Aug. 21, 1962 J. G. MELCHIOR 3,050,456

CONVERSION PROCESS FOR THE PRODUCTION OF HIGH OCTANE NUMBER GASOLINE COMPONENTS

Filed Oct. 15, 1958 2 Sheets-Sheet 1

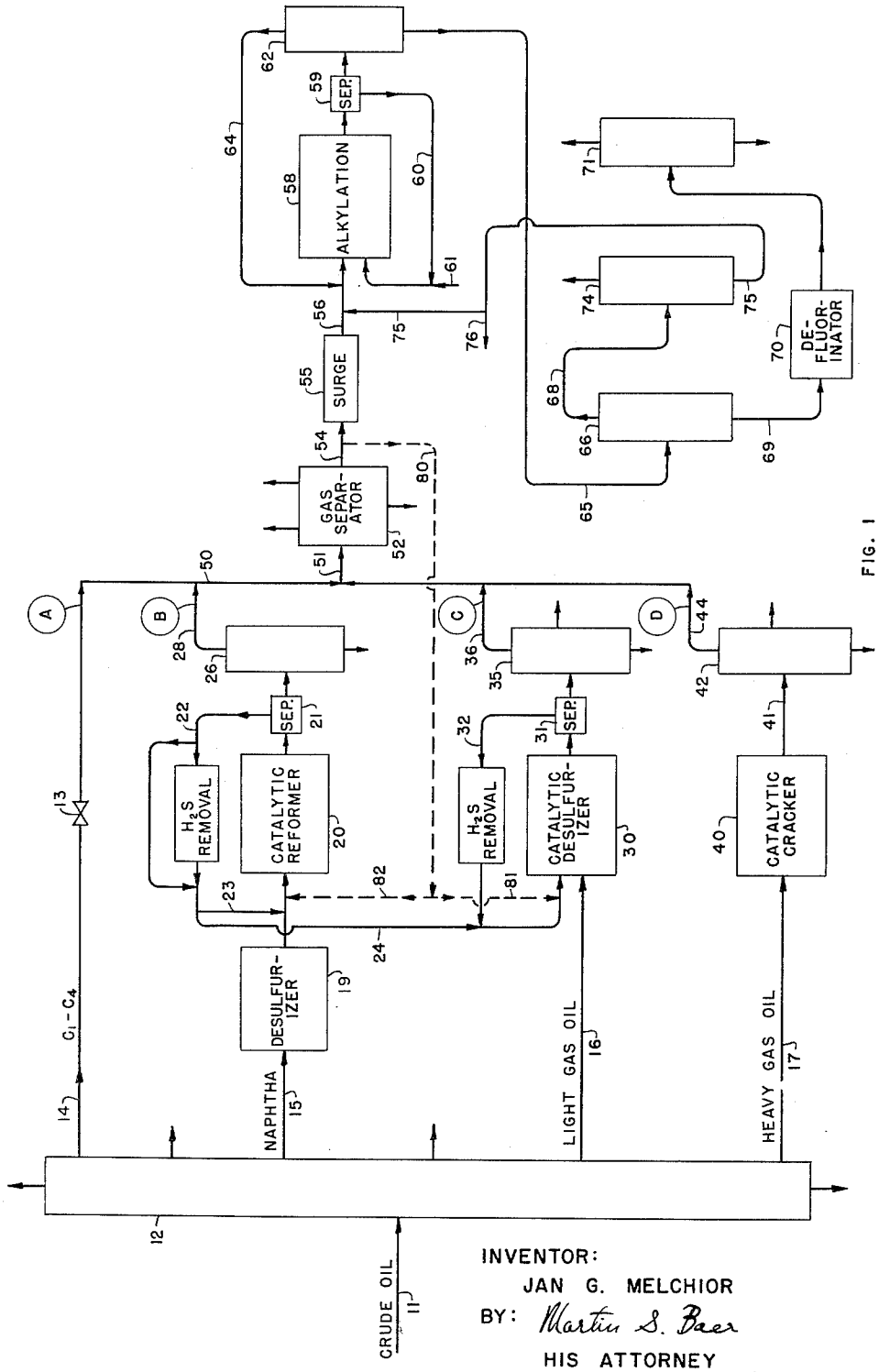


FIG. 1

INVENTOR:
JAN G. MELCHIOR
BY: Martin S. Baer
HIS ATTORNEY

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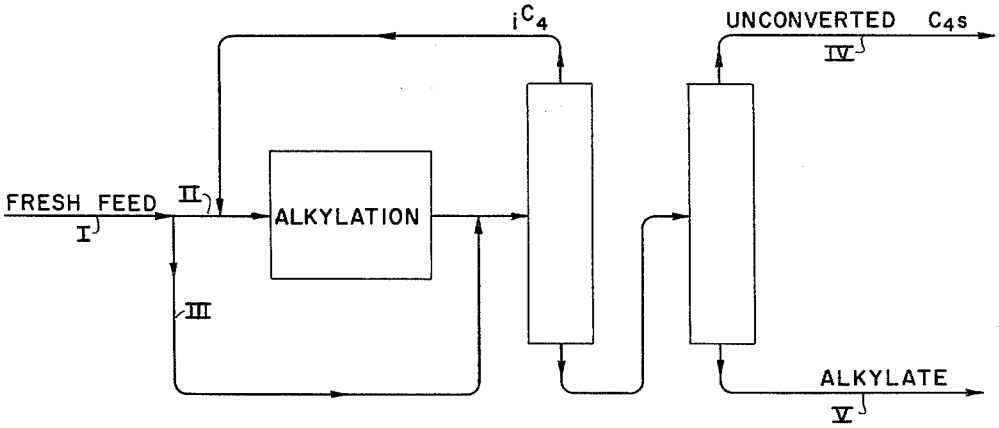


