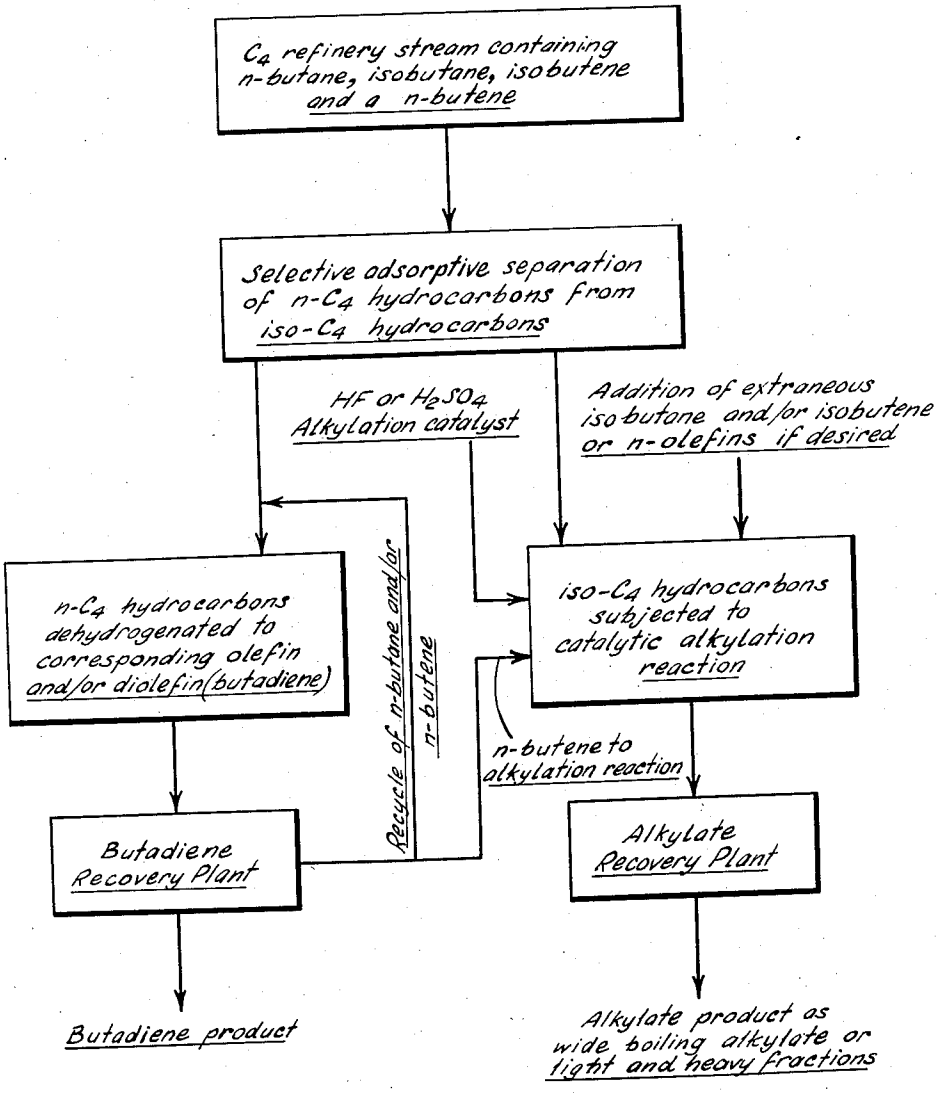
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METHOD OF TREATING A C_4 HYDROCARBON STREAM

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METHOD OF TREATING A C_4 HYDROCARBON STREAM

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2 Claims. (Cl. 260—680)

This invention relates to a method of treating a C_4 hydrocarbon stream. More particularly, this invention relates to an integrated combination method for handling a C_4 hydrocarbon stream such as may be produced in or recovered from a petroleum refinery or hydrocarbon synthesis plant.

