PETROCHEMICALS, FEEDSTOCKS

1. Introduction

By definition, petrochemicals are either isolated from or derived from natural gas or petroleum. Other sources of feedstocks, such as coal and agricultural products, remain very small sources of petrochemicals. The choice of feedstock for a given operator is an economic decision, but may be constrained by hardware limitations on the part of the operator or the availability of indigenous hydrocarbon supplies in a given geographical region. Because the primary uses of natural gas and petroleum are as sources of energy, the costs of petrochemical feedstocks are closely related to the alternative energy values of the various feedstocks. The petrochemical producer must buy feedstocks out of the alternative energy markets. Hence, the structure and economics of the energy industry in a given area affect the choice of petrochemical feedstocks. Seasonal effects in the prices of energy products introduce variability in petrochemical feedstock prices and affect the choice of preferred feedstock for a given operator at a point in time. International events such as the OPEC oil embargo of 1973–1974, the Iranian revolution of 1979, the Middle East war of 1990–1991, or the war in Iraq during 2003 have dramatically affected the costs and choice of petrochemical feedstocks for a period of time. Government regulations, such as the U.S. Clean Air Act Amendments of 1990 and major programs in the U.S. and Brazil to promote the use of ethanol as a vehicle fuel, also impact petrochemical feedstock availability, relative cost, and choice of alternative feedstocks.

It is convenient to divide the petrochemical industry into two general sectors: (*1*) olefins and (*2*) aromatics and their respective derivatives. Olefins are straight- or branched-chain unsaturated hydrocarbons, the most important being ethylene (qv), [74-85-1] propylene (qv) [115-07-1], and butadiene (qv) [106-99-0]. Aromatics are cyclic unsaturated hydrocarbons, the most important being benzene (qv) [71-43-2], toluene (qv) [108-88-3], *p*-xylene [106-42-3], and *o*-xylene [95-47-5] (see XYLENES AND ETHYLBENZENE). There are two other large-volume petrochemicals that do not fall easily into either of these two categories: ammonia (qv) [7664-41-7] and methanol (qv) [67-56-1]. These two products are derived primarily from methane [74-82-8] (natural gas).

Olefins are produced primarily by thermal cracking of a hydrocarbon feedstock that takes place at low residence time in the presence of steam in the tubes of a furnace. In the United States, natural gas liquids derived from natural gas processing, primarily ethane [74-84-0] and propane [74-98-6], have been the dominant feedstock for olefins plants, accounting for ~60–70% of ethylene production. Most of the remainder has been based on cracking naphtha or gas oil hydrocarbon streams that are derived from crude oil. Naphtha is a hydrocarbon fraction boiling between 40 and 170°C, whereas the gas oil fraction boils between ~310 and 490°C. These feedstocks, which have been used primarily by producers with refinery affiliations, account for most of the remainder of olefins production. In addition, a substantial amount of propylene and a small amount of ethylene are recovered from gas streams produced in petroleum refinery cracking units.

In most of the rest of the world, the olefins industry was originally based on naphtha feedstocks. Naphtha is the dominant olefins feedstock in Europe and

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Asia. In the mid 1980s, several large olefins complexes were built outside the United States primarily based on ethane feedstocks, most notable in western Canada, Saudi Arabia, and Scotland. During the 1990s, new large olefins complexes based on ethane feedstocks were also built in Kuwait, Qatar, and Malaysia. In each case, the driving force was the production of natural gas, perhaps associated with crude oil production, which was in excess of energy demands.

Recently, several large olefins complexes have been designed based on the use of condensates, a heavier natural gas liquid. Condensates are mixtures of liquid hydrocarbons, typically mixtures of pentane (C-5) and heavier components, which are recovered from natural gas either at the wellhead or in gas processing plants. Condensates usually are classified as either "light" or "heavy," according to their boiling range, and light condensates are sometimes classified as "natural gasolines". The typical properties of light condensates—$>65\%$ paraffins content and a boiling range of 30–180°C—make them desirable feedstocks for steam cracking to produce olefins.

Heavy condensates have a boiling range between 30 and 400°C and have characteristics of light crude oils. Like light crudes, heavy condensates contain naphtha, kerosene, gas oil, and minor quantities of heavier fractions, which makes them attractive feedstocks for refinery primary distillation, as well as olefins and aromatics production. A large U.S. Gulf Coast olefins complex based on naphtha feedstocks derived from heavy condensate streams started up in 2001 (1) and another world-scale olefins complex based on heavy condensate feedstocks is now under construction in China (2).

Since the early 1980s many olefin plants in the United States were designed to have substantial flexibility to consume a wide range of feedstocks. Most of the flexibility to use various feedstocks is found in plants with associated refineries, where integrated olefins plants can optimize feedstocks using either gas liquids or heavier refinery streams. Companies whose primary business is the production of ethylene derivatives, such as thermoplastics, tend to use ethane and propane feedstocks that minimize by-product streams and maximize ethylene production for their derivative plants.

