

- [54] **HYDROGEN FLUORIDE ALKYLATION WITH EFFLUENT REFRIGERATION**
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[58] Field of Search 260/683.48, 683.4 F

[56] **References Cited**
UNITED STATES PATENTS

2,664,452	12/1953	Putney	260/683.4 F
2,906,796	9/1959	Putney	260/683.48
2,977,397	3/1961	Putney	260/683.48
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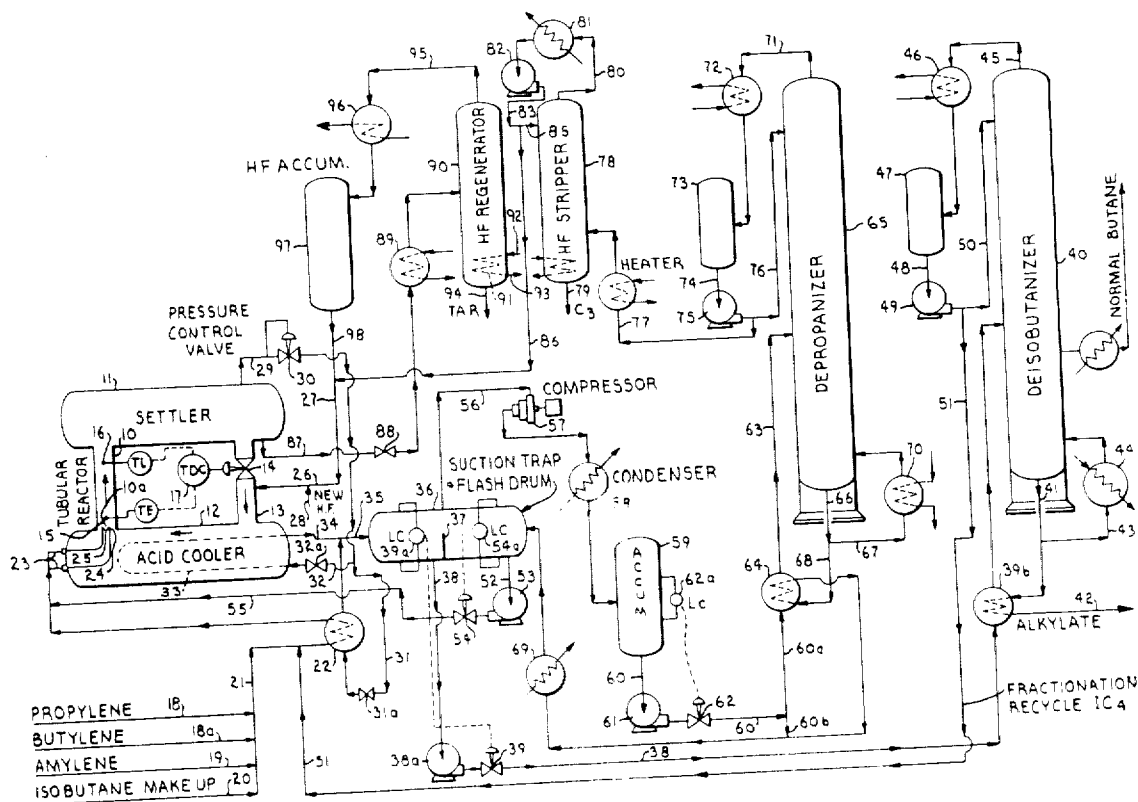
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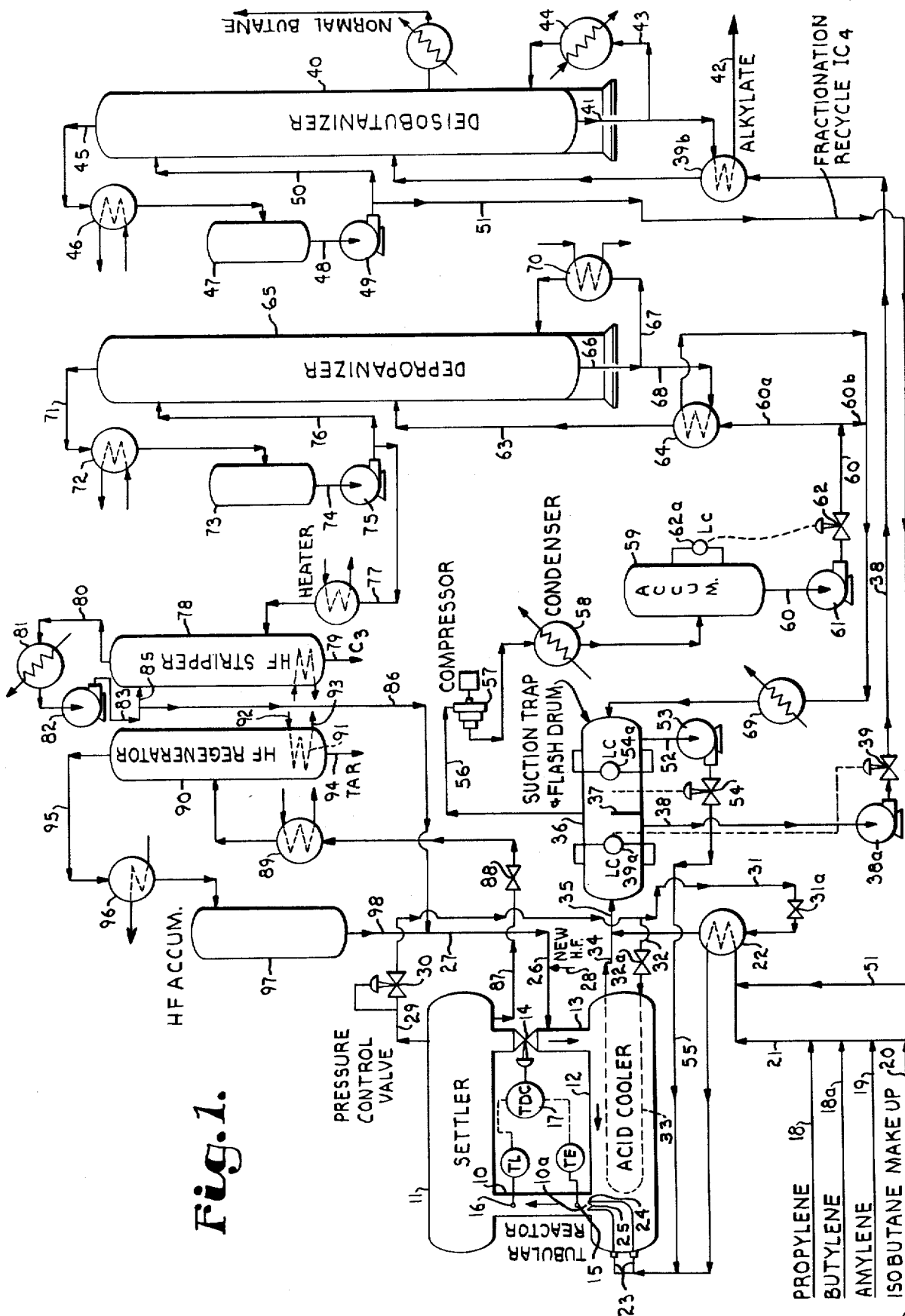
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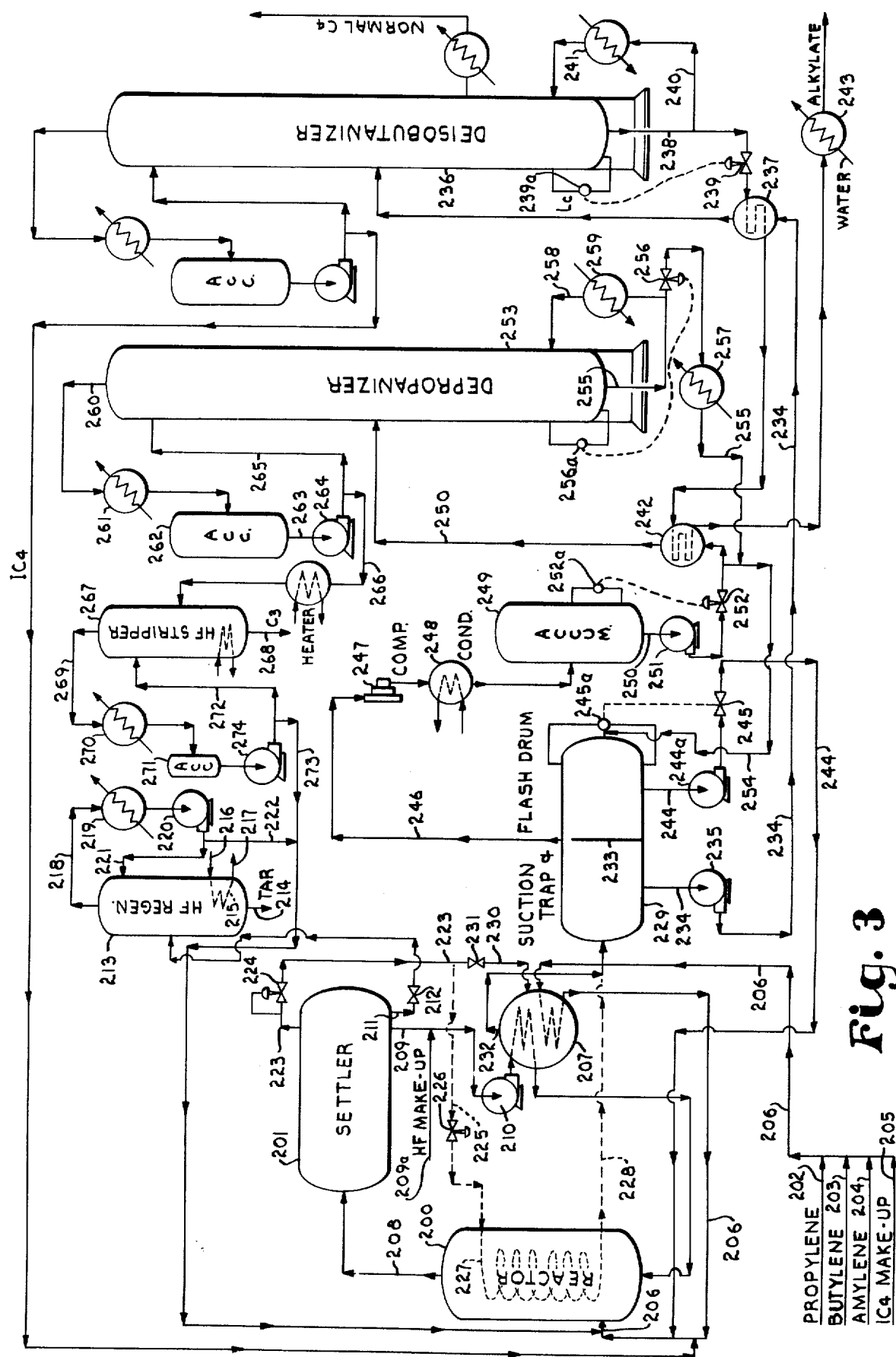
ABSTRACT

