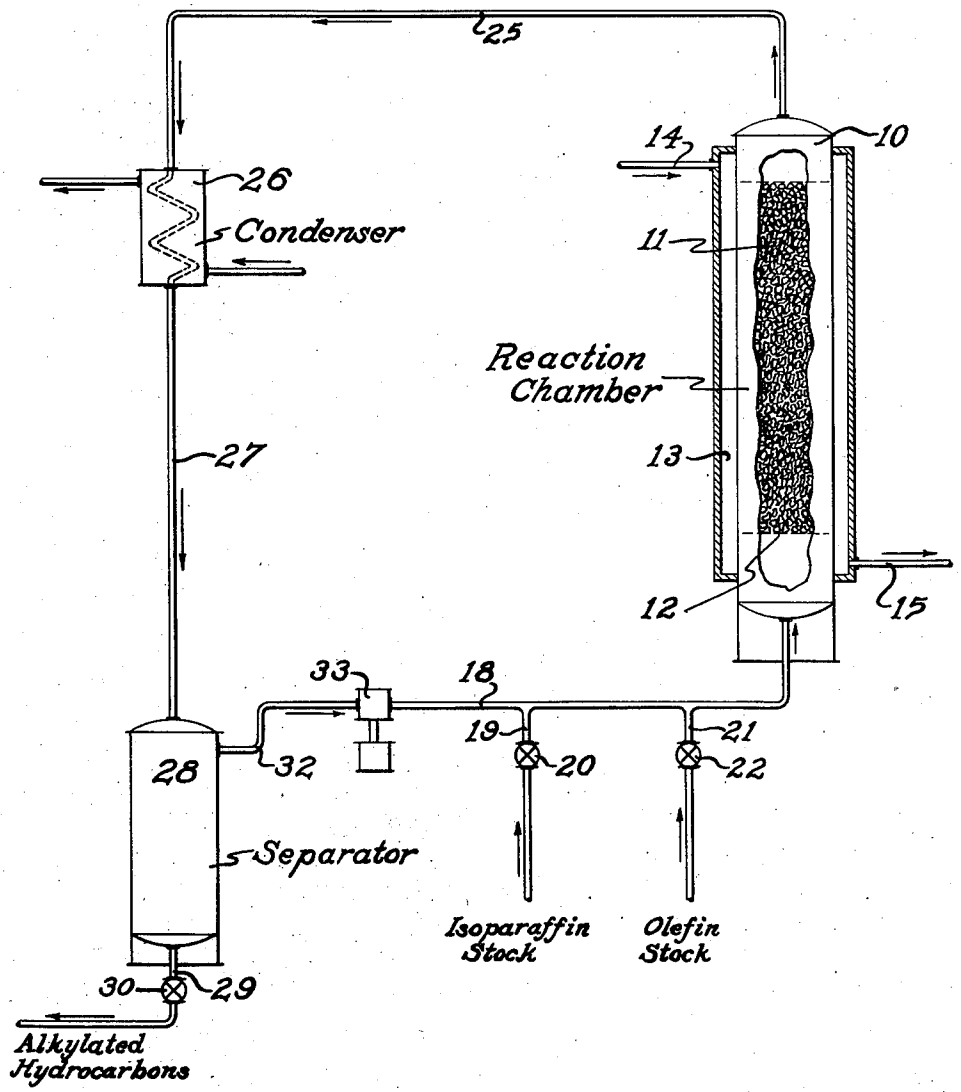
Dec. 26, 1944. W. E. BRADLEY ET AL 2,365,860

ALKYLATION OF ISOPARAFFINIC HYDROCARBONS

Filed June 18, 1941



INVENTORS

William E. Bradley & Karl J. Korpi

BY Ross J. Garofalo

ATTORNEY

Patented Dec. 26, 1944

2,365,860

UNITED STATES PATENT OFFICE

2,365,860

ALKYLATION OF ISOPARAFFINIC HYDROCARBONS

William E. Bradley, Los Angeles, and Karl J. Korpi, Redondo Beach, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Application June 18, 1941, Serial No. 398,645

