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ALKYLATION PROCESS

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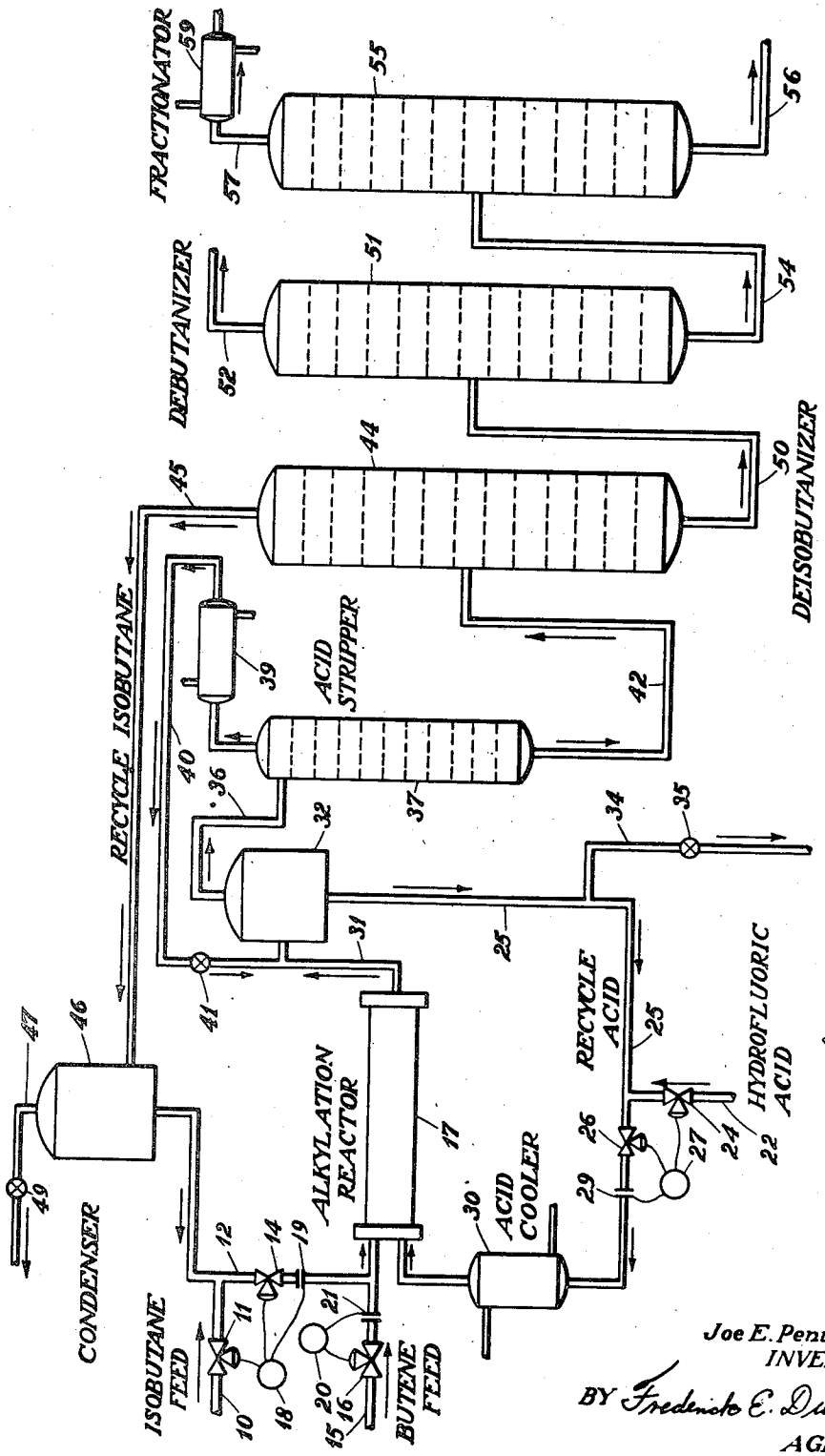

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ALKYLATION PROCESS

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4 Claims. (Cl. 260—683.4)

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This invention relates to the production of higher boiling hydrocarbons from lower boiling hydrocarbons in the presence of catalytic agents and relates more particularly to the alkylation of isoparaffins with olefins in the presence of acid catalysts.

