

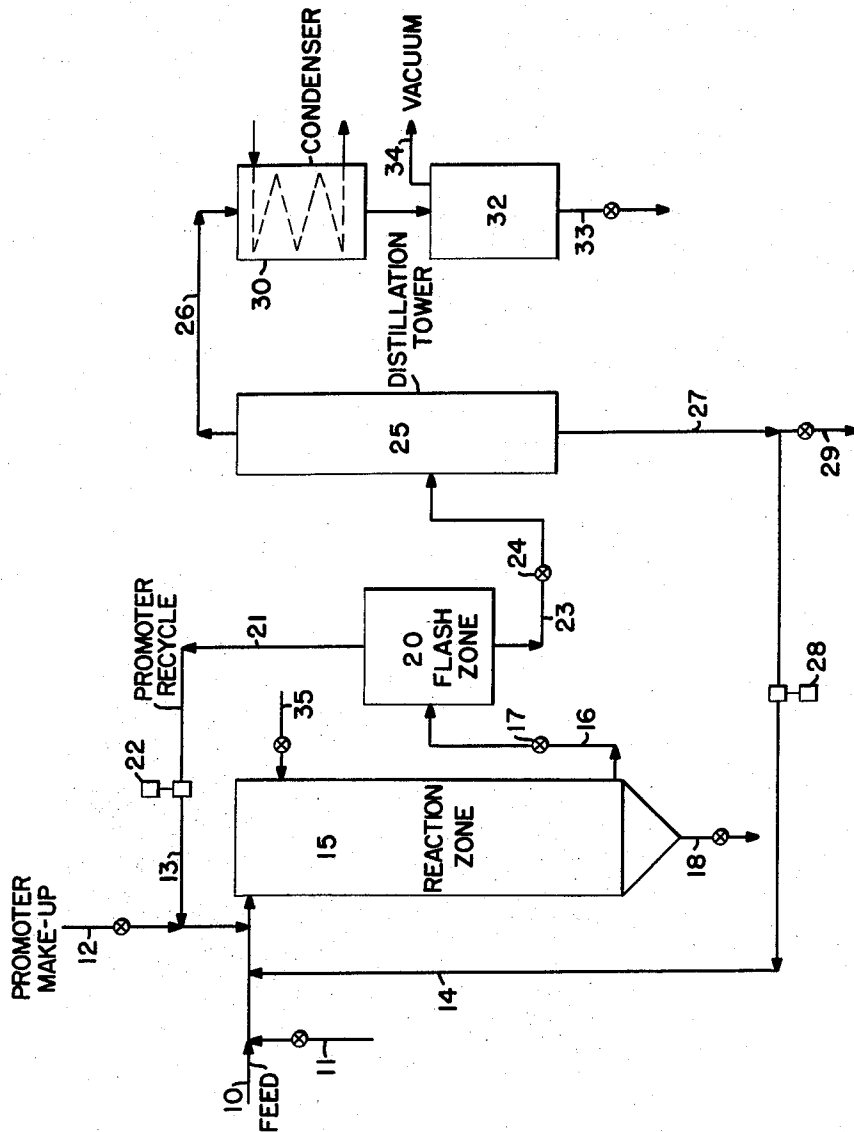
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PARAFFIN HYDROCARBON REACTIONS WITH ALUMINUM BROMIDE

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PARAFFIN HYDROCARBON REACTIONS WITH ALUMINUM BROMIDE

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This invention concerns improvement in the catalytic treatment of paraffin hydrocarbons. More particularly, the invention relates to improvements in the liquid phase conversion of normal or slightly branched chain hydrocarbons to commercially valuable, more highly branched isomers, employing aluminum bromide as the catalyst.

It is well known that the more highly branched isomers of the paraffinic hydrocarbons occurring in petroleum gasoline fractions are more valuable than the corresponding slightly branched or straight chain hydrocarbons because of their higher octane ratings. The demand for motor fuels of greater octane number has increased markedly as the automotive industry has provided gasoline engines with increasingly higher compression ratios to attain greater efficiency. One of the economically important ways in which the increased demands for high octane fuels can be met is through the isomerization of the light naphtha components of such fuels.

