

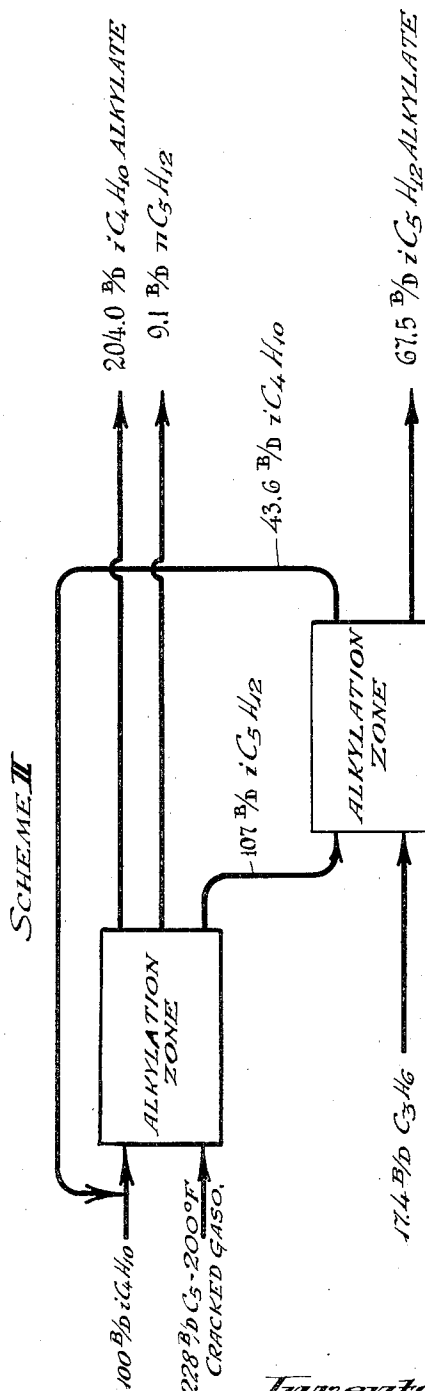
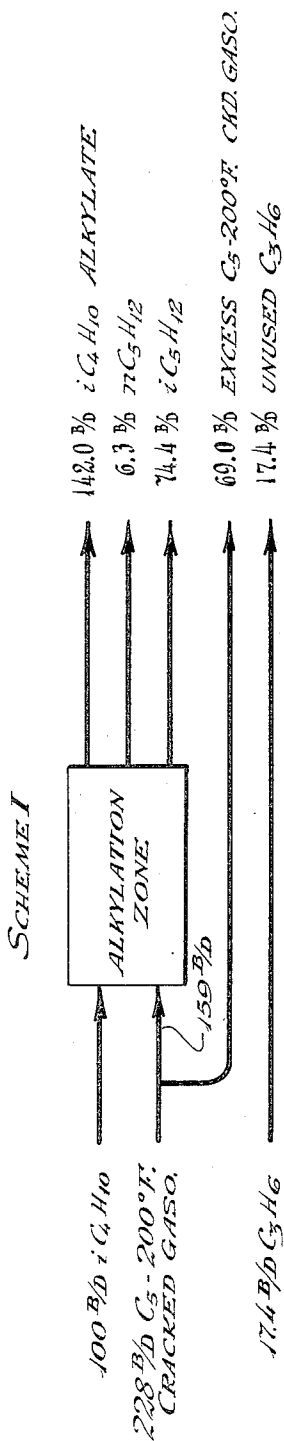
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R. J. NEWMAN

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ALKYLATION OF ISOPARAFFINS

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Inventor:
Robert J. Newman
 By *Lee J. Gary*
 ATTORNEY.

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ALKYLATION OF ISOPARAFFINS

Robert J. Newman, Riverside, Ill., assignor to
Universal Oil Products Company, Chicago, Ill.,
a corporation of Delaware

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4 Claims. (Cl. 260—683.4)

This invention relates to the production of branched chain saturated hydrocarbons by the catalytic alkylation of isoparaaffins with olefins, the present application being a continuation-in-part of my prior application, Serial No. 488,655, filed May 27, 1943.

The synthesis of relatively high molecular weight branched chain paraaffins by the catalytic alkylation of isoparaaffins with olefins is a process of considerable importance in the petroleum industry. The alkylation of lower boiling paraaffins containing at least one tertiary carbon atom per molecule, such as isobutane and isopentane, with normally gaseous olefins, such as propylene and butylenes, is of particular importance. Among the various alkylation catalysts which have been proposed are aluminum chloride and other metal halide catalysts, hydrogen fluoride, concentrated sulfuric acid, phosphoric acid, various halosulfonic acids, etc.

