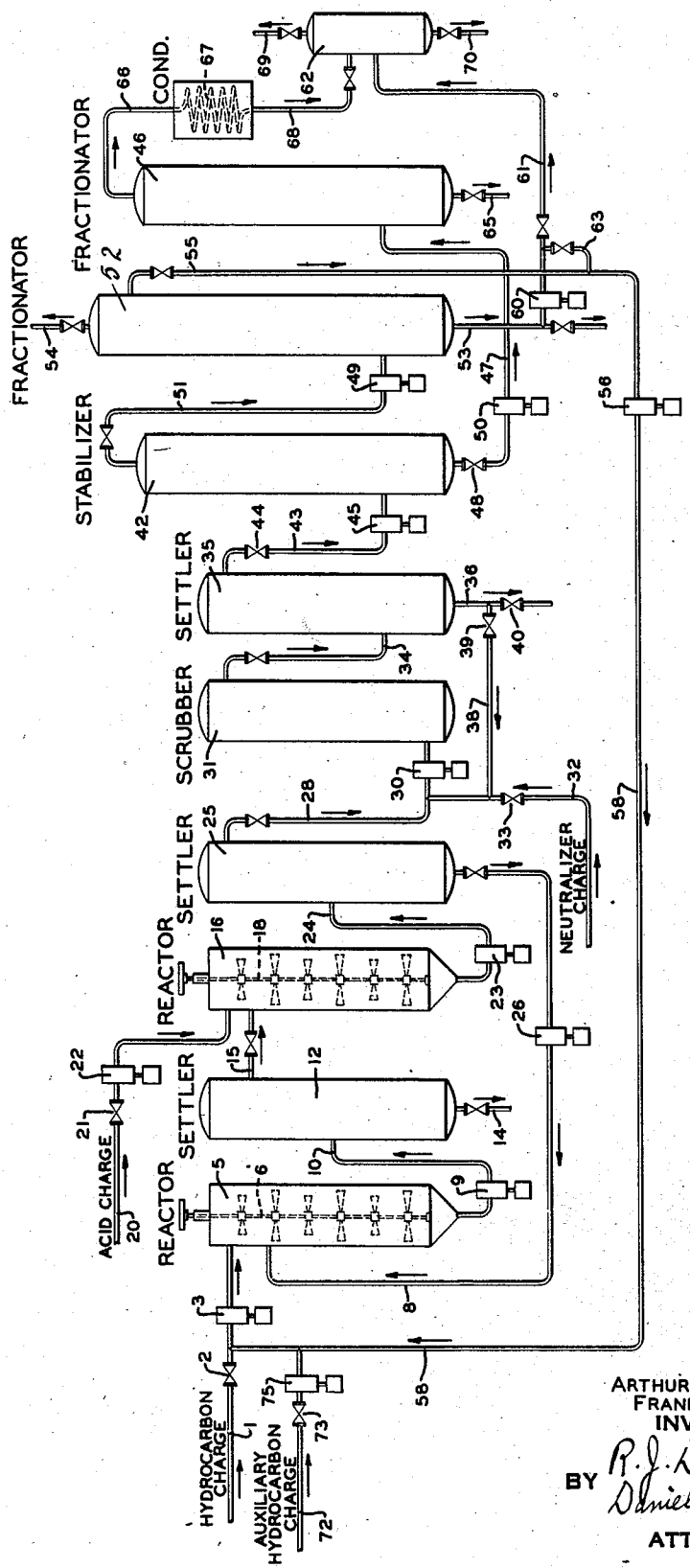
May 19, 1942. A. R. GOLDSBY ET AL 2,283,603

MANUFACTURE OF MOTOR FUEL

Filed March 18, 1938



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Patented May 19, 1942

2,283,603

UNITED STATES PATENT OFFICE

2,283,603

MANUFACTURE OF MOTOR FUEL

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Application March 18, 1938, Serial No. 196,669

8 Claims. (Cl. 196—10)

This invention relates to the manufacture of high antiknock hydrocarbons, particularly liquid motor fuel hydrocarbons such as gasoline, by the alkylation of paraffins, such as isobutane, with olefin hydrocarbons including normally gaseous olefins.

It has been found that isoparaffins, such as isobutane, may be readily alkylated with olefins in the presence of a catalyst, comprising strong sulfuric acid. This process is described in co-pending application, Serial No. 148,978, filed June 18, 1937, Korpi-Goldsby, and the present invention is an improvement in that type of process.

