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TREATMENT OF HYDROCARBONS

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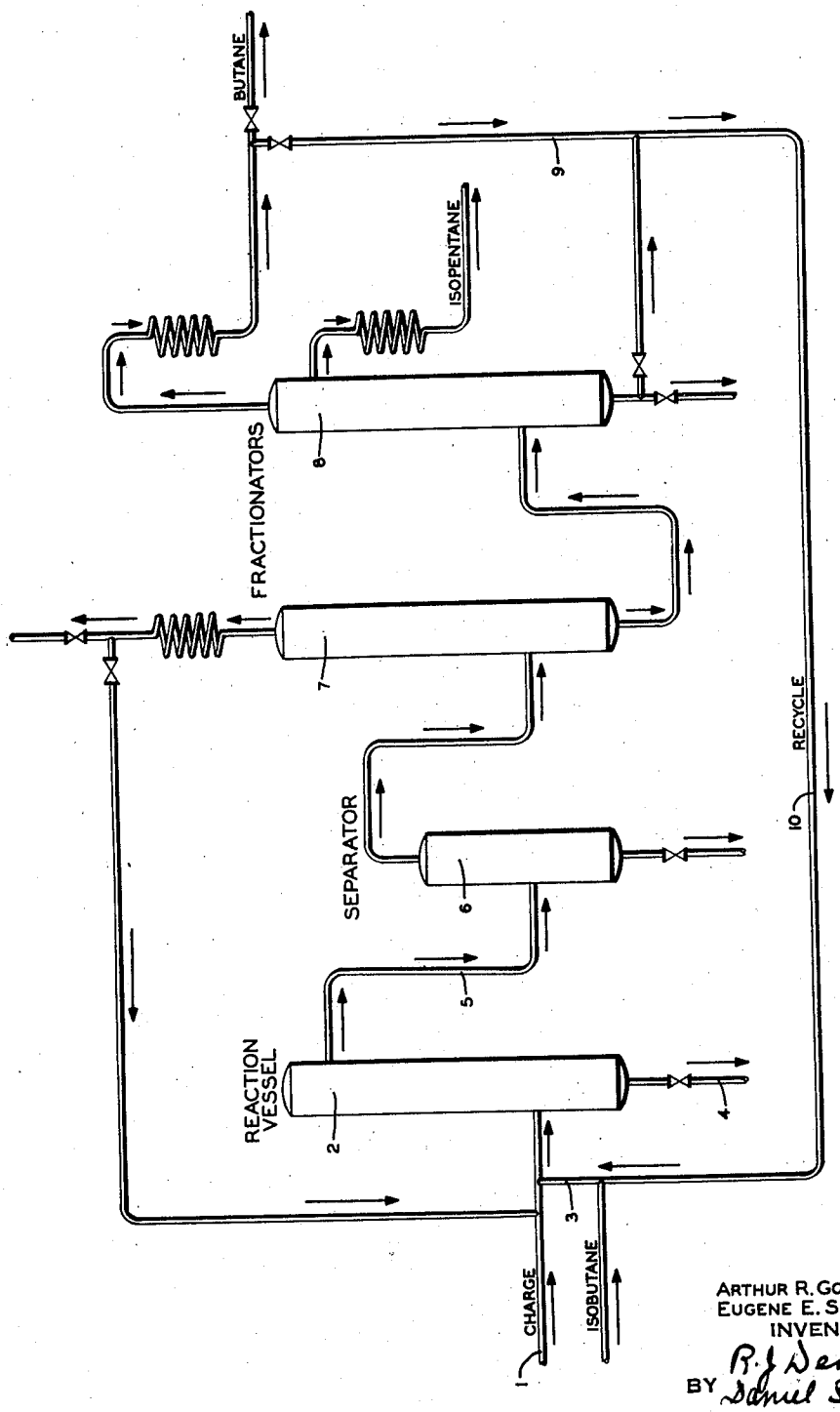

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TREATMENT OF HYDROCARBONS

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13 Claims. (Cl. 260—683.5)

This invention relates to the treatment of hydrocarbons and particularly to treatment with an isomerization catalyst to improve the anti-knock value and volatility.

