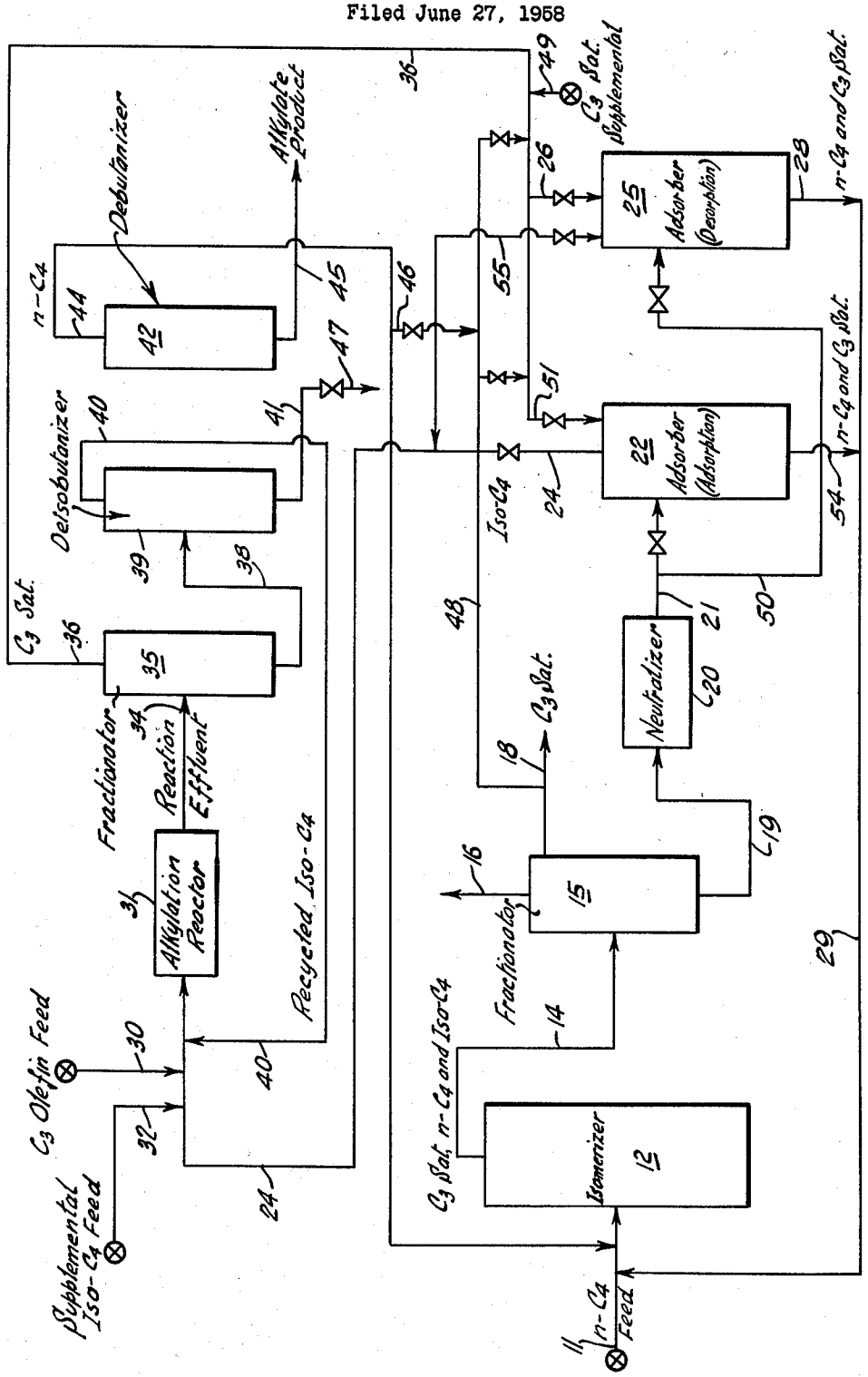
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ALKYLATION PROCESS

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ALKYLATION PROCESS

Randlow Smith, New Rochelle, N.Y., assignor to Texaco Inc., a corporation of Delaware

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1 Claim. (Cl. 260—683.49)

This invention relates to a petroleum treating process for the production of high octane motor fuel components. More particularly, this invention relates to an improved alkylation process. Still more particularly, this invention relates to an improved alkylation process involving in combination a number of treating steps coordinated with respect to each other for the production of a high octane motor fuel component.