Improved processes of alkylation of isoparaﬃnic hydrocarbons by olefinic hydrocarbons wherein hydrogen fluoride is the alkylation reaction catalyst; processes of hydrocarbon phase effluent (alkylate, excess isoparaﬃnic hydrocarbons and normal paraﬃnic hydrocarbons) refrigeration applied to the alkylation of isoparaﬃnic hydrocarbons by olefinic hydrocarbons wherein hydrogen fluoride is the alkylation reaction catalyst; such improved processes of effluent refrigeration in HF catalyzed alkylation applied to systems where the reaction vessel is an elongate vertical tube interconnecting an overhead settler vessel and a below situated acid cooler vessel or a simple tank with a separate settler; processes of hydrocarbon phase effluent (alkylate, excess isoparaﬃnic hydrocarbons and normal paraﬃnic hydrocarbons) refrigeration applied to the alkylation of isoparaﬃnic hydrocarbons by olefinic hydrocarbons using HF catalyst wherein the alkylation reaction step, as well as the input feeds thereto are cooled by the said effluent refrigeration.

13 Claims, 3 Drawing Figures







HYDROGEN FLUORIDE ALKYLATION WITH EFFLUENT REFRIGERATION

BRIEF SUMMARY OF THE INVENTION

Two U.S. Patents to David H. Putney disclose processes for alkylation of isoparaffinic hydrocarbons by olefinic hydrocarbons utilizing effluent refrigeration. These are U.S. Pat. No. 2,664,452 Dec. 29, 1953 for "Process for Alkylation Utilizing Evaporative Cooling" and U.S. Pat. No. 2,949,494, issued Aug. 16, 1960 for "Alkylation of Hydrocarbons Utilizing Evaporative Cooling". These two patents disclose effluent refrigeration for acid catalyzed alkylation wherein the reaction vessel or vessel wherein the alkylation reaction is carried out is a circulating mixing reactor of the Stratco contactor type. Such reactors are seen in the U.S. Patent to Putney U.S. Pat. No. 2,800,307, issued July 23, 1957 for "Apparatus for Controlling Temperature Change of Blends of Fluids or Fluids in Finely Divided Solids". Further, the U.S. Patent to Putney U.S. Pat. No. 2,977,397, issued Mar. 28, 1961, for "Hydrogen Fluoride Alkylation with Effluent Refrigeration" discloses hydrogen fluoride catalyzed alkylation carried out in such a Stratford contactor type mixing and reaction vessel.

