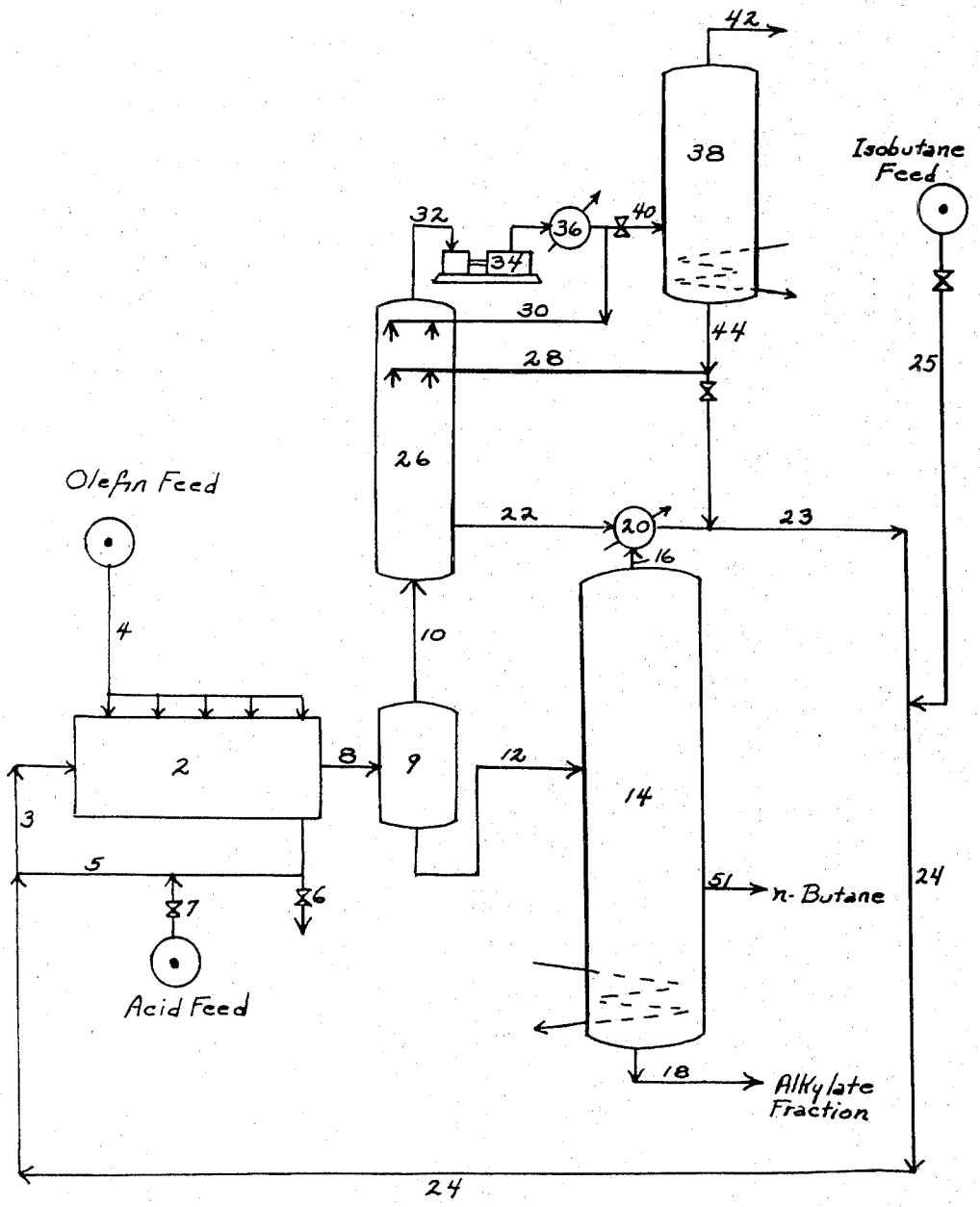
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ALKYLATION PROCESS

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ALKYLATION PROCESS

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ABSTRACT OF THE DISCLOSURE

The present invention relates to a method of concentrating materials boiling below the alkylatable hydrocarbons in the vaporous phase formed in an alkylation zone during liquid phase reaction. The process comprises contacting the vaporous phase, preferably in countercurrent manner, with a liquid alkylatable hydrocarbon stream which is rich in lower boiling materials to extract the lower boiling materials from the liquid stream in a concentrating zone; withdrawing, compressing and cooling vaporous phase enriched lower boiling material from the concentrating zone to form a condensate rich in lower boiling materials and passing said condensate to the concentrating zone as the liquid alkylatable hydrocarbon stream.