Flexibility allows the operator to pick and choose the most attractive feedstock available at a given point in time. The steam-cracking process produces not only ethylene, but other products as well, such as propylene, butadiene, butylenes (a mixture of monounsaturated C-4 hydrocarbons), aromatics, etc. With ethane feedstock, only minimal quantities of other products are produced. As the feedstocks become heavier (ie, as measured by higher molecular weights and boiling points), increasing quantities of other products are produced. The values of these other coproduced products affect the economic attractiveness, and hence the choice of feedstock.

Aromatics are produced primarily from two sources. The most important in the United States is refinery catalytic reformer operations. Catalytic reformers are high temperature catalytic dehydrogenation processes that convert naphthenes into aromatics in order to increase the octane level, and hence the gasoline blending quality of the stream being processed. Reformers produce large quantities of the primary aromatic chemicals. Benzene, toluene, and a mixed-xylene stream are subsequently recovered by extraction or extractive distillation using a solvent (see BTX PROCESSING). Recovery of *p*-xylene from a mixed-xylene stream requires a further processing step of crystallization and filtration or adsorption followed by desorption on beds of molecular sieves.

The second source of aromatics is pyrolysis gasoline from olefins plants. Pyrolysis gasoline is one of the by-product streams produced in olefin plants when cracking heavier feedstocks such as naphtha or gas oil. Pyrolysis gasoline contains hydrocarbon fractions from C-5 olefins through C-9 aromatics. Recovery of aromatics from this stream is by extraction and fractionation, just as in recovery from reformate. Pyrolysis gasoline is a more important aromatics feedstock in Europe and Asia than in the United States. A reason is that naphtha is the dominant feedstock for olefins production in these regions of the world, and less gasoline is produced in the refineries of these regions; hence, there is less reforming capacity. Otherwise there are only minimal differences in aromatics production in various regions of the world.

2. Olefin Feedstocks

Olefins are produced primarily by steam cracking of hydrocarbon feedstock. Steam cracking is a thermal cracking process in the presence of steam that takes place at low residence times in the tubes of a furnace. The thermal cracking process was originated in the early 1920s and has been the dominant route to olefins since that time (3). Olefin plants are complex and costly, with both complexity and cost increasing as the design feedstock increases in heaviness (molecular weight) from the lightest feed (ethane) to the heaviest feed (gas oil). Heavier feeds produce a wider array and larger quantities of products that require more complex separation and recovery processes. A new world-scale ethylene plant with a capacity of 1000×10^6kg/year based on naphtha feedstock will cost ~\$750 million (4). The total plant cost, including off-site facilities, is ~\$1.1 billion. Originally olefins plants were designed to consume a specific feedstock, such as ethane or naphtha, or a narrow range of feedstocks, most commonly ethane–propane mixtures. Starting ~1980, producers in the United States that were based on heavier feedstocks such as naphtha or gas oil, began to introduce feedstock flexibility to consume a wide range of feedstocks in their olefin plants. This was done to allow the operator to pick and choose the most attractive feedstock at a given point in time in order to maximize profitability. Olefin plants in the United States have incorporated more feed flexibility than those in Europe, and are therefore able to take advantage of a wider array of potential feedstocks.

Most of the flexibility to use various feedstocks is found in plants with associated refineries, where integrated olefins plants can optimize feedstocks using either gas liquids or heavier refinery streams. Figure 1 illustrates the many linkages between an olefin plant and a refinery that is typical of integrated complexes in the United States.

Companies whose primary business is the production of ethylene derivatives, such as thermoplastics, tend to use ethane and propane feedstocks that minimize by-product streams and maximize ethylene production for their derivative plants. Table 1 provides a summary of the 2003 production quantity and value of primary olefins petrochemicals and olefin feedstocks in the United States.

The cracking process produces not only ethylene, but other products as well. With ethane feedstock, only minimal quantities of other products are produced. As the feedstocks become heavier, increasing quantities of other products are produced. Most operators characterize these other products as either coproducts or by-products. In this article, coproducts are defined as other primary olefins (propylene and butadiene), and primary aromatics (benzene, toluene, and xylenes). By-products are everything else ranging from C-4 monoolefins to tars. The principal distinction between coproducts and by-products is that coproducts are the more desired and valuable products where operators often adjust feedstocks and operating conditions to maximize or minimize production, depending on the economics at the point in time. The values of these coproducts and by-products affect the economic attractiveness, and hence the choice of feedstock. Table 2 presents typical yields for a new plant employing the latest technology from various feedstocks as well as a characterization of the feedstock density and boiling range. Yields from older existing plants differ somewhat from these yields, generally being lower in ethylene production (see ETHYLENE).

