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PROCESS FOR PRODUCING PARAFFINIC HYDROCARBONS

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The present invention relates to the manufacture of paraffinic hydrocarbons of a branched chain structure particularly suitable for use as fuel in automobile and aviation engines. More specifically, the invention includes a process for combining certain isoparaffinic hydrocarbons with olefinic hydrocarbons to produce branched chain paraffinic hydrocarbons, these products of reaction being particularly suitable as a motor fuel, or as a constituent thereof, because of their high anti-detonating or slow burning characteristics. The invention further includes the use of special catalyst mixtures and of conditions of operation for the manufacture or synthesis of the described valuable compounds.

The adoption of high compression ratios for automobile and aviation engines has caused the petroleum industry to resort to the use of cracking operations as a general means of producing motor fuels having high anti-knock values. However, cracking operations produce undesirably large losses, for example in the form of gases which usually contain considerable proportions of olefins. Aside from these olefinic hydrocarbons of the normally gaseous and of the normally liquid types are also obtained from other sources. Thus, olefins occur along with paraffinic and other saturated hydrocarbons produced by gas-making processes, as well as by-products from various chemical industries. Also, olefinic hydrocarbons are obtained by a simple dehydrogenation of the corresponding paraffinic hydrocarbons.

In general, olefinic hydrocarbons are relatively more chemically active than other classes of hydrocarbons. Thus, even under comparatively mild catalytic influences, the olefinic hydrocarbons exhibit a high reactivity in their tendency to polymerize and to form substances of higher molecular weight. On the other hand, paraffinic hydrocarbons, for example isobutane, isopentane, etc., normally occurring in natural gas or any similar or related hydrocarbon fractions are usually considered to be more or less chemically inactive.

In one of its embodiments, the present process is directed to the efficient utilization of the above described isoparaffinic and olefinic hydrocarbons, and particularly the lower molecular weight or normally gaseous fractions thereof, such as those present in commercial gas mixtures, to produce high antiknock hydrocarbon fractions suitable for use as motor fuels. In another embodiment, the process includes the utilization of certain normally liquid olefinic hydrocarbons and of paraffinic hydrocarbons described more fully hereinbelow to produce motor fuels or constituents thereof having high anti-detonating characteristics and which are substantially free from products of polymerization. The process described herein is applicable to individual olefins and isoparaffins, and to their mixtures.

It has been previously discovered that certain isoparaffinic hydrocarbons, and particularly the relatively low boiling or low molecular weight isoparaffinic hydrocarbons, may be caused to react with olefinic hydrocarbons to form valuable derivatives thereof. This type of reaction consists in the joining of one or more olefin molecules with one molecule of an isoparaffinic hydrocarbon to produce an alkylated or branched chain paraffinic molecule. The product of this reaction is termed an "alkymer" to distinguish it from a "polymer" which is the product resulting from the union of two or more olefin molecules. Theoretically, the reaction of an isoparaffin with an olefin in the presence of a suitable alkylating catalyst is of a simple character. Thus, the reaction which takes place when isobutane is chemically combined with a butene in the presence of sulfuric acid may be expressed by the following equation:

$$C_4H_{10}+C_4H_8\rightarrow C_8H_{18}$$
isobutane butene octane

The above equation shows the union of one molecule of isobutane with one molecule of a butene to produce one molecule of an octane. Similar reaction equations may be written for the alkylation of the above or other isoparaffins with various olefins. As will be brought out more fully hereinbelow the term "alkylation" includes not only the simple chemical combination of an isoparaffinic molecule with an olefinic molecule introduced into the sphere of reaction but also the production of branched chain paraffinic hydrocarbons having a molecular weight less than obtained by this simple chemical addition of an isoparaffinic molecule to an olefinic molecule introduced into the reaction sphere.

Olefins, as stated above, when subjected to proper reaction temperatures and pressures, in the presence of catalysts of the type of sulfuric acid, tend to form polymers. In fact, this tendency to polymerize, at least under certain conditions, occurs in preference to alkylation, so that, if a mixture of isoparaffinic or even cyclic hydrocarbons and olefins is brought into contact with a sulfuric acid catalyst the reaction

products will be found to contain only a relatively small percentage of alkylated products of reaction, the greater portion of the olefins, and particularly the more reactive forms thereof, having undergone polymerization in preference to their addition to the isoparaffinic or cyclic hydrocarbons to produce alkyl derivatives or alkymers thereof.

