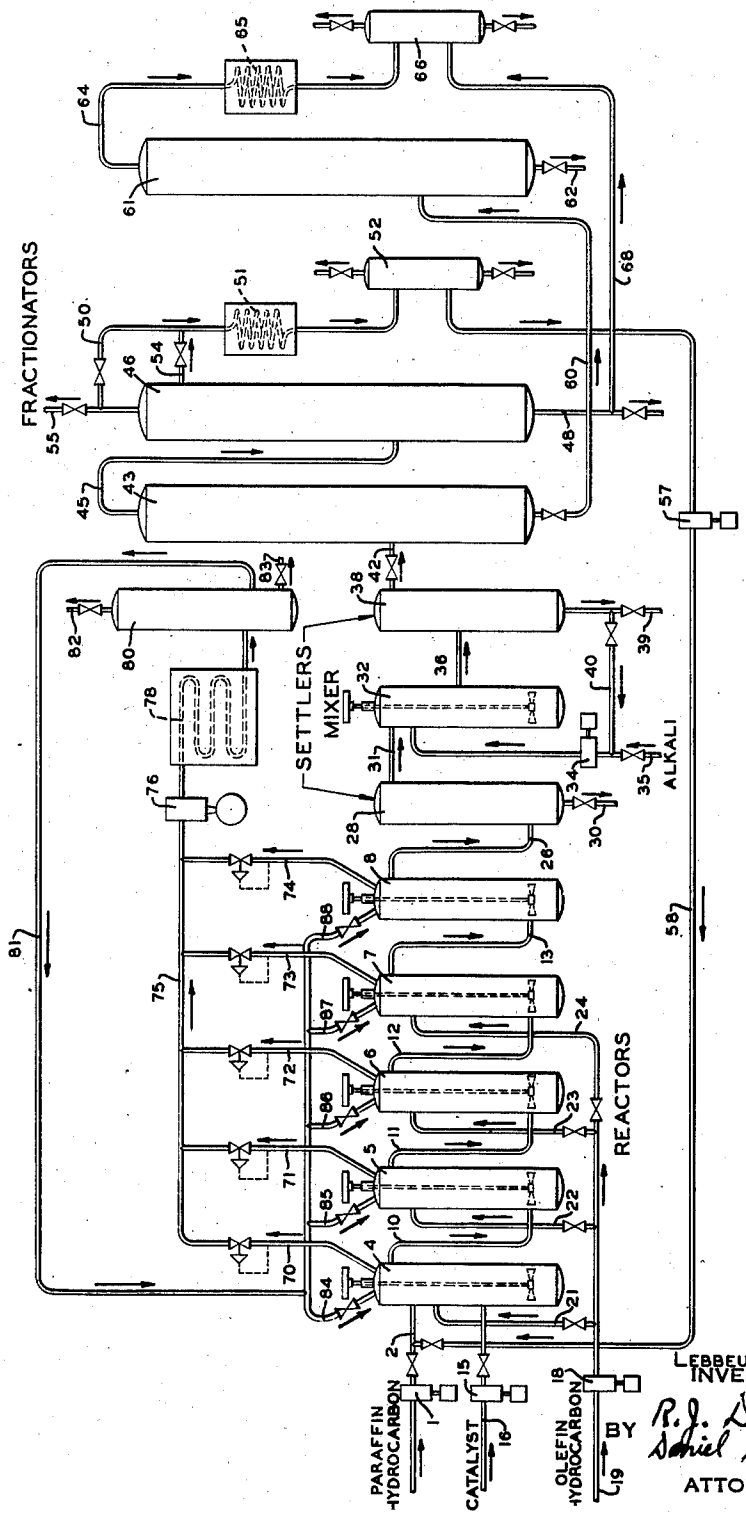
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MANUFACTURE OF ANTIKNOCK HYDROCARBONS

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MANUFACTURE OF ANTIKNOCK HYDROCARBONS

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This invention relates to the production of high antiknock hydrocarbons, suitable for the manufacture of gasoline, by the condensation or alkylation of paraffins with olefins, particularly isoparaffins with olefins, in the presence of a catalyst.

The invention has to do more specifically with improvements in an alkylation process, wherein isoparaffins, particularly low boiling isoparaffins, such as isobutane and isopentane, are intimately contacted with an alkylation catalyst, such as aluminum chloride, or, an acid catalyst of the sulfuric acid type, for example strong sulfuric acid.

