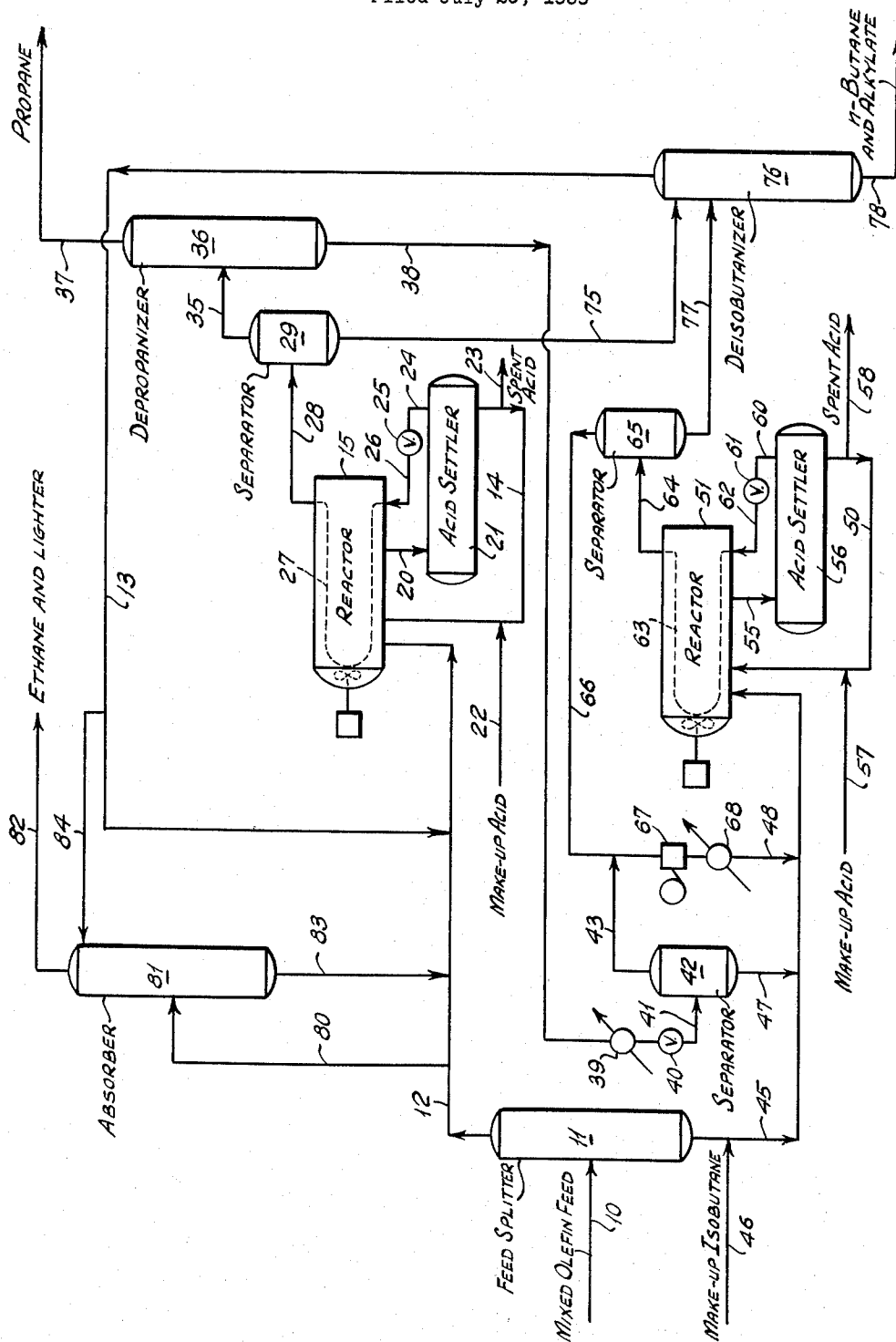


Nov. 7, 1961

F. A. CLAUSON
ALKYLATION PROCESS

Filed July 29, 1959

3,007,983



1

3,007,983

ALKYLATION PROCESS

Frank A. Clauson, Roslyn Heights, N.Y., assignor to Texaco Inc., New York, N.Y., a corporation of Delaware

Filed July 29, 1959, Ser. No. 830,304
6 Claims. (Cl. 260—683.46)

