

PLANT FOR PRODUCTION OF ISOCTANE FROM POLYMERIZATION OF BUTENES AND HYDROGENATION OF POLYMER TO ISOCTANES

Synthetic Chemicals in Fuels and Lubricants

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THE petroleum industry is today attracting wide attention as a potential producer of raw materials for chemical synthesis. Thus the manufacture of alcohol and of other solvents from the cracked gases which are produced in refining operations is now well established, and it is evident that petroleum offers a cheap and extensive source of carbon and hydrogen for many other syntheses.

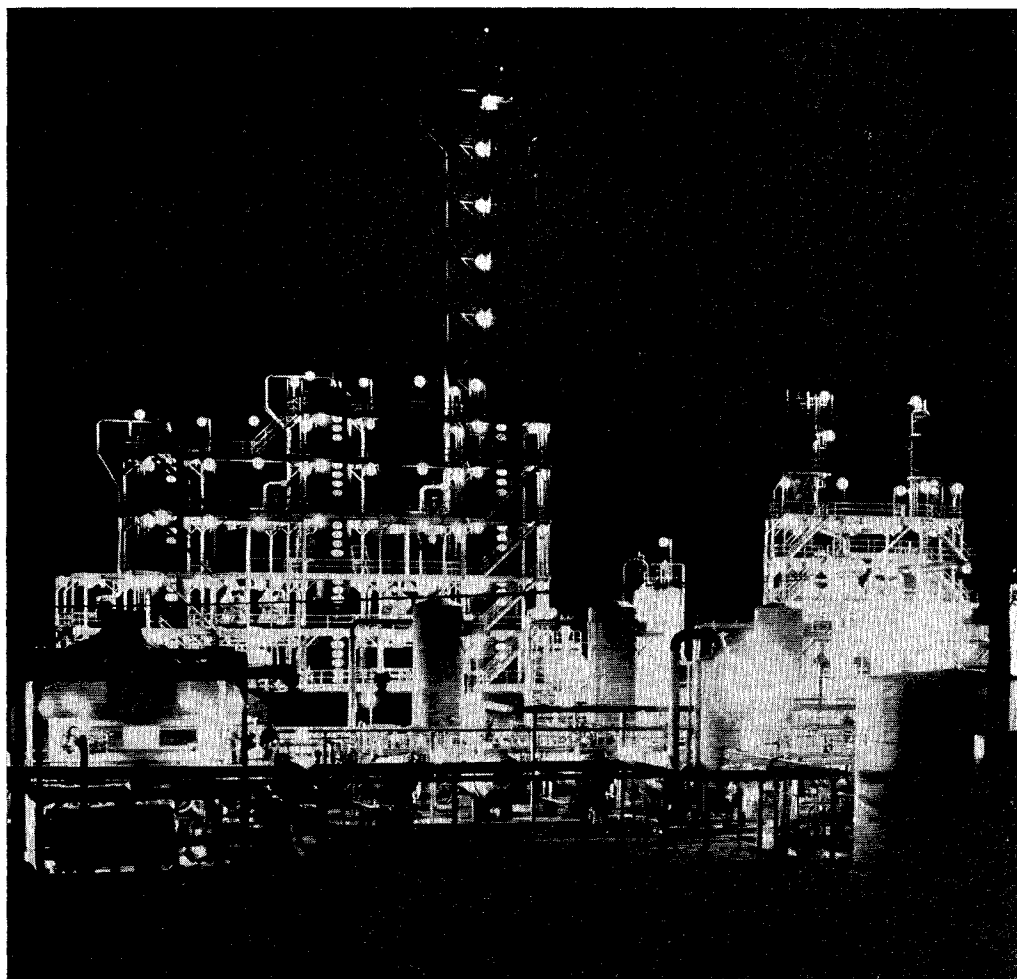
Emphasis on petroleum as a raw material has tended to overshadow the growing utilization of synthetic chemicals in the products which the petroleum industry markets. Some of these synthetics are supplied by the chemical industry, but an increasing volume is being made in the refinery itself. This paper aims to orient technologists of other industries as to the nature and scope of these product developments by a brief survey of typical examples.

