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ALKYLATION PROCESS

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This invention relates to the alkylation of paraffin hydrocarbons with olefin hydrocarbons and is concerned particularly with the production of high octane motor fuel by the catalytic alkylation of normally gaseous paraffins with normally gaseous olefins.

It is known that olefinic gases may be polymerized thermally to produce gasoline of an unsaturated character by treating at high temperatures and pressures, as disclosed, for instance, by Wagner Patent No. 2,088,824. Further, many processes are known for passing C_3 and C_4 hydrocarbon gases along with cracking stock or naphtha through a cracking furnace to crack and polymerize such gases to gasoline simultaneously with the cracking or reforming. Sullivan patents, Nos. 2,022,221 and 2,145,900, Youker Patent No. 2,027,460, and Ostergaard Patent No. 2,135,014, are a few of the many patents disclosing this latter process. Also Towne Patent No. 2,090,272 separately cracks paraffinic gases to olefinic gases before passing the gases through a polymerizing and reforming furnace with naphtha. Again, Tropsch Patent No. 2,063,133 discloses a catalytic process for cracking and polymerizing normally gaseous hydrocarbons, using elevated temperatures and pressures and an organic halide catalyst.

It is also known that a paraffinic hydrocarbon may be combined directly with an olefinic hydrocarbon by thermal or catalytic alkylation to produce a saturated alkylate product. Since conditions of alkylation also usually will polymerize olefins, it is necessary to maintain a relatively low concentration of olefins in the reaction mixture during alkylation. Several methods are known for the catalytic alkylation of iso-paraffins with olefins. For instance, it is known to alkylate iso-paraffins with olefins at low temperatures using sulfuric acid or aluminum chloride as a catalyst. However, such processes alkylate only isoparaffins. Further, the consumption of catalyst is comparatively high, amounting to 10% by weight or more with respect to the alkylate product. In the non-catalytic, thermal alkylation of paraffins with olefins, high temperatures above 900° F. and very high pressures above 3,000 lbs. per square inch are employed, which involve high initial and operation costs.

It is an object of our invention to provide an efficient process for catalytically alkylating paraffin hydrocarbons with olefin hydrocarbons. Another object of our invention is to provide an efficient process for catalytically alkylating either normal paraffins or iso-paraffins with olefins. A more specific object is to provide a process for catalytically alkylating normally gaseous paraffins with normally gaseous olefins to produce high yields of high octane gasoline.

Our invention comprises alkylating paraffinic hydrocarbons, which may be either normal paraffins or isoparaffins or a mixture of the two, with olefinic hydrocarbons at elevated temperatures and pressures in the presence of a catalyst consisting essentially of an organic halide and any non-volatile metal which is capable of reacting with hydrogen halide under the conditions of the process, and of these metals, aluminum and iron are preferred. In the co-pending Sachanen et al. application S. N. 355,818, filed September 7, 1940, it is disclosed that paraffins, either normal or iso-, may be alkylated with olefins in the presence of a catalyst consisting essentially of an organic halide. We now have found that similar alkylations also may be effected using catalysts which still consist essentially of an organic halide but which include certain metals in combination with the organic halides, the metals alone being inert. The purity and paraffinicity of the alkylate produced with the combination of organic halides and metals is somewhat higher than even that obtained in the case of the alkylation with organic halides alone. For instance, whereas the iodine number of the alkylates produced by the present process is around 0 to 8, that of the alkylates formed in the presence of organic halides alone is usually around 10 or somewhat higher.

An important feature of the present invention is the fact that, contrary to the conventional catalytic processes which are only capable of alkylating iso-paraffins, our process is capable of alkylating either normal paraffins or iso-paraffins, and we obtain high yields of a high grade product therefrom. Moreover, it should be pointed out that our process is capable of effecting essentially only alkylation so that an almost pure paraffinic product may be obtained.

An important feature of our process as compared to a strictly thermal process is the relatively low temperature used, not exceeding usually 650–750° F. in a continuous operation, and in general being between about 500 and about 800° F. As a result, degradation of the charging hydrocarbons, such as ethylene, propylene, butylenes, propane, and butanes, to low molecular weight hydrocarbons, such as methane is almost nil. Therefore, the final yield of gasoline in our process after recycling may be very high.

The pressure to be used may vary from about

500 to about 3,000 pounds per sq. in. or more, the most suitable pressure being more or less dependent upon the particular temperature employed. In general, the higher the pressure, the higher the yield of alkylate. Accordingly, the upper limit on pressure is set primarily by the feasibility of maintaining such pressure.

An operation feature of our process that is of considerable practical importance is the fact that a very small amount of catalyst is required. In our operations, we prefer to use only about 1% or less of the organic halide catalyst with respect to the total charge of paraffins and olefins. Further, the consumption of the metal in the process is very small. Usually the weight of the metal after the alkylation in a batch process is approximately equal to its original weight.

