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Jones

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[54] **ISOBUTANE FLASHING IN THE ALKYLATION OF C_2–C_5 OLEFIN HYDROCARBONS WITH ISOBUTANE**

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[58] **Field of Search**..... 260/683.45, 683.46, 683.48, 260/683.58, 683.59, 683.61, 683.49

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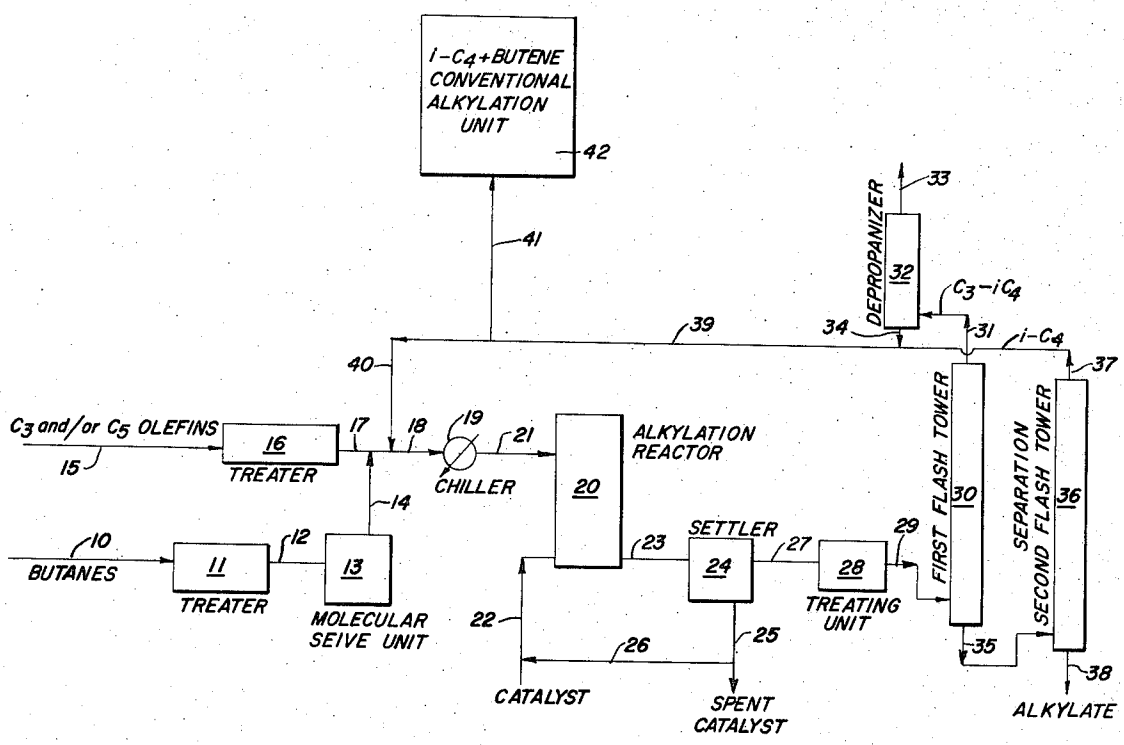
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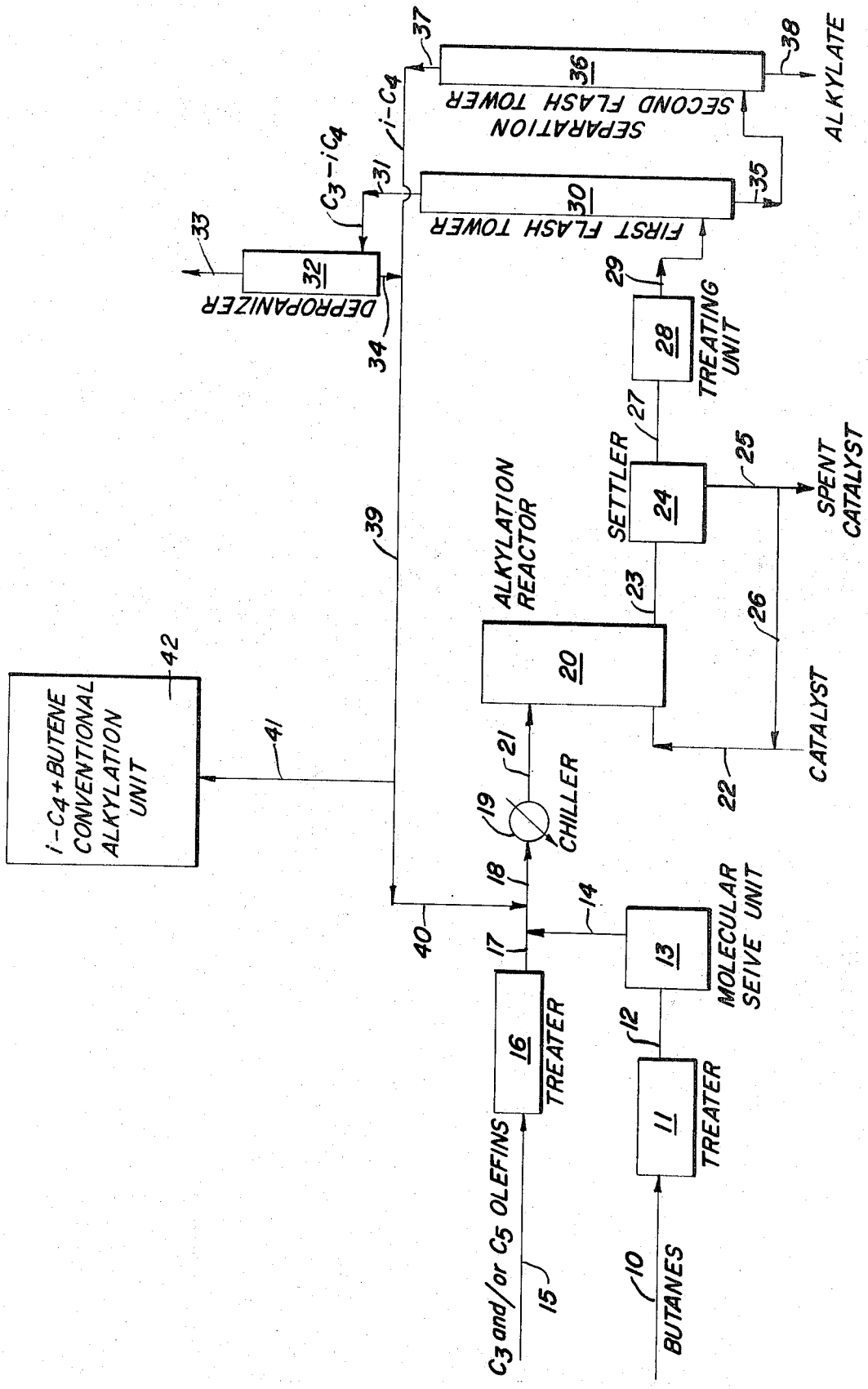
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[57] **ABSTRACT**