In accordance with one embodiment the practice of this invention is directed to the manufacture of a high octane motor fuel component, alkylate, from a feed comprising substantially only straight chain hydrocarbons, such as n-butane and another feed containing an olefinic hydrocarbon, such as propylene.

It is an object of this invention to provide an improved alkylation process for the manufacture of a high octane motor fuel component.

It is another object of this invention to provide an improved process for the manufacture of a high octane alkylate from relatively highly volatile starting materials.

Still another object of this invention is to provide an alkylation process which is adaptable to a variety of charge stocks.

Yet another object of this invention is to provide an improved alkylation process wherein normal butane is a feed component and wherein the normal butane feed is suitably treated in accordance with the practice of this invention to yield a high octane alkylate particularly useful as a motor fuel component.

How these and other objects of this invention are accomplished will become apparent in the light of the accompanying disclosure and drawing which schematically illustrates a process flow in accordance with one embodiment of the practice of this invention.

In accordance with this invention a feed comprising a saturated stright chain hydrocarbon is subjected to isomerization wherein the straight chain hydrocarbon is isomerized into an isomeric mixture comprising the aforesaid straight chain hydrocarbon and the corresponding isomeric branched chain hydrocarbon. Following the isomerization reaction the isomate is subjected to contact with a selective adsorbent which preferentially adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons from said isomate. The remaining unadsorbed isomeric branched chain hydrocarbons are then introduced into an alkylation reaction zone in admixture with a suitable olefinic hydrocarbon wherein said olefinic hydrocarbon reacts with and alkylates said isomeric branched chain hydrocarbon to yield an alkylation reaction effluent comprising unreacted said isomeric branched chain hydrocarbons and alkylate. The resulting alkylation reaction effluent is then subjected to fractionation to separate therefrom said unreacted isomeric branched chain hydrocarbon which is recycled to the aforesaid alkylation reaction zone. Alkylate as product is separately recovered from the alkylation reaction mixture. The adsorbed straight chain hydrocarbons, selectively adsorbed from the isomate by contact with said selective adsorbent, are desorbed therefrom and the resulting desorption effluent comprising the desorbed straight chain hydrocarbons is returned to the aforesaid isomerization reaction zone. By operating in the manner indicated hereinabove a feed stream comprising substantially only straight chain hydrocarbon and a suitable olefinic feed are reacted to yield as product substantially only high octane alkylate.

In the aforesaid combination of operations involving isomerization, selective adsorption and desorption and alkylation, any suitable isomerization process effective for isomerizing straight chain saturated hydrocarbons, such as butane, into the corresponding isomeric branched chain saturated hydrocarbons, such as isobutane, might be employed. Similarly, any suitable alkylation reaction wherein a branched chain saturated hydrocarbon, such as isobutane, is reacted with or alkylated with an olefinic hydrocarbon, such as propylene, might be employed therein.

With respect to the adsorption step wherein straight chain hydrocarbons are selectively adsorbed from admixture with non-straight chain hydrocarbons it is preferred in the practice of this invention to employ as the selective adsorbent a solid, alumino-silicate molecular sieve type adsorbent, i.e., adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons.

Any suitable isomerization process, vapor phase or liquid phase, may be employed in the practice of this invention and such isomerization processes are well known in the art. For the most part these isomerization processes are distinguished as to whether or not the hydrocarbons to be isomerized are isomerized in the liquid phase or in the vapor phase. In liquid phase isomerization a catalyst consisting of aluminum chloride dissolved in molten antimony trichloride is sometimes employed. Generally the hydrocarbon mixture undergoing liquid phase isomerization is admixed with hydrogen chloride gas which acts as a catalyst promoter during the isomerization reaction. Sometimes it is also desirable to admix hydrogen with the isomerization reaction mixture to improve the yield of the resulting isomerized hydrocarbons.

