Energy Bandwidth for Petroleum Refining Processes

Prepared by Energetics Incorporated for the
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Office of Energy Efficiency and Renewable Energy
Industrial Technologies Program

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Foreword

The Industrial Technologies Program (ITP) is a research and development (R&D) program within the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE). This program works in collaboration with U.S. industry to improve industrial energy efficiency and environmental performance. Research is conducted through partnerships with industry as well as academia, national laboratories, and private research institutes to reduce industrial energy consumption.

R&D projects within this program focus on manufacturing processes that use the most energy, ensuring that Federal funds are being spent effectively on areas with the greatest potential for improvement. ITP sponsors research on a variety of industrial processes, such as petroleum refining, metal casting, and steel making. Of these industrial sectors, petroleum refineries are one of the largest consumers of energy and the United States is the largest producer of refined petroleum products in the world. Because ITP strives to focus R&D on the most energy-intensive manufacturing processes and technologies in U.S. industry, the Petroleum and Coal Products industry is a worthwhile candidate for energy efficiency R&D.

ITP conducted a “bandwidth” study to analyze the most energy-intensive unit operations used in U.S. refineries. This study will help decision makers better understand the energy savings that could be realized in this area through energy recovery and improvements in energy efficiency. This report will be used to guide future ITP R&D decision-making and investments in petroleum refining processes.

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Overview

The Industrial Technologies Program (ITP), which is a part of DOE's Office of Energy Efficiency and Renewable Energy, is developing methods that will help quantify energy-efficiency improvements in the most energy-intensive process streams. Analyses such as energy bandwidth studies will enable ITP to focus on the processes or unit operations with the greatest potential for energy efficiency gains and maximize the impact of ITP's research investments.

Energy bandwidth analyses provide a realistic estimate of the energy that may be saved in an industrial process by quantifying three measures of energy consumption:

- ***Theoretical minimum energy (TME).*** TME is a measure of the least amount of energy that a particular process would require under ideal conditions. TME calculations are based on the thermodynamic analyses of primary chemical reactions using the change in Gibbs free energy (ΔG), and assume ideal conditions (standard state, 100% selectivity and conversion) and neglect irreversibilities. In some cases, the TME values were obtained through industry publications or using the heat of reaction (ΔH_r) due to insufficient Gibbs free energy data.

- ***Practical minimum energy (PME).*** The PME represents the minimum energy required to carry out a process in real-world, non-standard conditions (e.g., temperature, pressure, selectivities and conversions less than 100%) that result in the formation of by-products, the need for product separation, catalyst and equipment fouling, and other factors. These conditions impose limitations that make it impossible to operate at the theoretical minimum. The energy savings considered for the practical minimum analysis are primarily based on best practices and state-of-the-art technologies currently available in the marketplace. Energy savings technologies that are considered to be in the research and development stage are footnoted in Appendix A.

- ***Current average energy (CAE).*** CAE is a measure of the energy consumed by a process carried out under actual plant conditions. This measure exceeds both the theoretical and practical minimum energies due to energy losses from inefficient or outdated equipment and process design, poor heat integration, and poor conversion and selectivities, among other factors.

The bandwidth is the difference between PME and CAE and provides a snapshot of energy losses that may be recovered by improving current processing technologies, the overall process design, current operating practices, and other related factors.

The North American Industry Classification System (NAICS) classifies the Petroleum and Coal Products industry (represented by NAICS code 324) as including petroleum refineries that produce fuels and petrochemicals and manufacture lubricants, waxes, asphalt, and other petroleum and coal products. This report primarily focuses on NAICS 324110, Petroleum Refineries, which are defined as establishments primarily engaged in refining crude petroleum into refined petroleum.

NAICS 324 is one of the largest consumers of energy in the industrial sector, second only to NAICS 325, the chemicals sector. The petroleum and coal products industry represents a significant target for improving energy efficiency. In 2002, this sector consumed 3.2 quadrillion Btu (quads) of energy as fuel—accounting for 20% of the fuel energy consumed by U.S manufacturing industries. Petroleum Refineries, NAICS 324110, accounted for nearly 3.1 quadrillion Btu (quads) of this energy consumption [DOE 2005a].

This report examines the TME, PME, and CAE for five of the most significant processes in petroleum refining:

1. Atmospheric and vacuum crude distillation
2. Fluid catalytic cracking (FCC)
3. Catalytic hydrotreating
4. Catalytic reforming
5. Alkylation

These processes account for approximately 70% of the energy consumed by the refining industry and offer significant opportunities for increasing energy efficiency [DOE 1998].

Petroleum Refining Process Descriptions

Petroleum refining is a complex industry that generates a diverse slate of fuel and chemical products, from gasoline to heating oil. The refining process involves separating, cracking, restructuring, treating, and blending hydrocarbon molecules to generate petroleum products. Figure 1 shows the overall refining process.

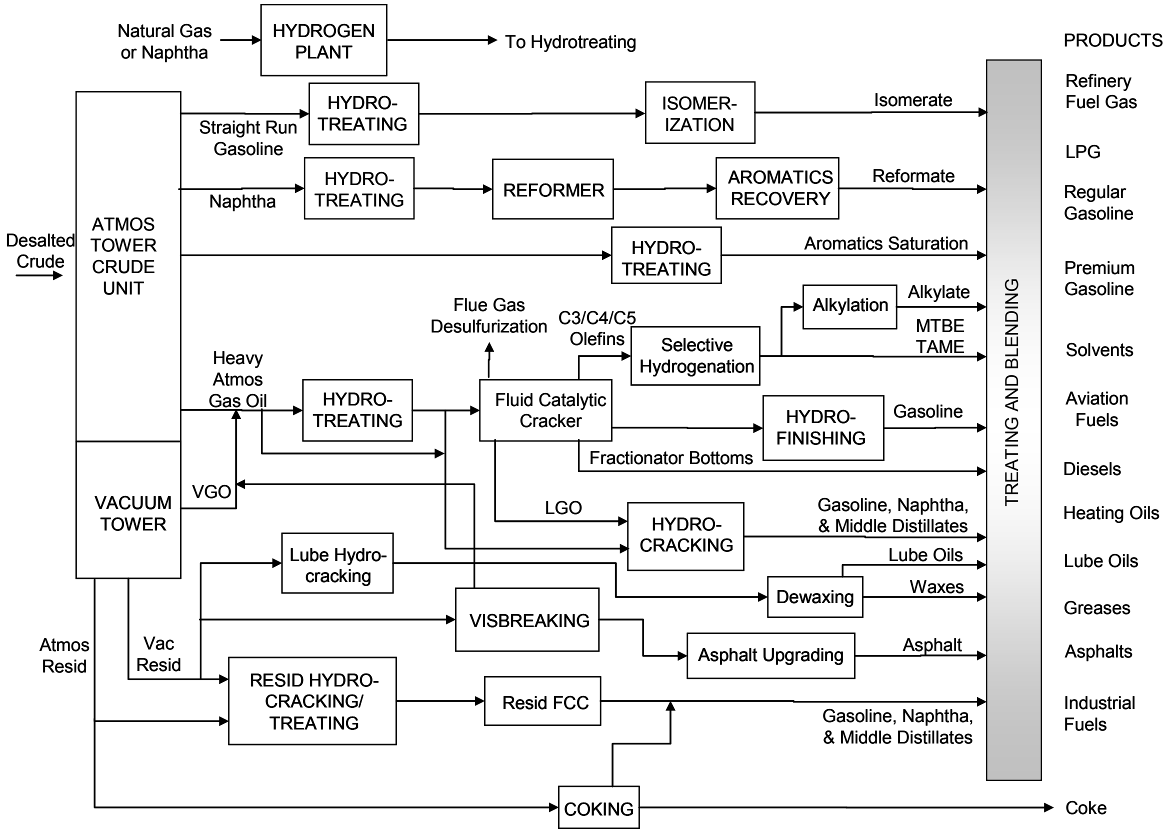


Figure 1. Typical Refinery Flow Diagram [DOE 1998]

There are approximately 150 refineries operating in the United States. Most of the larger refineries are concentrated along the coast due to the access to sea transportation and shipping routes. Figure 2 shows the geographic distribution of petroleum refineries in the United States.

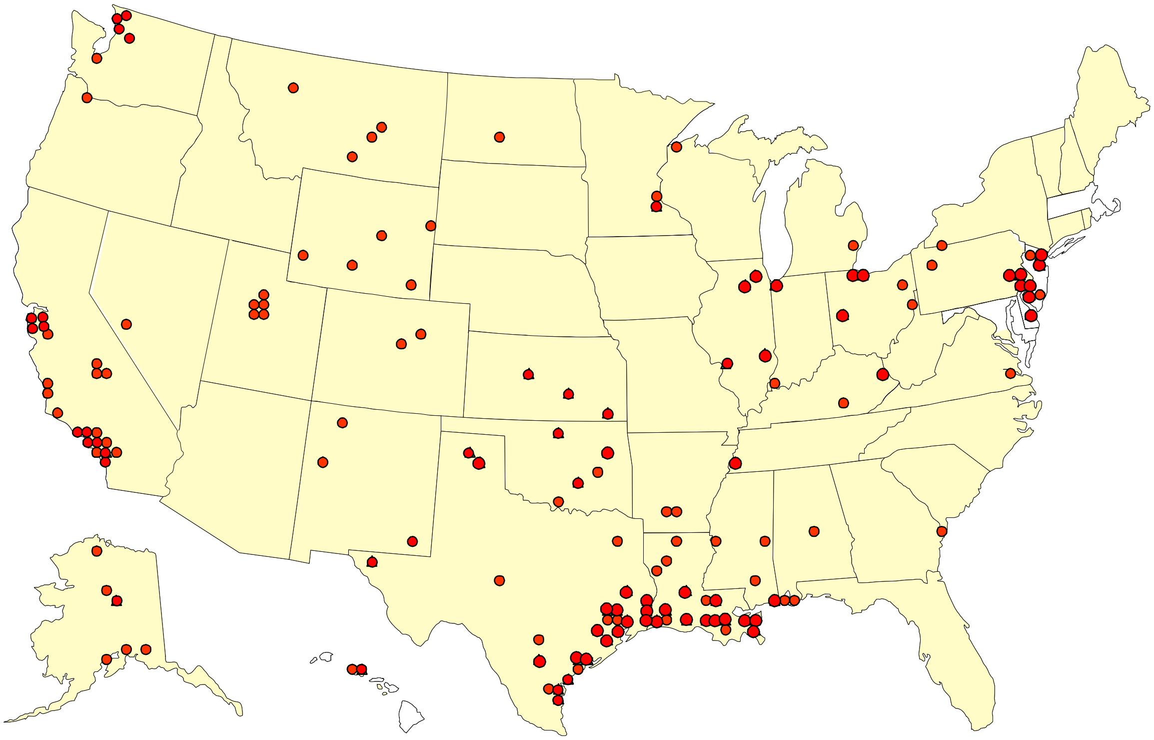


Figure 2. Geographic Distribution of Petroleum Refineries [DOE 2004]

The total crude distillation capacity of all the refineries in the U.S. is 18 million barrels per stream day (BPSD) [DOE 2005b]. The crude distillation capacity of individual refineries varies widely—from 4,000 to 843,000 BPSD [DOE 2004]. The U.S. Small Business Administration makes the following distinction between small and large refineries based on crude distillation capacity [SBA 2005]:

- small refineries – less than or equal to 125,000 BPSD
- large refineries – greater than 125,000 BPSD

Refinery size can impact operating practices and energy efficiency. Typically, small refineries are less complex than medium and large refineries and frequently contain fewer of the refining processes listed in Figure 1. In addition, some large refineries have parallel processes (i.e., two crude distillation towers or two reformers) due to refinery expansions over time. Figures 3 and 4 provide a snapshot of the refining capacity of large and small refineries for the five processes considered in this energy bandwidth analysis. Although there are more small refineries than large ones, they only account for 25% of the U.S. refining capacity.

