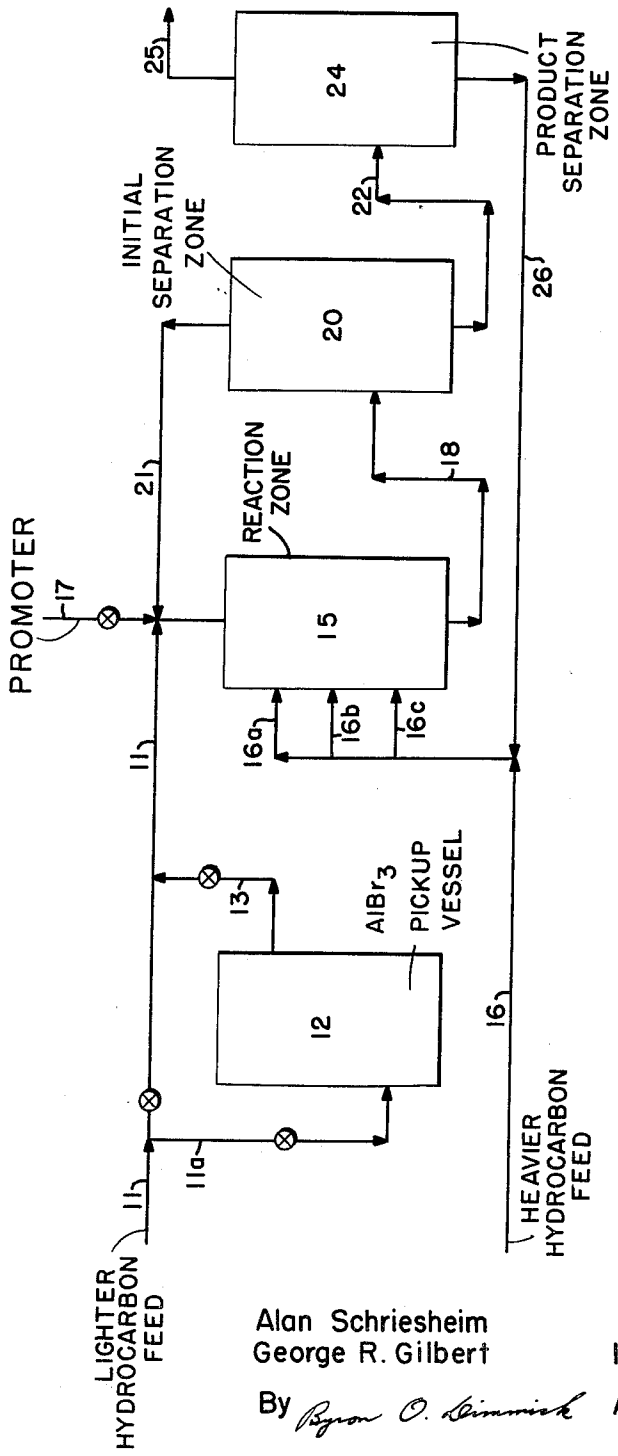
July 17, 1962 A. SCHRIESHEIM ET AL 3,045,056

SUPPORTED CATALYST PARAFFIN ALKYLATION PROCESS

Filed Nov. 3, 1958




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United States Patent Office 3,045,056 Patented July 17, 1962



3,045,056

# SUPPORTED CATALYST PARAFFIN ALKYLATION PROCESS

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Filed Nov. 3, 1958, Ser. No. 771,319
6 Claims. (Cl. 260—683.53)

The present invention relates to the alkylation of paraffin hydrocarbons with other paraffin hydrocarbons. It involves the preparation of branched chain paraffin hydrocarbons boiling in the motor fuel range by the reaction of a butane or a pentane, preferably isobutane, with other paraffin hydrocarbons of 6 or more carbon atoms in a process involving simultaneous cracking, isomerization and alkylation reactions. More specifically, the invention concerns a process wherein a butane or a pentane is reacted with a paraffin hydrocarbon of from 6 to 18 carbon atoms in the presence of aluminum bromide and a promoter support under conditions that favor the production of high yields of branched chain paraffin hydrocarbons of 5 to 7 carbon atoms.