In pending application, Serial No. 282,114, filed June 30, 1939, we have disclosed a process for treating straight run naphtha wherein hydrocarbon constituents of naphtha are subjected to contact with an isomerization catalyst in the presence of a large proportion of a low boiling isoparaffin hydrocarbon, such as isobutane.

The present invention relates to such a process, with particular reference to its application to the treatment of normal pentane, or a hydrocarbon fraction consisting essentially of normal pentane, for the production of isopentane.

It has been proposed heretofore to isomerize certain normally gaseous hydrocarbons and lower boiling normally liquid hydrocarbons, such as normal butane and normal pentane, to corresponding isoparaffins by contacting the normal paraffins in the liquid or vapor phase at temperatures of zero to 200° C., with certain anhydrous metallic halides, such as chlorides, bromides, etc., of aluminum, zinc, iron, zirconium, tin, barium, columbium, tantalum and boron, and small amounts of hydrogen halides, such as hydrogen chloride, as promoters. It has also been proposed to subject gasoline of boiling range of about 130° to 190° F. to isomerization in the presence of aluminum chloride and hydrogen chloride at temperatures of about 150° to 200° C.

Normal butane may be successfully isomerized to isobutane in the presence of anhydrous metallic halides and hydrogen halides, without a substantial amount of side reactions, providing correct operating conditions are used. In the case of the higher boiling normally liquid hydrocarbons, considerable difficulty is encountered due to cracking and/or other types of side reactions, whereby substantial deterioration of the catalyst is experienced and a substantial proportion of high boiling material outside of the gasoline boiling range is formed.

It has now been found that the side reactions and accompanying deterioration of the catalyst which normally occur with the higher boiling normal paraffins, may be substantially inhibited or minimized by carrying out the isomerization operation in the presence of a large proportion of a low boiling isoparaffin, such as isobutane. Thus, experiments have shown that when normal pentane (alone or in the absence of any added isobutane) is subjected to contact with a catalyst comprising aluminum chloride and a promoter such as hydrogen chloride, under conditions suitable to effect conversion to isopentane, the catalyst is completely converted in a relatively short time to a dark colored liquid complex. On the other hand, when the conversion is effected for the same length of time in the presence of a large proportion of added isobutane, no trace of the complex compound exists and the catalyst is recovered as a dry powder. Moreover, the formation of high boiling material is materially reduced.

The reactions involved are not fully understood. However, it is thought that the isobutane may inhibit the cracking and the resultant formation of unsaturated hydrocarbon fragments or olefins, which, either as such or as conversion products, react with the aluminum halide to form the complex. In addition the hydrocarbon fragments or olefins may react with the isobutane rather than with the catalyst. The catalysts which are useful in the process include any of the active isomerization catalysts, such as metallic halides, preferably used in the presence of small amounts of promoters, such as hydrogen halides. While any of the anhydrous metallic halides which will function as isomerization catalysts are contemplated, for practical purposes aluminum halides, such as aluminum chloride, and aluminum bromide, are preferred. Likewise, any of the hydrogen halide promoters, such as HCl, HBr, HI and HF, may be used, but it is preferable to use hydrogen chloride. The metallic halide catalyst may be in granular, solid, or lump form, or in the case of $AlBr_3$ at temperatures above 208° F. in liquid form, or supported on a solid adsorbent, such as synthetic and natural clays, silica gel, pumice, brick, coke, activated alumina, and activated carbon. The hydrogen halide promoter may be added as such or may be generated in situ from the metallic halide by adding the required amount of water, steam or alkyl halide which reacts with the metallic halide.

The process may be carried out in a batch or continuous type of operation, and preferably in a continuous operation. The process is preferably conducted as a cyclic operation in which the isobutane or a butane fraction of the reaction mixture is recycled together with any portion or all of the hydrogen halide promoter, as well as all or any portion of the unconverted normal pentane.