This invention relates to an improved process for catalytic alkylation and more particularly to such process wherein an olefin-based alkylatable material is alkylated with an isoparaffin in the presence of a catalyst. In one of its embodiments it is directed to a method of alkylating propylene and butylenes wherein the propylene is separated from the butylenes by fractionation under conditions effecting essentially complete removal of propane and lighter hydrocarbons from the butylene fraction and effecting inclusion of a promotional amount of butylene in the propylene fraction. The propylene is alkylated in a self-refrigerated first alkylation zone wherein a part of the low boiling hydrocarbon components including isobutane and propane are evaporated from the resulting hydrocarbon mixture of the first alkylation zone. The evaporated components, mainly isobutane, from self-refrigerating the first alkylation zone are depropanized and the depropanized isobutane stream is passed to a second alkylation zone. The aforesaid butylene fraction is alkylated in said second alkylation zone which is also self-refrigerated by evaporating a portion of the low boiling hydrocarbon components. The evaporated low boiling components from the second alkylation zone again mostly isobutane are condensed and recycled to the said second alkylation zone whereby substantially no propane is introduced into the second alkylation zone and depropanization of the evaporated components therefrom is unnecessary. Advantageously the isobutane from the deisobutanizer, which contains little normal butane, is employed as the source of isobutane fed to the propylene alkylation reactor. Effluent resulting liquid from the propylene alkylation zone contains relatively little normal butane and may be charged to the top of the deisobutanizing tower thereby displacing at least a part of the isobutane reflux required therein. Effluent resulting liquid from the butylene alkylation containing a larger portion of normal butane is introduced into the deisobutanizing tower at an intermediate point. When the propylene feed stream contains some ethylene, the propylene may be freed of the ethylene by distillation or by selective absorption. Advantageously, isobutane may be employed as absorption medium whereby propylene is absorbed in isobutane to provide a feed stream comprising both olefin and isoparaffin for the alkylation reaction zone.

In the catalytic alkylation of olefins with isoparaffins, a preponderance of isoparaffin (generally as much as 70 to 80 volume percent or more of the hydrocarbons in the reaction mixture) over olefin material and hydrocarbon diluents is used to direct the reaction towards production of the most valuable aviation or automotive fuels. Consequently a large quantity of isoparaffin must be recovered and recycled for reuse in the process. Isobutane is generally used as the isoparaffin for the manufacture of aviation or motor fuels although other isoparaffins, for example, isopentane may be employed.

The alkylatable material for reacting with isobutane is olefin-based, that is, it is generally an olefinic hydrocarbon itself such as propylene, butylene or the like, but it also can be an alkyl sulfate or fluoride (as obtained for example in a so-called "two stage" process wherein an olefinic hydrocarbon is absorbed in sulfuric acid or HF as a first stage in the alkylation operation), or an alkyl halide, suitably an alkyl fluoride or chloride which

2

can be made readily from olefinic hydrocarbons by other means.

The contacting of the excess isobutane with the alkylatable material and catalyst is done in liquid phase. With a catalyst such as hydrogen fluoride, alkylation temperatures as high as about 100° F. can be tolerated, but the most desirable alkylation temperatures are generally lower than this. With a catalyst such as sulfuric acid, alkylation temperatures substantially above about 75° F. are usually not used. A desirable temperature, preferably within the range of about 30° to 55° F., can be maintained in the alkylation zone by auto-refrigeration, or by effluent refrigeration applied to that zone.

In an effluent refrigeration system, the effluent of the alkylation zone comprising catalyst reactants and products is separated into a hydrocarbon phase and a liquid catalyst phase. The separated hydrocarbon phase is passed into a flash zone of lower pressure where any low boiling components, including some of the isobutane present, are vaporized with concomitant cooling of the vapor and remaining liquid hydrocarbons including alkylate. At least a part of the cooled hydrocarbons is used to refrigerate the reaction zone indirectly. In this operation, the alkylation zone and effluent separator are maintained under sufficient pressure to keep all components in the liquid phase. Flashing in a flash zone as referred to herein denotes the practically adiabatic forming of chilled vapors and residual liquid by reduction of pressure on a liquid hydrocarbon material. In an auto-refrigeration system the lower boiling hydrocarbons, including some of the isobutane present, are evaporated directly from the contents of the alkylation reaction zone to maintain a desirable reaction temperature. Effluent refrigeration and autorefrigeration are termed "self-refrigeration" since in each case refrigeration is effected by evaporation of components of the reaction mixture.