In refinery operations it is usually the practice to segregate hydrocarbon streams which may be produced during the refinery operations according to molecular weight and/or boiling point range. Accordingly, in a modern integrated petroleum refinery which may contain crude oil distillation units, catalytic cracking units, thermal cracking units and/or thermal or catalytic reforming units there are available, after suitable fractionation, various hydrocarbon or hydrocarbon-containing streams, such as a normally gaseous hydrocarbon stream containing methane and ethane, a C_3 hydrocarbon stream, a C_4 hydrocarbon stream, a stream containing hydrocarbons having boiling points in the gasoline range and the like. The C_4 hydrocarbon stream containing n-butane, isobutane, isobutene and sometimes varying amounts of n-butenes has been utilized as a source material for the production of butadiene.

When a refinery C_4 hydrocarbon stream is utilized for the manufacture of butadiene it usually must undergo a substantial amount of fractionation and, in some instances, chemical treatment, solvent extraction and the like in order to produce a suitable feed for the production of butadiene by catalytic dehydrogenation. For instance, a C_4 refinery stream comprising n-butane, isobutane, isobutene and n-butene is fractionated and treated for the removal of isobutene, by cold acid washing. The isobutane and a substantial amount of the n-butane are separated and recovered as an effluent in extractive distillation operations employing liquid furfural as the selective solvent, for the production of a C_4 hydrocarbon stream containing a major amount, in the range 50–90 mol percent and higher, on n-butenes for the manufacture of butadiene by catalytic dehydrogenation of the n-butenes. The above-mentioned fractionation, acid treating and extractive distillation operations require a substantial capital investment in equipment. As indicated, the above-mentioned operations are carried out principally to supply n-butene feed substantially free of non-straight chain hydrocarbons, such as isobutane, and containing only relatively minor amounts of isobutene, in the range 0–15 mol percent, for the production of butadiene by catalytic dehydrogenation of the n-butenes.

It is an object of this invention to provide an improved process for the handling and treating of a C_4 hydrocarbon stream utilized in the production of butadiene and/or n-butene.

It is another object of this invention to provide an improved process for the manufacture of butadiene from a C_4 hydrocarbon stream containing n-butane, isobutane, isobutene and n-butenes.

Still another object of this invention is to provide an improved integrated process for the treatment of a C_4 hydrocarbon stream containing normal C_4 hydrocarbons and iso-C_4 hydrocarbons wherein the normal C_4 hydrocarbons are utilized for the manufacture of butadiene and/or n-butenes and the iso-C_4 fraction is substantially exclusively utilized for the production of an alkylate suitable for use as a motor fuel component.

Still another object of this invention is to provide an improved process for the manufacture of butadiene.

In at least one embodiment of this invention at least one of the foregoing objects will be achieved. How these and other objects of this invention are achieved will become apparent in the light of the accompanying disclosure and drawing which schematically illustrates in a block flow diagram one embodiment of the practice of this invention.

In accordance with this invention we have provided an improved method for handling a C_4 hydrocarbon stream containing straight chain and non-straight chain C_4 hydrocarbons wherein said C_4 hydrocarbon stream is contacted with a selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, thereby producing a treated effluent having a substantially reduced straight chain C_4 hydrocarbon content or substantially free of straight chain C_4 hydrocarbons which is subsequently treated in a suitable manner to upgrade the same. The adsorbed straight chain C_4 hydrocarbons are desorbed from the selective adsorbent to yield a C_4 hydrocarbon stream comprised predominantly of or consisting essentially of straight chain C_4 hydrocarbons. The desorbed straight chain hydrocarbons are subsequently treated, as by catalytic dehydrogenation, for the manufacture of corresponding unsaturated hydrocarbons, such as the n-butenes and/or butadiene.

Referring now to the drawing which schematically illustrates one embodiment of the practice of this invention, a C_4 refinery stream containing n-butane, isobutane, isobutene and n-butenes is contacted with a selective adsorbent to selectively adsorb n-butane and the n-butenes therefrom to the substantial exclusion of the isobutane and the isobutene with the resulting production of a treated effluent comprising predominantly isobutane and isobutene. This treated effluent is subsequently subjected to an alkylation reaction for the production of high octane, branched chain hydrocarbons (alkylate) which are particularly suitable for use in aviation gasolines and as blending components in motor fuels.