In the alkylation of ethylene, propylene, butylenes and amylenes, contained in refinery streams, with isobutane in the presence of acidic catalysts, refinery streams containing such olefins, but which are essentially free from normal butane, and a refinery stream containing isobutane, but which is essentially free from normal butane, are segregated and interacted in an alkylation unit, employing a relatively high ratio of isobutane to olefin to produce alkylate, which is thereafter recovered from unreacted isobutane by low cost flashing or other low cost separation operations, and a portion of the recovered isobutane recycled internally to said alkylation unit; if desired any possible excess isobutane may be used as feed or as supplemental feed to an alkylation unit for the conventional alkylation of isobutane with butylenes.

16 Claims, 1 Drawing Figure




BUTANES
10
MOLECULAR SEIVE UNIT
13
14
TREATER
11
12
TREATER
16
C3 and/or C5 OLEFINS
15
17
18
CHILLER
19
21
ALKYLATION REACTOR
20
22
CATALYST
23
SETTLER
24
25
SPENT CATALYST
26
TREATING UNIT
28
27
29
FIRST FLASH TOWER
30
31
C3-iC4
i-C4
SECOND FLASH TOWER SEPARATION
36
37
38
ALKYLATE
35
DEPROPANIZER
32
33
34
39
40
41
i-C4+BUTENE CONVENTIONAL ALKYLATION UNIT
42

ISOBUTANE FLASHING IN THE ALKYLATION OF C_2-C_5 OLEFIN HYDROCARBONS WITH ISOBUTANE

BACKGROUND OF THE INVENTION

Alkylates are very desirable components for motor fuel blends. Initially, the alkylation processes were used to produce light aviation grade alkylates for blending with isopentane in the manufacture of various grades of military aviation gasolines. Such alkylates were made by the interaction of isobutane and butylene in the C_4 fraction obtained from the catalytic cracking of gas oil. Isobutane from external sources was added if the ratio of isobutane to butylenes were less than 1.2:1. In order to expand the amount of alkylates for use in motor gasolines it became desirable to supplement the olefin component by including additional propylene and/or amylene in the alkylation feed stock. The principal reaction in such alkylation processes is the coupling of the isobutane with the olefin, such as C_2, C_3, C_4 and C_5 olefins, or mixtures thereof, to produce liquid alkylate, i.e., isohexanes, isoheptanes, isooctanes and isononanes.