This invention relates to a process for alkylating hydrocarbons. More particularly, this invention relates to a method of concentrating low boiling compounds in the vaporous effluent from an alkylation reactor.

In the alkylation of hydrocarbons, notedly isoparaffins with olefins, the reactants are contacted and reacted in the presence of an acid catalyst, such as hydrofluoric acid or sulfuric acid or a Friedel-Crafts catalyst, such as aluminum chloride. During the course of alkylation, a portion of the alkylatable hydrocarbon and substantially all of the lower boiling hydrocarbons are vaporized and separated from the liquid alkylate effluent containing, in addition to alkylate, the remaining portion of alkylatable hydrocarbon and any higher boiling materials present in the system. The liquid alkylate effluent is treated for purification and separation of alkylate in one or more distillation operations.

For the most part, the vaporous effluent is condensed and recycled to the alkylation zone; however, a small portion of this vaporous effluent is passed to a separate distillation zone for removal of vaporous compounds boiling below the liquid alkylatable hydrocarbon. The removal of low boiling vapors from the system is necessary to avoid build up of these inerts in the reaction zone. While it is desirable to maintain the inert low boiling materials at a minimum in the alkylation reactor, it has been found impractical to distill the entire condensed vaporous effluent, since such distillation would require an excessively large depropanizer, and a large amount of heat would be consumed in heating up the entire condensed vaporous effluent.

While the inert materials are considered inert insofar as the alkylation reaction is concerned, these compounds reduce the concentration of the alkylatable hydrocarbons and thus reduces the quality of the alkylate produced.

Therefore, there is a need in the alkylation of hydrocarbons to develop a process which eliminates a major portion of the so-called inert low boiling materials at low capital and utilities cost.

It is an object of the present invention to provide an alkylation process which reduces the concentration of low boiling inert materials to a minimum without loss of alkylatable hydrocarbon.

Another object of this invention is to provide an economically feasible and commercial process for concentrating alkylatable hydrocarbon in the recycle streams to the reactor while concentrating low boiling hydrocarbons in the vaporous condensate feed to distillation.

These and other objects will become apparent to those skilled in the art from the accompanying description and disclosure.

According to the present invention, the vaporous phase from an alkylation reaction is separated from a liquid phase comprising alkylate product, alkylatable hydrocarbon and higher boiling materials; the vaporous phase is countercurrently contacted, preferably under adiabatic temperature conditions, with a low boiling liquid alkylatable hydrocarbon stream relatively rich in lower boiling inert hydrocarbons; the gaseous phase extracts the lower boiling inerts from the low boiling liquid stream containing alkylatable hydrocarbon and the resulting extracted liquid which contains a substantially reduced concentration of low boiling inerts is recycled to the reaction zone while the vaporous phase enriched in low boiling inerts is compressed and condensed to provide the low boiling liquid stream, of which at least a major portion is passed in countercurrent contact with the vaporous phase in the alkylatable hydrocarbon extraction or concentrating zone. If desired, a minor portion of the low boiling liquid stream or condensate, enriched in low boiling compounds, is passed to a distillation zone for removal of the low boiling inert materials as vapors from the alkylatable hydrocarbon which is withdrawn as a liquid from the distillation zone. The alkylatable hydrocarbon liquid from the low boiler distillation zone can be recycled to the alkylation zone or, preferably, can be passed into countercurrent contact with the vaporous phase at a separate point in the concentrating zone.