4 Claims. (Cl. 260—683.4)

The present invention relates to the synthesis of hydrocarbons, and refers more particularly to the manufacture of paraffinic hydrocarbons of a branched chain type suitable for use in automobile and aviation engines. In a more specific sense the invention comprises a process for the combining of isoparaffinic hydrocarbons of relatively low molecular weights with olefinic hydrocarbons to produce branched chain paraffinic hydrocarbons of higher molecular weight and boiling within the gasoline range, which are of particular value as motor fuels or constituents thereof in that they possess unusual anti-detonating characteristics. The invention further comprises the use of special catalysts and conditions of operation for the manufacture of these valuable compounds. This case is a continuation, in part, of our copending application, Serial No. 204,355, filed April 26, 1938.

The comparatively recent adoption of high compression ratios in automobile and aviation engines to increase their thermo-dynamic efficiency placed a demand upon the petroleum refining and similar industries to furnish hydrocarbon motor fuels of a high anti-knock or slow burning character. Thus, in the aviation industry there is an insistent demand for gasolines having knock ratings of 100 octane (as determined by the A. S. T. M. method) and containing not more than three milliliters of tetraethyl lead per gallon of gasoline.

In an attempt to provide motor fuels having the above characteristics and also satisfying other requirements, it has been recently proposed to produce synthetic fuels by combining aromatic or isoparaffinic hydrocarbons with olefinic hydrocarbons. This reaction, realized in the liquid phase, involves the contacting of the above mentioned hydrocarbons in the presence of a suitable catalyst. To prevent polymerization, i. e. the combining of two or more olefinic molecules into a single molecule, and to permit the addition of the olefinic hydrocarbon molecule to the aromatic or isoparaffinic molecule, this liquid phase "alkylation" is preferably realized by first commingling the aromatic or isoparaffinic hydrocarbons with a catalyst, such as sulfuric acid, and then introducing the olefins or olefin-containing gas, the mixture being maintained in a state of agitation to provide adequate contact between the two hydrocarbon fractions to be interacted. The catalysts employed for this alkylation reaction include sulfuric acid, aluminum chloride, etc.

The reaction between isoparaffinic hydrocarbons and olefins, to produce alkylated hydrocarbons or "alkylates," may, however, also be realized in the vapor phase, this alkylation reaction possessing certain advantages peculiar to the vapor phase treatment. Thus, the vapor phase alkylation of isoparaffins, of the type of isobutane and isopentane, with normally gaseous or normally liquid olefins does not require any subsequent fractional distillation of the products of reaction. This is because the vaporous or gaseous mixture leaving the reaction chamber may be conveyed into a condenser which is maintained at such a temperature that the alkylates are condensed without liquefying the unconverted hydrocarbons. As an example, the mixture of the isoparaffinic and olefinic hydrocarbons to be interacted may be conveyed as a gaseous or vapor mixture, and at optimum temperatures and pressures, through the reaction chamber containing a suitable alkylation catalyst described more fully hereinbelow. The products of reaction leaving this reaction chamber, aside from alkylated isoparaffins, also contain a certain proportion of unreacted hydrocarbons. This mixture may then be conveyed through the aforementioned condenser wherein the alkylates are caused to condense. These alkylates may then be easily removed, while the unreacted hydrocarbons, predominating in unreacted isoparaffins, may be recycled through the system after the addition of optimum or suitable quantities of the olefins.

Another advantage of the vapor phase process resides in the fact that it is possible to employ high temperatures without the necessity of operating at the vapor pressures of the hydrocarbon treated. These operations at the relatively high temperatures favor the rate of reaction, thus increasing the yield of alkylates per unit of time. A still further advantage resides in the fact that the treatment of the hydrocarbons in the vapor phase permits a control of the reaction, since it is possible to mix thoroughly the olefinic hydrocarbons with the isoparaffinic hydrocarbons to be alkylated before introducing the mixture into the reaction chamber. This thorough commingling prevents any possible local over-concentration of the olefins, thus decreasing the tendency of these olefins to polymerize, and simultaneously favoring the desired alkylation reaction.