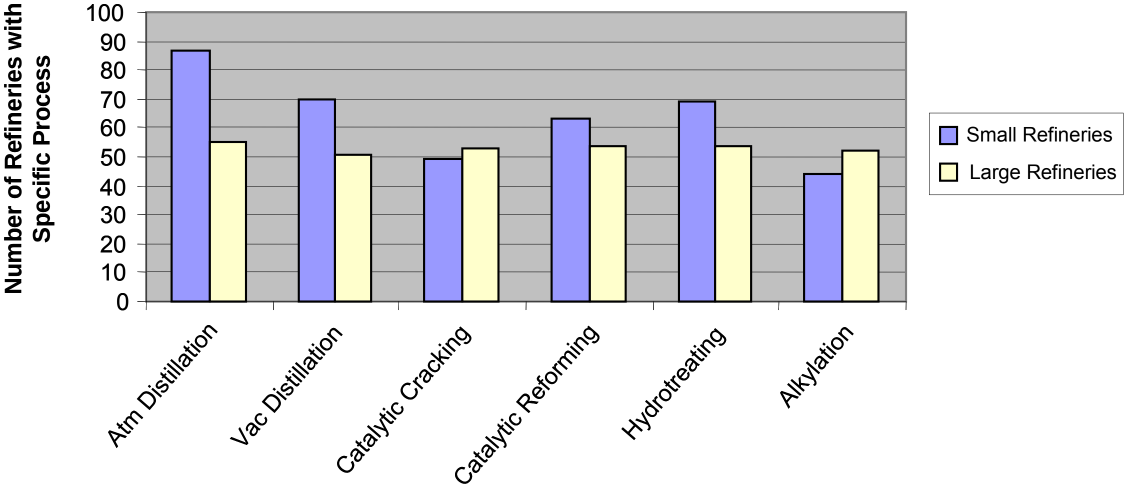


Figure 3. Industry Profile by Refining Process [DOE 2004]

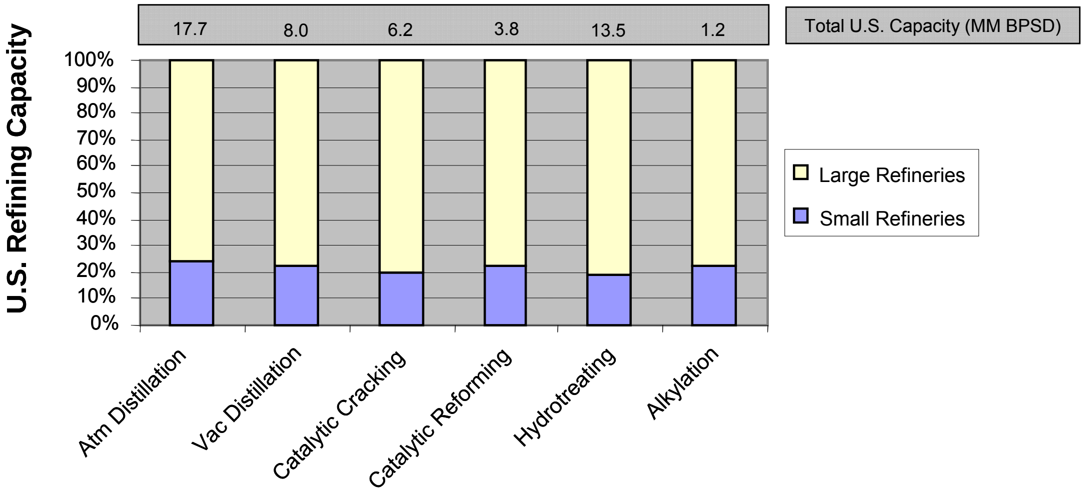


Figure 4. U.S. Refining Capacity [DOE 2004]

Following is a description of each of the five processes considered in this bandwidth analysis.

1. Crude Oil Distillation: Atmospheric and Vacuum

Crude distillation is one of the first and most critical steps of the petroleum refining process. It separates crude oil, a complex mixture of many different hydrocarbon compounds, into fractions based on the boiling points of the hydrocarbons. Characteristic boiling points of crude oil components range from 90°F to over 800°F [Humphrey 1991].

Atmospheric distillation begins with the crude desalting process, which is carried out before the crude enters the atmospheric tower. This removes chloride salts, which cause fouling and corrosion and contribute to inorganic compounds that deactivate catalysts in downstream processing units [DOE 1998]. Traditionally, crude oils were desalted if they had a salt content greater than 10 pounds per 1,000 barrel, but many companies are beginning to desalt all crude oils to minimize equipment fouling, corrosion, and catalyst deactivation and the costs associated with these problems [Gary 2001].

When the crude oil leaves the desalting process, its temperature ranges between 240°F and 330°F (115°C and 150°C). The crude then enters a series of heat exchangers known as the “preheat train” [Gary 2001]. The preheat train transfers heat from the hot atmospheric tower product and reflux streams to the crude oil, raising the crude temperature to approximately 550°F (288°C) [Gary 2001]. A direct-fired furnace heats the crude oil to 650-750°F (343-400°C) before it enters the flash zone of the atmospheric tower. All of the products that are withdrawn above the flash zone and 10-20% of the products withdrawn below the flash zone are vaporized [Gary 2001].

The atmospheric distillation tower operates at atmospheric pressure and contains 30 to 50 separation trays. Each tray corresponds to a different boiling temperature [DOE 1998]. When the crude oil vapor rises up the column, it passes through perforations in each tray and comes into contact with the condensed liquid inside. When the vapor reaches a tray in the column with a temperature equal to its boiling point, it will condense and remain on that tray. The higher (cooler) trays will contain a mix of more volatile (lighter) compounds while lower (hotter) trays will collect the less volatile (heavier) components.

At least two low-boiling point side streams from the atmospheric tower are sent to smaller stripping columns where steam is injected under the tray. The steam strips out the most volatile components from the heavier components. These volatile components are the desired products. The steam and remaining components are then fed back to the atmospheric tower [DOE 1998].

Atmospheric distillation produces a range of products, from liquid petroleum gases (LPG) to heavy crude residue. These streams are further processed into final products or blended with products from other processes downstream. A light, non-condensable fuel gas stream primarily composed of methane and ethane is also produced. It contains hydrogen sulfide and must be treated before it can be used as a fuel elsewhere in the refinery.

The heavy crude residue (or “bottoms”) is composed of hydrocarbons that have boiling points greater than 750°F [DOE 1998]. They cannot be heated to their boiling points at atmospheric pressure because many of the components decompose at that temperature. In addition, these extremely high temperatures exert a great strain on the equipment and can lead to the formation of coke deposits which must be physically removed for optimal equipment performance. Therefore, the bottoms stream is distilled under vacuum (10-40 mm Hg), which lowers the boiling points of the fractions and enables separation at lower temperatures. The products generated from vacuum distillation include light vacuum gas oil, heavy vacuum gas oil, and vacuum residue (asphalt or residual fuel oil) [Gary 2001]. Many of these products are further processed in downstream units such as hydrocrackers, visbreakers, or cokers.

For the purpose of this study, the atmospheric distillation system is defined as including the crude desalting process, crude preheat train, direct-fired furnace, atmospheric column, and smaller stripping towers. The vacuum distillation system is comprised of the fired heater and vacuum distillation column. Figure 5 shows the system boundaries for the bandwidth energy analyses.

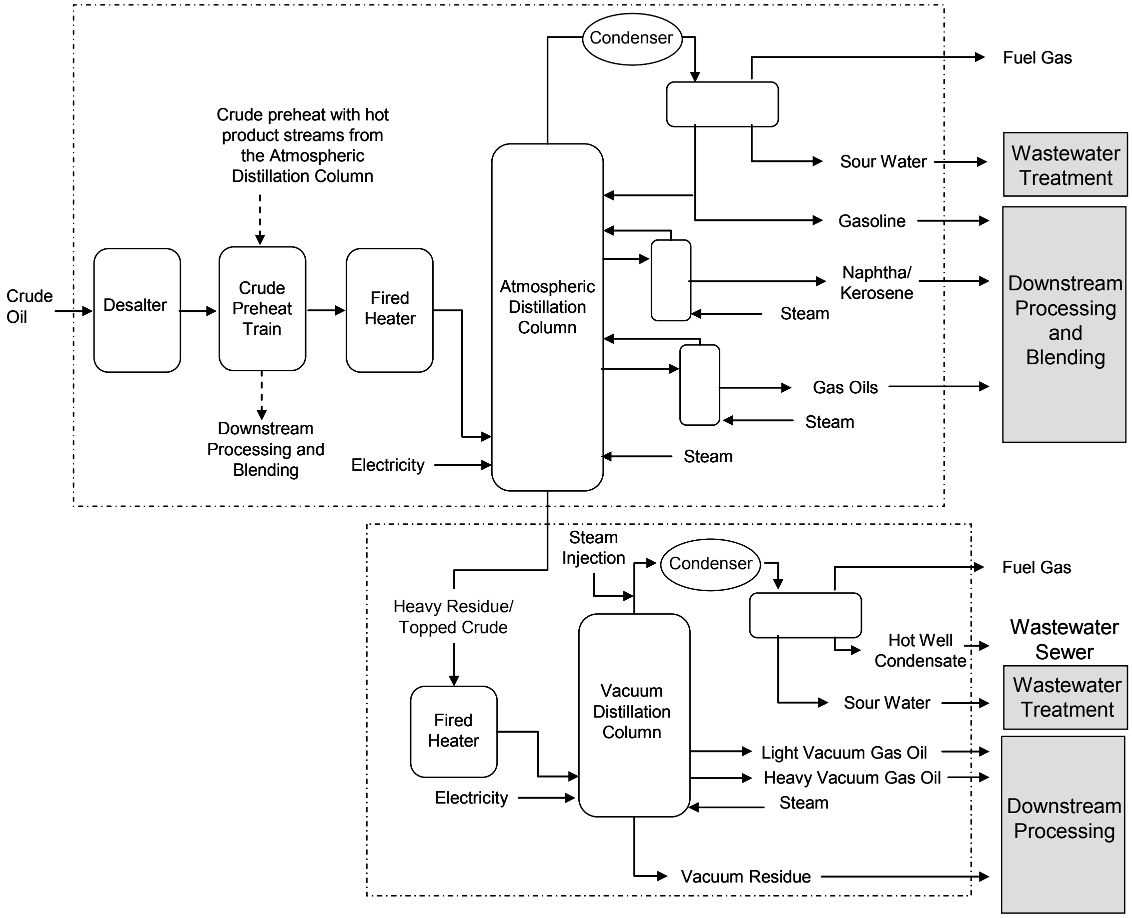


Figure 5. Atmospheric and Vacuum Crude Distillation Flow Diagrams and System Boundaries for Bandwidth Energy Analyses [DOE 1998]

2. Fluid Catalytic Cracking

Catalytic cracking is widely used in the petroleum refining industry to convert heavy oils into more valuable gasoline and lighter products. As the demand for higher octane gasoline has increased, catalytic cracking has replaced thermal cracking. Two of the most intensive and commonly used catalytic cracking processes in petroleum refining are fluid catalytic cracking and hydrocracking. “Fluid” catalytic cracking (FCC) refers to the behavior of the catalyst during this process. That is, the fine, powdery catalyst (typically zeolites, which have an average particle size of about 70 microns), takes on the properties of a fluid when it is mixed with the vaporized feed. Fluidized catalyst circulates continuously between the reaction zone and the regeneration zone. FCC is the most widely used catalytic cracking process [DOE 1998]; therefore, for the purpose of this petroleum bandwidth analysis, only the FCC process will be evaluated.

Catalytic cracking is typically performed at temperatures ranging from 900^{o}F to 1,000^{o}F and pressures of 1.5 to 3 atmospheres. Feedstocks for catalytic cracking are usually light and heavy gas oils produced from atmospheric or vacuum crude distillation, coking, and deasphalting operations [DOE 1998]. The fresh feed enters the process unit at temperatures from 500 -1,000°F. Circulating catalyst provides heat from the regeneration zone to the oil feed. Carbon (coke) is burned off the catalyst in the regenerator, raising the catalyst temperature to 1,150 - 1,350°F, before the catalyst returns to the reactor.

