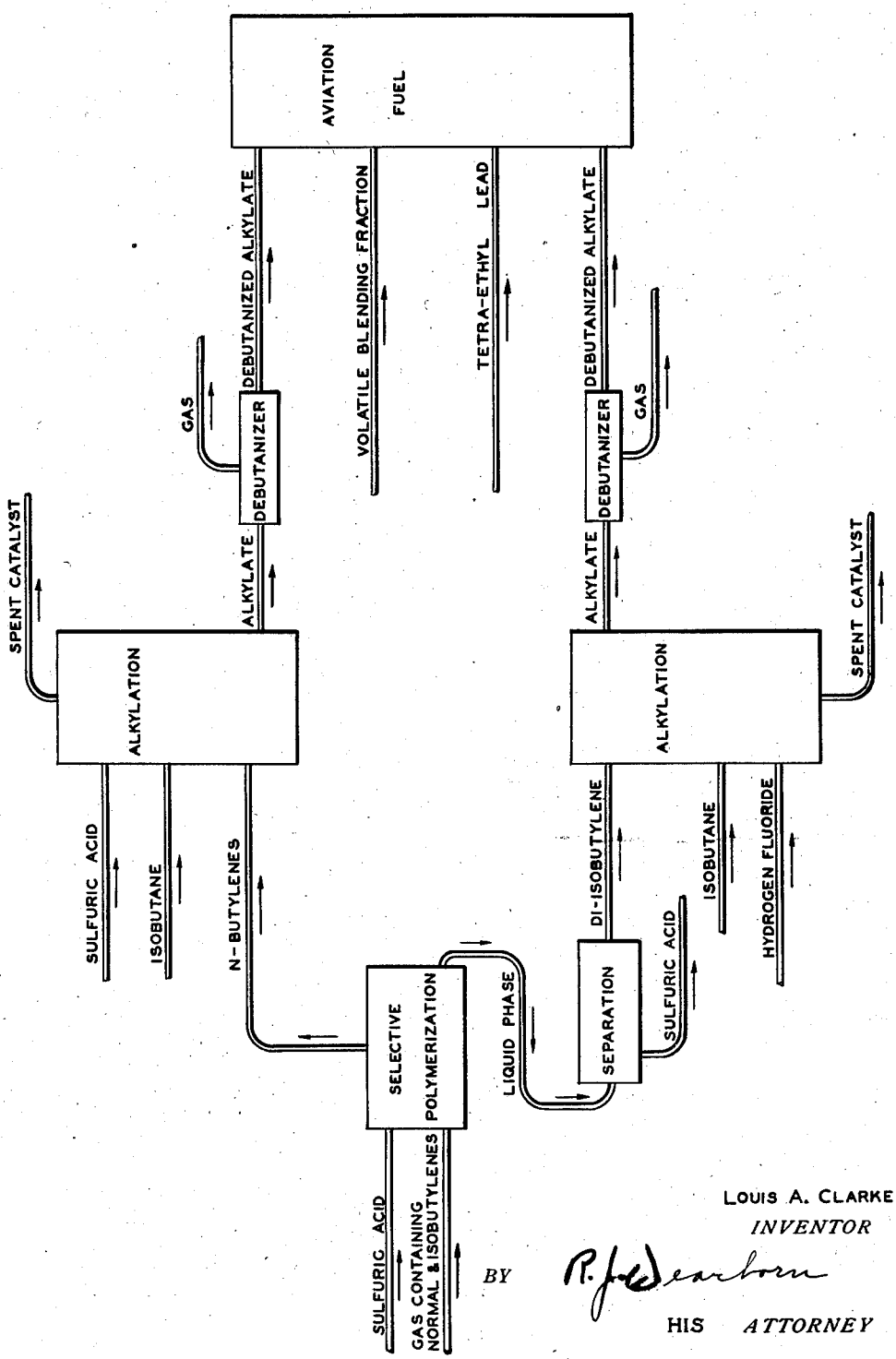
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MOTOR FUELS AND PROCESSES FOR MAKING SAME

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MOTOR FUELS AND PROCESSES FOR MAKING SAME

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12 Claims. (Cl. 44—69)

My invention relates to an improved process for the alkylation of isobutane, and for the production of superior anti-knock motor fuels. More specifically, my invention relates to the utilization of mixtures of normal and isobutylenes for the alkylation of isobutane, and to the production of improved aviation type motor fuels.

