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ALKYLATION OF ISOPARAFFINS WITH ETHYLENE

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The present invention relates to the synthesis of hydrocarbons, and more particularly refers to the manufacture of paraffinic hydrocarbons of a branched chain type especially suitable as fuel in automobile and aviation engines.

Recently, it has been proposed to produce branched chain hydrocarbon fractions boiling within the gasoline range and having high anti-detonating characteristics, by alkylating isoparaffinic hydrocarbons with olefins. This alkylation reaction was found to occur when the two hydrocarbon fractions were brought into contact with each other in the presence of a catalyzing agent, such as sulfuric acid.

The reaction between one or more olefin molecules and one or more isoparaffinc hydrocarbon molecules produced a branched chain paraffinic molecule. This reaction is called "alkylation," and the product is herein termed an "alkymer" in order to distinguish it from a "polymer" which is the product resulting from the interaction of two or more olefin molecules.

Theoretically, the interaction between an isoparaffinic hydrocarbon and an olefinic hydrocarbon in the presence of a suitable alkylating catalyst is of a simple character. Thus, the combination which takes place when isobutane is chemically combined with a butene may be expressed by the following equation:

$$C_4H_{10}+C_4H_8\rightarrow C_8H_{18}$$

Isobutane butene octane

The above equation shows a reaction in which the union of one molecule of isobutane with one molecule of butene produces one molecule of an octane. Similar alkylation equations may be written for the alkylation of the above and other isoparaffins with various olefins.

Motor fuels, and particularly fuels which are to be used in automobile and aviation engines contain different hydrocarbons having different boiling ranges, in fact, motor fuel specifications require the presence of these various hydrocarbons. Thus, the motor fuel fractions must have a relatively low initial boiling point for certain percentages boiling at different temperatures. Generally speaking, these motor fuels contain hydrocarbons ranging from the five-carbon molecules to and including the ten-carbon molecules. Therefore, to produce a motor fuel fraction of isoparaffins with olefins it is necessary to alkylate several of the relatively low boiling isoparaffinic hydrocarbons with different olefins. In view of the fact that the lowest isoparaffin is isobutane, and in order to produce an alkylated fraction which would satisfy the lower boiling bracket of the gasoline, it is necessary to alkylate isobutane with ethylene, this alkylation resulting in a fraction of isohexanes.

The ordinary known alkylating catalysts, however, are substantially ineffectual in causing the alkylation of isoparaffins with ethylene. Thus, under ordinary conditions of operation, namely at normal temperatures and at pressures sufficient to cause the maintenance of the hydrocarbons in a liquid phase, strong sulfuric acid will cause an efficient combining of isoparaffins, such as isobutane and isopentane, with the normally gaseous olefins of the class of propylene, butylene and pentenes, the products of reaction comprising branched chain saturated hydrocarbons boiling within the gasoline range, having high anti-detonating characteristics, and being susbtantially free from polymers boiling within this range. However, the treatment of the above isoparaffins with ethylene, under the same conditions and in the presence of the same catalyst, did not cause the combining of the isoparaffins with ethylene. It is, therefore, the main object of the present invention to provide a catalytic process which will cause the alkylation of the relatively low boiling isoparaffins with ethylene. It is a further object of this invention to provide a process which will utilize ethylene in the production of motor fuel fractions and constituents thereof, which possess high anti-detonating characteristics.

It is a further object of the invention to provide a process wherein alkylation of isoparaffins of the class of isobutane, isopentane, and isohexane with ethylene will be favored in preference to any polymerization of the ethylene introduced into the reaction zone for the purpose of combining with the isoparaffinic hydrocarbons to produce alkylated fractions suitable as motor fuels or constituents thereof. It is a still further object of the invention to provide a catalyst or a catalyst mixture which is adapted to cause this alkylation of the isoparaffins with ethylene to produce the above described motor fuel fraction of the branched chain saturated type, these fractions possessing high anti-detonating qualities.

The term "isoparaffins" or "isoparaffinic hydrocarbons," as employed in the present application and claims relates to the lower members, namely isobutane, isopentane and isohexane. The rates of alkylation of these isoparaffinic hydrocarbons, maintaining other conditions equal, are, however, 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.

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

The above and other objects may be attained by conducting the alkylation reaction in the presence of a catalyst comprising sulfuric acid and a modifying agent of the type of a metal oxide or a metal salt. The objects may further be attained by effecting a reaction between the isoparaffinic hydrocarbons and ethylene, or ethylene-containing gases in the presence of a catalyst comprising sulfuric acid and a reaction modifying agent of the type of the phosphates, sulfates, chlorides, nitrates, acetates or other salts or oxides of metals such as cadmium, zinc, mercury, copper, silver, barium or the like.