When an isoparaffin, such as isobutane, and olefins, particularly low boiling olefins between 3 and 5 carbon atoms, or polymers thereof, are intimately contacted with strong sulfuric acid up to 100% strength, the isoparaffin is alkylated by the olefins to produce high antiknock, saturated hydrocarbons within the gasoline boiling point range. The alkylation or condensation reaction is usually exothermic and an object of the present invention is to provide means for removing or dissipating the exothermic heat of reaction.

Furthermore, in an alkylation process of the type described, it is often advantageous to carry out the operation over a temperature range or, to utilize a plurality of reaction zones and to maintain a differential temperature in the various zones. Another object of the present invention is to provide means for obtaining this variable, or differential temperature, in the alkylation process.

In accordance with the present invention, evaporative cooling is obtained by vaporizing a portion of the hydrocarbons undergoing reaction. When a portion of the hydrocarbons is evaporated, the heat of vaporization may be extracted from the body of liquid to remove heat in situ from the remaining unvaporized hydrocarbons. The removal of such heat may be utilized to prevent undue rise in temperature, to regulate the temperature of reaction products, and to produce substantial cooling or refrigeration. The hydrocarbons evaporated may be a portion of the normal charging stock, including those intended for reaction. It is contemplated, moreover, that the hydrocarbons evaporated may be condensed and recycled to the system, whereby depletion in volume of the reaction products is avoided.

The alkylation process is usually carried out in the liquid phase at temperatures such that normally at least a portion of the hydrocarbons would be in the vapor phase. For example, when alkylating isobutane with a C_4 unsaturated hydrocarbon fraction, temperatures of about 60° to 100° F. are often used. At such temperatures the hydrocarbons would normally be substantially in the vapor phase, but it is customary to maintain sufficient pressure on the hydrocarbons undergoing treatment to maintain the liquid phase and one method of obtaining evaporative cooling, therefore, is to adjust the pressure, whereby the necessary vaporization is produced to obtain the desired amount of cooling.

In some cases it may be desirable to carry out the alkylation operation at sufficiently low temperatures, for example around 0° F., whereby the hydrocarbons would normally be in the liquid phase without the application of the pressure. In this case the evaporative cooling, according to the invention, may be obtained by reducing the pressure by means of a vacuum to obtain partial vaporization and simultaneous evaporative cooling.

The following description of the invention is to be read in connection with the accompanying drawing, which shows a diagrammatic sketch of one form of apparatus for carrying out the process of the invention.

Referring to the drawing, a paraffinic charging stock, comprising isoparaffins, such as isobutane or isopentane or mixtures thereof, is introduced by the pump 1 through the line 2 into the first of a plurality of reaction vessels 4, 5, 6, 7 and 8. The reactors are connected in series by the lines 10, 11, 12 and 13, and each is provided with a suitable stirring mechanism. A liquid catalyst, such as sulfuric acid, is introduced by the pump 15, through the line 16, into the reaction chamber 4. The olefin hydrocarbons, which may comprise any normally liquid or normally gaseous olefins heavier than ethylene, and preferably a cracked hydrocarbon fraction, such as a C_4 fraction, or polymers thereof, are introduced by the pump 18 through the line 19 into any one or all of the reactors 4, 5, 6 and 7 through the valve controlled branch lines 21, 22, 23 and 24 respectively. It is preferable to inject the olefins at multiple points, preferably into reactors 5, 6 and 7.

The reactive ingredients in the hydrocarbon charge are the isoparaffins and olefins, although any amount of unreactive hydrocarbons, such as the normal paraffins, may be present. It is desirable to maintain the ratio of isoparaffins to olefins at least 1:1 and preferably between about 3:1 and 5:1. The proportion of the catalyst is such as to provide in the case of sulfuric acid be-

tween about .5 and 1.5 parts of acid to one part by weight of olefin.

The hydrocarbons in the liquid phase are intimately contacted, while passing through the reactors, under time and pressure conditions to produce substantial alkylation of the isoparaffins by the olefins. When using an isoparaffin, such as isobutane, and a C_4 cracked hydrocarbon fraction, temperatures of about 60° to 90° F. and a reaction time of about 30 to 60 minutes have been found satisfactory.