In catalytic alkylation, the mol ratio of isoparaffin to olefin-based material supplied to the alkylation zone is maintained substantially in excess of 1 to 1, and preferably within the range of about 4 to about 20 to 1. The catalyst to liquid hydrocarbon volume ratio is maintained within the range of about 0.5 to 1 to about 5 to 1 and preferably within the range of about 1 to 1 to about 3 to 1. Catalyst strength is maintained of at least about 88% acid strength when sulfuric acid is used, of at least about 85% titratable acidity when hydrogen fluoride is used or of at least 15 weight percent aluminum chloride (expressed as equivalent aluminum) when aluminum chloride-hydrocarbon complex liquid catalyst is used. A liquid catalyst which is non-volatile under alkylation reaction conditions, for example, sulfuric acid, is preferred. Sulfuric acid strength is maintained at about 88 to 92% by purging spent acid from the system and by adding make-up acid of about 98 to 99.5 percent purity.

An important part of the isobutane employed in alkylation processing is a recycle stream produced by fractional distillation of alkylation products in a deisobutanizing fractional distillation zone, the isobutane being recovered as a distillate fraction of high isobutane concentration, for example, about 85 to 95 liquid volume percent isobutane. The higher-boiling alkylate in such distillation zone is recovered in the liquid bottoms fraction. This liquid bottoms fraction ordinarily is redistilled in conventional manner to separate light ends and to produce the high quality alkylate fuel blending stock.

In a self-refrigerated alkylation zone, the preponderant hydrocarbons present in the evaporated mixture include the highly volatile propane, if that is present in the reaction mixture, and isobutane. Very little alkylate escapes into the vapor phase in such evaporation for refrigeration purposes. The remaining hydrocarbon liquid, comprising unevaporated isobutane and higher boiling materials in-

cluding the alkylate, is sent to the deisobutanizing fractional distillation zone.

In the usual deisobutanizing fractional distillation operation, isobutane distillate is returned to the top of the distilling column as reflux at a high reflux ratio, for example 6 to 1, to maintain high isobutane purity in the distillate. As a result, only a small part of the distillate is withdrawn from the column for recycle to the alkylation reactor and only this small part withdrawn is available for maintenance of the isobutane excess required in the reaction mixture.

Broadly, my process is directed to a method of alkylating olefins in an olefinic mixture comprising propane, propylene and butylenes wherein said mixture is separated into fractions, the first fraction comprising all of the propane and propylene and a part of the butylene, and the second fraction comprising the remaining butylene free of propane, and said two fractions are separately alkylated in corresponding first and second self-refrigerated zones employing isobutane from product deisobutanization to provide isobutane in said first zone and depropanized refrigerant from said first zone and recycled refrigerant from said second zone to provide isobutane in said second zone.

Alkylation feed stocks containing only propylene as olefin react slowly even at high temperatures producing low yields of alkylate. Butylenes in amounts of at least 5 percent basis the olefin in the feed for a propylene alkylation process promote the propylene alkylation so that high yields of propylene alkylate at low reaction temperatures may be obtained. In accordance with the process of this invention, the feed stock is fractionated to effect inclusion of an effective promotional quantity of butylene in the propylene feed stock and at the same time effect separation of the olefin feed streams in a manner which assures that essentially all propane will be included in the propylene fraction and practically none will appear in the butylene fraction. This provides a feed mixture for the propylene alkylation zone which produces high yields of desirable products and concomitantly provides a feed stream for the butylene alkylation zone free of propane so that reaction zone products evaporated for self-refrigeration may be condensed and recycled without depropanization or the accumulation of propane in the recycle stream. The propylene stream containing all of the propane from the original olefin feed is charged with isobutane and catalyst to a first alkylation zone which is self-refrigerated by vaporization of a portion of the hydrocarbon components of the reaction mixture. The propane is concentrated in the evaporated components from the propylene alkylation zone. These evaporated components are then depropanized to separate propane, which is withdrawn from the system, and an isobutane stream substantially free of propane.

The depropanized isobutane stream, recycle isobutane, the butylene stream and catalyst are charged to a second self-refrigerated alkylation zone. Since substantially no propane is present in either of these hydrocarbon streams, the evaporated components of the reaction mixture from the second alkylation zone consist substantially of butanes, predominantly isobutane. These evaporated components may be condensed and recycled directly to the second alkylation zone without depropanization.

Liquid remaining after self-refrigerative evaporation of the light components, comprising alkylate and isobutane and some propane in the case of the liquid from the propylene alkylation zone, is deisobutanized to produce an isobutane fraction and an alkylate fraction containing normal butane. The isobutane fraction from the deisobutanizer is returned to the first stage alkylation zone to supply the isobutane required therein.