The invention may, therefore, be stated to reside in the treatment of isoparaffinic hydrocarbons of the type of isobutane, isopentane and isohexane, with ethylene, or with an ethylene-containing gas, in the presence of a sulfuric acid catalyst containing one or more of the above salts and/or oxides of the enumerated metals, whereby the products of reaction comprise or include alkylated branched chain hydrocarbons having a high antiknock value, said products of alkylation boiling within the gasoline range and being substantially free from polymers. The invention still further resides in the treatment of the relatively low-boiling isoparaffinic hydrocarbons such as isobutane, isopentane or isohexane, and mixtures thereof, with ethylene, or gases containing ethylene, in the presence of a catalyst comprising sulfuric acid of a 85% to 100% H_2SO_4 content, and containing a reaction modifying agent of the type of the phosphates, sulfates, chlorides, nitrates, acetates or oxides of cadmium, zinc, mercury, copper, silver, barium or the like, or mixtures of these salts and/or oxides, whereby the products of reaction comprise higher boiling alkylated or branched chain hydrocarbons having high anti-detonating characteristics and suitable as fuel for use in automobile and aviation engines, said products being substantially free from polymers.

The invention still further resides in the use of relatively small percentages of the above enumerated salts and/or oxides, in combination with the sulfuric acid catalyst. Thus, although larger percentages may be employed, excellent yields are obtainable by using a sulfuric acid catalyst containing between about 1% and 10% of the above salts, as calculated on the basis of the total quantity of the catalyst employed for the alkylation of the isoparaffins with ethylene. These percentages of the above salts, and particularly of the sulfates of mercury, copper, silver, zinc, cadmium or barium, when employed together with the relatively strong sulfuric acid, produce good yields of alkymers resulting from the addition of ethylene to the isoparaffins.

In operating according to the present invention, the isoparaffinic hydrocarbons, for example isobutane, or a mixture thereof with higher molecular weight isoparaffins, is first commingled with the catalyst described above. As stated the metal salt or oxide can comprise only a small percentage of the total quantity of the catalyst used. Nevertheless, there is no intention to be limited to any percentage since under some conditions the reaction may be carried out with as much as about equal quantities of sulfuric acid and of cadmium sulfate.

The ethylene used for the alkylation is introduced into the above mixture of isoparaffins and catalyst, this introduction being preferably gradual and accompanied by vigorous agitation. The preliminary commingling of the catalyst with the isoparaffins, as well as the gradual addition of the olefins and the agitation, aid in decreasing the tendency of the ethylene to polymerize, and at the same time aid in bringing the ethylene molecules into contact with the activated isoparaffinic molecules, thereby aiding in the formation of alkymers in preference to any polymerization of the ethylene.

It is obvious that the ethylene may be impure. Thus, it may be in a gas, or in the presence of some inert gaseous materials.

The introduction of the ethylene, or of the ethylene-containing gas, may be continued until the character of the products of reaction changes markedly. This is usually an indication that the alkylating effect of the catalyst is exhausted to such an extent that polymerization of the ethylene becomes the predominant feature of the reaction.

After settling, the hydrocarbon fraction is separated, and may be treated in any known manner, as by stabilization, etc. The alkymers thus produced have excellent anti-detonating characteristics, and are fully saturated, thus making them highly useful as addition agents capable of greatly increasing the knock rating of other motor fuel fractions.

The above described reaction may be in the liquid phase, in which case the reaction should preferably be realized at pressures sufficient to maintain at least the isoparaffins in the liquid state. The ethylene may then be conveyed into the mixture of isoparaffins and sulfuric acid catalyst containing the activating salt. For this purpose the pressures may be as high as 150 to 200 pounds, the reaction being realized at ordinary temperatures such as 70 to 75° F. It is obvious that these temperatures and pressures may be varied within a relatively wide range.

The term "gasoline boiling range" as employed herein refers to the average boiling range of fuels used in the ordinary automobile engines. Generally speaking, such gasoline has an initial boiling point of about 100° F. and a maximum end point of 425° 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 strength of acid and of the metal oxide or salt, the proportions thereof, etc., may be varied to suit the individual case. The quantity of the metal salt or oxide described above may be decreased or increased with a corresponding decrease or increase in the quantity of the acid necessary to promote the described alkylation with ethylene.