In commercial practice perhaps the most important alkylation reaction involves the interaction of isobutane with various olefins. Although isopentane, isohexane, etc., are capable of alkylation, these hydrocarbons are in themselves of substantial value and for that reason are often not available in sufficient quantities for extensive use in alkylation processes. Although isobutane is commonly alkylated with ethylene, propylene, and butylenes to produce branched chain hexanes, heptanes, and octanes, it is also possible to alkylate isobutane with the higher boiling or normally liquid olefins such as amylenes, hexenes, heptenes, etc. An isobutane alkylation process which is of particular importance at the present time involves the interaction of isobutane with a cracked gasoline fraction containing substantial quantities of normally liquid olefins. By this method of operation the cracked gasoline may be converted to a substantially saturated or low olefin content fraction which is then suitable for use as a base stock in aviation gasoline by blending with high octane number alkylate, isopentane, and tetraethyllead.

In many refineries the limiting factor in any isobutane-olefin alkylation process usually lies in the amount of isobutane which is available. In fact, there is often such a deficiency of available isobutane that it is necessary to resort to special methods for its production, e. g., by the isomerization of normal butane.

One object of the present invention is to produce greater amounts of isobutane alkylate from given amounts of isobutane and a normally liquid olefin fraction than have been produced by methods previously taught in the art. Another object of the invention is to utilize the maximum quantity of available olefins in the production of aviation gasoline stocks from cracked gasoline fractions. A still further object of the invention

is to provide a convenient method for the recovery and utilization of isopentane found in cracked gasoline fractions.

Broadly, the invention comprises alkylating isobutane with amylenes, separating isopentane from the alkylation products, separately alkylating said isopentane with propylene, and supplying isobutane produced in the isopentane alkylation step to said first named alkylation step.

In one specific embodiment the invention comprises alkylating isobutane with an amylenes-containing cracked gasoline fraction in the presence of hydrogen fluoride, separating isopentane from the alkylation products, alkylating said separated isopentane with propylene in a separate alkylation zone in the presence of hydrogen fluoride under alkylating conditions such that substantial amounts of isobutane are formed, separating isobutane from the alkylation products of said last named alkylation step, and supplying said separated isobutane to said first named alkylating step.

The usual components of aviation gasoline are a low olefin content base stock, a high octane number blending agent such as alkylate, sufficient isopentane to meet vapor pressure requirements, and the required amount of tetraethyllead. The base stock often consists of a substantially saturated straight run fraction, but in present day practice it has been found that base stocks having high aromatic contents are preferred. One of the most important methods in the production of aromatic containing base stocks comprises the catalytic cracking of hydrocarbon oils followed by retreatment of the gasoline boiling range product to reduce the olefin content thereof. Thermal cracking methods may also be employed for the production of aromatic-containing base stocks, but in general the catalytic cracking technique is preferred.

The catalytic cracking of hydrocarbon oils is usually characterized by the formation of substantial quantities of valuable isobutane along with C₃ and C₄ olefins. In addition, catalytically cracked gasoline fractions often contain substantial amounts of valuable isopentane. However, this isopentane is not easily recovered since it is usually present in admixture with amylenes having boiling points very close to that of isopentane. By the process of the present invention the amylenes present in a cracked gasoline fraction are interacted with isobutane leaving the isopentane behind in such form that it can be separated readily by fractionation from the alkylation products. Moreover, I have found that, particularly in the presence of a hydrogen fluoride catalyst, substantial amounts of isopentane are produced as a by-product during the alkylation of isobutane with amylenes. According to this invention the total isopentane which can thus be re-

covered is then reacted with propylene to produce a satisfactory quality alkylate and at the same time to produce additional quantities of isobutane which may be recycled to the first alkylation stage. The recycled isobutane thus becomes available for interaction with further quantities of cracked gasoline.

This invention is based on the experimental discovery that when isobutane is alkylated with amylenes and when isopentane is alkylated with propylene in the presence of a suitable catalyst and under suitable conditions substantial amounts of isopentane and isobutane are produced, respectively. The extent to which these side reactions occur will depend upon many factors especially the catalyst and operating conditions employed. In the case of isobutane-amylenes alkylation, the greatest amount of isopentane is produced when a hydrogen fluoride catalyst is employed, and the isopentane production is extensive over a relatively wide range of operating conditions. In the case of isopentane-propylene alkylation, I have found that greater amounts of isobutane are formed at higher temperatures and higher mol ratios of isopentane to propylene as hereinafter described in greater detail.

