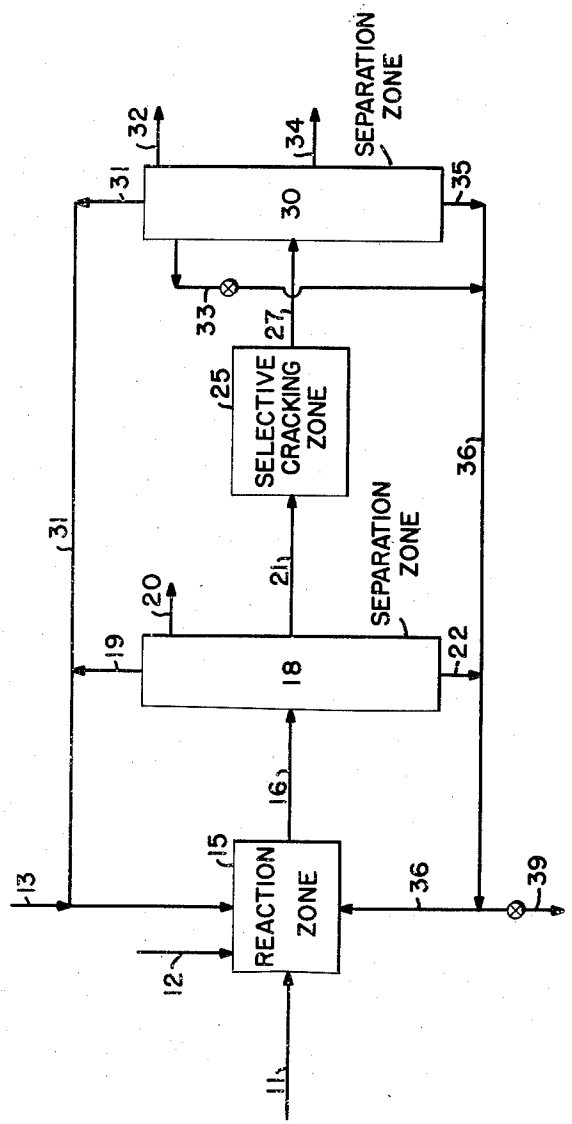
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COMBINED ISOMERIZATION AND CRACKING PROCESS

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John E. Hofmann
Henry T. Brown
Inventors

By Byron O. Simmick
Patent Attorney

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COMBINED ISOMERIZATION AND CRACKING PROCESS

John E. Hofmann, Summit, and Henry T. Brown, Elizabeth, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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The present invention concerns a process for upgrading the heptane fraction of a naphtha to enhance its value as a motor fuel component. In particular, the invention concerns a process wherein the less desirable isomers in a heptane fraction are selectively cracked while the more desirable isomers are essentially unaltered, thereby increasing the proportion of more desirable isomers in that fraction.

The use of modern high compression engines in motor cars has greatly increased the demand for motor fuels of high antiknock rating. In general, to provide such motor fuels, it is necessary to have available a supply of highly branched paraffin hydrocarbons boiling in the motor fuel boiling range. The petroleum refiner can employ for this purpose several processes, among which alkylation and isomerization are attractive from an economic standpoint.

The isomerization of normal paraffin hydrocarbons of from 4 to 7 carbon atoms into the corresponding branched chain homologs is well known. For effecting the isomerization, it is customary to employ certain metal halides, particularly aluminum chloride or aluminum bromide, in conjunction with certain promoters, such as hydrogen chloride, hydrogen bromide or boron fluoride. In the case of light naphtha it is preferred that the isomerization be conducted in the range of about 30° to about 140° F. in order to favor the formation of isomers of high antiknock rating. Aluminum bromide is particularly active in this temperature range.

It has recently been found that it is possible to bring about the liquid phase reaction of butanes and pentanes with higher paraffin hydrocarbons of from 6 to 18 carbon atom chain lengths to give good yields of C_5 to C_7 branched chain saturated paraffin hydrocarbons. For this type of reaction, temperatures in the range of from about 30° to about 140° F. are employed, and the catalyst used comprises aluminum bromide along with suitable promoters. Regardless of the particular heavier paraffin hydrocarbon that is used in the range of from about 6 to 18 carbon atoms in the latter type of reaction, the product distribution from the reaction predominates in C_5 to C_7 isomers. The quantity of the butane or pentane in the reaction is considerably greater than the quantity of the higher paraffin hydrocarbon and there is a net consumption of the lower hydrocarbon. In view of the fact that the process, in effect, brings about the alkylation of one paraffin hydrocarbon with another paraffin hydrocarbon, the process may be termed a paraffin alkylation process.

