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[54] ALKYLATION OF HYDROCARBONS

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[51] **Int. Cl.** **C07c 3/54**

[58] **Field of Search** 208/683.48, 683.42, 683.51

[56] **References Cited**

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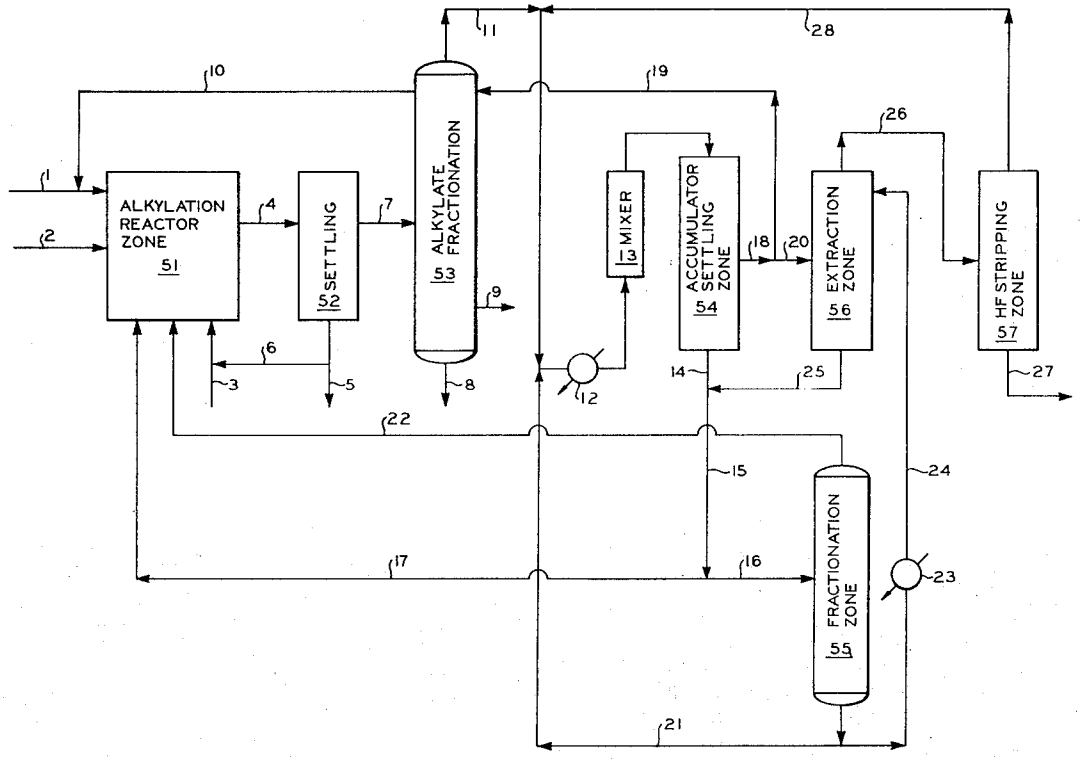
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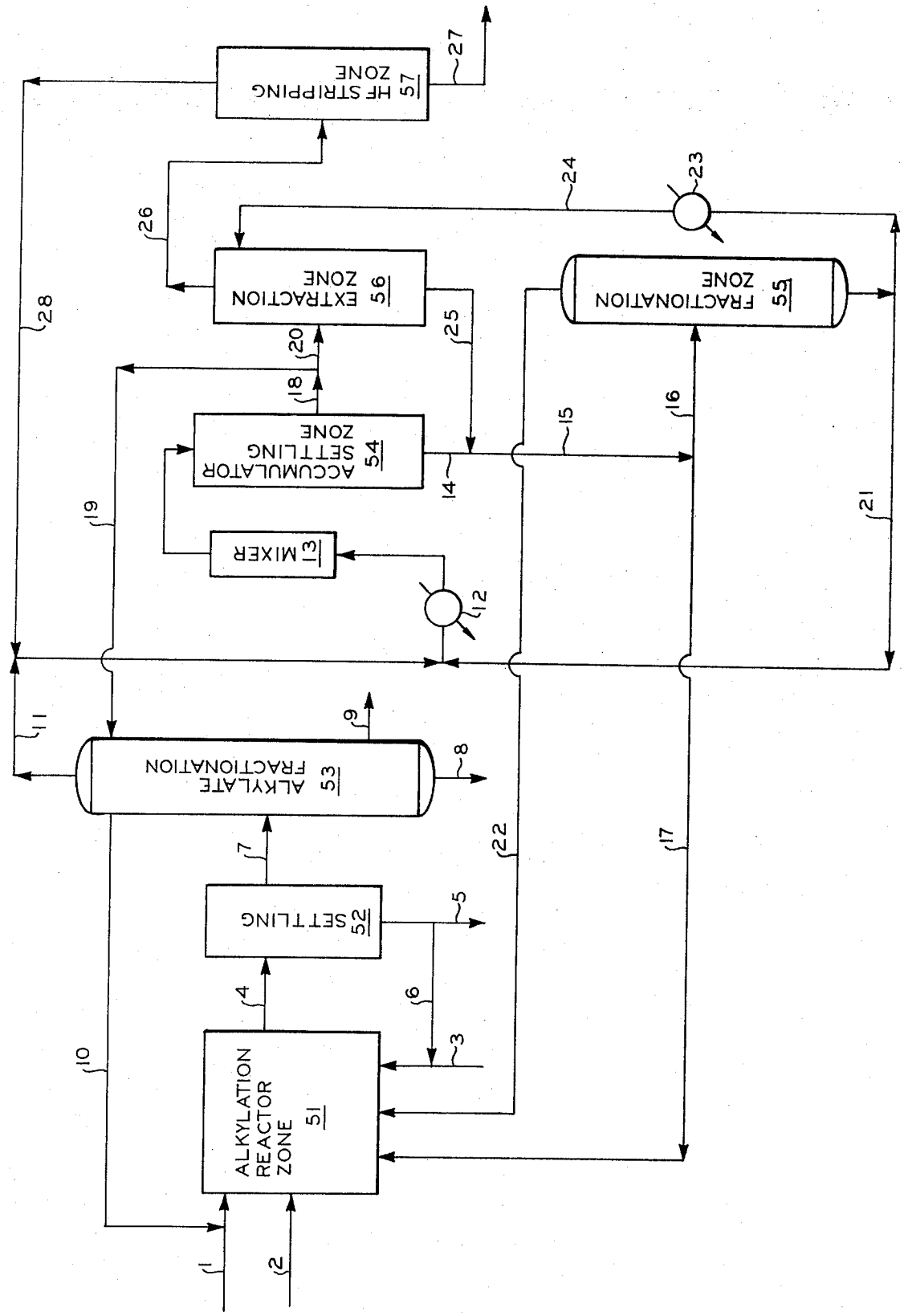
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[57] **ABSTRACT**