Although the preferred catalyst for the interaction of isopentane with propylene is substantially anhydrous hydrogen fluoride, it is possible to employ catalysts containing as much as about 10% water. In fact, the commercially available "anhydrous" hydrogen fluoride generally contains up to about 2% by weight of water. Excessive dilution with water is undesirable since it tends to reduce the alkylating activity of the catalyst and introduces corrosion problems. It is also within the scope of my invention to employ hydrogen fluoride containing relatively minor amounts of various additives or promoters such as boron trifluoride.

The alkylation of isoparaffins with olefins in the presence of a hydrogen fluoride catalyst is ordinarily conducted on a continuous scale by introducing the hydrocarbon charging stock and catalyst into a mechanically agitated reaction zone or any other zone suitable for effecting intimate contact between the hydrocarbons and catalyst. The hydrocarbon-catalyst mixture is maintained at the desired temperature and pressure for the required reaction time. It is desirable to maintain a substantial mol excess of isoparaffins over olefins in the hydrocarbon feed to the alkylation zone in order to promote alkylation as the principal reaction of the process. The reaction mixture is withdrawn and is introduced into a separation zone which ordinarily consists of a gravity settler. The lower catalyst layer is withdrawn and a major portion thereof may be recycled to the alkylation zone although another portion thereof may be withdrawn from the system and subjected to regeneration. Regenerated and/or fresh catalyst is supplied to the alkylation zone to maintain a relatively constant amount of catalyst within the reaction system. The upper hydrocarbon layer from the settler is subjected to fractionation for the recovery of gasoline boiling range products and for the separation of unconverted isoparaffins which are recycled to the alkylation zone.

The alkylation of isoparaffins with olefins in the presence of a hydrogen fluoride catalyst is carried out at a temperature of from about 0° F. to about 200° F. although the reaction temperature is preferably within the range of from about 50°

F. to about 150° F. In the alkylation of isopentane with propylene it is preferred to employ temperatures in the upper portion of this range, namely, from about 75° F. to about 150° F. in order to favor the production of isobutane during the reaction. The pressure on the alkylation system is ordinarily just high enough to maintain the hydrocarbons and catalyst in substantially the liquid phase, e. g., from about 50 to about 500 pounds per square inch. The time factor in the alkylation process is conveniently expressed in terms of "space time" which is defined as the volume of catalyst within the contacting zone divided by the volume rate per minute of hydrocarbon reactants charged to the zone. Usually the space time will fall within the range of from about 5 to 80 minutes although in certain cases it may be desirable to extend this range in either direction. It is preferable to maintain at all times a substantial mol excess of isoparaffins over olefins in the hydrocarbon feed to the alkylation zone, e. g., from about 3:1 to about 10:1 or higher. In order to promote the formation of isobutane during the alkylation of isopentane with propylene in the presence of hydrogen fluoride it is desirable to maintain a mol ratio of isopentane to propylene greater than 5:1, e. g., from about 5:1 to about 20:1. In general the volumetric ratio of hydrogen fluoride catalyst to hydrocarbons in the contacting zone should be about 1:1 although ratios of from about 0.5:1 to about 2.0:1 will give satisfactory results.

The invention can best be described by a typical illustration which, however, is not intended to limit the generally broad scope of the invention as defined in the claims.

Reference is now made to the drawing which illustrates schematically the advantages to be gained by the present invention. The olefinic charging stock comprises a C₅-200° F. catalytically cracked gasoline fraction having the following composition on a liquid volume per cent basis:

45	n-Butane.....	0.4
	Iso-amylenes.....	16.8
	n-Amylenes.....	7.9
	Iso-pentane.....	29.6
	n-Pentane.....	2.5
50	C ₆ and higher.....	42.8

This cracked gasoline fraction has a bromine number of 85 and contains 41% by weight of olefins. In scheme I, 100 barrels of isobutane are reacted with as much of the cracked gasoline fraction as possible. In scheme II, 100 barrels of isobutane are alkylated with the cracked gasoline fraction, but in addition the available isopentane in the alkylation products is separated and alkylated with propylene to produce isopentane-propylene alkylate and a substantial amount of isobutane which is recycled to the first alkylation zone and therein becomes available for alkylating additional quantities of the cracked gasoline fraction.