The adsorbed straight chain C_4 hydrocarbons, comprising substantially only n-butane and n-butenes, are desorbed from the selective adsorbent to produce a straight chain C_4 hydrocarbon stream comprising predominantly or substantially only n-butane and n-butenes. This stream is then subjected to catalytic dehydrogenation by contact with a suitable catalyst for the production of additional n-butenes and butadiene. The resulting produced butadiene is recovered from the dehydrogenation reaction effluent as a separate product and the unconverted n-butane and n-butenes together with the newly produced n-butenes are recycled to the catalytic dehydrogenation reaction. If desired, at least a portion of the n-butene content of the feed to the catalytic dehydrogenation reactor or the reaction effluent therefrom may be passed to the aforementioned catalytic alkylation operation to maintain a desired isoalkane/alkene ratio therein.

In view of the foregoing description which broadly outlines a practice of this invention, it is apparent that by treating a C_4 refinery stream in accordance with this invention for the production of butadiene a single operation, namely selective adsorptive separation of the straight chain C_4 hydrocarbons from the non-straight chain C_4 hydrocarbons, i.e., n-butane and n-butene from isobutane

and isobutene, takes the place of the operations of fractionation, acid treatment and solvent extraction or extractive distillation heretofore employed in the preparation of a suitable feed for butadiene manufacture when starting with a C_4 hydrocarbon refinery stream.

FEED STOCKS

The practice of this invention is particularly applicable to the treatment of C_4 hydrocarbon refinery streams containing n-butane, isobutane and isobutene. The presence of n-butene in the C_4 refinery stream is desirable. A C_4 hydrocarbon refinery stream might have the composition set forth in Table No. I.

TABLE NO. I

Component:	Mol percent
Propane and lighter	0–7.0
Isobutane	10–70
Isobutene	5–50
Butene–1	0–20
Butadiene	0–.5
n-Butane	5–70
Butene–2	0–35
Pentane and higher	0–7.0

Suitable C_4 hydrocarbon streams may be recovered and/or composited from refinery straight run distillation units, catalytic cracking units, catalytic reforming units, thermal cracking or thermal reforming units, isomerization units and the like.

Selective adsorptive separation of straight chain C_4 hydrocarbons from non-straight chain C_4 hydrocarbons

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. It is preferred, however, to employ as the selective adsorbent certain natural or synthetic zeolites or alumino-silicates, such as a calcium alumino-silicate, which exhibit the property of a molecular sieve, that is, material or adsorbents made up of porous matter or crystals wherein the pores are of molecular dimension and are of uniform size. A particularly suitable solid adsorbent for straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons is a calcium alumino-silicate manufactured by Linde Air Products Company and designated Type 5A Molecular Sieve. The crystals of this particular calcium alumino-silicate, apparently actually a sodium calcium alumino-silicate, have a pore size or diameter of about 5 Angstrom units, a pore size sufficient to admit straight chain hydrocarbons, such as n-butane and the n-butenes, to the substantial exclusion of the non-straight chain hydrocarbons, such as isobutane and isobutene. This particular selective adsorbent is available in various sizes and forms, e.g., in the form of a 1/16" and 1/8" diameter pellets or a finely divided powder.

Other suitable selective adsorbents are known and 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 straight chain hydrocarbons but sufficiently small to exclude the non-straight chain hydrocarbons. 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, yields a material which may be represented by the formula $(Ca,Na)Al_2Si_4O_{12}.2H_2O$ and which, after suitable conditioning, will adsorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons. Naturally occurring or synthetically prepared phacolite, gmelinite, harmotome and the like or suitable modifications of these materials by base exchange are also applicable for the practice of this invention. Other solid adsorbents which selectively adsorb straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons are known. It is contemplated that selective adsorbents may be obtained and prepared by suitable treatment of the various oxide gels, especially the metal oxide gels of the polyvalent amphoteric metal oxides.

The operation for the adsorptive separation of the straight chain C_4 hydrocarbons, n-butane and/or n-butene, from an admixture containing the same together with close boiling branched chain C_4 hydrocarbons, isobutane and isobutene, is effected by direct contact between the admixture and the particular selective adsorbent employed. The admixture being separated or treated for the adsorption separation of the straight chain C_4 hydrocarbons therefrom may be in the liquid phase or in the gaseous or vapor phase. Any suitable means for effecting liquid-solid contact or vapor-solid contact may be employed. For example, presumably the simplest operation, a liquid mixture containing straight chain and non-straight chain C_4 hydrocarbons is contacted with the solid selective adsorbent to form a slurry. After sufficient time has been allowed for the adsorption of the straight chain C_4 hydrocarbons the remaining liquid phase is separated from the slurry and the solid adsorbent subsequently separately treated for the removal or desorption of the straight chain C_4 hydrocarbons therefrom.