In vapor phase isomerization a catalyst comprising aluminum chloride promoted with hydrogen chloride is employed. Other catalysts suitable for use in vapor phase isomerization are known and include precious metal-containing catalyst as well as platinum-containing catalysts.

Alkylation processes which are suitably employed in combination treating operations in accordance with this invention are well known in the art. Suitable alkylation processes, identified by the type of alkylation catalyst employed, include sulfuric acid alkylation processes as well as HF alkylation and aluminum chloride alkylation processes. In sulfuric acid, HF and aluminum chloride alkylation processes a saturated branched chain hydrocarbon, such as isobutane, is contacted in the liquid phase at a suitable low temperature with an olefinic hydrocarbon, such as propylene. In the alkylation reactor the olefinic hydrocarbon reacts with the branched chain isomeric hydrocarbon to yield the corresponding alkylate. In the alkylation reaction it is desirable to maintain a great excess of isomeric saturated hydrocarbon therein, at least about 5:1, preferably at least 10:1, on a molar basis, to drive the reaction toward completion in the direction of consumption of the olefinic hydrocarbon. There is recovered from the alkylation reactor an alkylation reaction effluent comprising unreacted isomeric sat-

urated hydrocarbon and alkylate. The alkylation reaction effluent is fractionated into the above mentioned fractions, the alkylate being recovered as product and the unreacted branched chain saturated hydrocarbon is returned to the alkylation reaction zone to contact additional olefinic hydrocarbon.

The various isomerization processes and alkylation processes which are suitably employed in the practice of this invention are described in the Oil and Gas Journal, March 25, 1957, pages 153–165. The disclosures of this reference with respect to isomerization processes and alkylation processes are herein incorporated and made part of this disclosure.

Any suitable selective adsorption process effective for the removal of straight chain saturated hydrocarbons from branched chain hydrocarbons is satisfactorily employed in the practice of this invention. The invention, however, is particularly applicable to a selective adsorbent comprising certain natural or synthetic zeolites or alumino-silicates, such as a calcium alumino-silicate, which exhibits the property of a molecular sieve, that is, matter made up of porous crystals wherein the pores of the crystals are of molecular dimension and are of substantially uniform size. In general, zeolites may be described as water-containing alumino-silicates having a general formula $(R,R_2')O.Al_2O_3.nSiO_2.mH_2O$ wherein R may be an alkaline earth metal such as calcium, strontium or barium or even magnesium and wherein R' is an alkali metal such as sodium or potassium or lithium. These materials, when dehydrated for the removal of substantially all of the water therefrom, retain their crystalline structure and are particularly suitable as selective adsorbents.

A particularly suitable solid adsorbent for straight chain hydrocarbons is a calcium alumino-silicate, apparently actually a sodium calcium alumino-silicate, manufactured by Linde Air Products Company and designated Linde Type 5A Molecular Sieve. The crystals of this particular calcium alumino-silicate have a pore size or opening of about 5 Angstrom units, a pore size sufficiently large to admit straight chain hydrocarbons, such as the normal paraffins, to the substantial exclusion of the non-straight chain hydrocarbons, i.e., naphthenic, aromatic, isoparaffinic and isoolefinic hydrocarbons. This particular selective adsorbent is available in various sizes, such as in the form of ⅛″ or 1/16″ diameter pellets, or as a finely divided powder having a particle size in the range of 0.5–5.0 microns. In general, a selective adsorbent employed in the practice of this invention may be in any suitable form or shape, granular, spheroidal or microspheroidal.