In a hydrogen fluoride catalyzed alkylation process, particularly in such processes wherein primary alkyl fluorides are employed as catalyst activators, alkyl fluorides are separated from the secondary hydrocarbon product stream by condensing the overhead stream from the alkylation hydrocarbon fractionation zone to form a liquid acid phase and a liquid hydrocarbon phase. The acid phase is separated to obtain a hydrogen fluoride stream which is recombined in part with the overhead stream from the alkylation fractionation zone prior to condensation of said stream and in part with the hydrocarbon phase containing the secondary hydrocarbon product liquid stream in an extraction zone, wherein alkyl fluorides are removed from the secondary hydrocarbon product stream. The secondary hydrocarbon product-containing stream from the extraction zone is subsequently separated to recover a liquid hydrocarbon product stream essentially free of organic fluorides and hydrogen fluoride.

5 Claims, 1 Drawing Figure




ALKYLATION REACTOR ZONE 51
SETTLING 52
ALKYLATE FRACTIONATION 53
ACCUMULATOR SETTLING ZONE 54
FRACTIONATION ZONE 55
EXTRACTION ZONE 56
HF STRIPPING ZONE 57
MIXER 13
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ALKYLATION OF HYDROCARBONS

This invention relates to the alkylation of hydrocarbons. More particularly, the invention relates to the alkylation of paraffins with olefins in the presence of hydrogen fluoride catalyst. More particularly, the invention relates to the alkylation of isoparaffins with olefins in the presence of hydrogen fluoride and at least one primary alkyl fluoride reaction improver.