It is therefore the main object of the present invention to provide a process wherein alkylation of the isoparaffins shall be favored in preference to the polymerization of the olefins introduced into the reaction zone for the purpose of combining with the isoparaffinic hydrocarbons. It is a further object of the present invention to provide a process wherein valuable motor fuel fractions having high anti-detonating characteristics and substantially free of products of polymerization may be produced by alkylating the low boiling isoparaffinic hydrocarbons with normally gaseous or normally liquid olefins or with both types of olefins. It is a further object of the invention to modify the acid catalyst employed in such a manner that said modified catalyst will in effect tend to hinder polymerization of the olefins and simultaneously promote the combining of said olefins with the isoparaffinic hydrocarbons to form the alkymers thereof.

It has now been discovered that the above and other objects of the present invention may be realized by causing the reaction between isoparaffins and olefinic hydrocarbons to take place in the presence of a sulfuric acid catalyst containing a modifying agent which favors the alkylation of the isoparaffins in prefernce to the polymerization of the olefins introduced into the reaction zone. It has been further discovered that the mono-carboxylic and the di-carboxylic acids of relatively low molecular weights, such as acetic acid, propionic acid, butyric acid, oxalic acid, maleic acid, and other similar compounds, or mixtures thereof, are highly suitable as such addition compounds or modifying agents in that when combined with an acidic catalyst of the type of sulfuric acid, the substances or mixtures thereof tend to promote the combining of the olefins with the isoparaffins to produce alkylated isoparaffinic hydrocarbons, this reaction being favored in preference to the polymerization of the olefins.

The term "isoparaffins" or "isoparaffinic hydrocarbons," as employed in the present specification and claims, relates to the lower members, namely, isobutane, isopentane and isohexane. It has been discovered that the rates of alkylation of these isoparaffinic hydrocarbons, maintaining other conditions equal, are not the same. Thus, the rate of alkymer formation when isopentane is employed is considerably slower than the rate of alkylation of isobutane, while the alkylation rate of isohexane is even still lower.

As to the terms "olefins" and "olefinic hydrocarbons," as used herein, they relate to both the normally gaseous olefins, which comprise the hydrocarbons between about propylene and pentenes, and the normally liquid olefins, such as the hexenes and the higher olefins. It is to be noted, however, that it is not desirable to employ very high boiling olefins since the alkylation reactions become unfavorable when such olefins are employed. It has been found that, when normally liquid olefins are to be employed, it is preferable, although not absolutely essential, to use fractions having not more than about twelve carbon atoms per molecule.

It is to be understood that the reference to isoparaffinic and olefinic hydrocarbons includes the use of these hydrocarbons individually, or in mixtures with other hydrocarbons of the particular class, as well as mixtures thereof with other hydrocarbons.

The invention may be stated to reside broadly in reacting isoparaffins of the type of isobutane, isopentane and isohexane, with the described olefinic hydrocarbons in the presence of a sulfuric acid catalyst containing a modifying agent adapted to favor the alkylation of the isoparaffins in preference to the polymerization of the olefins introduced into the reaction zone. The invention further resides in reacting the described isoparaffinic hydrocarbons with normally gaseous or normally liquid olefins, at optimum temperatures and pressures, in the presence of a sulfuric acid catalyst containing a reaction modifying agent comprising the relatively low molecular weight mono- and di-carboxylic acids, such as acetic, propionic, butyric, oxalic and maleic acids, whereby the polymerization of the olefins is in effect hindered and the products of reaction comprise branched chain paraffinic hydrocarbons boiling within the gasoline range, having high anti-detonating characteristics, and being substantially free from polymers within said range.

In a more specific sense, the invention resides in the treatment of the described isoparaffins with normally gaseous olefins, between propylene and pentenes, at optimum temperatures and pressures, in the presence of sulfuric acid and a reaction modifying agent of the type of the relatively low molecular weight monocarboxylic and di-carboxylic acids, thereby producing high yields of branched chain saturated hydrocarbons boiling within the gasoline range, having high anti-detonating characteristics, and which fractions are substantially free from polymers boiling within this gasoline range.

The invention also resides in reacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with normally liquid olefins preferably below dodecenes, in the presence of sulfuric acid and the above described reaction modifying agent, whereby the products of reaction comprise branched chain paraffinic hydrocarbons boiling within the gasoline range, having high anti-detonating characteristics and being substantially free from products of polymerization boiling within the gasoline range.

