

総説

A Review of the State of the Art, and a Look at Trends

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Between 1960 and 1970 the world wide production of ethylene has increased from 3 million MAT to 18 million MTA as shown in Figure 1. Today

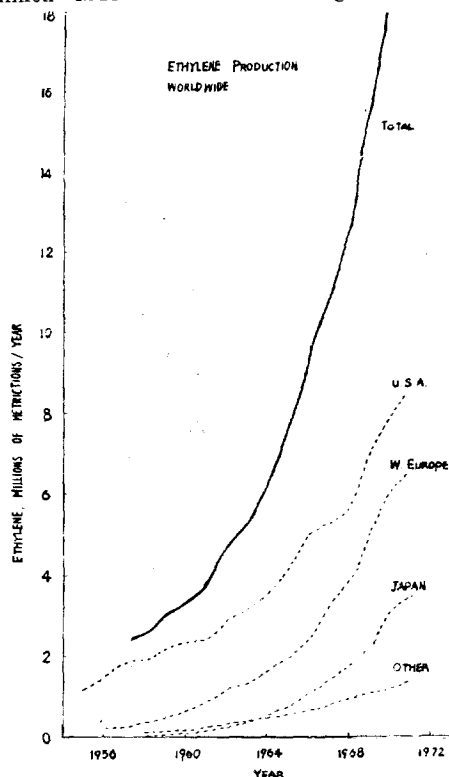


Fig. 1

ethylene is the most important petrochemical raw material. It is produced on all continents, and

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ethylene plants form the nucleus of new petrochemical industries in many developing countries.

The dramatic rise in production called for the development of larger and larger plants, which the builders of ethylene plants accomplished with remarkable swiftness and without any major technical difficulty.

High capacity equipment, notably centrifugal compressors, were readily available for these large plants. The tubular pyrolysis heater remains the dominant reactor for the conversion of aliphatic hydrocarbons to olefins. The development of high capacity pyrolysis heaters, however, did not coincide with the advent of the large ethylene plant.

It was only recently that large pyrolysis heaters became available.

A Lummus heater with a nominal capacity of 45,000 MTA ethylene started up three months ago.

Feedstocks

Ethane and propane are still the dominant feedstocks for ethylene plants wherever natural gas is in abundance. In Europe and Japan, Practically all ethylene is presently produced from naphtha. Contrary to many predictions, gas oil has not emerged as an important feedstock for ethylene plants although the necessary technology is available and thoroughly tested. Most petrochemical companies cannot obtain gas oil at attractive prices; only large refiners find themselves occasionally in a situation

with sufficient gas oil at an attractive cost for an ethylene plant. Refiners also have the advantage of being readily able to market the heavy fuel products which are produced by a gas oil cracking plant in significant quantities. It seems to us that the immediate future holds considerable uncertainty in regard to the supply of feedstock for existing and future ethylene plants.

It is probably safe to predict that the growth of ethylene production capacity in the seventies will be slower than it was in the last decade. Nevertheless, the question of the future ethylene plant, its feedstock, its flexibility, its byproducts, and its profitability is certainly of interest.

The feedstock question is probably the most important. It is surprising and was totally unforeseen that most future ethylene plants in the United States will be consuming liquid feedstock such as naphtha, raffinates and gas oil, whereas in Europe gas cracking plants may be built which will feed on ethane and propane recovered from North Sea and Russian natural gas. This development will have a profound impact on the petrochemical industry on both continents. The ethylene producer in the United States will be faced with the problem of handling and marketing a variety of byproducts, while the European producer will no longer produce the byproducts he was accustomed to. In Japan, with increasing quantities of imported liquefied natural gas, there will exist the opportunity of extracting the heavier components such as ethane, propane and butane for conversion into petrochemicals. In fact, plants that make use of the cold potential of liquid natural gas by combining the vaporization with an ethylene plant promise to be economically attractive.

Cracking technology for light gases, virgin naphtha and raffinates is well established. Extensive large scale tests have proven that naphtha technology with very minor modifications is applicable to the cracking of light gas oil.