Most units follow a heat balance design, where the heat produced during regeneration supplies the heat consumed during the endothermic cracking reactions. From a utility perspective, some units are net energy producers given the large quantities of hot flue gas produced in the regenerator that are used to generate steam and power.

A catalytic cracker constantly adjusts itself to stay in thermal balance. The heat generated by the combustion of coke in the regenerator must balance the heat consumed in the other parts of the process, including the temperature increase of feed, recycle and steam streams, temperature increase of combustion air, heat of reaction, and other miscellaneous losses including surface radiation losses.

The gasoline-grade products formed in catalytic cracking are the result of both primary and secondary cracking reactions. Carbonium ions are formed during primary thermal cracking. Following a proton shift and carbon-carbon bond scission, these small carbonium ions propagate a chain reaction that reduces their molecular size and increases the octane rating of the original reactants.

There are many other reactions that are initiated concurrently by the zeolite catalyst and are propagated by the carbonium ions [Gary 1984]. Figure 6 summarizes the principal types of reactions that are believed to occur in catalytic cracking. A complete list of chemical reactions occurring in a typical FCC unit is not readily available. There are dozens of significant reactions occurring simultaneously in this process unit.

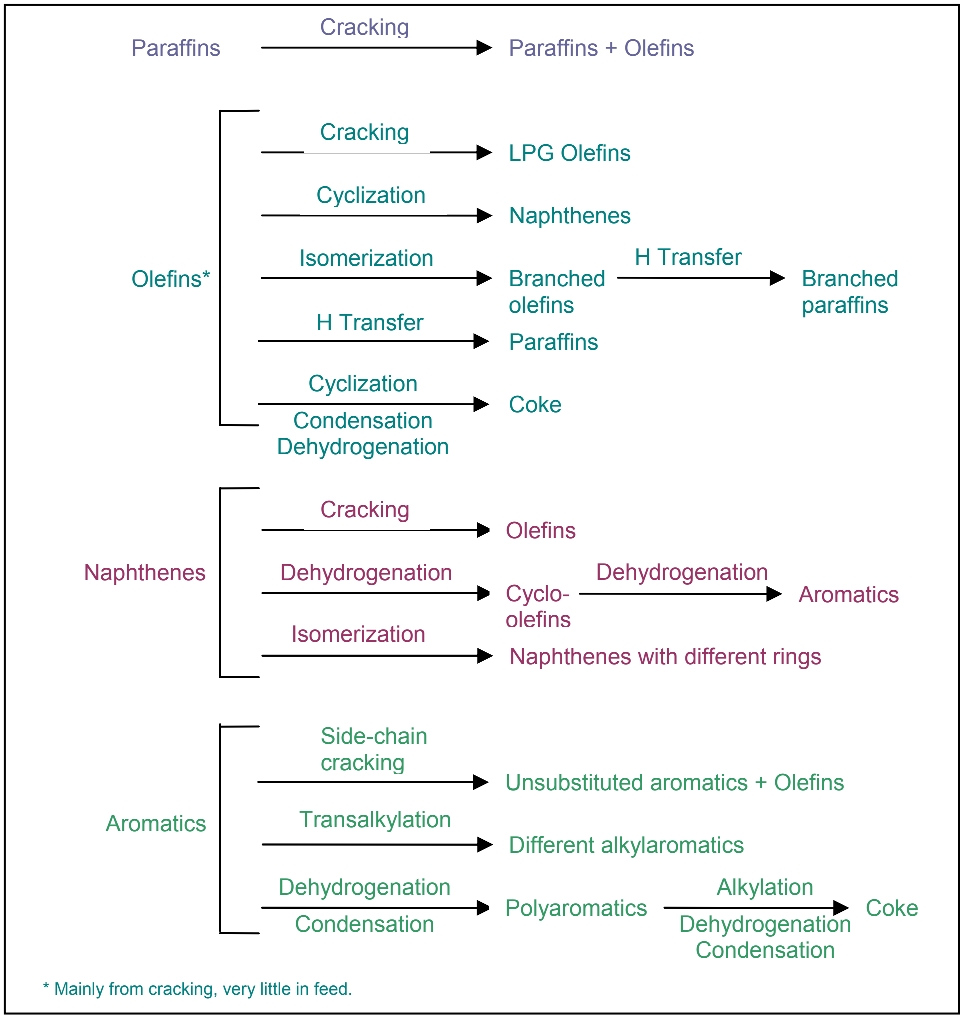


Figure 6. Principal Reactions in Fluid Catalytic Cracking [Davison 1993]

3. Catalytic Hydrotreating

Catalytic hydrotreating, also referred to as “hydroprocessing” or “hydrodesulfurization,” commonly appears in multiple locations in a refinery. In the hydrotreating process, sulfur and nitrogen are removed and the heavy olefinic feed is upgraded by saturating it with hydrogen to produce paraffins. Hydrotreating catalytically stabilizes petroleum products. In addition, it removes objectionable elements such as sulfur, nitrogen, oxygen, halides, and trace metals from products and feedstocks through a reaction with hydrogen [Gary 1984]. Most hydrotreating processes have essentially the same process flow. Figure 7 illustrates a typical hydrotreating unit.

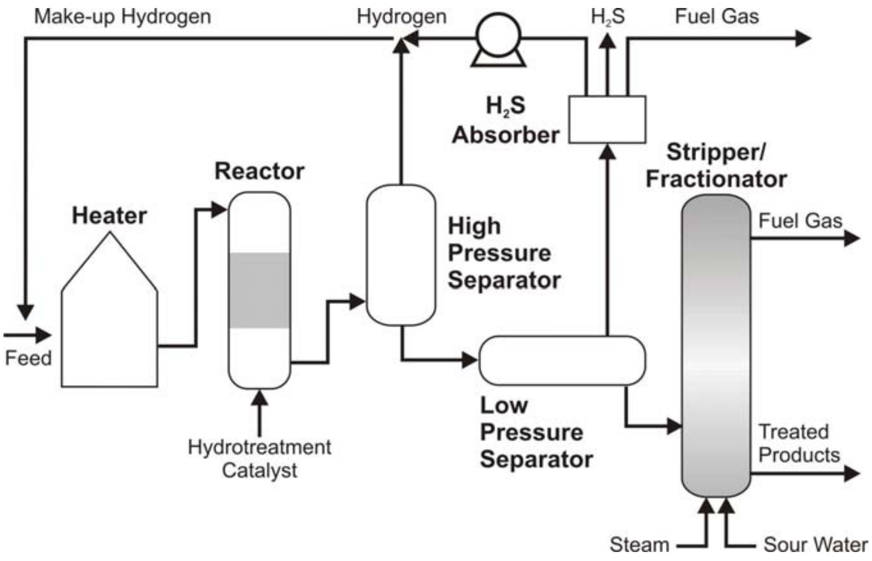


Figure 7. Catalytic Hydrotreating Flow Diagram [DOE 1998]

Hydrotreating units are usually placed upstream of units where catalyst deactivation may occur from feed impurities, or to lower impurities in finished products, like jet fuel or diesel. A large refinery may have five or more hydrotreaters. The following three types of hydrotreaters are typically found in all refineries:

- The **naphtha hydrotreater**, which pretreats feed to the reformer
- The **kerosene hydrotreater**, sometimes called "middle distillate hydrotreater," which treats middle distillates from the atmospheric crude tower
- The **gas oil hydrotreater**, sometimes called "diesel hydrotreater," which treats gas oil from the atmospheric crude tower or pretreats vacuum gas oil entering a cracking unit

The oil feed to the hydrotreater is mixed with hydrogen-rich gas before entering a fixed-bed reactor. In the presence of a metal-oxide catalyst, hydrogen reacts with the oil feed to produce hydrogen sulfide, ammonia, saturated hydrocarbons, and other free metals. The metals remain on the surface of the catalyst and other products leave the reactor with the oil-hydrogen stream. Oil is separated from the hydrogen-rich gas stream, and any remaining light ends (C_4 and lighter) are removed in the stripper. The gas stream is treated to remove hydrogen sulfide and then it is recycled to the reactor [Gary 1984].

Most hydrotreating reactions are carried out below 800°F to minimize cracking. Product streams vary considerably depending on feed, catalyst, and operating conditions. The predominant reaction type is hydrodesulfurization, although many reactions take place in hydrotreating including denitrogenation, deoxidation, dehalogenation, hydrogenation, and hydrocracking. Almost all hydrotreating reactions are exothermic and, depending on the specific conditions, a temperature rise through the reactor of 5 to 20°F is usually observed [Gary 1984]. Some typical hydrotreating reactions are shown in Figure 8.

Desulfurization

Dibenzothiophene + $2H_2$ → Biphenyl + H_2S

Hydrogenation, Olefin Saturation

1-Heptene + H_2 → n-Heptane

Hydrogenation, Aromatic Saturation

Naphthalene + $2H_2$ → Tetralin

Figure 8. Typical Hydrotreating Reactions [DOE 1998]

On average, the hydrotreating process requires between 200 and 800 cubic feet of hydrogen per barrel of feed [Gary 1984]. The hydrogen required for hydrotreating is usually obtained from catalytic reforming operations. This process is described below.

4. Catalytic Reforming

The catalytic reforming process converts naphthas and heavy straight-run gasoline into high-octane gasoline blending components. The feed and product streams to and from the reformer are composed of four major hydrocarbon groups: paraffins, olefins, naphthenes, and aromatics. Table 1 depicts the change in volume of these hydrocarbon groups as they pass through this unit. During this process, the octane value of the product stream increases with the formation of aromatics [Gary 1984].

Table 1. Typical Reformer Feed and Product Makeup

Chemical Family	Feed (Volume %)	Product (Volume %)
Paraffins	45-55	30-50
Olefins	0-2	0
Naphthenes	30-40	5-10
Aromatics	5-10	45-60

Source: Gary 1984

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. Catalytic reforming primarily increases the octane of motor gasoline rather than increasing its yield.

The four major reaction types that take place during reforming include dehydrogenation, dehydrocyclization, isomerization, and hydrocracking. The four reaction types are presented in more detail in Figure 9 with specific reactions that are typical of each type.

1) dehydrogenation of naphthenes to aromatics

Typical reaction a): (highly endothermic, high reaction rate)
Dehydrogenation of alkylcyclohexane to aromatic

Methylcyclohexane → Toluene + 3 H_2

Typical reaction b):
Dehydroisomerization of alkylcyclopentane to aromatic

Methylcyclopentane → Cyclohexane → Benzene + 3 H2

2) dehydrocyclization of paraffins to aromatics

Typical reaction:

n-Heptane → Toluene + 4 H_2

3) isomerization (fairly rapid reactions with small heat effects)

Typical reaction a):
Isomerization of n-paraffin to isoparaffin

n-Hexane → Isohexane

Typical reaction b):
Isomerization of paraffin to naphthene

Methylcyclopentane → Cyclohexane

4) hydrocracking (exothermic, relatively slow)

Typical reaction:

n-Decane → Isohexane +n-Butane

Figure 9. Catalytic Reforming Reactions [Gary 1984]

For the purposes of this bandwidth report, it is assumed that the four major catalytic reforming reactions presented in Figure 9 take place in the following volume ratio*:

Reaction 1) = 40 %
Reaction 2) = 17 %
Reaction 3) = 34 %
Reaction 4) = 9 %

* Based on conversations with industry representatives and Gary 1984 feed/product makeup analysis in Table 1.

This report does not account for additional reactions that form undesirable products, such as the dealkylation of side chains or the cracking of paraffins and naphthenes, which form butane and lighter paraffins.

Catalytic reforming reactions are promoted by the presence of a metal catalyst, such as platinum on alumina, or bimetallic catalysts, such as platinum-rhenium on alumina. The reformer is typically designed as a series of reactors, as shown in Figure 10, to accommodate various reaction rates and allow for interstage heating. Interstage heaters maintain the hydrocarbon feed stream at a temperature of approximately 950°F, which is required for the primarily endothermic reactions. Catalytic reforming can be continuous (e.g., cyclic) or semi-regenerative. In continuous processes, the catalysts can be regenerated one reactor at a time without disrupting operation [DOE 1998].