Particularly suitable solid selective adsorbents which may be employed in the practice of this invention include the synthetic and natural zeolites which, when dehydrated, may be described as crystalline zeolites having a rigid three dimensional anionic network and having interstitial dimensions sufficiently large to adsorb srtaight chain hydrocarbons but sufficiently small to exclude the non-straight chain hydrocarbons possessing larger molecular dimensions. The naturally occurring zeolite, chabazite, exhibits such desirable properties. Another suitable naturally occurring zeolite is analcite

$$NaAlSi_2O_6.H_2O$$

which, when dehydrated, and when all or part of the sodium is replaced by an alkaline earth metal such as calcium by base exchange yields a material which may be represented by the formula $(Ca,Na_2)Al_2Si_4O_{12}.2H_2O$ and which, after suitable conditioning, will absorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Other naturally occurring or synthetically prepared zeolites such as phacolite, gmelinite, harmotome and the like, or suitable base exchange modifications of these zeolites, may also be employed in the practice of this invention.

Other solid inorganic or mineral selective adsorbents are known. It is contemplated that selective adsorbents having the property of selectively adsorbing straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons in the manner of a molecular sieve may be obtained by suitable treatment of various oxide gels, especially metal oxide gels of the polyvalent amphoteric metal oxides.

The adsorptive separation of the straight chain hydrocarbons from the hydrocarbon fraction undergoing treatment may be carried out in the liquid or gaseous phase and at any suitable temperature and pressure effective in the adsorptive separation operation. It is desirable, however, to coordinate the adsorption separation conditions, e.g., temperature and pressure, with the desorption separation conditions, more fully described hereinafter, so as to effect the most economical use of the materials employed and for ease of control.

The adsorptive separation or adsorption of the straight chain hydrocarbons by the solid selective adsorbent may be carried out at any suitable temperature, such as a temperature in the range 50–500° F., sufficient to effect the adsorptive separation of the desired straight chain hydrocarbons, and at any suitable pressure, such as a pressure in the range 0–10,000 p.s.i.g. and higher, the temperature and pressure being adjusted with respect to the hydrocarbon mixture undergoing treatment depending upon whether or not it is desired to maintain the hydrocarbon mixture undergoing separation in liquid phase or in the vapor or gaseous phase.

Liquid phase adsorption may be carried out by simply slurrying the solid selective adsorbent with the liquid hydrocarbon mixture being treated, followed by separation or decantation of the resulting treated hydrocarbon effluent, now substantially free of or having a substantially reduced straight chain hydrocarbon content. Liquid phase adsorption may also be carried out by percolating the liquid hydrocarbon mixture to be treated through a bed of solid adsorbent material. It is usually preferred, however, to carry out the adsorptive separation operation in the gaseous phase, that is, to maintain the hydrocarbon mixture undergoing treatment in the vapor phase during the adsorption operation. In such an operation any suitable method for effecting gas-solid contact may be employed, for example, a fixed bed, a moving bed or a fluidized bed or a gas-entrained mass of selective adsorbent may be employed during the gas phase adsorptive separation operation. After sufficient time, the solid adsorbent is separated from the resulting treated hydrocarbon mixture, now having a reduced proportion of straight chain hydrocarbons, and the separated solid adsorbent is then subsequently treated to desorb the adsorbed straight chain hydrocarbons therefrom.

The desorption of the adsorbed hydrocarbons (straight chain hydrocarbons) from the solid adsorbent material may be made at any suitable temperature and pressure. For example, the desorption operation may be carried out at a pressure in the range 0–10,000 p.s.i.g. It is preferred, however, that the desorption operation be carried out in the gaseous phase, that is, the gaseous desorption or desorbing fluid and the resulting desorbed hydrocarbons are both present in the resulting desorption effluent in the gaseous or vaporous phase. Accordingly, the desorption temperature and the desorption pressure are adjusted to maintain the desorption fluid and the desorbed hydrocarbons in the gaseous phase. Generally a desorption pressure in the range 10–2,000 p.s.i.g. is suitable. It is sometimes desirable to carry out the desorption operation at a pressure substantially lower than the adsorption pressure. Isobaric adsorption-desorption operations are advantageous in some instances; however the pressure employed during the adsorptive separation operation is not determinative of the desorption pressure.

