroleum/feature_articles/2006/mtbe2006/mtbe2006.pdf.
- DOE 2006k “U.S. Imports by Country of Origin,” U.S. Department of Energy, Energy Information Administration, Updated 12 June 2006, <http://www.eia.doe.gov>.
- DOE 2006l “World Crude Oil Prices,” U.S. Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 6 December 2006, http://tonto.eia.doe.gov/dnav/pet/pet_pri_wco_k_w.htm.
- DOE 2006m *Petroleum Supply Annual 2005, Volume 1*. U.S. Department of Energy, Energy Information Administration, October 2006, DOE/EIA-0340(05)/1.
- DOE 2006n *Petroleum Marketing Monthly*. U.S. Department of Energy, Energy Information Administration, December 2006.

- DOE 2006o “Crude Oil Input Qualities,” U.S. Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 3 October 2006, <http://tonto.eia.doe.gov/dnav/pet/hist/mcrs1us2a.htm>.
- DOE 2006p “Exports,” U.S. Department of Energy, Energy Information Administration, *Petroleum Navigator*, Updated 30 November 2006, http://tonto.eia.doe.gov/dnav/pet/pet_move_exp_dc_NUS-Z00_mbb1_m.htm.
- DOE 2006q “A Primer on Gasoline Prices,” U.S. Department of Energy, Energy Information Administration, May 2006, DOE/EIA-X040.
- DOE 2005a “Hurricane Impact on US. Oil & Natural Gas Energy Markets.” U.S. Department of Energy, Energy Information Administration. 12/27/2005. http://tonto.eia.doe.gov/oog/special/eia1_katrina.html
- DOE 2005b *Manufacturing Energy Consumption Survey, 2002*. U.S. Department of Energy, Energy Information Administration, 2005.
- DOE 2005c *Petroleum Supply Annual 2004, Volume 1*. U.S. Department of Energy, Energy Information Administration, June 2005, DOE/EIA-0340(04)/1.
- DOE 2005d *2002 Manufacturing Energy Consumption Survey (MECS)*. U.S. Department of Energy, Energy Information Administration, 2005.
- DOE 2005e “Current (2005) Hydrogen from SMR Natural Gas with CO₂ Capture and Sequestration – Central Production Case,” U.S. Department of Energy, H₂A Analysis, Updated 14 August 2005, http://www.hydrogen.energy.gov/h2a_analysis.html.
- DOE 2004 *Petroleum Supply Annual 2003, Volume 1*. U.S. Department of Energy, Energy Information Administration, July 2004, DOE/EIA-0340(03)/1.
- DOE 2003 “Status and Impact of State MTBE Ban,” U.S. Department of Energy, Energy Information Administration, 27 March 2003, Accessed 4 August 2006, <http://www.eia.doe.gov/oiaf/servicerpt/mtbeban.index.html>.
- DOE 2003b *Emissions of Greenhouse Gases in the United States, 2002*. U.S. Department of Energy, Energy Information Administration, 2003.
- DOE 2003c *Petroleum Supply Annual 2002, Volume 1*. U.S. Department of Energy, Energy Information Administration, June 2003, DOE/EIA-0340(02)/1.
- DOE 2002 *Petroleum Supply Annual 2001, Volume 1*. U.S. Department of Energy, Energy Information Administration, June 2002, DOE/EIA-0340(01)/1.
- DOE 2001 “The Transition to Ultra-Low-Sulfur Diesel Fuel: Effects on Prices and Supply,” U.S. Department of Energy, Energy Information Administration, 8 June 2001, Accessed 10 November 2006, <http://www.eia.doe.gov/oiaf/servicerpt/ulsd/chapter3.html>.
- DOE 2001b *1998 Manufacturing Energy Consumption Survey (MECS)*. U.S. Department of Energy, Energy Information Administration, 2001.

- DOE 2001c *Petroleum Supply Annual 2000, Volume 1*. U.S. Department of Energy, Energy Information Administration, June 2001, DOE/EIA-0340(00)/1.
