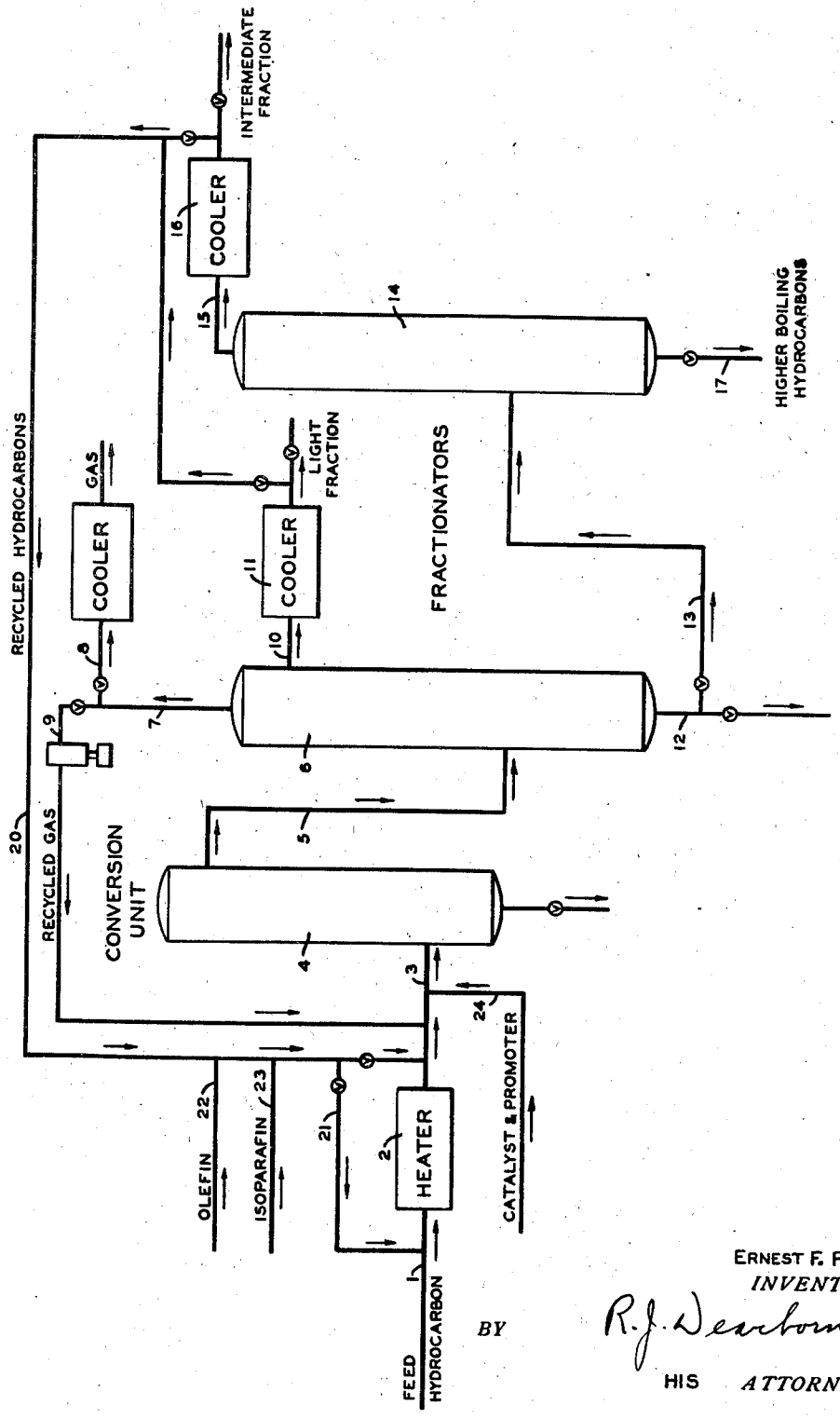
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CATALYTIC CONVERSION OF HYDROCARBONS

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CATALYTIC CONVERSION OF HYDROCARBONS

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This invention relates to the catalytic conversion of hydrocarbons for the production of hydrocarbons suitable in the manufacture of gasoline. More particularly, the invention relates to the catalytic conversion of relatively low boiling saturated hydrocarbons to produce hydrocarbons of highly branched chain character.

