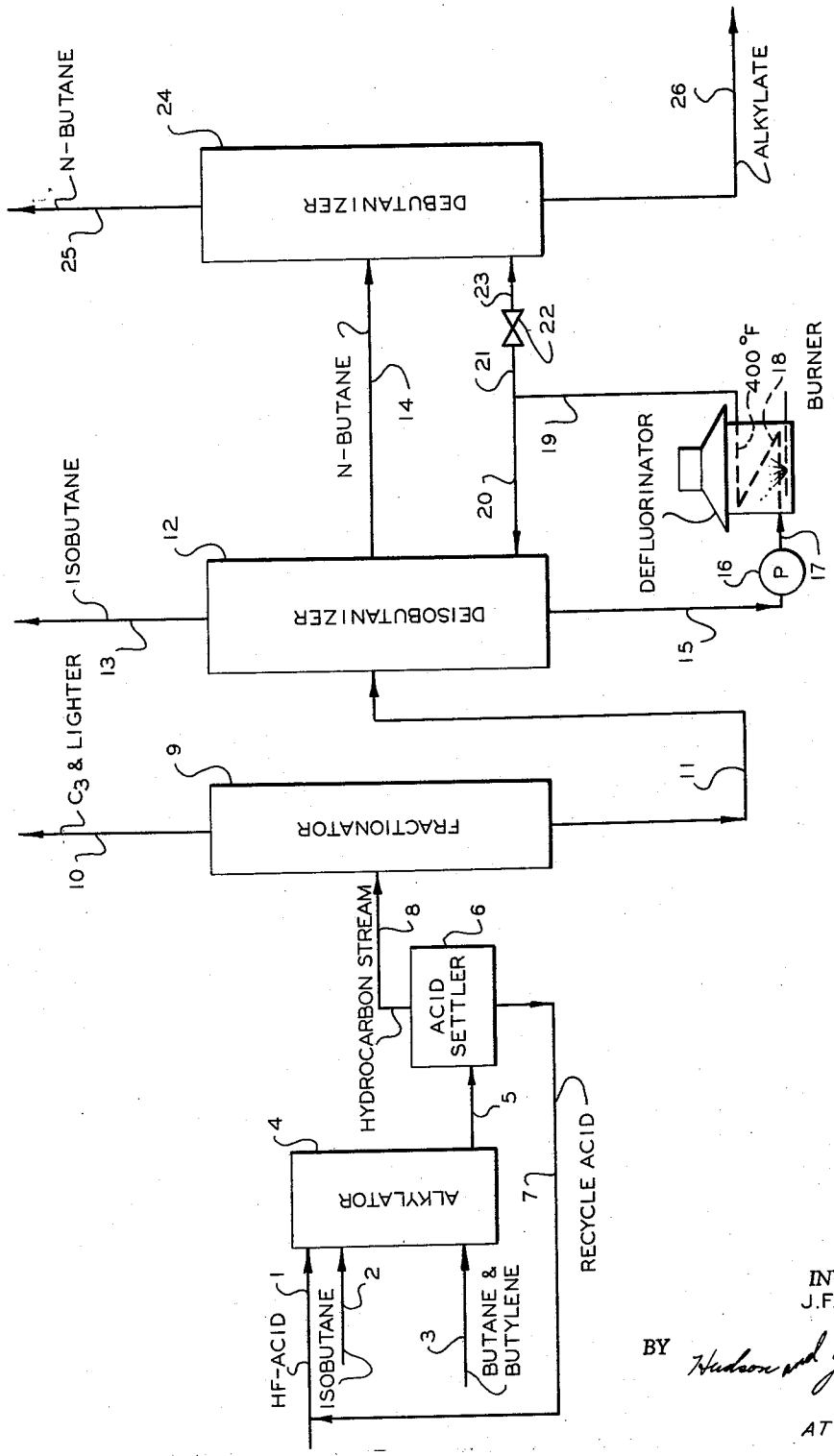
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ALKYLATION PROCESS

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ALKYLATION PROCESS

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This invention relates to alkylation. In one of its aspects, this invention relates to a process for the alkylation of hydrocarbons in which deisoparaffinizer bottoms are reboiled under conditions to cause defluorination of the same while at the same time there is removed from the deisoparaffinizer a normal paraffin stream.

It is well known that reboiling the deisobutanizer bottoms in an HF alkylation process will substantially defluorinate the alkylate provided sufficient time of heating is given. The residence time required at 400° F. is such that the ratio of feed to the reboiler to the net bottoms product is in the neighborhood of approximately 8:1. Such a ratio cannot be achieved at the temperature required for defluorination when there is a high concentration of normal butane in the kettle product since this normal butane concentration interferes with proper heat balance and equilibrium vaporization which are required for satisfactory operation of the column.