It can be seen that in the case of ethane, the yields of ethylene are the greatest and only minimal quantities of other products are produced. In the case of gas oil, the yields of ethylene are the lowest and large quantities of heavier coproducts and by-products are produced. When cracking heavier feedstocks, eg, naphtha, the severity of the cracking can be varied by adjusting the cracking temperature. Yields of ethylene can be maximized at the expense of propylene and butylene by increasing severity, or ethylene yields can be minimized and thus propylene and butylene yields maximized by lowering severity. Table 3 illustrates the effect of severity on yields for full-range naphtha cracking at high and low severity.

The selection of feedstock and severity of the cracking process are economic choices, given that the specific plant has flexibility to accommodate alternative feedstocks. The feedstock prices are driven primarily by energy markets and secondarily by supply and demand conditions in the olefins feedstock markets. The prices of individual feedstocks vary widely from time to time as shown in Figure 2, which presents quarterly prices of the various feedstocks in the United States from 1985 through 2003 in dollars per metric ton (1000 kg) (6).

It can be seen that the feedstock prices are not only volatile, but also vary with respect to each other. In 1985, high crude oil prices and natural gas price controls that tended to restrain the prices of natural gas liquids made gas liquids feeds much more attractive than heavier naphtha feeds. This situation encouraged olefin operators, whose plants were designed for heavy feeds, to modify their plants to increase their choice of feedstocks. On the other hand, at the end of 1991, temporary supply shortages of gas liquids caused ethane and propane prices to rise relative to heavier feeds. It can be seen that prices for all feedstocks have generally converged since 1991, with a key exception being during 1995 when depressed natural gas prices resulted in lower ethane prices.

The relative cost of various feedstocks can be more easily understood by examining the ratios of one to another. In Figure 3, the ratios of the various alternative feeds to ethane are shown. The high ratio of naphtha to ethane during most of the 1985–1991 period and in late 1995 clearly shows the relative disadvantage of naphtha feedstock during these periods.

Simply looking at the feedstock prices or price ratios is insufficient to accurately identify the most attractive feedstock because the values of all of the coproducts and by-products must also be taken into account. This is usually accomplished by calculating the cost to produce ethylene with all other coproduct and by-product yields credited against the cost of ethylene. An example of the cost of ethylene is presented in Table 4. The cash costs of ethylene from various feedstocks are compared for the first two quarters of 2003. Cash costs reflect all plant manufacturing costs except depreciation and are a measure of the out-of-pocket cash costs generated by the operation.

The data for the January–March period are generally typical of ethylene costs when natural gas and natural gas liquids prices are weak relative to prices for naphtha, and for crude oil and gasoline whose prices heavily influence the price of naphtha. During this period, crude oil and gasoline prices were particularly strong due to an oil workers' strike in Venezuela and tensions in the Middle East leading up to the war in Iraq. This situation more typically occurs during summer months when natural gas prices are weaker due to lower seasonal demand and prices for gas liquids are seasonally lower. Conversely, gasoline demand and prices are seasonally higher in the summer due to the peak driving season, and the cost of naphtha reflects this strength.

During the January–March 2003 period, the cash costs of producing ethylene from naphtha were ∼12¢ per kg of ethylene higher than the cash costs from ethane and about nine cents per kg of ethylene higher than the cash costs from propane. Therefore, gas liquids were the most economical source of feedstock during that period. Table 4 also presents the cash costs of ethylene from the same feedstocks during the April–June 2003 period when ethane became the least economical feedstock and naphtha was the preferred feedstock. Very low inventories of natural gas resulted in sharply higher natural gas prices, also forcing up ethane prices in order to provide an incentive to recover it from natural gas. Thus an ehtylene producer with feedstock flexibility would vary the feedslate over time in order to achieve the lowest possible costs. The historical feedstock sources for ethylene production in the United States are presented in Table 5. The shift to heavier feedstocks due to the high natural gas prices during 2003 is also shown.

The corresponding historical feedslate for ethylene production in the United States is presented in Table 6.

Most new plants built in the United States during the 1990s were based primarily on ethane and propane feeds because the companies constructing these facilities are predominantly thermoplastic producers requiring ethylene, but most industry observers expect that olefin feedslates in the United States will become progressively heavier in the future. Additional supplies of ethane will be limited, barring significant new discoveries of natural gas, and higher natural gas prices relative to prices for liquid fuels are expected to reduce the future attractiveness of ethane as a feedstock. Some additional propane will probably be imported from foreign sources. Adequate supplies of naphtha and gas oil are available to meet the remainder of growth demands for ethylene. On a worldwide basis, gas liquids accounted for ∼40% of ethylene production in 2003 and are expected to continue at that level in the future because of additional recovery of gas liquids associated with crude oil and natural gas production outside of the United States. As the United States olefins feedslate becomes somewhat heavier, the feedslate in the rest of the world will become somewhat lighter.