FIG. 2

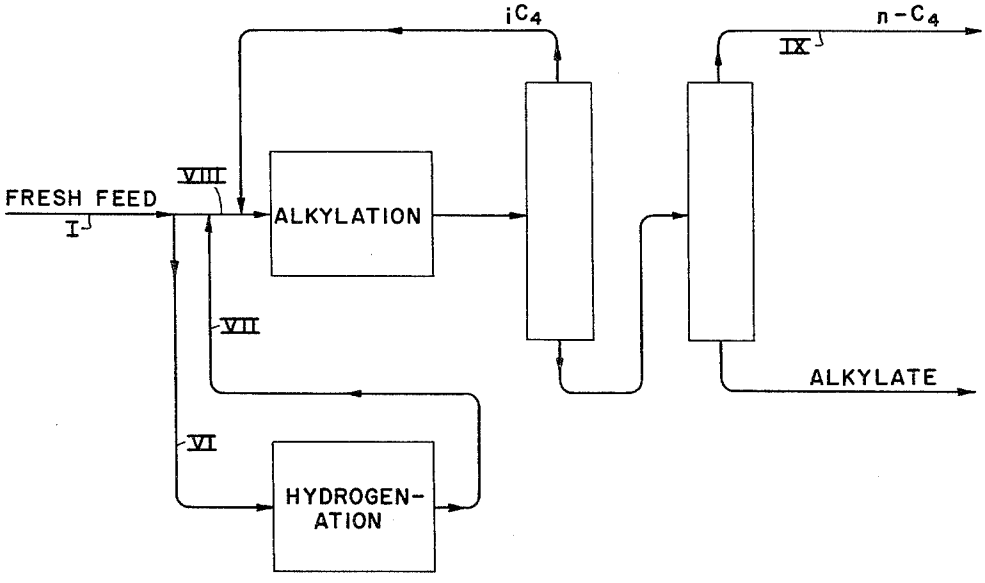


FIG. 3

INVENTOR:
JAN G. MELCHIOR
BY: Martin S. Baer
HIS ATTORNEY

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3,050,456

CONVERSION PROCESS FOR THE PRODUCTION OF HIGH OCTANE NUMBER GASOLINE COMPONENTS

Jan G. Melchior, The Hague, Netherlands, assignor to Shell Oil Company, a corporation of Delaware

Filed Oct. 15, 1958, Ser. No. 767,424
Claims priority, application Belgium Oct. 18, 1957
8 Claims. (Cl. 208—67)

This invention relates to a process for the alkylation of isoparaffins with olefins for the production of high octane number gasoline blending components.

It is well known to produce high octane number gasoline blending components by alkylating isoparaffins of from four to five carbon atoms per molecule with olefins of from three to five carbon atoms per molecule. A typical alkylation reaction is the addition of butylenes to isobutane to produce saturated branched octanes. The reaction is catalyzed by acids. Concentrated sulfuric acid or anhydrous hydrofluoric acid are the preferred commercial alkylation catalysts.

It is an object of this invention to provide an improvement in alkylation processes. It is a more specific object to provide a method for increasing the total production of alkylate from a fresh feed which is deficient in isoparaffins. It is a further object to provide a method for producing alkylate of improved octane number. Further objects will become apparent from the following description in which reference is made to the drawing, wherein:

FIG. 1 is a schematic representation of an arrangement of equipment used for carrying out a preferred mode of the process, and

FIGS. 2 and 3 are schematic representations of arrangements of equipment used in the process according to the prior art, and according to this invention, respectively.

In view of the fact that isoparaffin is commonly recovered from alkylation product and recirculated to the alkylation zone it should be understood that in this text "fresh feed" to the alkylation zone means the alkylation reactants before addition of isoparaffin recycle. The feed which is actually alkylated, which includes isoparaffin recycle, may be designated "total alkylation feed." The ratio of isobutane to olefin in the total alkllation feed is known as the "external isoparaffin-to-olefin ratio." The ratio of the amount of isoparaffin which is present at the point at which olefin is injected into the reaction mixture to the amount of olefin injected is known as the "internal isoparaffin-to-olefin ratio."

Saturated alkylation feed compounds are predominantly isobutane and in some cases isopentane. Unsaturated alkylation feed compounds are olefins having from three to five carbon atoms per molecule. The alkylation feed streams can consist of a single olefin or of a mixture of olefins on the one hand and of a single isoparaffin or of a mixture of isoparaffins on the other hand, or of mixed isoparaffins and olefins. Other components may be present, e.g., unbranched paraffins, which do not participate in the alkylation reaction to any appreciable extent but act merely as diluents.

Branched olefins, e.g. isobutylene, react readily with isoparaffins under alkylation conditions. However, in the sulfuric acid-catalyzed process, isobutane-isobutylene alkylate is of lower quality and is produced in lower yield than the alkylate produced from unbranched butylenes. In the HF-catalyzed process, isobutane-isobutylene alkylate is inferior to that produced from butene-2.

Mixtures of light branched and unbranched hydrocarbons are produced in the petroleum industry by the distillation of crude petroleum and by thermal or catalytic cracking of certain petroleum fractions.

In the distillation of crude petroleum, one can separate

a fraction boiling below gasoline which consists mainly of saturated C_1–C_4 hydrocarobns.

In the work-up of thermally or catalytically cracked petroleum fractions one can obtain a light fraction which consists mainly of saturated and olefinic C_1 to C_4 hydrocarbons.

In the stabilization of the product obtained by catalytic reforming of naphtha fractions, one can obtain a light hydrocarbon fraction which consists mainly of saturated C_3 and C_4 hydrocarbons, including substantial amounts of isobutane.

C_1–C_4 hydrocarbons may also be obtained by other refinery processes.

The predominant sources of isoparaffins for alkylation are isobutane and possibly isopentane which are recovered from the distillation of crude petroleum; further amounts of isobutane and possibly isopentane can be produced by the catalytic isomerization of the corresponding saturated normal paraffins.