In conventional alkylation processes of the prior art, both the principal olefin source and the isobutane feed stocks contain substantial amounts of n-butane. The isobutane feed stock and the olefin reactants, e.g., ethylene, propylene, butylenes and amylenes, after being treated to remove any sulfur compounds, and other contaminants, therefrom, are introduced into the alkylation reactor wherein alkylation takes place in the presence of an acidic catalyst, such as sulfuric acid, hydrofluoric acid; aluminum chloride and complexes thereof, etc., and the alkylation reaction carried out under controlled conditions of temperature, isobutane-:olefin ratios, space velocity, etc. The effluent from the reactor is settled or otherwise treated to effect the separation of catalyst from the hydrocarbon products. The separated hydrocarbon products are then sent to a deisobutanizer to separate the unreacted isobutane, as over-head, from n-butane and the alkylate product. In practice, the separated isobutane is recycled to the alkyalation reactor. in conventional alkylation unit operations, one of the most expensive capital and operating costs for the production of aviation and/or motor gasolines is the deisobutanizer required for the difficult separation of unreacted isobutane from the n-butane. The deisobutanizer is often thhe capacity bottleneck to the unit. Insufficient isobutane for recycle leads to higher acid consumption and lower octane products. This undesirable result is aggravated by the inclusion of propylene and/or amylene to the olefin feed.

The conventional alkylation of isobutane with olefin alkylating agents for the production of aviation and/or motor gasolines components is described in many patents, such as, among others, U.S Pat. Nos. 2,308,560; 2,320,199; 2,429,205; 2,768,987; 2,818,458; 2,914;592; 2,920,124; and others.

SUMMARY AND PREFERRED EMBODIMENT OF THE INVENTION

The present invention provides a means for conducting the catalytic alkylation of isobutane with C_2, C_3 and/or C_5 olefins such that the alkylation reactor effluent can be separated into a recycle isobutane fraction and an alkylate fraction by a relatively inexpensive flashing or other relatively inexpensive separation operations without the necessity of employing a costly deisobutanizer to separate unreacted isobutane from unreacted n-butane such as is present in the alkylation reactor effluent when operated in accordance with conventional isobutane-olefin alkylation processes of the prior art.

While the herein described invention is applicable to processes for the alkylation os isobutane with C_2, C_3 and/or C_5 olefins, employing the well known catalysts therefor, such as sulfuric acid, hydrofluoric acid, phosphoric acid, and Friedel-Craft catalysts, the invention will be described as applicable to the alkylation of isobutane with C_3 and/or C_5 olefins in which sulfuric acid is used as the catalyst. Briefly, in such process the isobutane and the olefin, in the presence of sulfuric acid of above 80% strength, preferably above about 90% strength, are contacted in a reactor provided with means for adequate mixing and contacting of the reactants, with means for removing from the reactor the heat of reaction. The effluent from the reactor is treated and fractionated to recover unreacted isobutane and the alkylate product. A process for such sulfuric acid alkylation is described in U.S. Pat. No. 2,429,205 which describes the so-called "cascade" type alkylation process. The alkylation of isobutane with C_3 and/or C_5 olefins in the presence of sulfuric acid is preferably conducted with a molar ratio of isobutane to olefin being maintained in the ratio of from about 5:1 to about 30:1, respectively, at a temperature in the range of from about 30°F. to about 60°F., and at a pressure sufficient to maintain the reactants in the liquid phase.

The present invention will be described by reference to the accompanying drawing which is a schematic flow diagram of a novel alkylatin unit utilizing the herein described invention.

