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CONVERSION OF NAPHTHENE HYDROCARBONS

Filed May 30, 1942

2 Sheets-Sheet 1

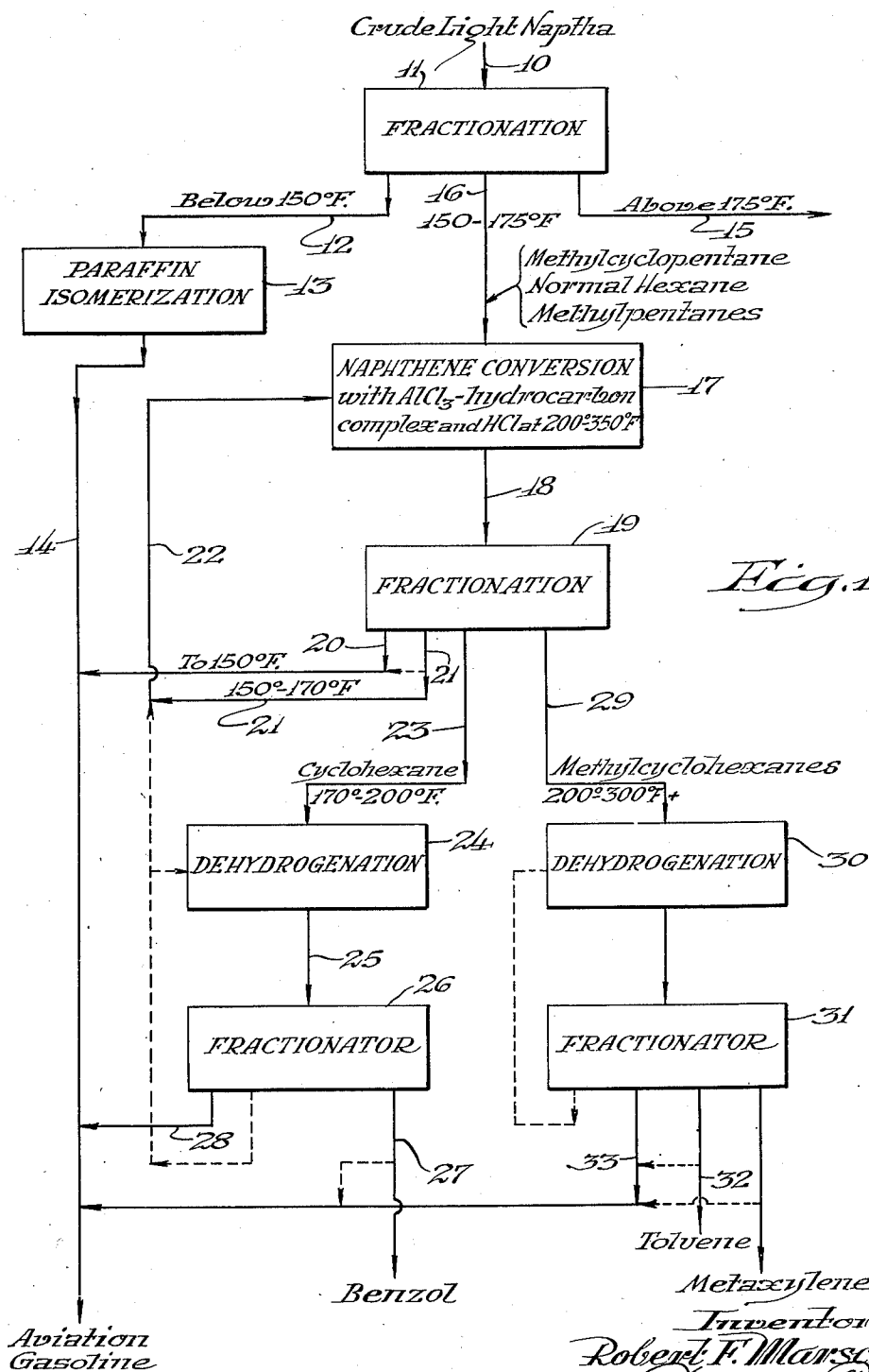


Fig. 1.