A major problem in petroleum refining is to secure from the hydrocarbon sources available a sufficient quantity of high octane rating hydrocarbons boiling in the motor fuel range to satisfy the demands of modern high compression engines. Processes for producing the high octane components must not be too costly and must have a reasonable degree of versatility. Hertofore a number of processes have been available which use $C_3$ and $C_4$ petroleum fractions from various sources such as natural gasoline plants, distillate recovery plants and various petroleum refinery streams, and which convert those fractions to motor fuel components by polymerization reactions or by alkylation reactions. For example, isobutane can be reacted with butylene in the presence of sulfuric acid to give a branched-chain 8-carbon-atom alkylate. Also butylene can be polymerized to a $C_8$ unsaturated hydrocarbon which upon hydrogenation will give isooctane. These processes have some disadvantages in that they require a number of separate operations and in that they necessitate the use of olefins, which are usually in relatively limited supply.

It has now been found that, by the use of a promoted aluminum bromide catalyst, butanes and/or pentanes can be reacted directly with higher paraffin hydrocarbons to give good yields of $C_5$ to $C_7$ branched chain hydrocarbons of high octane rating, provided certain specific conditions are employed. It has previously been proposed to conduct reactions of this type but yields have been low, reaction rates have been uneconomic and satisfactory product distribution has not been obtained.

In accordance with the present invention, a paraffin hydrocarbon of from 6 to 18 carbon atoms is reacted with a large excess of a butane or a pentane, preferably isobutane, employing as a catalyst $AlBr_3$ supported on or associated with calcined bauxite, at temperatures in the range of from about 30° to about 140° F. and at pressures sufficient to keep the reacting hydrocarbons in the liquid phase. The products of the reaction are saturated branched chain paraffin hydrocarbons predominantly in the $C_5$ to $C_7$ range. The preferred temperature range is from about 50° to about 120° F.



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

The process will be described with particular reference to the use of isobutane as the lighter component. Referring to the drawing in detail, a suitable butane feed stream containing at least initially a major proportion of isobutane is obtained by means of line **11** from a suitable source. A portion of the stream is conducted via line **11***a* through an aluminum bromide pick-up vessel **12** to dissolve aluminum bromide in a portion of the stream that is conducted to the reaction zone. The remainder of the feed stream is combined with the effluent leaving the pick-up vessel via line **13** and is conducted into a reaction zone **15**. The latter zone contains one or more beds of calcined bauxite saturated with aluminum bromide.

A stream of a higher paraffin hydrocarbon, as for example heptane, octane, dodecane or cetane, or of mixtures containing the higher paraffins, is conducted into the reaction zone by means of line **16**. Preferably the stream enters the reaction zone at a plurality of spaced points, **16***a*, **16***b*, etc., so as to insure as high a ratio as possible of isobutane to higher paraffin at any particular point in the reaction zone.

The reaction product leaves the reaction zone through line **18** and is conducted into an initial separation zone **20** wherein light materials, including unreacted isobutane and normal butane, are removed overhead and recycled to the reaction zone by means of line **21**. Hydrogen bromide, if present, will also be recycled via line **21**. The heavier material, including $C_5$ hydrocarbons and higher, is conducted by means of line **22** into a product separation zone **24** wherein $C_5$ to $C_7$ hydrocarbons are removed overhead by means of line **25** while heavier material comprising $C_8$ hydrocarbons and higher as well as any aluminum bromide that has been removed from the reaction zone is recycled to the reaction zone by means of line **26**. If desired, conditions can be adjusted in separation zone **24** to include normal heptane in the heavier material recycled through line **26**, while including the $C_7$ branched chain isomers in overhead line **25**.