The predominant sources of olefins are the light fractions recovered from the work-up of thermally and catalytically cracked petroleum fractions. These fractions are not in themselves suitable as complete fresh alkylation feed stocks because they are deficient is isoparaffin hydrocarbons. They are, therefore, preferably first admixed with other light fractions which are low in olefins, such as the straight-run light fractions. It is often preferable for economic reasons to admix all available light hydrocarbon fractions and fractionate the mixture to recover a C_4 fraction as alkylation feed, rather than fractionating each light hydrocarbon fraction separately to recover a C_4 fraction from each.

It is important in alkylation processes that the hydrocarbon mixture in the alkylation zone contain a substantial excess of the isoparaffin. The external isoparaffin-to-olefin ratio is usually maintained between 3.5:1 and 8:1 in sulfuric acid alkylation and even higher, e.g. between 6:1 and 12:1 in HF alkylation. The internal isoparaffin-to-olefin ratio is preferably at least 300:1 and may be as high as 800:1 or more. A substantial amount of the isoparaffin present in the alkylation zone remains unconverted while practically all the olefin is combined with isoparaffin.

It is especially important that the molecular ratio of isoparaffins-to-olefins in the fresh feed to the alkylation zone, including both normal and branched olefins, remain above a specified lower limit. The molecular ratio of isoparaffins to total olefins in the fresh alkylation feed should in every case be greater than 1.0:1 and preferably should be about 1.1:1. Ratios of 1.05 to 1.20 are satisfactory and ratios in the range from 1.1 to 1.15 are especially preferred. When the value of the ratio is less than 1:1, the yield and antiknock quality of the alkylate are substantially lower than at higher isoparaffin-to-olefin ratios, and greater acid losses are observed. This is especially objectionable in the case where hydrogen fluoride catalyst is employed because substantially greater amounts of the rather expensive HF are carried off in the form of alkylfluorides in the reaction product and are thus lost. When the molecular ratio exceeds 1:1 these undesirable side effects quickly decrease and in each case are substantially negligible at ratios of 1.1:1. Substantially higher values of the ratio may be employed; however, these lead, especially with total recycle of unconverted branched paraffins, to unnecessarily high isoparaffin-to-olefin ratios in the total alkylation feed and thus require an excessively large alkylation zone or reduce the capacity of a given system. This difficulty can be overcome by recirculating only a portion of the total isoparaffins; an excessively high isoparaffin-to-olefin molar ratio in the fresh feed to the alkylation zone is in that case not objectionable.

The present invention provides not only a means for improving the quality of total alkylate but also for increasing the output of total alkylate in a refinery in which the amount of available alkylating olefins is greater than the amount of alkylatable isoparaffins.

It has been proposed in the past in similar refinery situations to polymerize a portion of the available alkylatable olefins and thus bring the isoparaffin-to-olefin ratio into a desired balance. Obviously, the amount of alkylate produced by this expedient is only that which corresponds to the isoparaffin originally available in the refinery. By the process of this invention, however, a total amount of alkylate can be produced in a given refinery situation which is substantially greater than the amount of alkylate that could be produced by employing the prior art expedient of merely removing some of the olefins by polymerization. This will be further illustrated below by means of numerical examples.

The present invention is concerned with an improvement in the production of alkylate in refineries in which the availability of isoparaffins limits the production of total alkylate. In the past this has not been a serious problem because in the nation-wide economy isobutane has been available in excess and thus a refiner could purchase isobutane on the market if in his refinery sufficient isobutane was not available. It is not expected, however, that this situation will prevail much longer. In "Petroleum Refiner," 37, No. 7, 119–123 (1958), Sutherland and Belden show that by 1960 there is expected to be a substantial nation-wide deficiency of isobutane and even a deficiency of n-butane which could be isomerized to isobutane for the production of alkylate.

The process of this invention is particularly adapted for improving the alkylate yield for the refinery in which an olefin fraction is available which has a relatively high isobutylene-to-normal ratio. Catalytic cracking processes, and particularly the so-called two-stage catalytic cracking process which has recently come into commercial use, provide such a C_4 fraction. The two-stage process is described, i.a. in copending patent application Serial No. 436,004, filed June 11, 1954, now abandoned. Suitable apparatus is shown in U.S. 2,798,795 to Rehbein et al. A typical ratio of branched-to-normal butylenes produced in such a process is between 0.8 and 0.9:1. This compares with ratios in the range from 0.5:1 to 0.65:1 observed in conventional commercial catalytic cracking processes and from 0.3:1 to 0.5:1 in conventional commercial thermal cracking processes. A C_4 fraction from two-stage catalytic cracking is a preferred feed in the process of this invention; olefinic fractions from other catalytic cracking processes and including a substantial proportion of isobutylene are also suitable.

The present invention provides a method which makes it possible to increase the molecular ratio of branched paraffins to olefins in the fresh feed to an alkylation zone to exceed 1:1 to any desired extent. It thus becomes possible, according to the process of this invention, to produce a larger amount of better quality alkylate from a given refinery feed stock having an isoparaffin-to-olefin ratio below 1:1 than would otherwise be possible.

The process of this invention is a method for the production of high octane gasoline components from a fresh feed containing one or more olefins, one or more isoparaffins and possibly one or more unbranched paraffins at an isoparaffin-to-olefin molar ratio of less than 1:1 by alkylating the feed under the influence of an acid catalyst after a suitable part of the total fresh feed stream or of at least one of the components of the total fresh feed stream has been taken as a side stream and catalytically hydrogenated, preferably in a reaction zone wherein at the same time normally liquid hydrocarbons are catalytically treated in the presence of hydrogen, the light components of the hydrogenated side stream being recovered and recombined with the remainder of the feed

to produce a fresh feed in which the molecular ratio of branched paraffins to olefins is greater than 1:1.