Also, is has been found to be desirable to operate at as high a temperature as possible for maximum defluorination, the upper limit being determined by the color of the alkylate product (about 500° F. maximum). With this temperature limitation, it has been found that between 6 to 8, even to 10, volumes of bottoms must be circulated through the bottoms furnace for each volume of bottoms yield to effect sufficient contact time for desired defluorination. These conditions, however, provide too much reboiler duty, i.e., heat input (B.t.u.'s) for optimum tower operation at the desired tower operating temperature. This condition is governed to a large extent by the quantity of normal butane in the alkylate; i.e., as the normal butane content of the bottoms increases, the bubble point of the tower bottoms decreases, and the amount of vaporization in the reboiler furnace effluent increases.

It has now been conceived that in an HF alkylation of an isoparaffin with an olefin, for example, in the alkylation of isobutane with a butane-butylene stream in the presence of hydrofluoric acid, the deisobutanizer bottoms should be circulated through a heating zone back to the deisobutanizer while at the same time removing from the deisobutanizer a side stream containing normal butane. The normal butane can be removed from the operation or it can be passed to a debutanizer or otherwise treated as desired. One use for the normal butane is to isomerize the same to isobutane for reuse.

It is an object of this invention to provide an improved alkylation process. It is another object of this invention to provide an alkylation process in which improved defluorination of deisoparaffinizer bottoms is practiced. It is a further object of this invention to provide an alkylation process in which improved operation of a deisoparaffinizer, for example, a deisobutanizer, is obtained while at the same time, defluorinating the alkylate produced.

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

According to this invention, there is provided an alkylation of an isoparaffin with an olefin in the presence of hydrofluoric acid resulting in an alkylate-containing effluent which is fractionated, deisobutanized, and defluorinated, which comprises the steps of passing the effluent to a deisoparaffinizer zone, removing normal paraffin from said zone and circulating alkylate-containing fractionated alkylation effluent from said zone to a defluorinating zone maintained at a defluorinating temperature and returning the thus-heated and at least partially defluorinated effluent to said deisoparaffinizer zone.

The invention will now be described with respect to the alkylation of isobutane with a butylene-containing stream in the presence of HF acid. It will be obvious to those skilled in the art in possession of this disclosure that the invention has general applicability to defluorination of streams other than those given in the specific example.

Referring now to the drawing, hydrofluoric acid, isobutane and a butylene-containing stream, also containing some butane, are fed by way of conduits **1**, **2** and **3** into alkylator **4** from which an alkylation effluent is passed by way of conduit **5** to acid settler **6**. Acid from which substantially all desirable hydrocarbon has been separated by settling is passed by way of recycle conduit **7** to conduit **1** for reuse. Supernatant hydrocarbon stream is passed by way of conduit **8** to fractionator **9** from which an overhead of C_3 hydrocarbons and lighter is removed by way of conduit **10**. Bottoms from fractionator **9** are passed by way of conduit **11** to deisobutanizer **12** from which isobutane-containing stream is taken overhead by way of conduit **13**. According to the invention, a normal butane stream is removed from tower **12** by way of conduit **14**. Also, according to the invention, bottoms from the deisobutanizer are withdrawn by way of conduit **15** and pumped by way of pump **16** and conduit **17** into heated coil **18**, which is maintained in this example at approximately 400° F. and from coil **18** by way of pipes **19** and **20** back to the bottom of the deisobutanizer. Production quantities of defluorinated and deisobutanized alkylate are passed by conduit **21**, valve **22** and conduit **23** into debutanizer **24**. Normal butane is taken overhead from debutanizer **24** by way of conduit **25** and debutanized alkylate is sent to storage by way of conduit **26**. Although it is within the scope of this invention to take normal butane from conduit **14** to any desired place of utilization, in this example, it is passed to the debutanizer at a suitable place as will be understood by those skilled in the art of fractionation.

The residence time provided in the defluorinator is accomplished by maintaining the ratio of feed to the defluorinator to the net bottoms product at about 6–8 to 1. Thus, according to the combination of steps which constitute the essence of this invention, sufficient normal butane is taken off as a side stream by way of conduit **14** to permit effective fractionation in deisobutanizer **12** to be effected while at the same time maintaining the above-stated ratios. The stream in conduit **14** consists primarily of normal butane but it may contain some pentane and heavier. In this manner, the kettle product will contain only nominal amounts of butane and the correct residence time in the furnace is obtained. The pentane and heavier from the vapor side draw conduit **14** and kettle product can be recovered in the debutanizer according to practices known to one skilled in the art.

The location of vapor side stream conduit **14** is preferably at a point in the vapor space above the fourth or the fifth tray from the bottom of the column, in a fractionating column employing conventional bubble trays or the like; however, the normal butane containing side stream can be withdrawn from the column at any tray from about the second to about the tenth tray from the bottom.