The invention contemplates subjecting feed hydrocarbons, such as saturated relatively low boiling hydrocarbons derived from a petroleum source, to the action of a conversion catalyst in a reaction zone under conditions such that isomerization constitutes the principal reaction, and effecting the reaction in the presence of a small amount of olefinic hydrocarbon in such a way as to substantially promote the isomerization reaction.

More specifically the invention contemplates effecting the reaction so that a relatively small amount of low boiling olefin, in the presence of isoparaffin hydrocarbon, is maintained in the isomerization reaction, the isoparaffin advantageously being present in substantial amount relative to the olefin at and subsequent to the initial contact between the feed hydrocarbon and the conversion catalyst. Advantageously both isoparaffin and olefin are maintained present throughout the entire reaction.

It has been found that by carrying out the conversion in the foregoing manner and particularly at temperatures lower than normally used in isomerization, the hydrocarbon reaction product obtained contains a materially greater proportion of isomerized feed hydrocarbons than when the reaction is carried out in the substantial absence of olefin hydrocarbon. The reason for this is not clearly understood, but nevertheless the existence of a substantial promoting effect through having both olefin and isoparaffin present at least during the initial contact between feed hydrocarbon and catalyst appears to be substantiated by examples which will be described hereinafter.

In the isomerization of normal paraffin hydrocarbons with a metallic halide catalyst it has been found desirable heretofore to remove olefins from the feed to the reaction zone since under ordinary conditions olefins, if present, appear to cause catalyst deterioration and result in a substantial decrease in the yield of isomerized hydrocarbons per unit of catalyst employed.

The present invention, however, involves having a substantial amount of isoparaffin present with the olefin during the initial contact between the feed hydrocarbon and the catalyst and throughout substantially the entire reaction. Advantageously the isoparaffin is present in substantial molar excess over the olefin. It appears that under these conditions the olefin is utilized in alkylating isoparaffins present in the reaction

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zone and is thereby consumed in the production of valuable hydrocarbon products rather than entering into reaction with the catalyst to form complex. At any rate under such conditions a definite promoting effect is realized.

Moreover, the conversion reaction can be carried out at lower temperatures than prevail in the ordinary isomerization reaction. In addition the character of the product is different. For example, when isomerizing normal butane by the action of aluminum chloride and hydrogen chloride at a temperature of about 120° F. in the presence of a small amount of ethylene and in accordance with the method of this invention, the product contains very substantial amounts of neohexane and methylpentanes.

The following experiments comprise batch liquid phase experiments in which normal butane was converted by the action of aluminum chloride and hydrogen halide at a temperature of about 150° F. In each experiment anhydrous aluminum chloride, hydrogen chloride and some hydrocarbon were charged to a reaction vessel provided with a stirrer and means for heating the vessel. The stirrer was then started and the temperature adjusted to the desired point, following which hydrocarbon feed was added slowly over a period of 1 hour, the mixture being stirred for 30 minutes after completion of the addition of the hydrocarbon. Thereafter, the reaction mixture was drawn off and the hydrocarbon product separated into gaseous and liquid fractions, respectively. The gaseous fraction comprised essentially isobutane, normal butane and lighter hydrocarbons, while the liquid fraction comprised normally liquid hydrocarbons free from butanes.

The following tabulation compares the amount of catalyst, hydrocarbon charge, and hydrocarbon product in parts by weight. The composition of the gas and liquid fractions of the product is shown in per cent by weight.

	A	B	C
Catalyst:			
Aluminum chloride	110	110	110
Hydrogen chloride	10	10	10
Reaction temperature, ° F	150	150	150
Hydrocarbon charge:			
Normal butane	540	530	392
Isobutane	0	0	41
Ethylene	0	26	25
Mols of butane per mol of ethylene	0	10.0	8.3
Mols of isobutane per mol of ethylene	0	0	0.8
Hydrocarbon product: Gas fraction	530	500	404
Composition of gas fraction:			
Percent lighter than isobutane	0.1	0.5	1.8
Percent isobutane	11.0	19.4	42.1
Percent normal butane	87.5	76.0	51.9
Percent isopentane and heavier	1.4	4.1	4.2
Yield of isobutane, basis normal butane charged	10.2	18.0	32.9
Liquid fraction	None	40	58
Percent yield of liquid fraction basis ethylene		154	232

In experiment A the hydrocarbon charge con-

sisted solely of normal butane. In experiment B ethylene and normal butane was introduced continuously throughout the entire run. In experiment C isobutane was present initially in the reactor and ethylene and normal butane were introduced continuously throughout the entire run.

