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Energy Use in Petroleum Refineries

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OAK RIDGE NATIONAL LABORATORY

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OPERATED BY UNION CARBIDE CORPORATION FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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ENERGY USE IN PETROLEUM REFINERIES

V. O. Haynes

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FOREWORD

The information contained in this report was obtained primarily from open-literature sources, supplemented by discussions with authors and by information obtained from a few representatives of the petroleumrefining industry. Although it was not possible in this limited effort to quantify precisely the energy used in refining petroleum, the information is believed to be sufficiently representative to support the conclusions. Detailed descriptions of the various petroleum-refining processes are well documented in several publications; thus, this report describes the processes only to the extent felt necessary to make them relevant to their energy requirements.

Appreciation is hereby expressed to D. C. Azbill, Shell Oil Company; R. W. Wendes, Amoco Oil Company; R. B. James, Universal Oil Products; and several of their associates for detailed information on some specific processes and for general discussions. However, the information contained in this report should not be construed to be representative of these sources. Appreciation is also expressed to those who offered many helpful comments after reviewing a draft of the report: R. W. Wendes, Amoco Oil Company; O. L. Culberson, University of Tennessee; J. H. Smithson, U. S. Energy Research and Development Administration; and R. S. Carlsmith and S. A. Reed, Oak Ridge National Laboratory.

In view of the present accepted practice in this country for the petroleum refining industry, common U. S. units of measurement have been used throughout this publication. In recognition of the position of the U.S. as a signatory to the General Conference on Weights and Measures, which gave official status to the metric

SI system of units in 1960, appropriate conversion factors have been provided as follows:

TO CONVERT	TO	MULTIPLY BY
Btu	joule	1.055×10^3
kWhr	joule	3.600×10^6
barrels (bbl)	m ³	1.590×10^{-1}
ft ³	3	2.832×10^{-2}
Btu/bbl	joules/m ³	6.635×10^3

ABSTRACT

Refining petroleum accounts for about 4% of the total energy consumed in the United States and about 15% of all industrial consumption. The kinds of energy used and the manner in which energy is used are discussed on a process-by-process basis. Emphasis is placed on existing processes to identify and quantify process and equipment substitutions which might significantly conserve energy.

General industry and process information is given and estimates of potential savings are made. A few research and development opportunities are identified and nontechnical factors are discussed.

Nearly one-half the energy consumed by refineries is obtained from by-product refinery gas and coke, and about one-third is supplied by natural gas. On a regional basis, refineries were found to vary by a factor of two in the amount of energy used to refine a unit of crude oil. Refineries in regions traditionally abundant in inexpensive natural gas were found to use relatively more natural gas and energy.

About 36% of the energy used by petroleum refineries is consumed in the distillation units to separate the refinery streams into their basic components. Including energy for manufacturing hydrogen, about 24% of the total is used for cracking of the heavier components. Most of the remainder is used for reforming, hydrogen treating, and alkylation, distributed about 11, 17, and 6% respectively. Potential energy savings discussed in this report total 61 x 10^{13} Btu/yr based on 1974 capacities, a figure which represents about 20% of the energy consumed to refine petroleum.

SUMMARY

Petroleum refineries use slightly over 3×10^{15} Btu of energy annually — about 4% of yearly U. S. energy consumption. Plant size, product, and location affect refinery energy consumption. Processing has become more complex as plant size has increased, requiring more energy per unit output. Refineries in Texas and along the Gulf Coast use considerably more energy than the national average because their design was based on a relatively mild climate and inexpensive natural gas.

A little over half of the energy used to refine petroleum comes from refining streams — refinery gas, oil, liquified petroleum gas (LPG), and coke. The average energy required per unit output has declined about 0.8%/year since 1960 to a 1974 value of 707,000 Btu/bbl crude, but there are large regional variations in both the trend and the consumption. The increasing price of fuel will lead to more effective use of energy. However, because the growth of capacity is anticipated to be slow, conservation will have to be achieved by retrofitting existing plants and as a result will be more expensive and less effective.

The fuel-, steam-, and electricity-energy requirements, energy quality, and energy savings are estimated for most of the refining processes. Processes most important relative to energy consumption are distillation, thermal cracking, hydrocracking, hydrotreating, reforming, and alkylation. It appears that about 20% of the energy used to refine petroleum could be saved by the following measures:

Conservation measure	Savings (10 ¹³ Btu/year)
Adding distillation trays and reducing refluxing,	
operating with high tray flooding, and refining to minimum product quality	3.2
Use of more energy-efficient fluid catalytic crackers	15
Use of cyclic, bimetallic-catalyst reformers instead of semiregenerative units	5.0
Hydrotreating with no makeup hydrogen when possible	1.2
Use of hydrofluoric acid (HF) alkylation when analyses indicate it is more energy-efficient	0.6
Improved furnace design, furnace control, and furnace heat recovery	13
Greater use of heat exchange between process streams and exchanging to a lower temperature	10
Use of vacuum pumps instead of steam jets	1.1
Use of back-pressure turbines instead of condensing turbines for both direct drive and electricity generation	4.7

Conservation measure	Savings (10 ¹³ Btu/year)
Use of turbo-expanders and hydraulic turbines when	1.0
feasible	1.2

Use of more efficient pumps and motors and proper 4.6 sizing

Other factors that affect energy consumption in petroleum refining and can thus be explored for their practicability in conserving energy are: availability and price of fuel; product specifications; industry standards for products, equipment, operation, and maintenance; quality of crude oil to be refined; and integration of refineries with electric utilities and other industries.

INTRODUCTION

Historically, energy has been sufficiently cheap and abundant in the United States that minimizing energy requirements rarely has been a decisive factor in minimizing product cost. This observation is particularly true of the petroleum-refining industry in the Gulf Coast region where inexpensive gas has been readily available and was a significant influence in locating refineries in this region. The economics of energy have changed drastically in recent times and the adequacy of our energy supply has become a national concern. This report was prepared under the sponsorship of the U. S. Atomic Energy Commission to provide detailed information on the types, end-uses, and

respective quantities of energy consumed in major U. S. industries. Specific objectives of this study are to:

- Characterize the petroleum-refining industry by plant size, by products, and by location, including historical data.
- Describe the extent of energy consumption and the kinds of fuels used.
- Discuss current, planned, and proposed energy conservation practices, identify process choices which affect energy consumption, and identify opportunities for using alternate fuels.
- Identify areas of research and development having potential for conserving energy.

CONCLUSIONS AND REMARKS

General

Petroleum refineries use slightly over 3×10^{15} Btu of energy per year, a figure which represents about 4% of annual U. S. energy consumption and about 15% of annual industrial energy consumption. Although little of the refinery fuel is oil, energy consumption often is related to the equivalent amount of crude oil that would be required; expressed as such, refinery fuel consumption represents about 12% of the crude oil input to refineries.

Petroleum-refining-industry characteristics of plant size, product, and location all affect energy consumption. Size studies reveal that refining capacity is being concentrated in increasingly larger plants. As capacity has increased and the number of refineries has decreased, average plant size in the past decade increased about 60%.¹ Larger plants characteristically involve more complex refining processes, requiring more energy per unit of crude oil. However, this cost is not necessarily undesirable since the increased quality of the product might justify the increased energy consumption (e.g., clear, low-sulfur fuels; clear, high-octane gasoline; petrochemical feedstock).

From a location consideration, a large fraction of the petroleum refineries are located in the Texas and Gulf Coast regions where inexpensive supplies of natural gas have made it uneconomical to practice rigorous energy conservation. As shown by Fig. 1, energy consumption for the Texas refineries (districts 7 and 8) is substantially above the national average, with a wide variation of energy consumption among the districts. Because 26% of the total crude oil is processed in the two Texas districts, their refineries would save 23 x 10^{13} Btu of energy per year if consumption were reduced to the national average.

Fuels

Fuels are used almost exclusively for process heating and steam production. Steam is used as a stripping agent, in vacuum jets, in heat exchangers, and in powering turbines and pumps. Slightly over half of the energy comes from refinery streams — distributed about 60% from refinery gas, 20% from oil and LPG, and 20% from coke. About one-third of the energy is from natural gas. The electrical energy (four-fifths of which is purchased) is produced mainly from combustion of coal and natural gas and is used primarily for pumping.

Trends in Energy Use

The unit energy consumption for refining petroleum is subject to several competing demands — efforts to conserve energy, increased

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Fig. 1. Energy requirements for U.S. petroleum refineries by districts - 1972.

refining, and environmental restraints on products and refinery emissions. The unit energy consumption has been decreasing slowly in recent years and involves much retrofitting of existing plants. It appears that retrofitting and replacement of existing equipment and improved plant operation and maintenance will continue to predominate conservation efforts. Thus the degree to which energy conservation can be effected will be substantially less than could be achieved by an industry dominated by new energy-conserving plants. Substitution of other fuels for natural gas can also be expected at existing refineries.

The fuels and relative amounts used to supply energy for refining petroleum changed only slightly between 1961 and 1974. Between 1962 and 1974 the U. S. average of energy required to refine a barrel of crude oil dropped from 790,000 to 707,000 Btu/bbl, an average decrease of only 0.8%/year. Several major oil refiners have formed task groups to conserve energy in their refineries. Although some claim to have cut fuel consumption by a few percent as early as 1971, values from the Bureau of Mines show very little change within the refinery industry between 1971 and 1974; the reported energy consumption per barrel was essentially constant for this period. A shifting use of fuels is apparent by the increasing use of fuel oil and coke to replace natural gas. Recent efforts to conserve energy, then, appear to be obscured by a significant and approximately equal increase in energy used for additional petroleum refining (to produce, for example, high-octane. unleaded gasoline and low-sulfur products) and/or protection of the environment. A trend also exists to reduce reliance on natural gas. Large variations both in the magnitude of energy consumed per barrel of

oil refined and in recent fuel-use trends are found when comparing regional values, about half the regions showing increases and half showing decreases.

The increasing value of fuel undoubtedly will lead to more effective use of energy. According to historical values, though, the increasing emphasis on conservation of fuel for transportation and heating will retard expansion of the petroleum-refining industry, and capacity probably will be dominated by existing plants for many years. Thus, most conservation measures will necessarily be of the retrofitting type which are characteristically more expensive and less effective.

Refineries are in a unique position relative to the availability of fuel because their feed can be readily used to replace other fuels. The price, availability, and allocation of natural gas are of concern to refiners. Furthermore, there will be efforts to supply some energy with coal, possibly combusted in fluidized-bed units to minimize undesirable emissions. The energy from other low-grade waste materials also might be recovered in fluidized-bed combustion. Another long-range alternative under investigation is to use more efficiently the energy supplied by an electric-generating utility. In addition to electricity, for example, high-temperature process heat could be diverted through an appropriate heat-transfer system and supply steam which might furnish some of the petroleum-refining energy currently supplied from purchased fossil fuel, especially natural gas. If a joint venture were undertaken with an electric utility and other industries, it might even be possible to substitute nuclear fuel or coal for oil and gas.

Processes

The major petroleum refining processes and their representative requirements for fuel, steam, and electricity as discussed in this report are summarized in Table 1. Included is the energy required to refine a barrel of crude oil based on the feed to each process as a percentage of the crude oil input. The total energy, estimated to be 379,000 Btu/bbl of crude oil, includes energy for manufacturing hydrogen (a credit for the hydrogen produced by the reforming process). Not included in the total is energy for lubricating oil, wax, and asphalt processing, a contribution which might raise the total energy estimate to 455,000 Btu/bbl of crude oil. Other energy uses not included are those for catalyst and additive manufacture, product blending and storage, treatment of water and wastes, and terminal operations. The estimated unit energy usage is much below the U. S. average reported by the Bureau of Mines and about the same as values reported for U.S. districts with lowest consumption, suggesting that the estimated given here may be optimistically low relative to actual energy use. Reasons for major differences between estimates in this study and those of some other studies include the much lower energy requirements in this study for catalytic cracking and alkylation and a credit assignment for hydrogen produced by the reforming process. These factors together could account for about 190,000 Btu/bb1 of crude oil, distributed 110,000, 25,000, and 55,000 Btu/bbl for catalytic cracking, alkylation, and reforming respectively. The efficiency of heat recovery from the regeneration of the catalyst in the catalytic cracking process is likely to be the main reason for variations in the reported values.

	Process		Ener	gy requ	irement	
Process	feed		<u>Stu/bbl fee</u>	(10 ³ Btu/bb1		
	(% crude)	Fuel	Steam	Elect.	Total	crude oil)
Desalting	80	0.05	neg	0.6	0.65	0.5
Atm. distillation	100	80	10	6	96	96
Vac. distillation	35.2	75	22	3	100	35.2
Gas separation	10	0	62	1.8	63.8	6.4
Cracking Thermal Visbreaking Coking	1.4 ^a 1.4 ^a 6.5	700 160	162 30	15 10	877 200	12.3 2.8
Delayed Fluid Catalytic	5.7 0.8 28.9	80 0	45 100	70 15	195 115	11.2 0.9
Fluid ^b Gas lift ^C Hydrocracking	26.5 2.4 5.4	0/51 140	35/-177 - 67	50/57 22	85/-69 95	22.5/-18.3 2.3
w/o Hydrogen w Hydrogen		200 588	13 13	100 119	313 720	16.9 38.9
Reforming Cyclic w/o Hydrogen w Hydrogen Semiregenerative w/o Hydrogen w Hydrogen	21.2 6.0 ^d 15.2 ^d	280 2 355 189	0 0 0 0	50 36 75 67	330 38 430 256	19.8 2.3 65.4 38.9
Hydrorefining w/o Hydrogen w Hydrogen	6.4	73 228	0 0	22 30	95 258	6.1 16.5
Hydrotreating w/o Hydrogen w Hydrogen	29.9	39 106	34 34	14 17	87 157	26 46.9
Alkylation H ₂ SO ₄ HF	5.4 3.4 2.0	100 13	323 373	48 15	471 401	16.0 8.0
Isomerization C_4 feed C_5/C_6 feed	0.7 0.5 0.2	32 42	23 45	12 15	67 102	0.4 0.2
Miscellaneous ^e				20.9	20.9	20.9
Total (with	hydrogen ch	arge and	credit)			379.1

Table 1. Energy requirements for petroleum-refining processes

^a0.1 added to account for "other."

 $^{\rm b}{\rm Numbers}$ to right of / are for a new, grass-root plant.

^CIncludes 0.4 of Houdriflow.

 d 0.3 added to account for "other."

^eLighting, shops, etc. from: W. L. Nelson, *Guide to Refining Costs*, 2nd ed., The Petroleum Publishing Company, Tulsa, Okla. (1970), p. 158.

Table 2 gives the energy requirements per barrel of crude oil refined, separated according to temperature, for U. S. average process capacities. From steam requirements shown and assuming steam is generated at 750 psi and 566°C (1050°F), it is estimated that energy equivalent to 3 kWhr could be developed per barrel of crude oil for direct drive of large compressors and pumps or for electric generation. That is, at a high fuel utilization energy could be generated by letting steam down to the process requirements through back-pressure turbines. This contribution would represent about 40% of the refinery's electricity needs and is about twice the average amount of electricity generated onsite, some of which is generated by low-efficiency condensing steam turbines and by gas turbines. The estimate of 3 kWhr should not be considered an upper limit of electricity generation at a high fuel utilization for several reasons:

- Summing up what might be possible at each refinery might vary substantially from this average estimate.
- Steam could be generated at higher temperatures and pressures, making more electrical energy available for a given processheat requirement. This increased generation often would require new equipment.
- 3. Some of the lower-temperature-process-heat requirements could be served with steam. However, the merit of substituting steam for a low-temperature-process-heat requirement would be questionable since fuel utilization would be only slightly improved or even lowered.

			Ener	gy (10 ³ Btu/bb1	crude)			
Process		n at:	Fuel for process temperature of:					
1100000	500 ⁰ F	750 ⁰ F	650-750 ⁰ F	750-1000 ⁰ f	1650 ⁰ F	Electricity	Total	
Desalting			0.04			0.5	0.5	
Atm. distillation	10		80			6.0	96	
Vac. distillation	7.7			26.4		1.1	35.2	
Gas separation	3.1		3.1			0.2	6.4	
Thermal cracking	2.3			9.8		0.2	12.3	
Visbreaking	0.4			2.2		0.1	2.7	
Coking Delayed Fluid	0.8	2.6		4.6		4.0 0.1	11.2 0.9	
Catalytic cracking FCC Gas-lift	9.3 - 1.6			3.4		13.2 0.5	22.5 2.3	
Hydrocracking	0.7			10.8		5.4	16.9	
Reforming Cyclic Semiregenerative				16.8 54.0		3.0 11.4	19.8 65.4	
Hydrorefining			4.7			1.4	6.1	
Hy d rotreating	10.2		11.6			4.2	26.0	
Alkylation H ₂ SO ₄ HF	7.5	11.0	3.4 0.3			1.6 0.3	16.0 8.1	
Isomerization C_4 feed C_5/C_6 feed	0.1 0.1		0.2 0.1			0.06 0.03	0.4 0.2	
Hydrogen					9.0	0.4	9.4	
Miscellaneous						20.9	20.9	
Total	50.6	13.6	105.4	128	9.0	74.6	379.2	

Table 2. Energy quality for petroleum-refining processes

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*

- Gas turbines utilizing waste exhaust heat can be used to generate electricity.
- Additional use of 150-psi steam can be achieved by substituting it for some direct heating.