- DOE 1998 *Monthly Energy Review*, April 1998. U.S. Department of Energy, Energy Information Administration DOE/EIA-0035(98/04).
- DOE 1997 *1994 Manufacturing Energy Consumption Survey (MECS)*. U.S. Department of Energy, Energy Information Administration, 1997.
- DOE 1994 *1991 Manufacturing Energy Consumption Survey (MECS)*. U.S. Department of Energy, Energy Information Administration, 1994.
- DOE 1994 U.S. Department of Energy (DOE). 1994. Manufacturing Energy Consumption Survey 1991 (MECS). Energy Information Administration, DOE/EIA-0512(91).
- DOE 1993 U.S. Department of Energy (DOE) . 1993. *The U.S. Petroleum Industry: Past As Prologue, 1970-1992*. Energy Information Agency, Office of Oil and Gas. Washington, D.C. DOE/EIA-0572. September.
- DOE 1991 *Petroleum: An Energy Profile*, U.S. Department of Energy, Energy Information Administration, August 1991 (DOE/EIA-0545(91)).
- DOE 1991 *1988 Manufacturing Energy Consumption Survey (MECS)*. U.S. Department of Energy, Energy Information Administration, 1991.
- DOE 1988 *1985 Manufacturing Energy Consumption Survey (MECS)*. U.S. Department of Energy, Energy Information Administration, 1988.
- DOE 1990 *The U.S. Petroleum Refining Industry in the 1980's*, U.S. Department of Energy, Energy Information Administration, October 1990 (DOE/EIA-0536).
- EI 1990 *Industry Profiles Series: Petroleum Refining*, Energetics, Inc. Columbia, MD, 1990.
- EM 2007 "MAX-DEWAX™ Solvent Dewaxing Technology," ExxonMobil Corporation, Accessed 2 January 2007, http://www.exxonmobil.com/Refiningtechnologies/lubes/mn_max_dewax.html.
- EPA 2007 *Registration and Health Effects Testing*, U.S. Environmental Protection Agency, updated October 2007, www.epa.gov/otaq/additive.htm
- EPA 2006 *2004 Toxic Release Inventory*. U.S. Environmental Protection Agency, updated 9 June 2006, <http://www.epa.gov/triexplorer/>.
- EPA 2006b "Regulatory Announcement: Removal of Reformulated Gasoline Oxygen Content Requirement and Revision of Commingling Prohibition to Address Non-Oxygenated Reformulated Gasoline," U.S. Environmental Protection Agency, February 2006, EPA420-F-06-020.
- EPA 2006c "Guide on Federal and State Summer RVP Standards for Conventional Gas Only," U.S. Environmental Protection Agency, 7 March 2006, <http://www.epa.gov/otaq/volatility.htm>.

- EPA 2006d “Direct Final Rule and Notice of Proposed Rulemaking for Amendments to the Nonroad and Highway Diesel Fuel Regulations,” U.S. Environmental Protection Agency, April 2006, EPA420-F-06-033.
- EPA 2006e “National Ambient Air Quality Standards (NAAQS),” U.S. Environmental Protection Agency, updated 21 September 2006, <http://www.epa.gov/air/criteria.html>.
- EPA 2006f “Visibility Regulatory Actions,” U.S. Environmental Protection Agency, updated 23 October 2006, <http://www.epa.gov/oar/visibility/actions.html#barttradingfinal>.
- EPA 2006g “Fact Sheet – Final Amendments to the Regional Haze Rule and Guidelines for Best Available Retrofit Technology (BART) Determinations,” U.S. Environmental Protection Agency, updated 4 October 2006, http://www.epa.gov/oar/visibility/fs_2005_6_15.html.
- EPA 2006h “Petroleum Refinery Initiative Fact Sheet,” U.S. Environmental Protection Agency, updated 3 March 2006, <http://www.epa.gov/compliance/resources/cases/civil/caa/petroleumrefinery-fcsht.html>.
- EPA 2006i *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2004*. U.S. Environmental Protection Agency, April 2006, EPA 430-R-06-002.