In experiment A it will be observed that under the conditions employed, the yield of isobutane amounted to 10.2% by weight of the normal butane charged. However, in experiment B with a small amount of ethylene present the yield of isobutane obtained amounted to 18.0% by weight of the normal butane charged. On the other hand, in experiment C where a small amount of isobutane was initially present along with the ethylene the conversion of normal butane to isobutane was nearly doubled. The results in experiments B and C calculated on the basis of 100 pounds of normal butane charged may be tabulated as follows:

	B	C
Charge:		
Normal butane	100	100
Ethylene	4.9	6.4
Isobutane	0	10.5
Products:		
Normal butane	71.6	53.5
Isobutane	18.3	43.5
Normal liquid fraction	7.6	14.8

The liquid fractions obtained in experiments B and C comprised hydrocarbons boiling over the range about 85 to 175° F. and consisted mainly of pentanes and hexanes.

The following additional experiments afford a comparison of the yield and product character when reducing the reaction temperature from 150 to about 120° F. These experiments were carried out in a similar manner to that described above.

	D	E
Catalyst:		
Aluminum chloride	110	110
Hydrogen chloride	30	15
Reaction temperature, ° F	150	120
Hydrocarbon charge:		
Normal butane	331	257
Isobutane	85	66
Ethylene	32	25
Mols of butane per mol of ethylene	6.3	6.2
Mols of isobutane per mol of ethylene	1.1	1.1
Hydrocarbon product: Gas fraction	310	250
Composition of gas fraction:		
Percent lighter than isobutane	1.7	5.7
Percent isobutane	43.5	36.7
Percent normal butane	53.1	55.4
Percent isopentane and heavier	1.7	2.2
Yield of isobutane, basis normal butane charged	31.1	23.3
Liquid fraction	67	40
Percent yield of liquid fraction basis ethylene	210	160

The liquid fraction from experiment D was analyzed and found to comprise hydrocarbons boiling over the range about 86 to 145° F. and about 60% of this fraction comprised isopentane, the remainder being largely mixed hexanes.

The liquid product from experiment E was analyzed and found to comprise hydrocarbons boiling over the range about 86 to 196° F. About 30% of the liquid comprised isopentane, about 14% comprised neohexane and about 12% comprised a mixture of 2-, and 3-methylpentanes.

While normal butane was charged in the foregoing experiments it is, of course, contemplated that the invention has application to the conversion of other paraffin hydrocarbons having from about 4 to about 11 carbon atoms per molecule and in particular hydrocarbons of about 4 to 6 carbon atoms as well as light naphtha fractions boiling in the range up to about 150 to 170° F., for the purpose of converting normal and branched chain saturated hydrocarbons into branched and more highly branched chain saturated hydrocarbons. In addition it is contemplated that other types of hydrocarbons such as relatively low boiling naphthene hydrocarbons may be isomerized.

Other normally gaseous olefins may be employed besides ethylene, for example propylene, butylenes, amylenes, and mixtures thereof, although the lower molecular weight olefins are preferred. The proportion of olefin charged to the reaction may range from about 0.5 to as much as 10% and advantageously not exceeding about 5% by volume of the total feed to the reaction.

The isoparaffin introduced to the reaction advantageously comprises a relatively low boiling isoparaffin such as isobutane or isopentane. It may be obtained from an extraneous source or may be separated from the reaction product and recycled to the reaction zone. The isoparaffin is maintained in the reaction in the ratio of from about 1 to 10 mols of isoparaffin per mol of olefin. As indicated in experiment C good results were obtained with a ratio of nearly 1. In no case, however, should the isoparaffin exceed about 50% by volume of the normal paraffin undergoing conversion in the reaction zone.

Reference may be had to the accompanying drawing comprising a flow diagram illustrating one mode of practicing the invention in a continuous flow operation.