As is well known, hydrocarbon products may be produced by alkylation reactions involving the combination or condensation of two dissimilar hydrocarbon reactants in the presence of suitable catalytic agents. While various types of alkylate products may be obtained by employing various types of reactants, the alkylation of low boiling isoparaffins such as isobutane and isopentane with low boiling olefins such as ethylene, propylene, the isomeric butenes, and the isomeric pentenes, for the production of aviation fuels and high grade motor fuels has become of particular importance. Sulfuric acid has been employed as a catalyst in isoparaffin-olefin alkylation and more recently liquid hydrogen fluoride has found favor as a catalyst. The alkylation of isobutane with butenes is representative of these reactions and has been commonly carried out by feeding isobutane and butene feed stocks in the liquid state along with liquid hydrogen fluoride to a multi-pass alkylation reactor such as the reaction loop type reactor, wherein the hydrocarbons and catalyst are vigorously agitated and continuously circulated within a closed circuit. The reaction is exothermic and temperature control is important to prevent localized or general overheating of the reaction mixture with consequent deleterious effect on the yield and quality of the alkylate product as a result of side reactions occurring at elevated temperatures. Temperature control is obtained by means of internal heat exchangers over which the reaction mixture passes or by passing a portion of the continuously circulating mixture through an external heat exchanger. A portion of the circulating reaction mixture is continuously withdrawn from the reactor and the acid allowed to settle therefrom, after which the hydrocarbon product is treated for removal of excess isobutane reactant and removal of normal butane and any lighter hydrocarbons which may be present, the acid and the isobutane being recycled to the reactor. It has been proposed to carry out the alkylation reaction in single pass reactors, i. e., reactors in which the reaction mixture is not continuously circulated, but such reactors have not been extensively used, despite the fact that they possess advantages not possessed by multi-pass reactors, primarily because of the difficulty of obtaining

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proper control of the reaction temperature and because of the belief that very high ratios of saturated hydrocarbons to unsaturated hydrocarbons were essential to prevent olefin polymerization therefore making it desirable to recirculate the saturated hydrocarbon products.

It is an object of this invention to provide an improved alkylation process. It is another object of this invention to provide a process for the alkylation of isoparaffins with olefins in single-pass reactors. It is another object of this invention to provide a method for controlling the temperature of isoparaffin-olefin alkylation mixtures in single-pass reactors. Further objects and advantages of the invention will become apparent from the following description thereof.

In accordance with the invention, the above objects are achieved by a process which involves feeding to a single-pass reaction zone a volume ratio of acid catalyst to total hydrocarbons of at least three to one, separating the acid catalyst from the reactor effluent, recycling at least a portion of the separated acid, and cooling at least a portion of the recycled acid to maintain the temperature of the reaction mixture at a predetermined level.

The amount of heat evolved in alkylation reactions is a function of the type of alkylation reactants, i. e., the heat of alkylation will vary with different reactants, and the temperature rise of the reaction mixture will be a function of the heat of alkylation and the relative amounts and specific heats of the reactants, acid catalyst, alkylate product, and any inert hydrocarbons which may be contained in the hydrocarbon feed stocks. The acid catalyst has a relatively high specific heat and when employed in volume ratios of at least three to one is capable of absorbing the exothermic heat of reaction and preventing an undesirably large increase in the temperature of the reaction mixture. The acid catalyst separated from the reactor effluent and recycled to the reactor will contain the heat absorbed from the alkylation reaction minus or plus, of course, that heat which may be conducted to or taken from the atmosphere through the walls of the reactor, separator, pipe lines, etc., and the cumulative effect of the heat contained in the recycle acid increasing the temperature of the reaction mixture with repeated recycling is avoided by cooling the recycle acid, or a portion of the recycle acid, to a sufficiently low temperature.

The effect of acid catalyst-hydrocarbon ratio on the rise of temperature of the reaction mixture is shown in the following table. The data were

obtained by alkylating isobutane feed stock with butene feed stock in a single-pass reactor and employing varying volume ratios of hydrofluoric acid to total hydrocarbons. The isobutane and butene feed stock combined analyzed 5% propane, 60% isobutane, 12% butene, 21% normal butane, and 2% pentane by volume.