- EPA 2006j “Regulatory Announcement: Removal of Reformulated Gasoline Oxygen Content Requirement” U.S. Environmental Protection Agency, May 2006, EPA420-F-06-035.
- EPA 2005 “State Winter Oxygenated Fuel Program Requirements for Attainment or Maintenance of CO NAAQS,” U.S. Environmental Protection Agency, November 2005, EPA420-B-05-013.
- EPA 2000 “Heavy-Duty Engine and Vehicle Standards and Highway Diesel Fuel Sulfur Control Requirements,” U.S. Environmental Protection Agency, December 2000, EPA420-F-00-057.
- EPA 1999 33/50 Program: The Final Record. U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics. March 1999. EPA-745-R-99-004.
- EPA 1999b “Regulatory Impact Analysis – Control of Air Pollution from New Motor Vehicles: Tier 2 Motor Vehicle Emissions Standards and Gasoline Sulfur Control,” U.S. Environmental Protection Agency, December 1999, EPA420-R-99-023.
- EPA 1998 “Final Standards Promulgated for Petroleum Refining Waste,” U.S. Environmental Protection Agency, July 1998, EPA530-F-98-014.
- EPA 1998 *1996 Toxics Release Inventory*. U.S. Environmental Protection Agency, 1998.
- EPA 1997 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.
- EPA 1996a U.S. Environmental Protection Agency (EPA). 1996. *1987-1994 Toxics Release Inventory* (CD-ROM).

- EPA 1996b AP-42, *Chapter 1.3, Fuel Oil Combustion*, U.S. Environmental Protection Agency (EPA), October 1996.
- EPA 1995a *Sector Notebook: Profile of the Petroleum Refining Industry*. U.S. Environmental Protection Agency, Office of Compliance (EPA 310-R-95-013), September 1995.
- EPA 1995b AP-42, *Chapter 5.1, Petroleum Refining*, U.S. Environmental Protection Agency, January 1995.
- EPA 1993 *1993 Toxics Release Inventory*. U.S. Environmental Protection Agency, 1995. EPA 745-R-95-003.
- EPACT 2005 Energy Policy Act of 2005, H.R.6, <http://thomas.loc.gov>.
- Fransen 2004 Fransen, G., "New Control System Detects Desalter Problems Before Upsets Occur," *Proceedings of the AIChE 2004 Spring National Meeting*, Paper 88c, 2004.
- Gary 2007 *Petroleum Refining - Technology and Economics*, Gary, Handwerk, Kaiser, Fifth Edition, Taylor & Francis Group, 2007.
- Gary 1994 *Petroleum Refining - Technology and Economics*, Gary & Handwerk, 3rd Edition, Marcel Dekker, Inc., New York, N.Y., 1994.
- Gary 1984 Gary, J.H., Handwerk, G.E., *Petroleum Refining*, 2nd Edition, Marcel Dekker, Inc., New York, New York, 1984.
- Gould 2001 Gould, R.M., White, L.S., Wildemuth, C.R., "Membrane Separation in Solvent Lube Dewaxing," *Environmental Progress*, Volume 20, Number 1, p. 12-16, 2001.
- Gray 2000 Gray, D., Tomlinson, G., Mitretek Systems, "Opportunities for Petroleum Coke Gasification Under Tighter Sulfur Limits for Transportation Fuels," presented at the 2000 Gasification Technologies Conference, San Francisco, California, October 2000.
- HP 2006a "2006 Refining Processes Handbook (CD-ROM)," *Hydrocarbon Processing*, 2006.
- HP 2006b Weirauch, W., "HPImpact," *Hydrocarbon Processing*, April 2006.
- HP 2006c Weirauch, W., "HPImpact," *Hydrocarbon Processing*, May 2006.
- HP 2006d Weirauch, W., "HPImpact," *Hydrocarbon Processing*, August 2006.
- HP 2006e "Gas Processes Handbook 2006 (CD-ROM)," *Hydrocarbon Processing*, 2006.
- HP 2005a Dunham, D., "Upgrade alkylation for refining environment," *Hydrocarbon Processing*, September 2005.