A hydrocarbon such as a normal paraffin hydrocarbon or mixture consisting essentially of normal paraffin hydrocarbons is drawn from a source not shown through a pipe 1 and conducted to a heater 2 wherein it is heated to the reaction temperature. Olefin may be present in the feed in the requisite amount or may be added separately as mentioned later. The heated feed hydrocarbon or hydrocarbon mixture is conducted from the heater through a pipe 3 to a conversion unit 4 wherein it is subjected to the action of the conversion catalyst. For example, a suitable conversion catalyst comprises aluminum chloride activated with hydrogen halide.

The reacted, together with unreacted, hydrocarbons are drawn off from the conversion unit through a pipe 5 and advantageously introduced to a fractionator 6. The hydrocarbons are advantageously scrubbed upon removal from the conversion unit to remove entrained catalyst and promoter.

The fractionator 6 may be operated so as to separate the hydrocarbon mixture into any desired number of fractions or may be operated so as to remove only gaseous constituents, the degasified hydrocarbons passing to a separate fractionator for further treatment. However, as indicated in the drawing the fractionator 6 may be operated so as to remove overhead a gas fraction through a pipe 7 and branch pipe 8.

Since this gaseous fraction removed through the pipe 7 may comprise substantial amounts of hydrogen chloride or other gaseous agents used in the reaction it is usually desirable to recycle the gaseous material to the conversion reaction. In such case the recycled material is returned through a pipe 9.

A side stream comprising isomerized hydrocarbons may be drawn off through a pipe 10 and cooler 11 while a heavier fraction may be drawn

off in liquid form from the bottom of the fractionator through a pipe 12.

If desired the liquid fraction drawn off through the pipe 12 may be passed through a branch pipe 13 for introduction to another fractionator 14 wherein the hydrocarbons are subjected to further fractionation. In this instance an overhead fraction may be removed through a pipe 15 and a cooler 16 while a liquid fraction may be drawn off from the bottom of the fractionator through a pipe 17.

Any portion, of either or both of the fractions removed through the coolers 11 and 16, may be recycled to the conversion unit.

For example, when charging a feed hydrocarbon consisting of normal butane the product fraction removed from the cooler 11 may consist essentially of isobutane, while the product fraction removed from the cooler 16 may comprise essentially unreacted normal butane. The unreacted normal butane is advantageously recycled all or in part to the conversion unit together with a small amount of isobutane which may be obtained from the stream drawn off from the cooler 11. However, it is contemplated that the fractionation operations may be conducted so that the normal butane stream drawn off from the cooler 16 contains a small but sufficient amount of isoparaffin to supply the isoparaffin required in the conversion unit.

The recycled hydrocarbons may be returned through a pipe 20 communicating with the pipe 3 previously mentioned, or communicating by means of a branch pipe 21 with the pipe 1 previously mentioned.

Olefin hydrocarbon obtained from an extraneous source is conducted through a pipe 22 and advantageously commingled with the recycled hydrocarbons. On the other hand, it may be injected directly with the feed hydrocarbon or may be injected directly to the conversion unit whichever is desired. It may be injected in a stream which is rich in isoparaffin, or in a stream which is rich in normal paraffin.

Isoparaffin from an extraneous source and which may be necessary in the early stages of the operation may be introduced through a pipe 23.

Makeup catalyst and promoter may be passed to the conversion unit from a source not shown through a pipe 24.

The conversion unit may be of any conventional type depending upon the type of conversion operation employed. Thus, the catalyst may be employed in either solid or liquid form although the liquid form is usually preferred. In such case the catalyst may comprise a solid catalyst dissolved or suspended in a liquid carrier such as hydrocarbon or metallic halide-hydrocarbon complex. For example, an effective catalyst comprises solid aluminum halide dissolved or suspended in aluminum halide-hydrocarbon complex.

The conversion unit may comprise a vessel containing a substantially stationary body of fluid catalyst through which the hydrocarbons undergoing treatment rise merely by difference in density. On the other hand, the reaction vessel may be of the agitated type, such agitation being imparted either by mechanical stirring means or by rapid circulation of hydrocarbon or catalyst mixture through the reaction zone.

With the agitated type of apparatus it is usually desirable to provide adequate settling space or auxiliary settling chambers wherein separation between hydrocarbon and catalyst phases occurs, the catalyst phase being returned all or in part to the reaction zone, while the hydrocarbon phase is passed all or in part to the fractionating zone or subsequent treating zone, that portion not so disposed of being returned to the reaction zone.

