Advanced Petrochemicals

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ADVANCED PETROCHMICALS

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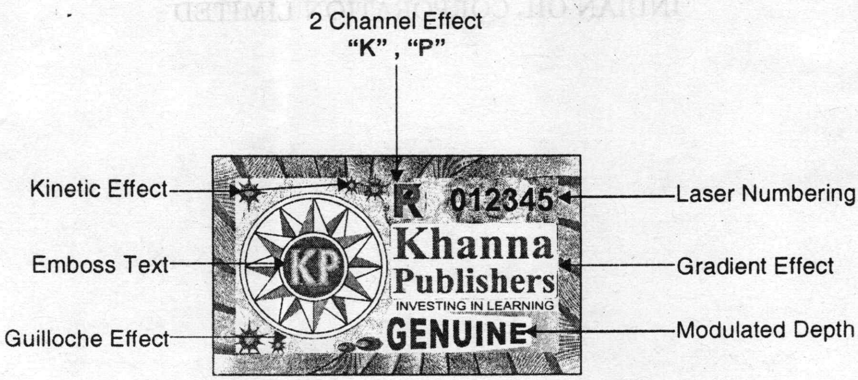

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PREFACE

The major task for the petroleum refineries in the very fast developing country like us is to achieve maximum lighter distillates from gradually obtainable heavy and sour crudes maintaining the various stringent environment norms from time to time specially for the transport fuels. As such the petrochemicals are literally chemicals from petroleum origin is hidden into the basic objective of the refineries along with the exploration of the heavier stocks from the bottom of the barrel. It also includes the optimum use other equivalent natural sources for eco-friendly products and development of low volume high priced value added products/chemicals.

The science of petroleum refining and petrochemical industries are very fluid and there are frequent changes in the technology, policies and demands. In this dynamic stage it is really a difficult task to write book in the developing field for which task has been given to me by constant request from many students in this field throughout our country who happens to read my book on "Advanced Petroleum Refining".

I have tried my best to collect informations on the petrochemicals and have compiled it for the engineering students with a hope it will also be helpful for faculty members as well research scholars in this field.

I have taken help from number of process licencers, academicians and experienced experts in the field for which I am ever grateful to each one of them and acknowledge them individually.

I am grateful to the management of Gujarat Refinery, Indian Oil Corporation for giving me permission to publish the book.

I have the gratitude and regards to Shri P.S. Rao, Executive Director of Gujarat Refinery, Indian Oil Corporation for his blessings in publications of this book by writing foreword of it.

The objective of publishing this book is entirely academic and I will be happy for the utilisation of it by those interested readers.

— **G.N. SARKAR**

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Introduction

Petroleum is a precious source of wealth today for man. Through chemistry he can convert it into fuels to generate power, a host of chemicals for trade and industry, pesticides for agriculture to control insects, dyes to add color to life, drugs to combat diseases, cosmetics to enhance beauty, perfumes for sensuous living, synthetic fibers for attractive easy-care apparels, and plastics a material for today, tomorrow and, may be the day after. All these chemical fantasies are made possible by the ingeneous technology of petrochemical process industry.

Petrochemical technology represents one of the most highly advanced and progressive frontiers of modern scientific and engineering endeavor. The advancement made in this field is so rapid that almost everyday a new product or a modification of exiting products is appearing in the consumer market. New process development or improvement through the use of better and highly selective catalysts replacing old methods of manufacture has frequently been reported.

Petroleum chemicals, or petrochemicals in short, are compounds or elements recovered or derived from petroleum or natural gas. As chemicals they do not represent any different class of compounds. They are organic chemicals, and have got the same composition, structure and properties as corresponding organic compounds derived from non-petroleum sources. For example, methyl alcohol from synthesis gas derived from petroleum or natural gas is exactly indentical to methyl alcohol produced by destructive distillation of wood. The name petrochemical refers only to the origin of the product.

The petrochemicals industry is one of the most competitive industries. New advances in catalyst development, process improvement, or even completely new routes to established chemicals from cheap raw materials are reported here more often than any other field of chemical process industries. All these have made the study of economics of petrochemicals industry important and necessary.

GENERAL COST CONSIDERATIONS

To start any industry and make products involve capital investment and expenditure. This may be divided under two heads. Viz. (*a*) *capital cost,* and (*b*) *production cost.*

Capital cost includes resources needed for obtaining the process know- how, building up of the plant and any other initial investments. If a process is simple and involves few steps for producing the desired product the capital cost would be small. To illustrate this let us consider the following hypothetical case.

Suppose the product *P* could be produced by two routes *A* and *B*. Route *A* is direct one-step process while route *B* involves two steps. So route *A* requires one reactor only while route *B* needs two reactors, which evidently increases the capital cost. Now again if the route *A* produces fewer by-products than route *B*. the separation and purification of product *P* becomes easier and involves less complicated and elaborate equipment. Similarly, if route *B* involves extreme reaction conditions such as very high temperature and pressure or corrosive reactants which require special and costly required for manufacturing a product depends on the nature of its process.