Aside from these considerations, the practicability of onsite electrical generation depends also on factors such as capital costs and reliability of the electrical supply.

The most energy-intensive petroleum refining processes are thermal cracking, hydrocracking, reforming, alkylation, and polymerization. However, based on extent of use, the less energy-intensive processes of distillation and hydrotreating also are relatively important energy consumers while polymerization is relatively unimportant. The distribution of energy consumption among the various processes is shown in Figure 2.

Table 3, based on 1974 capacities and processing rates, summarizes some of the potential for saving energy discussed in this report. Total savings equal 61 x 10^{13} Btu/year, about 19.7% of the energy used to refine petroleum.

It appears that a superior process to replace distillation does not exist, but there undoubtedly are variations of the process which can reduce energy consumption, such as adding trays combined with reduced refluxing, operating with high tray flooding, and evaluating product quality to reduce "overrefining." If 5% of the process heat used in the distillation-gas separation units could be saved (about 5800 Btu/bbl of crude oil), refining petroleum would require 3.2×10^{13} fewer Btu per year.

MISCELLANEOUS 5.5 --HYDROGEN 2.5 ISOMERIZATION 0.2-CRUDE SEPARATION 36.4 ALKYLATION 6.3--DESALTING 0.1 HF 2.1 ATM. DIST. 25.3 VAC. DIST. 9.3 H₂SO₄ 4.2 -GAS SEPAR. 1.7 HYDROGEN TREATING 8.5 -HYDROTREATING 6.9 -HYDROREFINING 1.6 --REFORMING 22.5 CRACKING 18.1 SEMIREGEN. 17.3-THERMAL 3.2 CYCLIC 5.2 -VISBREAKING 0.7 COKING 3.2 - DELAYED 3.0 - FLUID 0.2 CATALYTIC 6.5 - FCC 5.9 - GAS-LIFT 0.6 ^aLIGHTING, SHOPS, ECT. - HYDROCRACKING 4.5

(a) ENERGY DISTRIBUTION AMONG PROCESSES



(b) DISTRIBUTION AMONG TYPES OF ENERGY

Fig. 2. Distribution of energy in percent for petroleum processes and for types of energy used.

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	Potential energy savings (10 ¹³ Btu.year) by:							
	Improved combustion	Recovery of low-grade heat	Improved process	Alternate process	Other	Total	refinery energy consumption	
Atm. distillation	4.0	3.9	2.2 ^b		0.2 ^c	10.3	3.3	
Vac. distillation	1.4	1.5	0.8 ^b		1.2 ^{c,d}	4.9	1.6	
Gas separation	0.3	0.9	0.2 ^b			1.4	0.5	
Thermal cracking	0.5	0.1		1	0.1 ^{b,d}	0.6	0.2	
Visbreaking	0.1	٠٠٠ ()	0.1	0.2	0.1	
Coking	0.4	0.1				0.5 ^e	0.2	
FCC			15 ^f			15.0	4.8	
Hydrocracking	0.5	2.0			0.6 ⁸	3.1	1.0	
Reforming	2.6			5.0 ^h		7.6	2.4	
Hydrorefining	0.2	0.3	0.3 ¹		0.2 ^g	1.0	0.3	
Hydrotreating ^j	1.0	1.1	0.3 ^k	1.2	0.4 ^g	4.0	1.3	
Alkylation ²	1.0	0.2		0.6		1.8	0.6	
Hydrogen ^m	1.1	0.3				1.4	0.4	
Other					<u>9.3ⁿ</u>	9.3	3.0	
Total	13.1	10.4	18.8	6.8	12.0	61.1	19.7	

Table 3. Potential annual energy savings for petroleum refining^a

^aValues less than 5 x 10¹¹ not included.

^bImproved fractionation.

^cImproved insulation.

d Mechanical vacuum pumps.

^eAbritrary estimate of 10% savings.

f Modern, energy-conserving FCC process.

^gOne-fifth of estimated electrical energy (use of hydraulic turbines and more energyefficient prime movers).

^hConversion to cyclic units.

¹30% of electricity on 2/3 of capacity (lower pressure and less recycle and makeup of hydrogen).

j15% of feed processed with no makeup hydrogen.

 $$^{\rm k}20\%$ of electricity on 1/2 of capacity (lower pressure and less recycle and makeup of hydrogen).

^ZConversion of 1/2 of the less efficient capacity to the more efficient process.

 $^{\mathrm{m}}$ Based on 1/2 the estimated hydrogen requirement.

ⁿUse of back-pressure turbines for direct drives and electricity generation. More efficient pumping systems. The cracking process uses considerable energy but most of the thermal cracking units have been replaced by fluid catalytic cracking units (FCCU) which recover energy produced by the burning of coke (in the regenerators) deposited on the catalyst. By generating steam in carbon monoxide (CO) boilers and perhaps recovering energy with turboexpanders, FCCUs become low energy consumers and perhaps even net energy generators. Cracking in the FCCU is desirable because the units conserve energy relative to thermal cracking units which, except for coking units, appear to be phasing out. Although gas-lift catalytic crackers use about 12% more energy than do the fluid-bed types, there is such a small capacity of gas-lift units that estimated savings from replacing them with fluid-bed units total only 10^{12} Btu/year. By comparison, highly efficient FCCU is estimated to create potential savings of 15 x 10^{13} Btu/year.

The reforming process using a bimetallic catalyst appears to be quite advantageous because it allows operation at lower temperatures and pressures, increases yields, and extends the process operating period. Semiregenerative units operate at higher pressures and higher hydrogen-tooil ratios than do cyclic-type units in order to minimize carbon deposition on the catalyst, and thus require more compressor energy and charge heat and generate less hydrogen. For these reasons conversion to the more energy-efficient cyclic process would conserve energy. Assuming that half the units use bimetallic catalysts and the savings would be only half the differential energy consumption, and accounting for energy required for hydrogen manufacture, the potential savings is about 5×10^{13} Btu/year.

Hydrotreating and hydrorefining requirements vary widely and are difficult to access because of the wide variety of feeds. Hydrogen requirements are significant and the energy used to provide the hydrogen is about equal to other process-energy requirements. One hydrotreating process requires no makeup hydrogen and thus uses about 40% less energy; however, it is restricted to refining those feeds that will generate sufficient hydrogen for the hydrogen-treating reactions. It has not been established how much of the feed being hydrotreated could be treated by this process, but if a portion of 15% were used, and energy to manufacture hydrogen is taken into account, the energy savings is estimated to be 1.2×10^{13} Btu/year.

In alkylation processes sulfuric acid (H_2SO_4) is used twice as frequently as hydrofluoric acid (HF) as the catalyzing agent. One reference indicates that the H_2SO_4 process uses about 14% less energy than the HF process, but liscensors of the HF process claim the HF process uses less energy. Because fractionation equipment is essentially the same for both processes, HF process substitution would consist primarily of modifying or replacing the reactor section. Based on the liscensor information, conversion of half the 1974 H_2SO_4 capacity to HF units would save about 0.6 x 10^{13} Btu/year.

Isomerization is not highly energy-intensive and has such little capacity that it is insignificant in energy conservation studies. Polymerization, although energy-intensive, is not widely used and therefore insignificant relative to energy conservation because it is less than half as efficient as alkylation in producing gasoline from olefin feed and because the alkylation product is more compatible with modern engines.

Equipment

There are many opportunities for decreasing energy consumption in petroleum refineries by adding or changing equipment. The major areas for effecting energy conservation are associated with the furnaces and product-cooling equipment. Other conservation benefits would result from reducing heat losses from equipment and making efficient use of steam.

Furnace design, furnace control, and greater heat recovery from furnaces are areas where conservation could result in a potential for substantial energy savings. If the overall efficiency of two-thirds of the furnace units were improved from 75 to 88% by such means as recovery of energy from flue gas, optimizing excess air, and decreasing convectionradiation losses, fuel consumption would be reduced 10% — a savings of about 13 x 10^{13} Btu/year.

Despite the extensive use of heat exchange in refineries, a large fraction of the heat is rejected in air- and water-cooled heat exchangers. Thus further utilization of heat exchange between process streams or for other heating requirements, especially using the rejected low-temperature heat, warrants further attention. Recovery of one-fourth of the heat energy in cooling streams would result in an estimated energy savings of 10 x 10^{13} Btu/year.

Producing vacuum with mechanical pumps rather than with steam-jet ejectors has the potential for reducing related energy requirements by 75 to 90%, saving about 1.1 x 10^{13} Btu/year.

As previously discussed use of back-pressure turbines in lieu of inefficient condensing turbines has the potential for saving at least 4.7×10^{13} Btu/year.

Recovering energy from high-pressure process streams by letting the pressure down through turboexpanders or hydraulic turbines is applicable whenever the process streams are being reduced at pressure ratios greater than a value of about 2. This practice could save over half of the energy required to provide the high-pressure stream and is applicable to fluid catalytic cracking, hydrocracking, some reforming, hydrorefining, and hydrotreating processes. The estimated savings, assuming application to one-third of the 1974 hydrocracking, hydrorefining, and hydrotreating capacities, is about 1.2×10^{13} Btu/year.

Pumps and motors account for 10 to 15% of refinery energy consumption. Thus a 10% improvement in the efficiency of pumping systems would save about 4.6 x 10^{13} Btu/year.

These equipment-related conservation practices represent a potential energy savings to the refinery industry of about 11%. Other small energyconserving items would include the use of energy-efficient air-cooling towers in place of water cooling, more sophisticated instrumentation and control equipment, generation of electricity with turbines that exhaust at process-steam conditions, and more insulation.

Research and Development Opportunities

Some research and development needs related to petroleum refineries are: further determination of the effect of process parameters on energy consumption in the production of an equivalent or suitable product; development of reliable, instrumented systems to measure important process characteristics and control the processes at optimum conditions; development of improved catalysts; improvement in overall fuel utilization by considering both the efficiency of internal-combustion engines and

the petroleum refining necessary to produce fuel for the engine; and development of equipment and techniques for the beneficial use of lowgrade heat.

Improving the efficiency and reliability of existing processes and equipment, based on economic trade-offs involving capital and fuel costs, is a continuing effort in the refinery industries. Generalized effects of process parameters on energy use are well documented; however, because selecting and controlling the oil-refining process relates to the economic position among competitors, it is doubtful that there does or should exist free exchange of the "fine" effects of process variables. The only obvious ways to stimulate more efficient processes and equipment are through high fuel costs and creation of an energy-conscious as well as economic climate to encourage refiners to emphasize energy efficiency in optimizing process variables and in monitoring and controlling equipment.

Catalysts, used in nearly all refining processes, are related to about two-thrids of oil-refining energy consumption because of their influence on process temperatures, pressures, recycle rates, and product yields. Although current refining processes largely capitalize on the beneficial uses of catalysts, some limited in supply, significant basic catalyst research and development should continue.

Improving the octane rating of gasoline requires considerable energy. Thus analytical studies could be made in which optimized internalcombustion-engine performance as a function of octane rating is balanced with refinery-energy requirements to optimize overall utilization of the fuel. Several similar studies could consider the effect on gasoline quality of various amounts and kinds of antiknock additives. A confirmatory experimental program might also be required.

A fertile area for research and development for many industries besides petroleum refineries is beneficial use of low-grade heat [e.g., less than $149^{\circ}C$ ($300^{\circ}F$)] currently being rejected to the environment through air- and water-cooled heat exchangers. For refineries the amount of reject heat appears to equal at least one-fourth of the energy used to refine the petroleum and thus would represent about 10^{15} Btu/year. Some general areas of research are: inexpensive, efficient heat exchangers; use of absorption refrigeration systems; and low-temperature power generation cycles.

Other Factors

Several other significant factors which affect the energy used to refine petroleum include: the availability of fuel and its price; product specifications; industry standards for products, equipment, operation, and maintenance; quality of crude oil to be refined; and integration of refineries with electric utilities and other industries.

Fuel availability (including allocation) would become a factor of concern to oil refineries primarily in the event of a scarcity of natural gas when other users of natural gas probably would be given a higher priority. Because U. S. refineries use natural gas to supply about a third of their energy, a natural gas shortage would require major substitution of another energy resource and modification or replacement of existing equipment. Possible substitute fuels are refinery products (coke, fuel oils, and gas produced from crude oil), coal, and electricity which could be produced from nearly all resources including emerging ones like nuclear, solar, and geothermal. Increasing the value of fuel in general will motivate refiners to devote more effort to conserving energy.

Changing the relative value or availability of particular fuels could have marked effects on relative consumption of the various resources. Thus, allocation and pricing of fuels can greatly influence petroleumrefinery consumption of particular fuels. Government control through allocation and pricing schemes probably will determine the fuels consumed to refine petroleum. However, a large portion of the energy used to refine petroleum is refinery stream material, and all additional energy for a refinery could be obtained from the feed. Careful consideration also should be given to the end result, relative to energy consumption, of forcing a substitution between fuels. For example, using electricity would result in a lower overall efficiency unless beneficial use were made of the heat rejected in generating the electricity. Coal systems are also likely to be less efficient than a natural-gas system.

Product specifications such as sulfur content, lead content, and octane rating should be examined in detail to determine areas of unnecessary refining.

Standards for equipment and for operation and maintenance should be examined and expanded where necessary to reflect energy-conserving considerations.

Processing heavy crude oil, compared to higher-quality crude oil, requires somewhat greater quantities of energy to produce a given product. The only alternative is, of course, to locate and develop supplies of better-quality crude oil; however, this solution would be only temporary because eventually it undoubtedly will be necessary to use crude oil of all qualities.

Integration of petroleum refineries with electric utilities and other industries under a buy-and-sell arrangement for steam and

electricity is very desirable because much of the heat ordinarily wasted during electric generation could be used. Utilization of fuel would markedly improve and at the same time a highly reliable energy supply would be provided. In addition, a major substitution for oil and natural gas would be possible with other fuels like coal, nuclear, solar, and geothermal.

INDUSTRY DESCRIPTION

The petroleum-refining industry as considered here is defined by the Standard Industrial Classification Manual² under Code SIC-291 as follows:

"Establishments primarily engaged in producing gasoline, kerosine, distillate fuel oils, residual fuel oils, lubricants, and other products, through straight distillation of crude oil, redistillation of unfinished petroleum derivatives, cracking, or other processes."

Although U. S. refinery capacity has increased steadily since 1932, the number of refineries reached a peak in the late 1930s and has since decreased steadily. Figure 3 shows the year-by-year changes since 1930 based on refs. 1 and 3. Reference 1 data for January 1, 1974 show that the 247 U. S. refineries having a total capacity of 14×10^6 bbl/day, vary in capacity from 300 to 445,000 bbl/day. Bureau of Mines data⁴ include 17 additional small refineries considered operable and having a combined crude-oil-processing capacity of 80,000 bbl/day, a negligible portion of industry capacity. In recent years capacity and input have increased in the range of 3 to 4% per year. Refineries seldom shut down and much of the difference between production and full utilization of the plants is attributed to operating with less than maximum feed. Input in 1970-1971 was above 90% of capacity; 1973-1974 input dropped slightly to about 87% of capacity.



Fig. 3. U.S. refinery capacity and number since 1930.

Although small refineries tend both to go out of business and to consolidate into larger refineries, there are still a large number of small refineries in the United States. Nearly half (47%) of the nation's refineries have capacities less than 25,000 bbl/day and account for only 7% of total industry capacity. Forty percent have capacities less than 17,000 bbl/day and account for 5% of total capacity. Similarly, 82% have capacities less than 100,000 bbl/day and account for 40% of total capacity. Thus 60% of the total U. S. refinery capacity is in 18% of the plants (capacities greater than 100,000 bbl/day), 44% of capacity is in 10% of the plants (capacities greater than 150,000 bbl/day) and 32% of capacity is in 6% of the plants (capacities greater than 200,000 bbl/day). Figure 4 shows the size distribution of refinery capacity and refinery number based on the survey of ref. 1.

About 80% of refinery capacity is located along the Gulf Coast, Great Lakes, West Coast, and East Coast — distributed 36, 18, 16, and 10% respectively. Figure 5 shows the distribution of refineries and capacity by both Petroleum Administration for Defense (PAD) districts and by Bureau of Mines (B of M) refining districts⁴ based on ref. 1.