The present invention relates to the application of effluent refrigeration to the cooling of alkylation reactions and the feeds (both initial and recycle) thereto wherein the reaction vessel is either: (a) a vertical tube connecting the underside of an overhead settler vessel to the upper portion of a below situated acid cooler or (b) a simple reaction vessel or tank with separate settler vessel. In the herebelow described processes, not only is the efficient effluent refrigeration of the alkylation reaction carried out in these types of vessels, together with the effluent refrigeration of the feed streams (both initial and recycle) thereto, but also efficient separations of alkylate product, excess isobutane, hydrogen fluoride catalyst and normal propane or paraffinic hydrocarbons are achieved. Suitable recycles are provided, as well as discharges from the system, thus to efficiently carry out the effluent refrigerated HF catalyzed alkylation reactions in these systems.

OBJECTS OF THE INVENTION

An object of the instant invention is to provide improved hydrogen fluoride catalyzed alkylation processes wherein the alkylation reaction is carried out in vessels (or a vessel) without internal mixing, yet wherein the benefits of hydrocarbon phase effluent refrigeration are essentially fully achievable.

Another object of the invention is to provide improvements in alkylation processes utilizing hydrogen fluoride as a catalyst, the alkylation reaction being carried out in a reaction vessel of the type having an integral settler and an integral acid cooler associated therewith, the improvements deriving from hydrocarbon phase effluent refrigeration.

Another object of the invention is to provide improved means, method and apparatus for cooling hydrogen fluoride catalyzed alkylation reactions by hydrocarbon phase effluent refrigeration, the hydrocarbon phase effluent also employed to pre-cool the feed streams to the alkylation reaction vessels.

Another object of the invention is to provide methods of and means for obtaining the evaporative cooling benefits disclosed in the U.S. Patent to David H. Put-

ney, U.S. Pat. No. 2,949,494, issued Aug. 16, 1960 for "Alkylation of Hydrocarbons Utilizing Evaporative Cooling" for alkylation processes which are catalyzed by hydrogen fluoride and additionally have little or no alkylation reaction vessel internal mixing and circulation.

Another object of the invention is to provide methods of and means for efficiently separating (for recycle) the hydrogen fluoride catalyst of an alkylation reaction from the hydrocarbon phase effluent from the settler in an alkylation system where the hydrocarbon phase effluent is employed in effluent refrigeration both of the alkylation reaction step in the vessel and feed streams thereto.

Another object of the invention is to improve alkylation reaction processes catalyzed by hydrogen fluoride wherein the alkylation reactor comprises a tubular conduit between an overhead settler vessel and a below situated acid cooler vessel, the improvements comprising passing the hydrocarbon phase effluent from the settler through a pressure reducing valve, thereby to chill same by self-evaporative cooling, thereafter passing the effluent through cooling elements in the acid cooler vessel, whereby to remove heat from and aid in controlling the temperature of reactants in the tubular reactor.

Another object is to improve such described processes by passing the chilled hydrocarbon phase effluent, after use as a refrigerant in the acid cooler vessel and, optionally, as a refrigerant with the incoming feeds to the tubular reactor, to a separating phase or stage where any entrained hydrogen fluoride is taken off overhead as vapors (with propane) same passed to a depropanizer and HF stripper step, one portion of the liquid bottoms from the separating step comprising isobutane and alkylate passed to a deisobutanizer and a second liquid bottoms portion comprising isobutane passed in recycle to the feeds to the alkylation reactor.

Another object of the invention is to provide improved means of and methods for hydrogen fluoride catalyzed alkylation in systems wherein the alkylation reactor has no internal circulation means and there is a separate settling vessel, the hydrocarbon phase effluent overhead from the settler being passed through a pressure reducing valve where it is chilled by a self-evaporative cooling, the chilled, pressure-reduced hydrocarbon phase effluent, both liquid and vapor phases, then being passed through cooling elements in the alkylation reaction vessel to remove heat from and control the temperature of the reactant mixture, as well as being passed in indirect heat exchange with the feed elements to the reactor, the acid bottoms from the settler being recycled to the non-circulating reactor as catalyst and optionally being passed in indirect heat exchange with at least a portion of the chilled, pressure-reduced hydrocarbon phase effluent.

Another object of the invention is to provide such described process wherein the chilled, pressure reduced hydrocarbon phase effluent, after use as refrigerant in the alkylation reactor and with the recycle acid phase and hydrocarbon feeds to the reactor, is then passed to a vapor-liquid separating step where compressed vapor, including some hydrogen fluoride, is passed to depropanizing and HF stripping steps for recycle of the hydrogen fluoride to the feed to the reactor, the liquid bottoms from the vapor-liquid separating stage comprising a first part, including alkylate, sent to a deisobutanizer and a second part, largely comprising isobutane which is recycled to the feed to the reactor.

It is well known that there are distinct process advantages obtainable by operating a hydrogen fluoride alkylation plant at temperatures lower than obtainable with water cooling of the reactor. These benefits include increased octane number and yield of the resulting alkylate. This invention makes that possible since the HF alkylation units built in the past and now being built are water cooled.

Other and further objects of the invention will appear in the course of the following description thereof.

The three drawings comprise schematic flow diagrams of embodiments of the invention.

FIG. 1 is a schematic flow diagram of one embodiment of the improved hydrogen fluoride catalyzed alkylation process, the alkylation reactor comprising a vertical tube communicating between an overhead settler vessel and a below located acid cooler vessel, effluent refrigeration being applied to the feeds to the tubular reactor and the acid cooler.

FIG. 2 is a schematic flow diagram of a second embodiment of the improved hydrogen fluoride catalyzed alkylation process, the alkylation reaction vessel, settler and acid cooler being of the same type as that seen in FIG. 1, the process differing in the handling of the recycle hydrogen fluoride from the HF stripper and the regenerator, as well as the disposition of the hydrocarbon phase effluent after same is used as effluent refrigerant in the acid cooler and the hydrocarbon feeds to the alkylation reactor.