- HP 2005b Sayles, S., Bailor, J., "Upgrade FCC-Feed Hydrotreating," *Hydrocarbon Processing*, September 2005.
- HP 2005c Letzsch, W., "Improve Catalytic Cracking to Produce Clean Fuels," *Hydrocarbon Processing*, February 2005.

- HP 2005d Huchler, L.A., "Monitor Cooling Water Quality – Part 1," *Hydrocarbon Processing*, November 2005.
- HP 2005e Weirauch, W., "HPImpact: Gasoline blending rules could pit refiners against petrochem operators," *Hydrocarbon Processing*, June 2005.
- HP 2005f Henderson, Rodwell, M., and Harji, A., "Consider modifying your refinery to handle heavy opportunity crude oils," *Hydrocarbon Processing*, September 2005.
- HP 2005g Swaty, T.E., "Global refining industry trends: the present and future," *Hydrocarbon Processing*, September 2005.
- HP 2005h Jackson, K.M., "Industry Development: New Technologies and Regulations are Spurring Growth," *Hydrocarbon Processing*, February 2005.
- HP 2005i Micucci, L., "Optimize Claus Operations," *Hydrocarbon Processing*, December 2005.
- HP 2005j Nagl, G.J., "Update Your Sulfur Management Program," *Hydrocarbon Processing*, November 2005.
- HP 2005k Patel, N., Ludwig, K., Morris, P., "Insert flexibility into your hydrogen network – Part 1," *Hydrocarbon Processing*, September 2005.
- HP 2005l Patel, N., Ludwig, K., Morris, P., "Insert flexibility into your hydrogen network – Part 2," *Hydrocarbon Processing*, October 2005.
- HP 2003a Kilian, M., Wozny, G., "Optimize your search for sulfur-recovery technology," *Hydrocarbon Processing*, January 2003.
- HP 2003b Heguy, D.L., Nagl, G.J., "Consider Optimizing Iron-Redox Processes to Remove Sulfur," *Hydrocarbon Processing*, January 2003.
- HP 2003c Zagoria, A., Huycke, R., "Refinery hydrogen management – the big picture," *Hydrocarbon Processing*, February 2003.
- HP 2002 Siecke, M.J., Weber, R.J., "Is Regulatory Compliance a Burden or an Opportunity?," *Hydrocarbon Processing*, June 2002.
- HP 2001 Niemiec, B., Nagl, G.J., Watson, G., Baker, C., "Increase Flexibility and Efficiency of Claus Unit with Liquid Redox Technology," *Hydrocarbon Processing*, May 2001.
- HP 1998 Riddle, A.L., Bhat, A.N.V., Hopper, J.R., "Neural Networks Help Optimize Solvent Extraction," *Hydrocarbon Processing*, November 1998.
- HP 1996 "Refining Processes '96," *Hydrocarbon Processing*, (pps. 91-145), November 1996.
- HP 1994 Roy, G.K., "Improve FCCU expander reliability," *Hydrocarbon Processing* (pp. 67), March 1994.
- HP 1993a D.T. Cindric, B. Klein, A.R. Gentry, and H.M. Gomaa, "Reduce crude unit pollution with these technologies," *Hydrocarbon Processing*, (pps. 45-48), August 1993.

- Humphrey Humphrey, J.L., Seibert, A.F., Koort, R.A., *Separation Technologies* 1991. *Advances and Priorities, Final Report*, J.L. Humphrey and Associates, Austin, Texas February 1991, for the U.S. Department of Energy (DOE/ID/12920-1).
- IHS 2000 “ESDU Introduces New Process and Environmental Technology,” IHS, Inc. press release, 6 July 2000, Accessed 24 August 2006, <http://infoenlace.ihserc.com/engineering/press-releases/00esdu.html>.
- Kane 2004 Kane, L., Romanow, S., Eds., “New Catalyst Yields High-Octane Isomerate,” *Hydrocarbon Processing*, June 2004.