In the alkylation of isoparaffins with olefins, it is desirable to maintain an excess of isobutane in the reaction mixture and the principal object of the present invention is to provide means for a continuous recycle process in which the excess isoparaffins are recycled.

The present invention contemplates broadly the treatment of isoparaffins with olefinic hydrocarbons wherein the excess isoparaffins may be separated and recycled in the process. The invention is specifically intended for the alkylation of isobutane with olefins which are normally liquid or normally gaseous, particularly normally gaseous olefins, such as C_4, C_3 or a mixture of C_4 and C_3 olefins, with or without the presence of paraffins of the same number of carbon atoms. The invention is particularly suitable for the alkylation of isobutane with unsaturated normally gaseous hydrocarbon fractions, such as C_4 cracked hydrocarbon fractions or mixtures of C_3 and C_4 cracked gases.

In the alkylation of isoparaffins with olefins, according to the herein described process, strong sulfuric acid of preferably about 92 to 98%, for example 94%, is used. Temperatures may range from around normal atmospheric temperatures to 120° F. or over, and preferably about 75 to 90° F. A ratio of acid to olefins of about 1:1 or more may be used and the acid may be recycled in a concurrent or countercurrent type of operation. The molar ratio of isobutane to olefins may range between about 1:1 and 20:1, and preferably at least about 3:1, and up to 5:1 and higher is advantageous. The advantages of the high ratios of isoparaffin to olefin include an increased yield of alkylate within the aviation gasoline boiling range, and an improved octane of such alkylate.

According to one method of the present invention, a hydrocarbon charge containing an excess of isobutane above that which normally may be alkylated with the olefins present, is alkylated in the presence of sulfuric acid catalyst and a recycle fraction containing the excess isobutane is separated from the reaction products and recycled. Ordinarily the reaction products, after separation from the acid, are fractionated to separate the normally liquid hydrocarbons, and then unreacted normally gaseous hydrocarbons, all or in part, are fractionated to obtain a fraction rich in isobutane which is recycled. The recycled fraction may contain, in addition to the isobutane, a small amount of normal paraffins, such as propane and butane. It is sometimes advantageous to retain all or part of the n-butane in the normally liquid products to impart volatility thereto. In case there is an excess of paraffins, such as n-butane or propane, it is undesirable to retain the n-butane in the normally liquid products, and it may be necessary to provide means for eliminating the paraffins such as n-butane or propane in the system in order to avoid the building up of such paraffins therein. This may be done by fractionating the gaseous hydrocarbons whereby a cut is made between the paraffins and isoparaffins, for example between the n-butane and isobutane. The isobutane or fraction rich in isobutane is then recycled. When operating as described above to fractionate between the paraffin and the isoparaffin hydrocarbons to provide an isobutane-rich fraction, which fraction is recycled to the alkylation reaction zone, there is inherently effected a reduction in the proportion of normal paraffin, such as normal butane, in the reaction zone during continuance of the process to a proportion substantially below that in the fresh hydrocarbon charge where the latter comprises a hydrocarbon fraction, such as a customary refinery cracking gas, containing a substantial proportion of normal paraffin. Certain advantages are inherent in this disclosed method of operation, since this avoids normal paraffin concentrations in the reaction zone which result in decreased yields of total alkylate and aviation fractions thereof on the basis of the olefin charged while enabling available refinery cracking gas to be employed as charging stock.

According to another method of operation, a charging stock may be deficient in isobutane whereby insufficient isobutane to react with the olefins is present or the isobutane is insufficient to give the optimum results, particularly from the yield and antiknock standpoint. In such a case it is undesirable to recycle the small amount of unreacted isobutane. Since it is advantageous to have a high proportion of isobutane, for ex-

ample a molar ratio of isobutane to olefins of at least about 3:1 and up to 5:1 and higher, it is desirable when using such a charging stock to provide an auxiliary charging stock comprising isobutane in sufficient amount to provide a mixture in which the desired ratio of isobutane to olefins is obtained. This auxiliary charging stock may be substantially pure isobutane or a charging stock suitable for alkylation but containing a proportion of isobutane higher than the preferred range. It is intended that whenever using charging stocks deficient in isobutane, that this deficiency may be overcome by adjusting the proportion of isobutane or by the addition of auxiliary charging stocks or by the use of multiple charging stocks, whereby a mixture containing the desired proportion of isobutane is obtained. It is also intended that there will be an excess of isobutane which may be recycled in the process to maintain the desired ratio of isobutane to olefins in the reaction mixture.