The alkylation of isobutane by means of mixed normal and isobutylenes, using mineral acid catalysts, produces alkylates having desirable anti-knock characteristics for ordinary automotive and aviation uses. In accordance with the present invention, superior alkylates are produced which have unusually high anti-knock properties and lead susceptibilities desirable for the production of highly leaded aviation type "super fuels."

The process of my invention is illustrated in the single figure of the accompanying drawing showing the process diagrammatically with the aid of legends.

I have found that improved alkylates, suitable for use in aviation fuels of high power output, can be obtained from mixtures of normal and isobutylenes by separate alkylations of isobutane by means of the normal and isobutylene components of such mixtures, using different catalysts for the two alkylations. In my preferred process, an isobutylene alkylating agent derived from the butylene mixture, is employed in conjunction with a hydrogen fluoride catalyst for the alkylation of isobutane; and a normal butylene alkylating agent, derived from the same butylene mixture, is employed in conjunction with a sulfuric acid catalyst for the alkylation of isobutane. The resulting alkylates may be blended to produce motor fuels of high clear octane values and high lead susceptibilities. These blends may be heavily leaded to produce high power output aviation fuels having excellent performance in supercharged engines.

In the process of the present invention, preferably at least a major portion of the isobutylene is separated from the butylene-containing mixture in the form of an isobutylene alkylating agent of the class consisting of monomeric isobutylene, polymeric isobutylenes such as di-isobutylene and tri-isobutylene, and isobutylene addition products such as tertiary butyl alcohol and tertiary butyl fluoride. Isobutane is alkylated with the resulting isobutylene alkylating agent in the presence of a hydrogen fluoride catalyst; and the residual gas mixture, in the form of a n-butylene alkylating agent of the class consisting of n-butylenes and n-butylene addition products such as secondary butyl alcohol and secondary butyl acid sulfate, is employed for the alkylation of isobutane in the presence of a sulfuric acid catalyst.

Any of the butylene-containing gas mixtures commercially available in refineries may be employed in the present process, but the advantages of this process are best realized in the utilization of mixtures in which neither isobutylene nor n-butylenes predominate to any great extent. Suitable mixtures contain substantial amounts of isobutylene and either or both butylene-1 and butylene-2. Commercially available mixtures usually also contain isobutane, which is utilized as one of the reactants in the present process, and may also contain normal butane and lesser amounts of other gaseous hydrocarbons. The preferred mixtures contain only hydrocarbons with four carbon atoms, and in such mixtures, normal butane is preferably maintained at as low a concentration as is economically practical.

The separation of isobutylene from the butylene-containing mixtures may be effected by any of the known methods. This operation, however, is preferably carried out in a manner such as to yield directly an isobutylene alkylating agent suitable for use in the hydrogen fluoride alkylation, and to yield a normal butylene alkylating agent suitable for use in the sulfuric acid alkylation.

Selective absorption of isobutylene in dilute sulfuric acid, e. g., 60 to 70 per cent strength, constitutes a desirable procedure for separating this component from the gas mixtures. Isobutylene may be regenerated from the resulting solution by suitable methods, or the solution may be neutralized and then distilled to yield tertiary butyl alcohol, which may also serve as an alkylating agent in the hydrogen fluoride alkylation. In the latter case, water of reaction will be formed during the alkylation, and must be taken into consideration, in view of its diluting action on the catalyst.

A desirable modification of the above procedure is to heat the sulfuric acid solution to form isobutylene polymers, for example, in accordance with the procedure of U. S. Patent 2,258,368. The di-isobutylene and tri-isobutylene which may be obtained by this procedure are satisfactory alkylating agents for the hydrogen fluoride alkylation, but I generally prefer to form largely the di-isobutylene for this purpose.