In place of isobutane the feed in line **11** may comprise normal butane, in which case no higher hydrocarbon feed stock will be sent initially to the reaction zone but the butane will be recycled through line **18**, zone **20** and line **21** until a considerable amount of the butane has been isomerized to isobutane. The process may then continue in the manner already described, the recycle isobutane being sufficient to make the desired reaction proceed while the fresh butane feed becomes isomerized to isobutane in the reactor.

A number of factors in the process of the present invention are critical to its operation in order that proper distribution of the products may be obtained. For example, at temperatures above about 140° F. considerable cracking occurs and the principal products are propane and lighter materials. Also it has been established that aluminum bromide alone or even in the presence of conventional hydrogen halide promoters such as hydrogen bromide, in the absence of the support, is very much less active than the catalyst system of the present invention. Furthermore in order for the reaction to proceed satis-

factorily it is necessary that sufficient aluminum bromide be present not only to saturate the support under the reaction conditions employed but also to leave at least a small amount dissolved in the reacting hydrocarbons.

A mixed catalyst in which a portion of the aluminum bromide is replaced with aluminum chloride may be used provided that at least some aluminum bromide is present in the reacting hydrocarbons over and above that which is adsorbed on the support.

Although the reaction may proceed in the absence of hydrogen bromide promoter it is preferred that it be used as an auxiliary promoter in addition to the calcined bauxite. A range of from about 0.1 to 8% or more of HBr by weight based on total feed may be used, while from about 0.3 to about 5% is preferred. When hydrogen bromide is employed it is introduced into the reaction zone by means of line **17** and will be recycled to the reaction zone along with unreacted butanes by means of line **21**.

Although the process as described in conjunction with the drawing contemplates downflow of the stream through the catalyst bed, which is preferred, upflow can also be used. Also in place of a fixed bed process, a moving bed of catalyst could be used. Alternatively, a slurry type of operation could be employed wherein a suspension of catalyst is maintained in the reacting hydrocarbons, the slurry being stirred in the reactor with suitable mechanical stirring means or recirculated through the reactor by pumping means. Where slurry operation is used, the slurry is removed from the reactor at the end of the reaction period, in the case of batch operation, or as a fraction of the circulating stream in the case of continuous operation, and sent to suitable separation equipment to separate the catalyst from the hydrocarbons. The separation equipment may comprise a simple settling tank, a centrifuge, or a filter, for example, or suitable combinations of such means.

It is preferred that the minimum mol ratio of isobutane and/or isopentane to higher paraffin be about 3 to 1 but should preferably be no higher than about 12 to 1. If sufficient iso-$C_4$ is not present in the reaction zone to effect alkylation of the materials obtained when a higher paraffin or other higher product of the reaction is cracked by the catalyst, catalyst sludging will result. The feed stock must be essentially free of aromatic hydrocarbons and not more than about 0.02% of such material should be present. An added advantage of the catalysts of the present invention is that naphthene hydrocarbons may be tolerated in the feed stock up to about 20 volume percent. With increased naphthene content the reaction severity must be increased somewhat as compared to a reaction in the absence of naphthenes. This may be accomplished by raising the temperature and/or lowering the feed rate, for example.

Feed rates may vary from about 0.3 to about 2 v./hr./v. (liquid volume of total feed per hour per volume of total catalyst plus support) the higher feed rates being preferred when little or no naphthenes are present.

To remove aromatics from the feed stock conventional techniques may be employed such as solvent extraction, hydrogenation, acid treating and the like, as well as treatment with selective adsorbents such as molecular sieve zeolites. It is not necessary that the higher hydrocarbons used be individual hydrocarbons such as heptane or octane or cetane, for example, but mixtures may be used, such as a petroleum fraction containing paraffinic hydrocarbons in the range of 6 to 18 carbon atoms. Although, as stated, hexane is one of the higher hydrocarbons that may be used, it is preferred to employ heptane or higher. Essentially the same product distribution is obtained with hexane as with heptane but the reaction rate is lower by a factor of about 3. Other sources of the higher paraffin hydrocarbons for the reaction include light virgin naphthas, and paraffin raffinates from the extraction of hydroformed petroleum fractions.