Production cost of a material includes cost of raw materials and other chemicals, cost of operation of the plant in the form of labor, supervision, utilities *i.e.* electricity, gas, steam, water etc. cost for quality control, research and development and marketing, sales, advertising and service costs. Production cost, like capital cost, also depends on the process. The simpler the process the lower becomes the cost of production. However, cost of raw materials and other chemicals used in the process is the most important and controlling factor in the production cost. If a process is based on costly raw materials and/or the by-products formed are relatively cheaper and undesirable, the process turns out to be unattractive.

Phenol, for example, may be prepared from benzene via chlorobenzene or via benzenesulfonic acid, or via cumene.

Let us compare the three routes to phenol from benzene. All of them involve three steps. The first route via chlorobenzene requires chlorine and caustic soda. Both of these, raw materials are costly and, after the reaction, are converted to sodium chloride, which has no market. In a sense, costly chlorine and caustic soda are converted to a worthless materials. In the second route via benzenesulfonic acid concentrated sulphuric acid and caustic soda which are again costly, are consumed and converted to sodium sulphate, which has got little demand. Both these routes involve handling of corrosive chemicals, which demand larger capital investment. In the third route via cumene, propylene and air are necessary to produce phenol. Propylene is a relatively cheaper raw material available from a refinery or a naphtha cracker as by-product. Moreover, in this process acetone is obtained as a by-product, and the demand for acetone is growing faster than even the demand for phenol. Hence the cumene route to phenol is the most economic and industrially attractive process.

The production cost of ethylene, for example, from different raw materials differs considerably (Table-0.1). Although the investment cost of ethylene production is the least from ethane but the production cost is found to be higher than that from full range naphtha.

Table 0.1 Production Cost of Ethylene from Various Raw Materials

(Plant Capacity 4,50,000 mta)*

	Raw Materials				
	Ethane	*Propane*	*Full range Naphtha*	*Light fuel Oil*	*Heavy fuel oil*
Investment cost (million US dollars)	31	33	36	42	44
Production cost (US dollars/ton)	61	54	44	78	47

*Adapted from *The Petrochemical Industry.* (Perspective for Industrial Development in the Second United Nations Development Decade), United Nations, New York, 1973, p. 3.

Once a suitable process for a particular product has been carefully selected the effective cost reduction may be achieved by scale-up of the production. In general, the production cost decreases with the increase of plant size. That is present-day petrochemical technology has developed a bias for building giant-size plants. The average capacity of a modern ethylene plant in Europe, Japan and USA is of the order of 400,000 tpa or larger. But here also the law of diminishing return of economics is valid. There is an optimum plant size depending on local conditions, market and raw material supply, after which further increase in plant size will not result sufficient cost reduction.

It is not merely the plant size but the efficient running of the plant to its full capacity that really counts in cost reduction. If the large size plant is not operating at or near its full capacity, it will lead to higher cost of production compared to a moderate size plant which is running at full capacity. To what extent the plant capacity utilization can influence the production cost depends, in turn, on the plant capacity (Table 0.2).

Table 0.2 Influence of Underutilization of Ethylene Plant Capacity on its Production Cost*

Capacity utilization, %	*Relative production cost*	
	Plant capacity 400,000 tpa	*Plant capacity 70,000 tpa*
100	100	100
75	115	125
50	145	160

*Source: The *Petrochemical Industry,* (Perspective for Industrial Development in the Second United Nations Development Decade), United Nations, New York, 1973, p. 3.

Another important cost consideration is the energy cost associated with the petrochemical process. The energy cost involved electricity, steam, compressed air or oxygen. Any attempt to cut down energy cost either by efficient utilization of the energy or developing new routes requiring less energy would result in the lowering of production cost.

Petrochemical industry is highly capital intensive and involves highly-developed technology. The pace of development and innovations of technology in this area is also very fast. Under this trend of rapid technological change, new products and processes are replacing old ones.

This speed of technological advancement is possible due to heavy investment in research and development activities of petrochemical industries. Such heavy financial commitment to R & D is possible only in advanced countries. Moreover, in developing nations technically competent personnel and equipped R & D centers are hardly available. So it is highly unlikely that indigenous technology can successfully compete with foreign know-hows. Technology will not be available initially in a less developed country in such a competitive industry as petrochemicals. The example of Japan has experienced tremendous growth in this field during a decade know-how. Japan has experienced tremendous growth in this filed during a decade or so, and is now in a position to export new technology even to her donor country.

All the petrochemical industries in India-either in private or in public sector have imported the foreign technology either in the form of a collaboration agreement or by outright purchase. Indian Petrochemical Corporation Ltd has decided to purchase foreign know-hows for all its plants. The imports of foreign technology is expected to generate skilled technical personnel and expertise in the developing countries.