- Kremer 2004 Kremer, L., Nguyen, J., Weers, J., “Removal of Calcium and Other Metal Species from Crude Oil in the Desalting Process,” *Proceedings of the AIChE 2004 Spring National Meeting*, Paper 88d, 2004.
- Letzsch 2002 Letzsch, W., “Synthetic Crude to Petro Chemicals,” **The Refiner**, Issue 7, Summer/Fall 2002.
- LBNL 2005 Worrell, E. and Galitsky, C. *Energy Efficiency Improvement and Cost Saving Opportunities for Petroleum Refineries: An ENERGY STAR Guide for Energy and Plant Managers*. Lawrence Berkeley National Laboratory, February 2005, LBNL-56183.
- Lindemuth Lindemuth, P.M., Lessard, R.B., Lozynski, M., “Improve Desalter Operations,” *Hydrocarbon Processing*, September 2001.
- LLNL 2006 “Sleuthing MTBE with Statistical Data,” Lawrence Livermore National Laboratory, Accessed 4 August 2006, <http://www.llnl.gov/str/Happel.html>.
- Marano 2003 Marano, J.J., “Refinery Technology Profiles, Gasification and Supporting Technologies,” prepared for the U.S. Department of Energy, National Energy Technology Laboratory, Energy Information Administration, June 2003.
- Master 2003 Master, B.I., Chunangad, K.S., Pushpanathan, V., “Fouling Mitigation using Helixchanger® Heat Exchangers,” 2003, Accessed 24 August 2006, <http://www.technology.novem.nl/en/heat-exchange/downloads/ECI-FoulingArticle-2003-R3.pdf>.
- MEES 2006 A.F. Alhajji. “2005 Lessons from the Oil Market.” Middle East Economic Survey, Volume XLIX, No. 27, July 3, 2006. Gulf Research Center, Dubai, UAE. www.mees.com/postedarticles/oped/v49n27-5OD01.htm
- Meyers 2004 Meyers, R.A., Editor in Chief, *Handbook of Petroleum Refining Processes*, 3rd Edition, McGraw-Hill, New York, N.Y. 2004.
- Meyers 1997 R. A. Meyers, Editor in Chief, *Handbook of Petroleum Refining Processes*, 2nd Edition, McGraw-Hill, New York, N.Y. 1997.
- MPCA 2002 “Ethanol Production in Minnesota,” Minnesota Pollution Control Agency, October 2002.
- MSNBC 2006. Schoen, J.W., “What’s pushing oil prices higher?” MSNBC Commentary. 2006. <http://msnbc.msn.com/id/13862677>

- NARA 2006 National Archives and Records Administration, *Petroleum Refining Point Source Category*, 40 CFR Part 419, Revised 7 August 2006.
- NARA 2006b National Archives and Records Administration, *Identification and Listing of Hazardous Waste*, 40 CFR Part 261, Revised 7 August 2006.
- NBB 2005 “U.S. Navy Calls for Broad Use of Biodiesel at Navy and Marine Facilities,” National Biodiesel Board press release, March 11, 2005, <http://www.biodiesel.org>.
- Ng 2006 Ng, S., et al., “Production of Light Olefins through Gas Oil Cracking,” American Institute of Chemical Engineers (AIChE) 2006 Annual Meeting, San Francisco, California, November 2006.
- Nowak 2003 Nowak, F-M., Himes, J.F., Mehlberg, R.L. “Advances in Hydrofluoric (HF) Acid Catalyzed Alkylation,” Presented at the National Petrochemical & Refiners Association Annual Meeting, March 2003.
- NPRA 2006a “Facility Security,” National Petrochemical and Refiners Association (NPRA), Accessed 18 December 2006, <http://www.npra.org>.
- NW 2006 Banta, H., “Speculators – not supply and demand – are to blame for skyrocketing gas prices,” Nieman Watchdog, 11 July 2006, <http://www.niemanwatchdog.org/index.cfm?fuseaction=background.view&backgroundid=100>
- OGJ 2006a Radler, M., “Slim 2006 US Energy Demand Growth Projected,” *Oil & Gas Journal*, 16 January 2006.