Ratio of Hydrofluoric Acid to Total Hydrocarbons	Increase in Temperature of Reaction Mixture
	°F.
1 to 1	34.8
3 to 1	12.7
4.7 to 1	7.2
9 to 1	5.0
19 to 1	2.4

It will be seen from the table that the use of hydrofluoric acid-hydrocarbon ratios of at least three to one results in only small increases in temperature of the reaction mixture. Additionally, at high acid-hydrocarbon ratios, the temperature rise is relatively uniform due to the much greater degree of dispersion of the reactants in the reaction mixture. By suitably cooling the acid separated from the reactor effluent and recycled to the reactor, compensation may be made for the rise in temperature of the reaction mixture and the desired inlet temperature and outlet temperature of the reaction mixture may be continuously maintained.

The use of hydrofluoric acid-hydrocarbon ratios of at least three to one results not only in minimizing localized and general overheating of the reaction mixture by absorbing the exothermic heat of reaction but has the additional effect of improving the quality of the alkylate product through the catalytic effect of the large volumes of acid catalyst. Heretofore, isoparaffin-olefin alkylations, particularly isobutane-butene alkylation, have been carried out by employing hydrofluoric acid-hydrocarbon ratios of about one to one or slightly higher, i. e., the volume of hydrofluoric acid employed, including the recycle acid, has been equal to or slightly greater than the volume of isobutane and butene feed stock, including any normal paraffins or other inert hydrocarbons contained therein, plus the recycled isobutane. It has been recently discovered, as disclosed in my co-pending application with Urban H. Wagner and Carl S. Kuhn, Jr., Serial No. 561,888, filed November 4, 1944, that significant increases in the octane numbers of the alkylate products are obtained by employing hydrofluoric acid-hydrocarbon ratios of at least three to one. As the co-pending application discloses, it appears that the controlling factor in isoparaffin-olefin alkylation producing high yields of branched chain compounds having high octane numbers, for example, high yields of 2,2,4-trimethyl pentane (iso-octane) by the alkylation of isobutane with butenes, is a low concentration of olefin dissolved in the acid phase of the reaction mixture or, which is the same thing since isoparaffins are only slightly soluble in the acid phase, a high ratio of dissolved isoparaffin to olefin. As the co-pending application further discloses, effectively low concentrations of dissolved olefin or high ratios of dissolved isoparaffin to olefin are obtained by employing volume ratios of acid catalyst to total hydrocarbons fed to the alkylation reactor of at least three to one. Thus, the use of acid to hydrocarbon ratios of at least three to one is an important feature of the present invention when employing hydrofluoric acid as the catalytic agent in the alkylation of isoparaffins from the standpoint of obtaining the catalytic effect of the high ratios of acid to hydrocarbons on the quality of the product and the effect of minimizing localized and general rise in temperature of the reaction mixture.

While satisfactory results may be obtained by employing ratios of acid to hydrocarbon of at least three to one, it is desirable to employ higher ratios, as, for example, ratios of 10 to 1 to 50 to 1. Even extremely high ratios, such as ratios of 200 to 1 and higher, may be employed since both the catalytic effect and the temperature controlling effect of the acid increases with increasing acid ratios.

The entire amount of acid being fed to the reactor may be cooled or only a portion of the acid may be cooled. For example, the recycle acid alone or only a portion of the recycle acid may be cooled, or the entire amount or only a portion of the recycle acid plus fresh or regenerated make-up acid may be cooled. The extent to which the acid is to be cooled will depend upon the temperature rise of the reaction mixture and the amount of acid being cooled. Thus, where the entire amount of acid is cooled the extent of cooling will be less than where only a portion of the acid is cooled. Preferably, the entire amount of acid is cooled or the cooled portion thoroughly premixed with the rest of the acid going to the reactor in order to avoid localized under-cooling at the inlet portion of the reactor. The extent of cooling required will vary for each particular case and can be determined by those skilled in the art by actual operation or by calculation.

The essential feature of single pass reactors is a substantially steady forward flow of the reaction mixture from the inlet to the outlet of the reactor and the process of the invention is applicable to any type of reactor fulfilling this condition. The reactor may be a straight chamber or may be a curved tubular reactor. If desired, the reactor may be provided with baffles or other flow distributing means of such nature as to increase the turbulence of the reaction mixture without substantial interference with its predominantly forward flow through the reactor.