Alternatively, the di-isobutylene may be formed directly, in a single step, by contacting the butylene mixture with sulfuric acid under conditions to effect selective polymerization of the

isobutylene. This modification is shown in the accompanying drawing, which represents a flow diagram of a preferred method for carrying out the present invention.

The butylene-containing gas mixture may also be treated with hydrogen fluoride to form tertiary butyl fluoride for use as an alkylating agent in the hydrogen fluoride alkylation step of the process. Selective hydrofluorination of isobutylene is desirable for this purpose, but it is also possible to form both tertiary butyl fluoride and secondary butyl fluoride, and to decompose the latter to regenerate normal butylenes for use in the sulfuric acid alkylation. The hydrofluorination may be effected in the vapor phase in the presence of catalysts such as fluorides of zinc, manganese, cobalt, iron or aluminum. Conversely, the hydrofluorination may be effected in the liquid phase in the absence of catalysts, for example, in accordance with the process Grosse and Linn (J. Org. Chem., 3, 26).

In the above processes, or any equivalent processes for the separation of isobutylene, the isobutylene alkylating agent produced may suitably be either monomeric or polymeric. On the other hand, for the production of high quality alkylates in the sulfuric acid alkylation step, I prefer to employ only monomeric n-butylene alkylating agents, i. e., alkylating agents of the class consisting of butylene-1, butylene-2, and n-butylene addition products, such as secondary butyl alcohol and secondary butyl acid sulfate.

The alkylation of isobutane by means of the isobutylene alkylating agent is effected in the presence of a hydrogen fluoride catalyst in accordance with the procedure of my co-pending application, Serial Number 429,471, filed February 4, 1942. For the production of high quality alkylates in this step of the process, a high ratio of isobutane to isobutylene alkylating agent should be employed in the reaction mixture. This ratio should not be less than 4:1, and should preferably be at least 5:1. Although the isobutane to olefin ratio is the most important factor in this step of the process, it is also desirable to employ optimum reaction temperatures, and other reaction conditions, as described in my co-pending application. When using the preferred reaction conditions for the hydrogen fluoride alkylation, alkylates may be secured having CFRM octane numbers as high as 97 or even higher, and having high lead susceptibility and excellent performance in supercharged engines when leaded to the extent of 3 c.c. or more of tetraethyl lead per gallon.

The residual gas mixture containing the n-butylene alkylating agent may be employed to alkylate isobutane in the presence of a sulfuric acid catalyst, using any of the known conditions for sulfuric acid alkylation. Here again, optimum conditions are desirable for the production of highest quality alkylates. As examples of suitable reaction conditions, there may be mentioned temperatures of 35 to 60° F., isobutane to olefin ratios of at least 5.5:1 in the feed mixture, acid strength of 94 to 100 per cent, an acid to hydrocarbon ratio of at least 1:1 by volume and preferably about 1.7:1, and a contact time of at least 20 minutes and preferably at least 30 minutes. In continuous operation, an acid strength of at least 95 per cent is preferably maintained in the reaction zone by the use of make-up acid of 98 to 100 per cent concentration. For continuous operation, it is also desirable to employ emulsion recycle and isobutane recycle to effect an internal isobutane to olefin ratio of at least 100:1 and preferably about 150:1, and to employ a space velocity below 5 and preferably below 1, calculated as volumes of total hydrocarbon feed, including external recycle, per volume of acid catalyst per hour. It is to be understood, however, that these conditions are not limiting, but are merely illustrative of known reaction conditions which are suitable for this step of the process.