The invention will be further described in connection with the accompanying drawing which shows diagrammatically one form of apparatus for carrying out the process of the invention.

Referring to the drawing, a hydrocarbon charging stock is drawn through the line 1 and valve 2 by the pump 3 and introduced into a reactor 5. In this reactor the hydrocarbon is intimately contacted by means of stirring mechanism 6 with used acid catalyst introduced through the line 8. The mixture of catalyst and hydrocarbon is transferred by the pump 9 through the line 10 to a settler 12, wherein the spent acid is allowed to separate and collect in the lower portion thereof and may be withdrawn through the valve controlled line 14. The partially reacted hydrocarbon mixture flows through valved line 15 to a second reactor 16, also provided with a stirring mechanism 18. In this reactor the hydrocarbon mixture is intimately contacted with fresh acid catalyst charged through line 20 in which is located a valve 21 and pump 22. The mixture of acid and hydrocarbon is drawn from the bottom of the reactor 16 by the pump 23 and charged through the line 24 to a settler 25. In this settler the acid is allowed to separate from the hydrocarbon and collect in the lower portion thereof. This spent acid is withdrawn from the bottom of the settler by the pump 26 and recycled to the reactor 5 through the line 8. While a countercurrent type of operation for contacting the hydrocarbon and acid is shown, it is to be understood that a concurrent flow type may be used, or any other well known or preferred type of apparatus whereby intimate contact between the hydrocarbon and acid is obtained.

The hydrocarbons, or a portion thereof, are passed from the settler 25 through the valve controlled line 28 and forced by the pump 30 into a scrubber 31. A neutralizing agent, such as caustic soda or soda ash solution, is drawn from a suitable source of supply, not shown, through the line 32 in which is located valve 33 communicating with the line 28. The alkali so introduced is intimately contacted with the hydrocarbon in the scrubber 31 to effect neutralization of the acid bodies in the hydrocarbon. The scrubber 31 may contain suitable mixing devices, such as orifice plates or baffles. The mixture of hydrocarbon and neutralizing agent is transferred from the upper portion of the scrubber 31 through the valve controlled line 34 to settler 35 in which the neutralizer is allowed to settle out in the lower portion thereof. This spent neutralizer may be withdrawn through the line 36 or all or any part thereof recirculated through the by-pass line 38 by suitable regulation of valves 39 and 40. The neutralized hydrocarbons are transferred from the settler 35 to a stabilizer 42 by means of the line 43 in which is located valve 44 and pump 45. In the stabilizer the normally liquid hydrocarbons and a portion or all of the butane are separated and transferred from the lower portion of the stabilizer to a fractionator 46 by means of the line 47 in which is located valve 48 and pump 50. The normally gaseous hydrocarbons including the isobutane, and all or a portion of the n-butane and hydrocarbons lighter than C_4 hydrocarbons, are removed as vapors from the upper portion of the stabilizer through the line 51, in which is located a pump 49, and introduced into a fractionator 52.

The operation of the fractionator 52 may vary considerably, depending on the composition of the vapors to be fractionated therein. If the vapors are low in butane content, it may be unnecessary to make a separation between the butane and isobutane and in such case the entire C_4 fraction may be recycled to the system. This fraction may be withdrawn as a liquid from the lower portion of the fractionator through the line 53 while the lighter hydrocarbons may be removed from the upper portion of the fractionator through line 54. If the hydrocarbon mixture contains substantial amounts of propane a portion of this may be retained in the liquid fraction withdrawn through the line 53 for recycling to the system, although it is desirable to prevent building up of propane in the system, and most of such propane would be taken off overhead through line 54. If the hydrocarbons to be fractionated in the fractionator 52 contain an excess of n-butane, it is desirable to make a separation of the n-butane in order to avoid building up thereof in the system. Accordingly, the butane may be fractionated and collected in the lower portion of the fractionator and withdrawn through the line 53.

A cut containing the isobutane may be removed as a side stream from the fractionator 52 through the valve controlled line 55. This side stream may comprise essentially isobutane but ordinarily contains in addition some normal butane. Also if C_3 hydrocarbons are present, the side stream may contain all or a portion of the C_3 hydrocarbons. The lighter gases undesirable for recycling with the isobutane through line 55, are removed overhead from the fractionator through the line 54. The isobutane fraction removed in the side stream through the line 55 is forced by the pump 56 through line 58 to the charge line 1 through which it is introduced into the reactor 5.