It may be generally stated that the isoparaffinic and branched chain paraffin hydrocarbons are of greater commercial value to the petroleum industry than the corresponding straight chain hydrocarbons. Thus, for example, 2,2-dimethylbutane has a higher octane rating than the isomeric normal hexane. Isobutane is more valuable than normal butane since the former can be used as the basis for the preparation of 8-carbon-atom branched chain hydrocarbons by alkylation with butylene.

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. Insofar as the isomerization of light naphthas is concerned, the lower the temperature of isomerization, within limits, the more favorable is the equilibrium for converting straight chain paraffin hydrocarbons into isomers of high octane rating. Aluminum bromide has been found to be more active than aluminum chloride at lower isomerization temperatures, e.g. in the range of about 50 to about 120° F.

Aluminum bromide is also known to be an active catalyst for the alkylation of isoparaffinic hydrocarbons with olefinic hydrocarbons to produce branched chain hydrocarbons that are useful motor fuel components. The same catalyst, with suitable promoters, can be employed to effect the liquid phase reaction of paraffin hydrocarbons of from 6 to 18 carbon atoms with isobutane or isopentane at temperatures of about 30° F. to about 120° F. to give products predominating in C₅ to C₇ branched chain hydrocarbons of high octane rating; in a process involving simultaneous cracking, isomerization and alkylation reactions.

One disadvantage in the use of aluminum bromide in reactions of the types outlined above is that it is ap-

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preciably soluble in the products of those reactions. Because of this, a practical means must be available for recovering the aluminum bromide from the products so that it can be reused in those reactions. The recovery method employed must be one that will not cause degradation of the reaction products or of the catalyst.

It is one object of the present invention to provide means for effectively recovering aluminum bromide from the products of isomerization and alkylation reactions so that it can be reused as a catalyst and thus make the processes economic.

It is another object of this invention to provide optimum conditions for isomerization and alkylation reactions so as to obtain maximum yields of the most desired isomers while minimizing degradation of the products and of the recovered catalyst.

In accordance with the present invention the products of a reaction wherein paraffinic hydrocarbons are contacted with aluminum bromide are subjected to distillation under vacuum at temperatures no higher than 120° F., and preferably no higher than the temperatures used in the reaction zone. The aluminum bromide remains dissolved in the bottoms and is recycled with the bottoms to the reaction zone. If a promoter has been employed in the reaction, at least the major portion of the promoter is separated from the reaction product prior to the distillation step. Thus, a hydrocarbon feed comprising normal paraffin hydrocarbons of from 4 to 7 carbon atoms may be contacted with aluminum bromide in a suitable reactor in the presence of a hydrogen halide promoter at temperatures in the range of from 30° to 120° F. and under pressures that are preferably sufficiently high to maintain the reactants in the liquid phase. The product, which will contain some dissolved aluminum bromide, is removed from the reactor through a pressure reduction valve and conducted to a flash zone maintained at about atmospheric pressure and at a temperature no higher than about 150° F. In the flash zone the gaseous hydrogen halide promoter, along with a very small percentage of light material, is flashed from the product to be recycled into the feed stream entering the reactor. The products remain in the flash zone only a relatively short time. The bottoms from the flash zone are sent to a distillation tower wherein distillation is effected at a pressure less than atmospheric, e.g. 50 to 200 mm., and at a temperature no higher than 120° F. and preferably no higher than that used in the reaction zone. From about 50 to 80% of the product will be distilled overhead. The bottoms from the distillation tower, which will contain dissolved aluminum bromide, are recycled to the feed stream entering the reactor and thus will effect return of the catalyst to the reactor. By conducting the distillation at a temperature no higher than the temperature used in the reaction zone, catalyst deactivation and product degradation are prevented. Higher temperatures in the distillation zone would result in undesirable cracking of the isomerized product and consequent deactivation of the aluminum bromide catalyst. Furthermore, higher temperatures are less favorable for high concentrations of the highly branched isomers and would, therefore, result in some "back" isomerization of the product.