The petroleum-refining industry has experienced gradual but gross changes in its product stream. Kerosine, the major product of early refineries, was displaced by gasoline by 1915. Cracking, reforming, and alkylation processes have been developed to increase the quantity and octane rating of gasoline. Other less dramatic shifts in refinery procudts have occurred in response to demand for jet fuel, distillate fuel oil, residual fuel oil, lubes, asphalt, and petrochemical feedstocks. However, in recent years there have been no dramatic changes in the yield of refined petroleum products from crude oil. About half of the crude



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Fig. 4. Size distribution of U.S. petroleum refineries and refining capacity - January 1974.

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		REFINERY	REFINERY CAPACITY					
DISTRICT	T No. (% OF TOT		(10 ³ m ³ /day)	(10 ³ bbl/day)	(% OF IND.)			
PAD 1	28	11.3	266	1672	11.8			
2	66	26.7	616	3873	27.2			
3	77	31.2	928	5836	41.0			
4	27	10.9	83	520	3.7			
5	49	19.8	368	2315	16.3			
	247		2261	14216				

(a) PETROLEUM ADMINISTRATION FOR DEFENSE (PAD) DISTRICTS



(b) BUREAU OF MINES REFINING DISTRICTS

* INCLUDES ALASKA AND HAWAII

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Fig. 5. Distribution of refineries and crude-oil capacity in the United States - January 1974.

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oil is refined to gasoline; distillate fuel oil, jet fuel, and residual fuel oil account for about one-third of the crude oil; and the remainder is processed into more than a dozen other products.

Factors which could significantly change the product stream are: the supply of natural-gas liquids which represented about 6% of refinery input in 1974; changes in per-capita consumption of gasoline; and natural-gas users switching to fuel oils.

Table 4 gives percentage yields of the refinery products for several recent years.⁵

Products and the specific processes used to produce them vary considerably among refineries, causing the kinds and quantities of energy consumed also to vary markedly. Table 5, based on ref. 1, summarizes general refinery process and production capacities as they are related to refinery size as of 1974. Evaluation of the ref. 1 information also shows that smaller refineries are used more than larger refineries for lube and asphalt production and used less for other processes. The diverse character of petroleum refining practices is illustrated by Fig. 6 based on ref. 1; rather wide variations exist even after specific processes are grouped under general categories and refineries are aggregated into fairly large districts.

The kinds and qualtities of fuel consumed by U. S. petroleum refineries for recent years are given in Table 6. 6

The 3.1 x 10¹⁵ Btu of energy used by petroleum refineries in 1974⁶ represented 4% of U. S. energy consumption, 15% of U. S. industrial consumption, and 12% of the energy content of the crude oil being refined. Industry average energy consumption has decreased slightly in recent years and in 1974 was about 707,000 Btu/bbl of crude oil. Most

Finished products	1966	1967	1968	1969	1970	1971	1972	1973 ^b
Gasoline	44.4	44.0	43.9	44.8	45.3	46.2	46.2	45.6
Jet fuel	6.2	7.5	8.3	8.2	7.5	7.4	7.2	6.8
Ethane (including ethylene)	с	с	с	.2	.2	.2	.2	.2
Liquified gases	3.0	3.1	3.1	2.9	3.0	2.9	2.8	2.8
Kerosine	2.9	2.7	2.7	2.6	2.3	2.1	1.8	1.7
Distillate fuel oil	22.5	22.3	22.1	21.7	22.4	22.0	22.2	22.5
Residual fuel oil	7.6	7.7	7.2	6.8	6.4	6.6	6.8	7.7
Petrochemical feedstocks	2.1	2.4	2.5	2.5	2.5	2.7	2.9	2.9
Special naphthas	.9	.8	.7	.7	.8	.7	.7	.7
Lubricants	1.8	1.8	1.7	1.7	1.6	1.6	1.5	1.5
Wax	.2	.2	.2	.2	.2	.2	.1	.2
Coke	2.5	2.5	2.5	2.6	2.7	2.6	2.8	2.9
Asphalt	3.8	3.5	3.6	3.5	3.6	3.8	3.6	3.6
Road oil	.2	.2	.1	.2	.3	.2	.2	.2
Still gas	3.9	3.9	4.0	4.1	4.1	3.8	3.9	3.9
Miscellaneous	.5	.4	.4	.4	.3	.4	.4	.4
Shortage	- 2.5	- 2.9	- 3.0	- 3.1	- 3.2	- 3.4	- 3.3	- 3.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 4. Percentage yields of refined petroleum products from crude oil in the United States^a

^aOther unfinished oils added to crude in computing yields.

^bPreliminary.

^CIncluded with liquified gases.

Source: U.S. Department of the Interior, Bureau of Mines, Minerals Yearbook - Metals, Minerals, and Fuels, Vol. I, Washington, D.C., 1970, p. 888, and 1973, p. 982.

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Process	Percent of U.S. refineries ^a /percent of U.S. crude-oil capacity ^a for refinery size ranges (10 ³ bb1/day) of:						
riocess	0-25	25-50	0-50	50-100	100-450	0-450	
Vacuum distillation	46.1/23.0	76.1/28.8	54.7/26.6	95.2/32.0	100.0/39.1	70.0/35.2	
Thermal processes ^b	15.7/ 4.6	34.7/ 5.7	21.1/ 5.3	57.1/10.6	75.0/10.0	36.8/ 9.3	
Catalytic cracking	20.9/12.4	71.7/28.2	35.4/22.1	97.6/31.4	93.2/30.1	56.3/28.9	
Catalytic reforming	41.7/10.3	84.8/18.6	54.0/15.3	100.0/22.4	100.0/22.5	70.0/21.2	
Catalytic hydrocracking	2.6/ 0.6	13.0/ 2.4	5.6/ 1.7	14.3/ 3.4	56.8/ 7.3	16.2/ 5.4	
Catalytic hydrorefining	4.3/ 1.4	21.7/ 4.4	9.3/ 3.3	35.7/12.8	40.9/ 7.3	19.4/ 6.4	
Catalytic hydrotreating	31.3/10.0	87.0/24.4	47.2/18.9	97.6/31.7	100.0/32.8	65.2/29.9	
Alkylation	13.0/ 1.8	69.6/ 5.7	29.2/ 4.3	95.2/ 6.1	90.9/ 5.4	36.8/ 5.3	
Aromatics/isomerization ^C	2.6/ 0.2	15.2/ 0.7	6.2/ 0.5	45.2/ 3.0	47.7/ 2.3	20.2/ 2.2	
Lube production	13.0/ 2.8	8.7/ 0.3	11.8/ 1.2	7.1/ 0.4	38.6/ 1.7	16.2/ 1.3	
Asphalt production	36.5/10.6	58.7/ 7.2	42.9/ 8.5	38.1/ 3.6	59.1/ 3.3	44.9/ 4.3	
Coke production	4.3/ 0	21.7/ 0	9.3/0	30.9/ 0	52.2/ 0	20.6/ 0	

Table 5. Distribution of U.S. refinery process and product capacities relative to refinery size - January 1974

^aPercent by size range - not percent of all refineries.

^bCracking; visbreaking, coking.

^cBTX; hydroalkylation; cyclohexane; C_4 feed; C_5 feed; C_5 and C_6 feed. Production capacity.



Fig. 6. Frequency of refinery processes by district - January 1974.

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	Energy (10 ¹² Btu/year) consumed for the years:						Percent of		
Fuel	1962 1964		1966	1968	1970	1972 1973		1974	energy for 1974
Fuel oil	262.3	266.9	251.1	263.2	267.1	276.3 ^a	309.1	316.3	10.1
Acid sludge	1.6	1.2	0.9	0.5	0.3	Ъ	Ъ	Ъ	b
Gas LP Refinery Natural	1701.0 23.7 847.9 829.4	1685.0 45.0 785.6 854.4	1783.2 9.5 841.4 932.3	1942.5 23.7 91 3.6 1005.1	2070.5 16.2 993.6 1060.7	2169.8 53.8 1043.0 1073.0	2220.2 40.7 1072.5 1107.0	2154.9 39.5 1043.1 1072.3	68.9 1.3 33.3 34.3
Coke	309.1	321.5	322.2	325.7	313.6	338.3	400.0	374.0	11.9
Coal	19.1	21.2	25.7	19.2	12.4	8.1	7.9	5.2	0.2
Purchased electricity ^C	114.2	126.7	126.5	163.7	194.7	226.1	233.8	231.0	7.4
Purchased steam ^d	25.0	27.0	25.8	29.6	33.0	45.1	45.2	47.6	1.5
Total	2432.3	2449.5	2535.4	2744.4	2891.6	3063.7	3216.2	3129.0	
(Btu/bb1) ^e	792	756	735	727	729	716	70 9	707	

Table 6. E	Inergy consumed	at U.S.	petroleum	refineries
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^aIncludes 2.6 x 10¹² of crude-oil consumption.

^bIncluded in fuel oil.

^CAssumes 10,000 Btu/kWhr.

^dAssumes 1333 Btu/1b steam.

^eValues are about 5% higher than referenced data because of adjustment of purchased energy by efficiency factors. Only barrels of crude input used; total barrels input is about 8% higher because of unfinished rerun, natural gas liquids, and other hydrocarbons.

Source: U.S. Department of the Interior, Bureau of Mines, Mineral Industry Surveys, Crude Petroleum, Petroleum Products, and Natural-Gas-Liquids, Washington, D.C., 1962-1973 (final summaries) and April 1974 (monthly statement). of the energy is consumed at the refinery by burning natural gas and refinery gas, and slightly more than half of the energy is from refinery products. For example, 57% of the energy in 1974 was from refinery products — distributed about 60% from refinery gas, 20% from oil and LPG, and 20% from coke. About one-third of the energy comes from natural gas, and a trace (<0.3%) comes from coal. A small amount of energy (purchased electricity and steam) comes from oil, gas, coal, nuclear fuel, and hydropower.

A large regional variation exists in both the amount of energy consumed per unit of crude oil processed and in the kinds of fuel used. Appalachian No. 1 is the only district using a significant amount of coal. Use of natural gas is noticeably less in East-Coast, Appalachian, and North-Midwest districts, where the gas is being replaced primarily by fuel oil. Texas refineries use considerably more natural gas than do other refineries and rank highest in the amount of energy used per barrel, partially because of a higher-than-average amount of refining and probably because of past economic decisions based on inexpensive fuel. Table 7, based on ref. 6, shows the average energy consumption of various fuels per unit of crude oil and the large regional variation of energy consumption in 1974. The kinds of fuel used in each district from 1961 to 1973 are given in Appendix A.

Fuels are used to fire furnaces that heat the materials being processed; to run gas turbines; and to generate steam for injection into the process stream, for operating vacuum jets, for operating steam turbines, for operating steam pumps, and for heating via heat exchangers. About 20% of the electricity used by refineries is generated at the refinery. Most steam is generated at the refinery, but in six of the 13 Bureau of Mines districts a small amount of steam is purchased.

District	Energy consumption (10 ³ Btu/bb1) of:										
	Distil- late	Residual	LPG ^a	Natural Gas	Refinery Gas	Coke	Coal	Purchased Electricity	Purchased Steam	Total	
1		7.3	190	2.3	62	228	103		46	32	671
2		50	206	29	73	195	39	80	80	1.5	754
3			115	13	64	163	97	20	58		530
4		4.4	131	9,3	55	235	103		52		590
5			110	0.9	26	183	104		49		473
6	0.3	1.6	27	5.9	274	242	75		45		671
7		5.0	10	4.4	379	220	121		60	0.2	800
8		5.4	1	2.2	524	223	83		39		878
9		23	14	12	21 1	259	49		50	31	649
10	0.9	31	38	16	261	151	35		28		561
11			15	35	246	159	56		29		540
12		3.5	89	8.2	171	224	109		48		653
13		11	41	21	189	265	81		83	21	712

Table 7. Energy consumption per unit of crude oil in U. S. petroleum refineries by Bureau of Mines Districts - 1974

a Liquified petroleum gas.

Substitution among fuels is feasible and likely to occur as the relative prices and availability of fuels shift. For example, the introduction of new equipment could shift fuel-oil and natural-gas consumption to coal consumption. Modifying existing equipment so that coal can be used generally is impractical.

REFINING PROCESSES

General

Energy requirements for petroleum refineries vary rather widely because of the crude-oil composition, the processes and equipment used, and the products. Heavy crude oils require somewhat more energy to be refined than do light crude oils to yield similar products; likewise, high-sulfur crude oils require more energy than do low-sulfur crude oils. Energy requirements also increase as there is an increase in products such as lubricants, high-octane gasoline, and petrochemical feedstocks, and processes and equipment also affect energy requirements.

Modern refineries are reducing energy requirements by: using heat exchange; using more insulation; more effectively controlling combustion; recovering heat from exhaust gases; eliminating straight condensing-steam turbines; using back-pressured steam turbines; and using turboexpanders to "let down" process streams. Some refiners have established task groups to reduce energy consumption; reduction goals are on the order of 5% per year.

The purpose of this section is to indicate approximate refinery energy requirements and possible opportunities to conserve energy. Further information about the various processes is given in Appendix B.

For some processes only a representative energy-requirement value is given; for others a range of values is given. In all cases a representative value was used to estimate the potential for saving energy. Steam requirements were converted at the rate of 1333 Btu/1b, and electricity was converted at 10,000 Btu/kWhr. When fuel energy was given as heat absorbed, an efficiency of 75% (based on low-heating value) was used to determine fuel consumption. The energy savings estimated for this report are based on the following:

- 1. The process rate according to the 1974 values of ref. 6.
- 2. A 10% fuel savings by better furnace designs and control and by more use of heat recovery, based on literature articles^{7,8} and assuming that two-thirds of the units have efficiencies that can be improved from about 75 to 88%.
- 3. Recovery of energy by additional heat exchange between process streams before heat is rejected to the environment. The average temperature of energy entering the coolers is assumed to be $149^{\circ}C$ ($300^{\circ}F$). A reduction of this temperature to $121^{\circ}C$ ($250^{\circ}F$) is used to estimate the savings.⁹
- 4. Use of hydraulic turbines and more efficient prime movers to increase the energy efficiency from 30 to 70% on one-third of the applicable capacity requirements, giving a 20% savings of these electrical energy requirements.

Radiation-convection heat losses from refinery equipment and piping is common to all processes. In general, insulation has been provided based on an economic trade-off of the cost of the insulation vs the value of the heat. Even though the value of energy has been relatively low, a large fraction of the potential (uninsulated) heat loss has been eliminated. Still remaining is a potential for a small, economically justifiable energy savings based on a higher value of energy. Insulation requirements for new refineries can be expected to be based on higher energy values than in the past; additional insulation of existing refineries can be expected only where it is practical and economically justified. Quantitative estimates indicating the magnitude of radiationconvection losses and potential savings, based on a large modern refinery, are given for a few of the processes. The estimates indicated that, if refineries have provided enough insulation to limit surface temperatures to about $67^{\circ}C$ ($150^{\circ}F$), additional insulation to reduce surface temperatures to about $32^{\circ}C$ ($90^{\circ}F$) represents a rather small potential for energy savings relative to other items. Thus savings from insulation improvement are ignored for the other processes.

Electricity requirements for instrumentation and lighting of process areas are small compared to other electrical requirements for the process. Likewise, because most of the equipment is unenclosed, there is no significant space heating or cooling requirement for the processes. These miscellaneous requirements for electricity are considered to be small enough that their inclusion or exclusion in the consumption values for a process would not have an important effect. Moreover, they are amenable to generally known conservation measures such as reduction of light intensity within safe and legal limits and adjustment of temperature and humidity controls to levels requiring less energy.

Refiners often refer to the combined processes of desalting, atmospheric distillation, vacuum distillation, and gas separation as "crude distillation," but in this study these processes are considered separately.

Desalting

Energy requirements for desalting are quite low, consisting of: energy to pump the oil through the desalting system and to inject water into the system; heat to raise the oil and water temperature to about $121^{\circ}C$ (250°F); and electricity to maintain the high-potential electric field. Heating the oil to $121^{\circ}C$ will require about 30,000 Btu/bbl, but here this amount is included in the distillation requirements (heat losses from the desalting system are considered a desalting-process requirement). Crude-oil pumping energy is about 0.04 kWhr/bbl; pumping energy required to add water depends on the salt content of the crude oil. Low-salt crude oil requires about 1 vol % of water whereas high-salt crude oil may require water equal to 50% of the crude oil volume. As an example, the pumping energy required for desalting on a 5 vol % basis is about 0.01 kWhr/bbl.

The energy requirement for the high-potential electrical field is about 0.01 kWhr/bbl.

Assuming that most refineries have some insulation installed, the heat loss is estimated to be about 50 Btu/bbl. If half of this total were saved and if 80% of the crude-oil input were desalted, savings based on the 1974 processing rate would be about 10^{11} Btu/year.

If not being practiced, the recovery of energy from discharged brine by heat exchange to inlet feed (water or oil) would conserve energy. For example, if half of the energy in the discharged brine were utilized when 5 vol % of water is used for desalting, about 2500 Btu/bbl would be conserved, amounting to 10^{13} Btu/year.