The exact role of the catalyst mixture is not known at the present time. However, it is believed that the following theory may serve to explain the advantages realized when the aforementioned modifying agent is used in connection with the sulfuric acid catalyst to promote the alkylation of the isoparaffins. It is well known, as stated above, that the olefinic hydrocarbons are highly reactive and are readily polymerized when brought into contact with sulfuric acid, particularly when there is any degree of concentration of the olefins at any point of contact with the sulfuric acid. It is now believed that the presence of the modifying agent of the type of the lower molecular weight mono-carboxylic and di-carboxylic acids, prevents this undesirable polymerization of the olefins by combining with the olefins to form esters of these carboxylic acids. These esters then decompose or break down under the influence of the sulfuric acid into the carboxylic acid and the olefin.

In the meantime, however, the agitation of the mixture has caused the distribution or dispersion of the esters, thus increasing the chance of bringing the olefin molecules into contact with the isoparaffin molecules. The initial reaction of the above mono- or di-carboxylic acids with the olefins and the subsequent liberation of the olefins (after dispersion in the acid iso-paraffin mixture) is believed to decrease the tendency of polymerization of the olefins.

In one of its preferable embodiments the invention includes the realization of the alkylating reaction substantially in the liquid phase. In this case it is preferable to maintain substantially a concentration of isoparaffins in excess of the quantity theoretically necessary to combine with the olefins. For this purpose, the olefins, such as isobutane, isopentane, or is hexane or mixtures thereof, may first be commingled with the catalyst containing the described reaction modifying agent and the olefins may then be gradually introduced into this mixture. The reaction may be realized at ordinary or room temperatures, such as 70° to 80° F., it being understood that under certain conditions it may be advisable to conduct the reaction at higher or lower temperatures. The pressures employed are such as will cause the reacting hydrocarbons to be substantially in the liquid state. The mixture of isoparaffins and the alkylating catalyst should be preferably maintained in a state of vigorous agitation.

The presence of an excess of isoparaffins and the relatively gradual addition of the olefins prevents any local concentration of the olefins which would otherwise favor polymerization instead of the alkylation of the isoparaffins. In other words, the constant presence of an excess of isoparaffinic molecules increases the chances of the contact of an activated olefin with an activated isoparaffin molecule. Simultaneously, the relatively slow addition of the olefins decreases their concentration, thus also increasing the possibility of the alkylation reaction to take place in preference to the polymerization of the olefins.

The following examples are presented for the purpose of illustrating the advantages obtainable when using catalysts of the type described herein. In these experiments the isoparaffinic fraction employed comprised a narrow cut obtained from the stabilization of natural gasoline. This fraction consisted of substantially pure butanes in the proportion of approximately 85% isobutane and 15% normal butane. Obviously, the isoparaffinic fraction to be alkylated according to the present invention may consist of hydrocarbons other than the isobutane, such as isopentane, or may comprise a mixture containing these and other isoparaffins.

The specific olefin-containing fraction employed in the experiments was derived from cracking operations and had substantially the following composition:

	Percentage by volume of liquid
Ethylene	0.57
Ethane	4.50
Propylene	24.27
Propane	30.28
Isobutane	7.33
Isobutylene	12.63
n-Butylene	12.10
n-Butane	8.32
	100.00

It is thus seen that this olefin-containing fraction consisted of about 49% of unsaturates above ethylene, the ratio of propylene to the butylene being about 1 to 1.

In one of the runs, the catalyst consisted of a mixture containing 10% by volume of glacial acetic acid and 90% by volume of 92.3% H_2SO_4. The reaction, which continued for about nine hours, was realized by first commingling 1000 milliliters of the above catalyst with 3300 milliliters of the 85% isobutane containing fraction. The reaction temperature was maintained at 70° F., the pressure being sufficient to maintain the hydrocarbons substantially in a liquid state. Approximately 3800 milliliters of the olefin-containing fraction was then gradually and uniformly conveyed into the reaction zone. The yield of products of reaction based on the percentage by volume of the olefins added, was 126.3%. This fraction contained only 1.3% by weight of olefin polymers. The overhead fraction, distilled to an end point of 307° F. and comprising 103.6% by volume based on the olefins used, had a knock-rating of 89 and an olefin content of only 0.53%.