An advantage of the process of this invention is that propane is separated from the system efficiently by depropanization of a single stream having a relatively high propane concentration. The flashed liquid from the alkylation zones may be deisobutanized in a common fractiona-

tion facility to produce an isobutane stream to supply the isobutane requirements of the propylene alkylation zone. Isobutylene is more effective as a promoter in propylene alkylation than is the higher boiling normal butylene. In accordance with this method of separating propylene and butylene fractions, isobutylene which is lower boiling is preferentially included in the propylene alkylation feed stream whereas the normal butylenes are retained in the butylene alkylation feed stream.

In instances when the olefinic feed stream includes ethylene, it is desirable that the ethylene be removed before alkylation since ethylene results in excessive catalyst consumption and poor alkylate quality. Advantageously the propylene feed stream may be deethanized to remove ethylene by fractional distillation or the ethylene may be separated by subjecting the propylene feed stream to an extraction or absorption process. The isobutane recycle stream to the propylene alkylation reaction zone may be employed as absorbent in countercurrent contact with the propylene feed stream effecting absorption of propylene in isobutane. The resultant isobutane-propylene mixture may then be passed to the alkylation reaction zone to comprise at least part of the olefin and isoparaffin charged thereto.

The accompanying drawing diagrammatically illustrates one form of the process of this invention. Although the drawing illustrates one arrangement of apparatus in which the process of this invention may be practiced it is not intended to limit the invention to the particular apparatus or materials described.

A mixed olefin feed stock comprising propylene and butylenes is passed through line 10 to feed splitter 11. Feed splitter 11 is a fractional distillation column operated to effect separation of an overhead fraction comprising all of the propylene and propane contained in the mixed olefin feed together with some butylenes and a bottoms fraction consisting of components higher boiling than propane. The overhead propylene fraction is withdrawn through line 12, is combined with isobutane from line 13, and the combined stream is introduced into reactor 15. Acid catalyst is introduced into reactor 15 through line 14. Reactor 15 is shown as an impeller type reactor with forced internal circulation and a refrigerated internal coil. However other types of reactors may be employed, for example, time-tank, jet, and cascade reactors, any of which may be refrigerated by indirect heat exchange, by autorefrigeration, or by chilling one or more of the feed streams. The reaction zone temperature is maintained at about 45° F. and the pressure at about 50 pounds per square inch gauge whereby the reaction zone contents are maintained in liquid phase. In reactor 15 the olefin, isobutane and acid are mixed forming a hydrocarbon-acid emulsion. The olefin reacts with a part of the isobutane to form alkylate. A portion of the emulsion is withdrawn from reactor 15 through line 20 to acid settler 21 wherein the emulsion is separated into a hydrocarbon layer and an acid layer. Acid is withdrawn from settler 21 through line 14 for recycle to the reaction zone. Make-up acid as necessary to maintain system acidity is introduced through line 22 and spent acid is withdrawn through line 23.

Hydrocarbon liquid is withdrawn from settler 21 through line 24 and passed through pressure reducing valve 25 reducing the pressure to about 5 pounds per square inch gauge with resultant flashing of the lower boiling components and chilling of the liquid-vapor mixture formed. The chilled liquid-vapor mixture is passed through line 26, refrigeration coil 27 immersed in reactor 15, and line 28 to separator 29. Vapors comprising propane and isobutane from separator 29 are passed through line 35 to depropanizer 36. Depropanizer 36, a fractional distillation column, is operated to separate substantially all of the propane as an overhead fraction producing a depropanized isobutane stream. Propane is withdrawn as an overhead fraction through line 37 and

5

is discharged for use as fuel or for sale as L.P.G. De-propanized isobutane is withdrawn as a bottoms product from depropanizer 36 through line 38, is cooled in exchanger 39, and passed through pressure reduction valve 40 to effect flashing of a part of the isobutane and chilling of the liquid-vapor thus formed. The chilled liquid-vapor mixture is passed through line 41 to separator 42. Chilled liquid isobutane is withdrawn through line 47.