Because of the future requirements for low lead or lead-free high octane gasoline, there is an economic incentive to make gasoline by cracking heavier materials and by combining lighter hydrocarbons produced. One such method for upgrading these lighter or low boiling hydrocarbons is alkylation, using olefinic light hydrocarbons and light paraffins, particularly light isoparaffins, as feedstocks for alkylation. One widely used process for such upgrading is hydrogen fluoride catalytic alkylation. According to this process, substantially dry liquid feed comprising at least one paraffinic hydrocarbon and at least one olefinic hydrocarbon is charged to a reactor-settler system, wherein the hydrocarbon feed is contacted with liquid hydrogen fluoride catalyst. The hydrocarbon liquid phase which is produced in the settler is fed to a fractionator which accomplishes the needed separation to LPG-quality propane product, alkylate product and unreacted feedstock, e.g., isoparaffin for recycle to the hydrogen fluoride alkylation operation.

A recent improvement in such hydrogen fluoride alkylation processes involves the maintenance in the alkylation reaction zone of one or more primary alkyl fluorides within certain limits. In other words, while it had been known that certain alkyl fluorides were present in the reaction effluent as a byproduct of the alkylation reaction, it was not previously known that the presence of primary alkyl fluoride at certain minimum levels could be used in improving the octane of the product at the same reactor levels or obtain the same octane improvement with lower reactant isoparaffin to olefin ratios in comparison to hydrogen fluoride alkylation processes wherein no attention was paid to the amount of primary alkyl fluoride in the reaction zone.

Because of their corrosivity and other handling and cost problems, it is necessary to remove the hydrogen fluoride and other fluorine-containing materials from the product streams, in particular, from the secondary LPG-quality propane stream. This has been historically accomplished by stripping dissolved hydrogen fluoride from the propane product stream. While effective for the purpose of removing the hydrogen fluoride from the propane product stream, this stripping step has been found to be ineffective for the removal of primary alkyl fluoride dissolved in the propane product. Subsequent treatment of the propane product included bauxite treatment, KOH treatment, and the like, the agents being used up in such treatment.

It is an object of this invention to provide a process for the alkylation of paraffins with normal and branched chain olefins. It is another object of this invention to provide a process for the alkylation of normal and branched chain paraffins with normal and branched chain olefins. Another object of this invention is to provide for the modification of a hydrogen fluoride alkylation process effected in the presence of a reaction modifier, in which the olefin reactant is higher boiling or heavier than ethylene. Another object of the invention is to provide for the substantial removal of reaction modifiers from the LPG or secondary product stream. Other objects and the several advantages of the invention will be readily apparent from a study of the disclosure, the appended drawing, and the attached claims.

According to the present invention, there is provided a process for the alkylation of at least one paraffin with at least one olefin in the presence of hydrogen fluoride catalyst, wherein primary organic fluorides, whether produced during the reaction as a reaction byproduct, specifically introduced into the alkylation zone as a catalyst activator, or as a combination of such reaction byproduct and specific introduction, are essentially eliminated from the secondary or LPG hydrocarbon product stream.

More particularly, the present invention provides a process for the alkylation of at least one paraffin and at least one olefin in the presence of hydrogen fluoride catalyst which comprises:

a. contacting in an alkylation reaction zone under alkylation conditions at least one paraffin and at least one olefin in the presence of hydrogen fluoride catalyst to obtain a reaction product comprising alkylate, propane, organic fluoride, unreacted paraffins and hydrogen fluoride;

b. separating from said reaction product a first stream comprising alkylate, propane, unreacted hydrocarbons, a minor amount of hydrogen fluoride, and organic fluoride;

c. passing said first stream to a first fractionation zone and separating therefrom a second stream comprising alkylate product and a third stream comprising propane, a minor amount of hydrogen fluoride and organic fluoride;

d. condensing said third stream to obtain a propane phase to a first acid phase;

e. passing at least a portion of said propane phase to a liquid-liquid extraction zone;

f. passing at least a portion of said first acid phase to a second fractionation zone and separating therefrom a fourth stream rich in organic fluoride and hydrogen fluoride and a fifth stream rich in hydrogen fluoride;

g. passing at least a portion of said fifth stream to said extraction zone of step (e);

h. contacting in countercurrent fashion in said extraction zone said propane phase portion and said fifth stream portion;

i. separating said contacted portions into a sixth stream comprising propane and hydrogen fluoride; and

j. separately recovering from said sixth stream a seventh stream consisting essentially of propane.