The amount of catalyst and promoter will vary, depending on the type of operation used. The percentage of promoter may be varied within wide limits, say 0.1 to 10% by weight of the normal pentane-isobutane solution being treated. A concentration of 0.5% appears to be satisfactory for liquid phase isomerization, but a higher concentration of the order of around 2 to 3% may be desirable for gas phase isomerization.

The invention is not restricted to any particular temperature and pressure since the process may be operated successfully at temperatures and pressures selected from quite wide ranges. Thus, temperatures may range from about room temperature to about 300° F., although a temperature in the range of about 115 to 230° F. is preferable. In general, as the temperature is

increased, more isobutane is required to eliminate the formation of the hydrocarbon-catalyst complex. The operating pressure will depend upon the temperature as well as upon the type of operation, i. e., liquid or gas phase. A pressure just below the vapor pressure of the particular pentane-isobutane solution being treated at a given temperature may be used in gas phase operation in order to obtain the advantage of a greater through-put, although pressures from atmospheric up to the equilibrium vapor pressure can also be employed. For liquid phase operation a pressure in excess of the equilibrium vapor pressure is employed.

The proportion of isobutane used is influenced by the operating conditions and the nature of the charge. It is contemplated that the ratio by volume of isobutane to normal pentane charged may be as much as 5:1, or higher, the higher ratios being advantageous when using higher temperatures and higher percentages of promoter and catalyst. As indicated in the experiments referred to below, weight ratios of 2:1 and about 4:1 parts of isobutane per part of normal pentane have been found effective.

The contact time for the mixture being treated will depend upon the temperature, pressure and percentage of promoter used, which variables may be chosen to give the optimum conversion to isopentane. It is contemplated that the contact time may be around 1 to 4 hours for liquid phase operation. For vapor phase operation the contact time may be of the order of from 1 to 15 minutes.

The following examples compare the results obtained when isomerizing normal pentane with and without the presence of a substantial proportion of added isobutane at temperatures of 160 and 200° F., respectively. The results were obtained in batch experiments using powdered anhydrous aluminum chloride as a catalyst. A small amount of water was added to generate the promoter, i. e., hydrogen chloride.

	Experiments			
	1	2	3	4
Temperature ° F.	160	160	200	200
Time hours	4	3.7	4	2
CHARGE IN GRAMS				
n-Pentane	1,224	343	1,224	550
Isobutane	0	1,375	0	1,100
Aluminum chloride	129.9	182.2	129.9	175.1
Water	3	4.2	3	4.1
Catalyst converted to HCl	7.4	10.4	7.4	10.1
Catalyst effective as such	122.5	171.8	122.5	165
Hydrogen chloride generated	6.1	8.5	6.1	8.3
PRODUCTS IN GRAMS				
Hydrocarbon layer	1,155	1,699	1,140	1,600+
Catalyst layer	190	179	186	170+
Hydrocarbons recovered per cent	94.35	98.89	93.14	97.0+
Hydrocarbons converted to complex per cent	5.16	0.00	4.84	0.00
LOW TEMPERATURE DISTILLATION OF HYDROCARBON LAYER EXPRESSED AS MOL PER CENT				
Boiling below isobutane	0.0	0.0	0.7	0.1
Isobutane	63.5	74.3	57.6	74.5
n-Butane	0.2	3.8	5.1	0.9
Isopentane	21.9	16.6	20.6	20.5
n-Pentane	2.3	5.3	5.5	4.0
Boiling above n-pentane	12.1	0.0	10.5	0.0
Isopentane in C_5 fraction	89	76	80	84

As the foregoing data indicate, where the conversion was effected in the absence of isobutane there was substantial conversion of the catalyst to the complex compound, namely, 5.16% in Experiment 1 and 4.84% in Experiment 3. On the other hand, in the comparative runs, where isobutane was present, no complex formation was noted. Substantial conversion of normal pentane to isopentane occurred in each experiment. In Experiments 1 and 3, where isobutane was absent from the charge there was substantial formation of hydrocarbons boiling above normal pentane, while in the comparative experiments, where isobutane was present in the charge, no higher boiling hydrocarbons were formed.