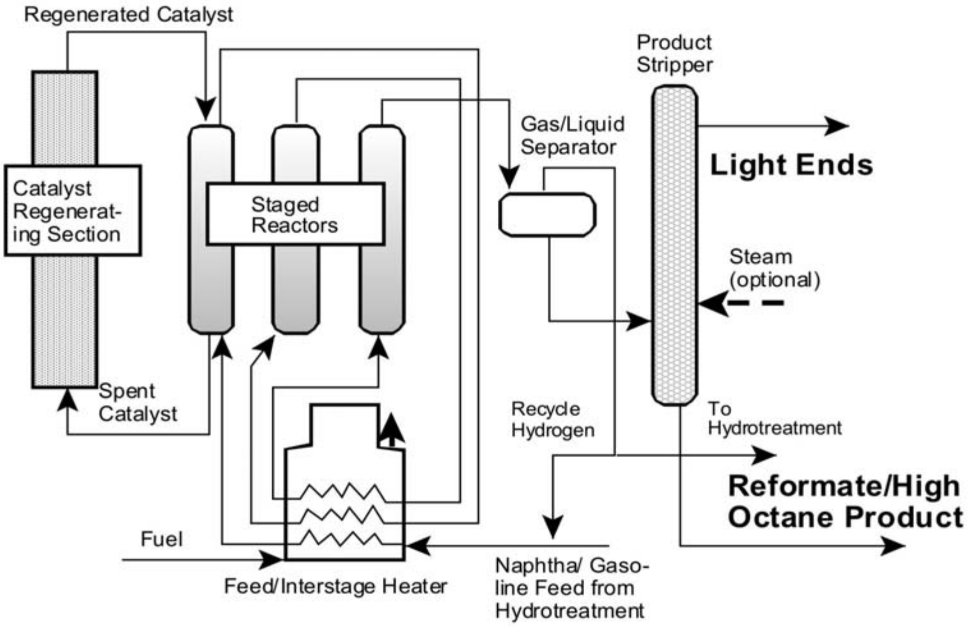


Figure 10. Catalytic Reforming Flow Diagram (Continuous Operation) [DOE 1998]

5. Alkylation

Alkylation involves linking two or more hydrocarbon molecules to form a larger molecule. In a standard oil refining process, alkenes (primarily butylenes) are reacted with isobutane to form branched paraffins that are used as blending components in fuels to boost octane levels without increasing the fuel volatility. There are two alkylation processes: sulfuric acid-based (H_2SO_4) and hydrofluoric acid-based (HF). Both are low-temperature, low-pressure, liquid-phase catalyst reactions, but the process configurations are quite different (see Figures 11 and 12). Several companies are also developing advanced HF catalysts to reduce the environmental and health risks of HF alkylation [Nowak 2003, CP 2004].

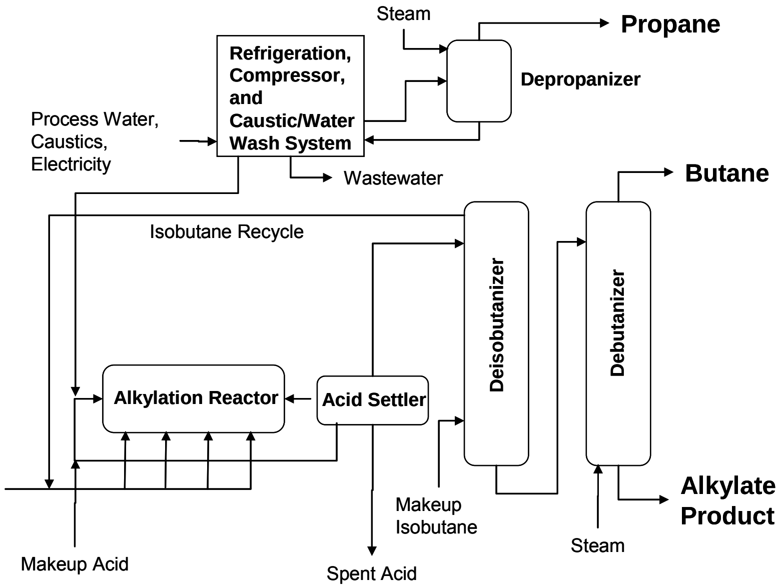


Figure 11. Sulfuric Acid-Based Alkylation Flow Diagram [DOE 1998]

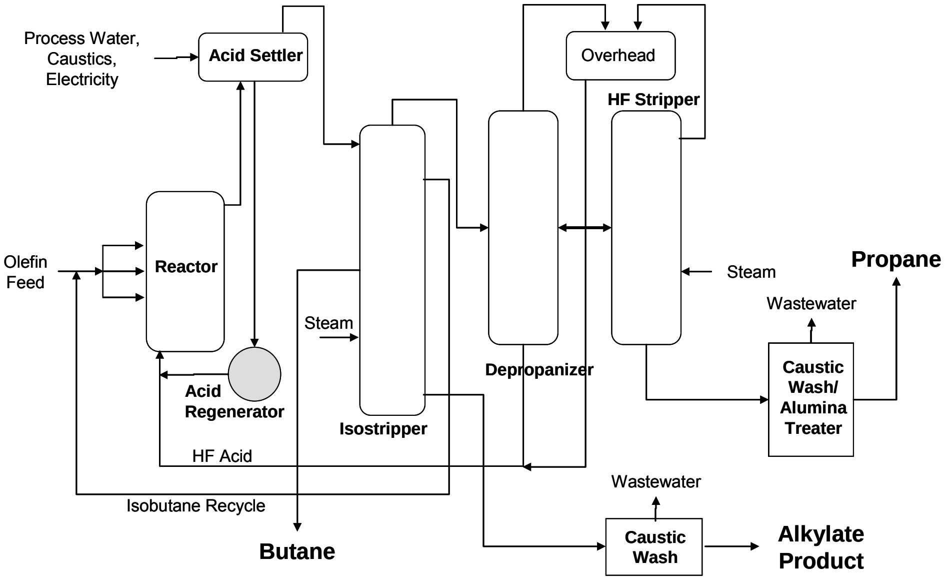


Figure 12. Hydrofluoric Acid-Based Alkylation Flow Diagram [DOE 1998]

The primary alkylation reaction is:

$$\underset{\text{Butylene}}{C_4H_8\,(l)} + \underset{\text{Isobutane}}{C_4H_{10}\,(l)} \xrightarrow{\text{acid catalyst}} \underset{\text{2,2,4-trimethylpentane}}{C_8H_{18}\,(l)} + \text{Heat}$$

In the H_2SO_4 process, the reactor must be kept at a temperature of 40-50°F (4-10°C) to minimize unwanted side reactions such as polymerization, hydrogen transfer, disproportionation, cracking, and esterification because these reactions can lower the alkylate octane or create processing issues [Meyers 1997, Stratco 2003, Ackerman 2002]. Heat is removed either through autorefrigeration or indirect effluent refrigeration. Autorefrigeration uses the evaporation of isobutane-rich vapors from the reaction mass to remove the heat generated by alkylation. The vapors are removed from the top of the reactor and sent to the refrigeration compressor to be compressed and cooled back to a liquid at the feed temperature [Meyers 1997]. In the indirect effluent refrigeration process, the alkylation is run at higher pressures to prevent vaporization of light hydrocarbons in the reactor and settler. Hydrocarbons from the settler are flashed across a control valve into heat transfer tubes in the reactor to provide cooling. Of the two systems, autorefrigeration is more energy efficient.

The HF process is run at higher temperatures, 70-100°F (20-30°C), in a reactor-heat exchanger [ANL 1981, Meyers 1997]. Cooling water is run through the heat exchanger tubes to remove the heat of reaction.

Energy Bandwidth for Five Principal Petroleum Refining Processes

The theoretical minimum, practical minimum, and current average energy requirements for the five refining processes evaluated in this report were derived from a variety of sources. TME calculations vary slightly for each of the five refinery processes as these values include thermodynamic analyses of process feed and effluent streams, thermodynamic analyses of primary chemical reactions, and published enthalpy and energy balance values. The CAE values, which represent actual plant data, were obtained from the Energy and Environmental Profile of the U.S. Petroleum Refining Industry [DOE 1998]. The PME values were estimated by considering assorted energy savings measures, primarily best practices and state-of-the-art technologies, and applying these savings to the CAE requirement.

Definition Recap

TME: The least amount of energy that a process would require under ideal conditions.

PME: The minimum energy required to carry out a process using best practices and state-of-the-art technologies under real-world conditions (including limiting factors such as heat transfer, non-ideal behavior of the reactants, byproduct formation, equipment fouling, etc.).

CAE: Energy consumed under actual plant conditions.

CAE – PME = Energy Bandwidth

The petroleum refining energy bandwidth is the amount of energy that may be recovered through the use of best available practices and state-of-the-art technologies. A small fraction of the PME energy savings technologies are considered to be in the research and development stage. Table 2 provides the TME, PME, and CAE values for each of the five principal petroleum refining processes as well as the energy bandwidth for each. To obtain the value for total energy requirement (Btu/yr), the U.S. total process unit capacity (bbl/yr) was multiplied by the Btu/bbl energy requirement. Note that the positive energy requirements in the table signify that energy is consumed by the processes (endothermic) while negative energy requirements represent processes that generate energy (exothermic). Although the alkylation reaction is exothermic, in practice, the process is an energy consumer. Other details regarding this table, such as data sources, calculations, and assumptions, are provided in Appendix A.

The largest potential bandwidth savings (difference between current average energy use and practical minimum energy as a percentage of the current average energy) is found to occur with distillation of the incoming crude (atmospheric, up to 54% and vacuum distillation, up to 39%). This is not surprising, given the typically low efficiencies of current distillation processes. Alkylation processes, both of which are acid-based, constitute the next largest bandwidth. Remaining processes exhibit significant inefficiencies as well. According to experts working in the field of petroleum refining and energy management, the plant-wide refinery energy savings potential is usually found to be around 30%. It should be noted that the bandwidth savings reported represent the maximum savings and in practice, the bandwidth savings will likely be less than the reported value due to (potential) overlap of the energy saving measures used in the bandwidth calculations.

Table 2. The TME, PME, and CAE and Energy Bandwidth Values for the Five Principal Petroleum Refining Processes

Process	TME	PME[a]	CAE	Energy Bandwidth (CAE-PME)	Potential Energy Bandwidth Savings (%)[d]	Total Annual CAE by Process (10^{12} Btu/yr)	Potential Energy Bandwidth Savings (10^{12} Btu/yr)
	10^3 Btu/bbl feed[b,c]						
1. Crude Distillation:							
Atmospheric	22	50	109	59	54%	658	356
Vacuum	46	54	89	35	39%	242	95
2. Fluid Catalytic Cracking	40	132	183	51	28%	377	105
3. Catalytic Hydrotreating	30	55	81	26	32%	382	123[e]
4. Catalytic Reforming	79	203	264	61	23%	339	78
5. Alkylation:							
H_2SO_4[f]	-58	156	250	94	38%	102[g]	38
HF	-58	152	245	93	38%		
					Total	2101[h]	

[a] This represents the minimum PME; in practice, the PME value may be greater due to overlap of the energy saving measures identified for each unit operation.

[b] A positive energy represents energy consumed by the process (endothermic). A negative energy represents energy produced by the process (exothermic).

[c] Energy values exclude losses incurred during the generation and transmission of electricity.

[d] This represents the maximum bandwidth savings; in practice, the savings may be less due to overlap of the energy saving measures identified for each unit operation.

[e] Energy value is based on the U.S. hydrotreating/desulfurization capacity.

[f] Energy values are based on the autorefrigeration-based sulfuric acid process.

[g] Energy value is based on the average CAE for the sulfuric and hydrofluoric acid processes.

[h] Total Annual CAE value is off by one due to rounding of the individual values.