A second experiment was conducted under substantially the same conditions as those described hereinabove with the exception of employing a sulfuric acid catalyst of a strength of 94.0%, this catalyst being used without the addition of any modifying agent of the class described hereinabove. The use of the slightly stronger acid should have favored the production of alkymers. However, the yield of products of reaction was 102% by volume based on the olefins employed, this fraction containing 14.5% of olefins. Similarly, the overhead fraction having a 307° F. end-point and which comprised only 64.6% by volume of the olefins employed, contained 2.5% by weight of olefins. It is thus seen that the amount of polymerization accompanying alkylation was greater when using the sulfuric acid alone as compared to the experiment in which the acid contained a modifying agent of the type described.

The above disclosure is presented in connection with the alkylation of isoparaffins with olefins and emphasizes the simple addition of the relatively low molecular weight normally gaseous olefins to the specified isoparaffins. In addition it was discovered that in reacting the isoparaffins with normally liquid olefinic hydrocarbons the reaction product comprised a large proportion of saturated hydrocarbons of a branched chain structure boiling substantialy within the gasoline range. Such hydrocarbons evidently could be formed by an initial scission of at least one of the original reacting hydrocarbons into two or more hydrocarbons of lower molecular weight, and the subsequent reaction of these lower molecular weight hydrocarbons to produce isoparaffinic molecules. Or, this may be the result of simple addition of the introduced olefinic molecules to the isoparaffinic molecules followed by scission of the product. Specifically, this alkylation reaction might be termed "cracking alkylation" in order to distinguish it from the straight or simple addition of an olefin to an isoparaffin, as already described hereinabove. The "cracking alkylation" reaction, therefore, may be described as including the step of reacting olefin molecules with isoparaffin molecules to produce one or more paraffinic alkymers which have molecular weights of less than that which would be obtained providing the reaction were one of simple addition in which one olefinic molecule reacts with one

isoparaffinic molecule to produce a branched chain saturated molecule having a molecular weight equal to the sum of the molecular weights of the reacting olefin and isoparaffin.

Therefore, it has also been discovered that the reaction between the isoparaffins and certain of the olefins (and particularly the normally liquid olefins) in the presence of the described catalyst comprising sulfuric acid and a reaction modifying agent of the class described hereinabove, may result in both the simple alkylation of the isoparaffins by the olefins added, and in the cracking alkylation in which, as stated, alkymers are produced which have a lower molecular weight than would be obtained by simple addition of an isoparaffin to an olefin. The higher molecular weight olefins, as olefins above dodecenes, however, appear to be unsuitable to react effectively with the isoparaffins to form alkymers, the product of reaction, when using these high molecular weight olefins, containing excessive percentages of polymers boiling above the gasoline range.

The term "gasoline boiling range," as employed herein, refers to the average boiling range of fuels used in ordinary automobile engines. Generally speaking, such a gasoline has an initial boiling point of about 100° F., and a maximum or end point of around 425° F. The term "atmospheric pressure" refers to pressures in the neighborhood of that extracted by a column of mercury 760 mm. in height while "atmospheric temperature" and "room temperature" relate to temperatures in the vicinity of 70° F. to 80° F.

In carrying out the invention the apparatus used and the conditions of operation chosen in respect to temperature, pressure, proportions of reacting constituents, choice of acid and of the modifying or solubilizing agents, etc., will be varied to suit the individual case. Thus, although the alkylation reactions described herein were realized at substantially room temperatures, under certain conditions lower or higher temperatures may be employed.

The quantity of the modifying agent as well as the concentration of the sulfuric acid catalyst may be increased or decreased with a corresponding decrease in the quantity or ratio of the acid necessary to promote the alkylation operation. The ratio of the modifying agent to the sulfuric acid may vary from a very small quantity of the modifying agent up to as much as equal parts of the modifying agent and of the sulfuric acid. It has been found, however, that relatively small quantities of the modifying agent, such as acetic acid, is sufficient to aid alkylation in preference to the polymerization of the olefins, these mixtures containing up to 15% by volume of acetic acid and the balance sulfuric acid gave excellent results as is indicated by the previous presented examples.

The above disclosure is merely illustrative of the preferred embodiments of the present invention, and is not to be taken as limiting, since many variations thereof may be made within the scope of the following claims without departing from the spirit of the invention.

We claim:

1. A process of forming alkylated paraffinic hydrocarbons which comprises interacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with olefinic hydrocarbons having more than two carbon atoms per molecule in the presence of strong sulfuric acid and a low molecular weight carboxylic acid.