In the case of isomerization, to prevent cracking and disproportionation during the reaction it is desirable to employ a cracking inhibitor. For a feed comprising C₅ and C₆ paraffin hydrocarbons, from about 10 to 20% of naphthenic hydrocarbons, such as methylcyclopentane or cyclohexane, should be present in the feed. For C₇ hydrocarbons, the amount of naphthenes should be somewhat higher. It is also necessary that the feed contain no more than a maximum of about 0.1% of aromatics. For this reason, it may be necessary to pretreat the feed

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to remove aromatics. For example, the feed may be treated with chlorosulfonic acid or with liquid sulfur trioxide or the feed may be solvent extracted or subjected to extractive distillation with such materials as butyrolactone. If the feed is a C_5 - C_6 naphtha containing cyclohexane and methyl cyclopentane, benzene can be removed by low pressure distillation. At atmospheric pressure benzene, cyclohexane and methyl cyclopentane form an azeotrope, but at reduced pressures, e.g. 50 to 400 mm. of mercury, methyl cyclopentane does not enter this azeotrope and can be taken overhead in an essentially benzene-free feed stock that still contains sufficient naphthenes for cracking inhibition, while benzene and cyclohexane remain in the bottoms.

The hydrogen halide activators, of which hydrogen bromide is preferred, are desirable not only to promote the isomerization but also to prevent deactivation of the catalyst. Thus, an important factor in isomerization is that the reaction zone is kept under a positive pressure of hydrogen bromide.

In the case of paraffin alkylation reactions wherein a paraffin hydrocarbon of from 6 to 18 carbon atoms is contacted with a molar excess of isobutane and/or isopentane in the presence of aluminum bromide, promoters are necessary, as aluminum bromide alone has been found to be relatively ineffective for catalyzing that reaction. A partially dehydrated calcined bauxite known commercially as Porocel is one promoter that is effective, and its action is further enhanced by the presence of hydrogen bromide. Paraffin alkylation reactions are run under conditions that are somewhat more severe than those existing in isomerization reactions, since some cracking must be permitted to take place. Hence the tolerance for naphthene hydrocarbons is not as great, and the catalyst must be active enough to effect the desired reaction even though up to 15 or 18 percent naphthenes may be present. Aromatics content must be considerably lower, preferably no more than 0.01 percent. Recovery of aluminum bromide catalyst from such reactions is effected in the same manner as for isomerization reactions, in accordance with the present invention. The solid promoter will remain behind in the reactor, while the hydrogen bromide is removed in the flash zone; thus the products of the reaction will be separated from the promoters prior to the vacuum distillation step.

The features of this invention will be more fully appreciated when reference is made to the accompanying drawing which illustrates schematically a suitable arrangement of apparatus for conducting a process for isomerizing paraffin hydrocarbons.

Referring to the drawing, a feed comprising hydrocarbons to be isomerized is mixed in line 10 with a recycle stream comprising aluminum bromide from line 14 and passed into reaction zone 15. The feed stream may comprise a naphtha cut consisting principally of C_5 and C_6 paraffin hydrocarbons along with 10 to 15 percent naphthenes, for example. The concentration of aluminum bromide in the hydrocarbons entering reaction zone 15 is in the range of about 0.3 to 5% by weight, preferably 0.5 to 2% by weight. It is preferred for most efficient operation that the reaction zone contain a bed of a suitable support material, such as alumina, silica, bauxite or the like. A particularly effective support material is a partially dehydrated calcined bauxite known commercially as Porocel.

After equilibrium has been established, the Porocel should contain of the order of 5 to 8 wt. percent of adsorbed aluminum bromide. In addition the hydrocarbons in contact with the Porocel in the reaction zone 15 contain 0.3 to 5 wt. percent, preferably 0.5 to 2 wt. percent, of dissolved aluminum bromide. Aluminum bromide is taken up by the Porocel until a maximum of about 8 wt. percent of aluminum bromide is adsorbed. Initially the aluminum bromide is introduced into the

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system through line 11, but after the process is underway the major portion of the aluminum bromide is introduced through recycle line 14 while only make-up aluminum bromide will enter through line 11. The amount of this make-up aluminum bromide will be in the order of 0.05 to 0.3 wt. percent, based on fresh hydrocarbon feed. Excellent control of the amount of aluminum bromide added can be effected by passing a portion of the feed stream through a bed of aluminum bromide and diluting the saturated stream with the remainder of the feed stream. By blending naphthenes with the portion of the feed that dissolves the aluminum bromide, any degradation that might occur by contact of paraffin hydrocarbons with a high concentration of aluminum bromide will be suppressed.