We have found that it is advantageous to effect isomerization of normal pentane in the absence of appreciable quantities of higher molecular weight hydrocarbons. The individual normal paraffin hydrocarbon apparently isomerizes most effectively at a temperature lower than that necessary in the case of a fraction containing it, together with higher molecular weight hydrocarbons. Experiments have indicated, for example, that normal pentane may be subjected to isomerization at a temperature of around 130° F. so as to obtain a 50% conversion to isopentane. However, when subjecting a pentane-hexane mixture from naphtha to isomerization under similar conditions and at the same temperature, very little conversion of normal pentane to isopentane occurs.

The invention will be understood further from the accompanying drawing showing a flow diagram for carrying out the process of the invention.

Referring to the drawing:

A charge comprising n-pentane is introduced through a pipe 1 to a catalyst chamber 2. Isobutane or a mixture of iso and normal butane is introduced through a pipe 3. Any partially spent catalyst may be withdrawn from the catalyst chamber through a pipe 4.

The reaction products are transferred from the upper portion of the catalyst chamber through a pipe 5 to a stabilizer or separator 6 wherein any catalyst carried over with the hydrocarbons may be separated and withdrawn. The separator, or the reaction products entering the separator, may be cooled to facilitate precipitation of the catalyst. The hydrocarbons are passed from the separator 6 to a fractionator 7.

The fractionator 7 is advantageously operated so as to remove hydrogen chloride and other gaseous constituents which may be discharged from the separator. If the gas removed comprises essentially hydrogen chloride, it is advantageously recycled to the reaction vessel 2.

The hydrocarbons withdrawn from the bottom of the fractionator 7 are passed to a fractionator 8. This fractionator is advantageously operated so as to remove an overhead fraction comprising butanes. A side stream is removed comprising isopentane, while the fraction drawn off from the bottom of the fractionator comprises normal pentane.

As indicated, the butane fraction may be conducted, all or in part, through pipes 9 and 10 and thus recycled to the reaction vessel 2. Likewise, the normal pentane fraction may be transferred, all or in part, through the pipe 10 for recycling to the reaction vessel.

Thus, in actual practice, the fractionation of the reaction products may be regulated so as to remove the promoter, isobutane, normal

butane and normal pentane, which are recycled, while the remaining product, comprising isopentane, is withdrawn from the system. The isopentane so withdrawn is advantageously disposed of as a blending stock in the manufacture of aviation gasoline. Isomerization of normal pentane to isopentane raises the octane number (CFRM) from approximately 60 to 93. It also increases the volatility, since normal pentane has a boiling point of 96.8° F., whereas isopentane boils at 82.4° F.

Consequently, the isopentane produced in the process is of particular benefit when blended with gasoline fractions for the production of aviation gasoline.

While recycling the unconverted pentane has been mentioned, it is contemplated that this may not be necessary. As indicated by the experimental data set forth above, the concentration of isopentane in the pentane fraction of the product may be around 76 to 85% so that recycling of the normal pentane may not be necessary.

It is also contemplated that mixtures of isobutane and normal butane may be recycled to suppress deterioration of the catalyst and resultant formation of the catalyst-hydrocarbon complex. Moreover, it is contemplated that the make-up isobutane, in a continuous system, may be obtained by the addition of normal butane or a butane fraction. In such case normal butane is converted to isobutane with formation of an equilibrium mixture of normal and isobutane.

Although aluminum chloride was used in the above-described experiments, eutectic or other mixtures of two or more of the aluminum halides can be used. Other isomerization catalysts besides the anhydrous aluminum halides can be employed. Mixtures of hydrogen halides can be used as promoters. Alkyl halides or mixtures of alkyl halides, acyl halides or mixtures thereof, aryl halides or mixtures thereof, water, steam, alcohols, aldehydes, ketones, organic acids, and other oxygenated compounds can also be used as promoters.