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

As to the terms "olefins" and "olefinic hydrocarbons," they are used herein to denote both the normally gaseous olefins and the normally liquid olefins. The normally gaseous olefinic hydrocar-

bons comprise the unsaturates between propylene and the pentenes, while the liquid olefins include the hexenes and other olefins of greater molecular weight. However, as will be brought out more fully hereinbelow, it is preferable not to employ the very high boiling olefins since the conditions then become unfavorable for the alkylation of the specified isoparaffins. It is now believed 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, in mixtures with other hydrocarbons of the same class, or mixtures thereof with other hydrocarbons.

The catalytic vapor phase alkylation described herein may be conducted at relatively low temperatures and pressures. Thus, even for the lowest molecular weight isoparaffinic hydrocarbons to be alkylated, as for example when isobutane is to be alkylated according to the present process, the temperature need not exceed about 750° F. These temperatures, depending on the hydrocarbons to be alkylated, may preferably be between about 100° and 600° F. Also, the pressures necessary are comparatively low, being preferably in the neighborhood of 20 to 300 pounds per square inch. Obviously, the optimum operating temperatures will vary with the pressures employed. For example, instead of operating at the above relatively low pressures, the reaction may be realized at considerably higher pressures, for example, up to 1000 pounds per square inch and even higher without in any way impairing, and even increasing, the reaction rates.

The alkylation reaction may be performed in the presence of any suitable catalyst, for example, sulfuric acid, mixtures thereof with phosphoric acid, or of these catalysts with other substances, such as certain metallic salts which tend to favor the alkylation reaction. When using a liquid catalyst, the mixture of hydrocarbon vapors or gases to be treated may be bubbled through the catalyst maintained at a suitable temperature. It has been discovered, however, that the use of solid catalysts is highly effective and results in high yields of alkylates without the formation of polymers and similar undesirable side reactions. It has been further discovered that metallic halide aluminates such as, for instance, the sodium, potassium or iron chloraluminates as such, or on a suitable support and in the presence or absence of a halogen acid are excellent catalysts for the alkylation in a vapor phase. Also solid acid sulphates and mixtures of these with acid phosphates, such as zinc or cadmium acid sulphates or phosphates alone or on suitable supports may be employed very effectively. Another group of catalysts which has been found to cause the alkylation of the isoparaffinic hydrocarbons, when realizing the reaction in the vapor phase, includes the solid catalysts formed by the partial saturation of activated carbon or bleaching clays and similar earths with sulfuric acid or mixtures of sulfuric and phosphoric acids, as well as with these acids in combination with certain metallic activators which tend to favor the alkylation in preference to the polymerization of the olefins conveyed through the reaction zone. These metallic activators include the sulphates, phosphates, acetates, chlorides, nitrates and oxides of metals such as cadmium, zinc, copper, mercury, silver and barium. The use of the above described solid alkylation catalysts has been found to increase considerably the yield of alkylates as well as the possible rate of throughput of the hydrocarbons to be treated.

The invention may therefore be stated to reside broadly in the vapor phase alkylation in the presence of an alkylating catalyst. The invention still further resides in the vapor phase alkylation of isoparaffinic hydrocarbons of less than seven carbon atoms per molecule, with olefins having more than two carbon atoms and preferably less than thirteen carbon atoms.

The invention still further includes the catalytic alkylation of isoparaffinic hydrocarbons of less than seven carbon atoms per molecule, in a gaseous or vapor state, said reaction being conducted at temperatures below about 750° F., and preferably in the neighborhood of 100 to 600° F., depending on the hydrocarbons being alkylated. Still further, the invention includes the realization of the above vapor phase alkylation at pressures of between about 20 and 300 pounds per square inch.

More specifically, the invention may be stated to reside in reacting low molecular weight isoparaffinic hydrocarbons of the type of isobutane, isopentane, and isohexane, with olefinic hydrocarbons above ethylene and below about dodecene, said reaction being realized in a vapor phase, in the presence of an alkylating catalyst, and at temperatures of below about 750° F. and pressures in the neighborhood of 20 to 300 pounds per square inch, whereby the products of reaction comprise branched chain hydrocarbons boiling within the gasoline boiling range, having high anti-detonating characteristics, and being substantially free from polymers within said gasoline boiling range. As previously stated, the above vapor phase reaction may be conducted at temperatures between about 100° F. and 600° F., depending on the hydrocarbons treated and on the pressures employed.