There are several well-known commercial processes for carrying out the alkylation step of this invention. Typical processes for alkylation using concentrated sulfuric acid catalyst are described in "Petroleum Refiner," 34, No. 9, 148 (1955) and "Petroleum Refiner," 35, No. 9, 251 (1956). Typical processes for alkylation using concentrated hydrofluoric acid are described in "Petroleum Refiner," 34, No. 9, 126 (1955); in "Trans. Am. Inst. Chem. Engrs." 39, 793 (1943), and in the book "Hydrofluoric Acid Alkylation," Phillips Petroleum Company, 1946.

The sulfuric acid alkylation may be advantageously carried out by the method described in the "Petroleum Refiner," supra, or by the methods described, for example, in the United States Patents 2,232,674, 2,260,945, 2,283,603 and 2,370,164; other methods of batch, intermittent or continuous operation may also be used.

The titratable acidity of the sulfuric acid employed as catalyst in the alkylation reactor is generally in the range from 85% to 100% H_2SO_4 and preferably between 88% and 94% H_2SO_4. It is general practice to charge to the process sulfuric acid having between 96% and 100% concentration and to use it until its titratable acidity has dropped to a lower value, e.g., about 85% to 90%. The alkylation reaction is conventionally carried out at temperatures in the range from about 0° C. to about 22° C. and preferably from 4° C. to 16° C. and pressures in the range from atmospheric to 135 p.s.i.g., but sufficiently high to maintain the reactants in liquid phase. It is generally desirable to employ a volume of liquid acid catalyst phase equal to from about 75% to about 250% of the volume of hydrocarbon phase used. An acid-to-hydrocarbon volume ratio of about 1:1 is generally preferred.

In the continuous alkylation processes the fresh feed is admixed with isoparaffin recycle and the total mixture contacted with concentrated sulfuric acid catalyst. The hydrocarbon product, separated from the acid catalyst, is passed to a fractionation zone in which at least some of the following are separated: unconverted branched paraffins; normal paraffins, if present, and crude alkylate. In a typical C_4 alkylation process the total alkylate is deisobutanized and isobutane recycled to the reaction. The deisobutanizer bottoms is debutanized to remove normal butane and obtain a total alkylate fraction as bottoms and the alkylate is re-run to separate alkylate bottoms, or it may be fractionated into a light alkylate and heavy alkylate fraction.

The alkylation employing concentrated hydrofluoric acid as catalyst may also be carried out in different types of process equipment, typically in the manner described in the publications, supra. The alkylation may be carried out at a temperature between 0° C. and 65° C. and preferably between 25° C. and 45° C. Acid-to-hydrocarbon ratios are not critical but may be in the range mentioned above for sulfuric acid or lower, down to about 1:10. The concentration of the hydrofluoric acid is in the range between 80% and 100%, and suitably between 86% and 90%; care is taken to keep water out of the reaction system.

The total hydrocarbon layer is separated from the HF acid layer in a separator. Part of the acid is recycled to the reaction zone and part is regenerated prior to being returned to the reaction zone. The hydrocarbon product is fractionated to recover isoparaffin for recycle, normal paraffin for removal from the system and alkylation product. Means are provided for separating hydrogen fluoride present in the hydrocarbon phase.

The catalytic treatment in the presence of hydrogen to which the normally liquid hydrocarbon fractions are subjected is preferably a catalytic desulfurization or a catalytic reforming process.

The catalytic desulfurization of normally liquid hydro-

carbon oils is a well-known process in which crude oil, straight-run crude oil fractions or fractions which have been subjected to one or more thermal or catalytic treatments are passed at elevated temperatures and pressures in the presence of hydrogen or of a hydrogen-containing gas over a suitable catalyst.

Depending on the kind of material to be desulfurized and on the circumstances, the starting material together with hydrogen or with the hydrogen-containing gas is passed over a catalyst either in vapor phase, in mixed phase, in liquid phase or in super-critical condition. The so-called trickle technique, described in U.S. 2,608,521 and in Petroleum Refiner, 32, No. 5, 137 (1953), and 34, No. 9, 155 (1955), is particularly suitable for such desulfurization. In this trickle technique the desulfurization feed, partly in liquid phase and partly in vapor phase, is passed co-currently with a hydrogen or a hydrogen-containing gas downward over a fixed bed of catalyst particles whereby the unvaporized portion of the feed passes over the catalyst in a thin film and the vaporized portion diffuses through the thin film to contact the catalyst. In the trickle technique, relatively low hydrogen-to-oil ratios can be employed. The following conditions are suitable: pressures of 10–100 atmospheres, temperatures of 300° C.–500° C., space rates of 0.5–15 kg. of oil per liter of catalyst per hour, and gas-to-oil ratios of 50–500 l. gas per kg. oil.

Suitable desulfurization catalysts are those which contain one or more elements of the sixth and/or eighth group of the periodic system, either as metals or in the form of one or more compounds with one or more other elements and suitably supported on a catalyst carrier. Particularly suitable catalysts are those containing one or more of the elements iron, nickel, cobalt, chromium, molybdenum, or tungsten as metal or in the form of one or more compounds with one or more other elements, e.g. oxygen or sulfur, suitably on an alumina carrier.

Especially preferred desulfurization catalysts comprise aluminum oxide as catalyst carrier and supported thereon 5%–15% by weight cobalt or molybdenum as metals and/or in the form of one or more compounds thereof with one or more of the elements oxygen, sulfur or aluminum, and in which the atomic ratio of cobalt to molybdenum is in the range between 1:20 and 18:20 and preferably between 1:10 and 9:10.