Any suitable desorption temperature sufficiently high to effect desorption of the adsorbed straight chain hydro-

carbons may be employed in the practice of this invention. Usually a temperature in the range 400–1100 F. is employed during the desorption operation. It is generally preferred, however, to carry out the desorption operation at an elevated temperature in the range 300–1100° F. The desorption temperature employed, however, should not be excessively high, for example not greater than about 1100–1300° F., particularly in the instance wherein a material such as Linde Type 5A Molecular Sieve, that is, a calcium alumino-silicate, is employed as the selective adsorbent since these temperatures are excessive and lead to the destruction of the adsorbent, presumably by collapse of the crystal structure, with resultant loss of the selective adsorption properties of this particular adsorbent.

Although desorption of the adsorbed straight chain hydrocarbon from the adsorbent containing the same may be accomplished by the mere application of heat it is preferred in the practice of this invention to employ a hot gaseous or vaporized desorbing fluid. Particularly useful as a desorbing fluid in the practice of this invention is a gaseous or vaporized straight chain hydrocarbon, such as ethane, propane or butane and the like. When a straight chain hydrocarbon is employed to effect desorption of the adsorbed straight chain hydrocarbon the desorption operation should be carried out at a temperature above the critical temperatures of not only the adsorbed straight chain hydrocarbons to be desorbed but also above the critical temperature of the straight chain hydrocarbon employed as the desorbing fluid or agent. For example, when propane or normal butane is employed to desorb adsorbed n-butane from the adsorbent material, the desorption operation is carried out at a temperature above the critical temperature of n-butane, i. e., above 307° F.

Although it is preferred in the practice of this invention to employ a straight chain hydrocarbon, such as ethane, propane or n-butane, as the desorbing agent to effect desorption of the adsorbed straight chain hydrocarbons from the adsorbent, other desorbing agents, such as hydrogen, methane, branched chain hydrocarbons and the like or mixtures of desorbing agents, are also suitably employed. When, however, a straight chain hydrocarbon such as n-butane is employed as the desorbing agent there results from the desorption operation a desorption effluent which is comprised substantially only of straight chain hydrocarbons such as n-butane. A feed comprising substantially only straight chain hydrocarbon is particularly desirable as feed to an isomerization reaction.

Referring now to the drawing which schematically illustrates one embodiment of the practice of this invention directed to the alkylation of a C_4 hydrocarbon, isobutane, with a C_3 olefinic hydrocarbon, propylene, a feed stream of normal butane supplied from a suitable source, such as from the bottoms of a C_4 fractionator tower, is supplied via line **11** as feed to isomerizer **12** wherein the n-butane is isomerized employing aluminum chloride as the isomerization catalyst together with HCl as the catalyst promoter. There is recovered from isomerizer **12** via line **14** an isomate mixture containing n-butane and isobutane. The resulting isomate mixture is fractionated in fractionator **15** from which there is recovered overhead via line **16** any light ends, such as HCl, which might have issued overhead via line **14** from isomerizer **12**. There is also withdrawn from the upper portion of fractionator **15** via line **18** a side stream comprising a C_3 saturated hydrocarbon, propane. The bottoms from fractionator **15** comprising substantially only n-butane and isobutane is recovered via line **19** and introduced into neutralizer **20** wherein any catalytic material, such as aluminum chloride, carried over from isomerizer **12** with the isomate mixture in line **14** is neutralized and effectively removed. The resulting neutralized isomate mixture is then passed via line **21** into adsorber **22** where it is contacted with a suitable selective adsorbent for straight chain hydrocarbons to effect the selective adsorption and removal of the n-butane from the isobutane. There is recovered from adsorber **22** via line **24** a treated effluent comprising substantially only isobutane.