In a more specific sense the invention resides in the vapor phase treatment of the above isoparaffins with normally gaseous olefins above ethylene, in the presence of an alkylating catalyst and at optimum temperatures and pressures, to produce alkylates boiling substantially within the gasoline range and being substantially free from polymers boiling within said range. The invention also includes the vapor phase treatment of isoparaffins below isoheptane with normally liquid olefinic hydrocarbons having less than thirteen carbon atoms per molecule, at temperatures of below 750° F. and pressures of between about 20 and 300 pounds per square inch, and in the presence of a suitable alkylating catalyst, to produce predominantly alkylates boiling within the gasoline range and substantially free from products of polymerization within said range.

The invention also covers the treatment of the above isoparaffinic hydrocarbons with the defined olefins, in the vapor phase and in the presence of a solid catalyst, to produce branched chain saturated hydrocarbons boiling within the gasoline range, having high anti-detonating characteristics, and being substantially free from olefin polymers boiling within said range. The invention still further includes the commingling of the vapors or gases of the above described isoparaffinic and olefinic hydrocarbons, and the bringing of said mixtures, at optimum temperatures and pressures, in contact with solid catalysts of the type of the metallic halide aluminates, such as the sodium, potassium and

iron chloraluminates, in the presence of a halogen acid, acid sulfates, mixtures of said sulfates and phosphates, sulfuric acid and mixtures of phosphoric and sulfuric acid on suitable supporting materials, with or without the addition of the above described metal salt activators.

In one of its specific embodiments, the invention resides in the continuous vapor phase alkylation of isoparaffinic hydrocarbons of less than seven carbon atoms per molecule with olefins of more than two and less than about thirteen carbon atoms, which comprises conveying the mixtures of these hydrocarbons to be alkylated with the olefins, in a vapor state, through a reaction zone containing an alkylating catalyst maintained at a suitable temperature, continuously withdrawing the products of reaction from the reaction zone, and continuously cooling these products to a temperature at which the products of alkylation formed during the reaction are caused to condense without liquefaction of the unreacted or nonalkylated hydrocarbons. The invention further includes the separation of the alkylates from the uncondensed hydrocarbons, and the continuous recycling of the vaporous or gaseous hydrocarbons through the reaction zone, after the addition of and the commingling with suitable or necessary quantities of the olefinic hydrocarbons. In this embodiment of the invention, additional quantities of the hydrocarbons to be alkylated may be continuously or periodically introduced into the system to make up for the hydrocarbons which have been used up in the formation of the alkylates. Obviously, to conduct this vapor phase alkylation, these hydrocarbons must necessarily be in a vapor or gaseous state prior to the time when they come in contact with the alkylating catalyst. Also, the outlined continuous vapor phase alkylation may be realized at temperatures below about 750° F. (and preferably between about 100° F. and 600° F.) and at pressures in the neighborhood of between about 20 and 300 pounds per square inch or higher.

The term "gasoline boiling range" as employed herein refers to the average boiling range of fuels employed in ordinary automobile engines. Generally speaking such a gasoline has an initial boiling point of around 100° F., and a maximum or end point of about 425° F.

Reference is now had to the accompanying drawing which shows diagrammatically one embodiment of the present invention. As will be described hereinbelow, the drawing discloses a continuous method of vapor phase alkylation of an isoparaffinic hydrocarbon of the class described with an olefin to produce motor fuels having high anti-detonating characteristics and substantially free from polymers. It is obvious, however, that the method described can be employed equally in connection with a discontinuous or batch system.