As a result of the present method of concentrating low boiling inerts in the vaporous phase, the subsequent distillation of said low boiling materials from alkylatable hydrocarbon liquid is enhanced due to improved efficiency in the fractionation of the material undergoing distillation of low boilers. By the present process the concentration of these low boiling materials in the vapors can be increased tenfold or more at low temperature and pressure in the alkylatable hydrocarbon extraction zone so that a vaporous fraction containing low boilers in high concentration can be removed in the subsequent distillation step and the resulting liquid reactant stream from the distillation zone rendered suitable for recycle to the alkylation zone at minimum concentration of reaction diluent. The purification of recycle streams results in formation of alkylate of increased octane number. It has been found possible to increase the octane number by as much as one point or more, e.g., from 94 to 96 octane.

The alkylatable hydrocarbons of the present process are those usually employed in alkylation processes and include isobutane and isopentane as the preferred species. However, it is to be understood that hydrocarbons of from two to ten carbon atoms, including benzene and methyl and/or ethyl-substituted butanes, pentanes, hexanes and heptanes are also suitably employed in the process of the present invention.

Among the olefins which are reacted with the alkylatable hydrocarbon, propene and butene are most preferred. However, olefins of from two to ten carbon atoms can be employed in the present process. These include the unsaturated and branched chain derivatives of the paraffins recited above.

The alkylation reaction can be initiated at a temperature within the range of from about 0° C. to about 130° C., preferably from about 5° C. to about 70° C. under a pressure sufficient to maintain liquid phase conditions, e.g., from about 2 to about 10 atmospheres.

Typical vaporous phases obtained from alkylation when

the alkylatable hydrocarbon is isobutane, contain between 50 and about 95 weight percent isobutane, between 5 and about 25 weight percent propane and between about 0.5 and about 2 weight percent of lower boiling materials. When the alkylatable hydrocarbon is isopentane the vaporous phase usually contains between about 70 and about 90 weight percent isopentane, between about 10 and about 20 weight percent n-pentane, between about 5 and about 20 weight percent propane, and between about 0.5 and about 2 weight percent lower boiling materials. Generally, the alkylatable hydrocarbon comprises between about 50 and about 80 weight percent by volume of the vaporous phase from the reactor and this percent can be increased to between 70 weight percent and about 90 weight percent in the vapors removed from the alkylatable hydrocarbon extraction zone of the present process.

The separation of vaporous phase from liquid alkylate phase can be effected during stages in an alkylation zone or it can be separated by flashing an entire liquid hydrocarbon mixture from the reactor or by any other known method of splitting the hydrocarbon reaction mixture into vaporous and liquid phases at the alkylatable hydrocarbon level.

The resulting vaporous phase at ambient temperature and pressure or at a temperature and pressure slightly lower than that employed in the alkylation zone can be pressurized or can be directly introduced into an alkylatable hydrocarbon extraction or concentrating zone, e.g., a trayed or packed tower, for counter-current contact with the low boiling liquid alkylatable hydrocarbon stream containing excess low boiling materials, e.g., containing between 2 and 30 weight percent low boilers. In the extraction zone the vaporous phase acts as a stripping agent to remove low boilers from the low boiling liquid stream which enters the upper portion of the column relatively rich in low boilers and which is withdrawn from the lower portion of the column relatively lean in low boilers. In the extraction zone of the present process, the low boiling materials in the liquid recycle stream can be reduced to less than 1 percent or can be reduced as much as 20 fold as compared to the original concentration.

With the increased concentration of low boilers in the resulting vapor phase extractant recovered from the upper portion of the extraction zone, the depropanizer of prior processes can be eliminated entirely and a portion of the vapors vented to avoid build-up of low boilers, if desired. As alternatives, the condensed vapors can be passed to a depropanizer markedly reduced in size to separate liquid isobutane from lower boiling material. In this event a sharper separation of isobutane from low boilers is attainable for a given size depropanizer as compared with prior depropanization which omitted the preconcentration step. In cases where the depropanizer is used in conjunction with the concentrator, the condensate of the extractant is distilled in the top of a fractionation column at a temperature of between about 25° C. and about 90° C. under a pressure of from about 10 atmospheres to about 40 atmospheres, preferably between about 35° C. and about 50° C., from about 12 to about 15 atmospheres, to eliminate a major portion of the low boilers from the system.