Butylene is withdrawn from feed splitter 11 through line 45 and is passed with isobutane from lines 46, 47 and 48 to reactor 51. Acid is introduced into reactor 51 through line 50. An emulsion of hydrocarbon and acid is formed in reactor 51 and the olefin reacted with a part of the isobutane to form alkylate. Emulsion is withdrawn through line 55 to acid settler 56 wherein the emulsion is resolved into liquid hydrocarbon and acid layers. Acid is recycled from settler 56 through line 50 to reactor 51. Make-up acid is required as introduced through line 57 and spent acid is withdrawn through line 58. Hydrocarbon is withdrawn from acid settler 56 through line 60 and pressure reducing valve 61 to effect flash vaporization of a part of the liquid and chilling of the liquid-vapor mixture thus formed. The chilled liquid-vapor mixture is passed through line 62 and refrigeration coil 63 immersed in reactor 51 and discharged through line 64 to separator 65. Vapor comprising isobutane is withdrawn from separator 65 through line 66 and is condensed by compressor 67 and cooler 68 to form liquid isobutane recycled to the reactor through line 48. Vapor from separator 42 may be passed through line 43 and combined with the vapor in line 66 to effect condensation and recycle of this isobutane stream.

Liquid comprising propane, butanes and alkylate from separator 29 is withdrawn through line 75 and passed to deisobutanizer 76. Liquid from separator 65 comprising butanes and alkylate is withdrawn through line 77 and discharged to deisobutanizer 76. Deisobutanizer 76, comprising a fractional distillation column, is operated to separate isobutane and lighter components from the normal butane and alkylate.

The hydrocarbon liquid in separator 29, which is the flashed effluent from the propylene alkylation zone, comprises isobutane and contains substantially no normal butane. Since deisobutanizer 76 is operated to separate isobutane from normal butane, this liquid stream from separator 29 may be introduced on the top tray of deisobutanizer 76 in place of at least a part of the isobutane which would normally be employed as reflux. The liquid from separator 65, which is the flashed liquid effluent from the butylene alkylation zone, contains most of the normal butane introduced into the system with the feed streams. This liquid is advantageously introduced into deisobutanizer 76 at an intermediate tray thereby effectively integrating the deisobutanization of the propylene alkylate and butylene alkylate in a single deisobutanizer tower.

The normal butane-alkylate stream is withdrawn as a bottoms fraction through line 78 and is discharged for further processing such as debutanization and rerunning if desired. Isobutane is withdrawn as an overhead fraction from deisobutanizer 76 through line 13 and is recycled to reactor 15.

When olefin feeds are employed which have not been deethanized, substantial quantities of ethylene may be present in the propylene olefin feed. Ethylene is an undesirable component of feed to the alkylation reactor in that it results in excessive catalyst loss. When ethylene is present in the propylene feed, the propylene in line 12 may be passed through line 80 to absorber 81. Isobutane from line 13 is passed through line 82 to the top of absorber 81 to provide absorption medium. The absorber 81 is operated as a reboiled-absorber wherein the lighter or lower boiling components are vaporized. The vapor passes in countercurrent flow with the descending

6

liquid isobutane and liquid components of the olefin feed. Absorber 81 is operated to effect separation of ethylene and lighter hydrocarbons as vapor which are discharged through line 82. Isobutane losses in the off gas may be reduced to a negligible amount by chilling the liquid isobutane passed to the top of the absorber. Chilling of the isobutane absorbent may be effected by flashing to a lower pressure. Isobutane absorption liquid and absorbed propylene and higher boiling hydrocarbons are withdrawn from the bottom of absorber 81 through line 83 and returned to line 12 for ultimate introduction into reactor 15.

Example

In the following example, all flow rates are given in barrel (42 gallons) of liquid per day regardless of whether the stream is in the liquid or the vapor state. All compositions are given in liquid volume percent.

A mixed olefin feed stock comprising propylene and butylenes from thermal and catalytic cracking at a rate of 3,231 barrels per day is fractionated to separate 2,443 barrels per day of an overhead propylene fraction and 788 barrels per day of a butylene fraction withdrawn as bottoms. Analyses of the fractionator charge and products are as follows:

	Mixed Olefin Feed	Propylene Fraction	Butylene Fraction
30 Methane and Ethane.....	9	12	
Ethylene.....	1	1	
Propylene.....	25	33	
Propane.....	17	22	
Isobutane.....	16	20	6
Isobutylene.....	7	7	9
N-butylene.....	15	3	51
N-butane.....	9	2	28
35 Pentanes.....	1		6
	100	100	100