It will be ovious to one skilled in the art that if one operates without the normal butane side draw-off, there can be encountered a situation wherein normal butane is present in such large amounts that total vaporization occurs at the temperature required for optimum defluorinating. Total vaporization would make it impossible to maintain the residence time required for optimum defluorination and at the same time satisfy the heat bal-

ance requirements of the deisobutanizer column. Total vaporization also increases any tendency of the materials being heated to form coke in the reboiler coils.

The following example includes operating conditions and flow rates for a process according to the drawing.

	Bbls./stream day	P.p.m.
Feed to Deisobutanizer	7,098	
Composition:		
HF	22	
C_3	380	
iC_4	4,405	
C_4	766	
C_5+	1 525	
Organic Fluorides		600
Deisobutanizer Bottoms (alkylate product)	1,534	
Composition:		
iC_4	28	
C_4	68	
C_5+	1,408	
Fluorides		30

N-butane is withdrawn from tray 3 of the deisobutanizer in the amount of 344 BPSD. This stream has the following composition.

iC_4	38
C_4	189
C_5+	117

A circulation rate is maintained through the reboiler of 18,000 BPSD. The material entering the reboiler has an organic fluoride content of 300 p.p.m.

The operating conditions of the deisobutanizer are as follows:

	Temperature, ° F.	Pressure, p.s.i.a.
Top	150	180
Bottom	340	

Reflux to deisobutanizer—6,975 BPSD.

The following conditions prevail in the debutanizer. A 30 tray column with feed entering on fifteenth tray is used.

	Bbls./stream day	P.p.m.
Feed to Debutanizer	1,878	
Composition:		
C_5+	1,525	
C_4	257	
iC_4	96	
Fluorides		30
DEBUTANIZER BOTTOMS		
Composition:		
C_5+	1,525	
C_4	1	
OH PRODUCT		
Composition:		
C_4	256	
iC_4	96	

The operating conditions of the debutanizer are as follows:

	Temperature, ° F.	Pressure, p.s.i.a.
Top	135	85
Bottom	315	

As will be understood by those skilled in the art in possession of this disclosure, the normal butane which is removed through conduit 14 can be partly contained in the feed to the alkylation operation. To the extent normal butane appears in the feed or in the effluent, the invention is operative to remove a sufficient amount of the same to make defluorination possible at optimum fractionation conditions in the deisobutanizer. Thus, it is immaterial from a viewpoint of the invention, as claimed, just what are the feeds so long as there is obtained a hydrocarbon which interferes with the defluorination operation, which in the case of the specific example described, has been normal butane.

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 in the deisobutanizing operation in which an HF-alkylate is deisobutanized, there are practiced defluorination by circulating the bottoms of the deisobutanizer through a heater and returning the same to the deisobutanizer while at the same time removing a sufficient amount of normal butane from the deisobutanizer to obtain proper equilibrium-vaporization conditions suitable for effective fractionation.

I claim:

1. A method for the deisobutanization of an HF-alkylate and its substantially simultaneous defluorination which comprises the steps in combination as follows: feeding an HF-alkylate to a deisobutanizing zone, removing isobutane as overhead from said zone, removing normal butane as a side stream from said zone, removing bottoms from said zone, passing bottoms thus removed into a defluorinating zone heated to a defluorinating temperature, returning thus-heated bottoms to the bottom of said deisobutanizer zone, and withdrawing a portion of the thus-heated bottoms from the deisobutanizer zone as deisobutanized and defluorinated alkylate.

2. A method according to claim 1 wherein the ratio of feed to the defluorinating zone to the net bottoms product from the deisobutanizer zone is in the range of approximately 6–8 to 1.

3. A method for the deisoparaffinization of an HF-alkylate and its substantial simultaneous defluorination which comprises the steps in combination as follows: feeding an HF-alkylate to a deisoparaffinizer zone, removing isoparaffin as overhead from said zone, removing normal paraffin as a side stream from said zone, removing bottoms from said zone, passing bottoms thus removed into a defluorinating zone heated to a defluorinating temperature, returning thus-heated bottoms to the bottom of said deisoparaffinizer zone, and withdrawing a portion of the thus-heated bottoms from the deisoparaffinizer zone as deisoparaffinized and defluorinated alkylate.

4. A method for the deisobutanization of an HF-alkylate and its substantially simultaneous defluorination which comprises the steps, in combination as follows: feeding an HF-alkylate to a deisobutanizing zone, removing isobutane as overhead from said zone, removing normal butane as a side stream from said zone, removing bottoms from said zone, passing bottoms thus removed into a defluorinating zone heated to a defluorinating temperature of about 500° F., returning the thus-heated bottoms to the bottom of said deisobutanizer zone, circulating said bottoms into said defluorination zone at a ratio in the range 6–10:1 of bottoms yielded from said deisobutanizer zone, and withdrawing a portion of the thus-heated bottoms from the deisobutanizer zone as deisobutanized and defluorinated alkylate.

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