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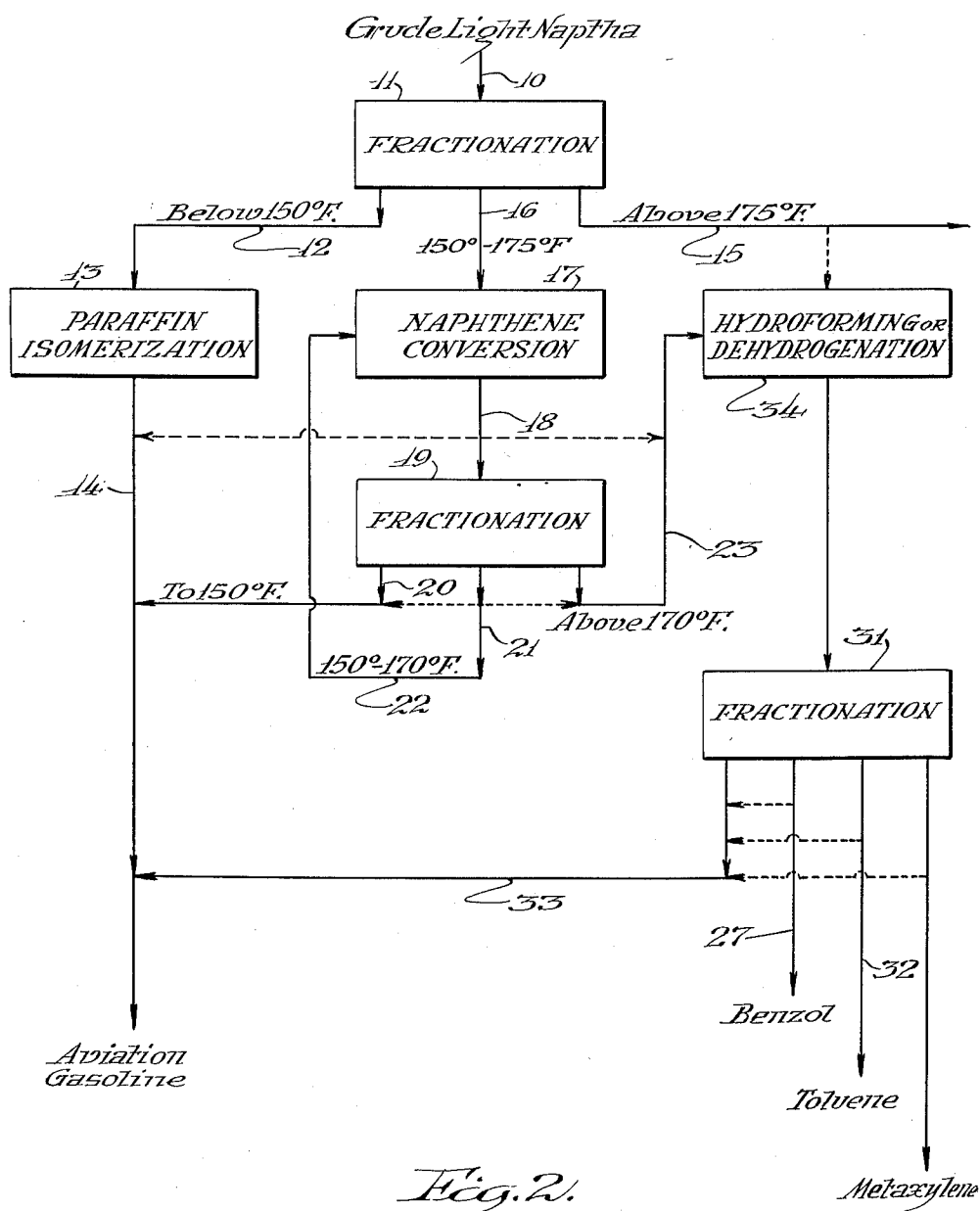


Fig. 2.

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UNITED STATES PATENT OFFICE

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CONVERSION OF NAPHTHENE
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ration of Indiana

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4 Claims. (Cl. 260—666)

This invention relates primarily to the conversion of naphthene hydrocarbons and it pertains more particularly to the alkylation of naphthenes by the addition of methyl groups thereto and to the conversion of five carbon ring to six carbon ring naphthenes. An outstanding feature of the invention is the conversion of a narrow-cut methylcyclopentane-normal hexane fraction of crude naphtha into valuable products such as high quality aviation gasoline, benzol, toluene, etc.

It is known that paraffinic hydrocarbons, such as pentane and hexane, may be isomerized with an aluminum chloride catalyst in the presence of an activator to produce branched-chain or more highly branched-chain paraffinic hydrocarbons. The charging stocks to such processes have included small amounts of naphthenes but such charging stocks have heretofore been selected with a view toward minimizing the content of aromatics and naphthenes. An object of my invention is to provide an improved method and means for converting into valuable products the fraction of crude light naphtha boiling between about 150 and 175° F., which fraction has heretofore been considered as of little or no value for the manufacture of high quality aviation fuel, toluene, etc.