The propylene fraction is charged to a reboiled absorber wherein it is contacted with 15,500 barrels per day of isobutane effecting absorption of about 95 percent or more of the propylene. Absorber off gas containing substantially all of the ethylene and a small amount of isobutane is discharged to other facilities for recovery of the isobutane. The isobutane and absorbed hydrocarbon from the absorber, at a rate of 17,291 barrels per day, are admixed with sulfuric acid and introduced to a reactor maintained at 45° F. and at 50 pounds per square inch gauge pressure. Reactants and catalyst are withdrawn to a settler. Hydrocarbon liquid is withdrawn at a rate of 16,973 barrels per day and passed through a reducing valve wherein the pressure is reduced to 5 pounds per square inch gauge. A part of the hydrocarbon liquid vaporizes chilling the liquid-vapor mixture. The chilled liquid-vapor mixture is passed through refrigerating coils in the reaction zone to maintain the desired reaction temperature therein. Liquid-vapor mixture from the refrigeration coils is discharged into a separator from which is withdrawn 13,472 barrels per day of liquid, and 3,501 barrels per day of vapor. The vapor is depropanized to produce 439 barrels per day of liquid propane and 3,062 barrels per day of depropanized isobutane containing 94 percent isobutane, 5 percent normal butane and 1 percent propane.

The butylene feed stream at a rate of 788 barrels per day is admixed with the 3,062 barrels per day of depropanized isobutane, 832 barrels per day of isobutane from outside sources and 2000 barrels per day of recycle isobutane and the combined stream passed with sulfuric acid to a reactor maintained at 40 pounds per square inch gauge pressure and 45° F. Emulsion is withdrawn from the reactor, settled, and the acid recycled to the reaction zone. Hydrocarbon from the separator is withdrawn at a rate of 6,480 barrels per day and is passed through a pressure reducing valve wherein the pressure

is reduced from 40 pounds per square inch gauge to 5 pounds per square inch gauge effecting vaporization of a part of the liquid and chilling of the resultant liquid-vapor mixture. The chilled liquid-vapor mixture is employed as refrigerant in the reaction zone and discharged to a separator from which is withdrawn 4,490 barrels per day of liquid and 2,000 barrels per day of vapor. The vapor comprises 88 percent isobutane, 9 percent normal butane and 3 percent propane. This vapor is condensed and recycled to the reaction zone to comprise a part of the isobutane introduced thereto.

Flashed liquid from the propylene alkylation step at a rate of 13,472 barrels per day is introduced to the top tray of a debutanizer. This stream comprises 6 percent propane, 79 percent isobutane and 10 percent alkylate. Flashed liquid from the butylene alkylation reactor at a rate of 4,490 barrels per day is introduced at an intermediate point in the deisobutanizer. This stream comprises 6 percent normal butane and 19 percent alkylate. Deisobutanizer overhead, comprising 6 percent propane, 89 percent isobutane and 5 percent normal butane, at a rate of 15,500 barrels per day, is withdrawn and used as the absorption medium employed in deethanizing the propylene feed. Deisobutanizer bottoms comprising alkylate and normal butane is rerun to separate 572 barrels per day of normal butane and 2,257 barrels per day of alkylate.

Although fractionation as applied in the various steps of the process of this invention is effected advantageously by fractional distillation, it is obvious that fractionation may be effected in whole or in part by other separating techniques, for example, adsorption, absorption, extraction, diffusion and crystallization, or by a combination of several separating techniques.

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

I claim:

1. In an alkylation process wherein an olefin-based alkylatable material is alkylated with an isoparaffin in the presence of an alkylation catalyst, the improvement which comprises: contacting a first feed stream comprising propane, propylene, and butylenes with an alkylation catalyst under alkylating conditions in a first alkylation zone, self-refrigerating said first alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane and propane from the resulting hydrocarbon mixture of said first alkylation zone, passing said evaporated components of said first alkylating zone to a depropanizing fractionation zone, passing remaining hydrocarbon liquid from said first alkylation zone containing alkylate and isobutane to a deisobutanizing fractionation zone, separately withdrawing depropanized isobutane and propane fractions from said depropanizing fractionation zone, contacting a second feed stream consisting of hydrocarbons higher boiling than propane and comprising butanes and butylenes with an alkylation catalyst under alkylation conditions in a second alkylation zone, self-refrigerating said second alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane from the resulting hydrocarbon mixture of said second alkylation zone, separately condensing said evaporated low boiling components from said second alkylation zone and returning thus condensed components to said second alkylation zone to supply a part of the isobutane passed to said second alkylation zone, passing remaining hydrocarbon liquid from said second alkylation zone to said deisobutanizing fractionation zone, separately withdrawing from said deisobutanizing fractionation zone an isobutane fraction containing isobutane and lighter hydrocarbons and deisobutanized liquid comprising alkylate from said first and second alkylation zones, and passing

at least a part of said isobutane fraction from said deisobutanizing fractionation zone to said first alkylation zone to supply at least a part of the isobutane passed to said first alkylation zone.