Refinery gas streams are a significant source of propylene and a minor source of ethylene in the United States. About one-half of the propylene produced in the United States is recovered directly from refinery gas streams, which are largely produced in fluid catalytic cracking (FCC) units (FLUID CATALYTIC CRACKING (FCC) UNITS, REGENERATION). FCC units are designed to convert heavy gas oil fractions into gasoline blend stocks and are used more extensively in the United States than in Europe and Asia. When used for producing a fuel, this propylene stream would be converted into heavier gasoline blend stocks by alkylation or dimerization processes or blended into liquefied petroleum gas (LPG). Refinery-grade propylene is usually in the 60–70% purity range, with the principal impurity being propane. Propylene prices are normally such that it is more attractive for refiners in close proximity to propylene consumers to sell or transfer the refinery-grade propylene to operators for the purpose of purification to chemical-grade quality (minimum 92% propylene) or polymer-grade quality (~99+% propylene). Other refiners also have facilities to perform this purification and thus are able to sell one of the higher purity grades of propylene. Purification consists of fractionation and removal of trace impurities. There are a few chemical processes that can utilize refinery-grade propylene without purification; cumene [98-82-8], 2-propanol [67-63-0], and higher olefins such as nonene (C-9 monoolefins) and tetramer (C-12 monoolefins).

3. Aromatics Feedstocks

Aromatics are produced primarily from two sources, refinery catalytic reformer operations and recovery from the pyrolysis gasoline fraction from olefin plants. The most important source in the United States is refinery catalytic reformer operations. Catalytic reformers are high temperature catalytic dehydrogenation processes that convert naphthenes contained in virgin naphthas into aromatics in order to increase the octane value, and hence the gasoline blend value of the stream being processed. Reformers produce large quantities of the primary aromatics; benzene, toluene, and isomers of xylene (see BTX PROCESSING).

The preferred feedstocks for aromatics production are naphthas containing high concentrations of the naphthene precursors to benzene, toluene, and xylenes. Naphthas are characterized according to their naphthene+aromatic (N+A) values and boiling range. Naphthas with N+A values in the range of ~40–45 or above are preferred reformer feedstocks and command premium prices. Naphthas with lower N+A values are poor reformer feedstocks and have lower values, but happily these low N+A naphthas are preferred for olefins plant feedstocks. The production of aromatic chemicals in the reforming process can be maximized by adjusting the distillation cut points on the naphtha feedstock to include the C-6 to C-8 cycloparaffins and aromatics. The resulting reformate contains from 4 to 8% benzene, with the higher level preferred. A typical composition (vol %) of the C-6 to C-8 aromatics fraction from a reformer operating at 100 Research Octane Number (RON) severity is benzene, 12%; toluene, 43%; and xylenes fraction, 45%. The xylene fraction is 25% *o*-xylene, 20% *p*-xylene, 40% *m*-xylene, and 15% ethylbenzene.

Benzene, toluene, and a mixed-xylene stream are subsequently recovered by extraction or extractive distillation using a solvent. Recovery of *p*-xylene from a mixed-xylene stream requires a further process step of either crystallization and filtration or adsorption on molecular sieves. *o*-Xylene can be recovered from the raffinate by fractionation. In *p*-xylene production, it is common to isomerize the *m*-xylene in order to maximize the production of *p*-xylene and *o*-xylene. Additional benzene can also be produced by the hydrodealkylation of toluene to benzene to balance supply and demand. Less common is the hydrodealkylation of xylenes to produce benzene and the disproportionation of toluene to produce xylenes and benzene, but the latter process has been more widely applied, particularly in Asia, during the past 10 years.

The second source of aromatics feedstock is pyrolysis gasoline from olefins plants. Pyrolysis gasoline is one of the by-product streams produced in olefin plants when cracking heavier feedstocks such as naphtha or gas oil. Pyrolysis gasoline contains hydrocarbon fractions from C-5 olefins through C-9 aromatics. Recovery of aromatics from this stream is by extraction and fractionation, just as in the recovery from reformate, following treatment to saturate diolefins. Pyrolysis gasoline is a more important aromatics feedstock in Europe and Asia than in the United States. This is because naphtha feedstocks are used more for olefins production in these regions of the world and less gasoline is produced in these regions; hence there is less reforming in refineries. A typical composition of C-6–C-8 aromatics stream from pyrolysis gasoline is benzene, 54%; toluene, 31%; and xylenes fraction, 15%. The xylene fraction is 17% *o*-xylene, 23% *p*-xylene, 37% *m*-xylene, and 23% ethylbenzene.

Pyrolysis gasoline is richer in benzene than reformate, 31% vs 7%. Essentially all of the pyrolysis gasoline in the United States is processed to recover aromatic chemicals because of the higher benzene content and problems associated with blending pyrolysis gasoline into motor gasoline. Pyrolysis gasoline contains higher molecular unsaturated compounds that tend to form gum materials in gasoline unless hydrogen treated.