A calcined bauxite that may be employed as the catalyst promoter in the present invention can be obtained commercially under the trade name "Porocel." Before the bauxite is used it should be dehydrated. A suitable pretreatment for this purpose involves heating for from about 3 to 5 hours at 1100° to 1200° F.

At the start of the process the calcined bauxite may be saturated with aluminum bromide and then placed in the reaction zone, or, alternatively, the bauxite alone 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.

The following examples serve to illustrate the practice of the present invention.

EXAMPLE 1

Comparative tests were made in which in each instance a mixture of 160 cc. of isobutane and 40 cc. of a normal heptane feed (containing 95% n-$C_7$ and 5% of methylcyclohexane) was stirred for 3 hours at 72° F. with one of the catalyst systems identified in Table I. At the end of each run the yield of products was determined, the results also being presented in Table I.

TABLE I

| | Test 1 | Test 2 | Test 3 | Test 4 |
|---|---|---|---|---|
| Catalyst, grams: | | | | |
| $AlBr_3$ | 23.6 | 23.6 | 23.6 | 23.6 |
| Porocel | ------ | ------ | 47.2 | 47.2 |
| HBr | ------ | 24.0 | ------ | 17.0 |
| Analysis of $C_5$+ Product, Weight percent: | | | | |
| iso-$C_5$ | 0.4 | 0.5 | 22.7 | 33.5 |
| n-$C_5$ | 0.3 | 3.6 | 2.9 | 5.9 |
| Total $C_5$ | 0.7 | 4.1 | 25.6 | 39.4 |
| iso-$C_6$ | 0.5 | 0.3 | 15.1 | 23.5 |
| n-$C_6$ | 0 | 0 | 0.6 | 1.1 |
| Total $C_6$ | 0.5 | 0.3 | 15.7 | 24.6 |
| iso-$C_7$ | 46.2 | 48.3 | 56.5 | 32.5 |
| n-$C_7$ | 52.6 | 47.3 | 2.2 | 3.5 |
| Total $C_7$ | 98.8 | 95.6 | 58.7 | 36.0 |

It will be seen from the results of these comparative tests that aluminum bromide alone, or even in the presence of hydrogen bromide, was not effective in producing the desired reaction. In both of these instances the major proportion of the reaction products comprised $C_7$ hydrocarbons. The aluminum bromide merely served as an isomerization catalyst. On the other hand, in the tests in which aluminum bromide and Porocel either alone or in conjunction with hydrogen bromide were employed as the catalyst, considerable yields of $C_5$ and $C_6$ isomers were obtained.

EXAMPLE 2

In a manner similar to that employed in Example 1 comparative tests were made with a number of other supports or promoters in addition to Porocel. These included $Fe_2O_3$ and $FeCl_3$ which are known to have high activity for promoting isomerization reactions. The results obtained are shown in Table II.

TABLE II

| | Test 3 | Test 5 | Test 6 | Test 7 | Test 8 |
|---|---|---|---|---|---|
| Catalyst: $AlBr_3$, grams | 23.6 | 23.6 | 23.6 | 23.6 | 23.6 |
| Promoter | Porocel | $Fe_2O_3$ | $FeCl_3$ | (1) | $Al_2O_3$ |
| Grams, promoter | 47.2 | 47.2 | 11.8 | 47.2 | 47.2 |
| Analysis of $C_5$+ Product, Weight percent: | | | | | |
| iso-$C_5$ | 22.7 | 1.2 | 1.5 | 1.7 | 1.7 |
| n-$C_5$ | 2.9 | 0.3 | 0.3 | 0.4 | 0.1 |
| Total $C_5$ | 25.6 | 1.5 | 1.8 | 2.1 | 1.8 |
| iso-$C_6$ | 15.1 | 1.8 | 0.8 | 1.1 | 0.2 |
| n-$C_6$ | 0.6 | 0.1 | 0 | 0 | 0.2 |
| Total $C_6$ | 15.7 | 1.9 | 0.8 | 1.1 | 0.4 |
| iso-$C_7$ | 56.5 | 93.2 | 62.9 | 46.1 | 65.0 |
| n-$C_7$ | 2.2 | 3.4 | 34.5 | 50.7 | 22.8 |
| Total $C_7$ | 58.7 | 96.6 | 97.4 | 96.8 | 97.8 |

[1] $Al_2O_3$—90%, $Fe_2O_3$—10%.