Sources: DOE 2005b; See Appendix A for TME, CAE, PME sources.

The energy requirement values for each process, as listed in Table 2, are shown graphically in Figures 13 and 14. The energy savings opportunity for each process is represented by the yellow band at the top of the bar. This is the average amount of energy currently used minus the practical minimum energy required.

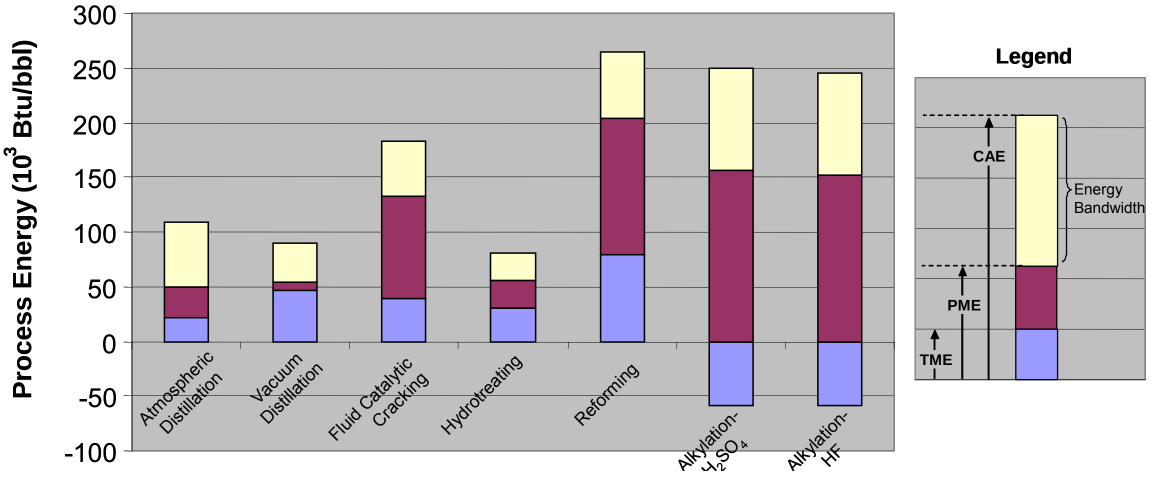


Figure 13. Petroleum Refining Industry Energy Bandwidth, Per Barrel Feed Processed Basis

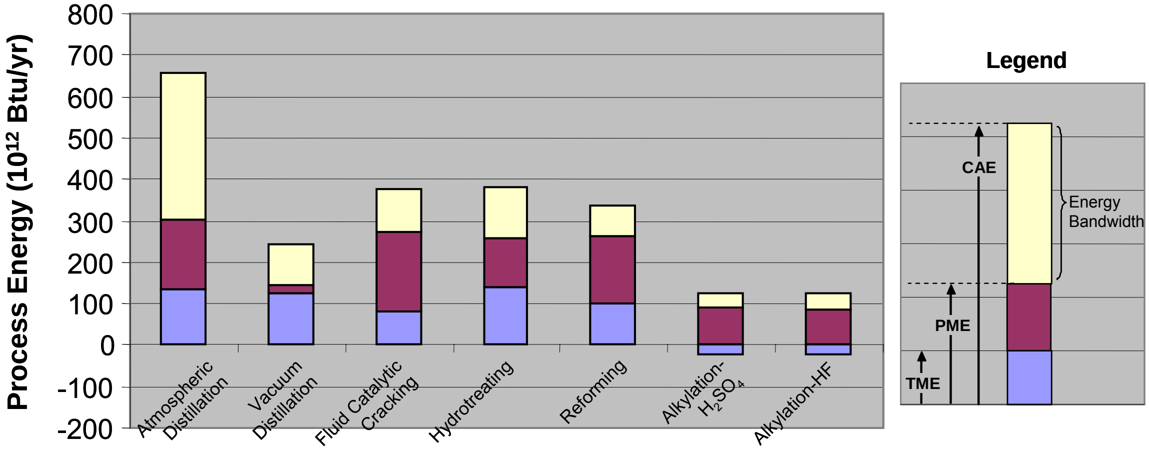


Figure 14. Petroleum Refining Industry Energy Bandwidth, Production per Year Basis

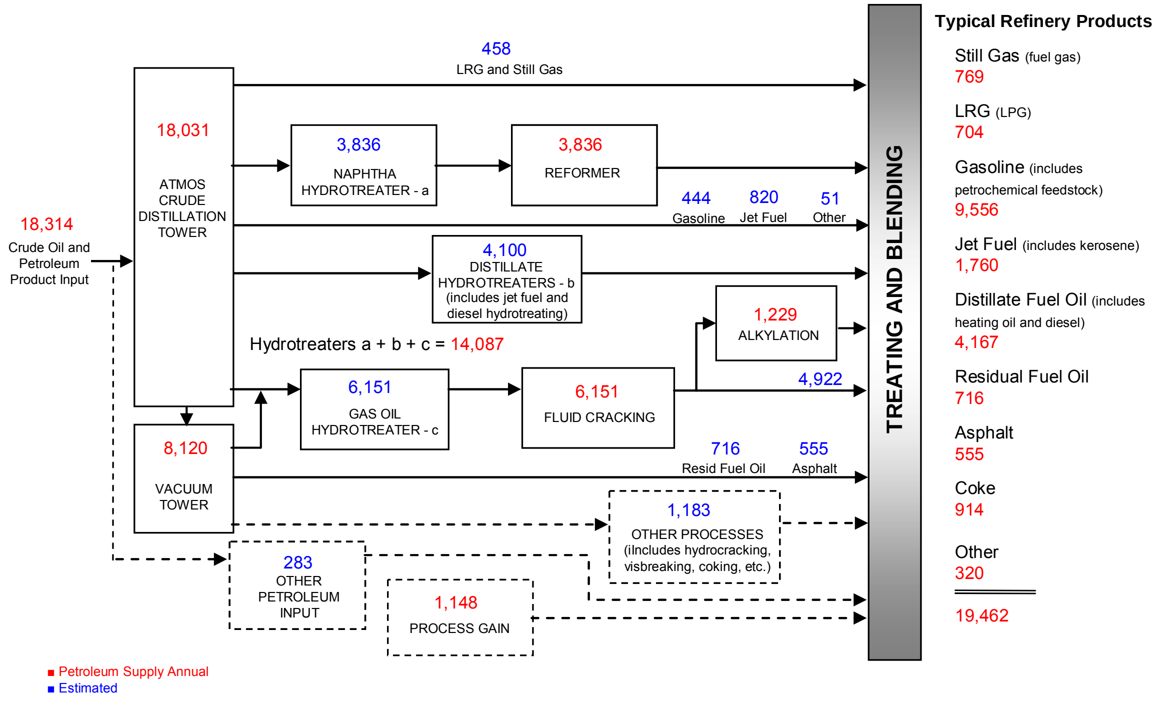
All five processes studied exhibit large enough bandwidths to warrant investigation for potential energy efficiency improvements. The economic feasibility of realizing these savings has not yet been evaluated. In many cases, the cost of upgrading a technology does not have sufficient energy saving payback.

From the perspective of refinery size, both large and small refineries operate distillation columns as a significant portion of their capacity, and opportunities to save energy in this area cut across all domestic refineries. Small refineries are about as energy efficient as large ones since the most inefficient refineries were shut down during the 1980s and early 1990s when the rules regarding crude pricing changed.

Petroleum Refining Product Energy Requirement

The energy used by petroleum refining processes can be further evaluated by considering the distribution of energy to produce various product streams. The first step is to compare the energy intensity of typical product streams. The total U.S. refinery input of crude and petroleum products can be compared to the total U.S. refinery product output. Total U.S. refinery incoming crude volumes, product volumes, and process unit capacities are available in the *Petroleum Supply Annual (PSA) 2004* [DOE 2005b]. For this analysis, flow volumes to and from the various process units were obtained from the PSA tables or they were estimated based on consultation with an industry expert.

Figure 15 shows a simplified refinery process flow diagram which includes input, output, and unit capacity flow volumes for those process units studied in this report. The values in Figure 15 represent total U.S. refinery flow in terms of 1,000 barrels per stream day (BPSD). Estimated values were derived with the help of an industry expert assuming that typical conventional crude oil is processed as shown in the simplified flow layout. A detailed breakdown of the flow volumes is provided in Appendix A.



VOLUME BALANCE:

18,314 input + 1,148 process gain = 19,462 produced
19,462 produced = 458 straight run still gas/LRG + 3,836 reformer +1,264 straight run gasoline and jet fuel + 51 other products + 4,100 dist HTs + 1,229 alkylation + 4,922 FCC + 1,271 straight run residual fuel oil and asphalt + 1,183 other processes + 1,148 process gain

* Barrel per stream day (BPSD) assumes 335 day per year

Figure 15. Simplified Refinery Flow Diagram Showing the Five Process Units Evaluated in this Report (Values Represent 2004 U.S. Total Flow Volumes x 10^3 BPSD*)

Table 3 provides the total annual energy requirements (Btu per year) and individual energy requirements of nine refinery products for each process unit being studied. The individual product energy requirement for each process was calculated by multiplying the annual production volume by the product output volume percent and the current average process unit energy requirement from Table 2.

Product stream heat capacities and process unit volume fractions are used to estimate the distribution of process unit CAE for the crude and vacuum units. For the remaining units where there are multiple reactions occurring simultaneously, it is assumed that the energy requirement is distributed evenly based on process unit volume percent.

Table 3. Total Annual Refinery Product Energy Requirement (T Btu/yr)

Process Unit	Product Energy Requirement	Still Gas	LRG	Gasoline	Jet Fuel/ Kero	Dist Fuel Oil	Resid Fuel Oil	Asphalt	Coke	Other
Crude Distillation:										
Atmospheric	658	1	1	295	54	180	38	30	49	12
Vacuum	242	0	0	61	0	33	39	45	64	0
Reformer	339	13	5	322	0	0	0	0	0	0
Hydrotreating	382	14	11	230	22	105	0	0	0	0
Alkylation	102	0	0	102	0	0	0	0	0	0
FCC	377	24	20	296	0	37	0	0	0	0
TOTAL	**2,101**	51	37	1,305	76	355	77	75	113	12
% of Total	**100%**	2.4 %	1.7%	62.1%	3.6%	16.9%	3.7%	3.6%	5.4%	0.6%

(Some values are off by one when columns and rows are summed due to rounding error)

The total annual product energy requirement, that is, 2,101 trillion Btu per year, is equal to the total annual CAE listed in Table 2. This value represents 68% of the 3,086 trillion Btu per year (or 3 quads) of process energy consumed by U.S. petroleum refineries in 2002 [DOE 2005a]. The flow volumes for “Other Processes,” “Process Gain,” and “Other Petroleum Input” shown in Figure 15 are not included in Table 3. These volumes contribute significantly to the remaining 32% of process energy consumed by the U.S. refining industry.

Gasoline requires the greatest amount of energy to produce. While gasoline makes up 49% by volume of refinery product output, its production consumes 62% of the refinery energy requirement. Distillate fuel oil is the next most energy-intensive product stream, consuming 17% of refinery energy requirement. The remaining 21% is distributed fairly evenly between the other product streams.

Appendix A

Data Sources, Assumptions, and Detailed Calculations

1. Crude Oil Distillation (Atmospheric and Vacuum) Energy Requirement Estimates

Theoretical Minimum Energy

Distillation of crude oil takes advantage of differences in boiling points to separate the crude. The overall heat balance is described by:

Theoretical Minimum Energy = Heat In – Heat Out

It is assumed for the TME calculation that:

- Crude oil behaves as an "ideal solution"; that is, the properties of the component in solution are equal to the properties of the pure component
- The heavier fractions must be distilled under vacuum (10 mm Hg) to prevent the heavy fractions from degrading
- The crude oil fractions exit the mass and energy balance at their respective boiling points
    - Heat Out = 0

As explained in the process description, the crude oil is heated so that the lighter fractions evaporate, allowing the vapor to rise up through the column until it contacts a tray that is at the vapor component's boiling point. The component condenses and exits the column as a liquid stream. Therefore, the energy input is the amount of energy required to raise the temperature of each component from 77°F (25°C) to its boiling point. The energy required to evaporate the crude oil component is cancelled out by the energy released when the component vapor condenses. As an *ideal solution*, the boiling point of the pure substance is used and any effects of intramolecular interactions are ignored. Also, due to a lack of thermodynamic data, the TME will be calculated as the heat or reaction, ΔH_{rxn}, rather than the change in Gibbs free energy, ΔG_{rxn} (heat of reaction and Gibbs free energy are related as follows: $\Delta G = \Delta H - T \cdot \Delta S$, where T is temperature in Kelvin and ΔS is the change in entropy).

