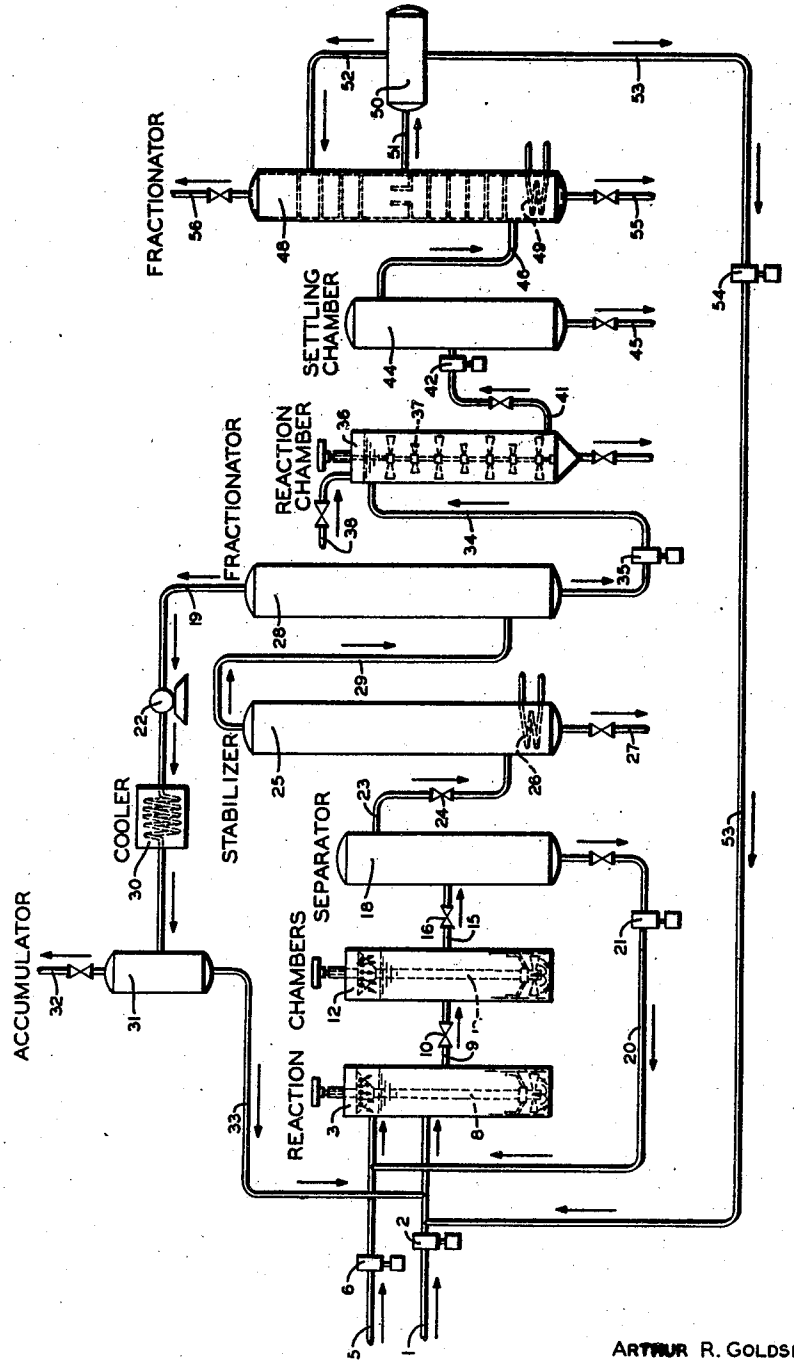
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of hydrocarbons and has to do particularly with the alkylation of paraffin hydrocarbons with olefins.

Paraffin hydrocarbons, particularly isoparaffins, may be alkylated with olefins under proper conditions and in the presence of a suitable catalyst. In such an operation it is customary to use as charging stocks, materials which contain normal paraffins, olefins and isoparaffins. In the alkylation reaction the isoparaffins and olefins are consumed thereby greatly increasing the proportion of the normal paraffins in the unreacted materials. In accordance with the present invention, the unreacted products from the alkylation reaction are treated whereby the normal paraffins are isomerized to isoparaffins which may be recycled to the system or otherwise treated with additional charging stock containing olefins to undergo alkylation.

The alkylation reaction may be carried out in the presence of a catalyst such as strong sulfuric acid of up to 100% concentration, and preferably about 94%. Other catalysts may comprise aluminum bromide and aluminum chloride. The temperature may range from −40 to +175° F. and preferably around 75 to 100° F. The reaction time may range from ten minutes to two hours and preferably about one hour. The ratio of isoparaffin to olefins may range from about 2:1 to 20:1 and good yields may be obtained with ratios of 3:1 to 5:1. Continuous or batch operation using counter current or concurrent flow may be employed.