Spray injection of the low boiling liquid stream into the upper portion of the packed column is recommended for better contact between the rising gases and the liquid, although other methods of promoting contact, e.g., bubble capped trays, can be employed, if desired.

The vaporous extractant from the top of the extraction zone is compressed to a pressure between about 5 and about 20 atmospheres, preferably between about 6 and about 8 atmospheres and condensed at a temperature between about 35° C. and about 60° C.

For a better understanding of the present invention reference is now had to the accompanying drawing which represents a specific embodiment of the process of the present invention. It is to be understood, however, that the present invention is not to be limited by the example described in the drawing and that many modifications and variations of the process described below will appear to those skilled in the art without departing from the scope of this invention.

In the drawing a mixture of isobutane and sulfuric acid is introduced into alkylation zone **2** from line **3**. The hydrocarbon content of this mixture comprises 10,702 lbs. moles/hr. isobutane, 1,807 lbs. moles/hr. n-butane, 13 lbs. moles/hr. of propene, and 200 lbs. moles/hr. propane and lower boiling materials. In the alkylation zone the liquid mixture is contacted in several stages with olefin feed comprising 865 lbs. moles/hr. butylene, 360 lbs. moles/hr. n-butane, 1 lb. mole/hr. of propene, and 10 lbs. moles/hr. propane and lower boiling materials introduced into zone **2** from line **4**. The alkylation is carried out at a temperature of 15° C. under about 25 p.s.i.g. with a molar excess of isobutane with respect to olefin. During the course of the alkylation a portion of the hydrocarbon, namely, 4473 lbs. moles/hr. of a mixture containing isobutane, n-butane and lower boiling materials, is vaporized. After the final stage of alkylation in alkylator **2** the remaining liquid is allowed to settle to separate liquid acid from the liquid hydrocarbon mixture. The liquid acid is recycled to reaction zone **2** by means of line **5** after sufficient acid has been withdrawn by means of valved line **6** and replenished with fresh acid from valved line **7** to maintain the acid concentration at at least a 92 percent level.

The liquid hydrocarbon mixture, together with vaporized hydrocarbons, is removed from reaction zone **2** by means of line **8** and passed to separation zone **9** wherein at under a pressure of about 14.2 p.s.i.g. at a temperature of about 12° C. a vaporous phase comprising 3,755 lbs. moles/hr. isobutane, 570 lbs. moles/hr. n-butane, 130 lbs. moles/hr. propane, and lower boiling materials is separated by means of line **10** from liquid phase comprising 6,082 lbs. moles/hr. isobutane, 1,597 lbs. moles/hr. normal butane, and 896 lbs. moles/hr. alkylate in line **12**. The liquid phase is introduced into deisobutanization zone **14** wherein at a top temperature of between 40° and 60° C. and a bottom temperature of between 150° and 180° C. under a pressure of 100 p.s.i.g. a vaporous fraction comprising 6.072 lbs. moles/hr. isobutane, 1,237 lbs. moles/her. n-butane and 80 lbs. moles/hr. propane and lower boiling materials are separated and withdrawn by means of line **16**, while from line **51** a n-butane product is removed, containing 300 lbs. moles/hr. n-butane and 10 lbs. moles/hr. i-butane, and from line **18** a liquid alkylate fraction comprising 60 lbs. moles/hr. normal butane and 890 lbs. moles/hr. alkylate is withdrawn from zone **14**. The liquid alkylate fraction is recovered as product or passed to subsequent stages of refinement (not shown).

The vaporous fraction from zone **14** withdrawn in line **16** is passed to condenser **20** by means of line **22** wherein the vapors are condensed and recycled to alkylation zone **2** by means of lines **23** and **24** after admixture with fresh isobutane feed introduced into line **24** by means of line **25**.