The energy consumed by atmospheric distillation includes energy that goes into heating the heavy fractions that must be distilled under vacuum. However, for the TME calculation, the energy consumption of atmospheric distillation is limited to the separation energy for the crude fractions that can be distilled at atmospheric pressure. In addition, the calculation excludes the energy content of the fuel gas stream generated via atmospheric distillation and excludes the heat recovery that takes place via the crude preheat train.

The vacuum distillation process is also simplified to calculate the TME. Similar to atmospheric distillation, it is assumed that all energy consumed by the vacuum distilled fractions as they are heated from ambient temperature to their boiling points is included in the vacuum distillation TME. In reality, the heavy components are heated from ambient conditions to a higher temperature as they pass through the atmospheric distillation tower. In addition, it is assumed that the residue stream produced is processed further in coking units, rather than used to generate heat for the vacuum distillation tower. Table A1 shows the physical and chemical properties of the crude oil fractions.

Table A1. Typical Cut Points, Crude Oil Fraction Compositions, Chemical/Physical/Thermodynamic Properties, and Theoretical Separation Heat Input

Crude Oil Fraction	Chemical Composition[a]	Product	Volume %	Specific Gravity (lb/gal)	Boiling Point of Pure Substance[b] (°F)	Cp[b] (Btu/lb·°F)	Theoretical Separation Heat Input (Btu/bbl$_{crude}$)
Atmospheric Distillation							
C2	C2	Fuel Gas	0.1	3.119	-128	0.549	0
C3	C3		0.3	4.245	-54	0.549	
iC4	iC4		0.2	4.704	-12	0.549	
nC4	nC4		0.6	4.871	32	0.533	
C5-180°F (82°C)	~C5	Gasoline (Light Straight Run)	4.3	5.652	97	0.541	110
180-350°F (82-177°C)	~C6-C10	Naphtha (Heavy Straight Run)	11.7	6.449	259	0.490	2,826
350-400°F (177-204°C)	~C10-C12	Kerosene	4.3	6.826	383	0.525	1,981
400-650°F (204-343°C)	~C12-C20	Light Gas Oil	24.7	7.195	513	0.527	17,150
Atmospheric Distillation TOTAL	**na**	**na**	**na**	**na**	**na**	**na**	**22,067**
Vacuum Distillation							
650-850°F (343-455°C)	~C20-C30	Light Vacuum Gas Oil	20.5	7.840	446[c]	0.501	12,479
850-1050°F (455-565°C)	~C30-C40	Heavy Vacuum Gas Oil	15.6	8.090	608[c]	0.501	14,101
1050°F+ (565°C+)	>C40	Residual Oil	18.0	8.298	707[c]	0.501	19,800
Vacuum Distillation TOTAL	**na**	**na**	**na**	**na**	**na**	**na**	**46,380**

[a] "C" refers to the number of carbon atoms in the hydrocarbon.
[b] These values represent a median value for the range of compounds at atmospheric pressure.
[c] Boiling points under vacuum (10 mm Hg) estimated using a nomograph.
na not applicable
Sources: Perry 1984, DOC 2003, CRC 1970, EPA 2005, SAS 2002, DOC 1995.

The energy required to raise the temperature of each fraction to its boiling point (bp) is calculated by:

$$\text{Heat Input}_{\text{crude fraction}} = \text{mass}_{\text{crude fraction}} * C_p * \Delta T = \text{mass}_{\text{crude fraction}} * C_p * (T_{bp} - 77°F)$$

$$\text{TME}_{\text{atmospheric}} = \Sigma \text{Heat Input}_{\text{atmospheric crude fraction}}$$
$$= 22{,}067 \text{ Btu/bbl crude}$$

$TME_{vacuum} = \Sigma Heat\ Input_{vaccum\ crude\ fraction}$
$= 46,380$ Btu/bbl crude

The TME for atmospheric distillation is 22 x 10^3 Btu per bbl crude. The heavy residue that is distilled in the vacuum distillation tower requires more energy to separate it. This residue has a TME of 46 x 10^3 Btu per barrel of crude oil.

Current Average Energy

Current process energy values from the *Energy and Environmental Profile of the U.S. Petroleum Refining Industry* were used to estimate CAE. Electricity losses incurred during the generation and transmission of electricity are excluded [DOE 1998].

Table A2. Estimated Energy Use in Atmospheric and Vacuum Crude Distillation[a]

Energy Source	Atmospheric Distillation Specific Energy (10^3 Btu/bbl feed)	Vacuum Distillation Specific Energy (10^3 Btu/bbl feed)
Fuel[b]	106.8	87.9
Electricity[c]	2.3	1.2
TOTAL ENERGY INPUT	**109.1**	**89.1**

[a] Includes energy used for desalting.
[b] Typical fuel mix at refineries includes natural gas, liquefied petroleum gas, refinery (fuel) gas, coke, crude oil, distillate and residual fuel oil, and purchased steam.
[c] Excludes losses incurred during the generation and transmission of electricity.
na not applicable
Source: DOE 1998

Practical Minimum Energy

The practical minimum energy can be calculated by considering improved operating practices and capital equipment. Below is a list of energy saving opportunities that may be realized to make the atmospheric crude distillation more energy efficient:

- Fouling mitigation in the crude preheat train and fired heater
- Improved fired heater efficiency
- Enhanced heat integration between the atmospheric and vacuum towers
- Improved tower and tray design for improved separation efficiency (vapor-liquid contact)
- Enhanced cooling (e.g., use of waste heat absorption chillers or compression and expansion of overhead vapors) applied to overhead condenser cooling water to lower the reflux ratio and reboiler duty

Implementation of these measures could reduce fuel consumption by the following percentages [ANL 1999, Gadalla et al. 2003]:

- Control of fouling in the crude preheat train and fired heater – 15%[a]
- Improved heat integration between the atmospheric and vacuum towers – 15%
- Improved tray design and heat integration between trays, and optimization of the number of trays and operating conditions for improved vapor-liquid contact and higher throughput – 15%[b]
- Enhanced cooling to lower overhead condenser cooling water from 75°F to 50°F – 10%

[a] 10% of this 30% estimate is considered to be technology in the research and development stage

[b] 5% of this 15% estimate is considered to be technology in the research and development stage

The potential fuel savings are estimated to be up to 55%; in practice, there may be overlap between the improvement areas resulting in a lower savings. Based on the CAE and the largest potential fuel savings, the practical minimum energy would be 50,400 Btu/bbl.

Vacuum distillation operations can also benefit from similar process and equipment improvements. Potential fuel savings are shown below [ANL 1999]:

- Control of fouling in the fired heater – 12%[a]
- Improved heat integration between the atmospheric and vacuum towers – 15%
- Improved tray design and heat integration between trays, and optimization of the number of trays and operating conditions for improved vapor-liquid contact and higher throughput – 6%[b]
- Enhanced cooling to lower overhead condenser cooling water from 75°F to 50°F – 7%

[a] 5% of this 15% estimate is considered to be technology in the research and development stage

[b] 2% of this 6% estimate is considered to be technology in the research and development stage

Vacuum distillation fuel savings are approximately 40%, resulting in a PME of 54,000 Btu/bbl. Similar to atmospheric distillation, the 40% reduction represents the maximum achievable and overlap between the improvement areas may result in a higher PME for a specific vacuum distillation unit.

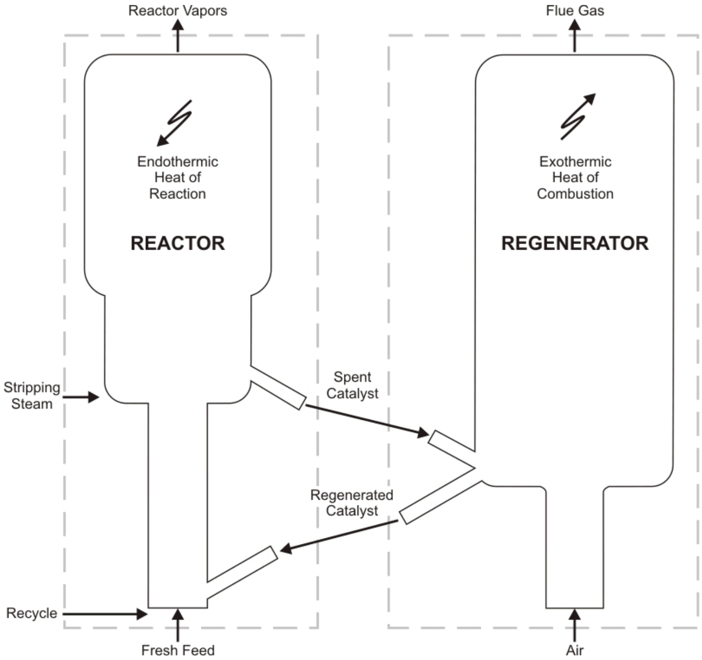
2. Fluid Catalytic Cracking Energy Requirement Estimates

Theoretical Minimum Energy

TME required by the FCC process is defined as “the energy required to complete the catalytic cracking reactions, assuming ideal conditions and 100% thermal efficiency.” As shown in Figure 6 (p. 9), there are multiple reaction types occurring simultaneously in this process unit. Given the complexity of considering heat of reaction for so many reactions, an energy balance is used to estimate theoretical minimum energy use. Performing an energy balance provides an accurate method to account for the energy generated within the process by the combustion of coke.

Catalyst manufacturer, Grace Davison, provides typical FCC operating data for the fictitious “Walden Oil Company” in their *Guide to Fluid Catalytic Cracking* reference manual. For the Walden Oil example, where the fresh feed enters the unit at 36,930 BPD and 28.5 API, energy produced by the combustion of coke is equal to 318 million Btu/hr or 206 x 10^3 Btu/bbl [Davison 1993].

A heat balance around the individual reactor and regenerator vessels for the Walden Oil example, as shown in Figure A1, identifies that heat of reaction is equal to 61.9 million Btu/hr, or 40 x 10^3 Btu/bbl [Davison 1993]. TME required to complete the catalytic cracking reactions in the Walden Oil example is equal to 40 x 10^3 Btu/bbl.



Regenerator Heat Balance

Heat In		Heat Out
Heat of coke combustion Heat content of coke Heat content of air	=	Heat to regenerated catalyst Heat to flue gas Radiation and miscellaneous losses

Reactor Heat Balance

Heat In		Heat Out
Heat from regenerated catalyst	=	***Heat to reaction*** Heat to fresh feed Heat to recycle stream Heat to stripping steam stream Radiation and miscellaneous losses

Figure A1. Simplified FCC Reactor and Regenerator Heat Balance

Current Average Energy

Some of the energy used in the FCC unit, such as electrical power, steam, and fuel, is obtained from utility sources. Another, larger, source of energy in the form of heat comes from the combustion of coke. The large amount of heat generated by coke combustion in the regenerator supplies the energy to heat the fresh feed, the recycle feed, and the stripping steam to reactor temperature, to heat the air to regenerator temperature, and to supply endothermic heat of reaction. Part of the feedstock is therefore consumed to supply the energy requirements of the process.

From a utility perspective the FCC process is typically a net energy producer. The process generates large quantities of hot flue gas that can be recovered in a waste heat or CO boiler to provide steam for reactor stripping or power for the regenerator air blower (compressor) [DOE 1998].