The selective adsorbent as employed in the adsorptive separation operation may be in the form of a fixed bed, a moving bed, a fluidized bed and the mixture of straight chain and non-straight chain C_4 hydrocarbons undergoing treatment may pass in direct concurrent or countercurrent contact with the selective adsorbent.

The adsorption operation may take place at any temperature in the range of 50–700° F. and higher depending upon whether or not it is desired to maintain the mixture undergoing separation in the liquid or vapor phase and depending to some extent upon the composition of the mixture of C_4 hydrocarbons and the amount of straight chain C_4 hydrocarbons to be removed. Also any desired adsorption pressure may be employed depending upon whether or not it is desired to carry out liquid or vapor phase adsorption. In a liquid phase adsorption operation it is preferred to maintain the adsorption temperature in the range 50–300° F., more or less. In a vapor phase adsorption operation it is preferred to maintain the adsorption temperature in the range 100–500° F., more or less.

After the adsorption of the straight chain hydrocarbons has been carried out to the desired extent, the selective adsorbent is treated to desorb and separately recover the straigth chain hydrocarbons therefrom. Desorption of the straight chain hydrocarbons is conveniently effected by the application of heat and is preferably effected by contacting the adsorbent with a hot stripping medium such as flue gas, nitrogen, methane, hydrogen, carbon dioxide, air or oxygen-containing gas under controlled temperature conditions, steam, preferably superheated steam, or any suitable inert normally gaseous material. Generally any gaseous stripping medium is suitable provided it possesses molecular dimensions sufficiently small to permit the entry of the molecules of the desorbing or stripping medium into the pores of the selective adsorbent and thereby desorb or displace the adsorbed straight chain C_4 hydrocarbons. Usually a desorption temperature in the range 200–1100° F., preferably a temperature in the range 300–800° F., is sufficient to effect substantially complete desorption of the adsorbed straight chain C_4 hydrocarbons from the selective adsorbent. Although the desorption temperature may be the same as the adsorption temperature, i.e. isothermal adsorption-desorption operations, it is sometimes desirable to maintain the desorption temperature about 100–300° F. higher than the adsorption temperature. As a gen-

eral rule the desorbing temperature should be high enough so that the adsorbed straight chain C_4 hydrocarbons are relatively quickly desorbed without at the same time causing destruction of the selective adsorbent or decomposition or cracking of the adsorbed-desorbed straight chain C_4 hydrocarbons.

Liquid water, such as superheated water, i.e. water at a temperature greater than 212° F. and at a superatmospheric pressure, may also be employed as a desorbing medium. It is advantageous to employ steam or superheated steam as the desorbing or stripping medium since, after the desorption of the straight chain hydrocarbons has been effected by superheated steam, the recovery of the straight chain hydrocarbons is effected by simply condensing the steam. Following steam desorption it is usually desirable to displace the steam now adsorbed to some extent within the pores of the adsorbent by contacting the adsorbent with a purge gas or stripping medium such as a flue gas, nitrogen, hydrogen, natural gas and the like, preferably at an elevated temperature, in order to sweep the steam from the pores of the adsorbent. It is mentioned that the desorption operation may be carried out at any suitable pressure, higher, lower or equal to the adsorption pressure. It is preferred, however, to carry out the desorption operation at a pressure substantially lower than the adsorption pressure, especially when an elevated adsorption pressure is employed.

After the adsorbed straight chain C_4 hydrocarbons have been desorbed from the adsorbent the resulting desorbed-regenerated adsorbent is now in condition to be contacted with additional fresh feed admixture of straight chain and nonstraight chain C_4 hydrocarbons to effect the desired separation. In actual practice it has been observed that the selective adsorbent, such as a calcium alumino-silicate, as exemplified by Linde Type 5A Molecular Sieve, may be employed substantially indefinitely in the adsorption-desorption operation without evidencing any substantial change in adsorptive capacity.