The vaporous phase withdrawn from separation zone **9** in line **10** is passed to the bottom of trayed tower alkylatable hydrocarbon extraction or concentrating zone **26** in countercurrent contact with a low boiling isobutane liquid stream comprising 268 lbs. moles/hr. isobutane, 43 lbs. moles/hr. n-butane and 13 lbs. moles/hr. propane and lower boiling materials. The low boiling isobutane liquid stream is spray injected from line **28** into the upper portion of the concentrating zone from which the liquid passes downwardly with a second liquid isobutane stream comprising 2,983 lbs. moles/hr. isobutane, 468 lbs. moles/hr. n-butane, 804 lbs. moles/hr. propane and lower boiling materials, spray injected from line **30** in countercurrent contact with rising vapors. The vapor

phase in zone **26** is contacted with the liquid streams under ambient conditions of temperature and pressure and extract 807 lbs. moles/hr. propane and lower boiling materials from the combined liquid streams. Although in the present case, zone **26** is at a temperature of about 8° C. under atmospheric pressure, it is to be understood that the concentrating zone **26** can be operated at temperatures between about 0° C. and about 80° C. under from 5 p.s.i.g. to about 180 p.s.i.g., if desired.

The resulting isobutane enriched liquid mixture is withdrawn from the lower portion of zone **26** by means of line **22** from which it is passed to condenser **20** in admixture with the vaporous fraction from deisobutanization zone **14**. It is to be understood, however, that the liquid mixture can be separately condensed and recycled to the alkylation zone without departing from the scope of this invention.

The extractant vapors from zone **26**, comprising 3,254 lbs. moles/hr. isobutane, 511 lbs. moles/hr. n-butane, 877 weight percent propane and lower boiling materials are withdrawn by means of line **32**, pressured to 80 p.s.i.g. in compressor **34** and cooled to 38° C. in condenser **36** in this particular embodiment, although compression to between about 60 p.s.i.g. and about 120 p.s.i.g. for condensation at temperatures between about 30° C. and about 50° C. can be effected with similar extractant mixtures or with extractant mixtures containing different components.

The resulting condensate is divided into two portions. One portion, about 324 lbs. moles/hr. is passed to distillation zone **38** which can be operated at a temperature between about 40° C. and about 90° C. by means of valved line **40**. The remaining portion is passed to the upper portion of zone **26** by means of line **30**.

In distillation tower **38** of this embodiment, at a temperature of 41° C. under 170 p.s.i.g., 60 lbs. moles/hr. propane and lower boiling materials are separated and withdrawn as a vaporous effluent in line **42** from liquid isobutane distilland. The liquid isobutane distilland and/or liquid effluent is recovered from zone **38** in line **44** and the isobutane distilland is preferably spray injected into concentrating zone **26** by means of valved line **28** at a point below entry of the condensed liquid isobutane stream which bypasses depropanization zone **38**. However, it is to be understood that a portion or all of the distilland can be passed to recycle line **22** or **24**, if desired.

A summary of process stream compositions in lbs. moles/hr. of components is presented below in Table I.

TABLE I

	C_3	n-Butane	Isobutane	Alkylate	Butylene
Hydrocarbon feed (in line 4)	10	180	----------	----------	865
Hydrocarbon feed (in line 25)	50	180	878	----------	----------
Isobutane recycle (in line 24)	200	1,807	[1] 10,702	----------	----------
Hydrocarbon (in outlet line 8)	80	1,597	[2] 6,082	896	----------
Vaporous effluent (in line 10)	130	570	3,755	----------	----------
Extractant vapors (in line 32)	877	511	3,254	----------	----------
Condensate (in line 30)	804	468	2,983	----------	----------
Distilland (in line 44)	13	43	268	----------	----------
Isobutane enriched liquid (in line 22)	70	570	3,752	----------	----------
Vaporous effluent (in line 16)	80	1,237	6,072	----------	----------

[1] 84%.
[2] 70.3%.
NOTE.—Octane number of alkylate recovered from process: 95.8.