The gas is suitably hydrogen or a hydrogen-containing gas mixture, preferably a mixture of hydrogen and light hydrocarbons; particularly suitable is the hydrogen-rich gas produced in the catalytic reforming of hydrocarbon fractions. It is suitable although not necessary to recirculate the hydrogen from the effluent, suitably after removing undesired components.

When the catalytic treatment of the normally-liquid hydrocarbons is catalytic reforming this is carried out in the well-known manner. Reforming processes are described in "Petroleum Refiner," 34, No. 9, 232–259 (1955). The catalytic reforming treatment, which is endothermic, can be carried out in a reaction vessel or pipe which is provided with means for addition of heat in order to maintain the total reaction space at a suitable temperature. It is also possible to carry out the reaction in a series of separate unheated reactors whereby intermediate streams passing from one reactor to the next are heated to the required temperature. Combinations of these two methods can also be employed. It is an advantage of the process of this invention that the hydrogenation reaction of the light hydrocarbons is exothermic so that a part of the heat of reaction of the catalytic reforming process can be supplied thereto internally by charging unsaturated light hydrocarbons thereto in accordance with the process of this invention.

Catalysts in the catalytic reforming process are employed in the form of fast-flowing or fluidized beds of catalyst powders or they may be employed in fixed-bed form. The naphtha to be treated is passed in vapor phase through the catalyst bed.

Reforming temperatures are in the range between about 420° C. and about 560° C. and preferably between about 470° C. and 540° C.

It is preferable to have relatively high partial pressures of hydrogen in the reaction zone. These partial pressures may be about 2 atmospheres, gauge, or higher, e.g. up to about 50 atmospheres, gauge. The total pressure in the reaction zone may be still higher.

Reforming catalysts are preferably one or more of the metals of the sixth and/or eighth group of the periodic table as metals and/or in the form of compounds with one or more other elements such as sulfur or oxygen. They may be supported on a suitable carrier such as aluminum oxide. A preferred type of catalyst consists of molybdenum oxide and/or chromium oxide supported on an aluminum oxide-containing carrier. At present the most widely used catalysts are those containing platinum. Such catalysts contain a small amount, e.g. between about 0.1% and 2% by weight of platinum supported on an acidic carrier. The acidic carrier my consist of compounds of silica and alumina or of a non-acidic carrier, such as aluminum oxide, which has been made acidic by applying a small proportion of an acidic material such as boria, phosphoric acid or a halogen. Thus, porous aluminum oxide containing a small proportion of fluorine and/or chlorine, e.g. 0.1% to 2% by weight, is a suitable acidic carrier for the platinum.

When using such platinum catalysts the partial hydrogen pressure is suitably between 15 and 50 atmospheres and preferably between 18 and 40 atmospheres for the temperatures between 440° C. and 540° C. and preferably between 470° C. and 540° C.

A preferred method of carrying out the process of this invention is illustrated by means of FIG. 1. Crude oil is passed through line **11** into fractionating zone **12**, which may consist of one or a multiplicity of fractionating columns. Among the fractions produced is a C_4-and-lighter straight-run fraction in line **14**, a naphtha fraction in line **15**, a light gas oil in line **16** and a heavy gas oil in line **17**. The naphtha is desulfurized in desulfurizer **19**, which may be hydrogenative or nonhydrogenative, and the desulfurized naphtha passed to catalytic reformer **20**. The catalytic reformer is suitably of the platinum reforming type, employing catalyst and conditions mentioned above. The reformate is separated into a gaseous and a liquid fraction in separator **21**, the gaseous fraction being taken through line **22** which may contain an H_2S removal unit. The fraction may be desulfurized, partly desulfurized and partly by-passed, or completely by-passed. This fraction, consisting essentially of hydrogen and some C_1 and C_2 hydrocarbons, is returned at least in part to furnish hydrogen to the catalytic reformer via line **23** and may be passed in part to a gas oil catalytic desulfurizer through line **24**. The total hydrocarbon fraction recovered from separator **21** is passed to fractionator **26** in which naphtha is taken as a bottoms fraction and a gas fraction, e.g. C_1 to C_4, is taken through line **28**.

The light gas oil from line **16** passes to catalytic desulfurizer **30** in which it is contacted with hydrogen-rich gas from line **24** at the above-mentioned conditions suitable for catalytic desulfurization in the presence of hydrogen. The reaction product passes to separator **31** in which a light gas fraction, consisting mainly of hydrogen and C_1 and C_2 hydrocarbons, is taken through line **32** containing an H_2S removal unit, the desulfurized hydrogen fraction being sent to line **24** for return to the desulfurizer. The hydrocarbon product from separator **31** is passed to fractionator **35** in which a desulfurized gas oil is taken as bottoms, an intermediate fraction may be taken if desired, and a gas fraction, e.g. a C_1–C_4 cut, is taken overhead through line **36**. It will be understood that the separation is indicated more or less schematically and that fractionation zone **35** may consist, for example, of a steam stripper

in which the separator liquid product is contacted with steam to strip therefrom all components lighter than gas oil, the overhead being recovered in an additional separator in which a liquid gasoline fraction is separated from a gaseous C_1–C_4-containing fraction.

The heavy gas oil in line **17** is passed to catalytic cracking unit **40** which may be of the fluidized or of the riser type or may be a fixed-bed catalytic cracking unit or a moving bed catalytic cracking unit. The cracked product is passed through line **41** to fractionation zone **42** in which a number of fractions may be separated, including a light hydrocarbon fraction such as a C_1–C_4 concentrate taken through line **44**.