The reactors as shown in the drawing are connected in series so as to provide a concurrent flow of the catalyst and hydrocarbons therethrough. It is to be understood, however, that a countercurrent system may be used, whereby the acid and hydrocarbons are intimately contacted while flowing in a countercurrent direction. It has been found that a five-stage system gives excellent results, but the number of reactors may vary.

The reaction products are withdrawn from the final reactor **8** through the line **26** to a settler **28**, wherein the catalyst separates by gravity from the hydrocarbons and may be withdrawn from the lower portion of the settler through the draw-off line **30**. The catalyst, if insufficiently spent, may be recycled to the system for further use. The hydrocarbons, collecting in the upper portion of the settler, are transferred through the line **31** to a mixer **32**, provided with a suitable stirring mechanism. An alkaline neutralizing agent, such as aqueous caustic soda, is introduced by the pump **34** through the line **35** into the mixer to contact intimately with the hydrocarbons and to effect neutralization of any acid constituents. The mixture of neutralizing agent and hydrocarbons passes from the mixer **32** through the line **36** to settler **38**, wherein the neutralizing agent is allowed to settle out in the lower portion thereof. The used neutralizer may then be withdrawn through the line **39**, or if insufficiently spent, recycled to the neutralizing operation, through the branch line **40** and charge line **35**.

The neutralized hydrocarbons are conducted from the settler **38** through line **42** to a fractionator or stabilizer **43** wherein the libuid hydrocarbons are stripped of substantially all the normally gaseous hydrocarbons. The normal butane and isobutane are vaporized and passed overhead from the fractionator **43** through the vapor line **45** to a fractionator **46**. In the fractionator a separation is made between the butane and lighter hydrocarbons, including isobutane. The normal butane is condensed and collected in the lower portion of the fractionator and may be withdrawn from the bottom thereof through the line **48**. In case the vapors consist essentially of isobutane, they may be withdrawn from the upper portion of the fractionator **46** through the vapor line **50** and condenser **51**, wherein they are condensed, and the resultant condensate collected in the accumulator **52**. If other hydrocarbons are present with the isobutane in substantial amounts, the vapors may be fractionated in the upper portion of the fractionator **46**, whereby a fraction rich in isobutane is separated and withdrawn as a side stream through the line **54**. The side stream is passed through lines **54**, **50** and condenser **51** to the accumulator **52**. Any light hydrocarbons undesirable for further reaction may be removed through the release line **55**. The isobutane fraction collected in the accumulator **52** may be recycled to the alkylation operation by the pump **57** through the line **58** and charge line **2**.

The liquid hydrocarbons, collected in the lower portion of the fractionator **43**, are passed through the line **60** to a still or fractionator **61**, and subjected to fractional distillation to remove overhead vapors of gasoline boiling point range. The higher boiling products are withdrawn as bottoms from the lower portion of the fractionator through the line **62**. The vapors are passed through the vapor line **64** and condenser **65** to an accumulator **66**. The product in the accumulator consists essentially of saturated hydrocarbons of high antiknock value suitable for the manufacture of gasoline. If desired, all or a portion of the normal butane, withdrawn from the fractionator **46** through the line **48**, may be combined with the gasoline product by passing it to the accumulator **66** through the branch line **68**.

The reactors **4**, **5**, **6**, **7** and **8** are provided with vapor or gas lines **70**, **71**, **72**, **73** and **74** respectively, which communicate with a header or main line **75**, in which is located a compressor **76**. Each of the vapor release lines is provided with relief valves for maintaining sufficient pressure on the reactors to maintain the hydrocarbons therein substantially in the liquid phase. The pressure usually ranges from slightly above atmospheric to 50 or 100 pounds, or over, depending on the type of hydrocarbons treated and the temperatures employed. When charging C_4 hydrocarbons, and using temperatures of about 60° to 90° F., pressures of about 15 to 50 pounds are ordinarily used. The relief valves may be set at a predetermined point, whereby an increase in pressure, for example as a result of a rise in temperature, causes vapors to be released through the valves. As a result of the evaporation, the temperature in the reactors will be reduced sufficiently to restore the desired pressure.