Capital and production costs also include cost of research and development activities. As has already been discussed that the rapid growth of development in petrochemical technology is due to the corporate R & D will result in lowering the cost of production by offering better processed or improving upon the existing ones, or introducing new products, or modification of exiting products. R & D activities when properly coordinated with marketing and technical customer service departments will create markets for newly developed products or modify the existing products to suit the customer demands. As most of the petrochemicals processed are highly capital intensive with large plant-output capacity, substantial savings would accrue from even a minor process improvement.

The role of catalyst reactions is well established in petrochemicals. An analysis of the recent advances in petrochemical technology will reveal that a large part of these advances is possible through the development of new catalyst process for ammoxidation of propylene will illustrate how R & D activities on petrochemical catalyst is responsible for the very success of this almost monopolistic technology.

Utilization of by-products is another area where R & D activities are likely to reduce cost of production. An example to the point is the polypropylene plant where almost 10% of the polypropylene produced is amorphous atactic variety which is considered as a waste. Petrochemical R & D centers may initiate research program to convert this by-product into a salable commodity. A very successful example of cost reduction by efficient utilization of by-products is the olefin production by steam-naphtha cracking. Ethylene production by this route would not have been commercially feasible if its by-products such as propylene, butadiene, C_4-streams and pyrolysis gasoline could not be efficiently utilized.

Petrochemical are derivatives of petroleum hydrocarbons. These are available mainly from two source, *viz,* crude oil and natural gas. Crude oil contains also some amount of dissolved gases. During atmospheric distillation, these dissolved gases are obtained as overhead products. However, main use of crude oil is as energy source in the form of motor spirit or gasoline, jet aircraft fuel, fuel, for diesel engines, furnace oil and as fuel for industrial heating. Only less than 10% of crude oil has found application as a petrochemical feedstock.

Formerly natural gas was mostly used as domestic and industrial fuels. But now its application in the chemical field is increasing.

Petrochemical feedstocks from crude oil may be grouped under two heads, *viz.* Refinery gases and liquid petroleum fractions. So petrochemical process industry depends mostly on the three source for their raw materials *viz,* natural gas, refinery gas and liquid petroleum fractions.

Natural gas essentially consists of methane, the lightest of hydrocarbons. Other constituents of natural gas include ethane, propane, butane, pentane and hexane, and non-hydrocarbon gases such as hydrogen sulfide, carbon dioxide and nitrogen. The composition of natural gas varies from source to source. Certain natural gases are almost pure methane (> 99%), and some contain as low as 64% methane.

Natural gas may be 'wet' or 'dry'. When it contains relatively greater proportion of higher hydrocarbon which are condensable such as propane, butane and pentane, it is regarded as wet. These gases when condensed and separated from methane and ethane form what is known as *natural gas liquids* (NGL) or liquefied *natural gas* (LNG). This natural gas liquid is also called *liquefied petroleum gas* (LPG). LPG consists of almost 95% propane, 5% butane, and a little amount of pentane and hexane. LPG may be used as a chemical feedstock, alternative to naphtha, for generating ethylene, propylene and other olefins. The alternative use of LPG is as domestic and industrial fuel for generation of power.

When natural gas contain very little amount of those condensable higher hydrocarbons, it is called dry. The chemical value of dry natural gas is much less than that of wet variety.

The higher hydrocarbons from natural gas are generally separated by two methods: (*a*) condensing these gases into liquids under high pressure, and (*b*) extraction of these hydrocarbons by a high boiling heavy petroleum fraction and subsequently distillation of the hydrocarbons-rich heavy petroleum fraction, when the gases are obtained as the overhead product.

Direct energy uses account for more than half of natural gas consumption. Until recently chemical use of natural gas is very limited. For example, onle 6% of natural gas consumption is as chemical feedstock in USA. With the growing scarcity of chemical feedstock natural gas consumption in the chemical field will be increasing.

The word petroleum comes from Greek word *Petra* meaning rock and oleum meaning oil, *i.e.* petroleum means 'rock oil' indicating its origin. Petroleum, or crude oil as it is customarily called, is a complex mixture of hydrocarbons with minor amounts of oxygen-, nitrogen- and sulfur-containing compounds. The hydrocarbons present in crude oil containing carbon atom C_1 to C_{40} belongs to paraffins, cycloparaffins (usually called *naphthenes*) and aromatics. Olefins, acetylenes, dienes and other unsaturated hydrocarbons are generally absent in crude oil. The composition of crude oil, like that of natural gas, varies from oil-fields to oil field. The Indian crude oils generally contain larger amount of paraffinic hydrocarbons. The sulfur compounds present in the crude oil are the most objectionable impurity. Petroleum with higher sulfur content is different to process and demands special desulfurization treatment.