The light hydrocarbon fractions from lines **14**, **28**, **36** and **44** are combined in line **50** and passed through line **51** to a gas separation unit **52**, which may be of the conventional type in which the light gases are compressed and the compressed gases are contacted countercurrently with an absorber oil in one or more stages. The gas separation unit may further contain an absorber oil debutanizer, an H_2S removal unit for the debutanizer overhead and a butane depropanizer so that the final product leaving gas separation zone **52** via line **54** consists essentially only of C_4 hydrocarbons. The products taken from gas separator **52** other than the C_4 cut in line **54**, are thus, for example, a C_2 and lighter fraction, a propane-propylene fraction and a gasoline fraction. The C_4 cut in line **54** passes to surge vessel **55** which provides feed to alkylation zone **58** via line **56**. Alkylation zone **58** is, for example, a reactor system in which butylenes are contacted with isobutane in the presence of concentrated anhydrous HF catalyst added via line **60**. Make-up acid is added through line **61**. The C_4 fraction in line **56** is admixed with recycle isobutane from line **64** before being passed to the alkylation zone.

The temperature in the alkylation zone is suitably between 30° C. and 40° C. and the pressure suitably about 10 atmospheres. The alkylation zone may be divided into several reactors, preferably substantially agitated and cooled to remove heat of reaction. The reaction mixture which leaves alkylation zone **58** is first passed through a pressure separator **59** wherein it is separated into two liquid layers, the lower layer consisting mainly of HF; this is recycled to the alkylation zone via line **60** which may contain an HF regeneration zone for removal of impurities. The hydrocarbon phase which, besides hydrocarbons, also may contain about 1% HF, passes from the separator to fractionator **62** in which the major portion of remaining HF is removed in admixture with some light hydrocarbons and recycled to line **56** via line **64**. The bottoms from column **62** are passed via line **65** to column **66** in which isobutane and lighter hydrocarbons are taken overhead in line **68** and heavier product, mainly alkylate, taken as bottoms in line **69**. The alkylate is defluorinated in defluorinator **70**, which may be, for example, a vessel containing alumina; the defluorinator product is distilled in column **71** to remove remaining butane overhead and take alkylate product as a bottoms fraction. The alkylate may be re-run to remove heavy alkylate, if desired. The fraction in line **68** is fractionated in column **74** to take overhead a fraction lighter than isobutane, e.g. propane present in the system, and to take as bottoms an isobutane concentrate which is returned via recycle line **75** to alkylation feed line **56**. If desired, some of the product in line **75** may be withdrawn as a bleed stream through line **76**.

In the above-described process it is essential that the isobutane-to-butylene ratio in line **56** ahead of the addition of recycle isobutane via lines **75** and **64** be at least 1:1 and preferably in the range from about 1.05:1 to about 1.15:1. This composition is generally the same as that in surge drum **55**. When the said ratio in surge drum **55** falls below the desired value and when the ratio in line **54** is not sufficiently high to permit prompt adjustment to the desired range in line **56**, then at least a substantial portion of the C_4 fraction in line **54** is withdrawn through line **80**, shown as a dashed line, and is passed therethrough either to catalytic desulfurizer **30** via line **81** or to catalytic reformer **20** via line **82**. Addition to the catalytic desulfurizer is ordinarily preferred. The butylenes present in the fraction added via lines **81** or **82** are completely hydrogenated in units **30** or **20**; the resulting saturated C_4 mixture is ultimately returned to surge drum **55** via the fractionation and gas separation system.

The following examples are presented for illustrative purposes only and are not to be considered as limiting the invention.

EXAMPLE I

The proportion of available olefins which is to be hydrogenated in a given situation is easily determined. The following is a typical calculation:

Isoparaffin: olefin ratio desired for charge to alkylation = 1.1.

Available feed (moles):

Isoparaffin	A
Normal paraffin	—
Isoolefin	B
Normal olefin	C
Total	$A+B+C$

Condition: $A<1.1\ (B+C)$

Let the amount of isoolefin to be hydrogenated by X moles.

Substitute into the relationship:

Total isoparaffin in fresh feed to alkylation
= 1.1 (total olefins in fresh feed to alkylation)
= 1.1 (originally available olefins–hydrogenated olefins)

$$A+X=1.1\left(B+C-\left(1+\frac{C}{B}\right)X\right)$$

$$X=\frac{1.1(B+C)-A}{2.1+\frac{1.1C}{B}}$$

The proportion of total feed to be hydrogenated is $\frac{X}{B}$.

The results, expressed in general terms, are as follows:

	Available	Sent to hydrogenation	Hydrogenated	Direct to alkylation	Total to alkylation
Isoparaffins	A	$\frac{X}{B}A$	$\frac{X}{B}A+X$	$A-\frac{X}{B}A$	$A+X$
Normal paraffins			$\frac{X}{B}C$		$\frac{X}{B}C$
Isoolefins	B	X		B−X	B−X
Normal olefins	C	$\frac{X}{B}C$		$C-\frac{X}{B}C$	$C-\frac{X}{B}C$
	$A+B+C$	$\frac{X}{B}(A+B+C)$	$\frac{X}{B}(A+B+C)$	$\left(1-\frac{X}{B}\right)(A+B+C)$	$A+B+C$

Without hydrogenation, the amount of alkylate produced is

$$\frac{A}{1.1} \text{ moles}$$

With hydrogenation, it is

$$\frac{A+X}{1.1} \text{ moles}$$

EXAMPLE II

Assuming numerical values for A, B and C, the following illustrates a specific case.

Let $A=35$, $B=30$, $C=35$.

The required calculations are:

$$X=\frac{1.1(B+C)-A}{2.1+\frac{1.1C}{B}}=\frac{1.1(65)-35}{2.1+\frac{1.1(35)}{30}}$$

$$=10.8$$

$$\frac{X}{B}=\frac{10.8}{30}=0.36$$

	Available	Sent to hydrogenation	Hydrogenated	Direct to alkylation	Total to alkylation
Isoparaffins	35	12.6	23.4	22.4	45.8
Normal paraffins			12.6		12.6
Isoolefins	30	10.8		19.2	19.2
Normal olefins	35	12.6		22.4	22.4
	100	36.0	36.0	64.0	100.0

By hydrogenating 36% of the total feed, the yield of alkylate is increased from 31.8 moles to 41.6 moles.