The above disclosure is merely illustrative of the preferred embodiments of the invention, and is not to be taken as limiting, since many variations thereof may be made within the scope of the following claims.

I claim:

1. A process of forming branched chain paraffinic hydrocarbons having high anti-detonating characteristics and suitable as motor fuel, which comprises interacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule

with ethylene in the presence of a catalyst comprising strong sulfuric acid and a modifying agent selected from the class consisting of the phosphates, sulfates, chlorides, nitrates, acetates and oxides of cadmium, zinc, mercury, copper, silver and barium.

2. In a process according to claim 1, wherein the quantity of the modifying agent comprises a relatively small percentage of the total quantity of the catalyst employed.

3. In a process according to claim 1, wherein the quantity of the modifying agent comprises between about 1% and 10% of the total quantity of the catalyst employed.

4. A process of producing alkylated isoparaffinic hydrocarbons, boiling within the gasoline boiling range and substantially free from polymers which comprises reacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule, with ethylene in the presence of a catalyst comprising sulfuric acid of a strength between about 85% and 100% H_2SO_4 and a modifying agent adapted to cause the alkylation of the isoparaffins in preference to the polymerization of ethylene and selected from the class consisting of the phosphates, sulfates, chlorides, nitrates, acetates and oxides of cadmium, zinc, mercury, copper, silver and barium.

5. A process of forming branched chain paraffinic hydrocarbons within the gasoline boiling range, which comprises reacting low boiling isoparaffinic hydrocarbons with ethylene in the presence of a catalyst comprising sulfuric acid of a strength of about 85% to 100% H_2SO_4 and a relatively small percentage of a modifying agent selected from the class consisting of the phosphates, sulfates, chlorides, nitrates, acetates and oxides of cadmium, zinc, mercury, copper, silver and barium.

6. In a process according to claim 5, wherein the quantity of the modifying agent comprises between about 1% to 10% of the total quantity of the catalyst employed.

7. A process to produce branched chain paraffinic hydrocarbons having high anti-detonating characteristics, which comprises commingling isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with a catalyst consisting of strong sulfuric acid and relatively small quantities of a modifying agent selected from the class consisting of the phosphates, sulfates, chlorides, nitrates, acetates and oxides of cadmium, zinc, mercury, copper, silver and barium, and bringing ethylene into contact with said isoparaffinic-catalyst mixture, thereby causing the alkylation of the isoparaffins with the ethylene to produce said branched chain paraffins substantially free from products of polymerization of ethylene.

8. In a process according to claim 7, wherein the addition of the ethylene is accompanied by vigorous agitation.

9. In a process according to claim 7, wherein the addition of ethylene into the isoparaffin-catalyst mixture is gradual and accompanied by vigorous agitation.

10. The process of forming alkylated isoparaffinic hydrocarbons having high anti-detonating characteristics and boiling within the gasoline range, which comprises commingling isoparaffinic hydrocarbons of less than seven carbon atoms per molecule with a catalyst comprising sulfuric acid of a concentration between about 85% to 100% H_2SO_4 and a modifying agent selected from the class of the phosphates, sulfates, chlorides, nitrates, acetates and oxides of cadmium, zinc, mercury, copper, silver and barium, gradually introducing an ethylene-containing gas into said isoparaffin-catalyst mixture to cause an alkylation reaction between the isoparaffins and the ethylene, and separating the alkylated isoparaffins from the unreacted mixture.

11. In a process according to claim 10, wherein the isoparaffinic hydrocarbon to be alkylated comprises isobutane, and wherein the alkylating reaction is aided by agitating the mixture.

12. A process of forming alkylated isoparaffinic hydrocarbons having high anti-detonating characteristics, which comprises commingling isoparaffinic hydrocarbons having less than seven carbon atoms per molecule, while under pressure sufficient to maintain said hydrocarbons in a liquid state, with a catalyst comprising strong sulfuric acid and a modifying agent selected from the class consisting of the phosphates, sulfates, chlorides, nitrates, acetates and oxides of cadmium, zinc, mercury, copper, silver and barium, and bringing ethylene into contact with said isoparaffin-catalyst mixture thereby causing the alkylation of isoparaffins with the ethylene to produce branched chain paraffins substantially free from products of polymerization of ethylene.

13. A process according to claim 12 wherein isobutane is employed as the isoparaffinic hydrocarbon fraction.

14. A process according to claim 7 wherein isobutane is employed as the isoparaffinic hydrocarbon to be alkylated and wherein the addition of the ethylene into the isobutane-catalyst mixture is gradual and accompanied by vigorous agitation.

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