The isomerization operation may be carried out in the presence of a catalyst such as aluminum bromide or aluminum chloride, either alone or in the presence of hydrogen chloride. Satisfactory results have been obtained with 5 to 30% of aluminum bromide, preferably 10%. Temperatures up to 200° F. may be used. A time of reaction is used ranging from a fraction of an hour to a day or more, and preferably as short a time as possible at the desired temperature. Charging stocks which may be treated according to the invention may comprise any mixture of isoparaffins, normal paraffins and olefins, such as normally gaseous hydrocarbons, normally liquid hydrocarbons or mixtures of normally gaseous and normally liquid hydrocarbons. Specific products which are contemplated are normally gaseous hydrocarbons, particularly C_3 and C_4 hydrocarbons, gasoline hydrocarbons, etc. The invention is particularly applicable to the treatment of unsaturated normally gaseous hydrocarbons such as cracking still gases predominating in C_4 hydrocarbons or C_4 and C_3 hydrocarbons. Mixtures consisting essentially of or comprising isobutane, normal butane and butenes may advantageously be treated.

The invention will be further understood from the following description of the invention read in connection with the accompanying drawing, showing diagrammatically one form of apparatus for carrying out the process of the invention.

Referring to the drawing, a charging stock comprising a mixture of isoparaffins, normal paraffins and olefins is charged through the line 1 by pump 2 to the reaction chamber 3. While only one line is shown for charging the hydrocarbons, it is to be understood that one or more charging stocks may be used; for example a mixture of isoparaffins and normal paraffins may be charged from one source of supply and the olefins from another source of supply. When recycling gases containing isobutane, it may be desirable to charge a gas high in olefin content along with the normal paraffins to thereby regulate the olefins charged to obtain the proper ratio of isobutane to olefins. The catalyst, such as 94% sulfuric acid, is charged through the line 5 by the pump 6 also to the reaction chamber 3. The reaction chamber is provided with a stirrer 8 for intimately mixing the catalyst and hydrocarbons. It is desirable that as intimate contact as possible be obtained and a high speed stirrer may be used, although other methods of efficient contact may be employed. The mixture is transferred through the line 9 controlled by valve 10 to a second reaction chamber 12 provided with a stirrer 13. While two reaction chambers are shown, it is to be understood that any number may be used to obtain the desired reaction. The products from reaction chamber 12 are transferred through the line 15 controlled by valve 16 to a separator 18. In the separator 18 a separation is allowed to take place between the catalyst and the oil. When using sulfuric acid, the acid will drop to the bottom of the separator and may be recycled through the line 20 by the pump 21 to the line 5, thence into the reaction chamber 3. The oil collecting in the top of the separator 18 is conducted through the line 23 controlled by valve 24 to the still 25.

In the treatment of normally gaseous hydrocarbons particularly, it is customary to maintain super-atmospheric pressures, for example 50 to 100 pounds or more, sufficient to keep the materials in the liquid phase. The pressure

may be reduced by means of the valve 24 whereby a separation between the unreacted normally gaseous hydrocarbons and the alkylation products which are normally liquid, may be effected in the stabilizer 25. If necessary, heat may be applied to the stabilizer, for example by means of the heating coil 26 in the lower portion thereof. The alkylation products are withdrawn from the lower portion of the stabilizer 25, through the line 27. The unreacted normally gaseous hydrocarbons are conducted through the vapor line 29 to fractionator 28, wherein separation is made between normal butane and isobutane. The isobutane and any lighter hydrocarbons are taken overhead from fractionator 28 through vapor line 19, compressed by compressor 22, cooled in the cooler 30 and the condensate collected in accumulator 31. Any light gases, such as C_1 and C_2 hydrocarbons, may be removed through gas release line 32. The isobutane is withdrawn from the accumulator through line 33 and returned to the reactor 2.

The normal butane collecting in the bottom of the fractionator 28 is transferred through the line 34 by the pump 35 to an isomerization or reaction chamber 36 which is provided with a stirrer 37 and a line 38 for the addition of a catalyst which may be aluminum bromide in the form of a hydrocarbon compound. The isomerization chamber 36 is usually of such size or a sufficient number of chambers used, whereby time and contact are provided for effecting the desired amount of isomerization which may be, for example, on the order of 50% conversion of paraffins to isoparaffins. The reaction products are transferred through the line 41 by pump 42 to a separation or settling chamber 44, wherein the catalyst is separated by settling or distillation of the hydrocarbons therefrom, and may be withdrawn from the lower portion thereof, through the line 45. The hydrocarbons are conducted through the line 46 to a still or fractionator 48 provided with heating means, such as coil 49, in the lower portion thereof. In the still 48 the hydrocarbons are fractionated to separate a fraction comprising the isoparaffins, such as isobutane, which is withdrawn from the intermediate point of the fractionator to a reboiler 50, through the line 51. The reboiler 50 is provided with a vapor line 52 for returning vapors to the still and a liquid line 53 for withdrawing the desired fraction. The higher and lower boiling point materials may be withdrawn from the lower portion and the upper portion of the fractionator through the lines 55 and 56 respectively. The fraction withdrawn through the line 53 from the reboiler 50 is recycled by the pump 54 to the charge line 1 leading to the reaction chamber 3.