It will be seen that neither alumina, ferric chloride nor $Fe_2O_3$ was effective in promoting the desired reaction. The alumina used in the above tests was found to be of the eta form. In each case the principal product comprised $C_7$ hydrocarbons although some isomerization of the latter had occurred.

EXAMPLE 3

In a similar manner, another series of tests were run at temperatures of 72 to 75° F. with the same feed composition and the same feed-to-catalyst support ratio as in Example 1 (200 cc. total feed to 47 grams of Porocel) using various metal halides other than aluminum bromide, in the ratio of 24 grams of halide to 47 grams of Porocel. The metal halides used were aluminum chloride, aluminum iodide, aluminum fluoride, bismuth trichloride, ferric chloride, tin tetrachloride and titanium tetrachloride. The concentration of aluminum fluoride on Porocel was slightly lower than with the other metal halides. None of these metal halides was found to have any apparent activity for the desired reaction under the conditions employed.

EXAMPLE 4

In another group of tests the effect of naphthenes on the reaction was determined. Using the catalyst system of Test 3 of Example 1 and the same reacting hydrocarbon mixture as in that test, but varying the percentage of naphthenes, it was found that as the concentration of methylcyclohexane in the normal heptane feed was increased from 1 volume percent to 20 volume percent the relative rate of conversion of heptane to $C_5$ and $C_6$ branched chain hydrocarbons was reduced by a factor of 3. It was also found that the inhibiting effect of naphthenes on the reaction can be overcome to some extent by raising the temperature. Thus, raising the reaction temperature from 100° F. to 115° F. when 8% of methyl cyclohexane was present brought about a doubling of the reaction rate, as measured by the weight percent of $C_7$ hydrocarbons in the $C_5$+ product after various reaction times. This is shown in Table III.

TABLE III

*Effect of Temperature on Reaction Rate in Presence of Naphthenes*

| Reaction Time, Hours | Weight percent $C_7$ in $C_5$+Product | |
|---|---|---|
| | 100° F. | 115° F. |
| 1 | 95 | 77.4 |
| 2 | 79 | 51.5 |
| 3 | 63 | 26.6 |
| 4 | 51.6 | 28 |



EXAMPLE 5

In another series of tests conducted in the same manner as described in Example 1, the effect of the ratio of isobutane to heptane on the yield of $C_5$ to $C_7$ branched chain hydrocarbons was determined. The catalyst in these tests consisted of 20 grams of aluminum bromide, 39 grams of aluminum chloride and 119 grams of Porocel. The reaction temperature was 100° F., the pressure was 300 p.s.i.g. and each reaction consumed 2 hours, the normal heptane being added gradually during the entire reaction period. The results obtained are given in Table IV and show that the yield of $C_5$+ hydrocarbons increased as the ratio of isobutane to heptane was increased over a mol ratio range of about 3 to 1 to about 10 to 1.

