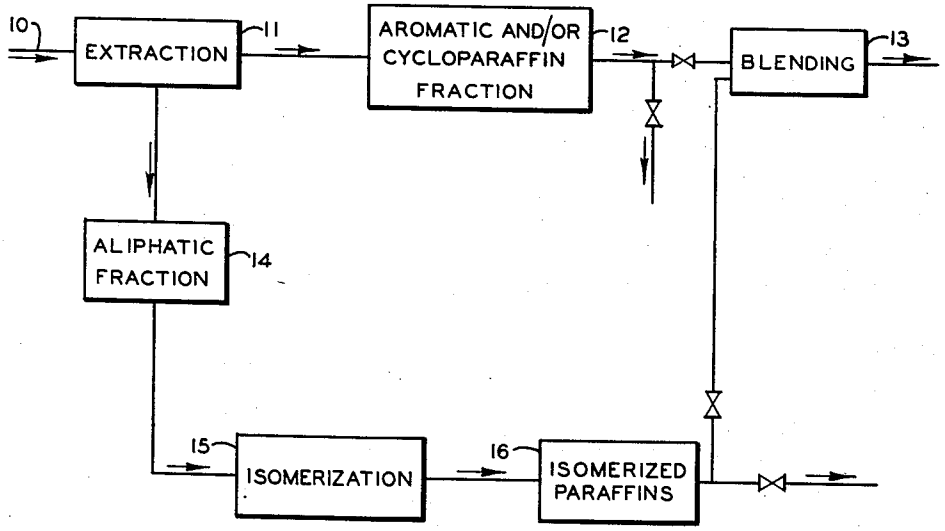
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PROCESS FOR ISOMERIZATION OF LIQUID HYDROCARBONS

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PROCESS FOR ISOMERIZATION OF LIQUID HYDROCARBONS

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This invention relates to the production of high quality gasoline by a process of isomerization.

In one of its aspects the invention relates to a treatment of a liquid hydrocarbon fraction containing desirably isomerizable hydrocarbons and aromatics and/or cycloparaffins prior to a catalytic isomerization of the said desirably isomerizable hydrocarbons. In another of its aspects the invention relates to the treatment of a gasoline to remove aromatics and/or cycloparaffins therefrom prior to a catalytic isomerization of said gasoline employing a molybdenum oxide catalyst. In yet another aspect the invention provides a process for the preparation of an improved gasoline, e. g. higher anti-knock value, by removing from a gasoline any aromatic and/or cycloparaffin compounds, isomerizing the remaining portion of the gasoline employing a supported, preferably prereduced, molybdenum oxide catalyst and then combining or blending the resulting isomerized portion with the said removed aromatic and/or cycloparaffin compounds.

It is known that liquid hydrocarbons consisting mainly of straight chain paraffin hydrocarbons of relatively low octane number may be substantially improved in octane number by treatment with an isomerization catalyst whereby the straight chain hydrocarbons are converted into branched chain or isoparaffin hydrocarbons of high octane number.

I have found that liquid hydrocarbons containing substantial amounts of aromatics and/or cycloparaffins, on isomerization with a supported molybdenum oxide catalyst, yield poor results, due to low octane improvement and to poisoning of the catalyst by accumulation of cyclic hydrocarbons on the catalyst, relative to results obtained when the said aromatics and/or cycloparaffins are first removed.

The aromatics and cycloparaffin hydrocarbons generally have a high octane number in their original form and as a result when they are present in paraffin hydrocarbons, the octane number of the mixture is higher than for naturally-occurring paraffin hydrocarbons alone. It has been found, according to this invention, that the aromatics and cycloparaffins are better used as blending agents than as feed stock to the isomerization process.

In accordance with the present invention, liquid hydrocarbons normally containing constituents which cause lowered effectiveness of the catalyst are treated under extracting conditions with a solvent selective for the removal of the constituents which cause lowered effectiveness of the catalyst. The refined hydrocarbon, mainly paraffins, after separation of the solvent and extract, is treated with the supported molybdenum oxide catalyst. The octane number of the treated paraffin hydrocarbon is substantially improved with increased effectiveness and yield per unit weight of catalyst. The aromatic and cycloparaffin hydrocarbons which are removed in the extract can be recovered for use in blending with the isomerized paraffins or with other motor fuel. The liquid hydrocarbons to be isomerized by this process are most

usually normal pentane, normal hexane and normal heptane but may include other liquid paraffin hydrocarbons such as normal octane, and longer chain paraffins.