Light gas oil in this context means a virgin material with a boiling range of 200 to 400°C. The modifications of the naphtha pyrolysis module for gas oil cracking service concerns only the transfer line exchanger, which has to be designed

for a higher outlet temperature to obtain a reasonable on-stream time. A Pyrolysis heater designed to crack light gas oil can economically process any higher feedstock including ethane (Table 1). Such flexibility will be one of the characteristics

Table 1. Heater Capacity for Various Feedstocks
(Srt II HC Heater)

Feedstock	Capacity Ethylene MT/HR
Gas Oil	32.6
Naphtha	35.7
Ethane/Propane	36.9

of future ethylene plants which are expected to utilize gas oil at one time or another. For this flexibility, however, a small penalty will be paid in the form of less high pressure steam production for the lighter feedstock operation. Since the transfer line exchangers will be designed for the gas oil effluent quenching, for naphtha feed operation the exchanger outlet temperature will be slightly higher, resulting in less high pressure steam production. In one case, this reduction amounted to roughly 3% of the high pressure steam production. This heat not recovered at the transfer line exchanger will be turned into medium pressure steam, and the net result will be the degradation of high pressure steam into medium pressure steam. One plant is presently in design which will produce between 0 and 50% of its total ethylene production from gas oil with the remainder to be derived from naphtha and light gases. Contrary to earlier predictions light gas oil cracking plants are only marginally more expensive than naphtha plants. For the equivalent ethylene production capacity, C_3 and lighter or C_4 and lighter gases are essentially the same for both naphtha and light gas oil feeds, and therefore, the charge gas compressor, chilling train and the subsequent processing units including refrigeration systems are practically the same for both cases. For gas oil feed, however, the front end will be a little larger, particularly the number of cracking heaters. Roughly 10% more heaters will be required for the gas oil plant. Considering the future demand for kerosene and light fuel oil it seems doubtful that light gas oil will ever become an important feedstock for ethylene

plants.

From a technical and economical point of view heavy and vacuum gas oils are ill suited as feedstocks for ethylene plants. Their hydrogen to carbon ratio is substantially lower than those of the light olefins which means that substantial quantities of heavy hydrogen deficient fuel oils will result as byproducts. In this respect all gas oil plants differ fundamentally from naphtha plants. The total fuel, that is gas and oil produced in a naphtha plant, nearly balances the fuel requirements of the plant. All other products are generally of a higher value than the naphtha feedstock.

However, heavy gas oils can be converted into suitable pyrolysis feedstocks through hydrocracking. Table 2 shows typical yields and gross margins for a heavy gas oil with and without hydrocracking. For this particular example, about 70% of the vacuum gas oil is hydrocracked to a lighter gas oil; the remainder being mainly naphtha and some light gases. Overall, the hydrocracked gas oil yields more

Table 2. Yields and Product Values for Heavy Gas Oil without and with Hydrocracking

	Virgin Heavy Gas Oil WT %	Hydrocracked Gas Oil WT %
Hydrogen	0.47	0.86
Fuel Gas	12.48	18.16
Ethylene	18.00	24.55
Propylene	13.20	12.50
C4's	6.21	7.34
Butadiene	5.33	4.95
NA Gasoline	11.40	8.67
Aromatics	7.91	11.53
Fuel Oil	<u>25.00</u>	<u>11.44</u>
	100.00	100.00
Total Value of all products		
\$/Ton Heavy Gas Oil	52.8	63.6

ethylene and less fuel oils. It also means a higher production of hydrogen and, in particular, aromatics, and for one set of product prices, the value of products increases from 52.8 to 63.6 dollars per ton of vacuum gas oil feed.

The economic justification of the hydrocracking

route is not self evident. The cost of hydrocracking, which is a function of the plant capacity and of the availability and the cost of the hydrogen, could be so high as to nullify the increase in product values. The demand for byproducts and the price for them would affect the economics greatly, and each specific case has to be looked at.

Hydrocracking will offer the advantage of desulfurizing the gas oil, which normally contains much sulfur and could cause problems if cracked directly.

In the United States, where a great demand for high octane non-leaded motor gasoline exists, raffinates will become an important source of ethylene plant feedstocks. Increased emphasis on the production of lead free high octane gasoline will make available more raffinate.

Ethylene plants will not only convert such relatively low valued hydrocarbons into petrochemicals but will also return a substantial portion of the feedstock as high octane gasoline.