Referring to the drawing, a paraffin stock, such as butanes, containing a major amount of isobutane, preferably about **80** percent or more, and a minor amount of n-butane, and possibly other low boiling paraffins, such as propane, is introduced through line **10** into treater **11** to remove sulfur compounds, and other feed contaminants, therefrom, and the effluent from treater **11** passed via line **12** to a molecular sieve unit **13** adapted to remove by adsorption essentially all of the n-butane from the butane feed stock to the substantial exclusion of the isobutane. Molecular sives employing any solid adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons can be employed in the practice of this invention. Adsorbents having a pore size or diameter of about 5–5.5 Angstrom units can be suitably used. One such adsorbent is a calcium aluminosilicate manufactured by Linde Air Products Company and designated Type 5A molecular Sieve. Another suitable adsorbent is a molecular screening activated carbon having pore sizes in the range of about 5.0–5.5 Angstrom units, identified as Type MSC-C offered by Pittsburgh Activated Carbon Division of Calgon Corporation. The isobutane effluent from molecular sieve unit **13** is removed via line **14.**

A propylene and/or amylene feed stock, substantially free of n-butane, introduced through line **15,** is passed through treater **16** to remove any sulfur compounds or other contaminants which it may contain, and the treated olefin effluent therefrom removed via line **17,** and combined with the isobutane feed stock free of n-

butane, in line **14**, and the hydrocarbons passed by way of line **18** through chiller **19** to the alkylation reactor **20** via line **21**. In the chiller **19** the feed stocks are cooled to a temperature of about 30°F. to about 60°F. The alkylation of the olefins with the isobutane in the presence of sulfuric acid catalyst, introduced to the reactor through line **22**, can be effected by any of the well known alkylation methods, such as, for example, described in U.S. Pat. Nos. 2,429,205; 2,768,987; 2,920,124 and others

The effluent from reactor **20** is passed through line **23** to settler **24** wherein catalyst is separated from the alkylate and unreacted isobutane, and possibly propane, if present. Separated catalyst is removed from settler **24** via line **25**; a portion of such recovered catalyst is recycled to the reactor **20** via lines **26** and **22**. Alkylate, together with unreacted isobutane, and possible propane, are removed from settler **24** via line **27** to a treating unit **28** to remove possible carry-over acid catalyst and esters. Effluent from the treater **28** is passed via line **29** to a first flash tower **30**, wherein propane and isobutane are flashed off, and taken overhead via line **31** to a depropanizer **32**, wherein propane is taken off overhead via line **33**, and isobutane, recovered as a bottom fraction, removed via line **34**.

The bottoms from the flash tower **30** are passed via line **35** to a second separation tower **36**, which may be provided with suitable stripping means, wherein the major proportion of the remaining isobutane is separated overhead, and removed via line **37**, and the alkylate removed as a bottoms fraction through line **38**.

A major proportion of the combined recovered isobutane fractions recovered from depropanizer **32** and from tower **36** are recycled via lines **39** and **40** to the alkylation reactor **20**. If desired, the remaining minor portion of isobutane can be passed via line **41** as isobutane feed or make-up to a satellite conventional alkylation unit **42** using butylenes as the alkylating agent. The satellite conventional alkylation unit **42** can be operated in conjunction with the alkylation unit using the process of the present invention. Recycled isobutane, obtained via lines **39** and **40** to the reactor **20**, is used to maintain the molar ratio of isobutane to olefin, i.e., propylene and/or amylene, substantially greater than that employed in the satellite conventional alkylation unit **42**, for example from about 5:1 to about 30:1, respectively.

Operating alkylation units in accordance with the present invention has many advantages. Thus, by being able to use less costly flash and/or stripping towers, existing costly deisobutanizers are freed for use in butane isomerization; the isobutane recycle can be raised to high rates to give high isobutane to olefin ratios, which in turn will give high octanes and low acid consumption at high alkylate production.

Although the the foregoing description of a preferred embodiment of the invention, isobutane feed stock, containing essentially no n-butane, is obtained by passing the feed stock, before it is introduced into the alkylation reactor, through suitable molecular sieves which remove the n-butane, the invention is not limited thereto. The isobutane feed stock, essentially free of n-butane, can be obtained from other sources. For example, in a conventional isobutane alkylation process, such as described in U.S. Pat. No. 2,768,987, the isobutane overhead stream from the conventionally empolyed deisobutanizer, can be used as the feed stock to the alkylation unit operated in accordance with the present invention, and in conjunction with the conventional isobutane-olefin alkylation unit; and only such additional isobutane, as may be needed, can be obtained by passing field butane, or other isobutane-containing stock through the molecular sieves to remove any n-butane contained therein.