- OGJ 2006b Jensen, J.D., Tamm, D.C., “RFS will require more blendstock production,” *Oil & Gas Journal*, 8 May 2006.
- OGJ 2006c “CGES: Global crude supplies will continue to get heavier,” *Oil & Gas Journal*, 26 September 2006.
- OGJ 2006d Stratiev, D., Galkin, V., Stanulov, K., “Most-active catalyst improves ULSD economics,” *Oil & Gas Journal*, 14 August 2006.
- OGJ 2006e Sayles, S., “Transition to ULSD, ethanol goes smoothly for US refiners,” *Oil & Gas Journal*, 04 December 2006.
- OGJ 2006f Fletcher, S., “Alternative fuels gaining transport market share,” *Oil & Gas Journal*, 04 December 2006.
- OGJ 2005a Radler, M., “Industry Spending to Rise but at Lower Rate in 2005,” *Oil & Gas Journal*, 4 April 2005.
- OGJ 2003a Williams, B., “Refiners’ future survival hinges on adapting to changing feedstocks, product specs,” *Oil and Gas Journal*, 11 August 2003.
- OGJ 1996c P. Rao and S.R. Vatcha, “Solid-acid alkylation process development is at a critical stage,” *Oil & Gas Journal*, September 9, 1996.

- OGJ 1995a P.R.Cressman, M.L. Hurren, E.F. Smith, and D.L.Holbrook, "Caustic-Free jet fuel Merox unit reduces waste disposal," *Oil & Gas Journal*, p. 80, March 20, 1995.
- OGJ 1994 A. K. Rhodes, "New process schemes, retrofits, fine tune alkylation capabilities," *Oil & Gas Journal*, August 22, 1994.
- OGJ 1992a K.S. Eble and J. Feathers, "Process Water Reuse, Part I," *Oil & Gas Journal*, September 21, 1992.
- OGJ 1990 M.J.P.C. Nieskens, F.H.H. Khouw, M.J.H. Borley, and K.W. Roebischlaeger, "Shell's resid FCC technology reflects evolutionary development," *Oil & Gas Journal*, June 11, 1990.
- ORNL 1980 R.S. Mack and others, *Industrial Energy Use Data Book*, Oak Ridge Associated Universities, Oak Ridge, TN 37830. 1980.
- PNNL 2006 "Bio-based Research – Biomass to Clean Fuels," Pacific Northwest National Laboratory, updated December 2006, <http://www.pnl.gov/biobased/bcf.stm>
- RAND 2003 Peterson, D.J., Mahnovski, S., *New Forces at Work in Refining: Industry Views of Critical Business and Operations Trends*, RAND Science and Technology, 2003.
- RFA 2007 "RFA Responds to State of the Union Energy Initiatives," Press Release, Renewable Fuels Association, 23 January 2007, <http://www.ethanolrfa.org/media/press/rfa/2007/view.php?id=930>.
- RFA 2006 *Ethanol Industry Outlook 2006: From Niche to Nation*, Renewable Fuels Association, <http://www.ethanolrfa.org>.
- RFA 2006b "'Legislative Actions: State," Renewable Fuels Association, Updated March 2006, Accessed 3 August 2006, <http://www.ethanolrfa.org/policy/actions/state/>
- RFA 2006c "The Ethanol Production Process (Dry Mill)," Renewable Fuels Association, <http://www.ethanolrfa.org/resource/made/>.
- RFA 2005 *Ethanol Industry Outlook 2005: Homegrown for the Homeland*, Renewable Fuels Association, <http://www.ethanolrfa.org>.
- RFA 2004 *Ethanol Industry Outlook 2004: Synergy in Energy*, Renewable Fuels Association, <http://www.ethanolrfa.org>.
- RohMax 2007 "VISCOPLEX® Dewaxing Aids," RohMax Oil Additives, Accessed 2 January 2007, <http://www.rohmax.com/rohmax/en/productsapplications/viscoplexdewaxingaids/backroundbenefits/>.