The process of the invention may be employed for the alkylation of isobutane with ethylene, propylene, butenes, pentenes, etc., and the alkylation of isopentane with these same olefins. However, the process of the invention may be employed in connection with any type of alkylation. The feed stocks may consist entirely of the pure reactants such as pure isoparaffin and pure olefin, or mixtures of pure isoparaffins and pure olefins, or may contain normal paraffins or other inert hydrocarbons. Refinery butane-butene mixtures obtained, for example, by the fractionation of gas mixtures from cracking operations or by the partial dehydrogenation of butane fractions obtained from natural gas or from stabilization of natural or straight run naphthas and containing normal butane and hydrocarbons heavier and lighter than 4-carbon atom hydrocarbons may be employed in isobutane-butene alkylation. However, it is desirable to carry out the alkylation reaction with feed stocks containing minimum amounts of inert hydrocarbons.

Conventional alkylation conditions with respect to temperature, pressure and isoparaffin-olefin ratio may be employed. For example, the

alkylation of isobutane with butenes may be carried out at temperatures between about 0° F. and 150° F., at pressures at least sufficiently high to keep the hydrocarbons and hydrofluoric acid in the liquid phase and with isobutane-butene ratios of between 2 to 1 and 15 to 1, preferably between about 6 to 1 and 10 to 1. Ratios of isobutane to butenes of at least 2 to 1 are essential since lower ratios tend to cause polymerization of the butenes with resultant decrease in yield of the alkylate product and/or excessive reaction between the butenes and the primary alkylate product because of the relatively low ratios of isobutane to alkylate product in the reaction mixture. The hydrofluoric acid may be anhydrous hydrofluoric acid or may have a titratable acidity as low as 70% by weight. Following alkylation, the reaction products may be treated in known manner for separation and reuse of hydrogen fluoride catalyst, separation and recycling of unreacted isoparaffin and recovery and purification of alkylate product.

The accompanying drawing is a flowsheet illustrating one mode of carrying out the process of the invention in connection with the alkylation of isobutane with butene.

Referring now to the drawing, isobutane in the liquid state enters the system through line **10** provided with a suitable control valve **11** and is admixed in line **12** provided with a suitable control valve **14** with recycle isobutane obtained in the manner hereinafter described. The isobutane is admixed with liquid butene feed entering the system through line **15** provided with a suitable control valve **16**, and the combined feeds passed to alkylation reactor **17**. The volume of isobutane fed to the alkylation reactor is regulated by means of flow controller **18** operating valves **11** and **14** and activated by flow responsive means **19**, and the volume of butene is regulated by means of flow controller **20** operating valve **16** and activated by flow responsive means **21**.

Fresh and/or regenerated liquid hydrofluoric acid enters the system through line **22** provided with a suitable control valve **24** and is admixed in line **25**, also provided with a suitable control valve **26**, with recycle hydrofluoric acid obtained in the manner hereinafter described. The volume of hydrofluoric acid is regulated by means of flow controller **27** operating valves **24** and **26** and activated by flow responsive means **29**. The acid in line **25** passes through acid cooler **30** where it is cooled to the desired temperature and then passes to reactor **17**. The mixed hydrofluoric acid and hydrocarbon feeds pass through the reactor and are withdrawn through line **31** and passed to separator **32** for gravity separation of the acid from the hydrocarbons. Recycle acid catalyst is withdrawn from the lower portion of separator **32** and returned through line **25** to the reactor, fresh and/or regenerated acid entering through line **22** as necessary. Line **34** provided with valve **35** is connected to the line **25** for continuous or intermittent removal of a portion of the recycle acid for regeneration. After regeneration, the acid may be returned to the system through line **22**.