Cyclopentane is a valuable aviation fuel component and may be recovered from associated hydrocarbons together with neohexane by fractional distillation. Methylcyclopentane, however, does not exhibit the superior antiknock qualities of cyclopentane and furthermore, methylcyclopentane boils so close to normal hexane that a fractionation between these hydrocarbons on a commercial scale is practically impossible. An object of my invention is to provide an improved method and means for processing this methylcyclopentane fraction of a crude light naphtha so that it may be converted into high quality aviation motor fuel components and so that valuable aromatic hydrocarbons such as benzol and toluene may be produced therefrom.

A further object is to provide an improved method and means for preparing alkyl benzenes and particularly methyl benzenes from normally liquid hydrocarbons of lower molecular weight such, for example, as a mixture of methylcyclopentane with normal hexane or other paraffinic hexanes or pentanes. Other objects will be apparent as the detailed description of the invention proceeds.

I have discovered that when a charging stock rich in methylcyclopentane, i. e., one containing

about 10 to 40% or more, preferably 20 to 30% of methylcyclopentane along with paraffinic hydrocarbons of approximately the same boiling point, are contacted with an aluminum chloride-hydrocarbon complex catalyst in the presence of hydrogen halide activators at temperatures of the order of 200 to 350° F., preferably about 250° F., there is not only a conversion of methylcyclopentane into cyclohexane but also a substantial amount of methylation of the cyclohexane. Charging stocks which initially contain only a small amount of cyclohexane and absolutely no methylcyclohexane are thus converted into products with large amounts of cyclohexane and of methylcyclohexane and with smaller but considerable amounts of dimethylcyclohexane. The methylcyclopentane of the charging stock is evidently converted first into cyclohexane and is then alkylated to methylcyclohexanes although, of course, the methylcyclopentane may be further methylated to a certain extent to form dimethyl or polymethyl cyclopentane. These in turn may be isomerized to the corresponding methylcyclohexanes. Simultaneously with this methylation of the naphthenes, which is an outstanding feature of my invention, I effect isomerization of the normal hexane and produce branched-chain pentanes and hexanes which are, of course, extremely valuable components of aviation fuel.

The cyclohexane produced in my process may be dehydrogenated to benzol or it may be recycled to the process for methylation. The methylated cyclohexanes may be dehydrogenated to methylbenzenes such as meta-xylene and toluene, which are extremely valuable for the preparation of explosives. If desired, the entire liquid product from my naphthene treating step may be dehydrogenated under such conditions as to convert the naphthenes into aromatics without converting the branched-chain paraffins into olefins, thereby producing an aviation fuel of extremely high quality both from the standpoint of knocking and from the standpoint of total heat content, volatility, range, stability against oxidation and gum-forming and over-all performance. The invention will be more clearly understood from the following detailed description read in conjunction with the accompanying drawings which form a part of the specification and in which:

Figure 1 is a flow diagram illustrating the application of my invention wherein the treated naphthene products may be separately dehydrogenated and

Figure 2 is a similar flow diagram illustrating the dehydrogenation of my naphthene products

simultaneous with the hydroforming of heptanes and heavier hydrocarbons.

The charging stock from my process is preferably a close cut fraction of crude light naphtha boiling within the approximate range of 150 to 175° F. Generally speaking, the 10% point should not be substantially lower than 150° F. and the 90% point should not be substantially higher than 175° F. While this particular narrow cut of crude light naphtha has been found to be particularly desirable and to give outstandingly good results, it should be understood that many features of the invention are applicable to somewhat heavier charging stocks, i. e., charging stocks which are considerably richer in cyclohexane. In fact, cyclohexane or a cut rich in cyclohexane may be employed per se for effecting methylation without having any substantial amount of methylcyclopentane in the original charge but in such cases methylcyclopentane will be formed in the reaction and will thus be present in recycled material. The narrow cut of crude light naphtha may have other hydrocarbons admixed therewith and, of course, a synthetic mixture of methylcyclopentane with normal hexane or other hexanes and pentanes may be utilized instead of the specific fraction of crude light naphtha.