In scheme I the total available isobutane comprising 100 barrels per day is interacted with 159 barrels per day of the cracked gasoline fraction. The alkylation is conducted in the presence of a hydrogen fluoride catalyst at 100° F., 180 pounds per square inch, 37 minutes space time, and a mol ratio of isoparaffin to olefin in the charge of about 8.1. From this step there is a total production of 142.0 barrels per day of isobutane alkylate, 6.3 barrels per day of normal pentane, and 74.4

barrels per day of isopentane. For the sake of comparison it is shown in scheme I that there are 69.0 barrels per day of excess cracked gasoline fraction and 17.4 barrels per day of unused propylene which would be utilized in the process of the present invention as shown in scheme II.

In scheme II the same quantities of available isobutane, cracked gasoline fraction, and propylene are shown. In the first alkylation zone 100 barrels per day of isobutane and 228 barrels per day of cracked gasoline fraction are charged. A hydrogen fluoride catalyst is employed under substantially the same conditions as described in connection with scheme I. From this operation there is recovered 107 barrels per day of isopentane. This isopentane comprises the isopentane originally present in the C₅-200° F. cracked gasoline and also the isopentane produced during the alkylation reaction. The 107 barrels per day of isopentane is alkylated with 17.4 barrels per day of propylene in a separate alkylation zone employing a hydrogen fluoride catalyst at 100° F., 220 p. s. i., 35 minutes space time, and a mol ratio of isopentane to propylene of about 7:1. In addition to 67.5 barrels per day of isopentane-propylene alkylate produced in the latter alkylation step there is also a production of 43.6 barrels per day of isobutane which as shown is recycled to the first alkylation step. It is obvious that the recycle of this additional isobutane permits the utilization of an additional 69 barrels per day of cracked gasoline fraction. The overall result in scheme II is the production of 204.0 barrels per day of isobutane alkylate, 9.1 barrels per day of normal pentane, and 67.5 barrels per day of isopentane-propylene alkylate.

The advantages of the present invention are summarized in the following comparison of the two schemes:

Table

	Scheme I	Scheme II
Charge, barrels per day:		
Isobutane.....	100	100
C ₅ -200° F. gasoline.....	159	228
Propylene.....	0	17.4
Products, barrels per day:		
Depentanized isobutane alkylate.....	142	204
Depentanized isopentane alkylate.....	0	67.5
Isopentane.....	74.4	0
Normal pentane.....	6.3	9.1

It is evident that the production of isobutane

alkylate is increased by approximately 44% in scheme II and in addition a considerable quantity of isopentane-propylene alkylate is obtained. It will be seen that my invention provides a convenient solution to a serious problem which arises during the commercial operation of the alkylation process, namely, the shortage of isobutane. The invention enables the refiner to utilize readily available propylene for the production of a satisfactory isopentane-propylene alkylate while at the same time producing additional quantities of isobutane which can be reacted with cracked gasoline to increase the overall yield of aviation gasoline stock from a given quantity of available hydrocarbon reactants.

I claim as my invention:

1. An alkylation process which comprises alkylating isobutane with amylene to form alkylated isobutane and isopentane, separating isopentane from the resultant products, alkylating the separated isopentane with propylene in the presence of hydrogen fluoride at a temperature of from about 75° F. to about 150° F. while maintaining a molar ratio of isopentane to propylene of from about 5:1 to about 20:1, whereby to produce a substantial amount of isobutane concurrently with the alkylated isopentane, and supplying the isobutane thus produced to the first-mentioned alkylating step.

2. An alkylation process which comprises subjecting isobutane and a cracked gasoline fraction containing amylene and isopentane to alkylating conditions to react amylene with isobutane, separating isopentane from the resultant products, alkylating the separated isopentane with propylene in the presence of hydrogen fluoride at a temperature of from about 75° F. to about 150° F. while maintaining a molar ratio of isopentane to propylene of from about 5:1 to about 20:1, whereby to produce a substantial amount of isobutane concurrently with the alkylated isopentane, and supplying the isobutane thus produced to the first-mentioned alkylating step.

3. The process as defined in claim 1 further characterized in that the first-mentioned alkylating step is effected in the presence of hydrogen fluoride catalyst.

4. The process as defined in claim 2 further characterized in that the first-mentioned alkylating step is effected in the presence of hydrogen fluoride catalyst.

ROBERT J. NEWMAN.