FIG. 3 is a schematic flow diagram of a modified form of the improved hydrogen fluoride catalyzed alkylation process, the alkylation reactor comprising a simple vessel without internal circulation or mixing means, there being a separate settler vessel, the hydrocarbon phase effluent from the settler being used as effluent refrigerant to (1) the alkylation reactor, (2) the recycle acid from the settler and (3) the hydrocarbon feed to the reactor vessel.

FIG. 1 HG CATALYZED ALKYLATION — EFFLUENT REFRIGERATION — TUBULAR REACTOR WITH OVERHEAD SETTLER AND BELOW LOCATED ACID COOLER

Referring first to FIG. 1, therein is shown an alkylation system wherein isoparaaffinic hydrocarbons are alkylated by olefinic hydrocarbons in the presence of hydrogen fluoride as a reaction catalyst. In this system, effluent refrigeration is employed. The reaction vessel comprises an elongate vertical tube interconnecting an overhead settler vessel and a below situated acid cooler vessel, there being an additional, valve controlled recycle flow line interconnecting the settler and acid cooler, whereby circulation of liquids occurs upwardly from the acid cooler to the settler in the reaction vessel and vice versa in the flow line (clockwise in this view of FIG. 1) by gravity flow because of the difference in specific gravity of the liquids in the two vertical tubes.

At 10 there is seen the tubular reactor connecting and communicating at its upper end with a settler vessel 11 and connecting and communicating at its lower end with an acid cooler 12. A valve controlled second vertical tube 13 communicates between and connects settler 11 and acid cooler 12, the control valve indicated at 14. Tubes 10 and 13 connect the upper side of the acid cooler 12 with the underside of settler 11.

Sensor 15 measures the entering temperature of liquids circulating upwardly in tubular reactor 10, while sensor 16 measures the leaving temperature of such liquids

adjacent the upper end of the tubular reactor. These sensors are coupled with a temperature difference control 17 which operates or throttles valve 14. Briefly stated, the greater the temperature differential between sensors 15 and 16, the more valve 14 is open, whereby to increase the circulation and obtain more cooling of the alkylating reactants in the tubular reactor.

Looking at the lower left-hand corner of FIG. 1, input flow lines 18–20, inclusive for propylene, butylene, amylene and isobutane make-up, respectively, join in common line 21. The contents of line 21, after joiner thereto of isobutane recycle line 51 (to be described) are cooled in indirect heat exchanger at 22, passing to input feed lines 23 which have input venturiers or nozzles 24 and 25, respectively, at the ends thereof positioned at the inlet 10a of tubular reactor 10.

Circulating in the vessel configuration of tubular reactor 10, settler 11, return line 13 and acid cooler 12 are an excess of isobutane, olefinic hydrocarbons, hydrogen fluoride catalyst and alkylate. Catalyst input to this system is through line 26 fed by line 27 from the HF regeneration and stripping systems, respectively, to be described, with make-up HF catalyst added through line 28, as required. In settler 11 there is a gravity separation of HF catalyst which fails and tends to return to cooler 12 through line 13. The lighter hydrocarbons: alkylate, excess isoparaaffinics and normal hydrocarbons rise to the top of settler 11. The entire vessel system (10, 11, 12 and 13) is liquid full.

Line 29 comes off overhead from settler 11 and has back pressure control valve 30 thereon. Valve 30 maintains the settler, reactor and acid cooler system under sufficient back pressure so as to maintain all of the reactants and fluids therein in liquid phase. Withdrawn overhead through line 29 is the hydrocarbon phase effluent, including primarily alkylate and isobutane with some propane and HF catalyst. After passing back pressure control valve 30, the pressure is so reduced on the hydrocarbon phase effluent as to refrigerate it and vaporize excess volatile hydrocarbons. Any alkylate therein is non-evaporable under the pressures and temperatures existing in this system. Line 29, after back pressure valve 30, divides into lines 31 (having valve 31a thereon) and 32 (having valve 32a thereon).

Some portion of the refrigerated hydrocarbon phase effluent, controlled by valves 31a and 32a, may be passed through line 31 in indirect heat exchange with the input feed components (olefins and isobutane) in line 21 at heat exchanger 22. The majority (or all) of the flashed hydrocarbon phase effluent is passed through line 32 (controlled by valves 31a and 32a) into a tube bundle 33 schematically indicated in the acid cooler 12. The return line 34 out of acid cooler 12 from tube bundle 33 is joined by line 31 after heat exchange at 22. All of the hydrocarbon phase effluent, then, after indirect heat exchange (effluent refrigeration) of the acid cooler and, optionally, heat exchanging of (cooling) the feed inputs to the tubular reactor 10, are passed via line 35 to suction trap and flash drum 36.

Suction trap and flash drum 36 is an elongate horizontal tank having a vertical divider 37 therewithin. A first withdrawal line 38 (on the left hand side of the divider 37 in the view of FIG. 1 adjacent the hydrocarbon phase effluent input from line 35) takes a first quantity of liquid bottoms (largely comprising alkylate) from vessel 36 through pump 38a in a quantity controlled by valve 39 and level control 39a. Line 38 thereafter

passes through a heat exchanger at 39b to deisobutanizer vessel 40. Bottoms from deisobutanizer 40 are taken off through line 41 through heat exchange at 39b, with the majority of the bottoms from the deisobutanizer thereafter being passed from the system through line 42 comprising alkylate and butane. Circulating line 43 with heat exchanger (heater) 44 is also provided for reboiling tower bottoms. The overhead from deisobutanizer 40 through line 45 is condensed at 46, thereafter passing to accumulator vessel 47. Isobutane is taken from accumulator 47 by line 48 through pump 49 which drives the isobutane either in recycle back to tower 40 via line 50 or to join line 21 of the feed through line 51.

Returning to trap and drum 36, a second liquid bottoms line 52 is driven by pump 53 as controlled by valve 54 and level control 54a in recycle via line 55 to join the input olefin and isobutane feeds to the system, as well as the fractionation recycle isobutane, in line 21.

Light hydrocarbon vapors are taken overhead from vessel 36 through line 56, passing through compressor 57 and condenser 58 to collection in accumulator vessel 59. The liquefied light hydrocarbons are taken from vessel 59 through line 60 driven by pump 61 and controlled by valve 62 and level control 62a from whence line 60 splits into two lines 60a and 60b. Through line 60b, a portion of the liquefied light hydrocarbons from vessel 59 are recycled to the right hand cell of trap-drum 36. A greater quantity, at least, of the lighter hydrocarbons are taken via line 60a through heat exchange at 64 to depropanizer 65.