Therefore, according to this invention, there is provided an improved process for the isomerization of gasoline components which comprises the steps of first removing any aromatics and/or cycloparaffins therefrom and then subjecting the remainder of the said gasoline to isomerization conditions in contact with a molybdenum oxide catalyst. As stated, the removed compounds or fraction can then be used to prepare an improved blend.

In case the proportion of aromatics and cycloparaffins in the hydrocarbon liquid is low, it may be desirable to treat the paraffinic hydrocarbons with sulfuric acid to remove the small amount of aromatics and the cycloparaffins and then isomerize the treated paraffin, rather than to isomerize the hydrocarbon directly, or to solvent extract the feed and then isomerize.

Therefore, as a feature of this invention, and based upon its concepts, the gasoline can be first treated with an agent such as sulfuric acid forming desirable aromatic sulfonates which can be used as such or as intermediates or processed to recover the aromatics by known means.

It is believed now evident that the invention provides a flexible operation by means of which different charge stocks or gasoline can be most economically, yet effectively treated to obtain an improved gasoline and/or sulfonates.

The preliminary solvent refining or extraction step may be carried out by conventional processes and with any solvent suitable for this purpose. The solvent extraction of light hydrocarbon oils is quite well known in the art, and it is intended that any of these methods may be used. Specific solvents which may be mentioned are sulfur dioxide, furfural, methyl alcohol, benzyl alcohol or mixtures of these. In carrying out the extraction process, the solvent is contacted with the hydrocarbon under temperature and pressure conditions to cause an extraction of aromatics and cycloparaffins, thereby forming an extract and raffinate layer, and then separating the two layers. Any solvent retained in the two layers may be removed, for example by distillation or washing with water. The raffinate layer will contain the paraffin hydrocarbons of low antiknock value suitable for treatment by isomerization with supported molybdenum oxide catalyst. The extract layer after separation of the solvent will usually contain high antiknock hydrocarbons which may be used for motor fuel, for example, by reblending with the isomerized raffinate. The solvent will extract unsaturates along with the aromatics and cycloparaffins. These unsaturates also have a high octane number and may be used for blending with the isomerized raffinate.

For the isomerization catalyst, molybdenum oxide catalyst supported on alumina or on silica-alumina is preferred, although the molybdenum oxide may be supported on other materials known to the art. The catalyst may be prepared by impregnating the supporting material with an ammonium molybdate solution and subsequent calcining to form the supported molybdenum oxide catalyst. Preferably, the catalyst is prereduced although this is not essential to operativeness or good yields.

The isomerization of normal hexane with the supported molybdenum oxide catalyst is decreased by as much as 25 to 50 percent by the presence of cycloparaffins. This finding is wholly unexpected. Thus, cycloparaffins have no ill effect on aluminum chloride catalyst. The cycloparaffins are beneficial to the aluminum chloride catalyst, in fact, in that disproportionation is suppressed.

The deterioration of the molybdenum oxide catalyst activity may be retarded by carrying out the process in the presence of hydrogen. One function of the hydrogen appears to be that of minimizing deposition of carbon on the catalyst. The hydrogen-to-paraffin mol ratio should

be larger than 0.03:1, preferably greater than 0.3:1 and less than 10:1. If the hydrogen in the feed is too low, the activity of the catalyst is so decreased by carbon deposition that the conversion per pass is disadvantageously low, and the selectivity of the catalyst, as indicated by the ultimate yield of isoparaffin or branched paraffins is similarly adversely affected. Furthermore, when the hydrogen in the feed is too low, an appreciable proportion of olefins appear in the effluent. The hydrogen may at least in part be recycled without purification and may contain an appreciable amount of gaseous by-products such as methane, etc. The probability that the hydrogen enters into the isomerization reaction should also be noted.

The reaction is effected, usually, under temperature and pressure conditions which maintain the vapor phase. The temperatures are preferably in the range of 815 to 860° F., although temperatures in the range of 780 to 885° F. may be used. Specifically, the preferred temperature range for the isomerization of normal pentane is 830 to 860° F. and for normal hexane the preferred temperature range is 815 to 830° F. The pressure may range from 100 to 950 p. s. i., however, a pressure of 250 to 550 p. s. i. is preferred. Specifically, the optimum pressure for isomerization of normal pentane is 250 to 500 p. s. i. and for normal hexane the preferred pressure range is 400 to 915 p. s. i. A contact time of 50 seconds to 350 seconds and preferably 100 to 150 seconds is used to obtain optimum conversion. Optimum conversion may be maintained with decreasing contact time by increasing the reaction temperature.