While the C_5 and C_6 components of the product of a paraffin alkylation reaction are of acceptably high antiknock rating, the same is not true of the C_7 fraction of the product. Similarly when there are C_7 components in [illegible] reaction involving a light naphtha fraction [illegible] relatively poor antiknock rating. It has been found that the equilibrium distribution in the C_7 fraction from both types of process is such that a high proportion of methylhexane isomers is present. Accordingly, there is a need for upgrading the quality of the C_7 fraction from isomerization and paraffin alkylation reactions.

It is one object of the present invention to provide a process wherein the C_7 fraction from the treatment of paraffinic hydrocarbons with aluminum bromide can be improved.

In accordance with the present invention, the C_7 fraction that is obtained from a catalytic treatment involving contacting with a Friedel-Crafts catalyst, particularly aluminum bromide, wherein said C_7 fraction contains a large proportion of methylhexanes, is subjected to a selective cracking reaction in the presence of an aluminum halide selected from the class consisting of aluminum chloride and aluminum bromide at a temperature in the range of from about 150° F. to about 250° F., whereby the methylhexanes are selectively cracked to C_4 to C_6 isomers while the more highly branched isomers of the C_7 fraction are relatively undisturbed in the cracking treatment.

The nature and objects of this invention and the manner in which the invention may be practiced will be readily understood when reference is made to the accompanying drawing in which the single figure is a schematic flow plan showing one method for practicing the invention.

The process will be first described with reference to the isomerization of a fraction containing heptane, followed by selective cracking of the products. A reaction zone **15** is provided in which an isomerization catalyst is present. This catalyst may comprise a fixed bed or a slurry. Preferably the catalyst comprises promoted aluminum bromide. However, other Friedel-Crafts catalysts can be employed provided they exhibit the desired isomerization activity in the preferred temperature range. A feed stream containing normal heptane enters the reaction zone through line **11**. Conditions of temperature and contact time are maintained in reaction zone **15** to bring about the desired reaction. Preferably the reaction pressure is high enough to keep the reacting hydrocarbons in the liquid phase. The preferred range of isomerization temperatures is from about 30° to about 140° F. If an auxiliary promoter is employed, such as hydrogen bromide, this may be introduced into the reaction zone through line **12**. Also, it may be preferred to conduct the isomerization in the presence of isobutane to suppress undesired side reactions. The isobutane is introduced into the reaction zone through line **13**. Preferably, the proportion of isobutane to feed hydrocarbon in reaction zone **15** is in the range of from about 25 to about 100 volume percent based on feed.

The products of the reaction leave the reaction zone through line **16** and are conducted into separation zone **18** where fractionation of the products may be carried out. If isobutane and a hydrogen halide are employed in the reaction, these will leave overhead through line **19** and be recycled to the reaction zone by means of lines **31** and **13**. A side stream of C_5 and C_6 hydrocarbons may be removed through line **20**. The C_7 fraction is

conducted by means of line 21 to selective cracking zone 25. Heavier materials may be removed through line 22 and recycled to the reaction zone by means of line 36.

The isomerization reaction in zone 15 is preferably conducted in the presence of a supported aluminum bromide catalyst. Among the supports that may be used are included silica gel, gamma alumina, activated carbon and calcined bauxite. The latter is available commercially under the trade name Porocel. To prepare the supported catalyst at the start of the process, the support may be saturated with aluminum bromide and then placed in the reaction zone, or, alternatively, the support may be placed in the reaction zone and then saturated with aluminum bromide carried in with a portion of the feed. Another method of preparation is to mix the aluminum halide with the support and to heat the mixture to effect impregnation. If desired, loosely held aluminum halide may be removed from the catalyst mass by heating the mass and passing through it a gas such as carbon dioxide, methane, hydrogen or nitrogen.

Alternatively, the support may be impregnated by dissolving the aluminum halide in a suitable solvent such as ethylene dichloride or dioxane, for example, and the porous carrier impregnated with this solution, followed by heating to remove the solvent and loosely held aluminum halide. Still another alternative is to employ a powdered support or promoter, mix the aluminum halide with it, and compress the mixture into pellets.

In place of a fixed bed operation, a moving bed of catalyst or a slurry type of operation may be used. In the latter case, a suspension of catalyst is maintained in the reacting hydrocarbons in zone 15, suitable stirring or recirculating means being employed to maintain the suspension. If slurry operation is used, the slurry will be conducted by means of line 16 along with the products of the reaction into separation zone 18. The latter zone will thus include suitable separation means for recovering the slurry, as for example a simple settling tank, a centrifuge or a filter or suitable combinations of such means. The recovered catalyst will be recycled to the reaction through lines 22 and 36.

