Sept. 28, 1965 R. D. BAUER ETAL 3,209,051

ALKYLATION OF HYDROCARBONS BY REDUCING ORGANIC FLUORIDE CONTENT OF A STREAM IN THE OPERATION

Filed April 17, 1962

2 Sheets-Sheet 1

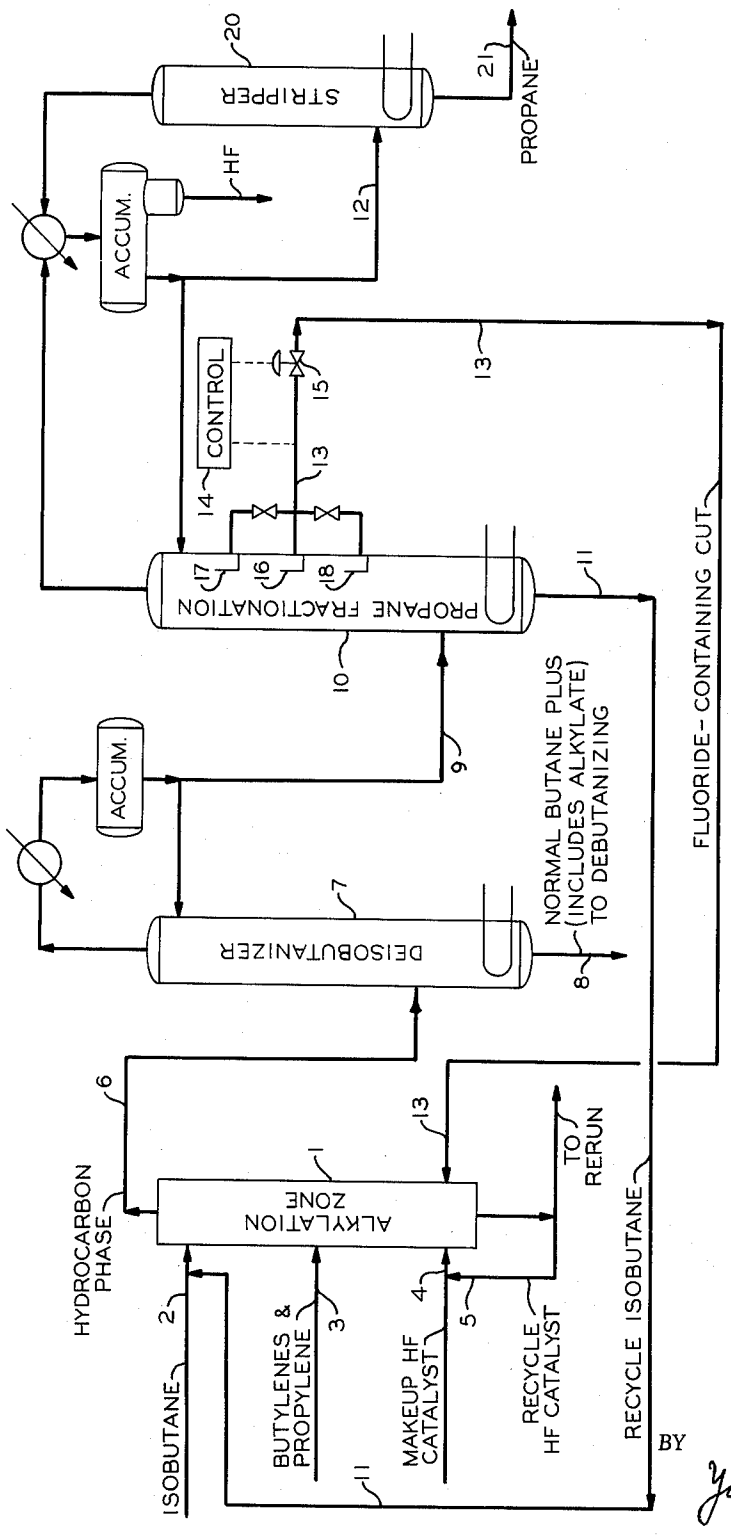


FIG. 1

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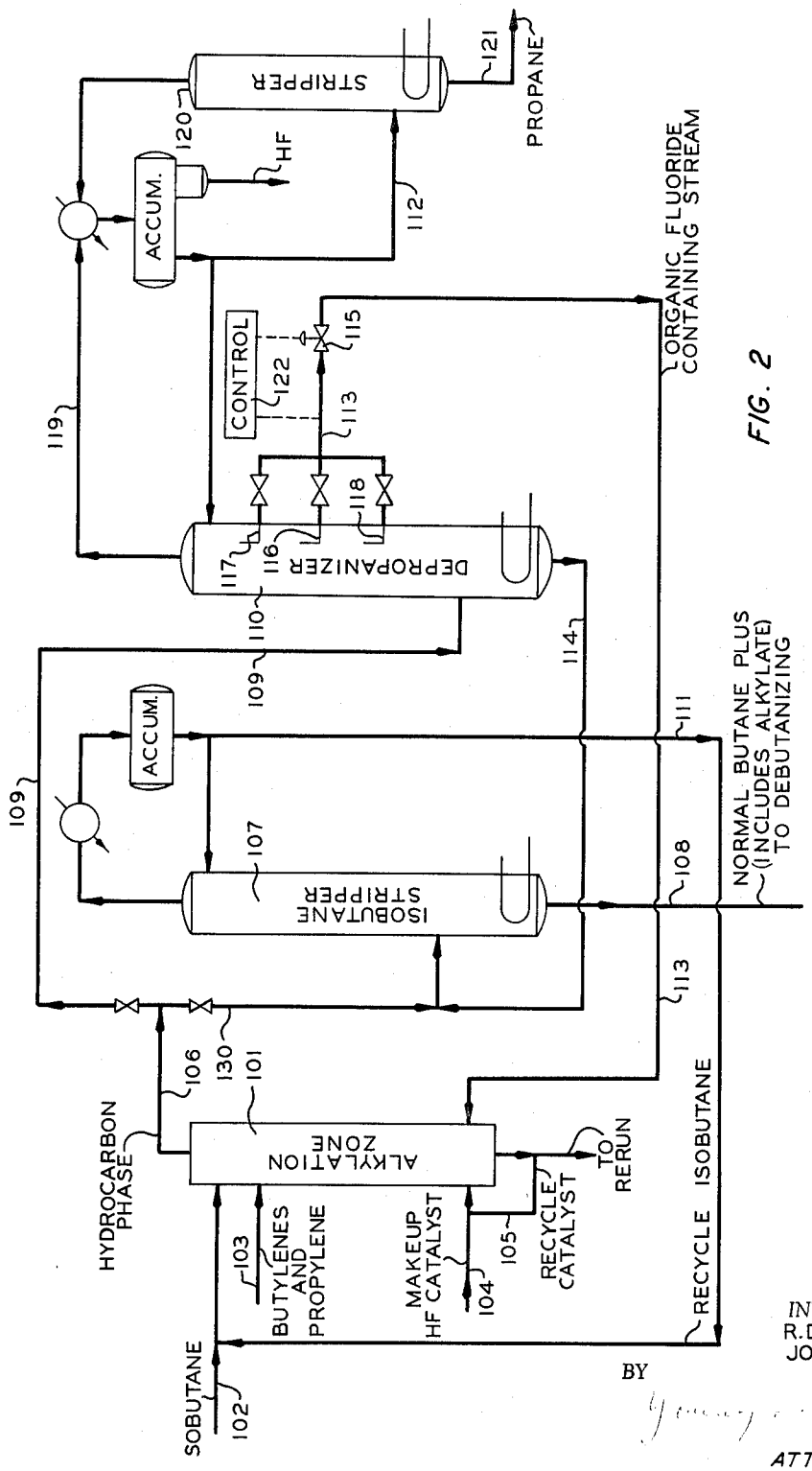


FIG. 2

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ALKYLATION OF HYDROCARBONS BY REDUCING ORGANIC FLUORIDE CONTENT OF A STREAM IN THE OPERATION

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8 Claims. (Cl. 260—683.42)

This invention relates to alkylation of hydrocarbons. In one of its aspects, it relates to the reduction of organic fluorides in a stream in the operation by removing the organic fluorides at a place at which these have been found to tend to concentrate. In another aspect of the invention, the organic fluorides which have been recovered, as stated, can be returned to the alkylation operation, for example, to the alkylation reactor or settler for further reaction according to methods now known or described in copending application of W. E. Plaster, Serial No. 182,847, filed March 27, 1962.

The alkylation of hydrocarbons, for example, the alkylation of an isoparaffin such as isobutane, with an alkylating agent such as propylene and/or butylenes is known. It is also known to alkylate aromatics with olefins and with olefin-forming materials.