Distillation of Petroleum

Distillation of petroleum is carried out in two stages. First is the atmospheric distillation and the second is the vacuum distillation.

Distillation of petroleum at normal atmospheric pressure separates crude petroleum into the following main products: (*a*) gases, (*b*) straight-run gasoline, (*c*) naphtha, (*d*) kerosene, (*e*) gas oil, and (*f*) heavy residue. Heavy residue is sent to vacuum distillation unit where it is further fractionated into (*a*) vacuum gas oil, (*b*) Lubricating oil, and (*c*) tar or asphalt.

Chemical from petroleum may range from basic petrochemicals such as ethylene, propylene, benzene, xylenes to finished end-products like plastics, rubbers, fibers, detergents, pesticides, dyes etc. They may be classified as (*a*) first generation, (*b*) second generation, and (*c*) third generation petrochemicals. However, this distinction is not very rigid but somewhat arbitrary.

First Generation Petrochemicals

These are chemicals directly available from petroleum crude oil or natural gas either by fractionation, isomerization, cracking etc. These generally represented the basic petrochemicals which are the building blocks for various chemical syntheses. Examples of this class of chemicals are methane, ethane, propane, ethylene, propylene, toluene, xylenes (known collectively as BTX) etc. Generally these could be subgrouped as aliphatic, olefinic, diene, naphthenic and aromatic basic petrochemicals.

Second Generation Petrochemicals

These chemicals are not present as such in petroleum fractions not they could be obtained by simple operations such as reforming, cracking or hydrocracking. They are the derivatives of the first generation petrochemicals. Example of such products are styrene (derived from benzene and ethylene), dimethyl terephthalate or terephthalic acid (derived from *p*-xylene), acrylonitrile (derived from propylene), ethylene glycol (derived from ethylene), vinyl chloride monomer (derived from acetylene or ethylene), adipic acid (derived from benzene) etc. Second generation petrochemicals constitute the intermediate chemicals which serve as the raw materials for consumer industries like plastics, rubbers, fibers, dyes, detergents etc.

Third Generation Petrochemicals

These are the consumer commodities derived generally from second generation petrochemicals. They represent the most important commercial products such as plastics, rubbers, fibers, detergents etc. Examples are polystyrene (from vinyl chloride monomer), DDT from (chlorobenzene), azo dyes (from styrene), polyvinyl chloride (from aniline) etc. However, some of the products may be directly synthesized from first generation petrochemicals, Polybutadiene rubber, for instance, is obtained by polymerizing butadiene, which is a basic petrochemical. Since most of the plastics or rubbers are derived from second generation petrochemicals, polybutadiene rubber is regarded as a third generation petrochemical. The classification is, therefore, somewhat arbitrary.

Typical Petrochemicals from various raw materials are given in the flow diagrams.