CAE and PME requirements for this process were calculated by considering both the utility sources and the internal energy produced by combustion of coke.

(CAE, PME) = utility energy + heat of combustion of coke

Table A3 provides specific energy use values for the FCC that are based on average energy requirements from several licensed FCC technologies.

Table A3. Estimated Energy Use in Fluid Catalytic Cracking

Energy Source	Specific Energy (10^3 Btu/bbl feed)
Fuel	62
Electricity [a]	13
TOTAL ENERGY INPUT	**75**
Steam Produced	-98

[a] Excludes losses incurred during the generation and transmission of electricity.
Source: DOE 1998

Average utility energy use for the FCC, excluding electrical losses during generation and transmission, is 75 x 10^3 Btu/bbl feed. The average rate of steam exported from the process is estimated to be 98 x 10^3 Btu/bbl feed [DOE 1998]. On average, the FCC process unit produces 23 x 10^3 Btu/bbl feed of utility energy.

Referring again to the Walden Oil example provided by Grace Davison, CAE can be estimated by summing the negative utility energy value (-23 x 10^3 Btu/bbl) and the positive heat of combustion of coke (206 x 10^3 Btu/bbl). For the example case, total CAE required in a FCC unit is equal to 183 x 10^3 Btu/bbl.

Practical Minimum Energy

PME can be calculated by considering improvements to operating and control practices and upgrades to process equipment. Implementation of the following technologies and practices could reduce energy consumption as shown (percent savings represent percent savings from overall energy requirement, or CAE) [conversations with industry representatives, DOE 2003b, Linhoff March 2002, ANL 1999]:

- Addition of a power recovery turbine – 15%
- Conversion of condensing turbine drive to electric motor drive (wet gas compressor) - 5%
- Improved heat integration, pinch analysis – 6 %
- Minimization of other miscellaneous losses including surface losses – 2%

Total potential energy savings is up to 28% (these energy savings may not be additive due to overlap). PME requirement is therefore equal to 132 x 10^3 Btu/bbl.

3. Catalytic Hydrotreating Energy Requirement Estimates

Theoretical Minimum Energy

When considering a typical gas oil hydrotreater, a number of hydrogenation reactions, such as olefin saturation and aromatic ring saturation, take place. Cracking is almost insignificant at the operating conditions. The exothermic heat of reaction for desulfurization and denitrogenation is relatively high (about 65 to 75 Btu/scf of hydrogen consumed). Another reaction contributing to heat release in gas oil hydrotreating is the saturation of olefins—the heat of reaction for olefin saturation is about 140 Btu/scf of hydrogen consumed. The overall heat of reaction for most hydrotreating reactors used for preparing hydrocracker feed is approximately 25,000 to 35,000 Btu/bbl feed (Note: Due to insufficient data, the heat of reaction, ΔH_r, is used in place of the change in free energy, ΔG. ΔH and ΔG are related by $\Delta G = \Delta H - T \cdot \Delta S$, where T is the temperature in Kelvin and ΔS is the change in entropy.) [Gary 1984].

For a typical gas oil hydrotreater, TME requirement, or minimum energy required to complete the catalytic hydrotreating reactions assuming ideal conditions, is estimated to be approximately 30 x 10^3 Btu/bbl feed. This value is assumed to be representative of all refinery hydrotreaters.

Current Average Energy

Table A4 summarizes specific energy use values for catalytic hydrotreating that are based on average energy requirements for several licensed hydrotreating technologies. For the purposes of this bandwidth report, the total estimated energy input in Table A4 was used to represent the current average energy requirement for a single typical hydrotreating process unit. As explained in the process description, a typical refinery employs three or more hydrotreating units throughout the plant. CAE requirement is estimated to be 81 x 10^3 Btu/bbl.

Table A4. Estimated Energy Use in Catalytic Hydrotreating

Energy Source	Specific Energy (10^3 Btu/bbl feed)
Fuel	62
Electricity[a]	19
TOTAL ENERGY INPUT	**81**
Hydrogen Consumed	223
Steam Produced	-31.1

[a] Excludes losses incurred during the generation and transmission of electricity.
Source: DOE 1998

Practical Minimum Energy

Practical minimum energy for a typical gas oil hydrotreater can be calculated by considering improvements to operating and control practices and new reactor technologies. Implementation of the following technologies and practices could reduce energy consumption as shown (percent savings and Btu/bbl savings represents savings from overall energy requirement, or CAE) [conversations with industry representatives, ANL 1999, Gary 1984, Plantenga et al., 2001, UCE 2001, Linhoff March 2002] :

- Improved preheater performance – 15 x 10^3 Btu/bbl savings[a]
- Improved catalyst – 5 x 10^3 Btu/bbl savings[b]
- Improved heat integration, pinch analysis – 5%
- Minimization of other miscellaneous losses including surface losses – 2%

[a] 50% of the estimate, or 7.5 x 10^3 Btu/bbl, is considered to be technology in the research and development stage

[b] 100% of the estimate is considered to be technology in the research and development stage

Total potential energy savings is estimated to be 31.5%, although in practice, the energy savings may be less due to overlap of the energy saving measures. PME requirement is equal to 55 x 10^3 Btu/bbl.

4. Catalytic Reforming Energy Requirement Estimates

Theoretical Minimum Energy

Four typical catalytic reforming reactions are presented in Figure 9. Assuming that these reactions are representative of the overall process unit chemistry, theoretical minimum energy (TME) can be estimated by calculating the standard Gibbs free energy of formation using the following equation:

$$\Delta G_r = \Sigma \Delta G_f \text{ products } - \Sigma \Delta G_f \text{ reactants}$$

Table A5 lists the change in Gibbs free energy of formation, ΔG_f, for the various products and reactants. Total average Gibbs free energy is calculated by multiplying the standard Gibbs free energy by the proportion variable for each reaction and summing the total. The proportion variable is based on an assumed reaction volume, as was discussed in the process description.

Table A5. Total Average Gibbs Free Energy Change for Typical Reforming Reactions

				ΔG (Btu/lbmole)	**Proportion Variable**
Dehydrogenation of alkylcyclohexane to aromatic					
	Methylcyclohexane → Methylbenzene + $3H_2$				
Gibbs Free Energy (Btu/lbmole)	11,736	52,704		40,968	20%
	Methylcyclopentane → Cyclohexane → Benzene + $3H_2$				
Gibbs Free Energy (Btu/lbmole)	15,390	13,662	55,780	40,390	20%
Dehydrocyclization of paraffins to aromatics					
	n-Heptane → Methylbenzene + $4H_2$				
Gibbs Free Energy (Btu/lbmole)	3,762	52,704		56,466	17%
Isomerization of paraffins to isoparaffins					
	n-Hexane → Isohexane				
Gibbs Free Energy (Btu/lbmole)	90	-1,728		-1,818	17%
	Methylcyclopentane → Cyclohexane				
Gibbs Free Energy (Btu/lbmole)	15,390	13,662		-1,728	17%
Hydrocracking – saturation of olefins and cracking of paraffins					
	n-Decane → Isohexane + n-Butane				
Gibbs Free Energy (Btu/lbmole)	14,814	-1,728	-28,272	-44,814	9%
Total Average ΔG for Combined Reactions (Btu/lbmole)				**21,235**	
Total Average ΔG for Combined Reactions (Btu/bbl)				**78,738**	

Sources: CRC 1970, Perry 1984
Gibbs free energy at 25°C

Total average Gibbs free energy for a typical reformer is estimated to be 21,235 Btu/lbmole. The average Gibbs free energy can also be presented in terms of barrel of feed by considering the molecular weight (g/gmole) and density (lb/gal) of the reaction products. TME for catalytic reforming is positive, or endothermic, representing heat required in the process. TME for catalytic reforming is estimated to be 78.7 x 10^3 Btu/bbl feed.

Current Average Energy

Table A6 summarizes specific energy use values for catalytic reforming that are based on average energy requirements for several licensed reforming technologies. For the purposes of this bandwidth report, the total estimated energy input in Table A6 will be used to represent the current average energy requirement for the process unit. CAE requirement is estimated to be 264 x 10^3 Btu/bbl.

Table A6. Estimated Energy Use in Catalytic Reforming

Energy Source	Specific Energy (10^3 Btu/bbl feed)
Fuel	254
Electricity[a]	10
TOTAL ENERGY INPUT	**264**
Hydrogen Produced	-479.2
Steam Produced	-15.4

[a] Excludes losses incurred during the generation and transmission of electricity.
Source: DOE 1998

Practical Minimum Energy

PME for the catalytic reforming process was calculated by considering improvements to operating and control practices, upgraded process equipment and additional product recovery process cooling. Implementation of the following technologies and practices could reduce energy consumption as shown (percent savings and Btu/bbl savings represents savings from overall energy requirement, or CAE) [conversations with industry representatives, ANL 1999, Gary 1984, Packinox 2003, DOE 1999]:

- Improved feed and interstage process heater performance (e.g., improved convection section heat recovery) – 18.5 x 10^3 Btu/bbl savings [a]
- Replace horizontal feed/effluent heat exchangers with vertical plate and frame exchanger – 30 x 10^3 Btu/bbl
- Improved equipment efficiency (e.g., recycle and net gas compressor, reactor product air cooler) – 2% Additional process cooling to improve light ends recovery (vapor compression vs. ammonia absorption) – 2 x 10^3 Btu/bbl savings
- Minimization of other miscellaneous losses including surface losses – 2%

[a] 50% of the estimate, or 9 x 10^3 Btu/bbl, is considered to be technology in the research and development stage

Total potential energy savings is estimated to be up to 23% (these energy savings may not be additive due to overlap). PME requirement is equal to 203 x 10^3 Btu/bbl.

5. Alkylation Energy Requirement Estimates

Theoretical Minimum Energy

The primary alkylation reaction below is used to calculate the theoretical minimum energy for both the sulfuric acid-catalyzed (H_2SO_4) and hydrofluoric acid-catalyzed (HF) processes.

$$\underset{\text{Butylene}}{C_4H_8\ (l)} \quad + \quad \underset{\text{Isobutane}}{C_4H_{10}\ (l)} \quad \xrightarrow{\text{acid catalyst}} \quad \underset{\text{2,2,4-trimethylpentane}}{C_8H_{18}\ (l)} \quad + \quad \text{Heat}$$

Table A7. Selected Thermodynamic and Physical Properties of Alkylation Compounds[a]

Compound	Molecular Weight (lb/lbmole)	Density (lb/gal)	ΔG_f (Btu/lbmole)
Butylene	56.1	5.0[c]	29,043
Isobutane	58.4	5.0[b]	-7,795
2,2,4-TMP	114.2	5.8[c]	5,679

[a] All properties are measured at 25°C unless otherwise indicated.
[b] Measured at 0°C.
[c] Measured at 20°C.
na not applicable
Sources: CRC 1970, Perry 1984, DOC 1995, DOC 2003.

This reaction is a net energy producer as shown in the following calculation:

$$\begin{aligned}\Delta G_r^{25^\circ C} &= \Sigma\Delta G_f^{25^\circ C}\text{ products} - \Sigma\Delta G_f^{25^\circ C}\text{ reactants}\\ &= 5{,}679\text{ Btu/lbmole} - (-7{,}795\text{ Btu/lbmole} + 29{,}043\text{ Btu/lbmole})\\ &= -15{,}569\text{ Btu/lbmole}\\ &= -58{,}280\text{ Btu/barrel feed}\end{aligned}$$

The theoretical minimum energy for the H_2SO_4 and HF alkylation processes is -58,280 Btu/bbl feed.

Current Average Energy

This analysis uses the current process energy values from the *Energy and Environmental Profile of the U.S. Petroleum Refining Industry* and excludes electricity losses incurred during the generation and transmission of electricity [DOE 1998].

Table A8. Actual Process Energy for Alkylation Processes

Fuel	10^3 Btu/bbl feed	
	H_2SO_4 Process	**HF Process**
Fuel	209.0	239.7
Electricity[a]	41.3	4.9
TOTAL ENERGY INPUT	**250.3**	**244.6**

[a] Excludes losses incurred during the generation and transmission of electricity.
Source: DOE 1998.