As illustrated in the drawing a companion adsorber **25** having therein adsorbent material containing adsorbed n-butane is undergoing desorption by contact with gaseous propane introduced into the upper portion of adsorber **25** via line **26**. The resulting desorption effluent comprising n-butane and propane is recovered from the adsorber **25** via line **28** and returned via lines **29** and **11** to isomerizer **12** wherein the thus recycled n-butane undergoes isomerization in the presence of the propane employed to effect desorption of the adsorbed n-butane from the adsorbent within adsorber **25**.

The isobutane recovered from adsorber **22** via line **24** is introduced in admixture with a suitable C_3 olefin-containing feed, propylene, supplied from a suitable source via line **30** into alkylation reactor **31**. The C_3 feed supplied via line **30** to alkylation reactor **31** comprises propylene and propane. The C_3 olefin feed may be derived from any suitable source, such as a C_3 fraction separated from a catalytic cracker off-gas or from the pyrolysis of propane. If desired, additional or supplemental isobutane in a C_4 feed stream containing substantially only isobutane or isobutane and n-butane, may be introduced from a suitable source via lines **32** and **24** into alkylation reactor **31**.

Within alkylation reactor **31** the isobutane and propylene undergo reaction with a resulting formation of the corresponding alkylate. There is recovered from alkylation reactor **31** via line **34** an alkylation reaction effluent comprising unreacted isobutane, alkylate and any propane originally contained in the C_3 olefin feed and any normal butane contained in the supplemental isobutane supplied to alkylation reactor **31**. The resulting alkylation reaction effluent is passed via line **34** into fractionator **35** where it undergoes fractionation with the resultant recovery overhead via line **36** of propane. The bottoms fraction recovered from fractionator **35** via line **38** is introduced into deisobutanizer **39** wherein there is recovered overhead via line **40** the unreacted isobutane which is recycled via lines **40** and **24** to alkylation reactor **31**. The bottoms issuing from deisobutanizer **39** via line **41** are introduced into debutanizer **42** wherein there is recovered overhead via line **44** any normal butane which might have been introduced into the alkylation reactor with the supplemental isobutane feed which is added via lines **32** and **24** to alkylation reactor **31**. There is recovered as bottoms from debutanizer **42** via line **24** the alkylate product, i.e., the resulting reaction product of propylene and isobutane.

As illustrated in the drawing the propane recovered overhead from fractionator **35** via line **36** is employed to effect desorption of the adsorbed normal butane from the adsorbent in adsorber **25**. The propane is introduced into adsorber **25** from fractionator **35** via lines **36** and **26**. If desired, the normal butane recovered overhead from debutanizer **42** via line **44**, alone or in admixture with the propane, may be employed to effect desorption of the adsorbed n-butane within adsorber **25** by introducing the n-butane recovered from debutanizer **42** into adsorber **25** via lines **44**, **46** and **48**. Further, as indicated in the drawing supplemental propane as may be needed to effect complete desorption of the n-butane from the adsorbent in adsorber **25** may be supplied from a suitable source via line **49** into line **36**.

The propane employed to effect desorption of the adsorbed n-butane from the adsorbent within adsorber **25**, and which is returned in the resultant desorption effluent via lines **28** and **11** to isomerizer **12**, is recovered via lines **18** and **48** from the isomate mixture in line **14** after undergoing fractionation in fractionator **15**. In the above-indicated manner the propane employed to effect desorption of the adsorbed n-butane is retained within the isom-

erization-adsorption-desorption system and does not enter the alkylation-fractionation and -recovery system.