For the purpose of this paper "synthetic chemicals" are defined in a loose and somewhat arbitrary fashion to cover reaction products which consist of a single or of a few closely similar compounds. Many of the products of oil refining result from chemical reactions. Thus cracked gasoline, a major constituent of present-day motor fuel, is made by subjecting oils heavier than gasoline (kerosene, gas oil, etc.) to conditions of high temperature for a sufficient time to effect thermal decomposition and thereby produce a high percentage of

material of the proper volatility to be used as motor fuel. Marked chemical changes take place in the cracking operation, and the cracked gasoline is distinctly different in composition and properties from the so-called straight-run gasoline naturally occurring in crude oil. However, the material which is produced and utilized is still a conglomeration of thousands of different chemical components, and it would not be classified as a synthetic chemical under the above definition.

Synthetic chemicals are used in fuels and lubricants in two ways: as addition agents which are incorporated in very small percentages, and as blending agents which are utilized in considerable proportions and which themselves contribute much of the fuel or lubricating value of the product.

The justification for using synthetic materials in fuels and lubricants is almost invariably the improvement in quality which can be effected. Synthetics are expensive in comparison with the natural materials. It is interesting to note that the bulk price of fuels and lubricants at the refinery is of the general order of magnitude of one cent per pound. Addition of relatively expensive synthetic materials can therefore be made to only a limited extent, and the quality advantage from their use must be significant. Thus one per cent of any addition agent which is priced at a dollar a pound would double the cost of the product.



PLANT FOR ALKYLATION OF ISOBUTANE WITH BUTENES; USED IN AVIATION GASOLINE

Addition Agents

ANTIKNOCK AGENTS. A notably successful example of the use of addition agents is tetraethyllead. While the addition of lead to gasoline is by no means new, the extent of its present use may not be adequately appreciated. The concentrations are very low, with a maximum of around 0.1 and an average of perhaps 0.02 per cent, but the volume of gasoline which is thus treated to improve its antiknock properties is so large that the dollar sales of Ethyl fluid today are understood to be greater than that of any other single organic synthetic material.

ANTIOXIDANTS. Small amounts of organic materials are added to gasoline to prevent deterioration by oxidation in storage. This deterioration, resulting in gum formation, would occur in refinery storage tanks, in bulk stations, in service stations, and in the tank of the automobile. The materials employed, called "antioxidants", are used in concentrations which are measured in thousandths of a per cent. They have been well described as "policemen" who preserve order in the gasoline. Typical materials are benzylaminophenol and butylaminophenol. Despite the extremely low concentrations, the extent of usage is so widespread that production of these synthetics can be measured in tons per day.

METAL DEACTIVATORS. The oxidation of gasoline is catalytically accelerated by the presence of metals and particu-

larly of copper. To prevent such catalytic action at normal temperatures in systems where copper must be present, the addition of a very small amount of disilycylalethylene diamine has proved remarkably effective.

CETANE IMPROVERS. The improvement in antiknock properties of gasoline by additions of tetraethyllead has been mentioned. In the case of Diesel fuels a similar problem is to improve the ignition quality of the fuel, a property which is measured by its cetane number. It has been found that certain addition agents, such as amyl nitrate and organic polysulfides, will raise the cetane number, although to date there has been very little commercial use of this discovery.