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.

We claim:

1. A process for isomerization of normal pentane which comprises subjecting normal pentane in the presence of a substantial proportion of added hydrocarbon comprising isobutane to contact with aluminum chloride and hydrogen chloride at a temperature of 130 to 300° F. for a period of time of around one minute to not in excess of four hours and thereby forming a reacted hydrocarbon mixture rich in isopentane, the amount by weight of the aforesaid isobutane being added being substantially in excess of the weight of pentane charged and sufficient to substantially reduce cracking and retard catalyst deterioration.

2. A process for the isomerization of a hydrocarbon feed consisting essentially of normal pentane which comprises continuously passing a stream of said feed through a reaction zone containing a metallic halide isomerization catalyst maintained under isomerizing conditions at a temperature not in excess of about 300° F., continuously introducing to said zone isobutane in an amount sufficient to maintain a substantial molar excess over the normal pentane undergoing treatment therein, subjecting the normal pentane feed to contact with the catalyst in the presence of the added isobutane and a small amount of hydrogen halide during passage through the reaction zone such that there is substantial conversion of normal pentane to isopentane with substantial reduction in cracking and catalyst deterioration, and removing from said zone a reacted hydrocarbon mixture containing isopentane in substantial amount.

3. The method according to claim 2 in which the ratio of isobutane to normal pentane maintained in the reaction zone is about 2 to 4 parts of isobutane to 1 part of pentane by weight.

4. A process for the isomerization of a hydrocarbon feed consisting essentially of normal pentane which comprises continuously passing a stream of said feed through a reaction zone containing a metallic halide isomerization catalyst maintained under isomerizing conditions, continuously introducing to said zone isobutane sufficient in amount to maintain a substantial molar excess over the normal pentane undergoing treatment therein, subjecting the normal pentane feed to contact with the catalyst in the presence of the added isobutane and a small amount of hydrogen halide during passage through the reaction zone for a period of about 1 to 15 minutes, maintaining within said reaction zone a reaction temperature of about 130 to 200° F. such that there is substantial conversion of normal pentane to isopentane with substantial reduction in cracking and catalyst deterioration, and removing from said zone a reacted hydrocarbon mixture containing isopentane in substantial amount.

5. A process for the isomerization of a hydrocarbon feed consisting essentially of normal pentane which comprises continuously passing a stream of said feed through a reaction zone containing a metallic halide isomerization catalyst, continuously introducing to said zone isobutane in an amount sufficient to maintain a substantial molar excess over the normal pentane undergoing treatment therein, subjecting the normal pentane feed to contact with the catalyst in the presence of the added isobutane and a small amount of hydrogen halide during passage through the reaction zone, maintaining isomerizing conditions within said zone at a temperature not in excess of about 300° F. such that there is substantial conversion of normal pentane to isopentane with substantial reduction in cracking and catalyst deterioration, removing from the reaction zone a reacted hydrocarbon mixture containing isopentane and butanes, fractionating said mixture to form a hydrocarbon fraction rich in butanes and recycling at least a portion of said butane fraction through the reaction zone.

6. In a process for isomerization of a hydrocarbon fraction comprising essentially normal pentane by contact with an isomerization catalyst for normal paraffin hydrocarbons maintained in a reaction zone under isomerizing conditions at a temperature not in excess of about 300° F. such that conversion of normal pentane to isopentane is normally accompanied by formation of substantial amounts of hydrocarbons of higher molecular weight than pentane, the step which comprises introducing isobutane to the reaction zone in an amount sufficient to maintain a substantial molar excess of isobutane over nor-

mal pentane undergoing treatment therein such that the aforesaid formation of hydrocarbons of higher molecular weight than pentane is substantially inhibited.