In a more preferred embodiment, a portion of the propane liquid phase is returned as reflux to the first fractionation zone and at least a portion of the remainder of the propane phase is passed to the extraction zone where it is contacted with a lqiuid stream enriched with hydrogen fluoride.

In still another embodiment, the stream from the second fractionation zone which is rich in organic fluoride and hydrogen fluoride can be returned to the alkylation reaction zone to provide part of the catalyst and catalyst activator for the alkylation reaction.

In yet another embodiment, a portion of the stream from the second fractionation zone which is rich in hydrogen fluoride is combined with the vapor stream comprising propane, a minor amount of hydrogen fluoride and organic fluoride, prior to condensation of said

stream, to obtain a propane phase and an acid phase.

In a further embodiment, the stream comprising propane and hydrogen fluoride is separated into a stream consisting essentially of propane and a stream comprising propane and hydrogen fluoride, with the latter stream being combined with the effluent stream comprising propane, a minor amount of hydrogen fluoride and organic fluoride from the first fractionation zone and the stream rich in hydrogen fluoride from the second fraction zone prior to condensation of the stream comprising propane, a minor amount of hydrogen fluoride and organic fluoride.

In accordance with the present invention, at least one paraffinic hydrocarbon, preferably a branched chain paraffinic hydrocarbon such as isobutane, is contacted with at least one olefinic hydrocarbon higher boiling than ethylene, including straight chain, branched and mixtures thereof, in an alkylation zone under alkylation conditions with hydrogen fluoride catalyst, preferably in combination with at least one catalyst activator selected from the group consisting of primary alkyl fluorides, preferably such alkyl fluorides having from 1 to 8 carbon atoms, more preferably ethyl fluoride, said alkyl fluorides being present in an amount in the range of from about 5 to about 30 weight percent, based upon the weight of combined hydrogen fluoride catalyst and catalyst activator.

The crude liquid reaction product comprising crude alkylate and hydrogen fluoride catalyst is passed to a phase separation zone from which the liquid crude alkylate product is separated from a major portion of the liquid hydrogen fluoride catalyst.

The crude alkylate stream, comprising alkylate, propane, alkyl fluoride, unreacted hydrocarbons, and a minor amount of hydrogen fluoride, from the phase separation zone is passed to a fractionator from which the alkylate is recovered as a bottoms kettle product and from which a propane stream comprising propane, alkyl fluoride and hydrogen fluoride is taken overhead.

The propane-containing overhead vapor stream from the alkylate fractionation zone is condensed and passed through a suitable mixing device, e.g., a static mixer, to an accumulator-phase separation zone where the stream is separated into a liquid hydrocarbon phase comprising propane and alkyl fluorides and a liquid acid phase comprising hydrogen fluoride and alkyl fluorides.

From the phase separation zone, the hydrocarbon phase is passed to an extraction zone. A portion of the hydrocarbon phase can be recycled as reflux to the primary alkylate fractionation zone. The acid phase from the phase separation zone is passed, at least in part, to a fractionation zone from which is taken an overhead stream comprising hydrogen fluoride and alkyl fluorides suitable for recycle to the primary alkylation zone as make-up catalyst, and a bottoms kettle product consisting essentially of hydrogen fluoride. If desired, a portion of the acid phase from the phase separation zone can be directly recycled to the primary alkylation zone to satisfy part of the catalyst requirements. At least a portion of the hydrogen fluoride bottoms stream from the acid phase fraactionation zone is combined with the propane-containing overhead vapor stream from the primary alkylate fractionation zone prior to condensing the stream in the manner heretofore mentioned. The combining of the essentially pure hydrogen fluoride stream with the propane-containing vapor stream from the alkylate fractionation zone enhances the subsequent separation of propane from the other components of the stream, thereby contributing to high purity propane yield, suitable as LPG product.

A portion of the essentially pure hydrogen fluoride kettle product from the acid fractionation zone is passed to the previously mentioned extraction zone, wherein the hydrocarbon phase from the phase separation zone, less the amount of such phase which is recycled as reflux to the alkylate fractionation zone, is contacted with the essentially pure hydrogen fluoride to further enhance the separation of propane from the other components of the hydrocarbon phase, in particular, from alkyl fluoride dissolved in such hydrocarbons.