POUR-TEST DEPRESSORS. The performance of lubricating oils at low temperatures, and to a

lesser extent that of Diesel fuels and of furnace oils, is seriously impaired by the separation of very small amounts of residual wax in the oil which prevent it from flowing freely. The pour test, a standardized test to determine the temperature at which an oil will no longer flow freely, is used as measure of this characteristic. Certain addition agents have proved very effective for securing fluidity at lower temperatures. Known as pour-test depressors, they are gaining wide commercial acceptance. Alkyl naphthalenes, used in concentrations between 0.1 and 1.0 per cent, are representative of the class. Their molecular structure is similar to that of the wax itself, and their function may be explained as that of setting up an interference to the regular pattern of wax crystallization and thereby lowering the temperature at which such crystallization can occur.

ADDITIVES TO IMPROVE MOTOR OIL PERFORMANCE. Today there is much interest in a class of additives designed to improve performance of the oil in the engine. Developments in automotive engine design have created conditions which are much more severe on the lubricating oil than was formerly the case, primarily as a result of higher operating temperatures. This has stimulated research to improve the resistance of oils to oxidation, to varnish formation, to ring sticking, sludge, corrosion, and wear. Such research is largely on the cut-and-try basis, and it often happens that an additive which improves performance in one respect may not impart any advantageous qualities when gaged by another index of

performance. Typical additives which are now being used to the extent of perhaps 1 per cent in the oil are phosphates and phosphites, both alkyl and aryl, sulfur-containing materials, and metallic soaps. Considerable progress is being made currently in the development of improved oil, even though the theory to explain the beneficial effects of the additions is obscure.

EXTREME-PRESSURE LUBRICANTS. Most lubricants are used in services where the lubricated surfaces are separated by a fluid film of lubricant. However, under extreme conditions of high pressure, such as are encountered in the hypoid rear axle gears of automobiles, the solid surfaces of the bearings make contact and establish an unusually severe problem in lubrication. Extreme-pressure lubricants used for such services contain materials which react with the metal surfaces and prevent bearing seizure caused by welding of the surfaces. Certain types of extreme-pressure lubricants, such as lard oil, high-sulfur oils, and oils with added lead soaps, have been in use for a long time. Recently the trend has been to add extreme-pressure agents which are more nearly synthetic materials containing sulfur, chlorine, or oxygen in the molecule.

Some years ago a superior lubricant was prepared by a process of polymerizing light, unsaturated naphtha with aluminum chloride. This naphtha was derived from the cracking of paraffin wax. The product proved excellent for numerous uses, including aircraft engine lubrication, but unfortunately it was too expensive to have wide utility. Today polymers are being prepared from isobutylene whose properties vary with the degree of polymerization. As described later, the lower polymers are valuable components of aviation gasoline. The intermediate polymers, in the lubricating oil range, have superior lubricating properties. The heavy polymers may be added in small amounts to lubricating oils to impart special properties to the product.

This discussion of additives to fuels and lubricants is by no means complete, but may serve to show the scope of present accomplishments and indicate the direction of research efforts in this field.

Blending Agents

Demand for high antiknock rating (high octane number) in aviation gasoline, particularly for military services, has created a problem which the refiner is meeting by making synthetic fuels. Thus 100-octane gasoline for tactical use might contain roughly 50 per cent of such synthetic fuel.

The reason why the refiner has had to resort to synthesis is indicated by Table I. About a third of the saturated paraffin hydrocarbons containing eight carbon atoms are listed with their boiling points and octane numbers by the C. F. R. motor method. The boiling points are reasonably similar, but the octane numbers vary from a low of -17 to a high of slightly above 100. Since ordinary gasolines consist of a large mixture of chemical compounds, many of which have approximately the same boiling range, it is impracticable to segregate those materials which have very high octane numbers from the rest by commercial fractionation. A mixture of around 70 octane number is readily obtainable, but if a superior fuel of around 100 octane number is desired, only selected compounds can be utilized. As a result synthetic methods for producing these special hydrocarbons had to be developed.