The n-butane fraction removed from the lower portion of the fractionator 52 through the line 53 may be withdrawn from the system but it is preferably pumped by the pump 60 through the branch line 61 to the accumulator 62 referred to hereinafter. Branch line 63 connects the line 61 with the line 55 whereby all or a portion of the material withdrawn from the lower portion of the fractionator 52 may be recycled to the system through line 55, pump 56 and line 58. This recycling of the fraction withdrawn from the lower portion of the fractionator 52 may occur when there is no separation between the n-butane and isobutane, as mentioned heretofore, or in other cases wherein it is desirable to

recycle a portion of the heavier fraction, for example when there is poor fractionation between the n-butane and isobutane.

The normally liquid hydrocarbons introduced into the fractionator **46** are fractionated therein to make a separation between the gasoline fraction and fraction heavier than gasoline. The heavier fraction is withdrawn from the lower portion of the fractionator through the valved line **65** while the gasoline fraction is removed as vapors overhead through the vapor line **66**. These vapors are condensed in the condenser **67** and pass through the run-down line **68** to accumulator **62** which is provided with a gas release line **69**, and a liquid draw-off line **70**. The gasoline fraction accumulated in the accumulator **62** may be deficient in butane for commercial gasoline specifications and accordingly any desired amount of excess butane from the system may be introduced therein through the line **61** referred to heretofore.

An auxiliary hydrocarbon charging line **72**, in which is located a valve **73** and pump **75**, is provided for introducing isobutane, or any charging stock containing isobutane, in sufficient amount to make up any deficiencies in the isobutane content of the main charging stock, or for supplying an adequate amount of isobutane in the system, to maintain the desired ratio of isobutane to olefins.

The system is ordinarily operated under sufficient pressure to maintain the hydrocarbons in the liquid phase, for example 25 to 150 pounds pressure. In some cases, for purposes of facilitating fractionation, the stabilizer **42** or the fractionator **52**, or both, may be maintained under pressures which may vary somewhat from those maintained in the treating system.

As an example of the operation of the invention, an unsaturated C_4 hydrocarbon charging stock, showing a ratio of isobutane to olefins of about 1.2:1, was mixed with recycled isobutane to bring the ratio of isobutane to olefin to about 3:1 and the mixture contacted with sulfuric acid of about 94% concentration at around 90° F., for sufficient time, for example about an hour, to alkylate the isobutane with the olefins, whereby substantially all the olefins were consumed. The reaction products were neutralized and the hydrocarbons fractionated to separate the normally liquid hydrocarbons. The unreacted gaseous hydrocarbons were fractionated to form a fraction, rich in isobutane and low in normal butane, which was recycled to the system and another fraction, comprising essentially normal butane, which was added all or in part to the normally liquid hydrocarbon fraction to improve the volatility thereof. The normally liquid hydrocarbon fraction was fractionated to separate a fraction containing hydrocarbons of gasoline boiling range. A gasoline yield of about 150%, based on the olefins consumed, was obtained. The gasoline fraction consisted essentially of saturated hydrocarbons and had an antiknock value of about 90.

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.

We claim:

1. A cyclic process for the manufacture of high anti-knock motor fuel from low-boiling hydrocarbons containing isobutane, normal butane and olefins, which comprises continuously introducing into an agitated reaction zone containing an alkylation catalyst a charge of hydrocarbons containing substantial proportions of isobutane and olefins and also a substantial proportion of normal butane, and reacting the hydrocarbons therein in liquid phase under conditions such that the isobutane is alkylated by the olefins to form normally liquid hydrocarbons within the gasoline boiling range, continuously withdrawing reaction products from the reaction zone to a settling zone where the reaction products separate into a hydrocarbon layer and a catalyst layer, continuously removing hydrocarbon from the hydrocarbon layer and catalyst from the catalyst layer, adding additional catalyst to the reaction zone to make up for that withdrawn, stabilizing the removed hydrocarbon to separate off-gases therefrom, fractionating the off-gases from the said stabilization to separate a fraction rich in isobutane and lean in normal butane, and continuously recycling the said isobutane fraction to the reaction zone to maintain a substantial excess of isobutane to olefin therein, the said isobutane fraction being sufficiently denuded of normal butane to thereby reduce the proportion of normal butane in the reaction zone during continuance of the process to a proportion substantially below that in the fresh hydrocarbon charge to said zone.