The propane-rich raffinate phase from the extraction zone is passed to a stripping zone wherein propane is recovered as a kettle product substantially free of hydrogen fluoride and alkyl fluorides. From the stripping zone is also taken a stream comprising hydrogen fluoride and propane which is subsequently combined with a propane-containing stream from the alkylate fractionation zone, prior to condensation of said stream as earlier mentioned.

The alkyl fluoride-enriched extract from the extraction zone is subsequently combined with the acid phase stream from the previously discussed phase separator, wherein the propane-containing stream from the alkylate fractionation zone was separated into its individual hydrocarbon and acid phase components.

The drawing is a schematic flow diagram illustrating the concepts of the invention as applied to the treatment of hydrocarbons containing primary alkyl fluorides resulting from an alkylation process effected in the presence of hydrogen fluoride.

Referring to the drawing in greater detail, an isoparaffinic feedstock and an olefinic feedstock higher boiling than ethylene are introduced through lines **1** and **2**, respectively, into alkylation zone **51**, wherein the charge stock is contacted with liquid hydrogen fluoride catalyst, which is introduced into alkylation reaction zone **51** through lines **3** and **6**. Preferably, there is also present as a catalyst activator at least one primary alkyl fluoride, which can be introduced into the alkylation zone through lines **3** and **6**. Preferably, the catalyst activator is initially introduced into the alkylation zone in admixture with the paraffinic feedstock through line **1** with a portion of the activator requirements being provided, after startup, by recycle from alkylation fractionation zone via lines **10** and **1**.

The alkylation reaction product is drawn off through line **4** and passed to settling-phase separation zone **52**, wherein the alkylation reaction product is separated into a liquid catalyst phase comprising hydrogen fluoride and primary alkyl fluoride and a liquid hydrocarbon phase comprising crude alkylate product, propane, unreacted hydrocarbons, and minor amounts of hydrogen fluoride and primary alkyl fluoride. The acid phase is withdrawn from zone **52** through line **5** and passed in part to catalyst recovery or rerun section, not shown, with a major portion of the acid phase being recycled through line **6** to the primary alkylation reaction zone **51**.

The hydrocarbon phase comprising crude alkylate product is drawn off from phase separation zone **52** and passed through line **7** to alkylate fractionation zone **53**. Liquid alkylate product is removed through line **8**, with

n-butane vapor being taken off through line **9.** Unreacted isoparaffinic feedstock, which can contain some alkyl fluoride, is recycled through line **10** to alkylation reaction zone **51.** A vapor stream containing propane and minor amounts of hydrogen fluoride and alkyl fluoride is taken overhead and passed through line **11** through condenser **12** and mixer **13** to accumulator-phase separation zone **54.**

The condensed propane-containing stream **11** from alkylate fractionation zone **53** is separated in accumulator-phase separation zone **54** into a liquid acid phase comprising hydrogen fluoride and primary alkyl fluoride and a liquid hydrocarbon phase comprising propane, HF, and primary alkyl fluoride.

The acid phase is withdrawn from zone **54** and passed through lines **14, 15** and **16** to acid phase fractionation zone **55.** If desired, at least a part of the acid phase from zone **54** can be recycled through line **17** as catalyst make-up to primary alkylation reaction zone **51.** Essentially pure hydrogen fluoride is recovered as a liquid bottoms product and combined through line **21** with vapor stream **11** from primary alkylate fractionation zone **53,** prior to condensation of stream **11** in condenser **12.** A portion of the hydrogen fluoride stream from zone **55** can be passed through cooler **23** and line **24** to extraction zone **56.** A mixed stream suitable for catalyst make-up containing hydrogen fluoride and primary alkyl fluoride is recovered from fractionation zone **55** and can be recycled through line **22** to primary alkylation reaction zone **51.**

The hydrocarbon phase from accumulator zone **54** is passed through line **18** and line **20** to extraction zone **56** where it is contacted in counter-current fashion with liquid hydrogen fluoride **24** from fractionation zone **55.** Extract from extraction zone **56** is combined through line **25** with the acid phase from accumulator zone **54.** The propane-rich raffinate from zone **56** is passed through line **26** to stripping zone **57,** wherein the raffinate is separated into a liquid bottoms product **27** consisting essentially of propane, and an overhead stream comprising hydrogen fluoride and propane. The overhead stream comprising hydrogen fluoride and propane is passed through line **28** and combined with vapor stream **11** from alkylate fractionation zone **53** prior to condensing stream **11** in condenser **12.** A portion of hydrocarbon liquid phase from **54** is charged via line **19** as reflux in fractionator **53.**

The following example is illustrative of the present invention.