The U.S. Clean Air Act Amendments of 1990 limited the amount of benzene in reformulated gasoline in the United States to 1% (7). Initially there was some concern that this would disrupt the benzene supply and demand balance in the chemical industry because at that time gasoline contained benzene >1%. If it had been necessary for refiners to extract all of the benzene >1%, substantial additional benzene could have been produced. However, only modest increases in the quantity of benzene produced from catalytic reformer sources occurred when reformulated gasoline became required in 1995 as most refiners adjusted the composition of reformer feed and reformer severity to produce less benzene. In addition, reformulated gasoline accounts for about one-third of U.S. sales since its use is only required in metropolitan areas with the most severe summertime ozone levels. Therefore, benzene levels >1% are still permissible in the other two-thirds of gasoline sold in the United States, making it possible for refiners to preferentially use low benzene streams for reformulated gasoline blends.

4. Other Feedstocks

The only other petrochemical feedstock of significant commercial use is methane (natural gas) that is used primarily to produce ammonia and methanol. Consumption factors are ~28 and 31 GJ/metric ton, respectively (58,300 and 64,700 BTU/lb) (8). Approximately 339×10^6GJ (321×10^{12} BTU) of methane was processed into $8{,}770 \times 10^6$kg of ammonia (9) and ~3000×10^6kg of methanol in the United States in 2003. Natural gas prices generally follow crude oil prices in the United States because they compete in energy markets and traditionally have been lower in cost on a fuel basis. Historical natural gas and crude oil prices are shown in Figure 4. In contrast, the price of natural gas is decoupled from crude oil prices in countries with extensive natural gas reserves and limited domestic markets for natural gas. Global ammonia and methanol production is increasingly being concentrated in these locations and U.S. production of these products has declined as U.S. natural gas prices have increased since 2000.

The relationship between natural gas and crude oil prices can be more easily understood by examining the ratios of one to another. In Figure 5, the ratio between the U.S. benchmark prices for natural gas and crude oil on a fuel basis is shown. The ratio was well below 1.0 during the entire period from 1985 through late 2000 when U.S. natural gas supplies were plentiful. Due to increasing U.S. natural gas demand and limited increases in supplies, the ratio has risen >1.0 several times since 2000 and a ratio near 1.0 is forecast to continue in the future.

5. Alternative Feedstocks

Alternative feedstocks for petrochemicals have been the subject of much research and study over the past several decades, but have not yet become economically attractive. Chemical producers are expected to continue to use fossil fuels for energy and feedstock needs for many decades in the future. The most promising sources that have received attention include coal, tar sands, oil shale, and biomass. Near-term advances in coal-gasification technology offer the potential to replace oil- and gas-based feedstocks in selected applications (10) (see FEEDSTOCKS, COAL CHEMICALS). Processes for the production of olefins from alternative feedstocks are in the development phase with no commercial plants operating. Several processes using methanol as a feedstock are considered to be the most promising and are economically attractive since the methanol could be produced from natural gas in locations having cheap, abundant natural gas reserves.

Lurgi's MTP technology has been demonstrated in relatively small scale. This technology converts methanol into propylene at high selectivity. The UOP/HYDRO MTO process converts crude methanol into an olefinic gas rich in ethylene and propylene. The ratio of propylene to ethylene produced can be adjusted within the MTO process. The process yield performance for the UOP/HYDRO MTO process as presented in public domain literature is presented in Table 7 (10). The effect of operational severity enables the ethylene/propylene ratio to be changed. UOP has reported that this ratio can be varied from 1.5 to 0.64 by changing reactor conditions.

Because oil and gas are not renewable resources, at some point in time alternative feedstocks will become attractive; and as natural gas and petroleum prices rise, the timetable for commercialization of alternative feedstocks will accelerate. Of the alternatives, only agricultural-based materials are a renewable resource (see BIOMASS ENERGY). Currently, the only chemical produced from a natural product in large-volume commercial quantities is ethanol via fermentation of natural sugar and starches. The vast majority of fermentation ethanol is used for fuel applications and this is likely to grow significantly as U.S. production of ethanol for use as a gasoline blendstock increases. Ethanol (qv) can be converted into a number of petrochemical derivatives and could become a significant source of chemicals, especially if new technology for converting the cellulose and hemicellulose in low cost biomass, such as corn stalks, sugar cane residue and rice straw, to ethanol is successfully developed. Several start-up companies in the United States and Canada are in the throes of such development efforts.

Other notable developments for converting biobased materials to industrial chemicals include DuPont's process for taking glucose to a new monomer, 1,3-propanediol (PDO). This monomer, when condensed with terephthalic acid, makes a polyester, trimethylene terephthalate (PTT), that is an ideal polymer for making carpeting. PTT combines the inherent stain resistance characteristic of polyesters with the excellent resiliency of nylon. DuPont has formed a joint venture with Tate & Lyle to create products from bioderived PDO. In addition to carpeting, PDO based polymers may find use in textiles, clothing, and interior applications. In the late 1990s, Shell developed a petrochemical based process for making PDO and is also developing the market for PTT. It will be interesting to see which route, the bio based or petrochemical-based process, is the ultimate winner.