2. A process of forming alkylated paraffinic hydrocarbons which comprises interacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with olefinic hydrocarbons having more than two carbon atoms per molecule in the presence of strong sulphuric acid and a low molecular weight, di-carboxylic acid reaction modifying agent, wherein the alkylation of the isoparaffins is promoted.

3. In a process of forming motor fuels having anti-detonating characteristics which comprises reacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with normally gaseous olefins having a molecular weight above ethylene in the presence of a catalyst comprising strong sulfuric acid and a low molecular weight mono-carboxylic acid, thereby forming products of reaction which are substantially free from products of polymerization within the gasoline boiling range.

4. In a process of forming motor fuels having anti-detonating characteristics which comprises reacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with normally gaseous olefins having a molecular weight above ethylene in the presence of a catalyst comprising strong sulfuric acid and a low molecular weight di-carboxylic acid, thereby forming products of reaction which are substantially free from products of polymerization within the gasoline boiling range.

5. A process of forming branched chain paraffinic hydrocarbons falling within the gasoline range, having high anti-detonating characteristics and substantially free from polymers within the gasoline boiling range, which comprises reacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with normally gaseous olefinic hydrocarbons having more than two carbon atoms per molecule in the presence of strong sulfuric acid containing a low molecular weight mono-carboxylic acid whereby the polymerization of the olefins is hindered and the alkylation of the isoparaffinic hydrocarbons, by said olefins, is promoted.

6. In a process according to claim 5, wherein a relatively small percentage of the mono-carboxylic acid is employed in the catalyst.

7. In a process according to claim 5 wherein the mono-carboxylic acid is an amount less than about 15% of the catalyst employed.

8. In a process according to claim 5 wherein the mono-carboxylic acid employed as the reaction modifying agent is glacial acetic acid.

9. A process of forming alkylated isoparaffinic hydrocarbons having high anti-detonating characteristics suitable as motor fuel which comprises commingling isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with a catalyst mixture comprising strong sulfuric acid containing a low molecular weight mono-carboxylic acid, and introducing into said isoparaffin-catalyst mixture normally gaseous olefinic hydrocarbons having more than two carbon atoms per molecule thereby alkylating said isoparaffinic hydrocarbons and hindering the polymerization of the olefins.

10. In a process according to claim 9 wherein the reaction modifying agent comprises a relatively small proportion of the catalyst employed.

11. In a process according to claim 9 wherein the reaction modifying agent comprises glacial acetic acid.

12. In a process according to claim 9 wherein the reaction modifying agent comprises glacial acetic acid and wherein said glacial acetic acid

comprises an amount less than 15% of the volume of the catalyst employed.

13. A process of forming alkylated isoparaffinic hydrocarbons having high anti-detonating characteristics suitable as motor fuels which comprises commingling isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with a catalyst mixture comprising strong sulfuric acid catalyst containing low molecular weight di-carboxylic acid, and introducing into said isoparaffin catalyst a mixture of normally gaseous olefinic hydrocarbons having a molecular weight above ethylene, thereby alkylating said isoparaffinic hydrocarbons and hindering the polymerization of the olefins.

14. A process for producing branched chain saturated hydrocarbons having molecular weights within the gasoline boiling range and substantially free from polymers within said range which comprises commingling isoparaffinic hydrocarbons of less than seven carbon atoms per molecule with a catalyst mixture containing strong sulfuric acid and a relatively small percent of a di-carboxylic acid, maintaining said mixture in a state of agitation and at normal temperature and at a pressure sufficient to maintain the isoparaffins in a liquid state, introducing normally liquid olefins having less than thirteen carbon atoms per molecule into said mixture, thereby causing a reaction between said olefins and isoparaffins to produce said branched chain saturated hydrocarbons and to hinder polymerization of the olefins and separately recovering said products of reaction.

15. A process for producing branched chain saturated hydrocarbons having molecular weight within the gasoline boiling range and substantially free from polymer within said range which comprises commingling isoparaffinic hydrocarbons of less than seven carbon atoms per molecule with a strong sulfuric acid catalyst containing relatively small proportions of glacial acetic acid, maintaining said mixture in a state of agitation and at a normal temperature and at a pressure sufficient to maintain the isoparaffins in a liquid state, and introducing normally gaseous olefins having a molecular weight above ethylene into said mixture, thereby causing a reaction between said olefins and isoparaffins to produce said branched chain saturated hydrocarbons and to hinder polymerization of the olefins.

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