It is evident that modifications and variations within the scope of this invention will be apparent to those skilled in this art. For example, when employing hydrofluoric acid as alkylation catalyst about 1% HF may remain in the hydrocarbon phase after separation of the catalyst and thus flash overhead with the isobutane in the first flash tower. Shoud any such isobutane, alone or commingled with other paraffin hydrocarbon streams, be later subjected to adsorption treatment for removal of n-butane, such adsorptive treatment should, of course, be effected with a reagent unreactive with hydrofluoric acid, such as an appropriate activated carbon. Accordingly, the present invention is not limited by the foregoing description and discussion thereof but only as defined in the appended claims.

I claim:

1. In the alkylation of isobutane with C_2, C_3 and/or C_5 olefins, the improvement comprising, removing n-butane from a paraffin feed stock containing a major proportion of isobutane, alkylating said isobutane-containing feed stock, containing essentially no n-butane, with an olefin alkylating agent, essentially free of n-butane, selected from the class consisting of ethylene, propylene, amylenes and mixtures thereof, in the presence of an acid catalyst, separating the catalyst from the alkylation reaction mixture, flashing the catalyst-free alkylation reaction mixture to remove a portion of the unreacted isobutane as an overhead fraction and to separate the alkylate and the remaining unreacted isobutane as a bottom fraction, flashing said alkylate and said remaining unreacted isobutane to remove a major proportion of said remaining unreacted isobutane as an overhead fraction, withdrawing said alkylate, and recycling the recovered isobutane.

2. In the alkylation of isobutane with ethylene, propylene, amylenes or mixtures thereof, the improvement comprising, removing n-butane from a paraffin feed stock containing a major proportion of isobutane and minor amounts of n-butane, alkylating in a first alkylation reactor the isobutane feed stock, essentially free of n-butane, with an alkylating agent, essentially free of n-butane, selected from the class consisting of ethylene, propylene, amylenes and mixtures thereof, in the presence of an acid alkylation catalyst, separating the catalyst from the alkylation reaction mixture, flashing the catalyst-free alkylation reaction mixture to remove a portion of the unreacted isobutane as an overhead fraction and to separate the alkylate and the remaining unreacted isobutane as a bottom fraction, flashing said alkylate and said remaining unreacted isobutane to remove a major proportion of said remaining unreacted isobutane as an overhead fraction withdrawing said alkylate, recycling a major proportion of the recovered unreacted isobutane to said first alkylation reactor, and passing the remaining portion of said recovered isobutane as isobutane feed to a second alkylation reactor having a conventional deisobutanizer for separating isobutane and n-butane from the second alkylation reaction mixture of isobutane with butylenes.

3. The process of claim 2, wherein the alkylating agent is propylene and the catalyst is sulfuric acid of at least about 80 percent strength.

4. The process of claim 2, wherein the alkylating agent is amylenes and the catalyst is sulfuric acid of at least about 80 percent strength.

5. The process of claim 2, wherein the alkylating agent is a mixture of propylene and amylenes, and the catalyst is sulfuric acid of at least strength. 80 percent strength.

6. The process of claim 2 wherein the alkylating agent is propylene and the catalyst is hydrofluoric acid.

7. The process of claim 2 wherein the alkylating agent is amylenes and the catalyst is hydrofluoric acid.

8. The process of claim 2 wherein the alkylating agent is a mixture of propylene and amylenes and the catalyst is hydrofluoric acid.

9. The process of claim 2, wherein the n-butane is removed from the paraffin feed stock by means of molecular sieves.

10. The process of claim 9, wherein the molecular sieves are adsorbents having pore sizes of about 5.0 – 5.5 Angstrom units.