Also introduced with the feed is an amount of hydrogen halide promoter sufficient to maintain a positive pressure of hydrogen halide of from 5 to 100 p.s.i.g. in the reaction zone. Initially, this promoter is introduced through line 12. After the process is underway, the major portion of the halide will be introduced through recycle line 13 while make-up promoter will enter through line 12.

The feed is conducted through the reaction zone at rates of the order of 0.1 to 2 v./v./hr. For isomerization, reaction temperatures of from about 50° to about 120° F. are employed in reaction zone 15. Preferably, the reaction temperature is in the range of from about 60° to 80° F. for maximum production of highly branched isomers. Conditions in the reaction zone are preferably such that no sludge formation occurs. However, a relatively small amount of sludge may be formed in the reaction zone and this may be removed through valved line 18.

The reaction products together with dissolved aluminum bromide leave the reaction zone through line 16 and are flashed through pressure reduction valve 17 into a flash zone 20 which is maintained at about atmospheric pressure and at a temperature no greater than 150° F. In the flash zone, from 5 to 10% of the product will be removed overhead through line 21 along with the gaseous hydrogen halide promoter. The residence time in the flash zone should be short, i.e., not more than one to two minutes, so that cracking and disproportionation will be negligible at this higher temperature. The stream in line 21 is pressured to the pressure level existing in the reaction by means of compressor 22 and recycled to the reaction zone through line 13.

The bottoms from the flash zone 20 pass through line 23 and pressure reduction valve 24 into a distillation tower 25 which is run at a pressure less than atmospheric, preferably a pressure of about 50 to 200 mm. of mercury. From 50 to 80% of the product is distilled overhead at a temperature no greater than 120° F. in the distillation tower and is conducted by means of line 26 through condenser 30 into receiving vessel 32. Conveniently, the vacuum for the distillation is applied to vessel 32 through line 34. The desired isomerization product is obtained from the receiving vessel through line 33. Unconverted normal paraffins may be recovered from the product and sent back through the reactor via feed line 10 or via line 35.

The bottoms in the distillation tower 25 will contain the aluminum bromide that has been carried out of the reaction zone along with the reaction products. These bottoms are recycled through line 27, pump 28 and recycle line 14 to enter the reaction zone along with fresh feed in line 10. If it is found that there is a tendency toward an undesirable build-up of naphthenes or of other materials that may tend to impair the reaction if present, a portion of the recycle stream may be bled off through line 29 to prevent such build-up.

A somewhat similar procedure may be employed for aluminum bromide recovery in a paraffin alkylation reaction, as for example in the reaction of isobutane with

normal heptane under conditions favoring simultaneous cracking, isomerization and alkylation reactions wherein a net consumption of isobutane occurs and the products of the reaction predominate in isomers of C₅ to C₇ paraffin hydrocarbons. Conditions are somewhat more severe than for isomerization but not severe enough to cause undesired cracking. One way to increase severity is to employ lower feed rates. A high proportion of isobutane to normal heptane, e.g. 3 to 1 volume ratio, is employed in order to effect the desired alkylation reactions and to prevent catalyst sludging.

To conduct a paraffin alkylation reaction with the system shown in the drawing, feed line 10 is employed for the isobutane feed, feed line 11 for isobutane containing dissolved aluminum bromide make-up, and feed line 35 for the higher isoparaffin such as n-heptane. Separation of hydrogen halide promoter and recovery of dissolved aluminum bromide from the product are effected in the same manner as previously described.

As a specific example of a paraffin alkylation reaction, a mixture of 160 cc. of isobutane, 38 cc. of normal heptane and 2 cc. of methyl cyclohexane contacted with 24 grams of AlBr₃, 47 grams of Porocel and 17 grams of hydrogen bromide for 3 hours at 72° F. gave a product in which the C₅+ fraction consisted of 33.5% isopentane, 6% normal pentane, 23.5% isohexanes, 1% normal hexane, 32.5% isohexanes and 3.5% normal heptane.