Byproduct Cracking

Operating companies, and in particular petrochemical companies, are often faced with the problem of by-product disposal. Propylene, butanes-butylenes from butadiene extraction plants and raffinates of aromatics extraction facilities are often valued as fuel. The history of propylene demand is particularly interesting. Not long ago there existed a considerable shortage, and ethylene plants were designed for maximum propylene yield. Today, several ethylene plants crack propylene for additional ethylene, although propylene is one of the least attractive pyrolysis feedstocks. In naphtha cracking plants the ratio of propylene to ethylene production can, within limits, be controlled with the cracking severity. The lower practical limit of this ratio is approximately 0.4 to 0.45 depending on the feedstock.

Future ethylene plants will possibly contain hydrogenation facilities to convert at times unwanted propylene into propane, which is an ideal pyrolysis feedstock (at least one such plant already exists). Table 3 shows typical yields and the total value of

Table 3. Yields and Gross Margin

	Propylene WT %	Propane WT %
Hydrogen	0.8	1.2
Fuel Gas	19.3	33.5
Ethylene	27.0	51.4
Butadiene	7.7	3.7
C4's	10.1	1.5
NA Gasoline	14.7	5.1
Aromatics	15.4	3.6
Fuel Oil	5.0	0.
	100.0	100.0
Total Value of all products		
\$/Ton propylene	64.8	76.4

Table 4. Yields and Gross Margin
C4 Raffinate

	Hydrogenated C ₄ * WT %	with C ₃ Cracked to Extinction WT %
Hydrogen	1.0	.1
Fuel Gas	27.6	37.0
Ethylene	31.0	45.4
Propylene	26.4	—
Butadiene	3.2	4.2
NA Gasoline	4.4	5.8
Aromatics	4.6	5.7
Fuel Oil	1.8	1.8
	100.0	100.0
Total Value of all products		
\$/Ton of Butane		
C ₃ at premium value	65.6	—
C ₃ at fuel value	56.9	60.3

*Feed Composition : 50% normal butane
50% isobutane

Table 5.

Pyrolysis Yield	Pyrolysis Raffinate WT %	Reformer Raffinate WT %
Hydrogen	1.1	0.8
Fuel Gas	20.9	20.4
Ethylene	24.5	26.0
Propylene	15.0	18.7
C4's	5.1	7.7
Butadiene	4.5	4.9
NA Gasoline	12.7	8.8
Aromatics	11.2	9.2
Fuel Oil	5.0	3.5
	100.0	100.0

Reformer Yield	Pyrolysis Raffinate WT %	Straight Run Naptha WT %
C ₄ & Lighter	18.6	17.3
Benzene	22.7	3.6
Toluene	16.9	12.2
Xylene	11.7	15.9
C ₉ Aromatics	5.2	20.2
C ₅ -Ep Non Aromatics	24.9	30.8
	100.0	100.0

all products for propylene and propane cracking. The raffinate of butadiene extraction plants, which consists primarily of mixed butylenes, is often fed to alkylation facilities producing high octane motor gasolines. Almost as often this material is used as fuel. In its untreated state it is unsuitable as pyrolysis feedstock. After hydrogenation however, it is an excellent feedstock for propylene production. If ethylene is the only desired olefin, the resulting propylene can also be hydrogenated. Table 4 shows the yields for yields for hydrogenated butadiene raffinate without and with hydrogenated propylene cracked to extinction. Raffinates from aromatics extraction plants are poor pyrolysis feedstocks, if they are derived from a pyrolysis gasoline heart cut. Raffinates from catalytic reformer products are good pyrolysis feedstocks. Conversely, pyrolysis gasoline raffinates are good feedstocks for catalytic reformers. Table 5 shows the pyrolysis and reformer yields for these two kinds of raffinates. Reformer raffinate is not reformed normally, and the reformer yield of straight run naphtha is given for comparison with that of pyrolysis raffinate. Nevertheless, many petrochemical companies who do not operate a catalytic reformer, recycle raffinate to the pyrolysis section of their ethylene plants and crack it to extinction.