My invention may be further illustrated by the following specific example:

A gas mixture of the following approximate composition:

	Mol per cent
Propane	4.6
Propylene	0.9
Isobutane	22.0
Isobutylene	10.0
N-butylenes	10.7
N-butane	50.0
C_5 and higher	1.8

is contacted with 65 per cent sulfuric acid to absorb approximately 90 per cent of the isobutylene content, and to yield a residual gas mixture of approximately the following composition:

	Mol per cent
Propane	5.0
Propylene	1.0
Isobutane	24.2
Isobutylene	1.1
N-butylenes	11.7
N-butane	55.0
C_5 and higher	2.0

Isobutane is added to this residual gas mixture in sufficient quantity to produce an isobutane to olefin ratio of 22.3 and the resulting mixture is continuously introduced into a reaction vessel containing 100 per cent sulfuric acid in a quantity sufficient to produce an acid to hydrocarbon ratio in the reaction mixture of approximately 1.7:1 by volume. The reaction mixture is agitated and maintained at approximately 60° F. and the rate of feed is maintained sufficient to produce a contact time of 20 minutes. The resulting emulsion is drawn off from the vessel at a rate corresponding to the rate of hydrocarbon feed and catalyst recycle, is allowed to separate and the catalyst phase is continuously returned to the reaction vessel. The hydrocarbon phase is then distilled to yield a debutanized alkylate of 311° F. E. P.

The sulfuric acid solution resulting from the isobutylene absorption described above is heated to a temperature of 140° F. for a period of approximately 5 minutes to effect polymerization of the isobutylene, primarily to di-isobutylene. The resulting di-isobutylene is recovered by distillation of the separated hydrocarbon layer, and is employed for the alkylation of isobutane in the presence of substantially anhydrous hydrogen fluoride as the catalyst. For this purpose, the isobutane and hydrogen fluoride are charged into a reaction vessel equipped with a rotary agitator, and di-isobutylene is added to the agitated mixture over a period of 60 minutes, while maintaining a temperature of 70° F. The isobutane, di-isobutylene, and hydrogen fluoride are employed in a mol ratio of 5:1:5 respectively. Following the introduction of the di-isobutylene, agitation is continued for an additional 30 minutes, after which the emulsion is allowed to separate, and the hydrocarbon phase is distilled to recover debutanized alkylate.

In representative alkylations under the conditions described above, di-isobutylene alkylates have been obtained having total octane contents of at least 85 per cent by volume, contents of 2,2,4-trimethylpentane of at least 55 per cent by volume, and CFRM octane numbers of 95–97; and n-butylene alkylates have been secured having CFRM octane numbers of 94–96. These alkylates, when blended in the proportions produced from the original butylene mixture, result in motor fuels having clear octane values of 94.5–96.5. On the other hand, alkylations of mixed gases containing isobutylene and n-butylenes in the ratio of the olefin gas mixture of the above example have yielded alkylates having clear octane numbers of only 93 to 94.

The blended alkylates, produced as described above, also have superior lead susceptibilities, and may be leaded as heavily at 6.0 c.c. of tetraethyl lead per gal. to produce fuels of extremely high maximum power output. Very satisfactory aviation type motor fuels can be prepared from such blended alkylates by incorporating a more volatile blending fraction such as isopentane or 2,3-dimethylbutane, and leading the resulting mixture to the extent of 3–4 c.c. of tetra-ethyl lead per gallon. From 5 to 20 per cent by volume of isopentane, 2,3-dimethyl butane, or equivalent volatile blending fraction will usually be satisfactory for this purpose. Inhibitors, alternative or additional anti-knock agents, and other fuel additives may be incorporated in these fuels in accordance with prior practices in this art.

It is to be understood, of course, that the above examples are merely illustrative and do not limit the scope of my invention. As has previously been pointed out, other methods may be used to separate isobutylene from the gas mixtures, and other procedures and combinations of reaction conditions may be employed for the hydrogen fluoride alkylation step and the sulfuric acid alkylation step. Likewise, different proportions, or other equivalent components, may be used in the production of motor fuels from the alkylates produced by my process. In general, it may be said that the use of any equivalents or modifications of procedure which would naturally occur to one skilled in the art is included in the scope of my invention. Only such limitations should be imposed on the scope of my invention as are indicated in the appended claims.