The hydrocarbon phase from the separator **32** is taken overhead through line **36** and sent to hydrofluoric acid stripping column **37** where a major portion of dissolved and suspended hydrofluoric acid carried over in the hydrocarbon phase is vaporized and returned after condensation in condenser **39** to the separator **32** through line **40** provided with valve **41**. The bottoms from stripper **37** are passed through line **42** to deisobutanizer **44** for removal of isobutane. Residual traces of hydrofluoric acid and organic fluoride contained in the bottoms from stripper **37** may be removed by chemical treatment, as with bauxite, prior to introduction of the hydrocarbons in deisobutanizer **44**. The isobutane is removed as overhead through line **45** and passed to condenser **46** maintained under such conditions of temperature and pressure that the isobutane condenses while any lighter hydrocarbons which may have formed during the alkylation reaction or which may have been contained in the hydrocarbon feed remain in the gaseous state. The gases pass out of the condenser through line **47** provided with valve **49** and the liquid isobutane is recycled through line **12** to the alkylation reactor **17**. The bottoms from deisobutanizer **44** are passed through line **50** to debutanizer **51** where normal butane formed during the reaction or which may have been contained in the feed hydrocarbons is removed as overhead through line **52**. If desired, the normal butane from line **52** may be isomerized to isobutane and recycled to the reactor **17**. The debutanizer bottoms are passed through line **54** to fractionator **55** where the alkylate product is separated into aviation alkylate and heavy alkylate. The heavy alkylate is removed as bottoms through line **56** and the aviation alkylate is removed as overhead through line **57** and condensed in condenser **59**.

The following examples are illustrative of the results obtainable by the process of the invention. In these examples, isobutane feed stock was alkylated with butene feed stock employing hydrofluoric acid as the catalyst. The feed stocks analyzed as follows:

Hydrocarbon	Volume Per Cent	
	Example 1	Example 2
Propane and Propylene	1.24	1.21
Isobutane	65.15	67.82
Isobutene	2.90	2.83
Butene-1	3.11	3.24
Normal Butane	21.78	19.64
Butene-2	4.99	4.45
Pentane, Pentenes, and heavier	0.83	0.81

and were used in proportions to give the isobutane-butene ratios indicated in the table below. The reaction was carried out in a single-pass reactor comprising a section of straight pipe one inch in diameter and twenty-feet long. The reactor effluent was sent to a separator where the hydrofluoric acid was allowed to settle from the hydrocarbon phase and the separated acid was recycled to the reactor. The entire amount of recycle acid plus the make-up acid was cooled before entering the reactor. The hydrocarbon phase was stripped of dissolved hydrofluoric acid and chemically treated for removal of any remaining hydrofluoric acid and was then deisobutanized, the isobutane being recycled to the reactor. Thereafter, the hydrocarbon phase was fractionated for removal of normal butane and lighter hydrocarbons. The resulting product was regarded as the total alkylate product. The total alkylate product was then fractionated into heavy alkylate and aviation alkylate, the aviation alkylate being that portion of the total alkylate product boiling below 356° F. The reaction conditions and results obtained are given in the table following.

Table

Example Number	1	2
Isoparaffin-Olefin Ratio by Volume	5.9	6.4
Hydrofluoric Acid-Total Hydrocarbon Ratio by Volume	39 to 1	199 to 1
Titratable Acidity of Hydrofluoric Acid, Weight Per cent	89.6	89.3
Residence Time of Reactants in Reactor, Seconds	15	3
Mass Velocity of Reactants in Reactor, Pounds per Square Foot per Second	79	420
Inlet Temperature of Reactants, ° F.	90	90
Outlet Temperature of Reactants, ° F.	91.1	90.2
Yield of Total Alkylate on Basis of Butenes Consumed, Volume Per cent	179	184
Yield of Aviation Alkylate on Basis of Butenes Consumed, Volume Per cent	166	174
F-3 Octane Number of Aviation Alkylate: Clear [1]	90.8	91.2
F-4 Octane Number of Aviation Alkylate [2] 8+cc. of Tetraethyl Lead per Gallon	2.08	2.71

[1] Octane number of aviation alkylate per se.
[2] Aviation alkylate to which has been added 4.0 cc. of tetraethyl lead per gallon.
(The F-3 and F-4 octane numbers were determined by the standard Aviation Fuel Division motor methods.)

It will be seen from the above table that high yields of high octane number alkylate product are obtained by the process of the invention.

Having thus described my invention, it is to be understood that such description has been given by way of illustration and example only and not by way of limitation, reference being had for the latter purpose to the appended claims.