In the recovery of the products resulting from an alkylation in which propane is produced, as in the alkylation of isobutane with butylenes and/or propylenes in the presence of hydrofluoric acid as catalyst, there is practiced a removal of propane which otherwise tends to build up in the operation. Thus, there is fed in such an operation a stream containing propane, isobutane and hydrofluoric acid to a propane fractionator, the overhead from which is propane and HF and the bottoms from which is isobutane. Heretofore, the alkyl fluorides contained in the feed fed to the propane fractionator have been distributed in at least one product removed therefrom. It has now been found that these alkyl fluorides tend to concentrate in the fractionator reaching a maximum concentration at a point intermediate the removal of bottoms and the taking off of overhead. Based upon this concept, there is the additional concept to remove alkyl fluorides from the propane fractionator at a point of maximum fluoride concentration. Thus, a side cut rich in fluorides is obtained and this can be recycled to the contactors for alkylation or elsewhere to recover the "alkylatable" fluorides, i.e., the fluorides which will act as alkylating agents. The fluorides can otherwise be removed as may be desired.

It is an object of this invention to provide an improved alkylation operation. It is a further object of this invention to reduce the fluoride content of certain streams obtained in the recovery of effluents from an alkylation operation. It is a further object of this invention to substantially reduce or eliminate after treatment of certain streams resulting from a hydrofluoric acid alkylation operation, for example, to reduce the size or need for so-called "bauxite" defluorinators. It is a further object of the invention to reduce the fluoride content of the ultimate hydrocarbon or gasoline product which are produced by alkylation.

Other aspects, objects and the several advantages of this invention are apparent from a study of this disclosure, the drawing and the appended claims.

According to the present invention, alkyl fluorides, or other fluorides, are removed from a point in the operation at which these tend to produce a maximum concentration. For example, in the alkylation of an isoparaffin with an olefin wherein propane is formed, it is found, according to the invention, that the alkyl fluorides tend to concentrate at a point intermediate the propane overhead removal and the isobutane bottoms of a propane fractionator.

FIGURE 1 is a schematic diagram of an alkylation process wherein, in the fractionation section, the depropanizing has the side draw removal. The depropanizer has charged thereto the overhead product from the deisobutanizing zone.

FIGURE 2 is a schematic diagram of an alkylation process wherein the depropanizer has the side draw, and a portion of the reactor effluent is the feed to the depropanizer.

Referring now to the drawing, in FIGURE 1, there are passed to an alkylation zone **1** by way of **2**, **3**, and **4**, respectively, isobutane, a mixture of butylenes and propylene, and hydrogen fluoride. Upon alkylation, the admixture is allowed to settle, forming a lower acid phase which is returned by way of **5** and a hydrocarbon phase which is passed by **6** into alkylate fractionator **7**. In fractionator **7**, there is performed a separation of alkylate removed at **8**, obtaining overhead a stream containing in addition to some fixed gases propane, isobutane and hydrogen fluoride. The overhead passes by **9** into propane fractionator **10** from which an isobutane bottoms **11** is obtained. This isobutane is recycled to alkylator **1** by way of **2**. Propane overhead is taken off at **12**, together with some HF, and sent to the HF stripper **20** for recovery of propane **21**. HF which is recovered is returned for further use in the operation. Propane is flared, recovered as L.P.G., or otherwise disposed of. According to the invention, there is taken a fluoride-rich side cut **13** which, in this instance, is controlled as to flow by controller **14** and control valve **15**. The control is so effected as to maintain in tray **16** a high concentration of fluorides. The removed fluorides, as indicated, are returned to the alkylation reactor or to the settler or can be disposed of in fuel gas or any other suitable processing step. In this embodiment, the fluorides are returned to the alkylation operation.

According to the invention, by providing a plurality of trays as indicated at **17** and **18**, it is possible either during the operation or by prior calculation based upon data to determine just where will be the concentration of fluoride such that it should be removed from the tower according to the invention. If, for any reason, a change of position occurs, the plurality of trays **16**, **17** and **18** can be operated to yield the fluoride stream which is desired to be removed. One skilled in the art in possession of this disclosure, having studied the same, will understand how these trays can be operated to remove fluorides while removing the least amount of undesired propane. Any isobutane which is removed with the fluoride stream is helpful in conducting this fluoride stream back to the alkylation or otherwise disposing of the same. Obviously, since it is not desired to waste isobutane, at the very least the invention improves the operation by the recovery of the isobutane while at the same time reducing the need for extensive treatment of the propane stream to recover fluorides therefrom. By practicing the reduction of fluorides, in general, there is obtained a reduction of fluoride content in the various streams in which fluoride normally builds up and, to this extent, the alkylate is found to be low in fluoride content with consequent possibility of reduction or elimination of the after-treaters, for example, the bauxite defluorinators.