According to one method of operation, all the relief valves may be set at a given pressure, corresponding to a contemplated maximum temperature. In this way any rise in temperature above that maximum may be avoided by the evaporative cooling, resulting from the generation and release of vapors when the pressure to which the relief valves are set is exceeded. The temperature may be atmospheric, or whatever it happens to be above atmospheric as a result of the exothermic heat of reaction, and the evaporative cooling may be primarily for the purpose of removing the excess exothermic heat.

According to another method of operation, positive heat may be added to the system, in addition to the exothermic heat of reaction, and the temperature controlled entirely or in part by the evaporative cooling, the extent of which may be controlled by means of the relief valves. In this case the evaporation may be for the purpose of removing either the exothermic heat of reaction, or the excess heat that may be added unintentionally to the hydrocarbon charge above that necessary to maintain the desired temperature.

According to another method of operation, evaporation of the hydrocarbons is utilized to produce positive cooling or refrigeration of the reactors. This method is principally applicable to the maintenance of a temperature lower than atmospheric. In case substantially reduced temperatures are desired, for example around 0° F., it may be desirable to maintain a vacuum on the vapor lines, whereby vaporization is induced as a result of the reduction in pressure.

It is to be understood that in any or all cases the evaporative cooling may not be depended upon entirely for the regulation of the temperature or for producing the desired amount of cooling or refrigeration, but may be auxiliary to other means which may or may not be the principal source of heat control.

It is also to be understood that the evaporative cooling in each of the reactors may be independently controlled by suitable adjustment of the pressure on the vapor lines by the relief valves. Accordingly, the evaporative cooling may be used to produce a variable temperature during the reaction, or a differential temperature between the individual reactors during the reaction period. For example, it may be desirable in some cases to maintain substantially the same temperature in each of the reactors but vary the temperature over a considerable range during the course of the reaction. Also it may be desirable in some cases to maintain a progressive increase in temperature from one reactor to another through the series of reactors. Furthermore, any desired temperature may be maintained in a given reactor which may be different from any one or all of the other reactors.

In case it is desired to maintain a temperature gradient in the various reactors, the pressure on the successive reactors may be maintained under increasingly higher pressures. It has been found desirable in some cases to maintain a temperature gradient, for example from about 70 to about 110° F., and in order to assist in maintaining this temperature gradient, the relief valves may be set to operate over a pressure range of about 25 to 75 pounds. Thus, the first reactor may be set at about 25 pounds, whereby a temperature of about 70° F. is maintained, and the second set at about 35 pounds whereby a temperature of about 80° F. is maintained, the third reactor at about 45 pounds whereby a temperature of about 90° F. is maintained, the fourth reactor at about 55 pounds whereby a temperature of about 100° F. is maintained, and the fifth reactor at about 75 pounds whereby a temperature of about 110° F. is maintained. Suitable pumps (not shown) may be used between the several reactors when they are operated at varying pressures.

The hydrocarbon vapors collected in the header 75 are compressed by the compressor 76, condensed in the cooling coil 78 and the resulting condensate collected in the accumulator 80. All or a portion of this condensate may be returned to any one or all of the reactors through the line 81 and the manifold lines 84, 85, 86, 87 and 88, the excess being released as vapors from the top of the accumulator through the line 82 or withdrawn as liquid from the lower portion thereof through the line 83.

As an example of the operation of the invention, isobutane is mixed with a cracked hydrocarbon fraction predominating in C_4 hydrocarbons, the overall ratio of isobutane to olefins in the fresh feed being about 3:1. The hydrocarbons are intimately contacted in a five-stage concurrent system with sulfuric acid catalyst of about 95% strength, the proportion of catalyst being about 80% by weight based on the olefin charge. The isobutane and catalyst are charged to the first reactor and the olefins injected equally into the second, third, and fourth reactors. Each reactor is provided with a vapor line in which is located a relief valve set at approximately 45 pounds. Whenever the temperature in the reaction vessels rises above about 90° F., the pressure in the vessels increases above the 45 pounds, resulting in the opening of the relief valves and liberation of some of the hydrocarbons to bring the pressure back to the desired normal. Such reduction in pressure results in the evaporation of hydrocarbons within the vessel with resultant evaporative cooling to lower the temperature back to the normal 90° F., or somewhat below. Inasmuch as isobutane is the lowest boiling hydrocarbon of the C_4 charge stock, and as the isobutane is present in a large proportion to provide the substantial molar excess of isobutane to olefins as specified above, it is obvious that the vapor pressure in each of the reactors is mainly that of the isobutane. Consequently, hydrocarbons evaporated on a rise in temperature within the reactors consist largely of isobutane. The vapors released through the vapor lines are collected in a main gas line, wherein they are picked up by a compressor and compressed to about 100 pounds and then passed through a cooler to effect condensation. The condensate consisting largely of isobutane is returned to the first reactor to pass again through the system, thereby serving to maintain the substantial molar excess of isoparaffin to olefins in the reactors. A reaction time of about 45 minutes is allowed. The acid is then separated from the reaction products and the hydrocarbons neutralized. The neutralized hydrocarbons are stabilized to remove overhead the normally gaseous hydrocarbons, which are fractionated to separate an isobutane fraction which is returned to the system. The stabilized hydrocarbons are distilled to produce a fraction boiling within the gasoline range which is combined with sufficient excess butane to bring the volatility up to about that of commercial gasoline. A yield of about 160% based on the olefins charged is obtained. The gasoline is largely saturated and usually has an anti-knock value of about 90.