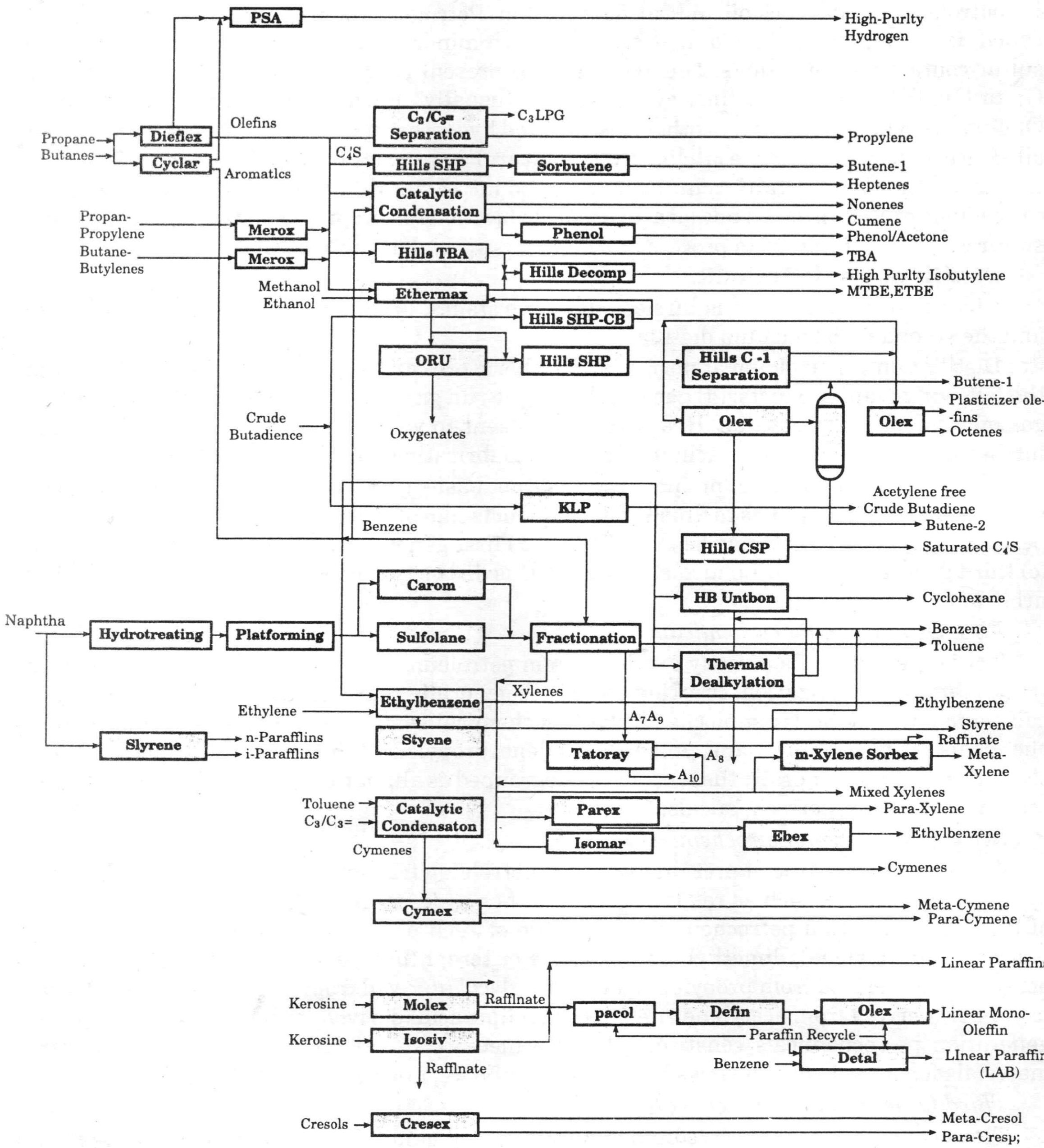
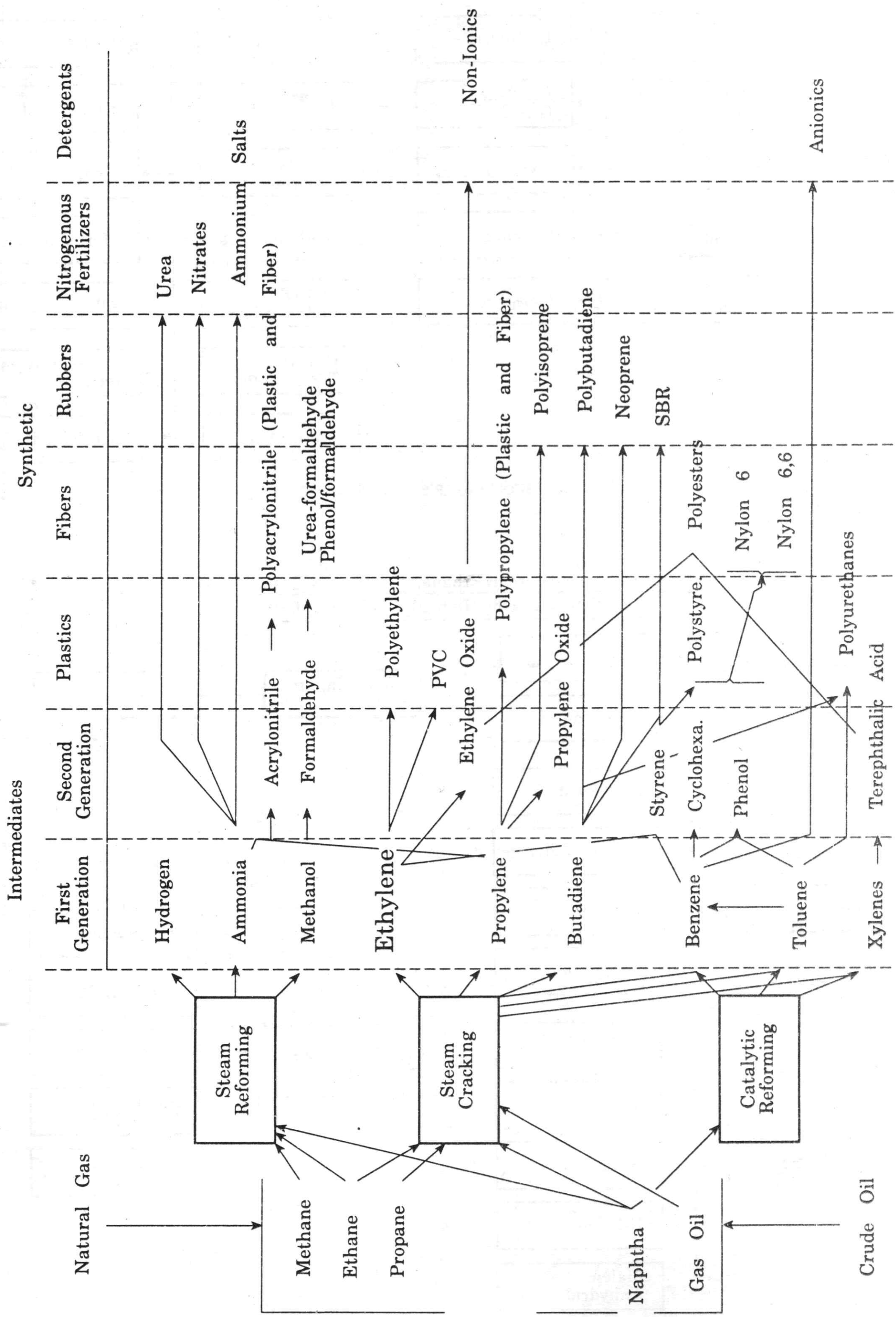