The organic halide catalyst of this invention comprises organic halogen derivatives, wherein a halogen has been substituted for part or all of the hydrogen of an organic compound, the efficiency of the catalyst apparently being somewhat in proportion to the ease with which it gives up hydrogen halide during the alkylation. In general, the preferred catalysts are halogen derivatives of hydrocarbons, and, particularly, cheap chlorine derivatives, wherein the halogen is substituted onto a non-ring portion, if any, of the hydrocarbon. It is to be understood herein that by "derivatives" of hydrocarbons, we mean compounds wherein all the hydrogen has been substituted, e. g., carbon tetrachloride, as well as compounds wherein only part of the hydrogen has been substituted, e. g., chloroform. We especially prefer to use as our catalysts chlorinated derivatives of light paraffinic hydrocarbons, including hydrocarbons of gasoline-boiling range. Thus, at the present time, we consider a chlorinated naphtha or a chlorinated butane as the most feasible catalyst from a practical standpoint. However, other specific catalysts that may be mentioned by way of example of the compounds that may be used are: chloroform; carbon tetrachloride; dichloro-difluoro methane; dichloro-monofluoro methane; ethyl chloride; ethyl bromide; ethylene dichloride; trichlor-acetic acid; chloral; acetyl chloride; benzoyl chloride; benzyl chloride; and so forth. It is to be understood also that free halogens or hydrogen halides, reacting with hydrocarbons, can be used to form our catalyst in situ.

To illustrate the invention further, we set forth below specific examples of operation without, however, intending to be limited to the specific details thereof.

Example I

600 parts by weight of iso-butane are reacted with 79 parts by weight of ethylene in the presence of 30 parts by weight of metallic aluminum (turnings), and 7 parts by weight of chloroform in an autoclave at 625° and 3,000 lbs. per square inch pressure for thirty minutes; the products of the reaction were as follows:

Unreacted gases and loss	Alkylate boiling up to 160° C.	Heavy ends
558 parts by weight or 82.2%.	110 parts by weight or 16.2%. Has a specific gravity of 0.671 at 20° C. and an iodine number of 5.	11 parts by weight or 1.6%.

Example II

600 parts by weight of iso-butane were reacted with 75 parts of ethylene in the presence of 16 parts by weight of steel wool, and 7 parts by weight of chloroform in an autoclave at 640° F. and 3,000 lbs. per square inch pressure for thirty minutes. The products of reaction were as follows:

Unreacted gases and loss	Alkylate boiling up to 160° C.	Heavy ends
569 parts by weight or 84.3%.	94 parts by weight or 13.9%.	12 parts by weight or 1.8%.

The alkylate boiling up to 160° C. had a specific gravity of 0.680 at 20° C. and an iodine number of 8.

We claim:

1. A process of alkylating paraffins with olefins which comprises contacting the olefins and paraffins at a temperature between about 500° F. and about 800° F. in the presence of a catalyst consisting essentially of an organic halide and a metal which is non-volatile and capable of reacting with hydrogen halide under the conditions of the process and controlling the concentration of olefins so that alkylation is the principal reaction.

2. A process of alkylating low boiling paraffins with low boiling olefins to produce saturated hydrocarbons of gasoline boiling range which comprises contacting said paraffins and olefins at a temperature between about 500° F. and about 800° F. and at a pressure above about 500 pounds per square inch in the presence of a catalyst consisting essentially of an organic halide and a metal which is non-volatile and capable of reacting with hydrogen halide under the conditions of the process and controlling the concentration of olefins so that alkylation is the principal reaction.

3. The process of claim 2 wherein the paraffin is selected from the class consisting of propane and butanes and the olefin is selected from the class consisting of ethylene, propylene and butenes.

4. The process of claim 2 wherein the organic halide is a halogen derivative of a hydrocarbon wherein a halogen is substituted onto a non-ring carbon atom.

5. The process of manufacturing high octane gasoline which comprises alkylating normally gaseous paraffins with normally gaseous olefins at a temperature between about 500 and about 800° F. and at a pressure above about 500 pounds per square inch in the presence of a catalyst consisting essentially of a small amount of a chlorinated derivative of a light paraffinic hydrocarbon and a metal which is non-volatile and capable of reacting with hydrogen halide under the conditions of the process, and controlling the concentration of olefins so that alkylation is the principal reaction.

6. The process of claim 5 wherein the paraffin is a butane and the olefin is ethylene.

7. The process of manufacturing high octane gasoline which comprises alkylating a butane with a normally gaseous olefin at a temperature between about 500° and about 750° F. and at a pressure above about 500 pounds per square inch in the presence of a catalyst consisting essentially of a small amount of a chlorinated derivative of a light paraffinic hydrocarbon, not ex-

ceeding about 1% of the charge, and a metal which is non-volatile and capable of reacting with hydrogen halide under the conditions of the process, and controlling the concentration of olefins so that alkylation is the principal reaction.

8. A process of alkylating paraffins with olefins which comprises contacting the paraffins and olefins under conditions of alkylation at a temperature between about 500° F. and about 800° F. in the presence of a catalyst consisting essentially of an organic halide and iron.

9. A process of alkylating paraffins with olefins which comprises contacting the paraffins and olefins under conditions of alkylation at a temperature between about 500° F. and about 800° F. in the presence of a catalyst consisting essentially of an organic halide and aluminum.

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