The fraction of most crude light naphthas boiling within the approximate range of 150 to 175° F. is characterized by the following approximate composition:

	Per cent
Methylcyclopentane -----	20-30
Normal hexane -----	30-60
Methylpentanes -----	10-40
Dimethylpentanes -----	3-5
Cyclohexane -----	4-8
Benzol -----	1-3

Thus this specific cut of a Mid-Continent naphtha may contain about 23% methylcyclopentane, 52% normal hexane, 14% methylpentanes, 6½% cyclohexane, 3½% dimethylpentanes and 1% benzol. A similar cut of Gulf Coast crude light naphtha may have approximately the following composition: methylcyclopentane 20%, normal hexane 34%, methylpentanes 37%, cyclohexane 5%, dimethylpentanes 2% and benzol 2%. Even a so-called paraffinic crude light naphtha fraction within this boiling range will contain substantial amounts of methylcyclopentane.

Referring to Figure 1, crude light naphtha from any source is introduced through line 10 to fractionation system 11 and the fraction boiling predominantly below about 150° F., i. e., with its 90% point not substantially higher than 150° F., is withdrawn through line 12 to an aluminum chloride isomerization system 13 for converting the straight-chain or slightly branched-chain hydrocarbons into branched-chain or more highly branched-chain hydrocarbons. The products from this isomerization step are withdrawn through line 14 for use in aviation gasoline.

The fraction boiling predominantly above about 175° F., i. e., with its 10% point not substantially below 175° F., is withdrawn through line 15 to a hydroformer operation or for conversion or utilization elsewhere in the refinery. The so-called "naphthene" or methylcyclopentane fraction boiling within the approximate range of 150 to 175° F., i. e. with its 10% point at least about 150° F. and its 90% point not substantially higher than 175° F., is withdrawn through line 16 to conversion system 17. The conversion system itself may be similar in design

and operation to the aluminum chloride isomerization system 13.

The closely cut charging stock may be introduced together with about 2 to 10% hydrogen chloride or other hydrogen halide activator into a mixing chamber provided with mechanical agitation but preferably at a low point in a tower containing an aluminum chloride-hydrocarbon complex. This complex may be prepared in situ by the reaction of the charging stock with aluminum chloride in the presence of hydrogen chloride or it may be preformed from the charging stock or from some other hydrocarbon. Paraffinic and particularly isoparaffinic hydrocarbons have been found to give excellent complexes for this type of conversion. The complex is a liquid at conversion temperatures of about 200 to 350, for example about 250° F., and the charging stock is passed upwardly through one or more columns of this liquid which are preferably about 10 to 20 feet high. Catalyst life may be prolonged by effecting the conversion in the presence of hydrogen, usually employing about 50 to 250 cubic feet or more of hydrogen per barrel of stock charged. The reaction is preferably effected under sufficient pressure to maintain the charging stock in liquid condition, such pressure being within the approximate range of 150 to 1500 pounds per square inch, for example, about 850 pounds per square inch. Make-up aluminum chloride may be added at the rate of about 1 or 2 pounds per barrel of stock charged and spent catalyst may be withdrawn from the system at substantially the same rate. The make-up catalyst may be introduced as a slurry in a portion of the product or in any conventional manner. Based on stock charged and the total amount of complex in the reactor (or reactors if more than one is employed) the space velocity should be within the approximate range of about .2 to 4 or more volumes of liquid feed per hour per volume of complex in the reactor, for example, about 1 volume of feed per hour per volume of complex.

Complex is settled from the hot reaction products and returned to the system after which the products stream is cooled to approximately atmospheric temperature and additional catalyst material is recovered and returned to the system. The products are then stripped free of hydrogen chloride, the stripped gas together with the gas from the cooled settler being returned to the system and the hydrogen chloride content thereof being absorbed in in-coming charging stock. The stripped products are neutralized with caustic, washed with water, fractionated and then introduced by line 18 to fractionation system 19.

The particular type of fractionation employed will depend of course upon the type of products which are desired. Components boiling below 150° F. may be withdrawn through line 20 to line 14 for use in aviation gasoline. The fraction boiling between 150 and 170° F. may be withdrawn through line 21 and either passed through line 20, debutanized, and introduced to aviation gasoline line 14 or it may be recycled through line 22 to the conversion step. The cyclohexane fraction boiling between about 170 and 200° F. may be passed by line 23 to a dehydrogenation step 24 and thence through line 25 to fractionation system 26 from which I may separately recover benzol through line 27. Other products from fractionation system 26 may be recycled to the dehydrogenation step 24 or to the conversion step 17 or withdrawn through line 28 to aviation gasoline line 14. It should be understood that

this and other fractionation systems may include solvent extraction, solvent distillation, azeotropic distillation, etc., instead of or in addition to simple fractionation according to boiling points.