Referring now to the drawing, the numeral 10 indicates a reaction chamber which contains a suitable catalyst 11. As shown, this catalyst may be held in place on a suitable support 12 which may be in the nature of a perforated plate. For the purpose of maintaining the catalyst at the desired temperature, reactor 10 may be provided with a jacket 13 which may be heated or cooled (as the case may be) by any suitable means, such as steam, water, etc., introduced through line 14 and withdrawn from jacket 13 through discharge line 15. It is clear that any other means may be employed to control and regulate the temperature within the reactor 10. The mixture of hydrocarbons to be reacted is introduced into reacting chamber 10 through line 18, the isoparaffinic hydrocarbons being fed into said line through branch 19 (provided with a valve 20). The olefins or olefin-containing gases are introduced into the system through line 21 also equipped with a valve 22.

The products of reaction leave reactor 10, and are conveyed through line 25 to a condenser 26 which is preferably maintained at a temperature which will cause the fractional condensation of the alkylates produced without liquefying the isoparaffinic hydrocarbons being treated. The liquid vapor mixture thus formed is then removed from condenser 26 and conveyed through line 27 to a separator 28 wherein the alkylates are caused to separate from the uncondensed fractions. These alkylated branched chain paraffinic hydrocarbons or alkylates may then be removed continuously or otherwise through discharge pipe 29 having a valve 30. The uncondensed hydrocarbons (which comprise or include the hydrocarbons to be alkylated) are withdrawn from the upper portion of separator 28, and conveyed, through pipe 32 and blower or vapor circulating pump 33, back into line 18 wherein they are commingled with new quantities of olefins before reintroduction into the alkylating reactor 10.

In operation, an isoparaffinic hydrocarbon, such as isobutane may be continuously or periodically introduced into the system through line 19. The olefinic hydrocarbons or gases containing the same, may be introduced through line 21, the rate of introduction being regulated by valve 22. Both hydrocarbon fractions are preferably brought to the desired temperature prior to their commingling in line 18. Obviously, however, either or both of these fractions may be in a liquid state and may be vaporized and heated to the optimum or desired alkylating temperature after their commingling in line 18. This mixture is then conveyed, at a predetermined rate, through reactor 10 and in contact with the catalyst 11 maintained therein. The products of reaction leaving through line 25 are continuously cooled in condenser 26 so that only the alkylates (alkylated isoparaffins) are liquefied. After separation in 28, the unconverted isoparaffins are then continuously recycled back into line 18 where they are again mixed with additional quantities of olefins. Since at least part of the isoparaffins are continuously alkylated and withdrawn as alkylates through line 29, additional quantities of the isoparaffins may be added either continuously or periodically through line 19.

The temperatures and pressures maintained in reactor 10, and in the other parts of the system, may be regulated to obtain optimum vapor phase alkylation of the given isoparaffinic hydrocarbon fraction or fractions. These operating conditions, as well as the proportions of the reacting constituents, rates of throughput, etc., may be varied to suit individual cases. Thus, in the case of alkylating isobutanes with olefins in the presence of a catalyst comprising sulfuric acid absorbed on active carbon, the hydrocarbons may be heated to between about 100° and 150° F., and may be conveyed at a pressure of 40 pounds per square inch through the reactor. Obviously, these pressures, etc., are only indicative, and are not to be considered as limiting, since various factors so far unmentioned

of hydrocarbons to be alkylated will effect these optimum operating conditions.

In operating according to the preferred embodiments, it is preferable to maintain, during the whole course of the reaction, an isoparaffin concentration in excess of that quantity theoretically necessary to combine with the olefins. For this purpose, the mixture of hydrocarbons being conveyed to reactor 10 should always contain an excess of isoparaffins. The isoparaffins remaining unaffected at the end of each cycle may then be recommingled with additional quantities of the given olefins. As stated, additional quantities of the isoparaffins may also be introduced to take the place of the portion alkylated. In the continuous process described, it is possible to add the olefins continuously, while maintaining an excess of the isoparaffins in the system. The presence of this excess of isoparaffins and the relatively gradual addition of olefins prevents any local overconcentration of the olefins which would otherwise favor polymerization instead of the alkylation of the isoparaffinic hydrocarbons. In other words, the constant presence of an excess of isoparaffinic molecules in the gaseous or vapor mixture, increases the chances of an immediate or substantially immediate contact of an activated olefin with an activated isoparaffin molecule. Simultaneously, the relatively slow addition of the olefins decreases their concentration in the mixture, thus also increasing the possibilities of the alkylation reaction to take place in preference to the polymerization of these olefins.