As illustrated in the drawing, two adsorbers 22 and 25 are employed. When one adsorber, such as adsorber 22, is employed in the adsorption cycle the other adsorber, such as adsorber 25, is employed in the desorption cycle. Accordingly, when the adsorbent material within adsorber 22 is saturated with n-butane and when the adsorbent material within adsorber 25 has been substantially completely depleted of any adsorbed n-butane, the isomate mixture issuing from neutralizer 20 via line 21 is then introduced into adsorber 25 via line 50 and the propane employed as desorbent fluid is introduced into adsorber 22 via lines 36 and 51. When the adsorbers 22 and 25 are so employed there now issues from adsorber 22 via line 54 a desorption effluent comprising n-butane and propane. This desorption effluent in line 54 is recycled via lines 29 and 11 to isomerizer 12. At the same time the adsorption effluent which issues from adsorber 25 via line 55 and comprising substantially only isobutane is introduced via line 24 into alkylation reactor 31 to undergo alkylation reaction therein with propylene. Accordingly, by employing in combination two adsorbers 22 and 25, one undergoing adsorption while the other undergoes desorption, the above-indicated combination of treating steps can be carried out substantially continuously.

As indicated in the accompanying drawing, the propane which is recovered overhead from fractionator 35 via line 36 was originally introduced into the alkylation reaction system together with the C_3 propylene-containing feed. Further, the n-butane recovered overhead from debutanizer 42 via line 44 was originally introduced into the alkylation reaction system when supplemental isobutane feed is supplied to the alkylation reaction system via line 32. In the event no supplemental isobutane feed is supplied to the alkylation reaction system via line 32 debutanizer 42 would not be required, the alkylate product fraction being recovered as bottoms from deisobutanizer 39 via lines 41 and 47.

Although emphasis in this disclosure has been placed upon the applicability of the practice of this invention to the alkylation of isobutane with propylene, it is mentioned that any suitable alkylation feed stocks, isomeric saturated hydrocarbon and olefinic hydrocarbon, are suitably employed in the practice of this invention. Suitable isomeric saturated hydrocarbons in addition to isobutane include the isomeric pentanes and hexanes and the like and suitable olefinic hydrocarbons include ethylene, the butenes including isobutylene, the pentenes, the hexenes and the like.

Further, as mentioned hereinabove it is desirable in the practice of this invention to carry out the desorption of n-butane from the adsorbent by employing a straight chain hydrocarbon under conditions such that the desorption temperature is greater than the critical temperature of the straight chain hydrocarbon employed as the desorbing agent as well as the adsorbed straight chain hydrocarbon (n-butane) itself. The advantages of carrying out a desorption operation above the critical temperature of the desorbing agent as well as the critical temperature of the hydrocarbon undergoing desorption are set forth in U.S. 2,818,455 issued December 31, 1957. The disclosures of the above-identified patent with respect to carrying out a desorption operation above the crtical temperature of the hydrocarbon to be desorbed as well as the desorbing agent itself are herein incorporated and made part of this disclosure.

It is mentioned that in the accompanying disclosure and particularly in the drawing no reference has been made to conventional operating equipment, such as heat exchangers, pumps, flow regulating devices, liquid level regulating devices and the like for reasons of clarity and not to clutter-up the specification and drawing. The employment of such devices in operations in accordance with the practice of this invention is readily apparent to those skilled in the art. Further, it is evident from the foregoing disclosure many modifications, substitutions and alterations are possible in the practice of this invention without departing from the spirit or scope thereof.

I claim:

A petroleum treating process which comprises subjecting n-butane to isomerization to yield an isomate mixture comprising n-butane and isobutane, contacting said isomate mixture with a selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb n-butane from said isomate mixture, passing the remaining isobutane to an alkylation reaction zone into admixture with an olefinic hydrocarbon stream containing propylene and n-butane wherein said propylene reacts with said isobutane to yield a corresponding alkylate, recovering from the alkylation reaction zone an alkylation reaction effluent comprising unreacted isobutane, n-butane and said alkylate, returning at least a portion of said unreacted isobutane to the aforesaid alkylation reaction zone, separating the aforesaid n-butane from the alkylation reaction effluent, employing the separated n-butane to desorb the adsorbed n-butane from said adsorbent, passing the resulting desorption effluent comprising only n-butane to the aforesaid isomerization reaction and recovering said alkylate as product from the aforesaid alkylation reaction effluent.

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