Other energy-conserving techniques associated with desalting, such as reducing pump energy by means of lower pressure drops and more efficient pumps, probably would be of very low priority and perhaps be uneconomical. Alternative measures might include longer storage periods and/or use of only chemicals to promote separation of salts from the oil. However, the small amount of energy required for the high-potential field appears to be easily justified.

Atmospheric Distillation

Energy requirements for atmospheric distillation consist of fuel to heat the crude oil, steam to be injected into the atmospheric tower and stripper, and energy to pump the fluids. Energy required to heat the crude oil depends on the extent of heat exchange, percent vaporized, and composition of the feed. Typically the required temperature increase supplied by furnace heat will be 66 to $135^{\circ}C$ (150 to $275^{\circ}F$) and will require 25,000 to 85,000 Btu/bbl of crude oil.³ Allowing for pipe-still efficiency results in an estimated fuel input (usually gas) of 35,000 to 145,000 Btu/bbl. Reboiling of reflux requires additional heat as shown by Table 8. Data from a large modern refinery indicate that about 80,000 Btu of fuel energy is required per barrel to vaporize 45% of a medium-gravity feed. Most of the electrical energy is used to pump the crude oil, the products, and the reflux, and to power the air-cooled heat-exchanger and air-preheat fans. The electricity required is about 0.06 kWhr/bbl.

Reflux ratio based on top product		at input (H ccentage va 40		
1	5,000	10,000	16,000	21,000
3	15,000	31,000	47,000	62,000
5	26,000	52,000	78,000	103,000
10	52,000	103,000	154,000	206,000

Table 8. Heat input for refluxing

Source: W. L. Nelson, *Guide to Refining Costs*, 2nd ed., The Petroleum Publishing Company, Tulsa, Okla. (1970), p. 35.

Steam requirements vary markedly depending on the crude-oil gravity and the fraction vaporized. Steam at 100 to 150 psig with some superheat at a typical rate of 1 to 2 and 4 to 8 lb/bbl may be used in the atmospheric column and stripper respectively.

Energy requirements for atmospheric distillation of crude oil in a plant making liberal use of heat exchange and air preheat are approximately as follows:

	Energy requirement	Process	temperature
	(Btu/bb1)	(°C)	(°F)
Electricity ^a	6,000		
Fuel	80,000	375	675
Steam	10,000	260	500
TOTAL	96,000		

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

Energy is lost from the atmospheric distillation system as: heat in the flue gases from the tube still; convection-radiation losses from the system; heat rejected by air- and water-cooled heat exchangers; and heat in blowdown water. Heat lost with the flue gas depends on furnace design, excess air, temperature of the charge, air preheat, and to a lesser extent the type of fuel (oil or gas). Gas is the preferred fuel because the flames radiate less intensely and because the burners are less expensive.¹⁰ If not being practiced, the recovery of heat from the flue gas, such as by preheating the combustion air or generating steam, can markedly improve energy efficiency.

Convection-radiation losses from the system are primarily from the pipe still (equivalent to 3 to 4% of the fuel heat); other potential losses are from the atmospheric tower and associated high-temperature piping (up to 700° F). Insulation usually is provided and will limit the equipment and piping losses, excluding losses from the furnaces, to about 700 Btu/bbl of feed. Thus a potential energy savings could result by using more insulation.

Air- and water-cooled heat exchangers are used to cool the recycle and product streams, such as saturate gas, naphtha, kerosine, and fuel oil. Atmospheric-tower residual can be transferred to a vacuum distillation system without cooling. Typically the atmospheric distillation portion of a modern integrated refinery rejects 35,000 Btu/bbl via the air-cooled heat exchangers used to cool product streams varying from 93 to 149° C (200 to 300° F). Thus these streams are potential supplies of low-temperature heat.

Blowdown water mainly comes from steam injected into the process stream, and because it is discharged at a low temperature [$\sim 38^{\circ}C$ ($100^{\circ}F$)] it does not represent a significant heat loss.

Apparently no competitive process exists to replace atmospheric distillation for primary separation. Opportunities to conserve energy in this process include improved insulation; optimization of equipment design and operation parameters (i.e., more fractionating trays, increased flooding of trays, and less refluxing); full use of heat exchange; and careful analysis and control of the process to preclude "overrefining."

Potential savings of energy in the atmospheric-distillation process are estimated for the 1974 process rate as follows:

Conservation measure	Savings (10 ¹³ Btu/year)
Better furnace design and control and more use of heat recovery (10% of consumption)	4.0
Improved fractionation (5000 Btu/bbl less energy)	2.2
Recovery and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	3.9
Better insulation (350 Btu/bbl)	0.2
TOTAL	10.3

This total is about 3.2% of the energy used for refining petroleum.

Vacuum Distillation

Energy requirements for vacuum distillation consist of fuel to heat the feed, reboil heat, motive steam for steam jet-ejectors and possibly for injection into the vacuum tower, and energy to pump the fluids. Feed to the vacuum still must be 399 to 427° C (750 to 800° F), a temperature range 66 to 93° C (150 to 200° F) hotter than the temperature of the residual discharged from the atmospheric column. The heat required also depends on the composition of the residual, the degree of vaporization desired, and the vacuum employed. Heating the feed will require 40,000 to 60,000 Btu/bbl of feed and, allowing for efficiency, the fuel (usually gas) input will equal 60,000 to 90,000 Btu/bbl of feed. Steam for operating steam jets at 100 to 150 psig depends on the quantity of noncondensibles that must be removed, a figure which in turn depends on whether or not steam stripping is used and on the amount of leakage into the system. When steam is injected into the tower, the minimum pressure is limited by the temperature of the condensing water. Other factors affecting steam-jet consumption are the design, the matching of operating conditions with the design, the desired vacuum, and the temperature of the condensing system. Although consumption can vary considerably, typical steam-jet usage is 5 lb of 100- to 150-psig steam per barrel of feed. This value is based on a two-stage ejector providing a 75-mm-Hg pressure when handling about 1.5 lb/bbl of noncondensibles.

Process steam is sometimes used to enhance the fractionation; the amount required varies widely depending on the pressure (vacuum), percent vaporized, and feed composition. Typically 7 to 12 pounds of 100- to 150-psig steam is required per barrel of feed.

Most of the electrical energy is used to pump the feed, the products, and the recycle and to power the air-cooled heat-exchanger and airpreheat fans. The electricity requirement is about 0.3 kWhr/bbl of feed.

Approximate energy requirements for vacuum distillation of the residual from atmospheric columns are as follows:

	Energy requirement (Btu/bbl feed)	Process (^o C)	temperature (⁰ F)
Electricity	a 3,000		
Fuel	75,000	413	775
Steam			
Jets	9,000	260	500
Process	13,000	260	500
TOTAL	100,000		

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

Energy is lost from the vacuum distillation system as: heat in the flue gases from the tube still; convection-radiation losses from the system; heat rejected by air- and water-cooled heat exchangers; and heat in blowdown water.

Heat lost in the flue gas depends on furnace design, excess air, temperature of the charge, air preheat, and to a lesser extent the type of fuel (oil or gas). Gas is the preferred fuel because the flames radiate less intensely and because the burners are less expensive.¹⁰ If not being practiced, recovery of heat from the flue gas, such as by air preheat or generation of steam, can markedly improve energy efficiency.

Convection-radiation losses from the system are primarily from the pipe still (equivalent to 3 to 4% of the fuel heat); other potential losses are from the vacuum tower and associated high-temperature piping. Insulation usually is provided and will limit the equipment and piping losses, excluding losses from the furnace, to about 700 Btu/bbl of feed. Thus a potential energy savings could result by using more insulation. Air- and water-cooled heat exchangers are used to cool recycle and product streams. Residual can be transferred for further processing, such as to the coker, without cooling. Typically the vacuum distillation portion of a modern integrated refinery would reject about 25,000 Btu/bbl of feed via air-cooled heat exchangers used to cool product and recycle streams varying from 121 to $177^{\circ}C$ (250 to $350^{\circ}F$). Thus these streams are potential supplies of low-temperature heat. An additional 9,000 Btu/bbl of feed is rejected to produce the vacuum. Assuming proper design and operation of the steam jet system, conserving energy can be achieved only by using different kinds of equipment to produce the vacuum.

Water is blown down from the steam-ejectors, and steam is sometimes injected into the process stream. But heat lost beyond the amount accounted for in the condensers is not significant.

Apparently no competitive process exists to replace vacuum distillation. Opportunities to conserve energy in this process include improved insulation, optimization of equipment design and operation parameters, and full use of heat exchange.

Use of mechanical pumps to evacuate the system would reduce energy requirements substantially. Capital and maintenance costs would be higher, but a considerable compensating savings in energy costs would result. Mechanical vacuum pumps would use 70 to 90% less energy than would steam jets, ¹¹ but adequate reliability would have to be demonstrated before refiners would be willing to consider a substitution.

Potential savings of energy in the vacuum-distillation process are estimated for the 1974 process rate as follows:

	S	avings
Conservation measures	(10 ¹³	Btu/year)
Better furnace design and control and more use of heat recovery (10% of consumption)		1.4
Improved fractionation (5000 Btu/bbl less energy)		0.8
Recovery and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers		1.5
Mechanical vacuum pumps (80% savings)		1.1
Better insulation (350 Btu/bbl feed) TOTAL		<u>0.1</u> 4.9

This total is about 1.3% of the energy used for refining petroleum.

Gas Separation

Energy requirements for the gas separation system consist of heating the feed and recycle streams and pumping the fluids through the system. Using the system shown in Fig. B.4 of Appendix B, feed to the debutanizer (cooled overhead from the atmospheric tower) is heated to about $149^{\circ}C$ $(300^{\circ}F)$ by heat exchange. Additional heat is added to the debutanizer tower by a circulating side stream. Overhead from the debutanizer is cooled, vented, and then fed to the depropanizer, the bottom fraction from the debutanizer is transferred to a gasoline splitter. In the depropanizer the propane is separated from the butane. The depropanizer feed is heated by heat exchange and additional heat is added to a circulating side stream. In the gasoline splitter the gasoline is separated into light and heavy components.

Steam may be used as the source of heat. As an example, the system shown in Fig. B.4 would require about 6.4 and 40 pounds of $260^{\circ}C$ ($500^{\circ}F$),

150-psig steam per barrel of feed for the depropanizer and gasoline splitter respectively.

Most of the electrical energy is used to pump the feed, the products, and the recycle and to power the air-cooled heat-exchanger fans.

Approximate energy requirements for gas separation are as follows:

	Energy requirement	Process temperature		
	(Btu/bb1 feed)	(°C)	(^o F)	
Electricity ^a	1,800			
Fuel or steam	62,000	260	500	
TOTAL	64,000			

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

In a plant using heat exchange to heat the feed, energy is mainly required by the reboilers to heat recirculating side streams of the fractionation towers. For example, providing this heat to the depropanizer and gasoline splitter requires about 43,000 Btu/bbl of feed to heat the streams to 121 to 149° C (250° to 300° F). Thus these are opportunities to provide energy by heat exchange from streams above 204° C (400° F).

Energy is lost from the saturate-gas-separation system as: convection-radiation losses from the system and as heat rejected by airand water-cooled heat exchangers.

Insulation usually is provided and will limit the convectionradiation losses from the equipment and piping to about 2000 Btu/bbl of feed. Thus a potential energy savings could result by using more insulation.

Air- and water-cooled heat exchangers are used to cool the recycle and product streams. Here this total equals about 80,000 Btu/bbl of feed. The fluids being cooled range in temperature from 77 to 110° C (170 to 230° F) and thus are potential supplies of low-temperature heat.

No apparent competitive process exists to replace the fractionation system. Opportunities for energy conservation in this process are improved insulation, optimization of equipment design and operation parameters (e.g., less refluxing), and full use of heat exchange. Providing more plates allows less refluxing for a given separation, and fractionation systems are designed with a trade-off between the number of plates and the reflux ratio. Refluxing is energy-intensive because it requires energy for the reboilers and energy removal in the condensers. Thus energy conservation is possible through capital expenditures for more trays.

Potential savings of energy in the gas-separation process are estimated for the 1974 process rate as follows:

Conservation measure	Savings (10 ¹³ Btu/year)
Better furnace design and control and more use of heat recovery (10% of consumption)	0.27
Recovery and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	0.91
Improved fraction (5000 Btu/bbl less energy)	0.22
Better insulation (1000 Btu/bbl feed) TOTAL	$\frac{0.04}{1.4}$

This total is about 0.5% of the energy used for refining petroleum.

Cracking

Thermal cracking and visbreaking

Energy requirements for a thermal-cracking system consist of fuel to heat the feed, energy to pump the fluids (sometimes steam-driven pumps), and sometimes steam to be used for stripping. Feed to the unit coming directly from the crude-oil distillation system would be at a temperature of about 371° C (700° F). Heat exchange in the fractionator recovers some of the heat from product streams. Energy reported to be required for the thermal-cracking process varies widely, partly because of the temperature of the feed to the process (i.e., feed which must be heated from ambient to process temperatures will require about 200,000 Btu/bbl more heat from fuel than feed which is transferred directly from the distillation unit at a high temperature) and the amount of recycling and refluxing practiced.

Energy consumption by a visbreaking unit is similar to that for a thermal-cracking unit, but somewhat less because of less recycling, and some steam is used to produce the vacuum (if vacuum fractionation is practiced).

Reported energy requirements for thermal cracking are as follows:³

	Energy requirement	Process t	emperature
	(Btu/bbl feed)	(°C)	(^o F)
Electricity ^a	6,000 to 24,000		
Fuel	400,000 to 1,000,000	521	970
Steam ^b	67,000 to 256,000	260	500
TOTAL	470,000 to 1,300,000		

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

^bAssumes feed, bottom, and recycle pumps are steam-driven.

	Process temperatur			
	Ref. 3 ^a	Ref. 12 ^b	(°C)	(⁰ F)
Electricity ^C	400 to 4,300	18,000		
Fuel	125,000 to 210,000	260,000	482	900
Steam	19,000 to 39,000	<u>-107,000^d</u>	260	500
TOTAL	144,000 to 253,000	171,000		

Energy requirements for visbreaking from two sources are as follows:

^aW. L. Nelson, *Guide to Refining Costs*, 2nd ed., The Petroleum Publishing Company, Tulsa, Okla. (1970), p. 87.

^b1974 Refining Process Handbook, Hydrocarbon Processing, vol. 53 (9), Gulf Publishing Company, Houston, Tex., September 1974, p. 123.

^CElectricity converted to energy requirement based on 10,000 Btu/kWhr.

^d9,000 Btu/bbl used for steam-jet ejectors and 116,000 Btu/bbl produced by the process.

Date from an industrial source are as follows:

	Energy requirement (Btu/bbl feed)
Electricity ^a	5,000
Fuel ^b	110,000
Steam	
Pumps	9,000
Process	8,000
TOTAL	132,000

^aElectricity converted of energy requirement based on 10,000 Btu/kWhr.

^bAnother 25,000 Btu/bbl was obtained by heat exchange with another refining process.

Although potential savings of energy from conservation techniques or use of alternate thermal-cracking or visbreaking processes are uncertain, an estimate based on mid-range requirements and the 1974 process rate is as follows:

Conservation measure	Savings (10 ¹³ Btu/year)
Better furnace design and control and more use of heat recovery (10% of consumption)	
Thermal cracking	0.53
Visbreaking	0.10
Improved fractionation (5000 Btu/bb1)	0.06
Mechanical vacuum pumps (80% savings)	0.05
Recovery and use of one-fourth of the low-grade heat	0.09
rejected by air- and water-cooled heat exchangers	
TOTAL	0.83

This total is about 0.3% of the energy used for refining petroleum. Coking

Energy requirements for delayed coking consist of steam for driving the water-jet pumps (used to remove coke from the soaking drums and sometimes to drive feed pumps), fuel for the heater, and electricity for other pumps. Sometimes steam is also used for reboiling in the fractionator section.

Energy requirements for fluid coking consist of steam for fluidizing the reactor bed (and for gasification in the alternate version) and sometimes for driving feed pumps. Electricity is also used for pump drives. No external fuel supply is required for process heating and a net production of steam can result.

The substantially lower energy consumption shown for the fluid process is misleading because energy is supplied by burning coke produced in the process. Overall differences in energy consumption probably are not significant, and the choice has been influenced by the kind of coke desired and other considerations such as maintenance and operating continuity.

Approximate energy requirements for coking are as follows:

	Ener	gy require	ement	Proce	ss te	mpera	ture
		(Btu/bbl feed)		Delayed		Fluid	
	Delayed	Fluid ^a	Fluid ^b	°c	°F	°c	°F
Electricity ^C	70,000	15,000	160,000				
Fuel	80,000	0	0	499	930	538	1000
Steam	45,000	100,000	-134,000	399	750	260	500
TOTAL	195,000	115,000	26,000				

^aWithout gasification.

^bWith gasification.

^CElectricity converted to energy requirement based on 10,000 Btu/kWhr.