TABLE IV

*Effect of Isobutane to Heptane Ratio on Yield*

| Feed Composition: | | | |
|---|---|---|---|
| Grams, Isobutane | 285 | 285 | 285 |
| Grams, n-Heptane | 170 | 85 | 33 |
| Yields, Wt. percent on Heptane Feed: | | | |
| $C_3$ and less | 6 | 10 | 36 |
| $C_5$+ | 122 | 153 | 170 |
| Analysis of $C_5$+Product, Weight percent: | | | |
| iso-$C_5$ | 33.5 | 42.1 | 36.4 |
| n-$C_5$ | 6.7 | 6.8 | 7.6 |
| Total $C_5$ | 40.2 | 48.9 | 44.0 |
| iso-$C_6$ | 21.1 | 24.2 | 12.7 |
| n-$C_6$ | 1.4 | 1.4 | 0.6 |
| Total $C_6$ | 22.5 | 25.6 | 13.3 |
| iso-$C_7$ | 23.9 | 22.1 | 30.2 |
| n-$C_7$ | 9.1 | 1.1 | 12.5 |
| Total $C_7$ | 33.0 | 23.2 | 42.7 |

EXAMPLE 6

Employing the same catalyst mixture as was used in Example 5, tests were made in which normal octane, normal cetane and normal octadecane were substituted for the normal heptane. The reaction temperature was 120° F. in the case of octadecane and 100° F. in the other runs. The reaction pressure in each instance was 300 p.s.i.g. and 2-hour reaction times were used. It will be seen from the data in Table V that the product distribution was essentially the same regardless of the higher paraffin used.

TABLE V

*Comparison of Reactions With Hydrocarbons of 7 to 18 Carbon Atoms*

| Feed Composition | Heptane | Octane | Cetane | Octadecane |
|---|---|---|---|---|
| Grams, Isobutane | 285 | 285 | 285 | 342 |
| Grams, Heavier Paraffin | 85 | 87.5 | 47.5 | 48.4 |
| Yields, Wt. Percent on Heavier Paraffin: | | | | |
| $C_3$ and less | 10 | 9 | 6 | 23 |
| $C_5$+ | 153 | 155 | 188 | 190 |
| Analysis of $C_5$+ Product, Weight Percent: | | | | |
| iso-$C_5$ | 42.1 | 48.0 | 35.7 | 42.4 |
| n-$C_5$ | 6.8 | 8.6 | 6.3 | 9.2 |
| Total $C_5$ | 48.9 | 56.6 | 42.0 | 51.6 |
| iso-$C_6$ | 24.2 | 24.2 | 21.1 | 25.5 |
| n-$C_6$ | 1.4 | 1.4 | 1.3 | 1.8 |
| Total $C_6$ | 25.6 | 25.6 | 22.4 | 27.3 |
| iso-$C_7$ | 22.1 | 9.7 | 9.6 | 7.9 |
| n-$C_7$ | 1.1 | 0.5 | 0.5 | |
| Total $C_7$ | 23.2 | 10.2 | 10.1 | 7.9 |
| $C_8$+ | 2.3 | 7.6 | 25.5 | 13.2 |

EXAMPLE 7

A catalyst composition comprising Porocel and aluminum bromide in a 1 to 1 weight ratio of $AlBr_3$ to support was tested in a continuous pilot unit consisting of a

jacketed reactor provided with a mechanical stirrer and with a settling chamber to permit slurry operation. Reaction conditions were 100° F. and 150 p.s.i.g. pressure. A feed mixture of normal heptane and isobutane which gave about 70 volume percent of isobutane in the reactor was passed through the reactor at a space velocity of about 0.05 volume of heptane per hour per volume of the reactor. As the catalyst occupied about 25 percent of the reactor volume this feed rate corresponded to about 0.2 v./hr./v. of catalyst. Aluminum bromide was continuously added to the reaction zone as a solution in the isobutane in sufficient quantity to constitute a 5 to 10 weight percent solution based on total feed. Hydrogen bromide was also added at the rate of 1 to 5 weight percent based on feed. The total liquid product from the reactor was scrubbed with 20 percent caustic to remove aluminum bromide and HBr, then dried, debutanized and analyzed. Continuous catalyst activity was observed for 150 to 200 hours operation, with good yields, of the order of 135 to 145 volume percent of $C_5+$ hydrocarbons, based on the normal heptane. A similar continuous run with cetane as the higher paraffin fed, using the same reaction conditions, the same catalyst mixture and the same ratios of isobutane to higher paraffin, gave yields of the order of 250 to 260 volume percent of $C_5+$ hydrocarbons, based on the cetane. In both runs, i.e. with heptane and with cetane, the ratio of $C_5$ to $C_6$ hydrocarbons was about 2 to 1.