I claim:

1. The process of manufacturing an aviation super-fuel which comprises alkylating isobutane with an isobutylene alkylating agent selected from the group consisting of isobutylene, di-isobutylene, tri-isobutylene, tertiary butyl alcohol, and tertiary butyl fluoride in the presence of substantially anhydrous hydrogen fluoride under conditions including a molar ratio of isobutane to monomeric isobutylene equivalent of the isobutylene alkylating agent in excess of 4:1, recovering a debutanized alkylate therefrom having a clear CFRM octane of at least 95, separately alkylating isobutane with an n-butylene alkylating agent substantially free from isobutylene and selected from the group consisting of butylene-1, butylene-2, secondary butyl alcohol and secondary butyl acid sulfate in the presence of strong H_2SO_4 of alkylation strength under conditions including a feed ratio of isobutane to n-butylene equivalent of the said n-butylene alkylating agent in excess of 5.5:1 and an internal ratio thereof in excess of 100:1 with a space velocity below 5, recovering a debutanized alkylate therefrom having a clear CFRM octane of at least 94, blending the said debutanized alkylates to produce a mixture having high lead susceptibility, adding thereto a minor proportion of a more volatile hydrocarbon selected from the group consisting of isopentane and 2,3-dimethylbutane, and also adding thereto an anti-knock agent.

2. The process of claim 1 in which the isobutylene alkylating agent comprises monomeric isobutylene, and the n-butylene alkylating agent comprises monomeric butylene-1 and butylene-2.

3. The process of claim 1 in which the isobutylene alkylating agent comprises di-isobutlyene, and the n-butylene alkylating agent comprises monomeric butylene-1 and butylene-2, .

4. The process of claim 1 in which the isobutylene alkylating agent comprises tri-isobutylene, and the n-butylene alkylating agent comprises monomeric butylene-1 and butylene-2.

5. A process for the manufacture of a high anti-knock motor fuel which comprises subjecting isobutane to the action of an isobutylene alkylating agent selected from the group consisting of isobutylene, di-isobutylene, tri-isobutylene, tertiary butyl alcohol and tertiary butyl fluoride at a temperature of 60–80° F. in the presence of a volume of substantially anhydrous hydrogen fluoride at least equal to the volume of hydrocarbons in contact therewith, while maintaining a molar ratio of isobutane to isobutylene alkylating agent of at least 5:1 based on the monomeric isobutylene equivalent of said isobutylene alkylating agent, recovering a debutanized alkylate therefrom having a clear CFRM octane of at least 95 and subjecting isobutane to the action of an n-butylene alkylating agent substantially free from isobutylene and selected from the group consisting of butylene-1, butylene-2, secondary butyl alcohol and secondary butyl acid sulfate at a temperature of 35–60° F. in the presence of a volume of 94–100 per cent sulfuric acid at least equal to the volume of hydrocarbons in contact therewith, while maintaining a molar ratio of isobutane to n-butylene alkylating agent of at least 5.5:1, recovering a debutanized alkylate therefrom having a clear CFRM octane of at least 94, blending the said debutanized alkylates, and adding an anti-knock agent thereto.

6. The process of claim 5, in which the isobutylene alkylating agent is monomeric isobutylene, and the n-butylene alkylating agent is a mixture of monomeric butylene-1 and butylene-2.

7. The process of claim 5, in which the isobutylene alkylating agent is essentially di-isobutylene, and the n-butylene alkylating agent is a mixture of monomeric butylene-1 and butylene-2.

8. The process of claim 5, in which the isobutylene alkylating agent is essentially tri-isobutylene, and the n-butylene alkylating agent is a mixture of monomeric butylene-1 and butylene-2.