2. In an alkylation process wherein olefins contained in a feed stream comprising propane, propylene and butylenes are alkylated with isobutane, the process which comprises the steps in combination as follows: fractionating said feed stream into a propylene fraction and a butylene fraction, said propylene fraction comprising propane, propylene, and butylenes wherein said butylenes comprise at least 5 percent of the olefin content of said propylene fraction, said butylene fraction consisting of hydrocarbons higher boiling than propane and comprising butanes and butylenes, passing said propylene fraction to a first alkylation zone, contacting said propylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said first alkylation zone, self-refrigerating said first alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane and propane from the resulting hydrocarbon mixture of said first alkylation zone, passing said evaporated components of said first alkylating zone to a depropanizing fractionation zone, passing remaining hydrocarbon liquid from said first alkylation zone containing alkylate and isobutane to a deisobutanizing fractionation zone, separately withdrawing depropanized isobutane and propane fractions from said depropanizing fractionation zone, passing said butylene fraction to a second alkylation zone, passing said depropanized isobutane to said second alkylation zone, contacting said butylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said second alkylation zone, self-refrigerating said second alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane from the resulting hydrocarbon mixture of said second alkylation zone, separately condensing said evaporated low boiling components from said second alkylation zone and returning thus condensed components to said second alkylation zone to supply a part of the isobutane passed to said second alkylation zone, passing remaining hydrocarbon liquid from said second alkylation zone to said deisobutanizing fractionation zone, separately withdrawing from said deisobutanizing fractionation zone an isobutane fraction containing isobutane and lighter hydrocarbons and deisobutanized liquid comprising alkylate from said first and second alkylation zones, and passing at least a part of said isobutane fraction from said deisobutanizing fractionation zone to said first alkylation zone to supply at least a part of the isobutane passed to said first alkylation zone.

3. In an alkylation process wherein olefins contained in a feed stream comprising propane, propylene, normal butane and butylenes are alkylated with isobutane, the process which comprises the steps in combination as follows: fractionating said feed stream into a propylene fraction and a butylene fraction, said propylene fraction being substantially free of normal butane and comprising propane, propylene, and butylenes wherein said butylenes comprise at least 5 percent of the olefin content of said propylene fraction, said butylene fraction consisting of hydrocarbons higher boiling than propane and comprising butanes and butylenes, passing said propylene fraction to a first alkylation zone, contacting said propylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said first alkylation zone, self-refrigerating said first alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane and propane from the resulting hydrocarbon mixture of said first alkylation zone, passing said evaporated components of said first alkylating zone to a depropanizing fractionation zone, passing remaining hydrocarbon liquid from said first alkylation zone containing alkylate and isobutane to the top tray of a deiso-

butanizing fractionation zone, separately withdrawing depropanized isobutane and propane fractions from said depropanizing fractionation zone, passing said butylene fraction to a second alkylation zone, passing said depropanized isobutane to said second alkylation zone, contacting said butylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said second alkylation zone, self-refrigerating said second alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane from the resulting hydrocarbon mixture of said second alkylation zone, separately condensing said evaporated low boiling components from said second alkylation zone and returning thus condensed components to said second alkylation zone to supply a part of the isobutane passed to said second alkylation zone, passing remaining hydrocarbon liquid from said second alkylation zone to an intermediate tray of said deisobutanizing fractionation zone, separately withdrawing from said deisobutanizing fractionation zone an isobutane fraction containing isobutane and lighter hydrocarbons and deisobutanized liquid comprising normal butane and alkylate from said first and second alkylation zones, and passing at least a part of said isobutane fraction from said deisobutanizing fractionation zone to said first alkylation zone to supply at least a part of the isobutane passed to said first alkylation zone.