The refiner has found the raw materials for his synthesis of high-octane hydrocarbons largely in a single fraction, the C_4 cut, which contains both saturated and unsaturated components. This mixture of butanes and butylenes is recovered from the gases which are produced in cracking operations. Butanes and butylenes are the lightest components which can desirably be incorporated in motor gasoline, but most modern

TABLE I. PROPERTIES OF SOME OF THE OCTANES

Name	Octane Rating	Boiling Point, ° F.
<i>N</i> -Octane	-17	258.4
2-Methylheptane	24	240.8
3-Ethylhexane	52	246
2,3-Dimethylhexane	76	240
2-Methyl-3-ethylpentane	91	240
2,2,4-Trimethylpentane	100	210.7
2,2,3,3-Tetramethylbutane	103	223

refineries produce them in excess of the amount which can be included in the gasoline. This excess would normally be burned as plant fuel.

Synthetic octanes of high antiknock value may be produced from the butane and butylene components by several optional methods, designated by the nature of the process as cold acid, hot acid or phosphoric acid, and catalytic alkylation.

Figure 1 shows in simple form the chemistry of the cold acid process. The mixture of butanes and butylenes is contacted with cold concentrated sulfuric acid, which has been refrigerated in order to make its action selective. Under these conditions isobutylene is absorbed, and two molecules of isobutylene then react to form a dimer. The dimer is later hydrogenated to produce a saturated product, which is principally 2,2,4-trimethylpentane, with an octane rating very close to 100 (pure 2,2,4-trimethylpentane has an octane number of 100 by definition). The product is excellent from the quality standpoint, but the yield is low because only the isobutylenes are utilized.

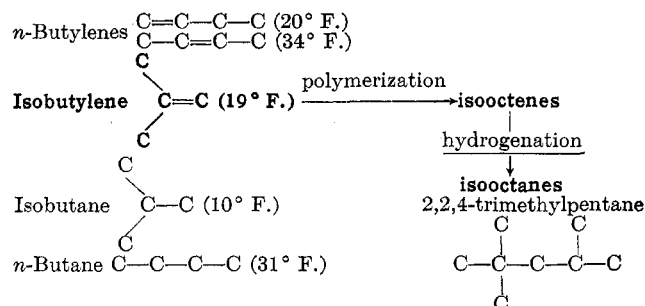


FIGURE 1. CHEMISTRY OF COLD ACID PROCESS FOR MAKING ISO-OCTANES

The hot acid process is also carried out with sulfuric acid but at somewhat higher temperature. Similar results are obtained by the phosphoric acid process which employs solid phosphoric acid as a catalyst. These processes involve reaction between isobutylene and *n*-butylene, as shown in Figure 2. After the dimer has been hydrogenated, the product is a mixture of branched-chain paraffins with an octane number of from 92 to 98. While the quality is somewhat below that of the cold acid product, the yield is roughly twice as great because the normal butylenes have been utilized as well as the isobutylenes.

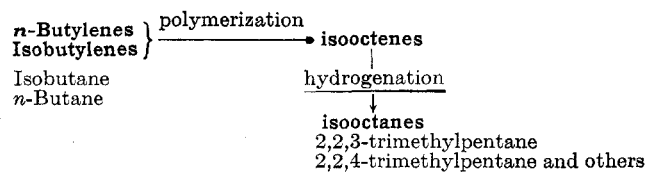


FIGURE 2. CHEMISTRY OF THE HOT ACID OR PHOSPHORIC ACID PROCESS FOR MAKING ISO-OCTANES

Catalytic alkylation involves reaction of the mixture of unsaturated C_4 hydrocarbons with isobutane at ordinary temperatures in the presence of very strong sulfuric acid and with vigorous agitation. Since the product is saturated, subsequent hydrogenation is unnecessary. The mixed octanes which result are nearly as high in antiknock value as those from the hot acid process, and the yields are much greater. The reaction is indicated in Figure 3.