Practical Minimum Energy

The PME for alkylation is approximately 156,000 Btu/bbl feed and 152,600 Btu/bbl feed for the sulfuric acid-catalyzed process and hydrofluoric acid-catalyzed process, respectively. The practical minimum energies are based on improved cooling and distillation operations. Table A8 shows the actual process energy consumption for the two processes that were used in the PME calculations.

For the sulfuric acid process, fuel is primarily consumed by the distillation reboiler and electricity is used to operate the compressors (which use about 71% of the electricity) and the pumps and mixers [Meyers 1997]. The PME is calculated by considering improved compressor efficiency, heat integration, and improvements to distillation column design. It is assumed that the compressors that cool and condense the isobutane vapors that have boiled off from the reaction mixture (autorefrigeration) operate at an efficiency of 25% [SWRI 2000]. A typical refinery could expect to generate significant energy savings by implementing the following measures [Gadalla et al., 2003, TDGI 2001, DOE 2003, Schultz et al., 2002].

- Improved compressor efficiency, from 25% to 50% – 14,500 Btu electricity/bbl feed
- Improved heat integration, pinch analysis – 10 %
- Use of a dividing wall column design or other advanced separation technology– 20% [a]
- Upgraded control system – 8%

[a] 100% of the estimate is considered to be technology in the research and development stage

The total potential energy savings are up to 14,500 Btu of electricity/bbl feed plus a 38% fuel reduction. PME is therefore 156,000 Btu/bbl feed. However, the energy saving measures presented may not be additive in real world applications leading to a reduced potential energy savings and higher PME.

For the HF process, almost all of the process energy is consumed in the separation units (isostripper, depropanizer) [Meyers 1997]. Improvements in column efficiency and/or implementation of advanced separation technologies could significantly reduce energy consumption in the HF alkylation process.[a] Using the methodology from the H_2SO_4 PME calculation, the fuel consumption could be reduced by 38%, resulting in a HF PME of 152,000 Btu/bbl.

[a] considered to be technologies in the research and development stage

Product Energy Requirement Estimates

U.S. Total Production Volumes

Table A9 lists the production volumes for typical refinery product streams. Daily production values represent U.S. refining total daily barrels per stream day (BPSD).

Table A9. Typical Refinery Product Streams

Product Stream	2004 Net Production (10^3 bbl)	Daily Production (10^3 BPSD)[a]
Still Gas (Fuel Gas)	257,689	769
Liquified Refinery Gas (LRG)[b]	235,975	704
Gasoline[c]	3,201,392	9,556
Jet Fuel/Kerosene	589,573	1,760
Distillate Fuel Oil	1,396,037	4,167
Residual Fuel Oil	239,907	716
Asphalt	185,921	555
Coke	306,065	914
Other[d]	107,194	320
TOTAL	**6,519,753**	**19,462**
Includes Process Gain of:	384,698	1,148

Source: DOE 2005b, Table 17

[a] Barrel per stream day (BPSD) calculated based on 335 stream days per year.

[b] Liquified refinery gas (LRG) is also referred to as liquefied petroleum gas (LPG)

[c] Includes petrochemical feedstocks and aviation gasoline.

[d] Includes lubricants, special naphthas, waxes and miscellaneous products.

U.S. Total Process Unit Capacities

Table A10 lists the total U.S. operable charge capacities for selected refinery process units. Capacity values represent U.S. refining total daily BPSD.

Table A10. Process Unit Capacities

Product Stream	Charge Capacity as of Jan 1, 2005 (10^3 BPSD)
Crude Distillation:	
Atmospheric	18,031
Vacuum	8,120
Reformer	3,836
Hydrotreating	14,087
Alkylation	1,229
FCC	6,151

Source: DOE 2005b, Tables 41 and 42

Product Volume Balance

Figure 1 on page 3 gives a glimpse of the complex arrangement of process units within a refinery. There are many interdependencies. One barrel of crude oil entering an atmospheric crude tower may continue on to a dozen or more downstream process units as the different crude oil fractions are refined into a variety of products. Table 11 provides an estimated breakdown of the product streams by the major process unit directly upstream of the treating and blending processes (see Figure 15). Estimating product flow through a refinery is a complicated task. The distribution varies greatly depending on crude type, refinery design, and market demands. The distribution in Table A11 was prepared through consultation with an industry expert assuming typical conventional crude and processing, as shown in the simplified flow layout (Figure 15).

Table A11. Refinery Product Output, U.S. Total Daily Production [a]

Process Unit	Refinery Product Output (10^3 BPSD)								
	Still Gas	LRG	Gasoline [b]	Jet Fuel/ Keros	Dist Fuel Oil	Resid Fuel Oil	Asphalt	Coke	Other [c]
	769	**704**	**9538**	**1690**	**4167**	**716**	**555**	**914**	**408**
Crude Distillation:									
Atmospheric	191	267	444	820					51
Vacuum						716	555		
Reformer	142	56	3637						
Distillate HTs				820	3280				
Alkylation			1229						
FCC	384	334	3599		605				
Other Processes								914	269
Process Gain[d]	52	48	647	119	282				

[a] Assuming typical conventional crude processed as shown in the Simplified Refinery Flow Diagram.
[b] Petrochemical feedstocks and aviation gasoline included in gasoline output.
[c] Includes lubricants, kerosene, special naphthas, waxes, and miscellaneous products.
[d] Assuming process gain is distributed on a volume basis between still gas, LRG, gasoline, jet fuel and distillate fuel oil product streams.

The values in Table A11 are shown on the basis of volume percent in Table A12.

Table A12. Volume % Breakdown of Refinery Product Output

Process Unit	Still Gas	LRG	Gasoline	Jet Fuel/ Keros	Dist Fuel Oil	Resid Fuel Oil	Asphalt	Coke	Other
Crude Distillation:									
Atmospheric	25%	41%	13%	0%	0%	0%	0%	0%	0%
Vacuum	0%	0%	0%	0%	0%	0%	100%	0%	0%
Reformer	18%	9%	37%	0%	0%	0%	0%	0%	19%
Distillate HTs	0%	0%	0%	100%	58%	0%	0%	0%	0%
Alkylation	0%	0%	13%	0%	0%	0%	0%	0%	0%
FCC	49%	51%	29%	0%	33%	0%	0%	0%	12%
Other Processes	0%	0%	0%	0%	0%	100%	0%	100%	0%
Process Gain	8%	0%	8%	0%	9%	0%	0%	0%	69%
TOTAL	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**	**100%**

Product Energy Requirement Calculation

Individual product energy requirement was calculated by multiplying the annual production volume by the product output volume percent and the current average process unit energy requirement provided in Table 2. An example of the calculation is provided below:

Gasoline Energy Requirement in the Alkylation Unit
3,201,392,000 bbl gasoline/yr x 12.86% x 248,000 Btu/bbl processed in the alkylation unit = 102 T Btu/yr

Table A13 (also shown as Table 3 on page 20) provides the total annual product energy requirement by process unit for all of the typical product streams shown in Figure 15. The atmospheric and vacuum crude distillation and FCC unit values include all downstream production volumes, whereas the reformer and alkylation unit values do not include any additional downstream processing, as shown in Figure 15. The hydrotreating energy requirement includes the naphtha hydrotreater, gas oil hydrotreater, and additional distillate hydrotreaters, as shown in Figure 15.

Table A13. Total Annual Refinery Product Energy Requirement (T Btu/yr)

Process Unit	Product Energy Requirement	Still Gas	LRG	Gasoline	Jet Fuel/ Kero	Dist Fuel Oil	Resid Fuel Oil	Asphalt	Coke	Other
Crude Distillation:										
Atmospheric	658	1	1	295	54	180	38	30	49	12
Vacuum	242	0	0	61	0	33	39	45	64	0
Reformer	339	13	5	322	0	0	0	0	0	0
Hydrotreating	382	14	11	230	22	105	0	0	0	0
Alkylation	102	0	0	102	0	0	0	0	0	0
FCC	377	24	20	296	0	37	0	0	0	0
TOTAL	**2101**	**51**	**37**	**1305**	**76**	**355**	**77**	**75**	**113**	**12**
% of Total	**100%**	**2.4%**	**1.7%**	**62.1%**	**3.6%**	**16.9 %**	**3.7%**	**3.6%**	**5.4%**	**0.6%**

(Some values are off by one when columns and rows are summed due to rounding error)

For the reformer, hydrotreater, alkylation, and FCC units, it was assumed that the CAE requirement was distributed on a process unit volume basis and therefore Btu/bbl feed was equal to Btu/bbl product, as shown in the following relationship:

Conversion of Btu/bbl Feed to Btu/bbl Produced for Gasoline in the Reformer Unit
264,000 Btu/bbl reformer feed x process unit volume % (3,637/3,836 = 94.81%) x 3,836,000 bbl reformer feed/3,637,000 bbl gasoline produced = 264,000 Btu/bbl gasoline produced

Therefore, the reformer energy required to produce a barrel of gasoline is equal to the reformer CAE.

In the case of atmospheric and vacuum crude distillation, distillation energy input is distributed based on volume fraction and boiling points of the product streams. Distillation separates stream components based on their boiling points. Because lighter components, such as LRG, have lower boiling points, they require less energy per unit mass to raise their temperature from the feed temperature to their boiling points. Heavier components have significantly higher boiling points and therefore require more energy per unit mass to raise their temperature from the feed temperature to their boiling point or exit temperature. Table A14 shows the distribution of the atmospheric crude distillation CAE among the different product streams. The distribution is a function of the change in temperature (boiling point – feed stream temperature) that a product stream must undergo as well as the volume fraction of the product stream (volume of product per volume of feed).

Table A14. Distribution of Atmospheric Crude Distillation CAE by Product Stream

Product	Fraction of Atmospheric Crude Distillation CAE (%)
Still Gas	0.07%
LRG	0.08%
Gasoline (includes petrochemical feedstocks)	41.9%
Jet Fuel/Kerosene	9.2%
Distillate Fuel Oil	27.8%
Residual Fuel Oil	6.7%
Asphalt	5.0%
Coke	7.1%
Other	2.2%
TOTAL	**100.0%**

Sources: Thermodynamic data sources are the same as those used in Crude Distillation TME calculation. Product volume fraction – API 2002

Gasoline and distillate fuel oil consume the most atmospheric crude distillation energy due to high volume fractions (gallons of product per barrel of crude processed) and two pathways through the atmospheric tower for these products. The analysis assumes that a portion of the gasoline and distillate (47% of total gasoline produced, 15% of total distillate fuel oil produced) is generated from the heavy fraction that exits the atmospheric tower and passes through the vacuum distillation tower before continuing on to the gas oil hydrotreater and FCC. It is also assumed that these portions consume more atmospheric distillation energy on an energy per volume of product basis than the gasoline and distillate that are generated from the naphtha hydrotreater/reformer, straight run, and distillate hydrotreater streams.

Still gas and LRG are similar to gasoline and distillate fuel oil in that approximately 50% of the products (see Table A11) are generated from the FCC and it is logical that the methodology described above would be followed for these products as well. However, due to the small production volumes of the gases and much lower distillation energy requirements (boiling points of these fractions are at or below atmospheric temperatures) compared to the other products, the atmospheric distillation energy distribution values (Table A14) for still gas and LRG were calculated assuming that none of the total production volume was generated from streams passing through the vacuum tower.

The vacuum distillation energy distribution between gasoline, distillate fuel oil, residual fuel oil, asphalt, and coke is shown in Table A15. The distribution was calculated following the same methodology used for the atmospheric distillation energy distribution.

Table A15. Distribution of Vacuum Distillation CAE by Product Stream

Product	Fraction of Vacuum Distillation CAE (%)
Gasoline (includes petrochemical feedstocks)	23.2%
Distillate Fuel Oil	13.4%
Residual Fuel Oil	18.4%
Asphalt	20.2%
Coke	24.8%
TOTAL	**100.0%**

Appendix B

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