It is also possible to operate the process with a liquid catalyst complex in place of the solid supported system or the slurry system described. In such instances, reaction zone 15 will be equipped with suitable agitation means such as a mechanical stirrer. A suitable liquid catalyst complex may comprise aluminum bromide and a halogen such as chlorine or bromine or aluminum bromide and an alkyl halide. The reaction product leaving zone 15 will carry with it some of the liquid complex as a separate phase which will be settled out in zone 18 and recycled to the reaction zone through lines 22 and 36.

The C_7 fraction leaving separation zone 18 by means of line 21 will comprise a mixture of C_7 isomers, from about 40 to 60 percent of which will be methyl hexanes while less than 10 percent will be normal heptane. This mixture is subjected to a selective cracking operation in zone 25 by contacting it with an aluminum halide selected from the group consisting of aluminum chloride and aluminum bromide, at a temperature in the range of from about 150° to about 250° F. The preferred temperature range is from about 160° to about 190° F. Preferably, feed rates of from about 0.1 to about 1.0 v./v./hr. are used.

The products of the selective cracking treatment will be removed from zone 25 by means of line 27 and conducted to a separation zone 30. Butanes separated from the product may be removed overhead by means of line 31 and recycled to isomerization zone 15. The C_5 and C_6 fractions may be removed through line 32. Alternatively, only the C_5 fraction may be removed through line 32 while the C_6 fraction will be removed as a separate side stream by means of line 33 and recycled to the isomerization zone through line 36. The C_7 product will be removed through line 34. Higher boiling materials including C_8 and C_9 hydrocarbons may be sent back to the isomerization zone through lines 35 and 36. If there is a tendency for naphthenes to build up in the system, a portion of these may be removed through line 39.

The present invention is particularly advantageous for improving the C_7 fraction of a paraffin alkylation reaction. In this type of reaction, the higher paraffin hydrocarbon of from 6 to 18 carbon atoms is caused to react with a butane or a pentane, the proportion of the butane or pentane to the higher hydrocarbon being at least 3 mols for each mol of the higher hydrocarbon. From an economic standpoint, there is no advantage in employing a mol ratio greater than about 10 to 1. In conducting a paraffin alkylation reaction, the higher hydrocarbon will enter the reaction zone through line 11 while the butane or pentane will enter through line 13. Preferably, the lower hydrocarbon entering the reaction is isobutane. Reaction conditions in zone 15 are somewhat more severe for a paraffin alkylation reaction than they are for an isomerization reaction. In either type of reaction, it is desirable that the feed be low in aromatic hydrocarbon content. For an isomerization reaction, it is preferred that no more than about 0.1 percent of such material be present, while for a paraffin alkylation reaction the feed should be essentially free of aromatic hydrocarbons. No more than about 0.02 percent of such material should be present in the feed to a paraffin alkylation reaction. Naphthenic hydrocarbons may be tolerated in the feed stock up to about 16 to 20 volume percent in the case of a paraffin alkylation reaction and may be present in somewhat higher concentrations in the case of an isomerization reaction. To remove aromatic hydrocarbons from the feed stock, any conventional technique may be employed, such as solvent extraction, hydrogenation, acid treating and contacting with selective absorbents such as molecular sieve zeolites. The same type of catalysts may be employed in the paraffin alkylation reaction as are described for the isomerization reaction. It is desirable, however, that sufficient aluminum bromide be present so that some of it is dissolved in the reacting hydrocarbons over and above the quantity held by the support. To insure this condition, it is desirable that the feed entering line 11 contain at least 0.1 percent of dissolved aluminum bromide. The aluminum bromide leaving the reaction zone will be recovered in the bottoms products in separation zones 18 and 30 and recycled to the reaction zone along with those bottoms products.

The benefits obtained in the practice of this invention will be appreciated from the results shown in the following example.

EXAMPLE I

The C_7 fraction from a paraffin alkylation reaction was subjected to a series of selective cracking tests with various catalysts. These included aluminum chloride, aluminum bromide, and aluminum bromide on a Porocel support. In each case a portion of the C_7 cut was placed in an agitated reaction zone along with the selected catalyst and agitated for a period of 2 hours at about 165° F. to 175° F. At the end of the reaction period, the products were collected and analyzed. The results obtained are presented in Table I.