I claim:

1. In an alkylation process of the type wherein a liquid isoparaffin, a liquid olefin, and hydrofluoric acid catalyst are fed into the inlet of a single-pass reaction zone wherein substantially forward flow of reaction mixture is maintained, the reaction mixture including alkylate product, isoparaffin, hydrofluoric acid, and any unreacted olefin is withdrawn from the outlet of said reaction zone and sent to a separation zone for separation into a hydrocarbon phase and an acid phase, and the acid phase recycled to the inlet of said reaction zone for admixture with fresh isoparaffin and olefin, the improvement in controlling the temperature of the reaction mixture in the reaction zone which comprises regulating the volume of hydrofluoric acid fed to said reaction zone including that recycled from said separation zone to the volume of total hydrocarbons fed to said reaction zone such that the volume of hydrofluoric acid in said reaction zone is at least ten times as great as the total volume of hydrocarbons in said reaction zone and cooling by indirect heat exchange at least a portion of the hydrofluoric acid to a temperature such that the average temperature of the entire portion of hydrofluoric acid entering said reaction zone is sufficiently below the maximum temperature desired therein that substantially the entire heat of reaction will be taken up by the reaction mixture without raising the temperature thereof in excess of the predetermined maximum value desired.

2. In an alkylation process of the type wherein a liquid isoparaffin, a liquid olefin, and hydrofluoric acid catalyst are fed into the inlet of a single-pass reaction zone wherein substantially forward flow of reaction mixture is maintained, the reaction mixture including alkylate product, isoparaffin, hydrofluoric acid, and any unreacted olefin is withdrawn from the outlet of said reaction zone and sent to a separation zone for separation into a hydrocarbon phase and an acid phase, and the acid phase recycled to the inlet of said reaction zone for admixture with fresh

isoparaffin and olefin, the improvement in controlling the temperature of the reaction mixture in the reaction zone which comprises regulating the volume of hydrofluoric acid fed to said reaction zone including that recycled from said separation zone to the volume of total hydrocarbons fed to said reaction zone such that the volume of hydrofluoric acid in said reaction zone is between ten and fifty times as great as the total volume of hydrocarbons in said reaction zone and cooling by indirect heat exchange at least a portion of the hydrofluoric acid to a temperature such that the average temperature of the entire portion of the hydrofluoric acid entering said reaction zone is sufficiently below the maximum temperature desired therein that substantially the entire heat of reaction will be taken up by the reaction mixture without raising the temperature thereof in excess of the predetermined maximum value desired.

3. In an alkylation process of the type wherein a liquid isoparaffin, a liquid olefin, and hydrofluoric acid catalyst are fed into the inlet of a single-pass reaction zone wherein substantially forward flow of reaction mixture is maintained, the reaction mixture including alkylate product, isoparaffin, hydrofluoric acid, and any unreacted olefin is withdrawn from the outlet of said reaction zone and sent to a separation zone for separation into a hydrocarbon phase and an acid phase, and the acid phase recycled to the inlet of said reaction zone for admixture with fresh isoparaffin and olefin, the improvement in controlling the temperature of the reaction mixture in the reaction zone which comprises regulating the volume of hydrofluoric acid fed to said reaction zone including that recycled from said separation zone to the volume of total hydrocarbons fed to said reaction zone such that the volume of hydrofluoric acid in said reaction zone is between ten and fifty times as great as the total volume of hydrocarbons in said reaction zone and cooling by indirect heat exchange the entire portion of hydrofluoric acid entering said reaction zone to maintain the inlet and outlet temperatures of the reaction mixture at predetermined values.

4. In an alkylation process of the type wherein a liquid isoparaffin, a liquid olefin, and hydrofluoric acid catalyst are fed into the inlet of a single-pass reaction zone wherein substantially forward flow of reaction mixture is maintained, the reaction mixture including alkylate product, isoparaffin, hydrofluoric acid, and any unreacted olefin is withdrawn from the outlet of said reaction zone and sent to a separation zone for separation into a hydrocarbon phase and an acid phase, and the acid phase recycled to the inlet of said reaction zone for admixture with fresh isoparaffin and olefin, the improvement in controlling the temperature of the reaction mixture in the reaction zone which comprises regulating the volume of hydrofluoric acid fed to said reaction zone including that recycled from said separation zone to the volume of total hydrocarbons fed to said reaction zone such that the volume of hydrofluoric acid in said reaction zone is 200 times as great as the total volume of hydrocarbons in said reaction zone and cooling by indirect heat exchange the entire portion of hydrofluoric acid entering said reaction zone to maintain the inlet and outlet temperatures of the reaction mixture at predetermined values.

JOE E. PENICK.

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