7. In a process for isomerization of a hydrocarbon feed comprising essentially normal pentane by contact with an isomerization catalyst for normal paraffin hydrocarbons maintained in a reaction zone under isomerizing conditions such that conversion of normal pentane to isopentane is normally accompanied by formation of substantial amounts of hydrocarbons of higher molecular weight than pentane, the method which comprises passing a stream of said normal pentane feed to the reaction zone, introducing isobutane to the reaction zone in an amount sufficient to maintain a substantial molar excess of isobutane over the normal pentane undergoing treatment therein and sufficient to inhibit substantial formation of the aforesaid hydrocarbons of higher molecular weight than pentane, effecting substantial conversion of normal pentane to isopentane during passage through the reaction zone, and removing from the reaction zone a hydrocarbon mixture containing isopentane in substantial amount.

8. In a process for the isomerization of a hydrocarbon feed comprising essentially normal pentane by contact with an isomerization catalyst for normal paraffins maintained in a reaction zone under isomerizing conditions such that conversion of normal pentane to isopentane is normally accompanied by formation of substantial amounts of hydrocarbons of higher molecular weight than pentane, the method which comprises passing said feed to the reaction zone containing a metallic halide isomerization catalyst, introducing isobutane to the reaction zone in an amount sufficient to maintain a substantial molar excess of isobutane over the normal pentane undergoing treatment therein, and sufficient to inhibit substantial formation of the aforesaid hydrocarbons of higher molecular weight than pentane, subjecting the pentane feed to contact with the catalyst in the presence of the added isobutane and a small amount of hydrogen halide such that substantial conversion of normal pentane to isopentane is effected, and removing from the reaction zone a hydrocarbon mixture containing isopentane in substantial amount.

9. The method according to claim 8 in which the ratio of isobutane to normal pentane maintained in the reaction zone is about 2 to 4 parts of isobutane to 1 part of pentane.

10. The method according to claim 8 in which the isomerization catalyst comprises aluminum halide.

11. The method according to claim 8 in which the isomerization reaction is effected at a temperature not in excess of about 300° F.

12. In a process for isomerization of a hydrocarbon feed comprising essentially normal pentane by contact with an isomerization catalyst for normal paraffin hydrocarbons maintained in a reaction zone under isomerizing conditions such that conversion of normal pentane to isopentane is normally accompanied by formation of substantial amounts of hydrocarbons of higher molecular weight than pentane, the method which comprises passing a stream of said feed to the reaction zone containing a metallic halide isomerization catalyst maintained under isomerizing conditions at a temperature not in excess of about 300° F., introducing isobutane to the reaction zone in an amount sufficient to maintain a substantial molar excess of isobutane over the normal pentane undergoing treatment and sufficient to inhibit substantial formation of the aforesaid hydrocarbons of higher molecular weight than pentane, subjecting the feed hydrocarbon to contact with the catalyst in the presence of the added isobutane and a small amount of hydrogen halide such that substantial conversion of normal pentane to isopentane is effected, removing from the reaction zone a mixture of hydrocarbons comprising C_4 and C_5 hydrocarbons including isopentane, separating C_4 hydrocarbons from said withdrawn mixture and returning the separated C_4 hydrocarbons at least in part to the reaction zone.

13. A process for the isomerization of a hydrocarbon feed consisting essentially of normal pentane which comprises continuously passing a stream of said feed through a reaction zone containing a metallic halide isomerization catalyst maintained under isomerizing conditions at a temperature not in excess of about 300° F., continuously introducing to said zone C_4 paraffin hydrocarbon in an amount sufficient to maintain a substantial molar excess of isobutane over the normal pentane undergoing treatment therein, subjecting the normal pentane feed to contact with the catalyst in the presence of the added C_4 paraffin hydrocarbon and a small amount of hydrogen halide during passage through the reaction zone such that there is substantial conversion of normal pentane to isopentane with substantial reduction in cracking and catalyst deterioration, and removing from said zone a reacted hydrocarbon mixture containing isopentane in substantial amount.

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