Oct. 28, 1941. A. R. GOLDSBY ET AL 2,260,990

MANUFACTURE OF MOTOR FUELS

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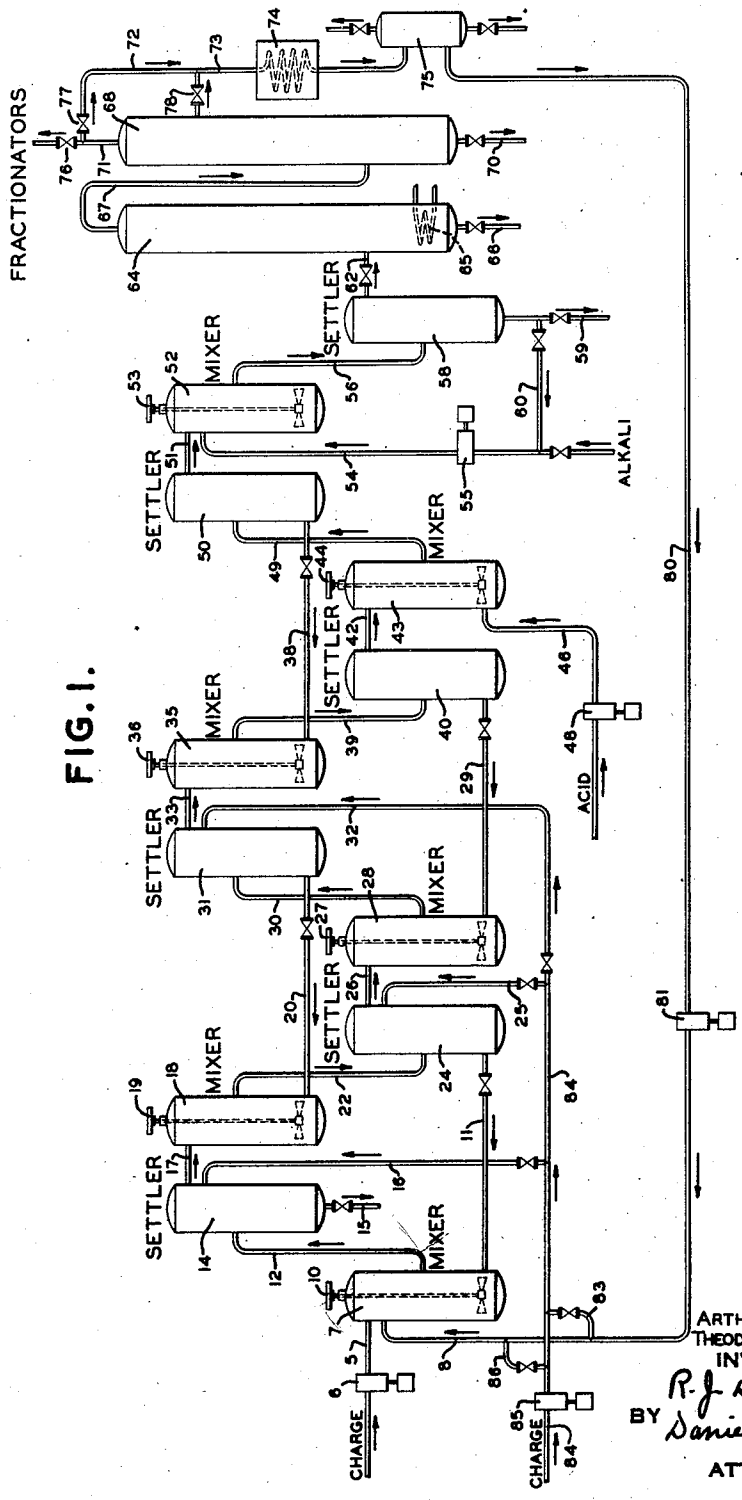


FIG. 1.

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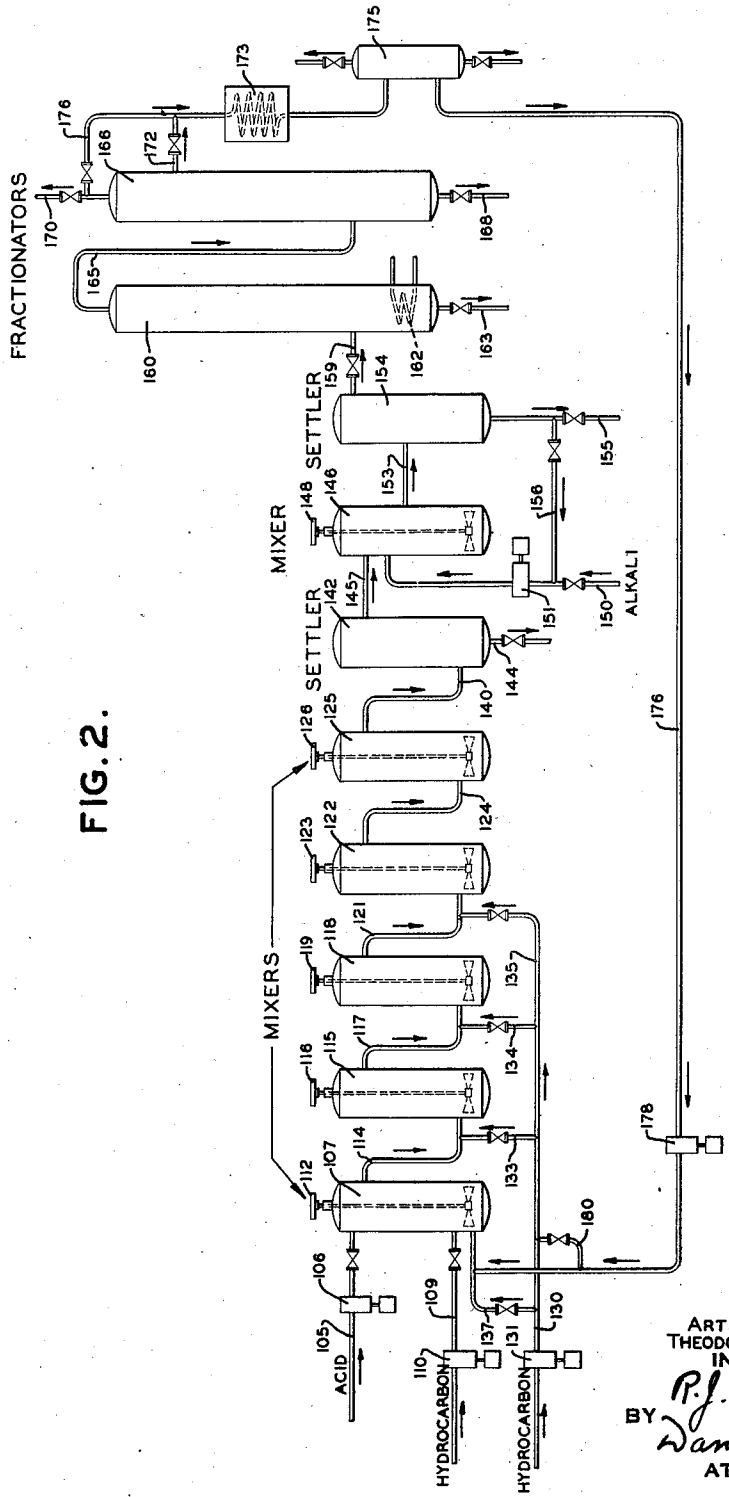


FIG. 2.

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MANUFACTURE OF MOTOR FUELS

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Application June 11, 1938, Serial No. 213,148

9 Claims. (Cl. 196—10)

This invention relates to the manufacture of motor fuel by the alkylation of paraffins with olefins, and has to do particularly with the liquid phase alkylation of low boiling isoparaffins and olefins in the presence of a liquid catalyst, such as sulfuric acid, to produce high anti-knock hydrocarbons of the gasoline boiling point range.

In the catalytic alkylation of isoparaffins with olefins, it is desirable to maintain a relatively high ratio of isoparaffins to olefins in the reaction mixture, whereby the yield and quality of the alkylation products are improved. In continuous operations, wherein streams of isoparaffins and olefins are charged to a reaction zone, the ratio of isoparaffin to olefin is determined by the proportion of these materials charged to the unit, and in order to obtain a large proportion of isobutane it is necessary to feed in a small proportion of olefin and recycle a large amount of isobutane. It has been found to be advantageous to charge the olefin portion-wise or in multiple injections; for example, by using a plurality of stages in which portions of the olefins are introduced into successive stages of reaction. By regulating the amounts of olefins injected in the multiple stages, and allowing time for substantial consumption of one portion of the olefin before the next portion is introduced, a local preponderance of isoparaffin may be maintained without using a large overall excess.

In one method of operation, the stream of paraffin hydrocarbon and catalyst may be passed in counterflow relationship through stages of reaction, and the olefin charge introduced into a plurality of the stages. It has been found satisfactory to use the step counterflow principle in which the hydrocarbon and catalyst are passed through alternating stages of mixing and settling, and the olefins introduced by multiple injection into a plurality of the steps. According to another method of operation, a concurrent flow may be used, in which the catalyst and paraffin hydrocarbons pass through a series of successive mixers and the olefin hydrocarbons introduced into a plurality of the mixing zones. Both methods of operation have been found to give good results.

The invention will be more fully understood by the following description read in connection with the accompanying drawings, which are diagrammatical sketches of apparatus suitable for practicing the process of the invention. Figure 1 shows an apparatus for practicing the invention according to the step counterflow principle. Figure 2 shows an apparatus for carrying out the invention using a concurrent flow operation.

Referring to Figure 1, a hydrocarbon charge is passed through the line 5 by the pump 6 to a mixer 7. The charge should contain a substantial amount of isoparaffins and may be any mixture of hydrocarbons containing isoparaffins which may be alkylated with olefins in the presence of a catalyst. A desirable product is one containing low boiling isoparaffins, preferably isobutane or a hydrocarbon mixture containing a large proportion of isobutane. For example, products from the debutanization or fractionation of cracked or straight run gasoline, or the product from the stabilization of natural gasoline, containing principally butane and isobutane, may be used. The hydrocarbon charge may be entirely saturated or may contain a certain amount of olefins present normally in the charge. Additional olefins may be introduced through the line 8, referred to hereinafter. In the mixer 7, the hydrocarbons are contacted by means of a stirring mechanism 10 with partially spent acid introduced through the line 11. The mixture passes from the mixer 7 through the line 12 to a settler 14. In this settler the acid and hydrocarbons separate, the acid settling to the bottom of the settler and may be withdrawn from the system through the valve controlled line 15. The hydrocarbons stratifying and settling in the upper portion of the settler 14 are mixed with additional olefinic charge introduced through the line 16 and the mixture passed through the line 17 to the mixer 18. The features of prediluting the olefin feed with alkylate or hydrocarbon phase separated from acid from a previous alkylation reaction, prior to contacting of the olefin with the catalyst in the alkylation reaction zone, and of the multi-stage serial flow process involving said step are disclosed and claimed in copending application, Serial No. 392,396, filed May 7, 1941, as a continuation-in-part of application, Serial No. 214,488, filed June 18, 1938.

In the mixer 18 the hydrocarbon is intimately mixed by stirrer 19 with partially spent acid introduced through the line 20. The mixture of acid and hydrocarbon is passed through the line 22 to a settler 24, wherein the acid and hydrocarbon are allowed to separate. The used acid collecting in the lower portion of the settler is conducted through the valve controlled line 11, referred to heretofore, to the mixer 7. The hydrocarbons collecting in the upper portion of the settler 24 are mixed with additional olefins from the line 25 and the mixture passed through

the line 26 to a mixer 28, wherein the hydrocarbons are intimately contacted by means of stirrer 27 with partially spent acid from the line 29. The reaction mixture passes through the line 30 to a settler 31 wherein a separation between acid and hydrocarbon takes place, the acid settling and being withdrawn from the lower portion of the settler by the valve controlled line 20 and introduced into the mixer 18. The layer of hydrocarbons in the upper portion of settler 31 is mixed with additional olefins from the line 32 and the mixture passed through the line 33 to a mixer 35, equipped with a stirrer 36. In this mixer the hydrocarbons are contacted with used acid from the line 38 and the reaction mixture passed through the line 39 to a settler 40. The partially spent acid settling in this settler is conducted through the valve controlled line 29 to the mixer 28. The separated hydrocarbons are conducted from the upper portion of the settler 40 through the line 42 to a mixer 43 containing a stirring mechanism 44.

In the mixer 43 the hydrocarbon is contacted with fresh acid introduced through the line 46 by the pump 48.

The amount of new acid introduced through the line 46 is usually between about one-half to five times the volume of the olefins, and preferably about three-fourths to one and one-half times the volume of olefins. The mixture from 43 is passed through the line 49 to a settler 50 wherein the acid is allowed to settle out and pass through the valve controlled line 38 to the mixer 35. The hydrocarbons from the last settler 50 are passed through the line 51 to a mixer 52 containing stirrer 53. In the latter mixer the hydrocarbons are neutralized by contact with an alkaline material introduced through the valve controlled line 54 by the pump 55. The mixture passes from the mixer 52 through the line 56 to a settler 58 wherein the neutralizing agent settles out and may be withdrawn from the system through the valve controlled line 59 or recycled to the mixer 52 through the lines 60 and 54 by the pump 55. The neutralized hydrocarbons from the settler 58 are passed through the line 62 to fractionator or still 64 equipped with a heating coil 65. In the fractionator 64 the hydrocarbons of higher boiling point than the desired fraction, for example higher boiling than gasoline, are drawn off as bottoms from the lower portion of the fractionator through the valve controlled line 66. The hydrocarbons, for example of gasoline boiling point range and lower, are vaporized and removed as overhead through the vapor line 67. The overhead vapors are passed through the line 67 to fractionator 68 wherein the desired liquid fraction, such as gasoline, is condensed and the stabilized product removed from the lower portion thereof through the valve controlled line 70. The uncondensed normally gaseous hydrocarbons are fractionated to obtain a fraction preferably comprising essentially C_4 hydrocarbons, such as isobutane or isobutane and butane, for recycling to the system.

The type of operation in the fractionator 68 will depend on the nature of the lower boiling hydrocarbons. If substantially only C_4 hydrocarbons have been charged to the system, the uncondensed gases may consist essentially of butane and isobutane which may be removed as a single fraction. In this case the vapors would be removed overhead through the lines 71, 72 and 73 to a condenser 74 and the condensate thereafter collected in the receiver 75. In case the charging stock to the system is a mixture of hydrocarbons containing a substantial amount of products below C_4 hydrocarbons, the gases in the fractionator 68 may contain a substantial amount of gases of more permanent nature. These gases, for example the hydrocarbons lower than C_3 and all or any portion of the C_3 hydrocarbons, may be discharged from the system through the line 71, the valve 76 therein being open and the valve 77 in the line 72 being closed. In such type of operation, a side stream comprising the C_4 hydrocarbons will be removed as a side stream through the line 73, the valve 78 therein being open.

The hydrocarbons collected in the receiver 75 are withdrawn through the line 80 in which is located pump 81 and returned to the mixer 7. A portion or all of the product recycled through the line 80 may be conducted through the bypass line 83 which communicates with the line 84 whereby these hydrocarbons may be introduced into one or more of the settlers 14, 24 and 31 by means of the valve controlled manifold lines 16, 25 and 32, referred to heretofore. The injection of the recycle stock through the lines 16, 25 and 32 may be desirable in starting up the system or in other cases wherein the recycle stock contains a substantial amount of unreacted olefins.

In some cases, particularly when there is an excess of normal butane in the overhead gases, it may be desirable to provide means for separating the isobutane from the normal butane. For example a stream of C_4 hydrocarbons, comprising essentially normal and isobutane, may be removed from fractionator 68 and a further separation or fractionation made to produce a fraction rich in isobutane which is recycled to the alkylation operation. These features are not shown in the drawing.

The olefinic charging stock is introduced through the line 84 in which is located a pump 85. This charging stock may comprise normally liquid or gaseous olefins, such as cracked hydrocarbon distillates of liquid or gaseous character or both, cracking still gases, refinery gases or gases from the cracking of normally gaseous paraffin hydrocarbons. It is preferable to use cracking still gases, for example C_4 hydrocarbons or a mixture of C_3 and C_4 hydrocarbons. Any portion or all of the charge from the line 84 may be introduced through any or all of the manifold lines 16, 25 and 32. Any portion or all of the charging stock may also be passed through the branch line 86 which communicates with the line 8 whereby the product may be introduced into the mixer 7. As an example equal portions of the olefinic charge may be introduced through the lines 16, 25 and 32 to the second, third and fourth stages of the system. The amounts of the charging stocks introduced through the charge lines 5 and 84 are regulated whereby the overall ratio of isobutane to olefins is at least 1:1 and preferably between about 3:1 and 5:1, although ratios considerably lower and higher have been used.

The alkylation taking place in the system is of the type disclosed in the copending application of Korpi-Goldsby, Serial No. 148,978, wherein the type of reaction is described more fully. The conditions of the reaction are temperatures of 0 to 125° F. and preferably about 60 to 90° F., and pressures sufficient to maintain a liquid phase, for example 25 to 150 pounds. The acid may be about 94 to 100% strength and prefer-

ably about 94 to 98% strength. The time of reaction is about 40 to 90 minutes and preferably about 50 to 60 minutes.