Byproduct Processing

Occasionally, benzene is the only desired product from an aromatics plant. Three processes are available which produce high purity benzene from the heart cut derived from pyrolysis gasoline through a combination of hydrocracking and hydrodealkylation. The ethylene plant delivers sufficient high purity hydrogen for this operation, provided all hydrogen

is recovered from the residue gas of the hydrodealkylation unit. The cryogenic section of ethylene plants is ideally suited for the treatment of hydrodealkylation residue gases. The hydrocracking of paraffins and naphthenes contained in the pyrolysis gasolines heart cut yields a significant amount of ethane which is easily recovered and recycled to the pyrolysis section for added ethylene production. A plant with a high degree of integration between the ethylene plant and the benzene unit is presently under construction.

Butadiene and aromatics extraction raffinates, surplus propylene and ethane from hydrodealkylation units are byproducts with little intrinsic value which can be recycled to the pyrolysis section of ethylene plants. The net effect of the recycling operation will be a higher total yield of petrochemicals from any given amount of feedstock.

There are other products which with some further processing can substantially improve the economics of ethylene plants. Isoprene extraction plants have recently started up in Japan and Germany.

Both plants were designed to recover isoprene from a mixed C_5 -hydrocarbon fraction separated in ethylene plants. The isoprene content of the mixed C_5 -stream is typically between 10 and 20 percent depending on the pentane content of the feedstock and the cracking severity. A low pentane content of the ethylene plant feedstock and high cracking severities will tend to increase the isoprene content of the C_5 -fraction. The pyrolysis of pentanes yields little isoprene just as the pyrolysis of butanes yields little butadiene. The isoprene raffinate, after complete hydrogenation, can be recycled to the pyrolysis section of an ethylene plant.

The mixed C_5 streams from several ethylene plants will be needed as feedstock for an isoprene recovery plant of economical size. The mixed C_5 -stream from a 500,000 MTA ethylene plant will only contain 14,000 MTA isoprene.

Acetylene is, at present, an unwanted pyrolysis byproduct. Most modern ethylene plants contain facilities for the selective hydrogenation of acetylene to ethane, which in turn can be recycled to the

pyrolysis section and cracked to extinction. High purity acetylene, however, can be recovered at very moderate expense. This may be of interest where a captive market for acetylene exists. A 500,000 MTA ethylene plant operating with moderate cracking severity can produce approximately 10,000 MTA acetylene. The acetylene production can be increased, if desired, by sending the ethane product to special acetylene furnaces instead of to the ethylene furnaces. Methylacetylene and propadiene can be separated similarly. Several plants are in operation which produce a mixed C_3 -stream containing between 20 and 40% C_3H_4 , which can easily be concentrated further. A 500,000 MTA ethylene plant can produce approximately 10,000 MTA C_3H_4 . Recent pilot plant tests demonstrated that the residual fuel oil from naphtha cracking plants is ideally suited for the production of premium needle coke and carbon block. The coking unit can easily be integrated with an ethylene plant. The gasoline and gas produced by the coker can be treated in the ethylene plant and its associated pyrolysis gasoline hydrotreater. However, the fuel oil produced in much larger quantities in gas oil cracking plants will contain more sulfur than the fuel oil derived from naphtha cracking.

At this time it is not quite certain if coke produced from this oil will meet the specification for electrode coke. It may again be more economical to treat pyrolysis fuel oil from several ethylene plants in one centrally located coking unit.

In ethylene plants cracking gas oil, a significant amount of pyrolysis gas oil is produced and separated. This material can be used as fuel for the pyrolysis heaters. It can also be hydrotreated resulting in a low sulfur and color stable light fuel oil product.

Plant Size

The future ethylene plant to be built in Europe, Japan or North America will have a capacity of 400,000 to 500,000 MTA in a single train. Still larger single train plants with capacities of 700,000 to 800,000 MTA can be built; centrifugal compressors of the required size are available. Although some

further reduction in investment cost per unit of annual capacity can be expected from such a large plant it is very doubtful that many will ever be built. Operating companies will have to weigh the risk of committing a truly huge investment to one single installation. Like any other plant, it will have to be operated in the first year at a minimum of 70-80% of its nominal capacity to give the expected economy of scale. There are only a few areas in the world accommodate the sudden increase in production of not only ethylene but of also an entire byproduct slate.

A 500,000 MTA plant will have ten to twelve cracking heaters depending on the feedstock. One heater will be a spare to assure full plant production during heater decoking and maintenance. Even new heaters designed for greater selectivity and higher severity will have to have a capacity of approximately 50,000 MTA of ethylene. A plant which will produce 450,000 MTA of ethylene with eleven cracking heaters is presently under construction. This number must be compared with 20 heaters for the first 450,000 MTA plant which started up three years ago.