Line 38 contains substantially all of the alkylate product, the external isobutane recycle in be fractionated to the deisobutanizer tower, the normal butane which entered with the feed stocks, some propane and hydrogen fluoride. Line 52 contains propane, considerable isobutane, some hydrogen fluoride, some normal butane but very little alkylate. Line 56 contains all of the effluent recycle isobutane, some hydrogen fluoride, propane, normal butane and a very small amount of alkylate.

Bottoms from depropanizer 65 are taken off through line 66 which splits into two lines 67 and 68. Line 68 passes in heat exchange at 64 and thereafter is recycled, after cooling at 69, back to suction trap and flash drum 36. A reflux may be taken via line 67 back to depropanizer 65 after heating at 70.

The overhead from depropanizer 65, comprising largely propane and catalyst HF passes via line 71 through cooling at 72 to accumulation in vessel 73. Bottoms from vessel 73 are taken out via line 74 driven by pump 75. The discharge from pump 75 separates into recycle line 76 back to the upper portion of the depropanizer tower and line 77 which passes to HF stripper vessel 78.

Bottoms from the HF stripper 78, comprising propane, pass out of the system via line 79. The HF overhead line 80 passes through a cooling step at 81 and through pump 82. Discharge from the pump through line 83 splits into a recycle line 85 to the stripper and a recycle line 86 which takes HF catalyst back to the system as will be described.

Returning to settler 11, since the system of tubular reactor 10, settler 11, recycle line 13 and acid cooler 12 is operated liquid full, there is a tendency for the heavier catalyst to fall to the bottom of settler 11, as well as a tendency for the lighter hydrocarbon phase

effluent of alkylate, excess isobutane and light hydrocarbons to rise to the top. Therefore, take off line 87 from the lower part of settler 11 spaced away from tubular reactor 10 is provided, having valve 88 thereon. HF catalyst liquid withdrawn from settler 11 is passed via heat exchange heating at 89 to HF regenerator 90. Regenerator 90 is heated by indirect heat exchange coil 91 having input and output lines 92 and 93. Tar is removed from the system through line 94. HF catalyst is taken off overhead of regenerator 90 via line 95 and passed through a cooling step at 96 to HF accumulator vessel 97. Accumulated HF catalyst is recycled to the system through line 98 which is joined by recycle line 86 from the HF stripper 78. As seen in FIG. 1, these lines combine at 27, thereafter joined by make up HF line 28 in feed to recycle tube 13 via line 26.

FIG. 2 — HF CATALYZED ALKYLATION IN REACTOR-SETTLER-ACID COOLER SYSTEM WITH EFFLUENT REFRIGERATION (SECOND FORM)

FIG. 2 is a schematic flow diagram of a process of alkylating isoparaffinic hydrocarbons with olefinic hydrocarbons in the presence of hydrogen fluoride as the alkylation reaction catalyst, the reaction vessel comprising an elongate vertical tube interconnecting an overhead settler vessel and a below situated acid cooler vessel. There is additionally provided a valve controlled recycle flow line interconnecting the settler and acid cooler, whereby circulation of liquids occurs upwardly from the acid cooler to the settler in the reaction vessel and vice versa in recycle flow. The system illustrated and described herebelow resembles that of the described system of FIG. 1 in numerous ways. However, it also differs in numerous respects, among which are included the use of a single section suction trap and flash drum.

Referring then to FIG. 2, a tubular vertical reactor 100 communicates between the lower portion of a settler vessel 101 and the upper portion of an acid cooler vessel 102. A recycle line or column 103 is provided communicating between the upper part of acid cooler 102 and the lower part of settler 101 spaced from tubular reactor 100. Valve 104 is controlled with respect to recycle flow down leg or tube 103 by temperature differential control 105. The latter is linked with entering temperature sensor 106 and leaving temperature sensor 107, the former positioned in the lower reaches of reactor 100, the latter positioned in the upper portion thereof. Circulation in the reaction vessel-settler-acid cooler system is upwardly in reactor 100 and downwardly in tube or pipe 103. This leads to a clockwise circulation of liquids in the system of FIG. 2. The impetus for such flow is, first, the input of new reactants to be described moving upwardly in leg or reactor 100 and, additionally, the driving force of the increased temperature within the reactor 100, which tends to cause the liquids therein to rise in the vessel's system. Likewise, the higher specific gravity of the liquids in the lower portion of the settler 101 adjacent tube 103 tends to cause the liquids to fall in such leg.

Looking at the lower left-hand corner of FIG. 2, input flow lines 109-111, inclusive provide propylene, butylene, amylene and isobutane make-up, respectively, joining in common line 112. Line 112, after receiving a recycle isobutane line (to be described) is optionally heat exchanged (cooled) at 113 and thereafter passes, after joinder by an HF catalyst recycle line, (to

be described) to input feed lines 114 and 115 which pass into acid cooler 102 to discharge nozzles or venturis 116.

Circulating in the vessel configuration of tubular reactor 100, settler 101, return line 103 and acid cooler 102 are an excess of isoparaffinic hydrocarbons (isobutane) olefinic hydrocarbons, hydrogen fluoride catalyst and alkylate. The primary alkylation takes place in the tubular reactor 100 between sensors 106 and 107. Catalyst input to this system is through line 117 joining line 112 immediately before tubular reactor 100 fed by line 118 from the HF regeneration and stripping systems, (to be described) with make up HF catalyst added through line 119, as required. In settler 101, there is a gravity separation of HF catalyst which falls and tends to return to cooler 102 through line 103. The lighter hydrocarbons including alkylate, excess isoparaffins and normal hydrocarbons, rise to the top of settler 101. The entire vessel system (101, 102, 100 and 103) is liquid full.

Taken overhead from settler 101 through line 120 is the hydrocarbon phase effluent comprising alkylate, some HF, excess isoparaffinic hydrocarbons and light normal paraffins. Back pressure valve 121 maintains the settler, reactor and acid cooler system under sufficient back pressure so as to maintain all of the reactants and fluids therein in liquid phase.

After passing back pressure control valve 121, the pressure is so reduced on the hydrocarbon phase effluent in line 120 as to refrigerate it and vaporize excess volatile hydrocarbons. Any alkylate therein is non-evaporable under the pressures and temperatures existing in the system. Line 120, after back pressure valve 121 divides into lines 122 (having valve 122a thereon) and 123 (having valve 123a thereon).

Some portion of the refrigerated hydrocarbon phase effluent, controlled by valves 122a and 123a, may be passed through line 122 in indirect heat exchange with the input feed components (olefins and isobutane) in line 112 at heat exchanger 113. The majority (or all) of the flashed hydrocarbon phase effluent is passed through line 123 (controlled by valves 122a and 123a) into a tube bundle 124 schematically indicated in the acid cooler 102. The return line 125 out of acid cooler 102 from the tube bundle 124 is joined by line 122 after the heat exchange at 113. All of the hydrocarbon phase effluent, therein, after indirect heat exchange (effluent refrigeration) of the acid cooler and, optionally, heat exchanging of (cooling) the feed inputs to the tubular reactor 100, are passed via line 126 to suction trap and flash drum 127.

Liquid bottoms from vessel 127 are taken off line 128 through pump 129 controlled by valve 130 and level control 130a, to deisobutanizer 133 via line 131. Bottoms from deisobutanizer 133 are removed through line 134 from which a circulating line 135 heated at 136 returns to tower 133. Valve 137, operated by level control 137a, controls the flow in line 134 which passes through heat exchange (optionally) at 132 and again at 138. Thereafter, line 134 departs from the system carrying alkylate product after optional cooling at 139.

Deisobutanizer overheads through line 140 condense at 141 and accumulate in vessel 142. Liquid isobutane is then recycled via line 143 through pump 144 partly back to the top of deisobutanizer 133 through line 145 as required for reflux with the balance to the feed inputs to tubular reactor 100 through line 146 which joins the feed line 112 before heat exchange at 113.

Returning to suction trap 127, the overhead vapors from vessel 127 are taken off through line 147, compressed at 148, condensed at 149 and accumulated in vessel 150. These condensed vapors, including HF catalyst and largely paraffinic hydrocarbons, particularly isobutane with some propane, are taken off through bottoms line 151 driven by pump 152 and controlled by valve 153 and level control 153a. After valve 153, line 151 splits into lines 154 and 155. The former, after joined by a line to be described, passes as line 156 to join the feed input line 112, comprising the isobutane effluent refrigeration recycle. Line 155, after heat exchange at 138 (optional) passes to depropanizer 157.

Bottoms from depropanizer 157 are taken off through line 158 controlled by valve 159 and level control 159a. Before valve 159, circulation line 160 may be provided with heater 161. Thereafter the depropanizer bottoms pass via line 162 through a cooling step at 163 to join line 154 as part of the isobutane effluent refrigeration recycle in line 156.

Overheads from depropanizer 157 pass out line 164 through condensor 165 to accumulation in vessel 166. Liquid from accumulator 166 passes via line 167 driven by pump 168 partly in recycle to the tower as reflux via line 169 and through line 170 to HF stripper 171.

Bottoms from HF stripper 171 pass via line 172a (largely propane) out of the system. The overhead hydrogen fluoride catalyst from stripper 171 passes via line 172 through condensor 173 to accumulation in vessel 174. The liquid from accumulator 174 passes via line 175 through pump 176 either in recycle via line 177 to the HF stripper 171 or as HF catalyst recycle via line 178 joining a line from the HF regenerator (to be described) becoming common line 118 already noted.

Returning to settler 101, as previously noted, there is a vertical separation of the catalyst (settles lower) and the hydrocarbon phase effluent (rises higher) in settler 101. Bottoms from settler 101 are passed via line 179 controlled by valve 180 to HF regenerator 181. Regenerator vessel 181 is heated via coil 182 with heating fluid input and output lines 183 and 184. Tar is passed out of the system from the regenerator via line 185. Overhead from vessel 181, hydrogen fluoride catalyst is passed via line 186 through condensation at 187 (accumulation), the liquid HF thereafter going via line 188 through pump 189 either in recycle to the regenerator through line 190 or back to the system in line 191 which joins stripper return line 178 thereafter becoming recycle line 118.

FIG. 3 — HYDROGEN FLUORIDE CATALYZED ALKYLATION IN NON-CIRCULATING REACTOR WITH SEPARATE SETTLER

Turning to FIG. 3, at 200 there is seen the reaction vessel which comprises a simple tank with little or no internal mixing or, at least, no circulated mixing utilizing a circulation tube as in the case of a Stratford contactor (U.S. Pat. No. 2,979,308 to Putney, issued Apr. 11, 1961 for "Apparatus for Controlling Temperature Change . . ." and U.S. Pat. No. 2,800,307 to Putney issued July 23, 1957 for "Apparatus for Controlling Temperature Change . . ."). There is a separate settling vessel 201.

Referring to the lower left hand corner of FIG. 3, propylene, butylene and amylene (olefinic hydrocarbons) in separate or individual streams 202-204, inclusive, as well as isobutane make-up through line 205, join in common line 206 which is passed in indirect

heat exchanging relationship (cooling of these streams) at 207. Line 206 thereafter passes to reactor 200 furnishing the basic olefinic and isobutane make-up feeds thereto, as well as other streams which have joined this line (which will be described herebelow). In the reactor 200, isoparaffinic hydrocarbons, particularly isobutane, are alkylated by olefinic hydrocarbons (propylene, butylene and amylene) in the presence of hydrogen fluoride as a reaction catalyst.

A mixture of HF catalyst, alkylate, excess isobutane and light paraffinic hydrocarbons such as propane are discharged via line 208 to settler 201. In settler 201, there is a gravity separation of the hydrogen fluoride catalyst (falls downwardly in the settler) and a hydrocarbon phase consisting of alkylate, isobutane and light paraffinic hydrocarbons. A first catalyst recycle line 209 from the underside of settler 201 passes to pump 210 carrying recycle HF catalyst which goes into indirect heat exchange (cooling of the catalyst) at heat exchanger 207, thereafter being recycled as catalyst feed to the reactor 200. Make-up HF line 209a may join line 209 as shown to provide additional catalyst as may be required by the system.

A second catalyst withdrawal line 211 with flow therethrough controlled by valve 212 passes to HF regenerator 213. Tar bottoms from the regenerator are passed out of the system through line 214. A heating coil 215 is provided in the regenerator fed by input and output lines 216 and 217. The overhead discharge of catalyst from regenerator 213 is through line 218 to condensation at 219 and passage to pump 220. From pump 220, a quantity of the catalyst is recycled to the regenerator through line 221, the balance returned to the system through line 222.

Turning back to settler 201, taken off overhead through line 223 is the entire hydrocarbon phase effluent comprising alkylate, excess isobutane, light paraffinic hydrocarbons and a small quantity of HF catalyst. Back pressure valve 224 maintains settler 201 and reactor 200 under sufficient back pressure to maintain all the reactants and fluid therewithin in liquid phase. In passing valve 224, the pressure is reduced on the hydrocarbon phase effluent whereby to refrigerate it and vaporize excess volatile hydrocarbons. The alkylate is non-evaporable under the pressures and temperatures existing in the system.

Flow line 225 having control valve 226 thereon passes to a heat exchanging coil or tube bundle 227 in reactor 200, the return line 228 passing to suction trap and flash drum 229. Line 223, after the take off for line 225, is numbered 230 with valve 231 thereon and passes to heat exchanger 207, the return line therefrom, 232, joining line 228 before it reaches suction trap and flash drum 229.

The reduced temperature, flashed hydrocarbon phase effluent, both liquid and vapor, in combination, may be passed in its entirety or just a portion thereof through line 225, controlled by valves 226 and 231, whereby to cool the alkylation reaction zone in reactor 200. Alternatively, all or a portion of the reduced temperature, flashed, hydrocarbon phase effluent, again controlled by valves 226 and 231, may pass through line 230 in indirect heat exchanging relationship with lines 209 and 206, whereby to cool the recycle catalyst feed to the reactor and the input hydrocarbon phase feed to the reactor. Generally speaking, the greatest proportion of the refrigerated hydrocarbon phase effluent will be passed in indirect heat exchange with the al-

kylation reaction itself in tube bundle or coil 227 in vessel 200.

At any rate, all of the flashed, refrigerated hydrocarbon phase effluent, both liquid and vapor in combination, is passed via line 228 to suction trap and flash drum 229.

Line 234 to deisobutanizer 236 via pump 235 contains substantially all of the alkylate product, the external isobutane recycle in be fractionated to the deisobutanizer tower, the normal butane which entered with the feed stocks, some propane and hydrogen fluoride. Line 244 contains propane, considerable isobutane, some hydrogen fluoride, some normal butane but very little alkylate. Line 246 contains all of the effluent recycle isobutane, some hydrogen fluoride, propane, normal butane and a very small amount of alkylate.

Bottoms from deisobutanizer 236 are taken off through line 238 controlled by valve 239 and level control 239a. Circulating line 240 is taken off line 238 and back to the deisobutanizer through heater 241. The contents of line 238 are passed in indirect heat exchange at 237 and thereafter (optionally) at 242 with the feed to the depropanizer (to be described), thereafter passing from the system as alkylate product after cooling at 243.

Returning to trap 229, bottoms from the right hand cell (in the view of FIG. 3) are taken off through line 244 driven by pump 244a. After pump 244a, line 244 has control valve 245 thereon controlled by level control 245a. Line 244 carries isobutane in recycle to join main feed line 206 leading to reactor 200.

Vapor overheads (light hydrocarbons with some catalyst contamination) from trap 229 are taken off through line 246, compressed at 247, condensed at 248 and accumulated in vessel 249. The accumulated liquids in vessel 249 are discharged through line 250 driven by pump 251 and controlled by valve 252 and level control 252a. The contents of line 250 are passed in indirect heat exchange at 242 with the alkylate product and thereafter go to depropanizer 253. Recycle line 254 taken off from line 250 after valve 252 returns some of the compressed, condensed overhead from line 246 to right hand cell of trap-drum 229.

Depropanizer bottoms are discharged through line 255 controlled by valve 256 and level control 256a. After cooling at 257, line 255 joins line 254 for recycle to the main feed to the reactor 200. Circulating line 258 may be taken off line 255 with heating at 259.

The overhead from depropanizer 253 is withdrawn through line 260 with condensation at 261 and accumulation at vessel 262. Bottoms from accumulator 262 are taken off through line 263 driven by pump 264 with this liquid either recycled to depropanizer 253 through line 265 as reflux to the depropanizer or passed via line 266 to HF stripper 267 (or both).

The bottoms from stripper 267, comprising largely propane, are withdrawn from the system at 268. The overhead line 269 from stripper 267, carrying hydrogen fluoride catalyst, is condensed at 270, and accumulated at vessel 271. The accumulated catalyst in vessel 271 is partly recycled to stripper 267 via line 272 and balance is passed back to the basic feed input to reactor 200 via line 273, by pump 274.

From the foregoing, it will be seen that this invention is one well adapted to attain all of the ends and objects hereinabove set forth together with other advantages which are obvious and which are inherent to the process.

It will be understood that certain process features, steps and sub-combinations thereof are of utility and may be employed without reference to other features, steps and process subcombinations. This is contemplated by and is within the scope of the claims.

As many possible embodiments may be made of the invention without departing from the scope thereof, it is to be understood that all matter herein set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

We claim:

1. A process of effluent refrigeration applied to the alkylation of isoparaffinic hydrocarbons by olefinic hydrocarbons wherein hydrogen fluoride is the alkylation reaction catalyst and

the reaction vessel comprises an elongate vertical tube interconnecting an overhead settler vessel and a below-situated acid cooler vessel,

there being an additional valve-controlled recycle flow line interconnecting the settler and acid cooler,

whereby circulation of liquid alkylation reaction mixture occurs upwardly through said reaction vessel to said settler and separated acid returns from said settler downwardly through said flow line to said cooler vessel, comprising the steps of:

- a. admixing said isoparaffinic hydrocarbons and said olefinic hydrocarbons with liquid hydrogen fluoride catalyst in an alkylation reaction step in said reaction vessel,
- b. passing said reaction mixture of hydrocarbons, including alkylate, propane and isobutane, and said catalyst from said reaction vessel overhead to said settler,
- c. maintaining said settler, said reactor and said acid cooler under sufficient back pressure to maintain all of said reaction mixture in liquid phase,
- d. withdrawing overhead from said settler a hydrocarbon phase which comprises primarily isobutane and alkylate and a minor amount of propane and catalyst,
- e. reducing the pressure on said hydrocarbon phase to vaporize excess volatile hydrocarbons, thereby refrigerating said hydrocarbon phase,
- f. passing at least a substantial portion of said refrigerated hydrocarbon phase, including both liquid and vapor without separation, in indirect heat exchange with said acid in said acid cooler whereby to lower the temperature thereof,
- g. passing said hydrocarbon phase, after use of same as a heat exchange medium in step (f) to a vapor-liquid separating step,
- h. the vapor phase from said separating step being passed to a depropanizing step and overhead from said depropanizing step being passed to an HF stripping step,
- i. recycling hydrogen fluoride catalyst from said stripping step to the alkylation reaction in step (a),
- j. passing a first portion of the separation step liquid bottoms from step (g) to a deisobutanizing step and recycling overhead liquids from said deisobutanizing step to the reaction step (a), and
- k. withdrawing alkylate product bottoms from said deisobutanizing step.

2. A process as in claim 1 including passing all of the said refrigerated hydrocarbon phase in indirect heat exchange with the liquid acid in said acid cooler.

3. A process as in claim 1 including passing a minor portion of the said refrigerated hydrocarbon phase in indirect heat exchanging relationship with the feeds to the reaction step (a).

4. A process as in claim 1 including recycling the depropanizing step bottoms to said vapor-liquid separating step (g).

5. A process as in claim 1 including passing a second portion of the separation step liquid bottoms from step (g) as recycle feed to the alkylation reaction step.

6. A process as in claim 1 wherein hydrogen fluoride catalyst is recycled from the HF stripping step to said flow line from said settler to said acid cooler.

7. A process as in claim 1 wherein hydrogen fluoride catalyst is recycled from said HF stripping step to join the hydrocarbon reactant feeds to the reaction step.

8. A process of effluent refrigeration applied to the alkylation of isoparaffinic hydrocarbons by olefinic hydrocarbons wherein hydrogen fluoride is the alkylation reaction catalyst and

the reaction vessel comprises an elongate vertical tube interconnecting an overhead settler vessel and a below-situated acid cooler vessel,

there being an additional valve-controlled recycle flow line interconnecting the settler and acid cooler, whereby circulation of liquid alkylation reaction mixture occurs upwardly through said reaction vessel to said settler and separated acid returns from said settler downwardly through said flow line to said cooler vessel, comprising the steps of:

- a. admixing said isoparaffinic hydrocarbons and said olefinic hydrocarbons with liquid hydrogen fluoride catalyst in an alkylation reaction step in said reaction vessel,
- b. passing said reaction mixture of hydrocarbons, including alkylate, propane and isobutane, and said catalyst from said reaction vessel overhead to said settler,
- c. maintaining said settler, said reactor and said acid cooler under sufficient back pressure to maintain all of said reaction mixture in liquid phase,
- d. withdrawing overhead from said settler a hydrocarbon phase which comprises primarily isobutane and alkylate and a minor amount of propane and catalyst,
- e. reducing the pressure on said hydrocarbon phase to vaporize excess volatile hydrocarbons, thereby refrigerating said hydrocarbon phase,
- f. passing at least a substantial portion of said refrigerated hydrocarbon phase, including both liquid and vapor, without separation, in indirect heat exchange with said acid in said acid cooler, whereby to lower the temperature thereof,
- g. passing said hydrocarbon phase, after use of same as a heat exchange medium in step (f) to a vapor-liquid separating step,
- h. a first portion of said vapor phase from said separating step being passed to a depropanizing step and overhead from said depropanizing step being passed to an HF stripping step,
- i. recycling hydrogen fluoride catalyst from said stripping step to the alkylation reaction in step (a).

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j. a second portion of said vapor phase separated from said separating step being recycled after compression and condensation to join the hydrocarbon reactant feeds to the reaction step (a), and

k. separating an alkylate product from the liquid bottoms from said separating step.

9. A process as in claim 8 wherein the liquid bottoms from said separating step (g) are passed in their entirety to a deisobutanizing step, the overhead from the deisobutanizing step being recycled to the reaction step (a) and the liquid bottoms from said deisobutanizing step being withdrawn as alkylate product.

10. A process of effluent refrigeration applied to the alkylation of isoparaffinic hydrocarbons by olefinic hydrocarbons where hydrogen fluoride is the alkylation reaction catalyst, there being separate vessels for reaction and settling steps comprising;

a. admixing said isoparaffinic hydrocarbons and said olefinic hydrocarbons with liquid hydrogen fluoride catalyst in an alkylation reaction step in said reaction vessel,

b. passing said reaction mixture of hydrocarbons, including alkylate, propane and isobutane, and said catalyst from said reaction vessel to said settler,

c. maintaining said settler and said reaction vessel under sufficient back pressure to maintain all of said reaction mixture in liquid phase,

d. separating hydrogen fluoride catalyst as liquid bottoms from said settling step and recycling a first portion of said catalyst to the reaction step (a),

e. withdrawing overhead from said settler a hydrocarbon phase which comprises primarily isobutane and alkylate and a minor amount of propane and catalyst,

f. reducing the pressure on said hydrocarbon phase to vaporize excess volatile hydrocarbons and thereby refrigerate said hydrocarbon phase,

g. passing at least a substantial portion of said refrigerated hydrocarbon phase, including both liquid

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and vapor without separation, in indirect heat exchange with said reaction mixture in the reaction step (a) whereby to lower the temperature thereof,

h. said refrigerated hydrocarbon phase, after being used as a heat exchange medium, being passed to a separating step wherein liquid and vapor phases are separated and a first portion of the liquid phase from said separating step is passed to a deisobutanizing step,

i. the overhead from said deisobutanizing step being recycled to the reaction step (a), the liquid bottoms from the deisobutanizing step being withdrawn as alkylate product,

j. a second portion of said catalyst from said settling step being passed to a hydrogen fluoride regenerating step, and the regenerated hydrogen fluoride catalyst from said regenerating step is recycled to the alkylation reaction step (a),

k. the vapor phase from said separating step being compressed, condensed and passed to a depropanizing step and overhead from said depropanizing step being passed to an HF stripping step, and

l. the propane bottoms from said stripping step being withdrawn from the process and hydrogen fluoride overhead from said stripping step being recycled to the alkylation reaction zone (a).

11. A process as in claim 10 wherein a portion of said refrigerated hydrocarbon phase is passed in indirect heat exchanging relationship with a catalyst recycle from the settling step (b) to the reaction step (a).

12. A process as in claim 10 wherein a minor portion of said refrigerated hydrocarbon phase is passed in indirect heat exchanging relationship with the hydrocarbon reactant feeds to the reaction step (a).

13. A process as in claim 10 wherein a minor portion of said refrigerated hydrocarbon phase is passed in indirect heat exchanging relationship with both the catalyst recycle from the settling step (b) and the hydrocarbon reactant feeds to the reaction step (a).

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