This is a continuation of my co-pending application, Serial No. 238,715, filed November 4, 1938.

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. The method in the manufacture of high anti-knock saturated hydrocarbons, which comprises reacting a low boiling isoparaffin with a somewhat higher boiling olefin in liquid phase in a plurality of reaction zones in the presence of an alkylation catalyst maintained under alkylating conditions whereby isoparaffin is alkylated by the olefin to produce liquid alkylate, introducing the olefin by split injection into a plurality of said zones, independently maintaining the pressure on each of said zones at about the boiling point of the said isoparaffin for the predetermined temperature employed in each zone, whereby heat of reaction produces vaporization of reacting constituents consisting largely of the isoparaffin to provide evaporative cooling of each alkylation reaction zone to maintain the predetermined temperature therein, releasing vaporized constituents from each of said reaction zones and combining the released vapors, compressing and cooling said combined vapors to produce a condensate consisting largely of said isoparaffin, and continuously recycling said liquefied isoparaffin to said alkylation reaction zones to main-

tain in each zone a substantial molar excess of isoparaffin to olefin therein.

2. The method according to claim 1, in which the recycled liquefied isoparaffin is returned in independently controlled amount to each of a plurality of said alkylation zones.

3. The method according to claim 1, in which the reaction products flow serially through a plurality of the alkylation zones, and the maintained pressures on the said plurality of zones are varied in the direction of flow to provide a temperature gradient throughout the said zones.

4. The method according to claim 1, in which the maintained pressure on at least one of said reaction zones is varied to thereby vary the temperature of said zone during the course of the reaction therein.

5. The method according to claim 1, in which the catalyst is strong surfuric acid of alkylation strength, and in which a portion of the vaporized constituents released from the several reaction zones, and which remains uncondensed in the subsequent compression and cooling, is removed from the system.

6. A process for the alkylation of isoparaffins with olefins, which comprises serially passing hydrocarbons containing as the lowest boiling essential constituent thereof a low boiling isoparaffin through a plurality of reaction zones wherein the hydrocarbons are intimately contacted in the liquid phase with an alkylation catalyst under alkylating conditions, introducing a somewhat higher boiling olefin in portions and in such amounts into a plurality of said reaction zones that an excess of isoparaffin is continuously maintained therein, whereby isoparaffin is alkylated by the olefin and heat is generated as a result of the reaction, causing a portion of said hydrocarbons consisting largely of the isoparaffin in each of said zones to evaporate as a result of the generation of heat and controlling the temperature by such vaporization.

7. A process for the alkylation of isobutane with olefins, which comprises serially passing isobutane through a plurality of reaction zones wherein the isobutane is intimately contacted in the liquid phase with concentrated sulfuric acid under alkylating conditions, introducing a normally gaseous C_4 olefin by split injection into said reaction zones, regulating the amount of said injections to maintain continuously an excess of isobutane in the mixture, whereby isobutane is alkylated by the olefins and heat is liberated as a result of the reaction, causing a portion of the isobutane in each of said zones to vaporize as a result of such liberation of heat, thereby controlling the temperature, condensing the vaporized isobutane and returning the condensate to the reaction zones to increase the concentration of isobutane therein.