- SB 2004 Science Blog, "Strict environmental Regulations Compel Petroleum Refiners to Opt for Catalytic Processes," 12 July 2004, Accessed 6 September 2006, <http://www.scienceblog.com/community/older/2004/8/20047499.shtml>.
- Senate 2006 "Levin-Coleman report finds speculation adding to oil prices: put the cop back on the beat," Press Release, Senate Committee on Homeland Security & Governmental Affairs, 27 June 2006, http://hsgac.senate.gov/index.cfm?Fuseaction=PressReleases.View&PressRelease_id=1278&Affiliation=C.

- SFA 1990 Personal communication with B. Schulman, SFA Pacific, Inc., Mountain View, CA, February 1990.
- Smaili 2002 Smaili, F., Vassiliadis, V.S., Wilson, D.I., "Optimization of Cleaning Schedules in Heat Exchanger Networks Subject to Fouling," *Chemical Engineering Communications*, **189**:1517-1549, 2002.
- Sulphur 1994 "Keeping Abreast of the Regulations: Improved Claus Sulphur Recovery," *Sulphur*, No. 231, pg 35(18), March-April 1994.
- UNFCCC 2006 "Kyoto Protocol," United Nations Framework Convention on Climate Change, Accessed 13 November 2006, http://unfccc.int/kyoto_protocol/items/2830.php.
- UOP 2006 UOP LLC, "Changing Refinery Configuration for Heavy and Synthetic Crude Processing," June 2006, <http://www.uop.com>.
- UOP 2004a UOP LLC, "UOP's New R-98™ Catalyst Increases Reformate Yield for Hunt Refining in First Commercial Application," Press Release, 4 April 2006, <http://www.uop.com>.
- UOP 2004b UOP LLC, "OMV Successfully Starts Up the First Installation of R-264™ Catalyst," Press Release 18 October 2006, <http://www.uop.com>.
- UOP 2004c UOP LLC, "Controlling FCC Yields and Emissions: UOP Technology for a Changing Environment," NPRA Annual Meeting, San Antonio, Texas, March 2003.
- USB 2006 "Market Opportunity Summary: Soy-Based Lubricants," United Soybean Board, January 2006, <http://www.unitedsoybean.org>.
- USDA 2004 Shapouri, H., "The 2001 Net Energy Balance of Corn-Ethanol," U.S. Department of Agriculture, 31 May 2004.
- van Rooijen 2005 van Rooijen, E., "ALKYCLEAN – A true solid acid gasoline alkylation process," *Catalysts Courier*, **60**, 11-12, 2005, http://www.albemarle.com/Products_and_services/Catalysts/Courier/.
- Vision 2020 *Technology Vision 2020: A Report on technology and the future of the U.S. petroleum industry*. American Petroleum Institute and National Petrochemical & Refiners Association. 1999.
- WA 2006 "Senate Bill Report ESHB 2738," Senate Committee on Water, Energy & Environment, State of Washington, 22 February 2006, <http://www.leg.wa.gov/pub/billinfo/2005-06/Pdf/Bill%20Reports/Senate/2738-S.SBR.pdf>.
- Weyda 2003 Weyda, H., Kohler, E. 2003. "Modern refining concepts—an update on naphtha-isomerization to modern gasoline manufacture," *Catalysis Today*, **81**, 51-55.
- Wilson 2002 Wilson, D.I., Polley, G.T., Pugh, S.J., "Mitigation of Crude Oil Preheat Train Fouling by Design," *Heat Transfer Engineering*, **23**:24-37, 2002.
- WP 2005 Vedantam, S., "Kyoto Treaty Takes Effect Today," *Washington Post*, 16 February 2005, p.A04.

- WP 2000 Rameshni, M. (WorleyParsons), *State-of-the-Art In Gas Treating*, WorleyParsons, British Sulphur 2000, November 2000.
- Yeap 2005 Yeap, B.L., Wilson, D.I., Polley, G.T., Pugh, S.J., “Retrofitting Crude Oil Refinery Heat Exchanger Networks to Minimize Fouling while Maximizing Heat Recovery,” *Heat Transfer Engineering*, **26**(1):23-34, 2005.