11. In the alkylation of isobutane with propylene, amylenes and mixtures thereof, the improvement comprising, removing n-butane from a paraffin stock containing a major proportion of isobutane and minor amounts of n-butane, alkylating in a first alkylation reactor said isobutane-containing paraffin stock, essentially free of n-butane, with an olefin alkylating agent, essentially free of n-butane, selected from the class consisting of propylene, amylenes and mixtures thereof, in the presence of an acid alkylation catalyst, separating catalyst from the alkylation reaction mixture, flashing the catalyst-free alkylation mixture to remove propane and a portion of the unreacted isobutane as an overhead fraction and to recover the alkylate and the remaining unreacted isobutane as a bottom fraction, depropanizing said overhead fraction to remove said propane and to recover unreacted propane-free isobutane, flashing said bottom fraction to separate a major proportion of said remaining unreacted isobutane therefrom, withdrawing said alkylate, combining said recovered unreacted propane-free isobutane and said recovered remaining unreacted isobutane, recycling a major proportion of said combined recovered unreacted isobutane to said first alkylation reactor, and passing the remaining portion of said combined recovered unreacted isobutane as isobutane feed to a second alkylation reactor having a conventional deisobutanizer for separating isobutane and n-butane from second alkylation reaction mixture of isobutane with butylenes.

12. The process of claim 11, wherein the n-butane is removed from the paraffin feed stock by means of adsorbents having pore sizes in the range of about 5.0 – 5.5 Angstroms, and the catalyst is sulfuric acid of at least 80 percent strength.

13. The process of claim 11, wherein the acid catalyst is hydrofluoric acid.

14. In the alkylation of isobutane with ethylene, propylene, amylenes or mixtures thereof, the improvement comprising, removing n-butane from a paraffin feed stock containing a major portion of isobutane and minor amounts of n-butane, alkylating in a first alkylation reactor the isobutane feed stock, essentially free of n-butane, with an alkylating agent, essentially free of n-butane, selected from the class consisting of ethylene, propylene, amylenes and mixtures thereof, in the presence of aluminum chloride catalyst and complexes thereof, separating the catalyst from the alkylation reaction mixture, flashing the catalyst-free alkylation reaction mixture to remove a portion of the unreacted isobutane as an overhead fraction and to separate the alkylate and the remaining unreacted isobutane as a bottom fraction, flashing said alkylate and said remaining unreacted isobutane to remove a major portion of said remaining unreacted isobutane as an overhead fraction, withdrawing said alkylate, recycling a major portion of the recovered unreacted isobutane to said first alkylation reactor, and passing the remaining portion of said recovered isobutane as isobutane feed to a second alkylation reactor having a conventional deisobutanizer for separating isobutane and n-butane from the second alkylation mixture of isobutane with butylenes.

15. The alkylation process comprising, introducing into a first alkylation reactor a paraffin feed stock containing a major amount of isobutane and a minor amount of n-butane, alkylating the isobutane in said feed stock with butylenes in the presence of an acid alkylation catalyst selected from the class consisting of sulfuric acid and hydrofluoric acid, separating catalyst from the alkylation reaction mixture, introducing the resultant alkylation reaction mixture from said first alkylation reactor into a conventional deisobutanizer to withdraw alkylate and to separate unreacted isobutane as an overhead fraction, passing said overhead fraction through molecular sieves having a pore size of 5.0 to 5.5 Angstrom units to produce recovered unreacted isobutane containing essentially no n-butane, combining said recovered unreacted isobutane, containing essentially no n-butane, with sufficient make-up isobutane, essentially free of n-butane, from an external source, introducing said combined recovered unreacted isobutane and make-up isobutane into a second alkylation reactor, alkylating said combined recovered unreacted isobutane and make-up isobutane with an olefin alkylating agent, essentially free of n-butane, selected from the class consisting of propylene, amylenes and mixtures thereof, in the presence of an acid alkylation catalyst, the ratio of isobutane to olefin in said second alkylation reaction being maintained in the ratio of from about 5:1 to about 30:1, withdrawing the resultant alkylation reaction mixture from said second alkylation reactor, separating the catalyst from the alkylation mixture, flashing the catalyst-free alkylation reaction mixture to remove and recover a portion of the uncombined isobutane as an overhead fraction and to separate the alkylate and the remaining uncombined isobutane as a bottom fraction, flashing said alkylate and said remaining uncombined isobutane to remove and recover a major proportion of said remaining uncombined isobutane as an overhead fraction, withdrawing said alkylate and recycling said recovered uncombined isobutane to said second alkylation reactor.

16. The process of claim 15 wherein said make-up isobutane essentially free of n-butane, from an external source, is obtained by passing an external paraffin stream containing isobutane and n-butane into a conventional deisobutanizer, separating therein isobutane from the external paraffin stream, recovering the isobutane as an overhead fraction, introducing said overhead fraction into molecular sieves having a pore size of 5.0 to 5.5 Angstrom units, and withdrawing the isobutane, essentially free of n-butane, from the molecular sieves.

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