8. The method in the manufacture of high anti-knock saturated hydrocarbons, which comprises serially passing isobutane in liquid phase through a plurality of alkylation reaction zones, introducing a C_4 cracked hydrocarbon fraction by split injection into a plurality of said zones, contacting the said isobutane with the C_4 fraction in said zones in liquid phase in the presence of strong sulfuric acid under alkylating conditions, whereby isoparaffin is alkylated by olefins of said C_4 cracked fraction to produce normally liquid saturated hydrocarbons of high anti-knock value, maintaining the pressure on each of said zones at about the boiling point of the isobutane for the predetermined temperature employed in each zone, whereby heat of reaction produces vaporization of reacting constituents consisting largely of isobutane to provide evaporative cooling of each zone to thereby maintain the predetermined temperature therein, releasing vaporized constituents from each of said reaction zones and combining the released vapors, compressing and cooling said combined vapors to produce a condensate consisting largely of isobutane, continuously recycling said liquefied isobutane to said alkylation reaction zones to maintain in each zone a substantial molar excess of isobutane over the stoichiometric equivalent monomeric contents of the olefin therein, continuously removing alkylate from said reaction zones, stabilizing the removed alkylate to separate off gases lighter than C_5 hydrocarbons, fractionating the separated off gases to separate an isobutane-rich fraction from a normal butane fraction, and recycling the isobutane-rich fraction to the alkylation reaction zones to assist in maintaining the substantial molar excess of isobutane to olefin therein.

9. The method according to claim 8 in which the recycled isobutane condensate is supplied in independently controlled amounts to a plurality of said alkylation reaction zones.

10. A continuous process for the alkylation of isobutane by means of normally gaseous olefins in the presence of concentrated sulfuric acid, which comprises concurrently flowing a mixture of sulfuric acid, liquefied isobutane and liquefied olefin gases through a long closed reaction zone, mechanically maintaining an intimate mixture and fine dispersion of the hydrocarbons in the acid throughout the length of said zone, withdrawing the heat of alkylation from said zone substantially as fast as it is generated, whereby long and intimate contact is obtained at a substantially constant temperature within the range of about 40° to 100° F., vaporizing isobutane and olefin hydrocarbons directly from the reaction mixture in said zone, condensing said vaporized hydrocarbons, and returning at least a substantial part of said condensed hydrocarbons to the reaction zone.

11. A continuous process for the alkylation of a low-boiling isoparaffin with an olefin in the presence of an alkylation catalyst, which comprises concurrently flowing a mixture of the alkylation catalyst and isoparaffin in liquid phase through a reaction zone, introducing the olefin at a plurality of spaced points along said reaction zone, whereby the olefin is intimately contacted with the mixture in liquid phase in said zone under alkylating conditions and isoparaffin is alkylated by the olefin, and withdrawing heat from said zone at a plurality of spaced points along said zone throughout the locus of olefin introduction by internal vaporization of hydrocarbon from the flowing mixture.

12. The method of catalytically alkylating a low boiling isoparaffin with normally gaseous olefins in the presence of concentrated sulfuric acid, which comprises concurrently flowing a mixture of sulfuric acid, liquefied low boiling ioparaffin and liquefied olefin gases through a long closed reaction zone, subjecting said mixture to intimate mixing in said reaction zone to obtain a fine dispersion of the hydrocarbons in the acid throughout the length of said zone, regulating the pressure throughout the length of said zone whereby the boiling point of the hydrocarbons therein is maintained at about 40° to 100 F..

removing from said zone the hydrocarbon vapors which are evolved therein, condensing at least a part of said evolved vapors and returning said condensed vapors to said reaction zone.

13. A continuous process for the alkylation of a low boiling isoparaffin by means of normally gaseous olefins in the presence of concentrated sulfuric acid, which comprises concurrently flowing a mixture of sulfuric acid, liquefied low boiling isoparaffin and liquefied olefin gases through a long closed reaction zone, mechanically maintaining an intimate mixture and fine dispersion of the hydrocarbons in the acid throughout the length of said zone, withdrawing the heat of alkylation from said zone substantially as fast as it is generated, whereby long and intimate contact is obtained at a substantially constant temperature within the range of about 40° to 100° F., and introducing further amounts of liquefied normally gaseous olefin hydrocarbons at spaced points along said reaction zone.