The following example illustrates some of the benefits to be derived from this invention. A mixture of 25 parts of normal hexane, 12.5 parts of aluminum bromide and 10 parts of silica gel (all parts by weight) was stirred for one hour at room temperature in a suitable reaction vessel. Vacuum was then applied to the vessel through a cold trap until ½ of the volume of hydrocarbon in the vessel had distilled into the cold trap. A volume of normal hexane equal to the volume of hydrocarbon removed was added to the reactor and the reaction continued for another hour. The results for four such cycles of operation are given in Table I.

Table I

Cycle	Percent Isomerization	Percent Cracking	22 DMB ¹	2 MP+23 DMB	3 MP ²	n-C ₆
1-----	49.9	0	11.2	31.6	7.1	50.0
2-----	69.8	0	25.0	34.4	10.4	30.2
3-----	63.8	0	22.4	32.3	9.1	36.4
4-----	58.2	0	18.4	30.6	9.2	41.8

¹ Dimethyl butane.

² Methyl pentane.

The data in Table I show that the catalyst remained active through several cycles of product removal.

It is to be understood that this invention is not to be limited to the specific embodiments described herein.

What is claimed is:

1. In the catalytic treatment of paraffinic hydrocarbons in the presence of aluminum bromide catalyst and a promoter at temperatures of up to about 120° F. in a reaction zone, wherein the products of the reaction comprise principally branched chain paraffinic hydrocarbons

of from 4 to 7 carbon atoms, and including the step of removing from the reaction zone hydrocarbon products containing dissolved aluminum bromide, the improvement which comprises the steps of separating the products of the reaction from at least the major portion of the promoter and thereafter subjecting the products to vacuum distillation in a distillation zone at temperatures no higher than 120° F. and recycling to the reaction zone a bottoms product containing dissolved AlBr₃, whereby recovery and re-use of catalyst may be effected without catalyst deactivation and without product degradation.

2. In a process for the formation of highly branched paraffinic hydrocarbon isomers of from 4 to 7 carbon atoms wherein paraffinic hydrocarbons are contacted with aluminum bromide in a reaction zone at temperatures of up to 120° F. in the presence of added hydrogen halide promoter and wherein the products of the reaction contain dissolved aluminum bromide, the improved method for recovering aluminum bromide catalyst from the reaction products which comprises conducting the reaction products to a flash zone maintained at about atmospheric pressure and at a temperature no greater than 150° F., removing hydrogen halide from said products in said flash zone while maintaining said products in said flash zone during a relatively short residence time, conducting the products to a distillation tower maintained at a pressure less than atmospheric, distilling isomerization products overhead at said reduced pressure and at a temperature no higher than 120° F. and recycling to said reaction zone a bottoms product containing aluminum bromide.

3. A process for the isomerization of paraffinic hydrocarbons of from 4 to 7 carbon atoms to more highly branched isomers which comprises contacting said hydrocarbons with aluminum bromide in a reaction zone at temperatures of up to 120° F. in the presence of added hydrogen halide promoter at pressures of from 5 to 100 p.s.i.g., conducting the reaction products to a flash zone maintained at about atmospheric pressure and at a temperature no greater than 150° F., removing hydrogen halide from said products in said flash zone while maintaining said products in said flash zone during a relatively short residence time, conducting the products to a distillation tower maintained at a pressure less than atmospheric, distilling isomerization products overhead at said reduced pressure and at a temperature no higher than 120° F. and recycling to said reaction zone a bottoms product containing aluminum bromide.

4. Process as defined by claim 3 wherein said hydrocarbons in said reaction zone include from about 10 to about 20 percent of naphthenic hydrocarbons.

5. Process as defined by claim 3 wherein said hydrogen halide comprises hydrogen bromide.

6. Process as defined by claim 3 wherein said pressure less than atmospheric in said distillation zone is in the range of about 50 to 200 millimeters of mercury.

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