Referring to the concurrent type of operation shown in Figure 2, the acid is introduced through valve controlled line 105 by the pump 106 into a mixer 107. The hydrocarbon charge containing the isoparaffins is also introduced into the chamber 107 through the valve controlled line 109 by the pump 110. The hydrocarbons and acid are intimately mixed by the stirrer 112, and the mixture passed through the line 114 to a second mixer 115 equipped with a stirrer 116. The product from the mixer 115 passes through the line 117 to the mixer 118 equipped with a stirrer 119. The products from mixer 118 are conducted through the line 121 to a fourth mixer 122 equipped with stirrer 123. The products from the mixer 122 are passed through line 124 to the final mixer 125 containing a stirring mechanism 126.

The olefinic charge is introduced through the line 130 by the pump 131 and may be introduced into the second, third and fourth mixers 115, 118 and 122, through the manifold lines 133, 134 and 135 respectively. Branch line 137 is provided, whereby olefinic charge may be introduced into the first mixer 107. The introduction of the paraffin and olefin hydrocarbons is in substantially the same manner and same proportions as described in connection with Figure 1. It is preferable, of course, to use a multiple injection of the olefins, preferably into the second, third and fourth mixers. It will be understood, of course, that hydrocarbons may also be introduced if desired into the 5th mixer by means not shown. This introduction into the last stage also applies to the operation in Figure 1, although such introduction into the last stage was not described therein.

The products from the final mixer 125 are passed through the line 140 to settler 142, wherein the spent acid settles in the lower portion of the settler and may be withdrawn from the system through the valve controlled line 144. The hydrocarbon layer collecting in the upper portion of the settler is passed through the line 145 to a mixer 146 provided with a stirrer 148. In this mixer the acid oil is intimately contacted with a neutralizing agent, for example aqueous alkaline solution, such as caustic soda solution, introduced through valve controlled line 150 by pump 151. The mixture of hydrocarbon and neutralizing agent is passed from the mixer 146 through the line 153 to a settler 154 wherein the neutralizing agent settles and may be withdrawn from the system through the line 155 or recycled through the valve controlled line 156 and line 150 by the pump 151. The neutralized hydrocarbons are passed from the upper portion of the settler 154 through the line 159 to fractionator or still 160. In the still, all the hydrocarbons except those of higher boiling point than the desired fraction are vaporized by heat, for example the coil 162. The higher boiling hydrocarbons or unvaporized bottoms are withdrawn from the lower portion of the fractionator through the valve controlled line 163. The vapors and gases are passed overhead from the fractionator 160 through the vapor line 165 to fractionator or stabilizer 166.

In the stabilizer 166 the desired fraction, for example gasoline, is condensed and the stabilized product withdrawn from the lower portion of the fractionator through the line 168. The normally gaseous hydrocarbons are fractionated to remove permanent gases, if any, through the valve controlled line 170. A fraction for recycling, preferably containing the unreacted isoparaffins including isobutane, is taken off as a side stream through the line 172 and condenser 173, forming a condensate which is collected in the receiver 175. In case there are no gases of a more permanent nature, such as C_3 hydrocarbons or lighter, a recycle product may be removed overhead through the valve controlled line 176. The operation of the fractionator 166 is intended to be substantially the same as fractionator 68 of Figure 1, wherein the operation is described more fully. The recycled product is passed from receiver 175 through the line 176 and forced by the pump 178 to the mixer 107. A portion or all of this recycle stock may be by-passed through the valve controlled line 180 to be introduced into one or more mixers 115, 118 and 122 by the line 130 and branch lines 133, 134 and 135.

As an example of the operation of the invention, a saturated C_4 hydrocarbon fraction, comprising a substantial amount of isobutane, was mixed with cracking still gas comprising a substantial amount of unsaturated C_3 and C_4 hydrocarbons, so that the ratio of isobutane to olefins was about 3:1. This mixture was passed through a five-stage step counterflow apparatus wherein the mixture was contacted at about 60° F. for about an hour with 98% acid in the ratio of about .9 to 1 by weight, based on the olefins. In this operation the hydrocarbons were all introduced into the first stage of the system. A yield of 311° F. end point product of about 116%, based on the olefins, and having an octane number of about 91 was obtained.