The methylcyclohexane fraction may be withdrawn from fractionation system 19 through line 29 to dehydrogenation system 30 and the products may be separated in fractionation system 31 to yield toluene withdrawn through line 32 and other components withdrawn through line 33 to aviation gasoline line 14 or for recycling. The charging stock for dehydrogenation system 30 may be a relatively narrow cut from 205 to 220° F. boiling range in which case the remaining heavy ends of naphthene conversion products and branched-chain paraffins may be introduced directly into aviation gasoline line 14. On the other hand, the entire heavy ends may be dehydrogenated under such conditions as to convert naphthenes into aromatics without converting paraffins into olefins, thus making possible the production of toluene and aviation fuel components of very high quality.

In Figure 2 I have illustrated a system wherein the total conversion products from the naphthene conversion step or the products boiling above 150° F., or the products boiling above 170° F. may be introduced into a hydroforming or dehydrogenation system 34 and if desired the same system may be employed for the hydroforming or dehydroaromatization of heptanes and other hydrocarbons boiling above about 175° F. from initial fractionation step 11. In this case the benzol, toluene and motor fuel fractions are obtained from the hydroformer product, the methylcyclohexane content of the original charging stock being dehydrogenated along with the methylcyclohexane produced in my naphthene conversion step.

The flow diagrams illustrated in Figures 1 and 2 are illustrative of how my invention may be utilized in refinery operations but it should be understood that my invention is not limited to these particular flow diagrams since numerous alternatives and modifications will be apparent from the above description to those skilled in the art. The operating conditions for the specific steps of dehydrogenation or hydroforming are well known in the art and will not require detailed description. A preferred catalyst for effecting the dehydrogenation or hydroforming is a group VI metal oxide such as molybdenum oxide mounted on active alumina. The dehydrogenation or hydroforming may be effected at temperatures of about 800 to 1050° F., under pressure of about 100 to 500 pounds per square inch in the presence of recycled hydrogen-containing gases and with a space velocity of about .1 to 10 volumes of charging stock per volume of catalyst space per hour. The mild conditions (required for dehydrogenating naphthenes without dehydrogenating paraffins) may be obtained by using higher space velocities or lower temperatures than are conventionally employed for effecting aromatization of open-chain paraffinic hydrocarbons. The hydrogen produced in the dehydrogenation step may be purified and employed in the naphthene conversion step.

When the desired product is an aviation fuel substantially the entire product from my naphthene conversion process may be utilized without any further fractionation or conversion. Thus a California crude light naphtha cut boiling predominantly within the range of 150 to 175° F. was converted in a two-tower system at a tempera-

ture of 275° F. in the first tower and 250° F. in the second tower under a pressure of about 850 pounds per square inch using about 180 cubic feet of hydrogen per barrel of stock charged, about 6% by weight of hydrogen chloride in stock charged to the reactors, about 1 pound of make-up aluminum chloride for each 30 gallons of stock charged and at space velocities of 1.4 volumes of naphtha feed per hour per volume of complex in the towers. The liquid yield (butane free) was upwards of 93 percent. Specific analyses of stocks charged and products produced showed that more than half of the methylcyclopentane disappeared in the conversion step, that the cyclohexane content in the product was more than twice the cyclohexane content of the charge and that substantial amounts of methylcyclohexanes were produced. The amount of product boiling above the distillation range of the feed stock was roughly equivalent to the methylcyclopentane content of the original charge. This higher boiling material was poorer in lead response than the lower boiling material when tested by the 1-C method of determining anti-knock value but it was characterized by a good response to lead tetraethyl when tested by the 3-C method. Thus the fraction boiling from about 100 to 150° F. had a clear A. S. T. M. octane number of about 80, an A. S. T. M. octane number with 4 cc. of tetraethyl lead per gallon of about 100 and a 3-C plus 4 cc. tetraethyl lead per gallon rating equivalent to S₁ (technical isooctane) plus 0.6. The heavier fraction which boils predominantly within the range of about 150 to 325° F. was characterized by a clear A. S. T. M. octane number of about 75, 1-C plus 4 cc. of tetraethyl lead per gallon of about 90 and a 3-C plus 4 cc. of tetraethyl lead per gallon of about S₁ plus 1 cc. Thus my naphthene conversion products with their associated branched-chain paraffins may be used per se as a high quality aviation fuel.

The aviation fuel may be increased in its anti-knock rating by dehydrogenating the methyl and polymethyl naphthenes under such mild conditions as to avoid dehydrogenation of the branched-chain paraffins. In this way I may provide methyl and polymethyl benzenes which are characterized by higher heat content than benzol and better antiknock qualities than the naphthenes.