Briefly stated, alkylation reaction between an isoparaffinic hydrocarbon and an olefin, in the presence of an alkylating catalyst may be of a simple character. Thus, an isobutane molecule may combine chemically with a butene to produce a branched chain paraffinic hydrocarbon which is an octane. In other words this straight alkylation is in the order of a simple addition of an introduced olefin molecule to an isoparaffinic molecule. However, the reaction is somewhat more complex. Thus, when the specified isoparaffins are reacted with the normally liquid olefinic hydrocarbons, the reaction product comprises a large proportion of saturated hydrocarbons of a branched chain structure boiling substantially 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 by the subsequent reaction between these lower molecular weight hydrocarbons to produce the alkylated branched chain saturated hydrocarbon molecules. In the alternative, the above phenomena may be the result of a simple addition of the introduced olefinic molecules to the isoparaffinic molecules, followed by a scission of the product. Specifically, this alkylation reaction may be termed "cracking alkylation" in order to distinguish it from the straight or simple addition of an introduced olefin to an isoparaffin, as this has been described hereinabove. Therefore, the "cracking alkylation" reaction may be described as including the step of reacting of olefin molecules with isoparaffin molecules to produce isoparaffinic alkylate molecules which have molecular weights of less than that obtainable if the reaction was of the simple addition type in which one olefinic molecule reacts with one isoparaffinic molecule to produce an alkylate molecule having a molecular weight equal to the sum of the molecular weights of the reacting olefin and isoparaffin molecules.

Therefore, the reaction between the isoparaffins of the class described and certain of the olefins, in the vapor phase and at the optimum temperatures and pressures outlined hereinabove, may result in both the simple alkylation of the isoparaffins by the olefins added, and in the cracking alkylation in which, as stated, alkylates are produced which have a lower molecular weight than would be obtained by the simple addition of an isoparaffin to an added olefin. The higher molecular weight olefins having molecular weights in the order of that of dodecenes and above, however, appear to be unsuitable to react with isoparaffins to form alkylates boiling within the gasoline range.

While the foregoing has been described in connection with an alkylation operation in the vapor phase, it will be observed that the alkylation process may be conducted under suitable temperature and pressure conditions in substantially the liquid phase. For example, relatively low temperatures of the order of 100° to 200° F. and relatively high pressures of the order of 300 pounds per square inch to maintain the hydrocarbons in the liquid phase may be employed. This liquid phase reaction is preferably carried out in the presence of the solid type catalyst herein mentioned such as the metallic halide aluminates, acid sulphates and acid phosphates.

It is to be understood that other modes of applying the principles of the present invention may be employed in lieu of those explained, all of these modifications and changes being deemed to be within the scope of the appended claims.

We claim:

1. A process for interacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with olefin hydrocarbons of more than two and less than thirteen carbon atoms per molecule to produce alkylated hydrocarbons boiling within the gasoline range which comprises commingling said isoparaffinic hydrocarbons with said olefinic hydrocarbons and conveying said mixture through a reaction zone containing a compound selected from the class consisting of solid acid sulphates and mixtures of said solid acid sulphates with acid phosphates.

2. A process for interacting isoparaffinic hydrocarbons having less than seven carbon atoms per molecule with olefin hydrocarbons of more than two and less than thirteen carbon atoms per molecule to produce alkylated hydrocarbons boiling within the gasoline range which comprises commingling a vapor of said isoparaffinic hydrocarbons with a vapor of said olefinic hydrocarbons and conveying said mixture through a reaction zone containing a compound selected from the class consisting of solid acid sulphates and mixtures of said solid acid sulphates with acid phosphates.

3. A process according to claim 1 in which the reaction is carried out in the presence of a metal salt activator.

4. A process according to claim 1 in which the compound is zinc acid sulphate.

WILLIAM E. BRADLEY.
KARL J. KORPI.