9. The process of manufacturing an aviation super-fuel which comprises alkylating isobutane with di-isobutylene, in the presence of substantially anhydrous hydrogen fluoride under conditions including a molar ratio of isobutane to monomeric isobutylene equivalent of the di-isobutylene of at least 5:1, recovering a debutanized alkylate therefrom having a clear CFRM octane of at least about 95 and containing at least 85% by volume of octanes of which more than

half is 2,2,4-trimethylpentane, separately alkylating isobutane with normal butylene substantially free from isobutylene in the presence of H_2SO_4 of at least 95% strength under conditions including a feed ratio of isobutane to normal butylene in excess of 5.5:1 and an internal ratio thereof in excess of 100:1 with a space velocity below 1, recovering a debutanized alkylate therefrom having a clear CFRM octane of at least 94, blending the said alkylates, adding thereto about 5-20% by volume based on the blended alkylates of a hydrocarbon selected from the group consisting of isopentane and 2,3-dimethylbutane, and also adding at least 3 cc. per gallon based on the resulting mixture of tetraethyl lead.

10. A process for the production of anti-knock motor fuels, which comprises subjecting isobutane to the action of an isobutylene alkylating agent selected from the group consisting of isobutylene, di-isobutylene, tri-isobutylene, tertiary butyl alcohol and tertiary butyl fluoride at a temperature of 60–80° F. in the presence of a volume of substantially anhydrous hydrogen fluoride at least equal to the volume of hydrocarbons in contact therewith, while maintaining a molar ratio of isobutane to isobutylene akylating agent of at least 5:1 based on the monomeric isobutylene equivalent of said isobutylene alkylating agent, subjecting isobutane to the action of an n-butylene alkylating agent substantially free from isobutylene and selected from the group consisting of butylene-1, butylene-2, secondary butyl alcohol and secondary butyl acid sulfate at a temperature of 35–60° F. in the presence of a volume of 94–100 per cent sulfuric acid at least equal to the volume of hydrocarbons in contact therewith, while maintaining a molar feed ratio of isobutane to n-butylene alkylating agent of at least 5.5:1 and an internal ratio thereof in excess of 100:1, debutanizing the resulting alkylation reaction products to produce debutanized alkylates having clear CFRM octanes of at least 95 and 94 respectively, and blending the resulting debutanized alkylates, together with a more volatile petroleum hydrocarbon fraction and tetraethyl lead, to form motor fuel.

11. An aviation super-fuel comprising a substantial proportion of debutanized diisobutylene-isobutane hydrogen fluoride alkylate formed under conditions including a molar ratio of isobutane to monomeric isobutylene equivalent of the diisobutylene in excess of 4:1, said alkylate having a clear CFRM octane of at least 95 and containing at least 85% by volume of octanes of which more than half is 2,2,4-trimethylpentane, blended with a substantial proportion of debutanized n-butylene-isobutane sulfuric acid alkylate formed under conditions including the substantial absence of isobutylene and with a molar ratio of isobutane to n-butylene in excess of 5.5:1, said last-mentioned alkylate having a clear CFRM octane of at least 94, together with about 5–20% by volume based on the volume of the blended alkylates of a light hydrocarbon selected from the group consisting of isopentane and 2,3-dimethylbutane, and at least 3 cc. per gallon based on the above mixture of tetraethyl lead.

12. An aviation super-fuel comprising a substantial proportion of debutanized hydrogen fluoride catalyzed isobutane alkylate formed from an isobutylene alkylating agent selected from the group consisting of isobutylene, di-isobutylene, tri-isobutylene, tertiary butyl alcohol and tertiary butyl fluoride, under conditions including a molar ratio of isobutane to monomeric isobutylene equivalent of the isobutylene alkylating agent in excess of 4:1, said debutanized alkylate having a clear CFRM octane of at least 95 and containing at least 85% of octanes of which more than half is 2,2,4-trimethylpentane, blended with a substantial proportion of debutanized sulfuric acid catalyzed isobutane alkylate formed from a normal butylene alkylating agent substantially free from isobutylene and selected from the group consisting of butylene-1, butylene-2, secondary butyl alcohol and secondary butyl acid sulfate, under conditions including a molar ratio of isobutane to n-butylene equivalent of the said n-butylene alkylating agent in excess of 5.5:1, said last mentioned debutanized alkylate having a clear CFRM octane of at least 94, together with about 5–20% by volume based on the volume of the blended alkylates of a light hydrocarbon selected from the group consisting of isopentane and 2,3-dimethylbutane, and an anti-knock agent.

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