In order to describe the invention in more detail reference will now be made to the accompanying drawing. A liquid hydrocarbon, mainly paraffinic, and usually containing substantial amounts of cycloparaffins, aromatics and/or unsaturates is conducted from a source not shown through pipe **10** to an extraction unit **11**. A paraffin hydrocarbon fraction consisting mainly of pentane will contain no aromatics but can have a substantial amount of cycloparaffins. A hexane fraction can contain from 1 to 5 percent benzene and up to 20 percent cycloparaffins. In this extraction unit the liquid hydrocarbons are treated so as to extract from them cycloparaffin, aromatic and unsaturated hydrocarbons. This extraction may be effected by treatment with a selective solvent such as sulfur dioxide. The cycloparaffin, aromatic and unsaturated hydrocarbons so extracted from the liquid hydrocarbons are separated from the extracting medium and passed to a tank **12** from which they may be passed, all or in part, to a tank **13**.

After being freed from dissolved solvent by any suitable means, the liquid hydrocarbons from which the cycloparaffin, aromatic and unsaturated constituents have been removed are passed to a tank **14** and from there conducted to an isomerization unit **15** wherein they are subjected to contact along with added hydrogen with the isomerization catalyst molybdenum oxide-on-silica-alumina. The resulting branched chain paraffins are passed to a tank **16** from which they may be passed, all or in part, to the previously mentioned tank **13** for blending with the aromatic, unsaturated and cycloparaffin constituents previously referred to. Hydrogen and unreacted hydrocarbons may be recycled.

The process of the present invention, wherein the liquid hydrocarbon is treated to remove aromatics, unsaturates and cycloparaffins prior to isomerization, produces an ultimate yield of about 85 to 90 percent of product showing an octane improvement of about 25 to 70 points. Similar isomerization treatment without the preliminary solvent extraction treatment produces ultimate yields of only about 40 to 60 percent. Moreover, the catalyst is poisoned in a short time.

In plant practice, normal paraffin concentrate would usually be isomerized, such concentrate having a normal paraffin content greater than the equilibrium amount at the conditions of isomerization.

Example I

A pure grade normal pentane of 99+ mol percent purity and having an ASTM octane number of 63, was admixed with hydrogen in a hydrogen-to-pentane mol ratio of 0.7:1, and the mixture was passed, in an isomerization step, through a solid fixed bed of molybdenum oxide-on-silica-alumina. The catalyst was prepared by impregnating with an ammonium molybdate solution a silica-containing "unigel" alumina in the form of ⅛ inch pills, which were then calcined. An analysis showed 6.4 percent molybdenum oxide and 4.6 percent silica. The isomerization was conducted at a temperature gradually increasing from 830 to 860° F., a pressure of 515 p. s. i. and a contact time of 105 seconds. An ultimate yield of isopentane of 90 percent with an ASTM octane number of 90 was maintained for 52 hours at a total per pass conversion of normal pentane of 48 weight percent.

Example II

A pure grade hexane having an ASTM octane number of 26, was admixed with hydrogen in a hydrogen-to-hexane mol ratio of 0.7:1, and the mixture was passed, in an isomerization step, through a solid fixed bed of molybdenum oxide-on-silica-alumina prepared as previously described. The isomerization was conducted at a temperature of 815 to 830° F., a pressure of 515 p. s. i., and a contact time of 105 to 112 seconds. An ultimate yield of branched hexanes of 85 percent with an ASTM octane number of about 81 was obtained at a total conversion of normal hexane per pass of 52.5 weight percent.

Example III

A mixture of 80 percent pure normal hexane and 20 percent methylcyclopentane was admixed with hydrogen, in a hydrogen-to-hydrocarbon mol ratio of 0.7:1 and the mixture was passed, in an isomerization step, through a solid fixed bed of molybdenum oxide-silica-alumina prepared as previously described. The isomerization conditions were the same as in Example II. The total conversion of normal hexane per pass was 28.8 weight percent, a decrease of 45 percent by the presence of cycloparaffin. The catalyst was poisoned by the methylcyclopentane.

Example IV

96 percent pure normal hexane and 4 percent benzene was admixed with hydrogen, in a hydrogen-to-hydrocarbon mol ratio of 0.7:1 and the mixture was passed, in an isomerization step, through a solid fixed bed of molybdenum oxide-on-silica-alumina prepared as previously described. The isomerization conditions were the same as in Example II. The total conversion of normal hexane per pass was 37.0 weight percent, a decrease of 30 percent by the presence of aromatics. The benzene accumulated on the catalyst during the run.

It can readily be seen from Examples III and IV that it is highly desirable to remove the aromatic and/or the cycloparaffin before isomerization with MoO_3, or a prereduced molybdena supported catalyst.