The extent to which a representative refinery might utilize the waste energy from coking units is unknown and dominates any attempt to estimate potential energy conservation. A limiting-type value based on the extent of coking in 1974, on the energy requirements, and on the assumption of a 10% savings, is 0.5×10^{13} Btu/year - less than 0.2% of petroleum refinery consumption.

Catalytic cracking

Energy requirements for catalytic-cracker units consist of energy to pump the feed, recycle, and products — including air to supply the regenerator and to move the catalyst. In the airlift (moving-bed unit) and sometimes fluid-bed units, fuel is used to heat the feed before it moves to the reactor vessel and steam is generated in cooling the catalyst. In the fluid-bed process the hot, regenerated catalyst supplies some and often all of the energy to heat the feed. The catalyst is regenerated at a temperature of 566 to 760°C (1050 to 1400°F) at pressures of 10 to 30 psig. Steam is used to strip the hydrocarbon products from the catalyst and sometimes is used in the fractionator system.

Flue gas from the regenerator is pressurized, hot, and combustible - conditions which provide opportunities for recovering energy and which if fully exploited could make FCCU net energy-generators.

Approximate energy requirements for catalytic cracking are as follows:

	Energy requirement	Process t	emperature
	(Btu/bbl feed)	(°C)	(^o f)
Airlift cracker ^a			
$Electricity^{b}$	22,000		
Fuel	140,000	482	900
Steam	- 67,000	260	500
Total	95,000		
FCUU			
$Electricity^{b}$	50,000		
Steam	35,000	260	500
Total	85,000		
FCUU ^C			
$Electricity^{b}$	57,000		
Fuel	50,700	482	900
Steam	-177,000	260	500
Total	- 69,000		

^aSource: 1970 Refining Process Handbook, Hydrocarbon Processing, Vol. 49 (9), Gulf Publishing Company, Houston, Tex., September 1970, p. 174.

^bElectricity converted to energy requirement based on 10,000 Btu/kWhr.

^CIndustry source estimate for a new, large refinery.

Airlift-type catalytic crackers appear to use more energy than fluid-bed-type crackers — the previous tabulation indicates about 12% more. Nelson data,³ although indicating considerably higher energy requirements for both types of crackers, also shows the air-lift type requiring about 12% more energy. Assuming 10,000 Btu/bbl savings and the 1974 process rate, replacing air-lift crackers with FCCU would conserve about 0.9 x 10^{12} Btu/year or about 0.03% of the energy used to refine petroleum.

Improvements in energy use of catalytic crackers, relative to the energy requirements for a large new refinery, indicate a substantial potential for energy conservation. Presumably required would be the use heat-recovery equipment like heat exchangers, air preheaters, CO boilers, and turboexpanders. Potential savings of energy based on the previously tabulated information are about 20 x 10^{13} Btu/year, or 8.2% of the energy used to refine petroleum. However, because of the uncertainty in determining the comparative amount of energy used from burning the carbon during regeneration, it is impossible to specify what percentage of this total represents a feasible savings. For the summary of this report, three-fourths of this amount is used.

Hydrocracking

Energy requirements clearly can vary considerably with the feed and product requirements. Literature information indicates a total requirement, excluding hydrogen, in the range of 240,000 to 400,000 Btu/bbl of feed. The energy requirement for the moving-catalyst bed is the lowest reported, but whether or not this value is actually because of this process characteristic is unclear. Althouth the reactions are

exothermic (55 to 70 Btu/scf of hydrogen absorbed), fuel is used to heat the hydrogen and feed streams. Heat is absorbed by the cold recycle gases and liquids, and heat exchange is used within the process. Energy is also required to pump the feed and products and to compress the hydrogen — this usage is equated to the electrical requirement. Sometimes steam is used for stripping in the fractionator section. In the following estimate, energy for manufacturing hydrogen used in the hydrocracker is based on a consumption and recycle of 1750 and 12,000 scf of hydrogen per barrel of feed respectively. In the hydrogen manufacturing process fuel is required to heat the feed and electricity is required to drive the pumps and compressors; it is assumed that steam is furnished by a waste-heat boiler at a "break-even" condition.

Approximate energy requirements for hydrocracking, with and without energy required for the hydrogen consumed, are as follows:

	Energy requirement	Process t	emperature
	(Btu/bbl feed)	(°C)	(^o F)
Electricity ^a	· · · · · · · · · · · · · · · · · · ·		
Hydrocracking	100,000		
Hydrogen	19,000		
Fuel	-		
Hydrocracking	200,000	380	716
Hydrogen	388,000		
Steam			
Hydrocracking	13,000	260	500
Subtotal			
Hydrocracking	313,000		
Hydrogen	407,000		
nyarogen			
TOTAL	720,000		

^aPumps and compressors electrically driven. Electricity converted to energy requirement based on 10,000 Btu/kWhr.

This tabulation assumes electric drives for the pumps and compressors, used mainly to compress the hydrogen. Some of this energy could be supplied from engines, turbines, or turboexpanders.

Hydrocracking is an energy-intensive process that converts most of the heavier portion of petroleum into more valuable, lighter materials. A large portion of the total energy demand is used to produce the hydrogen consumed in the process. Thus a judgment is made after weighing the utilization of the crude oil against the overall market for the many refinery products. A mitigating effect is the concurrent sulfur and nitrogen removal accomplished by the process.

At least seven variations of hydrocracker units exist. The main process difference is the fixed-bed vs the moving-catalyst-bed concepts, and whether or not this difference has a significant effect on energy consumption is unclear. Moving-catalyst units do not require elaborate "quench" systems, but they must maintain the catalyst and the feed in a fluidized condition. They also keep the catalyst in an active state by continuous withdrawal of spend catalyst and replacement with fresh catalyst. This practice not only avoids accumulation of solids on the catalyst, an occurrence which would result in plugging of the fixed-bed units, but also allows the catalyst to be more effective. Even though one small moving-catalyst-bed unit has been in operation for 12 years, this type of process has not been widely accepted; only one other U. S. unit and three foreign units are reported to exist.¹²

Potential savings of energy, with and without hydrogen manufacturing, are estimated for the 1974 processing rate as follows:

		Savings (Btu/bbl feed)		
Conservation Measure	Without H ₂	With H ₂		
Better furnace design and control and more use of heat recovery (10% of consumption)	0.5	1.4		
Recovery and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	2.0	3.5		
Use of hydraulic turbines and more efficient energy systems, e.g., turbines using the discharge as useful energy (one-fifth of electrical energy)	0.5	0.5		
TOTAL	3.0	5.4		

Not including conservation relative to hydrogen manufacture, this is 0.9% of the energy for refining petroleum; with hydrogen manufacture included, it is 1.7%.

Catalytic Reforming

Energy requirements for catalytic reforming consist of fuel to heat the feed and recycled hydrogen and energy to pump the feed, recycled hydrogen, and coolants. Feed and hydrogen entering the reactors must be at a temperature of 450 to 540° C (842 to 1004° F) and, because the predominate reactions in the first two reactors are endothermic, heat must be added to the process stream between reactors. In the last reactor(s) the balance between endothermic and exothermic reactions is more equalized. The amount of hydrogen recycle depends on the required hydrogen-to-oil ratio. This ratio affects energy consumption because of the circulation and heating requirements shown in the following tabulation:¹³

Hydrogen-to-oil mole ratio	6:1	8:1	10:1
Charge heat Btu/bbl feed	127,000	158,000	185,000
Compressor energy Btu/bbl feed	29,000	38,000	48,000

Thus, semiregenerative units that must be operated at higher pressures and higher hydrogen-to-oil ratios in order to minimize carbon deposition on the catalyst, require more compressor energy and more charge heat.

Approximate energy requirements for catalytic reforming are as follows:

	Energy requirement (Btu/bbl feed) for:		
	Cyclic	Semiregenerative	
Electricity ^a	50,000	75,000	
Fuel	280,000	355,000	
TOTAL	330,000	430,000	

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

Credit could be given for the hydrogen produced since it is useful as process hydrogen for catalytic cracking, hydrorefining, and hydrotreating. Because it relieves the need to manufacture some of the hydrogen used by these processes, it could be assigned the amount of energy that would be required to manufacture the hydrogen (estimates of this energy usage are given in this report's hydrocracking section). Applying this credit, energy requirements for catalytic reforming are as follows:

	Energy requirement		
	(Btu/bbl feed) for:		
	Cyclic	Semiregenerative	
Electricity ^a	36,000	67,000	
Fuel	2,000	189,000	
TOTAL	38,000	256,000	

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

Two features of catalytic reformers affect energy consumption. First, higher pressure and hydrogen-to-oil ratios of the semiregenerative units result in more energy consumption and less hydrogen production. Secondly, bimetallic catalysts allow operation at lower pressure, temperature, and hydrogen-to-oil ratios, resulting in an energy savings.

Potential savings of energy in the catalytic-reforming process are estimated for the 1974 processing rate, with and without credit for the excess hydrogen produced, as follows:

Conservation measure	S a vings (10 ¹³ Btu/year)		
	Without H ₂ credit	With H ₂ credit	
Conversion of semiregenerative units to cyclic units	5.0	10.8	
Better furnace design and control and more use of heat recovery (10% of consumption) ^b	2.6	0.02	
Recovery and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	0.01	2.5	
TOTAL	7.6	13.3	

^aBased on a savings of 100,000 Btu/bbl for conventional catalyst units and 50,000 Btu/bbl for bimetallic units.

^bOn the basis of cyclic-unit consumption.

Without credit for hydrogen, this savings is 2.4% of the energy used for refining petroleum; with credit for hydrogen, it is 4.2%.

Catalytic Hydrorefining

Energy for catalytic hydrorefining is required to heat the mixed feed and the gas stream to the necessary reaction temperature and to pump and compress the fluids. Steam is used for stripping in some units, usually those processing a heavy residual feed. But because little of the capacity is operating on this type of feed, a negligible amount of steam is consumed. The total energy requirement, as reported in ref. 12, varies from 17,000 to 133,000 Btu/bbl of feed for gas-oil-type feed and as high as 270,000 Btu/bbl of feed for a heavy residual feed.

Approximate energy requirements for catalytic hydrorefining with and without energy required for the manufacture of hydrogen are as follows:

F	Energy requirement (Btu/bbl feed)	Process ((^O C)	temperature ([°] F)
	· · · · · · · · · · · · · · · · · · ·		
Electricity ^a			
Hydrorefining	22,000		
Hydrogen	8,000		
Fuel			
Hydrorefining	73,000	385	725
Hydrogen	155,000	900	1,650
Subtotal			
Hydrorefining	g 95,000		
Hydrogen	160,000		
TOTAL	260,000		

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

The electricity requirement is for a relatively low pressure and low makeup-hydrogen rate; high pressure and high makeup-hydrogen could easily triple the requirement. Thus, to conserve energy, operation should be controlled at the lowest practical pressure and hydrogen conditions commensurate with a satisfactory product. The recycle-gas rate affects the fuel requirement as well as the compressor energy because the recycle gases must be heated.

It is doubtful that there are better process alternatives to accomplish the desired desulfurization and hydrogenation. Although chemical treatments can modify the form of the sulfur compounds, the treatments will not necessarily result in either separating the sulfur from the petroleum or in lowering the energy requirements. Some of the undesired components also might be removed by adsorbers. But in both of these processes the sulfur would not be extricated from the petroleum, causing reduced yields of the more desirable products.

Potential savings of energy in the catalytic-hydrorefining process are estimated for the 1974 processing rate as follows:

Conservation measure	Savings (10 ¹³ Btu/year)		
	Without H ₂ energy	With H ₂ energy	
Hydrorefine at more energy-efficient process conditions ^a	0.28	0.28	
Recover and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	0.28	1.0	
Better furnace design and control and more use of heat recovery (10% of consumption)	0.21	0.65	
Use of hydraulic turbines and more energy-efficient prime movers (one-fifth of electrical energy)	0.12	0.12	
TOTAL	0.89	2.0	

 $a_{30\%}$ of electricity on two-thirds of capacity and one-fourth of fuel used to heat the gases.

Not including conservation relative to hydrogen manufacture, this total is 0.3% of the energy for refining petroleum; with hydrogen manufacture included, it is 0.6%.

Catalytic Hydrotreating

Energy for catalytic hydrotreating is required to heat the mixed feed and the gas stream to the necessary reaction temperature and to pump and compress the fluids. Steam is used for stripping in some units. Total energy requirements, as reported in ref. 12, vary from 28,000 to 110,000 Btu/bbl of feed. However, a comparison including energy for manufacturing hydrogen yields a larger difference which becomes yet greater when compared to the process which does not require makeup hydrogen. Approximate energy requirements for catalytic hydrotreating with and without energy required for the manufacture of hydrogen are as follows:

	Energy requirement		Process temperature	
	(Btu/bb) a	l feed) b	(°C)	(^o F)
Electricity ^C				
Hydrotreating Hydrogen	14,000 3,000	11,000		
Fuel				
Hydrotreating Hydrogen	39,000 67,000	37,000	260 900	500 1,650
Steam Hydrotreating	34,000	48,000	260	500
Subtotal Hydrotreating Hydrogen	87,000 70,000	96,000		
TOTAL	160,000	96,000		

^aProcesses that require makeup hydrogen.

^bProcesses that do not require makeup hydrogen.

^CElectricity converted to energy requirement based on 10,000 Btu/kWhr.

The electricity requirement is for a relatively low pressure and low makeup-hydrogen rate. High pressure and high makeup-hydrogen could increase this requirement substantially. Thus, to conserve energy, operation should be controlled at the lowest practical pressure and hydrogen conditions commensurate with a satisfactory product. The recycle-gas rate affects the fuel requirement as well as the compressor energy because the recycle gases must be heated. Excluding the process which requires no makeup hydrogen, it is doubtful there are better process alternatives to accomplish the desired desulfurization. Although chemical treatments can modify the form of the sulfur compounds and absorbers might remove some of the undesireable components, the sulfur would not be extricated from the petroleum, causing reduced yields of the more desirable products.

Potential savings of energy in the catalytic-hydrotreating process are estimated for the 1974 processing rate as follows:

Conservation measure	Savings (10 ¹³ Btu/year)		
	Without H ₂ energy	With H ₂ energy	
Hydrotreat at more energy-efficient process conditions ^a	0.29	0.29	
Recover and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	1.1	2.5	
Better furnace design and control and more use of heat recovery (10% of consumption)	1.0	1.9	
Use of hydraulic turbines and more ener efficient prime movers (one-fifth of electrical energy)	0.37	0.37	
TOTAL	2.8	5.1	

а

20% of electricity and one-fourth of fuel used to heat the gases on half of the feed.

Not including conservation relative to hydrogen manufacture, this total is 0.9% of the energy for refining petroleum; with hydrogen manufacture included, it is 1.6%. As mentioned previously, one catalytic-hydrotreating process requires no makeup hydrogen. Excluding the energy for manufacturing hydrogen, the energy requirements for this process appear to be slightly higher than for the other catalytic-hydrotreating processes because of the gas-recycle rate. However, considering the energy required for the hydrogen, this process appears to use about 40% less energy. It is restricted to refining feeds which will generate sufficient hydrogen for the hydrogen-treating reactions, that is, reasonably high naphthene content and low olefin content. It also requires that process conditions be within a narrower range.¹³ Assuming that 15% of the feed to catalytichydrotreating processes could be treated by this process requiring no makeup hydrogen, the energy savings for the 1974 processing rate are estimated to be 1.2×10^{13} Btu/year or 0.4% of the energy used to refine petroleum.

Alkylation

Energy for alkylation units is required to pump the feeds, recycle, products, and coolant water; to run air-cooled heat-exchanger fans; to operate the refrigerant compressor for H_2SO_4 units; and to heat the reboilers of the fractionation columns. Most of the energy used by the alkylation process is for reboilers. HF units also use reboiler heat in the HF stripper. A less but substantial usage of energy is for the compressor (H_2SO_4 process), requiring about 12% of the process energy. About 80% of the electricity reported here is for pumping the coolant water. Using electricity for the compressors would increase electricity usage and decrease the high-pressure steam requirement.
The H₂SO₄ unit shown in Fig. B.14 of Appendix B illustrates using high-pressure steam to drive the compressor with the turbine exhaust being condensed in some of the heaters and reboilers.

The quantity of energy required for alkylation, especially for HFalkylation units, has not been well defined. Reference 14 information indicates that HF units use more energy than do H_2SO_4 units. However, one liscensor furnished information indicating just the opposite but pointed out that the energy varies depending on the particular application. Another liscensor of HF units would not furnish detailed information but also believed that H_2SO_4 units use more energy. Information from ref. 14 and the liscensor are given in the following tabulation:

	Ener	gy requirement	Pr	ocess t	emperat	ure	
		(Btu/bbl product)			so ₄	HF	
	^H 2 ^{SO} 4	HF^{a}	HF	(°C)	(⁰ F)	(°c)	(^o F)
Electricity ^b	48,000	37,000	15,000				
Fuel	160,000	1,040,000	13,000	260	500	260	500
Steam	520,000	15,000	370,000 [°]	399	750	260	500
TOTAL	730,000	1,100,000	400,000				

^aSource: R. E. Payne, Alkylation - What You Should Know About This Process, Petroleum Refiner, Vol. 37 (9), Gulf Publishing Company, Houston, Tex., September 1958.