2. A cyclic process for the manufacture of high anti-knock motor fuel from low-boiling hydrocarbons containing isobutane, normal butane and olefins, which comprises continuously introducing into an agitated reaction zone containing an alkylation catalyst a charge of the said low-boiling hydrocarbons, and reacting the hydrocarbons therein in liquid phase under conditions such that the isobutane is alkylated by the olefins to form normally liquid hydrocarbons within the gasoline boiling range, continuously withdrawing reaction products from the reaction zone to a settling zone where the reaction products separate into a hydrocarbon layer and a catalyst layer, adding additional catalyst to the reaction zone to make up for that withdrawn, continuously removing hydrocarbon from the hydrocarbon layer and catalyst from the catalyst layer, stabilizing the removed hydrocarbon to separate off-gases therefrom, separating a fraction rich in isobutane and lean in normal butane from the said off-gases, and continuously recycling the said isobutane fraction to the reaction zone, the said fresh hydrocarbon feed being correlated with the recycle of the said isobutane fraction to continuously maintain in the reaction zone a molar excess of isobutane over the stoichiometrical equivalent monomeric contents of the olefins which is about 5:1 and over.

3. A cyclic process according to claim 1, in which at least a portion of the normal butane fraction separated from the isobutane fraction in the fractionation of the off-gases is blended back with the gasoline fraction of the alkylate to adjust the volatility thereof.

4. A cyclic process according to claim 1, in which the catalyst is strong sulfuric acid.

5. A cyclic process for the manufacture of high anti-knock motor fuel from low-boiling hydrocarbons containing isobutane, normal butane and olefins, which comprises continuously introducing into an agitated reaction zone containing an alkylation catalyst a charge of hydrocarbons containing substantial proportions of isobutane

and olefins and also a substantial proportion of normal butane, and reacting the hydrocarbons therein in liquid phase under conditions such that the isobutane is alkylated by the olefins to form normally liquid hydrocarbons within the gasoline boiling range, continuously withdrawing reaction products from the reaction zone to a settling zone where the reaction products separate into a hydrocarbon layer and a catalyst layer, continuously removing hydrocarbon from the hydrocarbon layer and catalyst from the catalyst layer, adding additional catalyst to the reaction zone to make up for that withdrawn, stabilizing the removed hydrocarbon to separate an off-gas fraction rich in isobutane and lean in normal butane while leaving a substantial proportion of the normal butane in the hydrocarbon to adjust the volatility thereof, fractionating the stabilized hydrocarbon into a gasoline fraction containing normal butane and a heavier fraction, and continuously recycling the said off-gas fraction rich in isobutane to the reaction zone to maintain a substantial excess of isobutane to olefin therein, the said isobutane fraction being sufficiently denuded of normal butane to thereby reduce the proportion of normal butane in the reaction zone during continuance of the process to a proportion substantially below that in the fresh hydrocarbon charge to said zone.

6. A cyclic process according to claim 5, in which the fresh hydrocarbon feed is correlated with the recycle of the isobutane fraction to maintain in the reaction zone a molar excess of isobutane over the stoichiometrical equivalent monomeric contents of the olefins which is about 5:1 and over.

7. A cyclic process according to claim 5, in which the catalyst is strong sulfuric acid.

8. A cyclic process for the manufacture of high anti-knock motor fuel from low-boiling hydrocarbons containing isobutane, olefins and normal paraffins including normal butane, which comprises continuously introducing into an agitated reaction zone containing an alkylation catalyst a charge of hydrocarbons containing substantial proportions of isobutane and olefins and also some normal paraffins including normal butane, and reacting the hydrocarbons therein in liquid phase under conditions such that isobutane is alkylated by the olefins to form normally liquid hydrocarbons within the gasoline boiling range, continuously withdrawing reaction products from the reaction zone to a settling zone where the reaction products separate into a hydrocarbon layer and a catalyst layer, continuously removing hydrocarbon from the hydrocarbon layer and catalyst from the catalyst layer, adding additional catalyst to the reaction zone to make up for that withdrawn, stabilizing the removed hydrocarbon to separate offgases therefrom, fractionating the offgases from the said stabilization to separate an isobutane-rich fraction from normal paraffin hydrocarbons, and continuously recycling the said isobutane-rich fraction to the reaction zone to maintain a substantial excess of isobutane to olefin therein and to avoid build-up of normal paraffin hydrocarbons in the system.

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