EXAMPLE III

Reference is made herein to the flow illustrated in FIG. 1 of the drawing.

In a petroleum refinery, crude oil is distilled into several fractions including a light fraction (A) (line **14**) consisting predominantly of C_1–C_4 hydrocarbons, and several other fractions referred to hereinafter. Fraction (A) contains 13.6 t./d. (tons per day) isobutane and 59.9 t./d. n-butane.

A heavy naphtha fraction is taken via line **15**, desulfurized and catalytically reformed over a supported acidic platinum alumina catalyst. Part of the resulting hydrogen is recycled and part passed to catalytic desulfurizer **30**. The hydrogen fraction passing via line **24** to desulfurizer **30** contains 1.8 t./d. isobutane and 2.2 t./d. n-butane as well as other saturated light hydrocarbons. From the fractionation of the catalytic reformate there is recovered a light fraction (B) (line **28**) which contains 24.3 t./d. isobutane and 38.0 t./d. n-butane.

In desulfurizer **30** gas oil is desulfurized by means of cobalt oxide-molybdena-alumina catalyst, using the trickle technique. The pressure is about 60 atmospheres, the temperature about 380° C., the flow velocity about 2.5 v./v./hr. and the gas-to-oil ratio about 125 l. gas/kg. oil. From the product work-up there is recovered a light fraction (C) which contains the above-mentioned 1.8 t./d. isobutane and 2.2 t./d. n-butane.

Heavy gas oil is cracked in cracking unit **40**. In the distillation of its reaction product there is recovered a C_1–C_4 hydrocarbon fraction (D) (line **44**). This fraction contains 75.5 t./d. isobutane, 29.8 t./d. n-butane, 28.8 t./d. isobutylene and 67.2 t./d. normal butylenes.

The light fractions (A), (B), (C) and (D) are combined in line **50** and passed through gas separation zone **52**. The effluent (line **54**) contains 115.2 t./d. isobutane, 129.9 t./d. n-butane, 28.8 t./d. isobutylene and 67.2 t./d. n-butylene. When the system is in steady state, the butane composition in surge drum **55** has the same composition. The molecular ratio of isobutane to total butylenes is thus 1.16, which is in the correct range for satisfactory operation of the alkylation unit. Since even lower ratios are satisfactory, some isobutane may be recovered for other uses from line **76** when the system is in operation.

When fraction (A) is not available however, i.g. because of difficulties in the crude distillation while the reforming, desulfurizing and cracking units are still operating satisfactorily on stored feed stock, then valve **13** in line **14** would be closed and the butane feed would consist only of fractions (B), (C) and (D). These combined fractions contain 101.6 t./d. isobutane, 70.0 t./d. n-butane, 28.8 t./d. isobutylene and 67.2 t./d n-butylenes The molecular ratio of isobutane to total butylenes in line **54** is thus 1.02, which is undesirably low.

In order to remedy this, a portion of the fraction in line **54** is passed to line **80** to be hydrogenated, for example, by passing it through line **81** to catalytic desulfurizer **30**. For steady-state operation it is suitable to pass, for example, 283.5 t./d. of the C_4 fraction to surge drum **55**; this fraction would contain 109.3 t./d. isobutane, 78.2 t./d. n-butane, 28.8 t./d. isobutylene and 67.2 t./d. normal butylenes. Of the total passing through line **54** one recirculates via line **80**, for example to desulfurizer **30**, a total of 15.7 t./d. which leaves for alkylation a net of 267.8 t./d. of a C_4 fraction consisting of 103.2 t./d. isobutane, 73.9 t./d. n-butane, 27.2 t./d. isobutylene and 63.5 t./d. normal butylenes The molar ratio of isobutane to total butylenes in the alkylation feed is thus 1.10, which is a value in the desired range.

The passage of the small amount of C_4 fraction through the catalytic desulfurizer has no undesirable effect on the desulfurization of the gas oil. There is, of course, a slight increase in hydrogen consumption (circa 7.2 t./d. instead of 7.0 t./d.). This effect is so small as to have no substantial influence on the operation of the process.

The present invention is further illustrated by the following example in which reference is made to FIGS. 2 and 3. FIG. 2 is a schematic representation of an alkylation and fractionation system and FIG. 3 a similar schematic representation of an alkylation and fractionation system including hydrogenation in accordance with the process of this invention.

EXAMPLE IV

The present example illustrates how a substantially greater total production of alkylate can be achieved in a refinery in which the total butylenes available have a relatively high ratio of isobutylene to normal butylenes and in which isobutane is not present in the amount required for alkylation. Such a situation is found, for example, in a refinery in which all of the cracking is carried out in a catalytic cracking unit which produces a high ratio of iso- to normal butylenes.

Referring to FIG. 2, the alkylation unit is a conventional one, e.g. a sulfuric acid alkylation unit. The total feed fraction (I) passing to the alkylation unit has the following composition: isobutane, 210 b./d. (barrels per day); normal butane, 244 b./d., isobutylene, 226 b./d.; and normal butylene, 320 b./d., amounting to a total of 1000 b./d. This is passed to the alkylation unit which contains the usual reactors and associated equipment. The total effluent passes to a deisobutanizer in which isobutane is removed overhead for recycle, the bottoms passing to a debutanizer in which n-butane is removed as overhead and total alkylate is taken as the bottoms stream.

The compositions of the various streams are shown in Table 1, below. For convenience of presentation, volume ratios are employed in the calculation, although this causes a slight loss of precision, which is not of significant magnitude.