For purposes of comparison a standard alkylation process based on the above description was carried out wherein the vaporous phase (for example, a vaporous phase in line **10** at the same composition and conditions of temperature and pressure) is passed directly to compressor **34** and condenser **36**, operated under the same conditions of temperature and pressure discussed above in the drawing. A major portion of the total condensate, in this case about 93 percent, is passed from condenser **36** as recycle feed to the alkylation zone while the remaining portion is passed into a depropanization zone (such as zone **38**, operated under the same conditions of temperature and pressure as described in the drawing). The liquid effluent recovered from zone **38** is then recycled, together with the major portion of the total condensate, to the alkylation reactor as part of the feed thereto. In this operation, as in the embodiment described in the drawing, a liquid phase of the same composition as described in line **12** is passed to a deisobutanization zone (such as zone **14** operated under the same conditions of temperature and pressure) and the following composition of process streams is reported below in Table II in lbs. moles/hr. based on apparatus corresponding to that shown in the drawing.

TABLE II

	C_3	nC_4	$isoC_4$	Alkylate
Gas to compressor (34)	877	511	3,254	----------
Liquid from condenser back to reactor (36)	804	468	2,983	----------
Isobutane liquid from depropanizer (line 44)	13	43	268	----------
Isobutane vaporous fraction (in line 16)	424	1,237	5,814	----------
Isobutane feed to reactor (in line 24)	1,291	1,748	[1] 9,943	----------
Hydrocarbon in reactor outlet (line 8)	424	1,597	[2] 5,824	896

[1] 76.5%.
[2] 67.1%.
NOTE.—Octane number of alkylate recovered from process: 95.0.

From the above comparison it is noted that an increase of about 0.8 in octane number was achieved in the more efficient and commercially feasible process of the present invention, indicating a higher yield of pure alkylation product.

It is also observed that, by stripping in contactor **26** to concentrate propane in the vapor phase, the size of the high pressure depropanization zone can be markedly reduced to lend further economic savings in the process.

Having thus described my invention, I claim:

1. In the liquid phase alkylation of a hydrocarbon in an alkylation zone wherein a vaporous phase comprising alkylatable hydrocarbon and lower boiling materials and a liquid phase comprising alkylate, alkylatable hydrocarbon and higher boiling hydrocarbons are obtained and separated, the improvement which comprises: passing the vaporous phase through an alkylatable hydrocarbon concentrating zone to contact a liquid alkylatable hydrocarbon stream which is separately introduced into the concentration zone, said stream being rich in lower boiling materials; extracting the lower boiling materials with said vaporous phase and withdrawing a resulting alkylatable hydrocarbon enriched liquid effluent from the lower portion of the concentration zone for recycle to the alkylation zone; compressing and cooling the vaporous phase enriched in lower boiling materials to form a condensate; passing at least a portion of the condensate to the concentrating zone as the liquid alkylatable hydrocarbon stream rich in lower boiling materials.

2. The process of claim **1** wherein a portion of the condensate is passed to a distillation zone to remove the lower boiling materials as a vaporous effluent from liquid alkylatable hydrocarbon and the remaining undistilled portion of condensate is passed to the concentrating zone.

3. The process of claim **2** wherein at least a minor portion of the liquid alkylatable hydrocarbon from the distillation zone is recycled to the alkylation zone and the remaining distilled portion is passed to the concentration zone for contact with the vaporous effluent.

4. The process of claim **2** wherein all of the liquid alkylatable hydrocarbon from the distillation zone is passed to the concentration zone for contact with the vaporous phase at a point below the introduction of the undistilled condensate.

5. The process of claim 2 wherein less than 10 percent of the condensate is passed to the distillation zone.

6. The process of claim 1 wherein the liquid phase from the alkylation zone is passed to the lower portion of a deisoparaffinization zone wherein alkylatable hydrocarbon is separated from alkylate by distillation and the vaporous phase from said concentrating zone is employed as reflux to the upper portion of the deisoparaffinization zone.

7. The process of claim 1 wherein the vaporous phase and the liquid alkylatable hydrocarbon stream are countercurrently contacted in the concentration zone.

8. The process of claim 7 wherein the vaporous phase is passed upwardly and the liquid alkylatable hydrocarbon stream is passed downwardly in the concentration zone.

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