Variation and modification are possible within the scope of the foregoing disclosure and appended claims to the invention the essence of which is that an increase of both the yield and octane number can be obtained in the isomerization of a hydrocarbon fraction comprising aromatics and/or cycloparaffins by the prior removal of any of said aromatics and/or cycloparaffins when the catalyst is a molybdenum oxide catalyst, preferably a supported molybdenum oxide catalyst, and still more preferably which catalyst has been prereduced and that a process has been set forth for the said removal and the said subsequent isomerization of the remainder of the said hydrocarbon fraction, e. g. a gasoline.

We claim:

1. A process for the preparation in improved yield of a motor fuel having improved octane characteristics from an isomerizable hydrocarbon fraction containing hydrocarbons suitable as components of a motor fuel and containing at least one of an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of treating said hydrocarbon fraction to provide a portion rich in said aromatic hydrocarbon and cycloparaffin hydrocarbon and a portion poor in said aromatic hydrocarbon and said cycloparaffin hydrocarbon and isomerizing the said portion poor in said aromatic hydrocarbon and cycloparaffin hydrocarbon in presence of a molybdenum oxide catalyst supported upon a material selected from the groups consisting of alumina and silica-alumina, at a temperature in the range of 780 to 885° F., a pressure in the range 100 to 950 p. s. i. a. and a hydrogen to hydrocarbon mol ratio of 0.03:1 to 10:1.

2. The process of claim 1 wherein the temperature in the said isomerization zone is in the range 815° to 860° F., the pressure is in the range 250 to 550 pounds per square inch absolute, the hydrocarbons are maintained substantially in the vapor phase the hydrogen to hydrocarbon mol ratio is greater than 0.3:1 and less than 10:1, the time of contact is in the range of 50 seconds to 350 seconds and wherein the molybdenum oxide catalys is molybdenum oxide supported upon a carrier.

3. The preparation of an improved motor fuel in improved yield from a hydrocarbon fraction containing an isomerizable paraffin hydrocarbon, an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of removing substantially all of said aromatic and said cycloparaffin hydrocarbon from said hydrocarbon fraction, and subjecting the remainder of said hydrocarbon fraction to isomerization conditions in the presence of a molybdenum oxide isomerization catalyst supported upon a material selected from the group consisting of alumina and silica-alumina and a hydrogen to hydrocarbon mol ratio of 0.3:1 to 10:1.

4. The preparation of an improved motor fuel in improved yield from a hydrocarbon fraction containing an isomerizable paraffin hydrocarbon and an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of removing substantially all of said aromatic and said cycloparaffin hydrocarbon from said hydrocarbon fraction; subjecting the remainder of said hydrocarbon fraction to isomerization conditions in the presence of a molybdenum oxide catalyst and in the presence of hydrogen, the hydrogen to paraffin mol ratio being at least 0.03:1 and less than 10:1 and blending the isomerized hydrocarbon fraction with at least a portion of said removed aromatic and cycloparaffin hydrocarbon.

5. The preparation of an improved motor fuel component from a mixture containing a substantial proportion of normal hexane and a minor proportion of methylcyclopentane which comprises separating the methylcyclopentane from said mixture, admixing the normal hexane with hydrogen, and isomerizing said hexane hydrogen admixture in presence of a molybdenum oxide catalyst.

6. A process according to claim 5 wherein the isomerized admixture is treated to recover isomerized hydrocarbon and the said isomerized hydrocarbon is blended with the said methylcyclopentane.

7. The preparation of an improved motor fuel component from a mixture containing a substantial proportion of normal hexane and a minor proportion of benzene which comprises separating the benzene from said mixture, admixing the normal hexane with hydrogen, and isomerizing said hexane hydrogen admixture in presence of a molybdenum oxide catalyst supported upon a material selected from the group consisting of alumina and silica-alumina.

8. A process according to claim 7 wherein the isomerized admixture is treated to recover isomerized hydrocarbon and the said isomerized hydrocarbon is blended with the said benzene.

9. The preparation of an improved motor fuel in improved yield from a hydrocarbon fraction containing a paraffin hydrocarbon, an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of removing substantially all of said aromatic and said cycloparaffin hydrocarbon from said hydrocarbon fraction; subjecting the remainder of said hydrocarbon fraction to isomerization in the presence of a molybdenum oxide catalyst at a temperature in the range 780° to 885° F. and a pressure in the range 100 to 950 p. s. i. a. and a hydrogen to hydrocarbon mol ratio of 0.3:1 to 10:1 and blending the isomerized hydrocarbon fraction with at least a portion of said removed aromatic and cycloparaffin hydrocarbon.