Plant Design

Future plants may no longer contain one or two direct fired steam superheaters. Superheating of the waste heat steam can be accomplished in the convection section of each cracking heater. While this design will result in a lower total waste heat steam production, it will also result in a more uniform loading of the boiler during normal operation as compared to start-up. Total investment cost will be lower and total plant shutdowns due to malfunctioning or failure of the separate steam superheater will be eliminated.

Pollution Control

New plants will have to be designed to meet present and as much as possible any future pollution control requirements. Ethylene plants are not major polluters. The fuel gas fired in the cracking heaters

is essentially sulfur free. Pyrolysis gas oil which may at times be used as fuel for pyrolysis heaters will generally have a low sulfur content or can be desulfurized.

The blowdown from the dilution steam system and the spent caustic form the two most obnoxious aqueous effluent streams from ethylene plants. Both can be substantially reduced in quantity, the first, by a steam heated reboiler on the process water stripper as a substitution for the use of open stripping steam. The amount of spent caustic can be reduced with a regenerative acid gas removal system removing the bulk of the hydrogen sulfide and carbon dioxide from the process gas upstream of the caustic scrubber. MEA is being used for this purpose in several gas plants. A naphtha plant is under construction and a gas oil plant is in design with regenerative acid gas removal systems using Alkaid as solvent. In both plants the amount of spent caustic discharged will be small. Ultimately, the spent caustic may be completely regenerated. Tests along these lines are presently underway. Whether a caustic regeneration system will eventually eliminate the need for regenerative acid gas removal systems will solely depend on economic consideration. Either system will discharge hydrogen sulfide which may be burned if permissible or, more likely, be converted to elemental sulfur.

New, more efficient systems have been developed to separate coke from the decoking effluent of cracking heaters and to eliminate the nuisance of open polymer discharge during catalyst regeneration.

In a modern plant all continuous and a great number of intermittent drains are collected and recycled to the quench section. Similarly, the liquid accumulated in the flare drums can be recycled to the plant. Practically, all intermittent liquid and minor gaseous discharges can be recovered and recycled. This even applies to pump drains and the effluent from oil separators.

The flare will for some time remain a big problem in ethylene plants. There does not at present exist a flare design which permits without noise, smoke and light the combustion of 250 t/h of hydrocarbons,

which will be released from a 500,000 MTA plant upon a sudden shutdown of the charge gas compressor. There is no question, however, that this problem will eventually be solved. The ultimate solution should be a high capacity ground flare.

Driver Selection

Most ethylene plants in Japan and Germany use the high pressure steam (120 atm or 1700 psig) generated in the pyrolysis section directly, i.e. without pressure reduction, as motive steam for the turbines driving the main compressors. In America the highest pressure motive steam used in ethylene plants has been 56 atm or 800 psig. With the value of fuel increasing rapidly future American ethylene plants, in particular those cracking liquid feedstocks, may follow European and Japanese practice and use the 120 atm (1600 psi) steam generated in the pyrolysis section directly to drive the major compressors. American high pressure steam turbines are now readily available.

Recovery Plant Design

The recovery section of future ethylene plants will not differ fundamentally from present plants.

Increased use of high-flux and extended surface heat exchangers will give a significant cost reduction for the cryogenic section. Today's designs consume less utilities than older plants. The total compressor horsepower is in the order of 750 to 850 kwh/tc₂H₄ (0.45 to 0.50 bhp/hr/1b) for a typical naphtha plant.

So far only a few plants contain computer control systems, because the investment was not justified by a predictable saving in operating cost. However, more recently, operating companies express more interest in computer control systems as more experience has accumulated. A well designed computer control system will lead to a statistically improved plant performance. Plant instrumentation systems are now often designed for compatibility with a future process control computer.

In summary, the future ethylene plant will have a capacity of 400,000 to 500,000 MTA, it will achieve a higher yield of petrochemicals per unit feedstock than older plants, it will separate and upgrade additional products, it will meet all pollution control requirements, it will be computer controlled, it will do all of this with a lower utilities consumption and would do all of this at a lower total investment cost if it were not for the general trend of world wide inflation.