Referring now to FIGURE 2 (to which the example is directed), there are passed to an alkylation zone **101** by way of **102**, **103**, and **104**, respectively, isobutane, a mixture of butylenes and propylene, and hydrogen fluoride. Upon alkylation, the mixture is allowed to settle, forming a lower acid phase which is returned by way of **105** and a hydrocarbon phase of which a portion is passed by way of conduit **106** and conduit **130** into isobutane stripper **107**. The bottoms product **108** from stripper comprises normal butane and heavier (including alkylate), and the overhead from **107** is passed by way of

conduit **111** as recycled isobutane to the alkylation reaction zone **101**. Another portion of the hydrocarbon phase is passed from alkylation zone **101** by way of conduit **106** and conduit **109** as feed for depropanizer **110**. Bottoms from tower **110** is passed by way of conduit **114** and also charged to isobutane stripper **107**. The overhead yield from depropanizer **110** is charged by way of conduit **119** and conduit **112** to the propane stripper **120**. Propane, substantially free of organic fluorides is recovered by way of conduit **121**. HF which is recovered is recycled to the alkylation zone. According to the invention, there is removed an organic fluoride (isopropyl fluoride) -rich side stream **113** which, in this instance is controlled by controller **122** and valve **115**. The control is effected so as to maintain in tray **116** a high concentration of organic fluorides whose rate of removal substantially eliminates organic fluorides from the overhead stream **119**. The removed fluorides are returned to alkylation, as illustrated, or to any other suitable usage.

According to the invention, a plurality of side draws from trays **116**, **117**, and **118** are available for use, and the selection of the proper tray where fluoride concentration is the highest is made.

SPECIFIC EXAMPLE

Operation of propane column (**110**):

Feed temperature, ° F	150
Top temperature, ° F	130
Sidedraw tray temperature, ° F	142
Bottom temperature, ° F	220
Reflux temperature, ° F	85
Reflux feed volume ratio,	0.744
Pressure, p.s.i.a	285

STREAM FLOWS, MOLS/HOUR

Stream component	Feed (109)	Bottoms (114)	Side draw (113)	Overhead (Less reflux) (131)
Hydrogen fluoride	92.2		0.9	91.3
Propane	346.7	17.3	174.0	155.4
Isopropyl fluoride	(0.09660)	(0.04289)	(0.05371)	Nil
Isobutane	2,473.5	2,438.5	35.0	Trace
Normal butane	359.1	358.7	0.4	Trace
Isopentane	51.5	51.5	Trace	Trace
Light alkylate	151.1	151.1	Trace	Trace
Heavy alkylate	4.6	4.6	Trace	Trace
Total	3,478.7	3,021.7	210.3	246.7

Tower **110** is a 50-tray tower of 76 percent efficiency. The side draw is on the forty-third tray from the bottom. The depropanizer overhead is substantially free of isopropyl fluoride.

DEPROPANIZER COLUMN (110)

Tray number (From bottom)	Mol fraction iC_3F in liquid (Concentration gradient)
0	0.000015
4	0.000026
8	0.000036
12	0.000040
16	0.000044
20	0.000043
24	0.000042
28	0.000040
32	0.000065
36	0.000113
40	0.000200
42	0.000240
43	0.000255
44	*0.000260
45	0.000252
47	0.000240
50	0.000183

*The maximum isopropyl fluoride content is on the forty-fourth tray.

Conventional operation, same tower operating conditions

STREAM FLOWS, MOLS/HOUR

Stream component	Feed (109)	Bottoms (114)	Side draw (Not used)	Overhead (Less reflux) (131)
Hydrogen fluoride	92.2			92.2
Propane	346.7	17.3		329.4
Isopropyl fluoride	(0.09660)	(0.04289)		(0.05376)
Isobutane	2,473.5	2,469.3		4.2
Normal butane	359.1	359.1		Trace
Isopentane	51.5	51.5		Trace
Light alkylate	151.1	151.1		Trace
Heavy alkylate	4.6	4.6		Trace
Total	3,478.7	3,052.9		425.8

It has been estimated that with the use of this invention there is a savings of approximately $70.00 per day on a 2,000 barrel per day throughput in an alkylation unit in which isobutane is alkylated with isobutylene employing hydrofluoric acid as a catalyst. Upon improvement of the separation of the organic fluorides, according to the invention, it appears that eventual complete elimination of bauxite defluorinators might well be obtained. In any event, a great reduction in their use is permitted by practice of the invention. The invention is of particular interest at this time since it now appears that the Natural Gasoline Association of America will probably set requirements or specifications for alkylate to contain less than 50 parts per million of fluorides.