Cargill and Dow have teamed up to develop fermentation technology to convert corn starch to lactic acid at rates that will allow the resulting polymer, polylactic acid (PLA) to compete with large volume petrochemical based plastics such as nylon and PET. In addition to developing efficacious biocatalysts to speed up reaction rates, Cargill Dow is increasing the plant size as a means to lower costs. The capacity of Cargill Dow's first PLA plant, which came on stream in 2002, is 140,000 metric tons per year and they are already planning additional capacity. Cargill Dow believes the market potential for PLA could reach 500,000 metric tons by 2010. Products based on PLA offer many good properties and will find application in consumer goods, food packaging, bedding, clothing and other applications. PLA, in addition to being made from renewable resources, also has the benefit of being biodegradable or easily recycled back to its starting monomer. Lactic acid esters, such as ethyl or buty lactate, are also being explored as environmentally friendly substitutes for petrochemical-based solvents such as methylethyl Ketone (MEK) or isopropanol.

Cargill also has other programs in place to produce industrial chemicals from renewable agricultural resources. Some of these projects include conversion of glucose to 3-hydroxypropionic acid (3-HP). 3-HP, using conventional industrial chemistry, can be converted to acrylic acid, PDO, and other specialty polyesters;

production of urethane polyols from vegetable oils and using metathesis chemistry to cleave and modify unsaturated natural oils to olefins and difunctional olefins.

Another promising bioconversion process that has the potential to compete with petrochemical processes is the conversion of glucose to succinic acid. Several U.S. Government sponsored laboratories (Argonne National Laboratory, Pacific Northwest National Laboratory and National Renewable Energy Laboratory) have collaborated to develop fermentation technology to convert sugars to succinic acid. Succinic acid can undergo hydrogenolysis to 1,4-butanediol (BDO). In 2003, the global market for BDO is estimated to be over 800,000 metric tons per year. Besides the U.S. based development in this area, Mitsubishi Chemical, working together with Ajinomoto in Japan, is also investigating a similar approach.

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John T. Boepple
Nexant *ChemSystems*

Table 1. **Olefin Feedstocks and Olefins Production, 2003**[a]

Material	Quantity, million kg	Cost, million $
	Feedstocks	
ethane	13,813	4,043
propane	9,577	2,824
butane	1,917	576
heavier than C-4s	17,880	4,931
	Primary olefins	
ethylene	22,966	14,407
propylene	13,916	7,031
butadiene	1,901	1,247

[a] See Refs. 5 and 6. Courtesy of Nexant *ChemSystems*.

Table 2. **Yields[a] from Typical Ethylene Feedstocks,[b] wt %**

Feedstock	Ethane	Propane	Naphtha[c]	Naphtha[d]	Gas oil
density, g/L			683.0	706.3	890.5
ASTM ibp, °C[e]			37	37	310
ASTM ebp, °C[f]			141	167	488
		Products			
hydrogen	3.64	1.41	1.03	0.92	0.58
methane	3.13	23.64	17.50	15.80	9.40
acetylene	0.33	0.49	1.05	0.82	0.30
ethylene	50.04	37.15	35.40	31.70	20.50
ethane	40.00	4.23	3.85	3.80	2.90
propadiene	0.04	0.48	1.11	0.90	0.51
propylene	0.75	13.91	14.90	14.40	13.80
propane	0.16	8.00	0.35	0.30	0.27
butadiene	0.85	3.64	4.60	4.60	4.45
butylenes	0.19	0.98	3.90	3.90	4.10
butane	0.23	0.11	0.23	0.20	0.10
C-5–C-8 naphtha	0.39	1.83	3.40	4.90	4.75
benzene	0.20	2.26	5.50	5.80	6.50
toluene	0.05	0.52	1.60	2.80	2.25
C-8 aromatics	0.00	0.08	0.20	1.40	1.70
styrene	0.00	0.41	0.70	0.75	0.70
C-9-205 FBP naphtha	0.00	0.75	1.08	2.05	3.00
fuel oil	0.00	0.11	3.60	4.96	24.19
total	*100.00*	*100.00*	*100.00*	*100.00*	*100.00*

[a] Single pass.

[b] Courtesy of ABB Lummus Global Inc.

[c] Light naphtha.

[d] Full-range naphtha.

[e] Initial boiling point (bp).

[f] End bp.

Table 3. **Yields at High and Low Severity for Full-Range Naphtha Feedstock**[a,b]

Product	High severity yield, wt %	Low severity yield, wt %
hydrogen	0.92	0.74
methane	15.80	12.60
acetylene	0.82	0.35
ethylene	31.70	26.00
ethane	3.80	4.40
propadiene	0.90	0.60
propylene	14.40	17.50
propane	0.30	0.50
butadiene	4.60	4.40
butylenes	3.90	6.80
butane	0.20	0.85
C-5–C-8 naphtha	4.90	11.70
benzene	5.80	3.10
toluene	2.80	2.75
C-8 aromatics	1.40	2.50
styrene	0.75	0.57
C-9-205 FBP naphtha	2.05	2.30
fuel oil	4.96	2.34
total	*100.00*	*100.00*

[a] Courtesy of ABB Lummus Global Inc.