As an example of the operation of the invention, a C_4 hydrocarbon fraction comprising about 30% olefins, 30% isobutane and 40% normal butane, was treated with about an equal amount by volume of 94% sulfuric acid operating in a continuous manner. A total yield of alkylation products comprising normally liquid hydrocarbons with end point around 600° F. of about 140% based on the olefins charged was obtained, of which about 100% based on olefins charged were within the motor fuel boiling range having an end point below 400° F. The unreacted normally gaseous hydrocarbons, relatively rich in normal butane were subjected to isomerization by the treatment with about 10% aluminum bromide at room temperatures for approximately 40 hours. The reaction products contain approximately 50% isobutane along with a small proportion of lower and higher boiling hydrocarbons. The products were fractionated to obtain a fraction containing in excess of 50% of isobutane which was recycled to the alkylation operation. By operating in this manner, a total yield of liquid alkylation products of about 175% based on the olefins charged was obtained, with a yield of motor fuel products having end point below 400° F. equal to about 160% of the olefins charged, and having a high antiknock value.

The process is particularly advantageous in that it provides a means for utilizing substantially all the materials of an ordinary charging stock comprising isoparaffins, normal paraffins and olefins. By isomerizing the normal paraffins to isoparaffins, a much higher ultimate yield for a given charging stock is obtained and eliminates the necessity of supplying extraneous isoparaffins to the system.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the manufacture of higher boiling isoparaffins useful as motor fuel from low boiling isoparaffins and olefins, which comprises subjecting a hydrocarbon fraction containing low boiling isoparaffins, olefins and normal paraffins to alkylating conditions whereby the isoparaffins are condensed with the olefins to form higher boiling normally liquid isoparaffins, separating the normal paraffins from the reaction products, isomerizing the normal paraffins to isoparaffins and charging the last mentioned isoparaffins to the alkylation operation to increase the ratio of isoparaffins to olefins in the reaction mixture and to react with the olefins to produce further quantities of higher boiling isoparaffins.

2. A process for the manufacture of high antiknock gasoline hydrocarbons, which comprises subjecting a hydrocarbon fraction containing low boiling isoparaffins, normally gaseous olefins and low boiling normal paraffins, to the action of an alkylation catalyst whereby the isoparaffins are alkylated by the olefins to produce isoparaffins of high antiknock value of gasoline boiling point range, separating said gasoline hydrocarbons from the reaction products, also separating from the products of reaction normal paraffins including normal butane, isomerizing said normal butane to isobutane and charging the isobutane formed by said isomerization to the alkylation operation.

3. A process for the manufacture of high antiknock normally liquid hydrocarbons from normally gaseous hydrocarbons, which comprises subjecting normally gaseous hydrocarbons including normal and isobutane, and olefins containing between 2 and 5 carbon atoms, to the action of concentrated sulfuric acid whereby the isobutane is alkylated by the olefins to produce normally liquid isoparaffins, separating the normally liquid hydrocarbons from the reaction products, also separating from the reaction products a fraction rich in normal butane, subjecting said fraction to an isomerization operation whereby the normal butane is converted to isobutane and charging said isobutane from the isomerization operation to the alkylation operation.

4. A process for the manufacture of saturated liquid hydrocarbons of high antiknock value which comprises subjecting normal butane to an isomerization operation whereby normal butane is partially converted in substantial amount to isobutane, treating said isobutane, in mixture with unconverted normal butane, with olefins under alkylating conditions whereby the isobutane is condensed with the olefins to form normally liquid isoparaffins, maintaining an excess of isobutane in the reaction mixture, separating excess isobutane from the reaction products, recycling said separated isobutane to the alkylation operation, also separating normal butane from the reaction products and recycling said separated normal butane to the isomerization operation.

5. A process for the manufacture of antiknock motor fuel hydrocarbons, which comprises reacting isobutane in a hydrocarbon mixture containing isobutane and normal butane with olefins in the presence of an alkylating catalyst, while maintaining the isobutane in considerable excess of the olefins, separating the hydrocarbon reaction products into a normally liquid alkylate and unreacted hydrocarbons containing the excess isobutane and normal butane, fractionating said unreacted hydrocarbons to separate normal butane from isobutane, converting by isomerizing the normal butane to isobutane in the presence of an isomerizing catalyst and charging the isobutane formed in the isomerization stage to the alkylation stage.

6. A process according to claim 5 in which the isobutane from the fractionation stage is recycled to the alkylation stage.

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