^bElectricity converted to energy requirement based on 10,000 Btu/kWhr.

^cCould be obtained from direct firing or from hot oil.

Polymerization is an alternate process to upgrade the octane rating of fuels. However, alkylation has some basic advantages in that product yield is higher because the isobutane as well as the olefins are converted and the alkylate is free of gum-forming materials. Thus alkylation is expected to continue as an important refining process as long as there is a demand for high-octane fuel.

Based on ref. 14 energy requirements given in the previous tabulation, substitution of the H_2SO_4 process for HF alkylation indicates a potential energy savings of 14% of the energy used for alkylation. However, as discussed previously, HF process liscensors believe the HF process to be less energy-intensive. The fractionation equipment is essentially the same for both acid-catalyzed processes. Thus substitution would consist primarily of modifying or replacing the reactor section. Energy requirements for the refrigerant compressors of the H_2SO_4 units appear to be considerably higher than the energy required for the watercoolant and HF-stripper systems of the HF units. Thus the energy savings given here are based on estimates of this difference and assume that the energy for pumping the process streams and for fractionation are the same for both processes. The energy savings resulting from replacing half of the H_2SO_4 capacity with the HF process would be 0.6 x 10^{13} Btu/year or 0.2% of the energy used to refine petroleum.

The potential for other energy savings in the alkylation process are estimated for the 1974 processing rate, using the energy requirement data furnished by the liscensor, as follows:

Conservation measure	Savings (10 ¹³ Btu/year)
Better furnace design and control and more use of heat recovery (10% of consumption)	1.0
Recovery and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	0.23
TOTAL	1.2

This total is about 0.4% of the energy used to refine petroleum. If half of the H_2SO_4 process capacity were converted to HF units and the other measures were taken. the savings would increase by 0.2% to 0.6% of the energy used to refine petroleum.

Isomerization

Energy for isomerization is required to pump the feed, recycle, products, and coolant water; to run the air-cooled heat-exchanger fans; and to heat the feed and reboiler streams. For the butane isomerization units the energy required for the fractionator is disregarded here because these requirements are included in the alkylation unit for which the isobutane is being made. Therefore, for butane isomerization only the energy associated with the reactor and stabilizer is given. Energy for C_5/C_6 isomerization includes the deisopentanizer requirement.

Approximate energy requirements for isomerization are as follows:

			Pro	ocess t	emperat	ure
	Energy requirement (Btu/bbl feed)		C ₄ is	om.	C ₅ /C ₆ isom.	
C ₄ isom.		C_5/C_6 isom.	(°C)	(⁰ F)	([°] C)	(⁰ F)
Electricity ^a	12,000	15,000				
Fuel	32,000	42,000	177	350	260	500
Steam	23,000	45,300	260	500	260	500
TOTAL	67,000	102,000				

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

No apparent substitute exists for the conventional isomerization processes. The extent of its use clearly depends on factors such as the demand for high-octane components with these boiling characteristics and the demand for the materials used in petrochemical feedstock.

Potential savings of energy in the isomerization process are estimated for the 1974 processing rate as follows:

Conservation measure	s (10 ¹³	avings Btu/year)
	C ₄ isom.	C_5/C_6 isom.
Better furnace design and control and more use of heat recovery (10% of consumption)	0.010	0.012
Recovery and use of one-fourth of the low-grade heat rejected by air- and water-cooled heat exchangers	0.019	0.023
TOTAL	0.029	0.035

These energy savings represent 0.02% (0.009% for C_4 isomerization and 0.011% for C_5/C_6 isomerization) of the energy used to refine petroleum.

Polymerization

Energy for polymerization units is required to pump the feeds, recycle, products, and coolant water, to run air-cooled heat-exchanger fans, and to heat the reboilers of the depropanizer and debutanizer columns. Although the reactions are exothermic and heat exchange is practiced, the process is quite energy intensive, largely because of the fractionation columns.

Energy requirements for polymerization based on information in ref. 15 are as follows:

	Energy requirement	Process t	emperature
	(Btu/bbl product)	(°C)	(^o F)
Electricity ^a	48,000	<u> </u>	<u>_</u>
Steam	800,000	260	500
TOTAL	850,000		

^aElectricity converted to energy requirement based on 10,000 Btu/kWhr.

However, the utility requirements report by Nelson³ are much less, about one-fourth as much.

Utility requirements for the liquid-phosphoric-acid process are not published, but the energy requirements probably are not significantly different from those for the solid-catalyst process.

Potential energy savings in the polymerization process are not estimated here because the extent of use of the process is small and unknown.

Hydrogen Production

Energy for manufacturing hydrogen by steam reforming is required to compress and pump process fluids and coolant water; to run air-cooled heat-exchanger fans; and to heat the steam and feed gas. The amount of electricity required is very sensitive to the pressure at which the hydrogen leaves the plant, and the data presented in this report are representative of a plant delivering hydrogen at 150 psia. Steam requirements for the process are assumed to be on an internally-generated, break-even basis.

Approximate energy requirements for manufacturing hydrogen are as follows:

	Energy requirement (Btu/10 ¹³ scf H ₂)	Process (⁰ C)	temperature (^O F)
Electricity ^a	11,000		
Fuel	222,000	900	1,650
TOTAL	230,000		
a			

^aElectricity is converted to energy requirement based on 10,000 Btu/kWhr.

Potential savings of energy estimated for manufacturing hydrogen, based on the production rate suggested in this report for 1974 (i.e., $480 \times 10^6 \text{ scf/day}$) are as follows:

Conservation measure	Savings (10 ¹³ Btu/year		
Better furnace design and control and more use of heat recovery (10% of consumption)		0.4	
Recovery and use of one-fourth of the low- grade heat rejected by air- and water- cooled heat exchangers		0.6	
TOTAL		1.0	

This total is about 0.3% of the energy used for refining petroleum.

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APPENDIX A

Regional characteristics of energy consumption

in U. S. petroleum refineries

(based on ref. 6)

Notes:

Districts are identified by Fig. 5 of this report. Steam conversion - 1333 Btu/1b. Electricity conversion - 10,000 Btu/kWhr.

Legend:

LPG - liquified petroleum gas

RG - refinery gas

NG - natural gas

PE1 - purchased electricity

PSt - purchased steam



Fig. A.1. Energy consumption per barrel of crude oil in Bureau of Mines districts 1 and 2 - 1961-1973.



Fig. A.2. Energy consumption per barrel of crude oil in Bureau of Mines districts 3 and 4 - 1961-1973.



Fig. A.3. Energy consumption per barrel of crude oil in Bureau of Mines districts 5 and 6 - 1961-1973.

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Fig. A.4. Energy consumption per barrel of crude oil in Bureau of Mines districts 7 and 8 - 1961-1973.



Fig. A.5. Energy consumption per barrel of crude oil in Bureau of Mines districts 9 and 10 - 1961-1973.



Fig. A.6. Energy consumption per barrel of crude oil in Bureau of Mines districts 11 and 12 - 1961-1973.



Fig. A.7. Energy consumption per barrel of crude oil in Bureau of Mines district 13 and the United States - 1961-1973.



Fig. A.8. Energy consumption per barrel of crude oil in U.S. petroleum refineries by Bureau of Mines districts - 1961-1973.

APPENDIX B

Petroleum refining process descriptions

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Desalting

Salts in the brine associated with crude oil accumulate as solids in the refinery-process equipment. They also contribute to the fouling of heat exchangers and to coke formation in pipe-still tubes. Furthermore, it is desirable to remove the chloride salts because they may convert to hydrochloric acid which corrodes the process equipment. Thus to prolong equipment life and to reduce maintenance and the frequency of "wash out" of equipment, desalting is performed to decrease the salt content to 10 to 15 lb per 1000 bbl of crude oil.

Representative salt content of crude oil varies from 20 to 60 lb/1000 bbl except for that of Mississippi mix which is 220 lb/1000 bbl.³ Table B.1 gives the water requirement for a range of salt contents.³

Water requirement (vol % of crude oil)
-
1
2-5
4-10
10-25
20-50

Table B.1. Effect of salt content on water requirement

Source: W. L. Nelson, Guide to Refining Costs, 2nd ed., The Petroleum Publishing Company, Tulsa, Okla. (1970), p.49.

Techniques for desalting consist of the following:

1. Addition of water to dilute the brine followed by settling in tanks. Desalting is promoted by heating to 93 to $143^{\circ}C$ (200 to $300^{\circ}F$) with adequate pressure to prevent violent vaporization.

- Circulation through packed towers (sand, gravel, or excelsior) before or after settling.
- 3. Addition of caustic soda to a pH of 8-9.
- High-potential electric field across the settling vessel (16,000-33,000 V) to promote separation by assisting in breaking the emulsion.
- 5. Addition of chemicals (i.e., surfactants and wetting agents).

Figure B.1. illustrates a desalting system in which crude oil is heated to about $121^{\circ}C$ (250°F) via heat exchange, mixed with water which has been warmed by the extracted brine, and separated from the brine in a settling tank. An electrostatic field is used to promote the separation by breaking the emulsion.

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- PROCESS STREAM HEAT EXCHANGERS

Fig. B.1. Petroleum refinery desalting system.

Realization of the importance of adequate desalting is stimulating interest in better methods, such as two-stage electrostatic units, control of wash water, and mechanical-operational changes.¹⁶

Atmospheric Distillation

Following stabilization and desalting, if practiced, crude oil is separated into light distillates (gases, naphtha, and kerosine), gas oil, and residue. Each of these distillation products is processed further to provide usable products. Separation is accomplished by pumping crude oil through heat exchangers into a distillation column composed of a series of bubble-cap plates at a temperature high enough to separate the crude oil into its various fractions. Figure B.2. is a schematic diagram of an atmospheric-distillation system. Because the required temperature at atmospheric pressure often is high enough to decompose the crude oil, steam is injected into the tower to lower the required feed temperature to about 343 to $371^{\circ}C$ (650 to $700^{\circ}F$). Gases are withdrawn from the top of the column and the lighter liquid fractions are removed as side streams that are partially recycled through a stripper that may use steam. The heavier fraction is transferred for further processing such as vacuum distillation.

Vacuum Distillation

General

A common refinery practice is vacuum distillation of the residual from the atmospheric distillation tower to obtain heavy distillate suitable for cracking and for manufacturing lube oils. The bottoms from the vacuum tower may be used as asphalt, be coked, or be further cracked. As an overall average, vacuum-distillation capacity was 35% of crude-oil capacity in 1974.¹ Nearly all large refineries and about half of the small refineries perform vacuum distillation. Feed to the vacuum tower is heated to about 399 to 427°C (750 to 800°F). Pressure in the tower is



Fig. B.2. Single-stage crude oil distillation unit.

maintained at about 75 mm of Hg with usually a condenser-steam ejector system. Although some refineries may use barometric condensers, these units are being replaced by water-cooled heat exchangers to reduce environmental pollution. Mechanical pumps could be used instead of steam jets but capital and maintenance costs would be much higher and there is concern about achieving a comparable reliability. Sometimes steam is also injected into the tower as a stripper.

Figure B.3. is a schematic diagram of a vacuum-distillation system. Gas Separation

The overhead fraction from the atmospheric tower is cooled to about $38^{\circ}C$ ($100^{\circ}F$) and transferred to tanks from which the straight-run gas and water are withdrawn. The remainder is transferred to fractionation towers to separate it into its components — propane, butane, and light and heavy gasoline. The fraction of the crude oil processed through saturate-gas-separation systems depends on the composition of the crude oil and on the refinery process. No industry average is available, but an example for a large modern refinery is that the feed would be about 10% of the crude oil. The temperature of the feed is raised by heat exchange and sometimes by steam reboilers.

Figure B.4. is a schematic diagram of a gas-separation system. Approximate pressures and temperatures in the towers are as follows:

	Pressure (psig)	Temperature (⁰ C/ ⁰ F)
Debutanizer	175	177/350
Depropanizer	300	121/250
Gasoline splitter	30	132/270

Products are all cooled to about 100°F.



Fig. B.3. Vacuum-distillation unit.

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- PROCESS STREAM HEAT EXCHANGER

Fig. B.4. Gas-separation system.

Cracking

Cracking, the decomposition of large hydrocarbon molecules into smaller molecules, is identified as a thermal, catalytic, or hydrocracking process. Further separation of the processes and the extent of their capacity in U. S. refineries, based on the 1974 survey data of ref. 1, are given in Tables B.2.-B.4. Reforming, which involves hightemperature cracking of straight-run gasoline and naphtha, is discussed as a separate process.

Thermal processes, including coking, are used by 37% of U. S. refineries (60 to 75% of the large refineries but only 15% of the small refineries). Capacity for the thermal processes is 9% of the crude-oil capacity. Coking is by far the dominant thermal process (70%) with delayed coking used seven times more than fluid coking. Most of the remainder of thermal-cracking capacity is equally divided between gasoil cracking and visbreaking. Visbreaking is a mild form of thermal cracking used to maximize furnace oil and minimize gasoline production. Gas-oil cracking using steam dilution is primarily used to produce light olefins. The survey data do not give the extent of steam cracking, and energy requirements were not determined for this report.

Catalytic cracking is performed at 57% of U. S. refineries (nearly all of the large refineries but only about 20% of the small refineries). Capacity of catalytic crackers is 29% of the crude-oil capacity. Fluid catalytic crackers account for 92% of the capacity with most of the remainder being the Thermofor process, accounting for about one-fourth of the catalytic-cracking capacity of small refineries. Only about 1% of catalytic cracking is by the Houdriflow process (four refineries). Most

Thermal	Percent of thermal	<u> </u>	Percent	for ref (10 ³ bb]	inery si /cd) of:	ze range	
process	processes	0-25	25-50	0-50	50-100		0-450
			Percen	t of U.	S. refin	eries ^a	
Gas-oil cracking	13.4	6.1	6.5	6.2	11.9	11.4	8.1
Visbreaking	13.8	2.6	2.2	2.5	16.7	13.6	7.3
Fluid coking	8.7	0.9	4.3	1.9	2.4	4.5	2.4
Delayed coking	60.6	2.6	17.4	6.8		52.3	18.6
Other	3.5	3.5	4.3	3.7		4.5	3.2
Total	100.0	15.7	34.7	21.1	57.1	75.0	36.8
		Perce	ent of th	ermal-p	cocess ca	pacity ^b	
Gas-oil cracking		4.2	4.5	8.7	18.2	73.1	
Visbreaking		5.3	2.2	7.5	34.9	57.6	
Fluid coking		6.6	9.5	16.1	16.8	67.1	
Delayed coking		1.3	7.8	9.1	26.2	64.7	
Other		23.7	14.5	38.2	0	61.8	
			Percent	of U.S.	crude-oi	l capacit	ya
Gas-oil cracking		0.7	0.5	0.8	1.1	1.5	1.3
Visbreaking		0.9	0.2	0.4	2.1	1.2	1.3
Fluid coking		0.8	0.7	0.8	0.6	0.9	0.8
Delayed coking		1.1	3.9	2.8	6.8	6.1	5.7
Other		1.1	0.4	0.5	_0	0.3	0.3
Total		4.6	5.7	5.3	10.6	10.0	9.4

Table B.2. Relative U. S. refinery use of thermal processes

^aPercent by size range — not percent of all refineries. Total is not necessarily additive because some refineries have more than one kind of process.

 $^{\rm b}{\rm Percent}$ of a type of thermal process — not percent of all thermal processes.

Catalytic cracking	Percent of cat. cr.	Percent for refinery size range (10 ³ bb1/cd) of:						
process	processes	0-25	25-50	0-50	50-100	100-450	0-450	
			Perce	nt of U	.S. refi	neries ^a		
Fluid The r mofor Houdriflow	91.5 6.9 <u>1.6</u>	13.9 7.0 <u>0</u>	56.5 19.6 <u>4.3</u>	26.1 10.6 1.2	83.3 9.5 <u>4.8</u>	95.5 4.5 0	48.2 9.3 <u>1.6</u>	
Total	100.0	20.9	73.9	36.0	97.6	95.5	57.1	
Recycle	22.5	20.9	71.7	35.4	97.6	93.2	56.3	
	Per	rcent of	catalyti	c-crack	ing-proc	ess capac	ity ^b	
Fluid Thermofor Houdriflow		2.3 13.9 0	8.9 36.5 27.3	11.2 50.4 27.3	22.0 32.3 72.7	66.8 17.3 0		
		I	Percent of	e u.s.	crude-oi	1 capacit	ya	
Fluid Thermofor Houdriflow Total		8.5 3.9 <u>0</u> 12.4	20.8 6.3 1.1 28.2	16.0 5.4 0.7 22.1	26.9 3.0 <u>1.5</u> 31.4	29.6 0.5 <u>0</u> 30.1	26.5 2.0 0.4 28.9	

Table B.3. Relative U.S. refinery use of catalytic-cracking processes

^aPercent by size range — not percent of all refineries. Total is not necessarily additive because some refineries have more than one kind of process.