[b] Density = 706.3 g/L; ASTM ibp = 37°C; ASTM ebp = 167°C.

Table 4. **Cash Costs[a] of Ethylene from Various Feeds[b]**

	Ethane		Propane		Naphtha	
Cost	Jan.–March	April–June	Jan.–March	April–June	Jan.–March	April-June
feedstock	38.7	36.7	73.9	62.8	109.8	83.4
by-product credits	−14.8	−13.8	−50.5	−49.3	−86.5	−81.5
catalyst and chemicals	0.2	0.2	0.2	0.2	0.4	0.4
utilities	9.4	8.8	13.1	12.2	21.0	19.6
operating	2.1	2.1	2.2	2.2	2.5	2.6
plant overhead	2.5	2.6	2.7	2.8	3.2	3.3
total cash costs	*38.2*	*36.6*	*41.6*	*31.0*	*50.4*	*27.7*

[a] 2003.

[b] Courtesy of Nexant *ChemSystems*.

Table 5. **Historical U.S. Ethylene Production by Feedstock (million kg of ethylene production)**[a]

Feedstock	1999	2000	2001	2002	2003
ethane	11,523	11,328	11,098	10,798	10,109
propane	5,023	3,481	3,984	5,077	4,072
n-butane	810	912	1,116	900	778
naphthas	4,279	5,988	2,813	3,430	3,991
gas oil	2,539	2,054	2,288	2,904	3,001
refinery offgas recovery	977	1,021	1,034	1,076	1,010
total	*25,152*	*24,785*	*22,332*	*24,185*	*22,961*
	Percent from heavy liquids (naphtha and gas oil)				
	27.1	32.5	22.8	26.2	30.5

[a] Courtesy of Nexant *ChemSystems*.

Table 6. **Historical U.S. Ethylene Feedslate (million kg feedstock)**[a]

Feedstock					
ethane	14,058	13,821	13,540	13,174	12,333
propane	10,549	7,310	8,366	10,662	8,551
n-butane	1,782	2,005	2,454	1,980	1,712
naphthas	12,968	18,146	8,523	10,394	12,094
gas oil	10,233	8,279	9,221	11,703	12,094
refinery offgas recovery	977	1,021	1,034	1,076	1,010
total	*50,567*	*50,583*	*43,138*	*48,988*	*47,795*

[a] Courtesy of Nexant *ChemSystems*.

Table 7. **UOP/HYDRO MTO Process Product Yields (Weight Percent)**[a]

Product	Maximum ethylene mode	Maximum propylene mode
ethylene	48	34
propylene	31	45
butenes	9	12
other products	12	9
	Ethylene/propylene ratio	
	1.55	0.76

[a] Ref. 10.

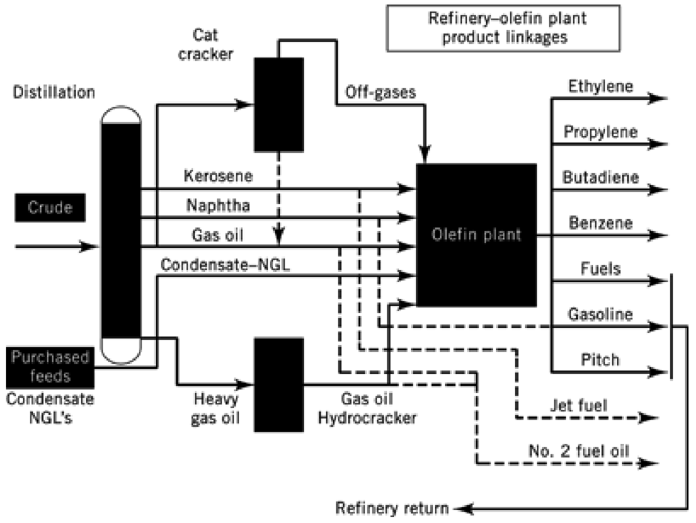

Fig. 1. Typical refinery–olefin plant complex. Courtesy of Shell Oil Co.