14. The method of catalytically alkylating a low-boiling isoparaffin with an olefin in the presence of an alkylation catalyst, which comprises concurrently flowing a mixture of the catalyst together with the low-boiling isoparaffin and olefin in liquid phase through a long closed reaction zone, subjecting said mixture to intimate mixing in said reaction zone to obtain a fine dispersion of the hydrocarbons in the catalyst throughout the length of said zone, regulating the pressure throughout the length of said zone whereby the boiling point of the hydrocarbons therein is maintained at about 0° to 100° F., removing from said zone the hydrocarbon vapors which are evolved therein, condensing at least a part of said evolved vapors and returning at least a part of said condensed vapors to said reaction zone.

15. A continuous process for the alkylation of a low-boiling isoparaffin with an olefin in the presence of an alkylation catalyst, which comprises concurrently flowing a mixture of the catalyst together with the low-boiling isoparaffin and olefin in liquid phase through a long closed reaction zone, mechanically maintaining an intimate mixture and fine dispersion of the hydrocarbons in the catalyst throughout the length of said zone, withdrawing the heat of alkylation from said zone substantially as fast as it is generated, whereby long and intimate contact is obtained at a substantially constant temperature within the range of about 0° to 100° F., and introducing further amounts of olefin in liquid phase at spaced points along said reaction zone.

16. A process for the alkylation of an isoparaffin with an olefin, which comprises serially passing the isoparaffin in liquid phase through a plurality of reaction zones containing an alkylation catalyst and maintained under alkylating conditions, introducing an olefin in portions and in such amounts into a plurality of said reaction zones that a molar excess of isoparaffin to olefin is continuously maintained therein, whereby isoparaffin is alkylated by the olefin and heat is generated as a result of the reaction, causing a portion of the hydrocarbons present in each of said plurality of zones to evaporate as a result of the generation of heat and controlling the temperature by such vaporization, releasing vapors from each of said zones and combining the released vapors, recovering a condensate consisting largely of the said isoparaffin from the released vapors, and recycling at least a portion of said condensate to the reaction zones to assist in maintaining the molar excess of isoparaffin to olefin therein.

17. The method in the manufacture of high anti-knock saturated hydrocarbons, which comprises reacting a low-boiling isoparaffin with an olefin in liquid phase in a plurality of reaction zones in the presence of an alkylation catalyst maintained under alkylating conditions to produce liquid alkylate, introducing the olefin by split injection into a plurality of said zones, independently maintaining the pressure on each of said zones at about the boiling point of said isoparaffin for the predetermined temperature employed in each zone, whereby heat of reaction produces vaporization of reacting constituents to provide evaporative cooling of each alkylation reaction zone to maintain the predetermined temperature therein, releasing vaporized constituents from each of said reaction zones and combining the released vapors, recovering a condensate consisting largely of said low-boiling isoparaffin from said released vapors and continuously recycling at least a portion of said condensate to said alkylation reaction zones to maintain in each zone a substantial molar excess of isoparaffin to olefin therein.

18. The method of catalytically alkylating a low-boiling isoparaffin with somewhat higher boiling olefins of a cracked hydrocarbon fraction in the presence of an alkylation catalyst, which comprises continuously introducing the low-boiling isoparaffin and the cracked hydrocarbon fraction, with the low-boiling isoparaffin in molar excess of the olefins of said fraction, into an alkylation reaction zone and reacting the same therein in liquid phase in the presence of an alkylation catalyst under alkylating conditions, maintaining a pressure on the alkylation reaction zone at about the boiling point of the said low-boiling isoparaffin at the predetermined temperature employed, whereby heat of reaction produces vaporization of hydrocarbon constituents including the low-boiling isoparaffin to provide evaporative cooling of the alkylation zone to maintain the said predetermined temperature, releasing the resulting hydrocarbon vapors from the said reaction zone, subjecting the released vapors to condensation by compression and cooling, passing the resulting compressed and cooled hydrocarbons to an accumulating zone, removing hydrocarbon vapors from said accumulating zone and discharging the same from the system, recycling resulting liquid condensate consisting largely of the said low-boiling isoparaffin from said accumulating zone to the alkylation reaction zone to assist in maintaining a molar excess of isoparaffin to olefin therein, and continuously removing alkylation reaction products from said reaction zone and recovering alkylate therefrom.

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