Table 1

COMPOSITIONS OF FRACTIONS

Fraction	I	II	III	IV	V	VI	VII	VIII	IX	X
Component, B/D:										
i-C_4H_{10}	210	70	140			105	214	319		
n-C_4H_{10}	244	81	163	244		119	277	402	402	
i-C_4H_8	226	75	151	151		110		116		
n-C_4H_8	320	107	213	213		157		163		
Total C_4H_8	546	182	364	364		267		279		
Total C_4	1,000	333	667	608		491	491	1,000	402	
Alkylate					312					460

The ratio of isobutane to total butylenes in the fresh feed is only about 0.385:1. There is, thus, a very substantial excess of butylenes since isobutane is limiting and since a ratio of 1.15:1 is desired in this example. The amount of butylenes that can be alkylated is only 182 b./d. It is, therefore, necessary to split the total feed and pass only fraction (II), which contains 182 b./d. of butylenes, to the alkylation zone while fraction (III) is by-passed and sent to the alkylation fractionation system so that the isobutane content thereof can be recovered and recycled back to the alkylation zone while the normal butane and butylenes content passes with the alkylate to the alkylate debutanizer in which fraction (IV) is taken as overhead. This contains 364 b./d. of unconverted butylenes. The amount of alkylate produced in this system is 312 b./d.

Instead of passing fraction (III) to the alkylate fractionating system it is, of course, also possible to split it separately because it is only necessary to recover its isobutane content for alkylation.

The improvement obtainable by treating the same feed fraction (I) in accordance with the present invention is illustrated by reference to FIG. 3.

The proportion of fraction (I) which must be hydrogenated in order to provide a complete balance between isobutane and butylenes is readily calculated.

If a portion of the total fraction (I) is to be hydrogenated to produce sufficient isobutane to alkylate the remaining butylenes, the required volume of isobutylene to be converted is 110 b./d., calculated as illustrated in Examples I and II. Thus fraction (VI) passing to the dehydrogenator must contain 110 b./d. of isobutylene. The hydrogenation may take place in the manner illustrated previously, e.g. by combining the fraction with the feed to a reforming or hydrogenative desulfurization unit or by a separate hydrogenation step. The hydrogenated C_4 fraction returned to feed to alkylation has composition (VII); the total fresh feed to alkylation thus has composition (VIII), the debutanizer overhead has composition (IX) and the total alkylate production (X) is 460 b./d. Thus, by the mere expedient of hydrogenating a portion of the total fresh feed, alkylate production has been increased from 312 to 460 b./d., or by approximately 50%.

Process variations within the scope of this invention will occur to those skilled in the art. For example, where separating means are available the isoolefin may be concentrated relative to normal olefins prior to the hydrogenation step.

I claim as my invention:

1. A process for increasing the yield of alkylate obtained from a feed fraction containing isoolefin and normal olefin and containing less than one mole of alkylatable isoparaffin per mole of alkylating olefin which comprises separating said feed fraction into a first portion and a second portion, hydrogenating in the presence of free hydrogen the first portion to convert the isoolefin and normal olefin therein to the corresponding isoparaffin and normal paraffin, recombining the hydrogenated first portion with the unhydrogenated second portion and alkylating said recombined portions by contact with a mineral acid alkylation catalyst at alkylating conditions, the relative proportions of said first portion and said second portion being adjusted so that the recombined first and second portions have a molar ratio of isoparaffin to olefin of at least 1.05:1.

2. A process according to claim 1 in which the mineral acid is concentrated hydrofluoric acid.

3. A process according to claim 1 in which the mineral acid is concentrated sulfuric acid.

4. A process according to claim 1 in which said first portion of the feed fraction is hydrogenated in the presence of free hydrogen by being admixed with the naphtha feed to a reforming process and at least the isoparaffinic components of the reformed product in the molecular weight range of the feed fraction are recovered from the reformed product and passed to the alkylation with said second portion of the feed fraction.

5. A process according to claim 1 in which said first portion of the feed fraction is hydrogenated in the presence of free hydrogen by being admixed with the gas oil feed to a desulfurization process and at least the isoparaffinic components of the product in the molecular weight range of the olefinic fraction are recovered from the desulfurization product and passed to the alkylation with said second portion of the feed fraction.

6. A process for the production of high octane number gasoline components which comprises catalytically cracking a hydrocarbon oil to produce a cracked product including a light hydrocarbon fraction having an iso- to normal butylene ratio of at least about 0.8:1 and having an isobutane to olefin ratio of less than 1:1, separating said fraction into a first portion and a second portion, hydrogenating in the presence of free hydrogen said first portion to convert the iso- and normal butylene therein to isobutane and normal butane, respectively, recombining the hydrogenated first portion with the unhydrogenated second portion and alkylating said recombined portions by contact with a mineral acid alkylation catalyst at alkylating conditions, the relative proportions of said first portion and said second portion being adjusted so that the recombined first and second portions have a molar ratio of isobutane to olefin of at least 1.05:1.

7. A process for the production of high octane number gasoline components which comprises catalytically cracking a hydrocarbon oil to produce a cracked product including a light hydrocarbon fraction having an iso- to normal butylene ratio of at least about 0.8:1 and having an isobutane to olefin ratio of less than 1:1, separating said fraction into a first portion and a second portion, hydrogenating in the presence of free hydrogen said first portion of said fraction to obtain isobutane and normal butane and recombining the hydrogenated first portion with said unhydrogenated second portion so that the recombined first and second portions have a molar ratio of isobutane to olefin of at least 1.05:1, recombining the portions and alkylating in an alkylation zone the recombined fraction by contact with a mineral acid alkylation catalyst at alkylation conditions whereby alkylate is formed, and recovering normal butane from said alkylation zone.

8. A process in accordance with claim 7 and further characterized by isomerizing in an isomerization zone in the presence of an isomerization catalyst under isomeriza-

tion conditions the normal butane recovered from said alkylation zone, whereby isobutane is formed, separating said isobutane from said isomerization zone and recycling said isobutane into said alkylation zone.

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