It will be noted that the concept to take advantage of the fact that fluorides will concentrate in the depropanizer appears new in the art. Indeed, the discovery that these fluorides will concentrate so that they can be removed as a side cut from a depropanizer appears to be novel in the art.

It will be evident to one skilled in the art having studied this disclosure, the drawing and the appended claims that there has been set forth a method for alkylating an alkylatable compound with an alkylating compound in the presence of hydrofluoric acid wherein organic fluorides are formed and tend to concentrate in the system which comprises passing a stream containing said fluorides to a fractionation operation, therein concentrating the fluorides, and removing the fluorides from said fractionation operation.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawing and the appended claims to the invention the essence of which is that a fluoride-rich side stream is removed from a product stream fractionator, such as a propane fractionator, in the conventional alkylation operation.

We claim:

1. In a method of alkylating in an alkylation reaction zone an isoparaffin with an olefin to produce an alkylate, wherein propane is formed, and wherein hydrofluoric acid is used as a catalyst, the steps which comprise in a first zone fractionating the alkylate produced to obtain a first alkylate stream and a second stream comprising propane, isobutane, hydrofluoric acid and alkyl fluorides, in a second zone fractionating said second stream to obtain overhead comprising propane and hydrofluoric acid vapors and a bottoms product comprising isobutane, in said second zone at an intermediate locus thereof concentrating alkyl fluorides, removing from said second zone and from said locus a side fraction containing said organic fluorides which have concentrated therein, and passing said side fraction to said alkylation reaction zone.

2. In a method of alkylating in an alkylation reaction zone an isoparaffin with an olefin to produce an alkylate, wherein propane is formed, and wherein hydrofluoric acid is used as a catalyst, the steps which comprise passing an alkylation reaction mass which is obtained to a settling zone, in said settling zone allowing the reaction mass to

settle into at least two phases, an acid phase and a hydrocarbon phase, in a first zone fractionating the hydrocarbon phase produced to obtain a first alkylate stream and a second stream containing propane, isobutane, hydrofluoric acid and alkyl fluorides, in a second zone fractionating said second stream to obtain overhead comprising propane and HF and a bottoms product comprising isobutane, in said second zone at an intermediate locus thereof concentrating alkyl fluorides, removing from said second zone at said locus a side fraction containing said organic fluorides which are concentrated therein and passing said side fraction into said settling zone.

3. An improved method for alkylating an isoparaffin and an olefin employing HF acid catalyst which comprises contacting said isoparaffin and said olefin in presence of said acid in an alkylation reaction zone forming an alkylation reaction zone effluent, separating an acid phase from said effluent, then fractionating said effluent to separate an alkylate product containing fraction and a second fraction containing unreacted isoparaffin, paraffin, alkyl fluorides and HF, fractionating said second fraction to recover therefrom, as separate fractions, unreacted isoparaffin, paraffin and HF, and an alkyl fluorides concentrate, and returning said concentrate to the alkylation reaction.

4. An operation according to claim 3 wherein the isoparaffin is isobutane and the olefin is at least one olefin selected from the group consisting of butylenes and propylene.

5. An improved method for alkylating isoparaffin and an olefin employing HF acid catalyst which comprises contacting said isoparaffin and said olefin in the presence of said acid in an alkylation reaction zone forming an alkylation reaction zone effluent, in a settling zone separating an acid phase from said effluent, then fractionating said effluent to separate an alkylate product containing fraction and a second fraction containing unreacted isoparaffin, paraffin, alkyl fluorides and HF, fractionating said second fraction to recover therefrom as separate fractions unreacted isoparaffin, paraffin and HF and an alkyl fluorides concentrate, and returning said concentrate to said settling zone.

6. An operation according to claim 5 wherein the isoparaffin is isobutane and the olefin is at least one olefin selected from the group consisting of butylenes and propylene.

7. An improved method for alkylating an isoparaffin and an olefin employing HF acid catalyst which comprises contacting said isoparaffin and said olefin in the presence of said acid in an alkylation reaction zone forming an alkylation reaction zone effluent containing low boiling paraffin, separating an acid phase from said effluent, in a first fractionation zone fractionating a portion of said effluent to remove therefrom an alkylate product containing fraction, in a second fractionation zone fractionating another portion of said effluent to separate therefrom a first fraction containing alkylate product and unreacted isoparaffin, a second fraction containing low boiling paraffin and HF, and a third fraction containing alkyl fluorides concentrated therein, which is obtained intermediate said first and second fractions, and returning said alkyl fluorides to the alkylation operation for further reaction therein.

8. A method according to claim 7 wherein said first fraction containing alkylate product and unreacted isoparaffin is passed to said first fractionation zone.

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