Other studies of continuous operation established that in order to maintain catalyst activity it is necessary to have present in the reaction zone sufficient aluminum bromide to furnish aluminum bromide in solution in the reacting hydrocarbons over and above the quantity required to satisfy the total adsorption capacity of the calcined bauxite. To ensure this in a continuous operation it is preferred that sufficient aluminum bromide be dissolved in at least one of the entering streams of reacting hydrocarbons so that at least 0.05 weight percent of aluminum bromide will be present in the products leaving the reaction zone.

Certain modifications of the process outlined hereinbefore will occur to those skilled in the art. Such modifications are contemplated within the scope of the present invention. For example, if the yield of $C_5$ hydrocarbons is larger in proportion to the $C_6$ hydrocarbons than is desired, the product may be distilled to separate a $C_5$ cut which may then be used in a conventional alkylation step with an olefin such as ethylene, propylene or a butene, employing the usual alkylation catalysts such as sulfuric acid, phosphoric acid, hydrogen fluoride, or an aluminum halide. Alternatively, the $C_5$ cut can be sent to a second reaction zone of the type herein described for reaction with higher normal paraffin hydrocarbons.

It is to be understood that this invention is not to be limited to the specific embodiments and examples herein described and presented but that its scope is to be determined solely by the claims appended hereto.

What is claimed is:

1. A liquid phase process for the preparation of high octane naphtha components consisting largely of branched chain paraffin hydrocarbons of 5 to 7 carbon atoms which comprises reacting a minor proportion of a straight chain paraffin hydrocarbon of from 6 to 18 carbon atoms with a major proportion of a lighter hydrocarbon selected from the group consisting of butanes and pentanes, at temperatures no higher than about 140° F., in a reaction zone in the presence of a catalyst comprising aluminum bromide and calcined bauxite, supplying to the reaction zone sufficient aluminum bromide to furnish at least 0.05 weight percent of aluminum bromide in solution in the reacting hydrocarbons over and above the quantity required to satisfy the total adsorption capacity of the calcined bauxite.

2. Process as defined by claim 1 wherein reacting hydrocarbons are continuously conducted into said reaction zone and reaction products are continuously removed from said reaction zone and wherein sufficient aluminum bromide is dissolved in at least one entering stream of reacting hydrocarbons so that at least 0.05 weight percent of aluminum bromide is present in the products removed from said reaction zone.

3. Process as defined by claim 1 wherein from about 0.1 to about 8 percent of hydrogen bromide, based on the reacting hydrocarbons, is present in the reaction zone.

4. Process as defined by claim 1 wherein the mol ratio of said lighter hydrocarbon selected from the group consisting of butanes and pentanes to said hydrocarbon of from 6 to 18 carbon atoms in the reaction zone is in the range of from about 3 to 1 to about 12 to 1.

5. Process as defined by claim 1 wherein naphthenic hydrocarbons are present in said reaction zone.

6. A process for the preparation of high octane naphtha components consisting largely of branched chain paraffin hydrocarbons of 5 to 7 carbon atoms which comprises reacting a straight chain paraffin hydrocarbon of from 6 to 18 carbon atoms with a lighter hydrocarbon selected from the group consisting of butanes and pentanes, wherein the mol ratio of said lighter hydrocarbons to said straight chain paraffin hydrocarbon is in the range of from about 3:1 to about 12:1, at temperatures in the range of about 50 to 120° F., in a reaction zone in the presence of a catalyst comprising aluminum bromide and calcined bauxite, supplying to the reaction zone sufficient aluminum bromide to furnish at least 0.05 weight percent of aluminum bromide in solution in the reacting hydrocarbons over and above the quantity required to satisfy the total adsorption capacity of the calcined bauxite.

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