EXAMPLE

As an example of the present invention, a mixed olefin feed stream comprising propylene and butylenes is reacted with isobutane in the presence of hydrogen fluoride catalyst and ethyl fluoride catalyst activator. The reaction is conducted under conditions such as to insure liquid phase operation. The hydrogen fluoride catalyst is added to the reaction vessel and contacted with the olefins and isoparaffin hydrocarbon, with ethyl fluoride being introduced in admixture with the isoparaffin feed stream. Nozzles located in the lower portion of the catalyst phase are used to charge the hydrocarbon phase to insure intimate contact between the hydrocarbon and catalyst liquid phases. The amount of ethyl fluoride catalyst activator is maintained at a level to insure a two-phase (hydrocarbon-acid) liquid system. The hydrocarbon phase from the alkylation reaction zone is fractionated to obtain debutanized alkylate product and a propane-containing vapor stream which is subsequently treated to produce LPG-quality propane. The results are reported in the following table:

Typical Operation

I. Conditions:	
HF Reaction Zone (51):	
Temperature, °F.	90
Pressure, psig	to maintain liquid phase
Fractionation Zone (53):	
Top Temperature, °F.	130
Bottom Temperature, °F.	425
Pressure, psig	300
Accumulator (54):	
Temperature, °F.	110
Pressure, psig	290
Fractionator (55):	
Top Temperature, °F.	150
Bottom Temperature, °F.	206
Pressure, psig	135
Extraction Zone (56):	
Temperature, °F.	136
Pressure, psig	285
HF Stripper (57):	
Top Temperature, °F.	130
Bottom Temperature, °F.	145
Pressure, psig	315

Mixer **13** is an in-line static mixer, known in the art. This can even be a pipe with baffles or the like.

II. Flow Rates:	
HF Reactor:	
Olefin Feed (2), B/D	2,800
Propylene, vol. %	18.4
Propane, vol. %	12.6
Butylenes, vol. %	20.9
Isobutane, vol. %	28.4
Normal Butane, vol. %	19.7
Isobutane (Feed & Recycle)(1, 10, 17),B/D	18,747
Ethyl Fluoride, vol. %	2.6
Propane, vol. %	6.9
Isobutane, vol. %	72.8
Normal Butane and heavies, vol. %	17.7
HF/Hydrocarbon vol. ratio	4:1
iC_4/olefin vol. ratio	13:1
Fractionator (53) Feed (7), B/D	21,398
Mixer (13):	
Feed (11, 28), B/D (100 wt. % vapor)	16,052
Propane, vol. %	87.0
Isobutane, vol. %	0.8
HF, vol. %	4.4
C_2H_5F, vol. %	7.8
Temperature, °F.	130
Feed (21), B/D	380
HF Catalyst, vol. %	98
C_2H_5F, vol. %	NIL
Temperature, °F.	206
Extractor (56):	
Feed (20), B/D	676
Propane, vol. %	90.0
Isobutane, vol. %	0.8
C_2H_5F, vol. %	6.2
HF, vol. %	3.0
HF Feed (24), B/D	315
HF, wt. %	98.0
Other, wt. %	2.0
Hydrocarbon (26), B/D	580
Propane, vol. %	97.0
Isobutane, vol. %	1.0
Organic Fluorides, PPM by wt.	(50)
HF, vol. %	2.0
HF-C_2H_5F Recycle (22), B/D	548
Propane, vol. %	47.8
C_2H_5F, vol. %	41.6
HF, vol. %	4.6
Propane Product (27), B/D	448
Propane, vol. %	99
Isobutane, vol. %	1
Organic Fluorides, PPM by wt.	(40)

-Continued

II. Flow Rates:	
HF Reactor:	
Acid to Reactor (Extractor Bypass)(17), B/D	336
Propane, vol. %	21.1
C_2H_5F, vol. %	20.8
HF, vol. %	58.1

Zones **51, 52, 53, 54, 56** and **57** are conventional zones well known in the field of hydrogen fluoride alkylation. The conditions at which these zones are or can be operated are well known to those skilled in the art; these parameters will not be discussed in detail herein. The paraffinic and olefinic feedstocks suitable for use in the practice of this invention are well known to those skilled in the art and will not be further discussed herein.