^bPercent of a type of catalytic-cracking process — not percent of all catalytic-cracking processes.

Process	Percent of cat.		Percent f		nery siz 1/cd) of		
used to:	hydrocr.	0-25	25-50	0-50	50-100	100-450	0-450
			Perce	ent of U	.S. refi	neries ^a	
Upgrade distillate Upgrade residual Lube-oil manuf. Other	91.5 0.4 0.8 <u>7.3</u>	0.9 0.9 0.9 0	13.0 0 0 0	4.3 0.6 0.6 0	14.3 0 0 0	52.3 0 2.3 <u>4.5</u>	14.6 0.4 0.8 <u>0.8</u>
Total	100.0	2.6	13.0	5.6	14.3	56.8	16.2
			Percent o	of proce	ss capac	ity ^b	
Upgrade distillate Upgrade residual Lube-oil manuf. Other		0.1 100.0 37.5 0	5.5 0 0 0	5.6 100.0 37.5 0	15.0 0 0 0	79.4 0 62.5 100.0	
			Percent o	f U.S.	crude-oi	1 capacit	ya
Upgrade distillate Upgrade residual Lube-oil manuf. Other		0.1 0.3 0.2 0	2.4 0 0 0	1.5 0.1 0.1 0	3.4 0 0 0	6.6 0 c 0.7	4.9 c 0.4
Total		0.6	2.4	1.7	3.4	7.3	5.3

Table B.4. Relative U.S. refinery use of catalytic hydrocracking

^aPercent by size range — not percent of all refineries. Total is not necessarily additive because some refineries have more than one kind of process.

^bPercent of kind of use - not percent of all catalytic-hydrocracking uses.

^c <0.1.

large refineries recycle about 22% of the catalytic-cracker feed (this percent is also the industry average), whereas the average recycle for small refineries is about 33% of the catalytic-cracker feed.

Hydrocracking is used primarily by large refineries — 57% of large U. S. refineries and 16% of all U. S. refineries. Hydrocracking capacity is 5% of crude-oil capacity. The main use is for upgrading distillate; other small uses are for upgrading residual and for lube-oil manufacturing.

Thermal cracking and visbreaking

Thermal cracking and visbreaking processes differ mainly in severity (i.e., time, temperature, and pressure). There are many variations of these processes depending on the characteristics of the feed and the desired products. Thus equipment classified as thermal cracking might be used for visbreaking and vice versa. Figures B.5. and B.6. show examples of thermal-cracking and visbreaking processes respectively. for the illustrated thermal-cracking process, topped crude oil (bottom stream from a distillation unit) is heated by direct heat exchange with the cracked products in a fractionating column. Light and heavy oil from the fractionating column are pumped through a furnace as separate streams. The lighter oil is heated to a higher temperature and pressure than the heavier oil, about $521^{\circ}C$ and 500 to 700 psig and $504^{\circ}C$ and 300 to 500 psig (970 and 940°F) respectively.¹⁷ Light oil is not recycled when heating oil is the desired product; otherwise recycle is about 2.5 and 3.5 times the throughput for the light and heavy oil respectively.¹⁰ The two streams from the furnace are combined and transferred through a reaction chamber to a flash chamber from which the heavy portion is

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Fig. B.5. Thermal-cracker system.

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Fig. B.6. Visbreaker system.

removed from the bottom and the rest is returned to the fractionator. Furnace distillate is drawn from the side of the fractionator. Gas and gasoline from the top of the fractionator are cooled and separated.

Visbreaking is a mild form of thermal cracking sometimes used to reduce the viscosity of heavy residues with little reduction of the boiling point, resulting less light heating oil being required to blend the residue to an acceptable fuel oil. For the visbreaking process illustrated in Fig. B.6., feed is heated to about 482°C (900°F) and mixed with a recycle stream of heated heavy gas oil.¹³ Pressure is in the range of 50 to 300 psig. The furnace is designed to provide a "soaking" section to allow time for the reactions to be completed. After quenching by a recycle stream of product heating oil, the gas, gasoline, heating oil, and residuum are separated in a fractionating section. The residuum is then passed through a vacuum tower with the overhead being returned to the fractionator and the bottoms becoming a fuel oil.

Coking

Coking is a form of thermal cracking in which heavy residues are converted into gas, naphtha, heating oil, and coke. Coking is a more severe process than ordinary thermal cracking in that the heavy oil is maintained at a high temperature for a longer period of time. Of the major coking processes, delayed coking is used much more than fluid coking.

The delayed-coking process is similar to the process described previously for thermal cracking except that only heavy oil is fed to the furnace and soaking drums are provided to prolong the reaction time. Coke which accumulates in the soaking drums must be removed every one or two

days; thus multiple soaking drums are provided to allow continuous operation. Coke is removed from the drums by drilling a hole in the deposit and using high-pressure water jets as cutting devices. Furnace outlet temperature is about 499° C (930° F); coke drum pressure and temperature are 10 to 70 psig and about 432° C (810° F). Figure B.7.a. is a schematic diagram of a delayed-coking system.

Fluid coking, shown schematically in Fig. B.7.b., is a continuous process with coke being deposited on coke fines coming from a heater chamber which receives coke from the reactor vessel. Air is supplied to the heater chamber where some of the coke is burned to supply some of the process heat requirements and to generate some steam. Heavy residue is fed to the reactor vessel in which there is a fluidized bed of coke particles. The top of the reactor vessel has a scrubber-fractionator to separate the particulate material and hydrocarbon fractions from the heavier oils being recycled. Because some of the coke is burned, the fluid-coking process has less coke product than the delayed-coking process. Operating temperatures and pressures are 480 to $565^{\circ}C$ (900 to $1050^{\circ}F$) and 0 to 15 psig.

A variation of the fluid-coking process is shown schematically by Fig. B.7.c. The process is similar to the fluid-coking process described previously, but the coke is transferred between the heater and a gasifier in which all the net coke produced is gasified by steam and air. After furnishing process heat and generating steam, the gases are cooled, scrubbed, and desulfurized to a low-sulfur fuel gas.

Catalytic cracking

Catalytic cracking using the fluid-bed-type unit, FCCU, is the dominant form of cracking process. Less used are catalytic cracking



à.

Fig. B.7. Coking processes.

Sources (a), (b): G. D. Hobson, Modern Petroleum Technology, 4th ed., John Wiley and Sons, New York, 1973, p. 283; p. 285.

> (c): D. E. Blaser, J. A. Rionda, and A. L. Saxton, Combine Desulfurizing and Coking, Hydrocarbon Processing, vol. 50 (9), Gulf Publishing Company, Houston, Tex., September 1971, p. 140.

units of the moving-bed type in which the catalyst moves by gravity through the reactor and regenerator vessels and is returned to the top of the unit by a gas lift. Most of the gas-lift units are Thermofor air-lift units; only four refineries have the Houdriflow type.

There are several versions of FCC units. The main obvious difference is in the height of the units caused by the relative placement of the reactor and regenerator sections. Functionally the fluid-bed catalytic units have evolved from those with a reactor vessel for the cracking region to those in which most of the cracking occurs in a riser leg which receives feed and regenerated catalyst at its lower end and delivers the cracked feed and coked-catalyst to a disengager tank. Insufficient information is available in the literature to reach conclusions about their relative energy consumption. However, it seems likely that for a given degree of processing and effectiveness of the catalyst, the smaller units and those in which most of the cracking occurs in the dilute phase during catalyst transfer would be more energy-efficient.

In any case, coke formed during cracking deposits on the catalyst and must be burned off to regenerate the catalyst. In FCCU removal is thus accomplished with low-excess oxygen at temperatures of 565 to $704^{\circ}C$ (1050 to $1300^{\circ}F$) and pressures of 15 to 35 psig. The resultant gas is a mixture of CO and CO₂ at sufficiently high temperature and pressure to provide a substantial supply of energy which can be recovered by use of heat exchangers, turboexpanders, and CO boilers.

Figures B.8. and B.9. show schematic diagrams of moving-bed and fluidized-catalytic-cracking units respectively.
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Fig. B.8. Thermofor moving-bed catalytic unit.

Source: G. D. Hobson, Modern Petroleum Technology, 4th ed., John Wiley and Sons, New York, 1973, p. 293.



Fig. B.9. Fluid-bed catalytic cracker units.

Sources: 1974 Refining Process Handbook, Hydrocarbon Processing, vol. 53 (9), Gulf Publishing Company, Houston, Tex., September 1974, p. 118.

1966 Refining Process Handbook, Hydrocarbon Processing, vol. 45 (9), Gulf Publishing Company, Houston, Tex., September 1966, p. 188.

Hydrocracking

Hydrocracking is a pressurized-hydrogen catalytic process used to convert refractory middle-boiling or residual material to high-octane gasoline, reformer feed, and high-grade fuels by cracking, hydrogenation, isomerization, and hydrotreating reactions. Upgrading of distillate is the predominate use made of hydrocracking. Most hydrocracker designs are of the fixed-bed type; however, at least one design involves a moving-catalyst bed operated such that upflow of fluid keeps the catalyst in an "abbullating" state. The temperature for hydrocracking is 340 to 420°C (644 to 790°F) and pressure is 1200 to 2000 psig. Hydrogen consumption is about 1500 to 2000 scf/bbl of feed and hydrogen recycle is about 8000 to 15,000 scf/bbl of feed. However, consumption is much less than this total if the unit is used solely as a desulfurizer and much higher (3000 scf/bbl) if used for gasoline production from high-boiling material.

Hydrogen from reforming can be used for the hydrocracking; however, assuming hydrotreating and/or hydrorefining are practiced, this supply is sufficient only if a limited amount of hydrocracking is performed. Usually a supplemental hydrogen supply is required. Because hydrogen has value, especially when also used to produce low-sulfur fuels, and requires energy for its production, it seems appropriate to assign an energy requirement to the hydrocracking process for the hydrogen used. For this study the energy required to produce the hydrogen is assumed to be as follows:

	Energy requirement (Btu/10 ³ scf H ₂)
Electricity	11,000
Fuel	222,000
Steam	break even
TOTAL	233,000

Figure B.10. shows schematic diagrams of fixed-bed and movingcatalyst-bed systems.

Catalytic Reforming

Catalytic reforming of low-octane naphtha to a high-octane material and to aromatics for petroleum feedstocks is preferred to thermal reforming because of better control of the reactions and better product vields. These factors also make the present (catalytic) reformers the more energy efficient type. There are about 15 variations of catalytic reformers of two basic types - cyclic or semiregenerative - each of which uses either a conventional (usually platinum-on-alumina) catalyst or bimetallic (rhenium or tin in addition to platinum). The extent and distribution of catalytic reforming by these types of units, based on the 1974 survey data of ref. 1, are given in Table B.5. Catalytic reforming is used by 70% of U.S. refineries (nearly all of the large refineries but only half of the small refineries). Catalytic-reformer capacity is 21% of crude-oil capacity (22% for large refineries and 10% for small refineries). Use of the semiregenerative type predominates with about equal use of conventional and bimetallic catalyst. Most of the remaining reforming is by the cyclic process using conventional catalysts.

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(b) MOVING - CATALYST UNIT (H-OIL)

Fig. B.10. Hydrocracker units.

Source: G. D. Hobson, Modern Petroleum Technology, 4th ed., John Wiley and Sons, New York, 1973, p. 313, 320.

Catalytic reforming	Percent of cat. ref.			<u>(10³ bb</u>	1/cd) of		
process	processes	0-25	25-50	0-50	50–100	100-450	0-450
		-	Perc	ent of U	.S. refi	neries ^a	
Semiregenerative Conventional Bimetallic	70.0 35.0 35.0	36.5 23.5 13.0	73.9 32.6 41.3	47.2 26.1 21.1	85.7 45.2 40.5	86.4 45.5 40.9	60.7 32.8 27.9
Cyclic Conventional Bimetallic	27.2 25.0 2.2	5.2 2.6 2.6	8.7 8.7 0	6.2 4.3 1.9	14.3 11.9 2.4	36.4 34.1 2.3	12.9 10.9 2.0
Other ^b	2.8	0	2.2	0.6	9.5	2.3	2.4
Total	100.0	41.7	84.8	54.0	100.0	100.0	70.0
	Perce	ent of	catalyti	c-reform	ing-proc	ess capac:	ity ^C
Semiregenerative Conventional Bimetallic		4.6 5.5 3.6	12.4 11.1 13.8	17.0 16.6 17.4	26.5 26.2 26.8	56.5 57.2 55.8	
Cyclic Conventional Bimetallic		1.2 0.4 9.6	4.1 4.4 0	5.2 4.8 9.6	8.8 8.4 13.7	86.0 86.8 76.7	
Other		0	6.4	6.4	72.3	21.3	
			Percent	of U.S.	crude-oi	l capacity	,a
Semiregenerative Conventional Bimetallic		9.4 5.7 3.7	16.1 7.2 8.9	13.5 6.6 6.9	18.1 8.9 9.2	14.0 7.1 6.9	14.9 7.5 7.4
Cyclic Conventional Bimetallic		0.9 0.3 0.6	2.1 2.1 0	1.6 1.4 0.2	2.3 2.0 0.3	8.3 7.7 0.6	5.7 5.3 0.4
Other ^b		0	0.4	0.2	2.0	0.2	0.6
Total		10.3	18.6	15.3	22.4	22.5	21.2

Table B.5. Relative U.S. refinery use of catalytic-reforming processes

^aPercent by size range — not percent of all refineries. Total is not necessarily additive because some refineries have more than one kind of process.

^bAll-bimetallic catalyst.

^CPercent of a type of catalytic-reforming process — not percent of all catalytic reforming processes.

The cyclic units ordinarily operate at lower pressure and higher temperature at the expense of more rapid deactivation of the catalyst by coke deposition because a "swing" reactor provides for reactivation of the catalyst on a regular three-to-five-day schedule. The advantage of this cyclic process is that the yields of aromatics and hydrogen are increased and the hydrogen-to-oil mole ratio may be lower.

For either process type, feed and the hydrogen which is recycled from the process are heated in furnaces and sometimes by heat exchange; sent to a series of three or four reactors; and further heated in furnaces between each reactor. The cyclic process always provides for by-passing one of the reactors so that the reactors may be rotated through catalyst-regeneration cycles. By proper choice of operating parameters the semiregenerative process is able to extend to several months the time between catalyst regenerations. Bimetallic catalyst also allow oepration at lower pressures, lower temperatures, and longer times.

Approximate operating characteristics for catalytic reforming are as follows:

	Cyclic	Semiregenerative ^a
Pressure (psig)	200 - 350	300 - 600
Temperature ([°] C/ [°] F)	500-540/932-1004	450-540/842-1004
Hydrogen/oil mole ratio	3:1 - 5:1	5:1 - 10:1
Hydrogen production (scf/bbl)	1000 - 1500	700 - 1500

^aSource: G. D. Hobson, *Modern Petroleum Technology*, 4th ed., John Wiley and Sons, New York, 1973, p. 338, 340.

Figure B.11 shows schematic diagrams of cyclic- and semiregenerativetype catalytic reformers.



(a) CYCLIC



(b) SEMIREGENERATIVE

Fig. B.11. Catalytic reformer units.

Source: G. D. Hobson, Modern Petroleum Technology, 4th ed., John Wiley and Sons, New York, 1973, p. 338, 342.

Catalytic Hydrorefining

Catalytic hydrorefining as discussed here follows the ref. 1 description of applications, identified along with the extent of U. S. capacity in Table B.6. Catalytic hydrorefining is used by 19% of U. S. refineries (predominately by large refineries). Capacity is 6% of the crude-oil capacity. Primary uses are to treat middle distillates and catalytic-cracker and stock feeds. Lesser uses are desulfurization of residual and gas oil.

Many variations of units to preform catalytic hydrorefining exist, all of which basically are very similar. Hydrogen and feed are heated and passed over a fixed-bed catalyst. The materials are then cooled and separated into several components; gases, after H_2S removal, are recycled and the liquids are further separated into the desired products. The catalyst commonly is cobalt molybdate on an alumina support. Regeneration of the catalyst is required only infrequently. Temperature and pressure are in the range of 315 to $455^{\circ}C$ (599 to $851^{\circ}F$) and 200 to 1000 psig. However, extremes of these values are avoided because at low pressure and high temperature there is excessive carbon deposition on the catalyst, increasing the frequency of regeneration, and high pressure and low temperature favor undesired reactions such as aromatics converting to naphthenes. Gas is recycled at a rate of 300 to 5000 scf/bbl and makeup hydrogen at 400 to 1000 scf/bbl.

Figure B.12. is a schematic diagram of a catalytic-hydrorefining unit.