While the methylcyclopentane cut of a crude light naphtha is a preferred charging stock, it should be understood that methylcyclopentane from any source may be processed in accordance with my invention by simply blending therewith a substantial amount of normal hexane, pentane or methylpentanes. The naphthene content should be within the approximate range of 10 to 40% or more and should preferably be at least about 20% by weight of the charging stock. If a charging stock consists predominantly of cyclohexane there will be a certain amount of methylation or addition of methyl groups to the cyclohexane but there will be a simultaneous conversion of some of the cyclohexane to methylcyclopentane. If it is desired to effect methylation of cyclohexane the methylcyclopentane may be continuously recycled so that the naphthene content of the final product may be almost entirely methylcyclohexanes which, in turn, may be dehydrogenated to form toluene and polymethyl benzenes. However, the methylcyclopentane produced in my process is not associated with any appreciable amount of normal hexane and it is

therefore a valuable aviation fuel component. An excellent aviation fuel can be made, for example, by blending a major amount of such methyl cyclopentane with minor amounts of isooctane and smaller amounts of isopentane. Such fuel may of course contain tetraethyl lead and it may also contain small amounts of ketones, ethers, amines, etc.

While I have described in detail a specific example of my invention and specific operating conditions and ranges it should be understood that my invention is not limited to these particular details since many alternative and modified operations and operating conditions will be apparent to those skilled in the art from the above description.

I claim:

1. A hydrocarbon conversion process which comprises fractionating a naphthenic light naphtha which is substantially free from olefins to obtain an intermediate fraction having a 10% distillation point of at least about 150° F. and a 90% distillation point below about 175° F. and at least one heavier fraction and one lighter fraction, isomerizing said lighter fraction, contacting the intermediate fraction with an aluminum chloride-hydrocarbon complex catalyst in the presence of added hydrogen chloride and added hydrogen at a temperature within the approximate range of 200 to 350° F. under a pressure within the approximate range of 150 to 1500 pounds per square inch and at a space velocity within the approximate range of .2 to 4 volumes of liquid charging stock per hour per volume of complex catalyst which space velocity is sufficiently low to effect both isomerization and methylation of naphthenes whereby C₈ naphthenes are converted into substantial yields of methyl cyclohexane, fractionating the products of the contacting step to obtain a fraction boiling below about 150° F., a fraction boiling chiefly within the approximate range of 150 to 170° F. and at least one fraction boiling above 170° F., recycling the 150-170° F. fraction to the contacting step in order to effect methylation of the naphthenes contained therein for increasing the yield of naphthenes boiling above 170° F., and blending with said isomerized lighter fraction

at least a part of the products from the contacting step which boil below 150° F.

2. A hydrocarbon conversion process which comprises fractionating a naphthenic light naphtha which contains substantial amounts of naphthenes and paraffins and which is substantially free from olefins to obtain an intermediate fraction boiling chiefly within the range of about 150° F. to 175° F. together with at least one lighter fraction and a heavier fraction, isomerizing said lighter fraction, contacting the intermediate fraction with an aluminum chloride catalyst in the presence of added hydrogen chloride at a temperature in the range of about 200 to about 350° F. under a pressure within the range of about 150 to 1500 pounds per square inch and with a space velocity sufficiently low to effect substantial methylation of naphthenes whereby methylcyclohexane is produced from C₈ naphthenes and branched chain paraffins of lower molecular weight are produced from paraffinic components in the charging stock, fractionating the products produced in the contacting step to obtain a methylcyclohexane fraction and at least one lower boiling fraction and combining said lower boiling fraction with said isomerized light fraction.

3. The process of claim 2 which includes the further step of selectively dehydrogenating the methylcyclohexane fraction to produce toluene therefrom.

4. A hydrocarbon conversion process which comprises preparing a charging stock containing about 10 to 40% by weight of C₈ naphthenes, less than 3% by weight of aromatics and the balance substantially entirely paraffins, contacting said charging stock with an aluminum halide catalyst in the presence of a hydrogen halide activator at a temperature in the range of about 200 to 350° F. and under a pressure within the range of 150 to 1500 pounds per square inch and with space velocity sufficient to effect substantial conversion of said C₈ naphthenes to methylcyclohexane and lower molecular weight branched chain paraffins, and fractionating products from said contacting step to obtain a methylcyclohexane fraction from at least one lower boiling fraction.

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