Acid phase fractionation zone **55** is a conventional fractionation zone analogous to alkylation fractionation zone **53.** Representative operating conditions are as shown in the Example. The exact operating conditions for any given charge to acid phase fractionation zone **55** is a function of the composition of streams **14, 15** and **16.** Fractionation zone **55** is to be operated at conditions such as to provide a product stream consisting essentially of hydrogen fluoride. To insure this end, it is desirable to operate the zone in such a manner that a portion of the hydrogen fluoride feed to the zone is taken off with the organic fluoride, e.g., alkyl fluoride such as ethyl fluoride. In addition to separating substantially all of the organic fluoride from the hydrogen fluoride product stream, this procedure also provides a product stream comprising hydrogen fluoride and primary alkyl fluoride which can be recycled as catalyst make-up to the alkylation reaction zone. The adjustment of the operating conditions of the zone in response to the feed composition is well known in the art.

Reasonable variations and modifications are possible within the scope of this disclosure without departing from the spirit and scope thereof.

I claim:

1. A process for the alkylation of hydrocarbons in the presence of hydrogen fluoride catalyst and a catalyst activator selected from the group consisting of primary alkyl fluorides having from 1 to 8 carbon atoms wherein said catalyst activator is present in an amount ranging from about 5 to about 30 weight percent, based on weight of catalyst and catalyst activator, comprising:

a. contacting in an alkylation reaction zone under alkylation conditions at least one paraffinic hydrocarbon and at least one olefinic hydrocarbon with said catalyst and said catalyst activator to obtain a reaction product comprising alkylate, propane, alkyl fluoride, unreacted hydrocarbons and hydrogen fluoride;

b. passing said reaction product to a phase separation zone and separating therefrom a hydrocarbon phase comprising alkylate, propane, alkyl fluoride, unreacted hydrocarbons and a minor amount of hydrogen fluoride;

c. passing said hydrocarbon phase to a first fractionation zone and withdrawing therefrom a liquid stream comprising alkylate product and a vapor stream comprising propane, alkyl fluoride and hydrogen fluoride;

d. condensing said vapor stream and passing said condensed stream to a separation zone wherein said condensed stream is separated into a liquid hydrocarbon phase comprising propane and alkyl fluoride and a liquid acid phase comprising hydrogen fluoride and alkyl fluoride;

e. passing at least a portion of said liquid hydrocarbon phase to an extraction zone;

f. passing at least a portion of said liquid acid phase to a second fractionation zone and separating therefrom a light stream comprising hydrogen fluoride and alkyl fluoride and a liquid stream consisting essentially of hydrogen fluoride;

g. combining a first portion of said liquid stream from step (f) with said vapor stream from step (c) prior to condensing said vapor stream in step (d);

h. passing a second portion of said liquid stream from step (f) to said extraction zone;

i. extraction in countercurrent fashion in said extraction zone said liquid hydrocarbon phase from step (d) with the liquid hydrogen fluoride from step (f) thereby separating said propane from said alkyl fluoride;

j. withdrawing from said extraction zone a raffinate comprising propane and hydrogen fluoride;

k. separately recovering from said raffinate a hydrocarbon stream consisting essentially of propane;

l. recovering from said raffinate an overhead stream comprising propane and hydrogen fluoride; and

m. combining said overhead stream with said vapor from step (c) prior to condensing said vapor in step (d).

2. The process of claim **1** wherein a further portion of said liquid hydrocarbon phase from step (d) is passed as reflux to said first fractionation zone.

3. The process of claim **1** wherein at least a portion of said light stream is passed to said alkylation reaction zone.

4. The process of claim **1** wherein said catalyst activator is ethyl fluoride.

5. The process of claim **4** wherein said paraffinic hydrocarbon is isobutane and said olefinic hydrocarbon comprises propylene and butylene.

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