Table I

Test	A	B	C	D	E	O
Parts Catalyst Per 100 Parts of Feed.	40 $AlCl_3$	20 $AlCl_3$	20 $AlBr_3$	4 $AlBr_3$+ 50 Support	12 $AlBr_3$+50 Support	Original Feed
Composition of Product, Liquid Vol. Percent:						
iso-C_4	15.3	16.4	12.5	6.7	14.5	0.4
n-C_4	0.1	0.2	1.1		0.3	
iso-C_5	13.0	13.1	12.8	9.3	13.8	0.6
n-C_5	0.6	0.9	1.0	0.2	0.6	
iso-C_6	11.4	11.8	12.9	9.7	12.9	2.8
n-C_6	1.3	1.4	1.7	1.4	1.5	1.1
2,2-DMC_5	12.6	12.0	14.0	13.4	12.1	12.3
2,4-DMC_5	4.2	3.8	3.3	8.6	6.8	18.0
2,2,3-TMC_4	4.1	3.9	5.1	6.3	4.2	5.7
3,3-DMC_5	7.3	7.8	6.0	6.5	7.4	7.6
2,3-DMC_5	2.0	2.5	2.1	3.4	1.8	5.7
2-MC_6	7.9	7.4	6.7	10.4	4.5	27.5
3-MC_6	5.7	6.6	7.9	12.3	4.5	13.3
3-EtC_5	0.4	0.2	0.4	0.2	0.2	0.5
n-C_7	3.9	3.7	4.5	4.6	3.3	3.8
C_8	5.6	5.2	3.5	5.4	5.8	0.3
C_9	4.5	3.4	2.9	1.9	5.7	

Inspection of Table I reveals that in each test where a catalyst was used there was selective cracking of certain of the components of the C_7 fraction. If column A is compared with column O, it will be seen that the concentrations of 2,2-dimethylpentane, 3,3-dimethylpentane, 2,2,3-trimethylbutane and normal heptane remained substantially unchanged. The low quality monomethylhexanes, which constituted more than 40 percent of the original feed, underwent considerable cracking to isobutane, isopentane and isohexane. Thus, the present invention provides a very effective means for converting the mono-methylhexanes to more desirable products while leaving the higher quality heptane isomers essentially unchanged. Although the normal heptane did not crack under the conditions employed, it is present in such low proportions in the C_7 fraction from an isomerization reaction or from a paraffin alkylation reaction that it does not significantly affect the quality of the product.

Comparing columns A and B of the table, it will be seen that essentially the same results were obtained with 20 parts of aluminum chloride per 100 parts of feed as with twice as great a proportion of catalyst to feed. Comparing columns B and C, it will be noted that aluminum bromide has about the same activity as aluminum chloride in the concentration of 20 parts of catalyst per 100 parts of feed. The results in columns D and E show that 4 parts of aluminum bromide on 50 parts of support per 100 parts of feed were not as active as the higher concentration of 12 parts of aluminum bromide per 50 parts of support. On the other hand, 12 parts of aluminum bromide and 50 parts of support were more active than 20 parts of aluminum bromide (column C) in cracking the methylhexanes. This indicates that the support increased the activity of the catalyst. However, it is not desirable to increase the activity of the catalyst too much since this will impair the selectivity of the reaction. Preferably the ratio of aluminum halide to support should not exceed about 50 parts of the former to 100 parts of the latter, by weight. While the support used in the described tests comprised a calcined bauxite, i.e., Porocel, other supports may likewise be used, including silica gel, molybdenum oxide, gamma alumina, activated carbon, and others. Liquid complexes of the aluminum chloride or aluminum bromide with halogen, alkyl halides, hydrocarbons, ethers, alcohols and the like may also be used.

The scope of the invention is to be determined by the claims appended hereto and is not to be limited by the specific examples herein presented.

What is claimed is:

1. A process for obtaining an upgraded heptane fraction which comprises converting paraffinic hydrocarbons in a conversion zone in the presence of aluminum bromide to form C_5–C_7 branched chain hydrocarbons wherein the C_7 fraction contains trimethyl butane, dimethyl pentane, from 40 to 60 percent methyl hexanes and less than 10 percent of normal heptane, segregating said C_7 fraction from said hydrocarbons and subjecting said C_7 fraction to a selective cracking action in the presence of an aluminum halide selected from the class consisting of aluminum chloride and aluminum bromide at a temperature in the range of from about 150° F. to about 250° F. whereby selective cracking of said methyl hexanes to isomers of butane, pentane and hexane is effected, while said trimethyl butane and said dimethyl pentane remain substantially unchanged.

2. Process as defined by claim 1 wherein said hexane isomers are segregated from said selective cracking step and recycled to said conversion zone.

3. A process for upgrading a heptane fraction of a naphtha which comprises isomerizing the said fraction at a temperature in the range of from about 30° to about 140° F. in the presence of an isomerization catalyst, whereby a mixture of isomers is obtained containing dimethyl pentanes, less than 10 percent normal heptane and from about 40 to about 60 percent methylhexanes, and thereafter subjecting said mixture thereby obtained to a selective cracking action in the presence of an aluminum halide selected from the group consisting of aluminum chloride and aluminum bromide at a temperature in the range of from about 150° to about 250° F., whereby selective cracking of said methylhexanes to isobutane, isopentanes and isohexanes is effected.

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