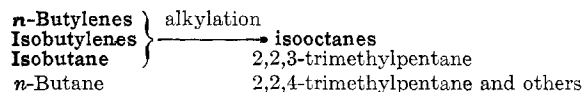


FIGURE 3. CHEMISTRY OF CATALYTIC ALKYLATION FOR ISO-OCTANE MANUFACTURE

Still another method for synthesizing a high-octane product involves the interaction of isobutane with ethylene at high temperatures and pressures, such as 900° F. and 5000 pounds per square inch. This process, known as thermal alkylation, gives a branched-chain paraffin containing six carbon atoms, 2,2-dimethylbutane, known as neohexane. The reactions are shown in Figure 4.

The photographs show views of plants which are producing high-octane blend agents for aviation purposes.

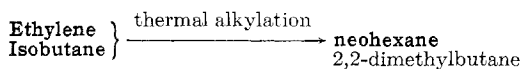


FIGURE 4. REACTIONS INVOLVED IN MANUFACTURE OF NEO-HEXANE

The developments described are representative of commercial organic syntheses which are coming to the fore in the oil industry under the stimulus of a demand for higher quality products. The synthetic products are expensive in comparison with natural fuels and lubricants from petroleum, but refiners' synthetics are relatively cheap when contrasted with synthetic chemicals as a group. The rapidity with which synthetic fuel production is developing is indicated by the fact that its annual volume already compares favorably with the production of the coal-tar industry.

Since this paper is restricted to a consideration of synthetic material, it deals with only a minor phase of the chemical and chemical engineering research of the oil industry. Within this field the industry's present advanced position is due primarily to the combination of large supplies of raw materials and an intense concentration of research and development activity.

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Behavior of Cotton Fiber

With Ammonium Oxalate and Cuprammonium Solution

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ACCORDING to Farr and co-workers (5, 6), the cell membrane of the cotton fiber and other plants is built up of cellulose particles surrounded by a cementing material. They state that the cell wall of young and of mature fibers may be disintegrated into the two constituents by certain treatments. In most cases the particle material was obtained by subjecting the fiber to treatment with hydrochloric acid of various concentrations. Since the cementing substance is said to consist chiefly of a noncellulosic pectic material, an aqueous ammonium oxalate solution, usually applied for removing pectin from plant material, is regarded as being most suitable for removing the bulk of the cementing substance from the cotton fiber (3). Simultaneously, provided the treatment is long enough, the fibers are said to disintegrate into particles. Thus, continuous treatment of raw cotton with a 2 per cent aqueous ammonium oxalate solution for 3126 hours (about 130 days) at 75° C. (4) supplied Farr with sufficient material of both particles and cementing material for further studies.

In evaluating these results, the interpretation of which is rather unusual from the viewpoint of the cellulose chemist, it appears desirable to distinguish between the two types of treatment under which disintegration of the fibrous material into cellulose particles was observed. For example, under the action of strong hydrochloric acid for 18 hours at

room temperature or of more dilute acid for a longer period disintegration of the fiber probably does take place. Such treatments lead to hydrocellulose, a cellulosic material which has lost its fibrous structure and appears in the form of fiber fragments. Farr claims without evidence other than stain and optical tests (3, 6) that the particles show no signs of degradation. But proof that the latter does occur is, without doubt, derived from the molecular weight of the particle material; this was determined by the ultracentrifugal method to be only about 40,000 (8). This value is less than one twelfth of that usually found for raw cotton which Farr used as a source for the isolation of the particles.

It appeared improbable, then, that treatment with such a neutral agent as ammonium oxalate should lead to the same result, unless the assumption was made that, under the conditions applied, oxidizing and hydrolyzing effects would be exerted.

To reduce the possibility of an oxidizing effect, Farr's experiments were repeated in the absence of air—i. e., in an atmosphere of nitrogen, carefully controlled for the duration of the treatments. For comparison some treatments were also carried out in air.

The cellulosic material was raw cotton lint. It was first extracted with alcohol and benzene in order to remove the wax, so that the extracted material would wet easily with the