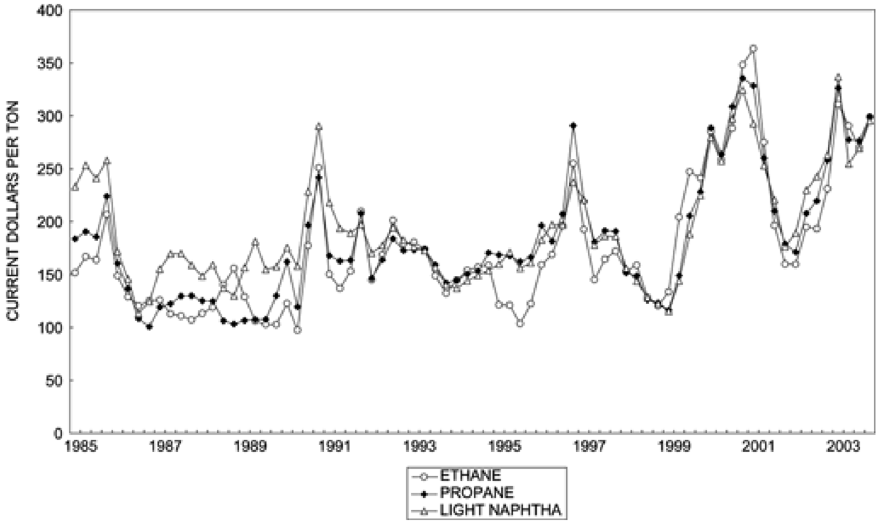

Fig. 2. Quarterly olefin feedstock prices, 1985–2003, for (○) ethane (◆) propane, and (△) light naphtha.

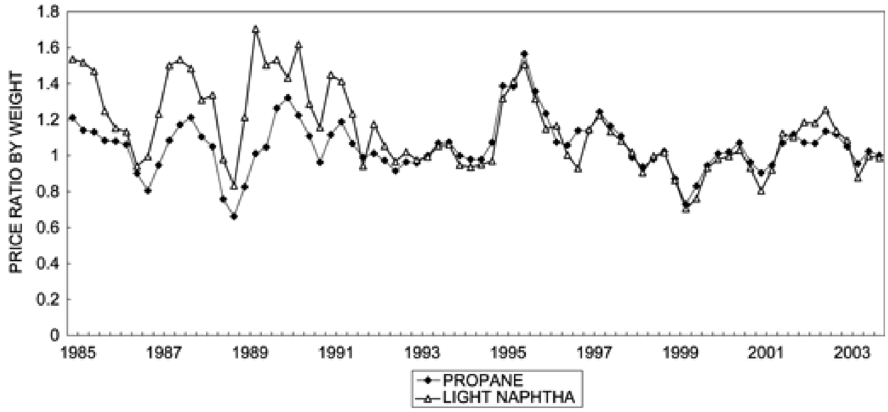

Fig. 3. Price ratio of various feeds to ethane, 1985–2003; (◆) propane and, (△) light naphtha.

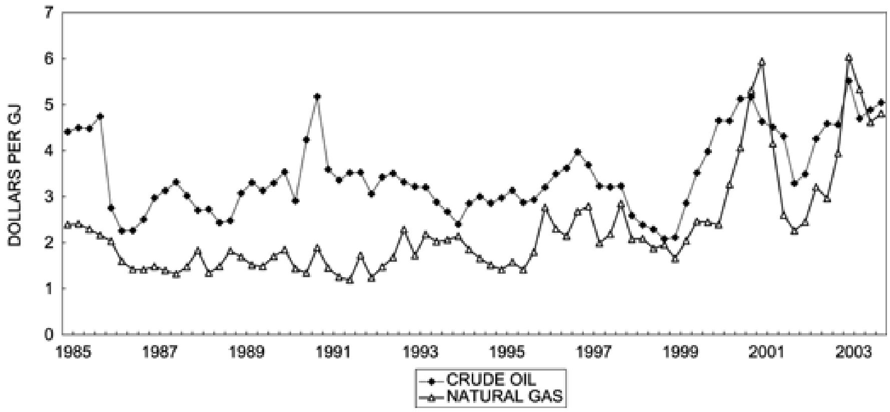

Fig. 4. Prices of natural gas (△) and crude oil (◆), 1985–2003. To convert ¢/GJ to ¢/BTU, multiply by 1.055×10^{-6}.

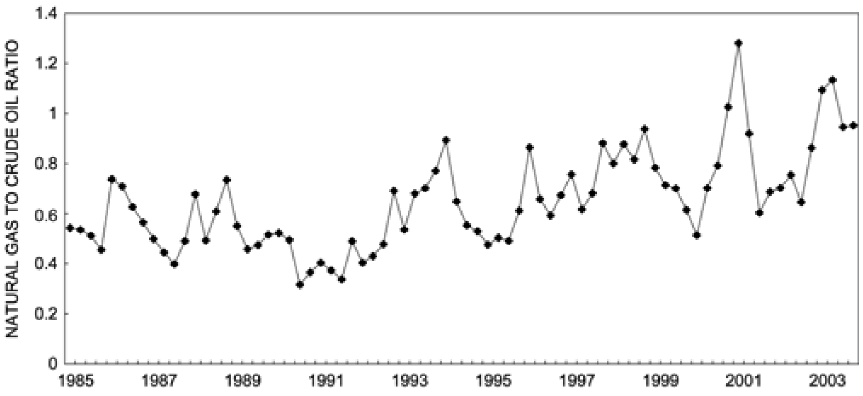

Fig. 5. Fuel price ratio of natural gas at Henry Hub to WTI crude oil, 1985–2003.