Fig. 0.0. Overall view of Petrochemicals.



Overall View of Petrochemicals

Fig. 0.1.

Petro Chemicals from Methane

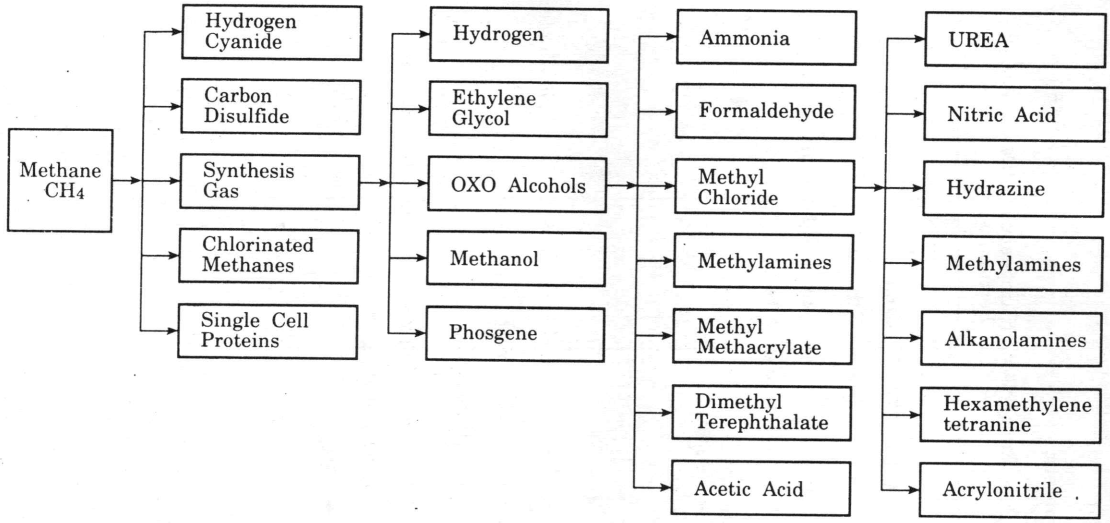


Fig. 0.2 Petrochemicals from Methane

Petrochemicals from Ethane, Propane, N-Butane, Light Naphtha & High Mol. Wt. Paraffins