The reaction may be carried out in the presence of extraneous agents such as hydrogen for the purpose of controlling or modifying the reaction.

Various metallic halide catalysts may be employed such as aluminum chloride, aluminum bromide, zirconium chloride, beryllium chloride, titanium tetrachloride, stannic tetrachloride, antimony chloride, or mixtures of halides such as $AlCl_3$-$SbCl_3$, $AlCl_3$-NaCl, etc.

Suitable promoters other than hydrogen chloride may be hydrogen bromide, hydrogen iodide, carbon tetrachloride, alkyl, aryl or acyl halides or any substance which is capable of liberating halogen halide after coming into contact with the metallic halide catalyst. Chlorine, bromine and iodine may be injected for purposes of promoting the reaction. Alkyl halide formed by chlorination of a portion of the feed hydrocarbon to the reaction may be utilized as the promoter.

Other catalysts or promoters besides those specifically mentioned above may be employed since it is contemplated that the process of this invention is applicable to the conversion of hydrocarbons by the action of any suitable catalyst wherein isomerization constitutes the principal reaction.

With an aluminum halide-hydrogen halide catalyst, such as aluminum chloride activated with hydrogen chloride, the temperature maintained in the reaction zone is preferably somewhat lower than that employed when effecting isomerization in the usual manner and in the absence of olefin. On the other hand, the temperature is somewhat above the range employed in the conventional alkylation reaction with this type of catalyst. For example, when isomerizing normal butane in the presence of ethylene in accordance with this invention the reaction temperature may range from about 100 to 175° F. When isomerizing normal pentane the temperatures may range from about 75 to 125° F.

The use of high promoter concentration facilitates employing low temperatures such that the reaction may be carried out at even lower temperatures, as for example 0° F.

The feed hydrocarbon may be treated to remove objectionable compounds such as sulfur compounds and aromatic constituents, the presence of which is undesired when employing a catalyst such as aluminum halide.

The process of promoting the isomerization of a normal paraffin hydrocarbon, such as normal butane, to the corresponding isoparaffin in the presence of an aluminum halide catalyst and a hydrogen halide promoter at temperatures within the range of about 75 to 250° F., by adding to the normal paraffin charge a small proportion of an olefin and also a small proportion of an isoparaffin, the olefin amounting to from a fraction of 1% to about 5% by volume of the total hydrocarbon feed, and the isoparaffin amounting to at least the molar equivalent of the olefin but not exceeding about 10% by volume of the normal paraffin undergoing conversion in the reaction zone, is disclosed and claimed in the copending co-owned application of Eugene E. Sensel, Serial No. 606,446, filed July 21, 1945, as a continuation-

in-part of the copending application, Serial No. 439,031, filed April 15, 1942.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method for catalytically converting normal butane to more valuable saturated hydrocarbons, which comprises forming a hydrocarbon feed mixture consisting mainly of normal butane and containing minor proportions of isobutane and a normally gaseous olefin, the olefin being present in about 0.5 to not in excess of about 10 volume per cent of the total hydrocarbon feed mixture, and the isobutane being present in from 1 to 10 mols per mol of olefin but not exceeding an amount which provides about 50% by volume on the basis of the normal butane undergoing conversion in the reaction zone, passing the said hydrocarbon feed mixture to said reaction zone and contacting the same therein in liquid phase with an aluminum halide catalyst and a hydrogen halide promoter under conditions including a temperature within the range of about 100 to 175° F., whereby isomerization of normal butane

to isobutane constitutes the principal reaction and the production of normally liquid branched-chain paraffin hydrocarbons higher boiling than n-butane constitutes a substantial but minor reaction, removing hydrocarbon reaction products from said reaction zone, separating isobutane from said removed products as a principal final product of the process, separating a normally liquid fraction consisting essentially of said higher boiling branched-chain paraffin hydrocarbons as a substantial but minor final product, also separating from said products an intermediate fraction consisting essentially of unconverted normal butane with a minor proportion of isobutane, and recycling said intermediate fraction to the reaction zone, the amount of normal butane thereby converted into isobutane and recovered as such in the final product being substantially greater than when the conversion is effected under the same conditions with a feed consisting of normal butane and free from said isobutane and olefin.

2. The method according to claim 1, wherein the normally gaseous olefin is ethylene, and the normally liquid product contains substantial amounts of neohexane and methylpentanes.

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