10. The preparation of an improved motor fuel in improved yield from a hydrocarbon fraction containing an n-paraffin hydrocarbon, an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of removing substantially all of said aromatic and cycloparaffin hydrocarbons from said hydrocarbon fraction; subjecting the remainder of said hydrocarbon fraction containing said n-paraffin hydrocarbon to isomerization in the presence of a molybdenum oxide catalyst supported upon a material selected from the group consisting of alumina and silica-alumina at a temperature in the range 815° to 860° F. and a pressure in the range of 250 to 550 p. s. i. a. and a hydrogen to hydrocarbon mol ratio of 0.3:1 to 10:1; recovering a hydrocarbon fraction containing a substantially increased amount of isoparaffins; and blending the isoparaffin containing hydrocarbon fraction with at least a portion of said removed aromatic and cycloparaffin hydrocarbons.

11. The process of claim 10 wherein the normal paraffin hydrocarbon is normal pentane.

12. The process of claim 10 wherein said normal paraffin hydrocarbon is essentially normal hexane.

13. In the preparation of an improved motor fuel component from a mixture containing a major proportion of isomerizable paraffin hydrocarbons and a minor portion of aromatic and cycloparaffin hydrocarbons which comprises contacting said mixture with sulfuric acid so as to sulfonate the aromatic and cycloparaffin hydrocarbons; separating the unreacted isomerizable paraffin hydrocarbons from said sulfuric acid containing sulfonates of said aromatic and cycloparaffin hydrocarbons; admixing the unreacted isomerizable paraffin hydrocarbons with hydrogen; and isomerizing said paraffin hydrocarbon-hydrogen admixture in the presence of a molybdenum oxide catalyst supported upon a material selected from the group consisting of alumina and silica-alumina.

14. In the preparation an improved motor fuel component from a mixture containing isomerizable paraffin hydrocarbons and aromatic and cycloparaffin hydrocarbons the improvement which comprises the steps of contacting said hydrocarbon mixture with a solvent selected for the removal of the aromatic and cycloparaffin hydrocarbons under extracting conditions; separating the isomerizable paraffin hydrocarbons from said solvent and dissolved aromatic and cycloparaffin hydrocarbons; admixing said paraffin hydrocarbons with hydrogen; and isomerizing said paraffin hydrocarbon-hydrogen admixture in the presence of a supported molybdenum oxide catalyst supported upon a material selected from the group consisting of alumina and silica-alumina.

15. The process of claim 14 wherein said solvent is at least one selected from the group consisting of sulfur dioxide, furfural, methyl aclohol, and benzyl alcohol.

16. The process of claim 15 wherein said solvent is sulfur dioxide.

17. The process of claim 15 wherein said solvent is furfural.

18. The process of claim 15 wherein said solvent is methyl alcohol.

19. The process of claim 15 wherein said solvent is benzyl alcohol.

20. The preparation of an improved motor fuel in improved yield from a hydrocarbon fraction containing normal pentane, an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of removing substantially all of said aromatic and said paraffin hydrocarbons from said hydrocarbon fraction, subjecting the remainder of said hydrocarbon fraction which is essentially normal pentane to isomerization at a temperature in the range of 830 to 860° F., a pressure in the range of 250 to 550 pounds per square inch and a hydrogen to hydrocarbon mol ratio of 0.3:1 to 10:1 in the presence of a molybedenum oxide isomerization catalyst supported upon a material selected from the group consisting of alumina and silica-alumina.

21. The preparation of an improved motor fuel in improved yield from a hydrocarbon fraction containing normal hexane, an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of removing substantially all of said aromatic and said cycloparaffin hydrocarbons from said hydrocarbon fraction, and subjecting the remainder of said hydrocarbon which is essentially normal hexane to isomerization at a temperature in the range 815 to 830° F., a pressure in the range of 400 to 915 pounds per square inch and a hydrogen to hydrocarbon mol ratio of 0.3:1 to 10:1 in the presence

of a molybdenum oxide isomerization catalyst supported upon a material selected from the group consisting of alumina and silica-alumina.

22. A process for the preparation in improved yield of a motor fuel having improved octane characteristics from an isomerizable hydrocarbon fraction containing hydrocarbons suitable as components of a motor fuel and containing at least one of an aromatic hydrocarbon and a cycloparaffin hydrocarbon which comprises the steps of treating said fraction to provide a portion rich in at least one of said aromatic and said cycloparaffin hydrocarbon and a portion poor in said last-mentioned hydrocarbons, admixing hydrogen with said portion poor in said last-mentioned hydrocarbons, and isomerizing said admixture in the presence of molybdenum oxide catalyst supported upon a material selected from the group consisting of alumina and silica-alumina.

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