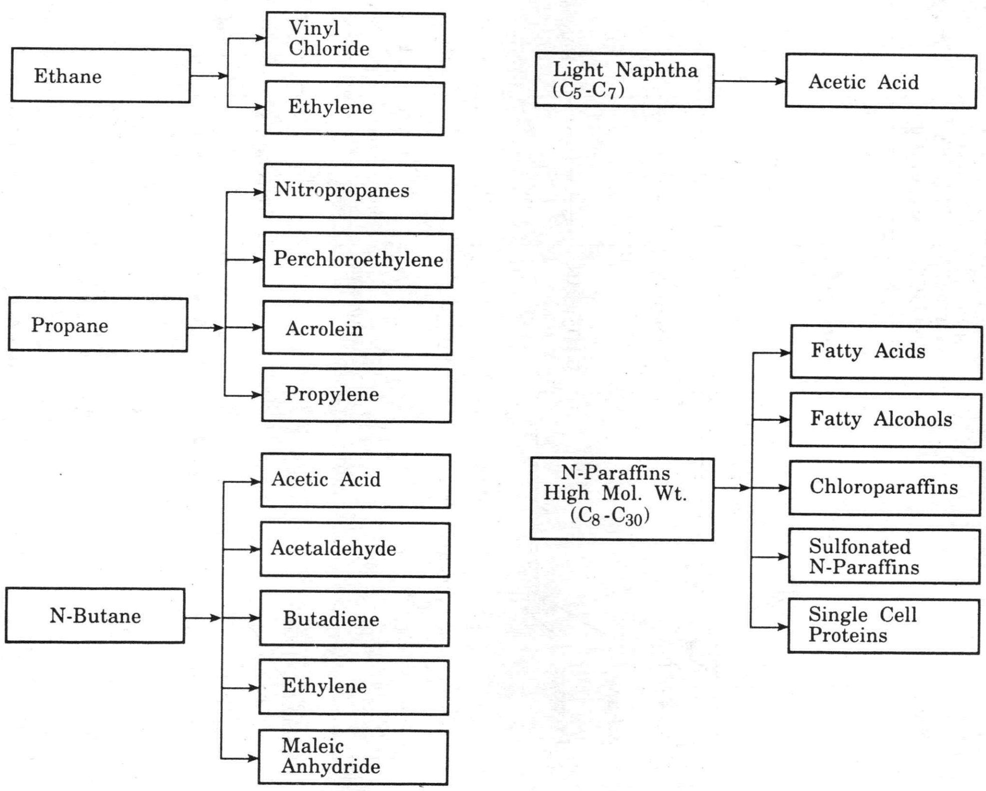


Fig. 0.3 Petrochemicals from Ethane, Propane, N-Butane, Light Naphtha and High Mol. Wt. Paraffins.