4. In an alkylation process wherein olefins contained in a feed stream comprising ethylene, propane, propylene and butylenes are alkylated with isobutane, the process which comprises the steps in combination as follows: fractionating said feed stream into a propylene fraction and a butylene fraction, said propylene fraction comprising ethylene, propane, propylene, and butylenes wherein said butylenes comprise at least 5 percent of the olefin content of said propylene fraction, said butylene fraction consisting of hydrocarbons higher boiling than propane and comprising butanes and butylenes, passing said propylene fraction to an absorption zone, contacting said propylene with liquid isobutane absorption medium in said absorption zone, effecting preferential absorption of said olefin heavier than ethylene in said liquid isobutane forming a liquid stream comprising olefins higher boiling than ethylene and isobutane, passing said last mentioned stream to a first alkylation zone, contacting said propylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said first alkylation zone, self-refrigerating said first alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane and propane from the resulting hydrocarbon mixture of said first alkylation zone, passing said evaporated components of said first alkylation zone to a depropanizing fractionation zone, passing remaining hydrocarbon liquid from said first alkylation zone containing alkylate and isobutane to a deisobutanizing fractionation zone, separately withdrawing depropanized isobutane and propane fractions from said depropanizing fractionation zone, passing said butylene fraction to a second alkylation zone, passing said depropanized isobutane to said second alkylation zone, contacting said butylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said second alkylation zone, self-refrigerating said second alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane from the resulting hydrocarbon mixture of said second alkylation zone, separately condensing said evaporated low boiling components from said second alkylation zone and returning thus condensed com-

ponents to said second alkylation zone to supply a part of the isobutane passed to said second alkylation zone, passing remaining hydrocarbon liquid from said second alkylation zone to said deisobutanizing fractionation zone, separately withdrawing from said deisobutanizing fractionation zone a liquid isobutane fraction containing isobutane and lighter hydrocarbons and deisobutanized liquid comprising alkylate from said first and second alkylation zones, and passing at least a part of said isobutane fraction from said deisobutanizing fractionation zone to said absorption zone as liquid isobutane absorption medium.

5. The process of claim 4 wherein said liquid isobutane fraction withdrawn from said deisobutanizing fractionation zone is flashed effecting formation of chilled liquid and vapor and said chilled liquid is passed to said absorption zone as liquid isobutane absorption medium.

6. In an alkylation process wherein olefins contained in a feed stream comprising ethylene, propane, propylene and butylenes are alkylated with isobutane, the process which comprises the steps in combination as follows: fractionating said feed stream into a propylene fraction and a butylene fraction, said propylene fraction comprising ethylene, propane, propylene, and butylenes wherein said butylenes comprise at least 5 percent of the olefin content of said propylene fraction, said butylene fraction consisting of hydrocarbons higher boiling than propane and comprising butanes and butylenes, passing said propylene fraction to an absorption zone, contacting said propylene with liquid isobutane absorption medium in said absorption zone, effecting preferential absorption of said olefin heavier than ethylene in said liquid isobutane forming a liquid stream comprising olefins higher boiling than ethylene and isobutane, passing said last mentioned stream to a first alkylation zone, contacting said propylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said first alkylation zone, self-refrigerating said first alkylation zone by evaporation of low boiling hydrocarbon components comprising part of the isobutane and propane from the resulting hydrocarbon mixture of said first alkylation zone, passing said evaporated components of said first alkylation zone to a depropanizing fractionation zone, recovering alkylate from the remaining liquid hydrocarbon from said first alkylation zone, separately withdrawing depropanized isobutane and propane fractions from said depropanizing fractionation zone, passing said butylene fraction to a second alkylation zone, passing said depropanized isobutane to said second alkylation zone, contacting said butylene fraction, isobutane, and an alkylation catalyst under alkylating conditions in said second alkylation zone, separating isobutane from the reaction mixture of said second alkylation zone, passing said isobutane from said second alkylation zone to said absorption zone to comprise at least a part of said liquid isobutane absorption medium, and recovering alkylate from the reaction mixture of said second alkylation zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,303,735	Goldsby	Dec. 1, 1942
2,385,123	Atkins	Sept. 18, 1945
2,417,251	Hemminger	Mar. 11, 1947
2,511,758	Weinreich	June 13, 1950
2,664,452	Putney	Dec. 19, 1953
2,820,073	Dixon et al.	Jan. 14, 1958

UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 3,007,983

November 7, 1961

Frank A. Clauson

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 14, for "debutanizer" read
-- deisobutanizer --; column 7, line 19, for "tray of a
deisobutanizer. This stream comprises 6 percent" read
-- prises 1 percent propane, 71 percent isobutane, 9
percent --.

Signed and sealed this 10th day of April 1962.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents