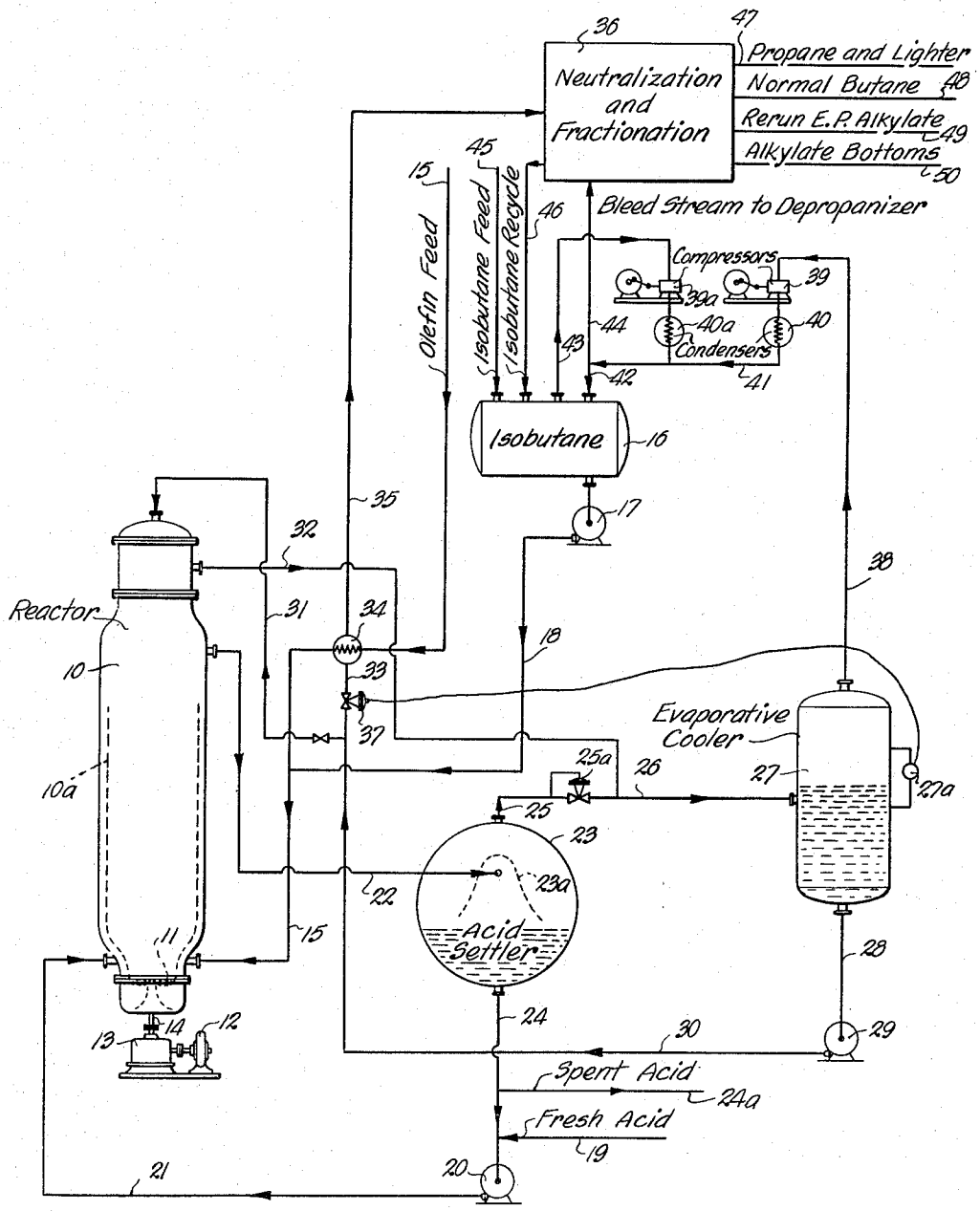
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PROCESS FOR ALKYLATION UTILIZING EVAPORATIVE COOLING

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PROCESS FOR ALKYLATION UTILIZING EVAPORATIVE COOLING

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This invention relates to improvements in a process for the alkylation of hydrocarbons in the presence of a liquid acid catalyst, and refers more particularly to a process in which evaporative cooling of the hydrocarbons is utilized to reduce the temperature of the reactants prior to and during the reaction step.

This application is a continuation-in-part of an application Serial No. 196,282, filed November 17, 1950, now U. S. Patent No. 2,649,486.

In the prior parent application there was disclosed a two-stage absorption type alkylation procedure, and one of the advantages of such process was the reduction in the amount of normal paraffin diluents present in the alkylation zone. This reduction in the amount of diluents not only promoted better quality alkylate, but also made it possible to utilize the hydrocarbon effluent from the reaction step as the refrigerating medium in the process.

In the process hereinafter described, a single stage alkylation operation is disclosed eliminating the absorption step. In this type process the quantity of diluents present in the reaction stage is in many cases so high that the effluent cannot be used as a refrigerating medium without building up a still larger quantity of diluents in the reaction zone. For example, in a typical alkylation unit without the absorption step, but in which hydrocarbon effluent is used as a refrigerant, the vapors separated from the hydrocarbon effluent may be composed conservatively of 50% to 60% isobutane, 35% to 45% normal butane, and approximately 5% other hydrocarbons represented by lighter fractions of the alkylate. The presence of this 35% to 45% normal butane in the condensate returned to the reaction zone not only does not contribute to the establishment of proper alkylation conditions, but actually has a detrimental effect thereon. Thus in the instant process, the presence of the 35% to 45% normal butane in itself has a detrimental effect on the alkylate quality and, in addition, the low percentage of isobutane in the refrigerant vapors, that is, 50% to 60%, makes it difficult to build up a satisfactory isobutane-olefin ratio.

The use of the effluent as a refrigerant, therefore, is advantageous principally in those cases where the hydrocarbons evaporated therefrom are richer in isobutane than the mixture of the fresh feed plus isobutane recycle from fractionation. There would be little advantage in using effluent refrigeration in a case where the vapors from the effluent when condensed and added back to the feed would decrease the percent of isobutane in the reactant mixture and increase the amount of normal paraffin diluents in the total combined feed.

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An object of the invention, therefore, is to provide a process wherein the effluent from the reaction stage is separated into a hydrocarbon phase and an acid phase, the hydrocarbon phase passed to an evaporative cooler where it is chilled by a reduction of pressure and the chilled liquid recycled to the reaction stage where it is brought into indirect heat exchange with the reactant mixture to reduce its temperature.

Another object is to provide a process in which the chilled hydrocarbons returned from the evaporative cooling step are used not only in the reaction zone as a cooling medium but in heat exchange with the feed to the reaction zone.

Still another object is to provide a process in which the vaporized hydrocarbons separated in the evaporative cooling step are compressed and condensed and themselves chilled by evaporative cooling prior to being recycled into the reaction step.

A further object is to provide a process wherein the chilled hydrocarbons used as a cooling medium in the reaction step are returned and combined with the hydrocarbon phase separated from the effluent mixture and directed thence to the evaporative cooling step.

Other and further objects will appear from the description which follows.

In the accompanying drawing which forms a part of the instant specification and is to be read in conjunction therewith, like reference numerals indicate like parts.

The single figure is a schematic flow diagram of one embodiment of the process.

Referring to the drawing, at 10 is shown a reactor comprising a vertical vessel preferably equipped with an open-ended circulating tube, shown in dotted lines at 10a, and a propeller 11 in the bottom of the tube driven by a motor 12 through gearing enclosed within the casing 13. The propeller is mounted on a vertical shaft 14 extending upwardly from the top of the gear case 13. To simplify an understanding of the apparatus, it will be described in conjunction with the process employed.

Olefinic hydrocarbons are introduced into the bottom of the reactor through a feed line 15, while the isobutane to be alkylated is supplied from tank 16 by means of pump 17 and line 18. The isobutane supply line 18 joins pipe 15 so the

mixture of isobutane and olefins is introduced into the bottom of the reactor through line 15. Fresh acid is supplied to the system through pipe 19 and is charged by means of pump 20 through pipe 21 into the bottom of the reactor. The olefinic and paraffinic hydrocarbons supplied through pipe 15 are combined with the acid and alkylation takes place while the mixture is rapidly agitated in the reaction vessel. The effluent-hydrocarbon-acid mixture is withdrawn from reactor 10 through pipe 22 and is discharged into an acid settler 23 beneath hood 23a, where the heavier acid phase is separated from the hydrocarbon phase. The acid is withdrawn from the bottom of the settler through pipe 24, and may be withdrawn from the system through pipe 24a or directed to the suction side of pump 20 to be recycled to the reactor with or without fresh acid, as the operation requires. The hydrocarbon phase is withdrawn from the top of settler 23 through pipe 25 and is directed through line 26 to the evaporative cooler 27. The settler 23 is maintained under sufficient pressure to keep all hydrocarbon constituents of the mix in liquid phase. Back pressure valve 25a in line 25 accomplishes this purpose. Upon being introduced into the cooler, pressure upon the hydrocarbon phase is reduced and the volatile fractions are evaporated. The liquid hydrocarbons chilled by evaporative cooling accumulate in the vessel 27 from which they are drawn off through pipe 28. These chilled liquids are recycled by means of pump 29 and pipes 30, and 31 to the top of the reactor 10 where the liquid is discharged into the header of a tubular heat exchanger extending substantially throughout the length of the reaction vessel, but not shown in the drawing. These heat exchange tubes are located within the circulating tube 10a and serve to chill the reactant mixture while it is being intimately mixed and rapidly circulated by the propeller 11. No back pressure is imposed upon the cooling medium in the heat exchange tubes, the pressure being substantially the same as that existing in the evaporative cooler 27. The lighter hydrocarbon components are thus permitted to vaporize within the tubes as heat is picked up from the reaction zone. The cooling medium after circulation through the heat exchanger is discharged as a mixture of liquid and vapor through pipe 32, which is connected into pipe 26 through which the hydrocarbon phase is withdrawn from the top of the acid settler 23. Thus it will be seen that the chilled hydrocarbons utilized as a cooling medium in the reactor 10 are combined with the hydrocarbons separated from the acid in the settler and returned to the evaporative cooling step 27 through pipe 26.

A portion of the cooling medium returned through pipe 30 to the reactor may be diverted through line 33 to cool the incoming olefin feed by means of heat exchanger 34 interposed in feed line 15. The portion of the cooling medium utilized for such purpose is then discharged through pipe 35 to neutralization and fractionation, diagrammatically shown at 36. The amount of cooling medium used for this purpose is governed by the liquid accumulation in cooler 27 through a liquid level control device 27a connected to valve 37 in pipe 33.

The volatile hydrocarbons separated from the liquid in cooler 27 are discharged through pipe 38 and are directed to compressor 39, after which they are cooled in condenser 40 and discharged through pipes 41 and 42 into the isobutane accumulator 16. To facilitate the cooling of the accumulated liquid in drum 16, a portion of the volatile material is removed through pipe 43, and passed to compressor 39a, then cooled in condenser 40a, and returned to the drum 16 through pipes 41 and 42. A diversion line 44 connected to pipe 41 permits the bleeding of a portion of the hydrocarbons from the system to a depropanizer included in fractionation, indicated diagrammatically at 36. The isobutane accumulator is also equipped with a fresh isobutane feed line 45 and an isobutane recycle feed line 46 for returning isobutane from fractionation into the isobutane accumulator 16. Connected into fractionation diagrammatically shown at 36, are discharge lines 47, 48, 49, and 50, through which are respectively withdrawn propane and lighter hydrocarbons, normal butane, rerun alkylate and alkylate bottoms.

Although the drawing shows evaporative cooler 27 located below the top of the tubular heat exchanger of the reaction vessel thus requiring a pump to circulate cooled hydrocarbons through the tubes, it is to be understood that vessel 27 may to advantage be located above the top of the reaction vessel so that cooled hydrocarbon liquid from it will flow by gravity through the elements of the tubular heat exchanger within the reactor. The mixture of liquid and vapor then issuing from the tubular heat exchanger is carried back up to vessel 27 by the gas lift effect of the vapor portion of the stream. When cooler 27 is so located pump 29 can be omitted. In this case however a pump will be required to pump the hydrocarbon product through control valve 37, line 33, exchanger 34 and line 35 to neutralization and fractionation.

In order to realize the benefits of effluent refrigeration, it is unnecessary to completely eliminate the normal paraffins from the feed as is substantially accomplished in the two-stage absorption type alkylation described in my prior application. There are however many instances in refineries where an isobutane fraction is alkylated with olefins originating from catalytic cracking units or other sources where the amount of normal paraffin diluents in the combined feed is very low, being of the order of 8% to 10% or lower. In some cases when recycling isobutane from fractionation containing approximately 80% isobutane and 20% normal butane, in quantities sufficient to build up an isobutane to olefin ratio in the total feed of 4:1, the vapors leaving the effluent refrigerant system or evaporative cooler will show as high as 75% to 85% isobutane, which is considerably greater than the percentage of isobutane in the total feed. In such cases effluent refrigeration works to great advantage not only in increased quality of alkylate, but also in reducing the requirements for fractionating recycle isobutane. The higher the percentage of normal paraffins such as normal butane and propane in the feed, the less attractive the effluent refrigeration system becomes. When the volumetric percentage of normal paraffin in the composite feed is of the order of 25%, the effluent refrigeration system has lost most of its advantages. Above 25% normal paraffins in the feed, it has little to offer as compared with closed cycle refrigeration. Approximately 30% normal paraffins in the feed would result in from 35% to 40% normal paraffins in the vapors evaporated from the evaporative cooler and sent to the compressors,

which, as suggested in my previous application, would be an unprofitable operation.

The instant process, then, eliminates the absorption step and is limited to the processing of feed stocks for which absorption is not required in order to realize a substantial portion of the benefits of effluent refrigeration. When absorption is not used, there is no necessity for chilling the acid to the low temperature required in the system where an absorber is used.

It should be noted that in this simpler embodiment of the alkylation method, the effluent from the settler is passed to an evaporative cooler which acts as a flash drum where the hydrocarbon effluent is self-refrigerated by evaporative cooling, and from which the chilled liquid is passed to the reactor as a cooling medium. A portion of this cooling medium may be employed to cool the incoming olefin feed and since the olefin feed is combined with the isobutane feed prior to their introduction into the reactor, this cooling effect is transmitted to the entire feed.

Also, in the alkylation process described, the content of the isobutane accumulator drum **16** is self-refrigerated by continuous evaporation of isobutane to the compressor **39***a*, after which it is liquefied and returned to the accumulator. Since isobutane compressors are available for evaporating isobutane from the hydrocarbon effluent, these same compressors can be utilized to self-refrigerate a portion or all of the isobutane feed, recycle and refrigerant condensate. The cooling of the isobutane feed in this manner reduces the load on the reactor cooling coils and the cost of these coils, as a consequence, is reduced. It is possible for this process to cool the isobutane feed in drum **16** to a temperature even below that of the reaction temperature without requiring subatmospheric pressures at the suction of compressor **39***a*, assuming that the reaction is carried out within the range of 45° F. to 70° F.

It should be noted also that evaporative refrigeration cannot be applied to the olefin feed since a portion of the refrigerant vapors must be continuously bled off to the depropanizer of the fractionation section in order that propane can be eliminated from the system. If the olefin feed were introduced into the isobutane accumulator **16**, olefins would be lost to fractionation and rejected from the system without reaching the alkylation zone. Only in very rare cases are alkylation feed stocks entirely devoid of propane. This propane is evaporated from cooling vessel 27, preferentially to the isobutane. The compressor condensate recovered from these hydrocarbons contains a higher percentage of propane than does the liquid bottoms taken from cooler 27 and it is, therefore, a portion of this lighter stream which should be diverted to the depropanizer, to prevent building up propane to a high value in the reaction or alkylation zone.

Thus it will be seen that under selected conditions where the feed stream to the alkylation stage is relatively low in normal paraffins, evaporative cooling may be employed efficiently and to great advantage.

Having thus described my invention, I claim:

1. In an alkylation process wherein isobutane and olefins are contacted with a liquid acid catalyst in a reaction step, and a mixture of hydrocarbons containing less than 35% normal paraffins is withdrawn with the acid catalyst as effluent from said reaction step, the improvement which comprises separating said effluent into a hydrocarbon phase and an acid phase in a separating step, reducing the pressure on the hydrocarbon phase in an evaporative cooling step to refrigerate the same, separating the vaporized hydrocarbons from the chilled liquid hydrocarbons and passing the latter in indirect heat exchange with the reactant mixture in the reaction step.

2. A process as in claim 1 wherein a portion of the chilled liquid hydrocarbons returned to cool the reaction mixture is brought into indirect heat exchange with the feed of reactants to said reaction step.

3. A process as in claim 1 wherein a portion of the chilled liquid hydrocarbons returned as a cooling medium to the reaction step is brought into indirect heat exchange with the feed of reactants to said reaction step, said portion thereafter diverted to a fractionation step, and controlling the amount of said diverted portion by the liquid level in the evaporative cooling step.

4. A process as in claim 1 wherein the chilled hydrocarbons returned from the evaporative cooling step and used as a chilling medium in the reaction step are passed from the reaction step back to the evaporative cooling step.

5. A process as in claim 1 wherein the vaporized hydrocarbons separated in the evaporative cooling step are compressed, condensed and recycled as a part of the feed to the reaction step.

6. A process as in claim 1 wherein the vaporized hydrocarbons separated in the evaporative cooling step are compressed, condensed, and a portion re-evaporated from the condensed body of liquid to reduce the temperature thereof prior to recycling as a part of the feed to the reaction step.

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