The above experiment was repeated substantially in the same manner, except that the olefins were introduced equally into the second and third stages of the system while the parafin charging stock only was introduced into the first stage. A yield of 311° F. end point product of about 153%, based on the olefins, and having an octane number of about 92 was obtained. The features of contacting used alkylation acid with substantially olefin-free low-boiling isoparaffin, such as isobutane, and passing the isoparaffin with stripped olefin product to an alkylation reaction zone, and the multi-stage alkylation process involving said step, are disclosed and claimed in copending application, Serial No. 214,488, filed June 18, 1938.

As another example of the operation of the invention, an experiment was carried out under substantially the same conditions as described above except that the products were treated in a five-stage concurrent system in which the paraffin hydrocarbons, olefin hydrocarbons and acid catalyst were all charged into the first stage. A yield of 311° F. end point product of about 113%, based on the olefins, and having an octane number of about 91 was obtained.

When the same operation was carried out in a five-stage concurrent system, but the olefin hydrocarbons charged into the second, third and fourth stages, the yield obtained was approximately 151% of 311° F. end point product, based on the olefins, and having an octane number of about 92 was obtained.

While five stages of reaction have been described and shown in the drawings, it is to be understood that any number of stages may be used to give the desired results. In general about

4 to 7 stages are satisfactory and preferably about 5 or 6 stages.

Although the invention has been described in connection with a recycle operation in which there is a substantial amount of isobutane recycled, it is contemplated that the invention may be applied to a once-through operation in which substantially all the isobutane is consumed in a single pass through the system. In such a modification, the amount of olefins injected in the multiple stages may vary from stage to stage. For example, the quantity of olefins introduced may be progressively less in the later stages as the amount of unreacted isobutane becomes smaller. In this way substantially all of the isobutane may be consumed and recycling of isobutane eliminated.

It will be observed that the present invention produces a substantial increase in yield. The invention also has the advantage of reducing the formation of products outside the gasoline range, particularly the high boiling materials, and decreasing the acid consumption. In some cases also the recycling of isobutane may be eliminated.

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 process for the alkylation of isoparaffins with olefins, which comprises passing strong sulfuric acid and low boiling isoparaffins in excess of the olefins serially through a plurality of reaction stages and introducing the olefins in portions into a plurality of said stages of reaction.

2. A process for the alkylation of isoparaffins with olefins, which comprises passing strong sulfuric acid and low boiling isoparaffins in excess of the olefins serially through a plurality of reaction stages, splitting the feed of olefins and simultaneously introducing portions thereof into a plurality of said stages of reaction.

3. A process for the alkylation of isoparaffins with olefins, which comprises passing strong sulfuric acid and low boiling isoparaffins concurrently and serially through a plurality of reaction zones, introducing olefins in portions into a plurality of said zones to react with the isoparaffins therein and regulating the proportions of olefins and isoparaffins whereby an excess of isoparaffins over olefins is maintained in each of said zones.

4. A process for the alkylation of isoparaffins with olefins, which comprises passing in countercurrent flow strong sulfuric acid and low boiling isoparaffins serially through a plurality of reaction stages and introducing the olefins in portions into a plurality of said stages while maintaining an excess of isoparaffins over olefins therein.

5. A process according to claim 2 in which 4 to 7 stages of reaction are used and the olefins are introduced into at least two of the first four stages through which the isoparaffins are passed.

6. A process according to claim 2 in which the relative size of the portions of olefins is progressively decreased in the successive stages to which the portions are introduced.

7. A process for the alkylation of isoparaffins with olefins, which comprises passing in continuous countercurrent flow strong sulfuric acid and isoparaffins serially through a plurality of reaction stages, and continuously and simultaneously introducing the olefins directly to each of several of said stages while maintaining an excess of isoparaffins over olefins therein.

8. In a continuous process of alkylating isoparaffin hydrocarbons with olefin hydrocarbons in the presence of an alkylation catalyst wherein a flowing stream of isoparaffin hydrocarbons is maintained and said stream subjected to intimate and countercurrent contact with the catalyst, the steps comprising continuously and simultaneously introducing feed olefins to said flowing stream of isoparaffins at successive intervals in the direction of flow of said stream in proportion such that there is an excess of isoparaffins over olefins therein, and subjecting the olefins so introduced to intimate contact with the isoparaffins in the presence of the catalyst whereby substantial alkylation of the isoparaffins is effected.

9. A process according to claim 8 in which the catalyst is strong sulfuric acid.

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