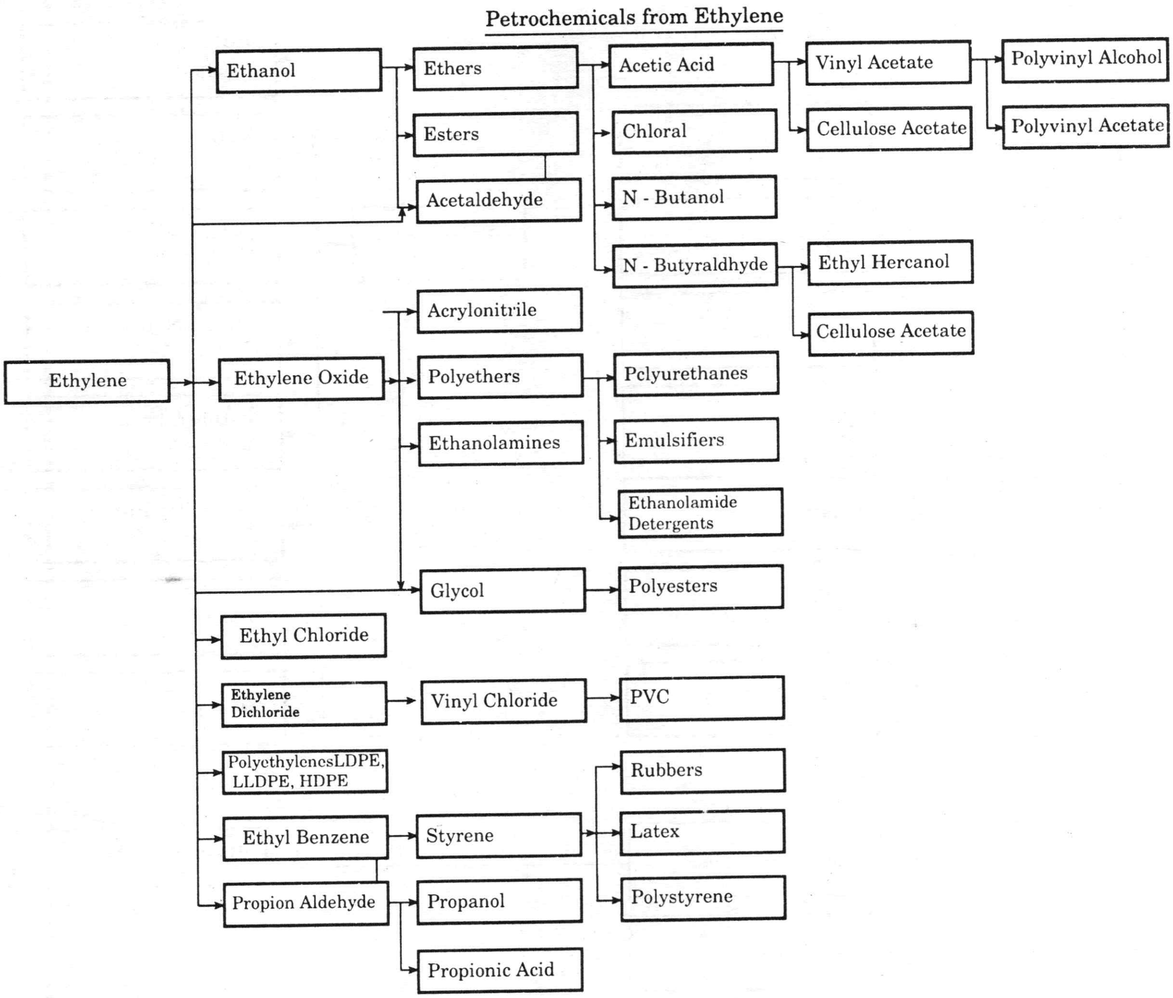


Fig. 0.4. Petrochamicals from Ethylene

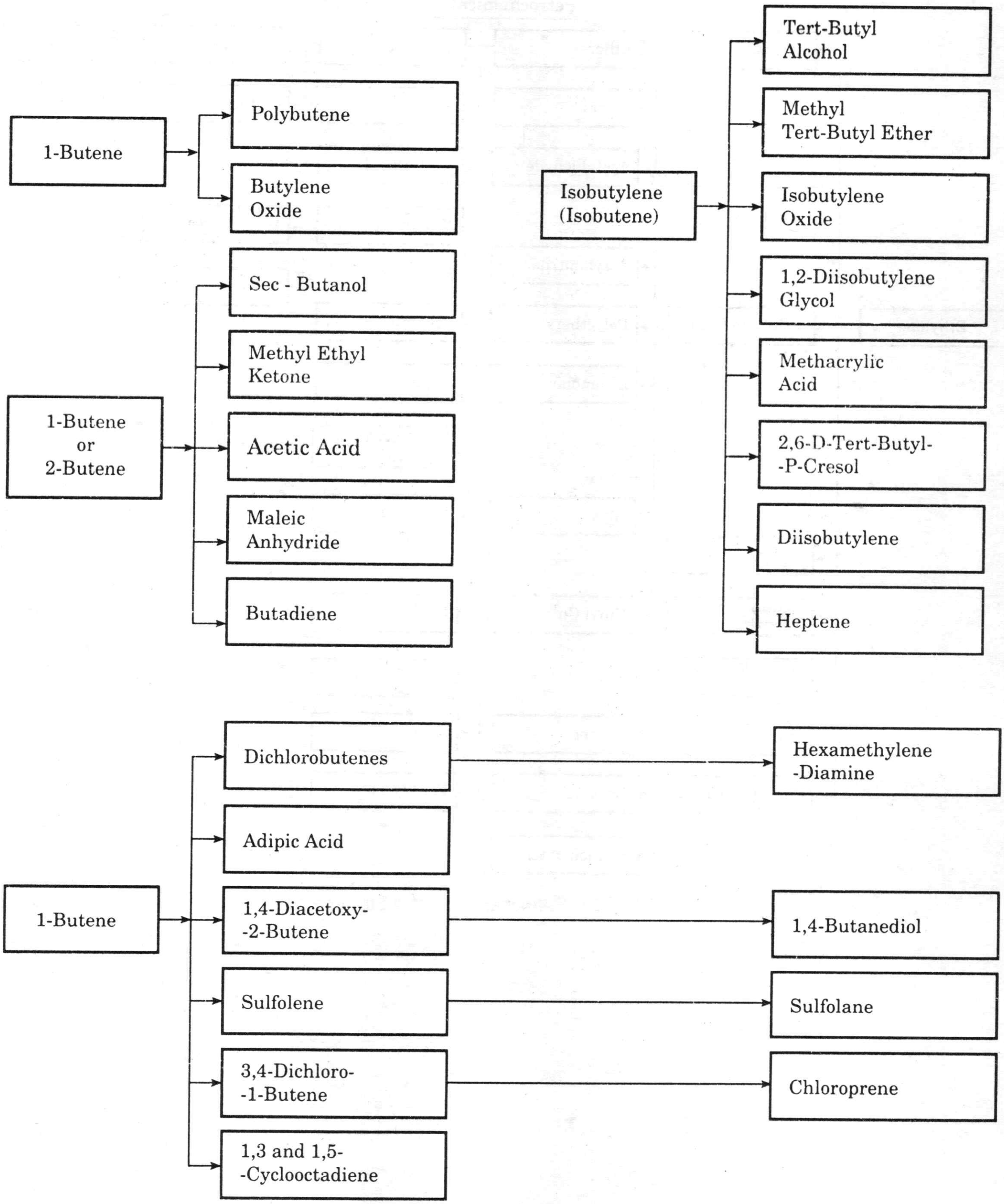
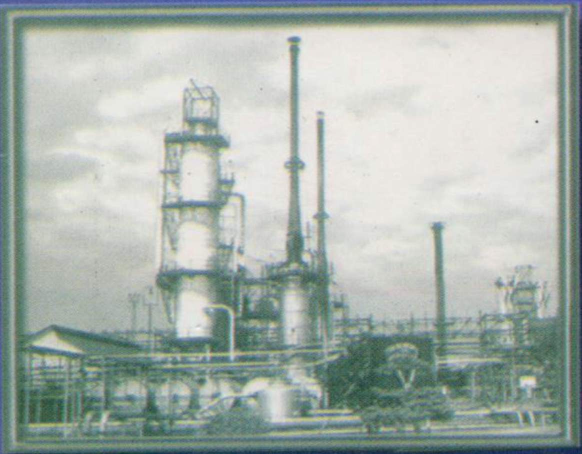


Fig. 0.5 Petrochemicals from Butylenes and Butadiene



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