Catalytic Hydrotreating

Catalytic hydrotreating as discussed here follows the ref. 1 description of applications, identified along with the extent of U.S.

Process	Percent of cat.		Percer	nt for re (10 ³ bł	efinery s ol/cd) of	ize range		
used to:	hydroref.	0-25	25-50	0-50			0-450	
			Perc	cent of U	.S. refi	neries ^a		
Desulf. residual	1.0	0.9	0	0.6	0	2.3	0.8	
Desulf. gas-oil Pretreat cat. cr.	15.7	0	2.2	0.6	2.4	6.8	2.0	
and stock feed	33.2	0.9	6.5	2.5	16.7	13.6	6.9	
Treat mid. dist.	48.5	0.9	19.6	6.2	16.7	20.5	10.5	
Other	1.6	1.7		1.2	0	4.5	1.6	
Total	100.0	4.3	21.7	9.3	35.7	40.9	19.4	
	Percent of process-capacity use b							
Desulf. residual		42.9	0	42.9	0	57.1		
Desulf. gas-oil Pretreat cat. cr.		0	5.0	5.0	13.8	81.2		
and stock feed		1.2	6.7	7.9	32.0	60.1		
Treat mid. dist.		0.2	10.0	10.2	20.4	69.4		
Other		36.0	0	36.0	0	64.0		
			Percent	of U.S.	crude-oi	l capacity	,a 7	
Desulf. residual		0.4	0	0.2	0	с	с	
Desulf. gas-oil Pretreat cat. cr.		0	0.4	0.3	1.2	1.4	1.0	
and stock feed		0.4	1.3	0.9	6.0	2.2	2.1	
Treat mid. dist.		0.1	2.7	1.7	5.6	3.6	3.1	
Other		0.5	0	0.2	0	0.1	<u>c</u>	
Total		1.4	4.4	3.3	12.8	7.3	6.2	

Table B.6. Relative U.S. refinery use of catalytic hydrorefining

^aPercent by size range — not percent of all refineries. Total is not necessarily additive because some refineries have more than one kind of process.

^bPercent of kind of use - not percent of all catalytic hydrorefining. ^c <0.1.

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Fig. B.12. Catalytic-hydrorefining unit.

Source: 1974 Refining Process Handbook, Hydrocarbon Processing, vol. 53 (9), Gulf Publishing Company, Houston, Tex., September 1974, p. 148. capacity in Table B.7. Catalytic hydrotreating is used by 65% of the U.S. refineries (nearly all large refineries but only about 30% of the small refineries). Capacity is 30% of crude-oil capacity. The predominate use (about one-half) is for desulfurizing catalytic-reformer feed. Other uses are desulfurization of various products.

The many variations of catalytic-hydrotreating processes are very similar to each other and to the catalytic-hydrorefining processes. Generally the feeds are the lighter, lower- and middle-boiling components, and the main purpose is to desulfurize the feed. Over half of the hydrotreating capacity in the United States is for desulfurizing reformer feed and most of the remainder is used for desulfurizing various light refinery liquid products. The schematic diagram shown for catalytic hydrorefining is also applicable to catalytic hydrotreating; operating temperatures are somewhat lower [175 to 430° C (347 to 806° F)] and pressures are in the lower part of the hydrorefining range (<600 psig). Hydrogen requirements, also generally less than requirements for hydrorefining, are 50 to 800 scf/bbl with an average of about 300 scf/bbl. One process requires no supplemental hydrogen but has a gas-recycle rate of 2000 to 4000 scf/bbl.¹³

Alkylation

Alkylation is a petroleum-refining process in which an olefin is reacted with an isoparaffin, usually isobutane, to yield high-octane, branched-chain paraffinic hydrocarbons. Although alkylation can be achieved thermally, essentially all existing U. S. units use a catalyst – either H_2SO_4 of HF. Table B.8. shows the extent of these types of alkylation processes based on the 1974 survey data of ref. 1; five-eights of the units are of the H_2SO_4 type and three-eights are of the HF type. Alkylation is performed by 37% of U. S. refineries (nearly all of the

Process	Percent of cat.	. <u>.</u> .	Percent	t for r (10 ³ b	bl/cd) o	size rang	
used to:	hydrotr.	0-25	25-50	0-50	50-100	100-450	0-450
			Perce	ent of	U.S. ref	ineries ^a	
Desulf. cat. ref. feed Desulf. naphta Sat. naphta olefin	55.4 12.0	25.2 5.2	71.7 15.2	38.5 8.1	83.3 11.9	81.8 36.4	53.8 13.8
and aromatics Desulf. lt. dist. Polish lube oil Desulf. med. dist. Other	$ \begin{array}{r} 1.0 \\ 5.8 \\ 2.8 \\ 16.7 \\ \underline{6.4} \end{array} $	1.7 2.6 0.9 3.5 <u>1.7</u>	4.3 10.9 0 4.3 <u>4.3</u>	2.5 5.0 0.6 3.7 2.5	2.4 7.1 2.4 21.4 <u>11.9</u>	13.6 20.5 20.5 27.3 29.5	4.5 8.1 4.5 10.9 <u>8.9</u>
Total	100.0	31.3	87.0	47.2	97.6	100.0	65.2
		Per	cent of	process	-capacit	y use ^b	
Desulf. cat. ref. feed Desulf. naphta Sat. naphta olefin		3.0 2.8	11.7 8.7	14.7 11.5	23.5 21.7	61.8 66.8	
and aromatics Desulf. lt. dist. Polish lube oil Desulf. med. dist. Other		2.9 2.5 1.2 0.8 0.9	7.1 18.0 0 3.2 2.5	10.0 20.5 1.2 4.0 3.4	9.6 21.9 6.5 26.0 22.1	80.4 57.6 92.3 70.0 74.5	2
		1	Percent	of U.S.	crude-c	oil capaci	ty ^a
Desulf. cat. ref. feed Desulf. naphta		7.0 1.4	16.9 2.8	13.1 2.3	18.0 3.7	17.1 4.1	16.6 3.6
Sat. naphta olefin and aromatics Desulf. lt. dist. Polish lube oil Desulf. med. dist. Other		0.1 0.6 0.1 0.6 0.2	0.2 2.7 0 1.4 0.4	0.2 1.9 c 1.1 0.3	0.1 1.8 0.2 6.0 1.9	0.4 1.7 1.3 5.8 2.4	0.3 1.7 0.8 5.0 <u>1.9</u>
Total		10.0	24.4	18.9	31.7	32.8	29.9

Table B.7. Relative U.S. refinery use of catalytic hydrotreating

^aPercent by size range — not percent of all refineries. Total is not necessarily additive because some refineries have more than one kind of process.

^bPercent of kind of use - not percent of all catalytic hydrotreating.

5

c <0.1.

Alkylation	Percent of alkylation		Percen		efinery b1/cd) o	size rang f:	e
process	processes	0-25	25-50			100-450	0-450
			Perc	ent of	U.S. ref	ineries ^a	
н ₂ SO4	62.8	2.6	28.3	9.9	47.6	70.5	27.1
HF	37.2	10.4	41.3	19.3	50.0	22.7	25.1
Total	100.0	13.0	69.6	29.2	95.2	90.9	36.8
		Percent	t of alk	ylation	-process	capacity	Ъ
H ₂ SO ₄		0.7	6.9	7.6	19.2	73.2	
HF		5.5	21.2	26.7	34.2	39.1	
		1	Percent o	of U.S.	crude-o	il capaci	ty ^a
н ₂ SO ₄		0.3	2.0	1.4	3.0	4.1	3.4
HF		_1.5	3.7	2.9	3.1	1.3	2.0
Total		1.8	5.7	4.3	6.1	5.4	5.4

Table B.8. Relative U.S. refinery use of alkylation processes

^aPercent by size range — not percent of all refineries. Total is not necessarily additive because some refineries have more than one kind of process.

^bPercent of kind of use - not percent of all alkylation processes.

large refineries but only 13% of the small refineries). The H_2SO_4 process is more common in large refineries and the HF process is more common in small refineries. Alkylation capacity is 5% of crude-oil capacity.

In thermal-catalytic alkylation processes feed is reacted at 52 to 232° C (125 to 450° F) and 300 to 1000 psig pressure using a metal halide catalyst (AlCl₃); thermal alkylation processes require higher temperatures and pressures. The H₂SO₄- and HF-catalyzed processes on the other hand, are very similar and operate at lower temperature and pressure - 2 to 15° C (36 to 59° F) and atmospheric pressure to 150 psig for the H₂SO₄ process, and 15 to 50° C (59 to 122° F) for the HF process. Removing heat from the reactions requires a refrigeration system for the H₂SO₄ units; HF units can use water cooling because they can operate at higher, less-controlled temperatures. HF is more readily recovered from the product than is H₂SO₄, but the HF units require somewhat higher temperatures in the HF stripper to break down the fluorides formed during the processing. The process choice often has been based on the economics of acid supply, recovery, and disposal.

For both acid-catalyzed processes the isobutane, olefin, and acid are fed to a reactor provided with a cooling system. The outlet stream from the reactor enters a settler tank (and caustic washer for the H_2SO_4 process) and then a fractionator(s) where isobutane is stripped for recirculation to the reactor and alkylate is separated from the butane and propane. Intimate contact of the acid catalyst with the hydrocarbons is provided by various means such as stirring or high-velocity circulation.

Figure B.13. shows schematic diagrams of H_2SO_4 - and HF-alkylation units. A variation of the H_2SO_4 -alkylation process is the autorefrigeration process where the refrigerant is mostly process isobutane



(a) H2SO4 ALKYLATION PROCESS



(b) HF ALKYLATION PROCESS



Source (b): 1974 Refining Process Handbook, Hydrocarbon Processing, vol. 53 (9), Gulf Publishing Company, Houston, Tex., September 1974, p. 208. with some propane content. Figure B.14. is a schematic diagram of the "cascade" type of reactor which requires much less isobutane recycle than the earlier "jet" type — about 2 recycle to 1 of product vs 5-to-1.¹⁸ The isobutane-to-olefin ratio in the reactor is about 25-to-1.

Isomerization

Isomerization is the process by which atoms of a hydrocarbon are rearranged without adding or removing material. It normally is used to form branched molecules from straight-chain molecules and to increase the branching of molecules. One important use, C_4 isomerization, converts normal butane to isobutane (a feed for alkylation units). C_5 and C_6 isomerization produces isoparaffins that can be blended into motor gasoline to improve the octane rating. Table B.9. shows the extent of isomerization capacity in the United States in 1974.¹ Isomerization processes are used by 11% of U. S. refineries; however, capacity is less than 1% of the crude-oil capacity.

The isomerization process consists of contacting the hydrocarbon with a catalyst under proper conditions of temperature and pressure. Aluminum chloride with hydrochloric acid or platinum-containing material are used as catalysts. Yield of branched paraffins is improved and side reactions are reduced at low reaction temperatures, but the reaction rate also is reduced as the temperature is lowered. Thus, the temperature chosen must be a trade-off between these effects in combination with use of side-reaction inhibitors. A common way to restrict side reactions is to carry out the reactions in the presence of hydrogen. Since little hydrogenation occurs the consumption of hydrogen is very low.

Operating conditions normally are in the same range for butane and pentane/hexane isomerization (i.e., 121 to $288^{\circ}C$ (250 to $550^{\circ}F$), 200 to

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Source: R. Stiles, The Alkylation Process, Petroleum Refiner, vol. 34 (2), Gulf Publishing Company, Houston, Tex., February 1955, p. 103.

Isomerization	Percent of isomerization	Percent for refinery size range (10 ³ bb1/cd) of:					e
process	processes	0-25	25-50	0-50		100-450	0-450
			Perce	ent of	U.S. ref	ineries ^a	
C ₄ feed	52.7	1.7	10.9	4.3	19.0	13.6	8.5
C_5 feed	30.6	0	0	0	4.8	4.5	1.6
C ₅ -C ₆ feed	16.7	0	2.2	0.6	2.4	2.3	1.2
Total	100.0	1.7	13.1	4.9	26.2	20.4	11.3
	P	ercent	of isome:	rizatio	n-proces	s capacit	y ^b
C ₄ feed		3.5	12.8	16.3	40.7	43.0	
C_{5} feed		0	0	0	63.3	36.7	
C ₅ -C ₆ feed		0	32.4	32.4	40.6	27.0	
5 0			Percent (of U.S.	crude-o	oil capaci	tya
C ₄ feed		0.2	0.4	0.3	0.6	0.3	0.4
C_5 feed		0	0	0	0.6	0.1	0.2
C ₅ -C ₆ feed		0	0.3	0.2	0.2	с	0.1
Total		0.2	0.7	0.5	1.4	0.4	0.7

Table B.9. Relative use of isomerization processes

^aPercent by size range — not percent of all refineries.

^bPercent of kind of use - not percent of all isomerization processes. ^c <0.1.

a

500 psig, and a hydrogen-to-oil mole ratio of 0.1 to 0.5:1) with butane isomerization tending to be performed in the lower portion of the ranges.

Figure B.15. shows schematic diagrams of isomerization units.

Polymerization

Polymerization involves the conversion of olefin gases to liquid, higher-boiling hydrocarbons. Initially the conversion was carried out as a thermal process but was soon replaced by the more efficient catalytic-polymerization process. Catalysts are sulfuric acid, copper pyrophosphate, and phosphoric acid (the most widely used type). No survey information was found to indicate the extent of use of the polymerization process. However, because alkylation compared to polymerization produces more than twice as much gasoline per barrel of olefin and because the product is more compatible with modern engines, alkylation is the more popular route to upgrade gaseous stocks.¹⁹ Thus in this report polymerization is considered to be an insignificant user of energy.

A solid phosphoric-acid-catalyzed polymerization process is shown schematically in Fig. B.16. Temperature in the reactor is about $200^{\circ}C$ ($392^{\circ}F$) and the pressure is from 400 to 1200 psig. The reactions are exothermic (670 Btu/1b of propylene and 400 Btu/1b of butene converted), and thus quenching is required to control the temperature. Control is accomplished by introducing C₃ recycle at several levels in the reactor vessel.

Hydrogen Production

The need for a refinery to produce hydrogen depends on the extent the refinery practices reforming, thereby producing hydrogen, and hydrogen-consuming processes such as hydrocracking, hydrorefining, and hydrotreating. Refineries practicing an average amount of reforming





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(a) SOLID PHOSPHORIC ACID CATALYST POLYMERIZATION PROCESS



(b) LIQUID PHOSPHORIC ACID CATALYST POLYMERIZATION PROCESS

Fig. B.16. Phosphoric-acid-catalyst polymerization units.

Sources (a): G. D. Hobson, Modern Petroleum Technology, 4th ed., John Wiley and Sons, New York, 1973, p. 360.

> (b): 1966 Refining Process Handbook, Hydrocarbon Processing, vol. 45 (9), Gulf Publishing Company, Houston, Tex., September 1966, p. 211.

probably produce enough hydrogen for their hydrotreating and hydrorefining units. However, if they also have a hydrocracker unit, they usually will require a hydrogen-production unit. Because no published survey gives the capacity of hydrogen-production units for U. S. refineries, an estimate was made based on the 1974 capacity¹ of the hydrogen-producing and hydrogen-consuming processes and on average hydrogen rates.^{*} The estimate indicates a need to manufacture 600 x 10^6 scf of hydrogen per day; if this amount is assumed to be produced in the 32 refineries having a significant hydrocracking capacity, an average hydrogen-production unit is indicated to have a capacity of about 20 x 10^6 scf/day.

Processes used to produce hydrogen are steam reforming of hydrocarbon gases and partial oxidation. Schematic diagrams of these processes are shown in Fig. B.17. Steam-reforming reactions are carried out in the presence of a nickel catalyst which is easily poisoned by contaminants such as sulfur. Thus the feed must be reasonably clean and often requires a purification unit. The reactions are endothermic (97,300 Btu/lb mole for the steam reforming of methane). Typical operating conditions are 900°C (1650°F) and a steam-to-oil ratio of 3-to-1. The reaction results in a volume increase compatible with the need to use the hydrogen at high pressure, but the reaction is favored by low pressure. For most units the pressure can be relatively high, up to 400 psig.

A survey is being made by the Oil and Gas Journal with a projected publishing date of April 1976.



(b) STEAM REFORMING PROCESS

Fig. B.17. Hydrogen manufacturing processes.

Source: G. D. Hobson, Modern Petroleum Technology, 4th ed., John Wiley and Sons, New York, 1973, p. 324, 326.

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The partial oxidation process does not require a catalyst and thus feed purification to remove sulfur is not necessary. Feed, which can be any hydrocarbon from gas to fuel oil, is mixed with steam, heated, and then reacted with oxygen in a vessel where part of the feed is burned, producing a flame temperature of about $1450^{\circ}C$ ($2640^{\circ}F$). Unless a market exists for nitrogen, the size of the unit must be relatively large (>10⁷ scf hydrogen/day) to economically justify the cost of the oxygen.

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