In accordance with a special feature of this invention the adsorptive separation of the straight chain or n–C_4 hydrocarbons is carried out at a temperature below about 307° F., the critical temperature of n-butane, in order to employ more effectively the adsorptive capacity of the selective adsorbent. Furthermore in the practice of this invention it is preferred to carry out the desorption of the adsorbed n–C_4 hydrocarbons at a temperature above about 307° F., the lowest critical temperature the n–C_4 hydrocarbons, including butene-1, butene-2 and butadiene, whose critical temperatures are 320° F., 311° F. and 325° F., respectively. Accordingly by contacting a n–C_4 hydrocarbon stream containing n-butane and an n-butene, e.g., butene-1 and/or butene-2 and/or a butadiene with a selective adsorbent of the type described hereinabove it is possible to fractionate such a stream into its various constituent n–C_4 hydrocarbons by carrying out the adsorption operation at a temperature above the critical temperature of a particular n–C_4 hydrocarbon, which particular hydrocarbon under these conditions would be substantially unadsorbed, or at most, only adsorbed to a minor extent. As an example it is possible to selectively adsorb butene-1 and the remaining n–C_4 hydrocarbons over n-butane by carrying out the adsorption operation at a temperature above the critical temperature of n-butane (307° F.) but below the critical temperature of the other n–C_4 hydrocarbon or hydrocarbons, e.g., butene-1, 320° F., or butadiene, 325° F. to be adsorbed. With respect to the selective desorption of adsorbed n–C_4 hydrocarbons from the selective adsorbent, e.g. to selectively desorb n-butane over butene-1, both adsorbed in an adsorbent, the desorption is carried out at a temperature above 307° F. but below 320° F.

Alkylation of the separated non-straight chain C_4 hydrocarbons

The resulting treated or separated branch chain C_4 hydrocarbon effluent comprising predominantly isobutane and isobutene is subjected to catalytic alkylation for the production of an alkylate which is particularly suitable as a high octane blending agent in aviation and/or motor gasolines. This treated effluent from the adsorption operation is particularly suitable as a feed stock to an alkylation reaction since it contains a substantial amount of isobutane and its corresponding branch chain olefinic hydrocarbon, isobutene. It is realized that depending upon the completeness or thoroughness of the adsorption operation the treated branch chain C_4 hydrocarbon effluent may contain minor amounts of straight chain C_4 hydrocarbons, such as n-butane and the n-butenes. The presence of n-butenes in the alkylation reaction, however, is desirable. The n-butane would pass through the alkylation reaction substantially unchanged, acting primarily as a diluent and may be separately recovered from the resulting alkylate. Any suitable catalytic alkylation operation may be employed, such as H_2SO_4 catalytic alkylation or HF catalytic alkylation.

Sulfuric acid catalytic alkylation is carried out in the liquid phase at a relatively low temperature, such as a temperature in the range 35–60° F. The liquefied branched chain C_4 hydrocarbons comprising isobutane and isobutene, namely a branched chain alkane and a mono-olefin, are contacted with concentrated, about 98%, sulfuric acid whereby isobutane is alkylated by the isobutene or any other mono-olefin which may be present in the alkylation reaction mixture. Since the alkylation reaction is exothermic the reaction temperature is controlled and the heat of reaction is removed by autorefrigeration wherein continuous vaporization of the alkylation reaction mixture is permitted. The resulting vaporized gaseous hydrocarbon fraction is compressed, condensed and returned to the alkylation reactor. Another method of effecting temperature control during the alkylation reaction is by means of the so-called effluent refrigeration system wherein the alkylation reaction mixture comprising hydrocarbons and acid is permitted to settle to form a hydrocarbon phase and an acid phase. A portion of the hydrocarbon phase is separated and flashed at reduced pressure, thereby reducing the temperature of the separated hydrocarbon phase. The resulting relatively cool hydrocarbon phase is then employed as a cooling medium for the alkylation reaction. Following the alkylation reaction the resulting alkylate is washed with caustic to remove the acid catalyst and fractionated for the recovery of the resulting alkylate.

In HF alkylation, which is suitable for feed stream comprising predominantly isobutane and isobutene, the liquefied reactants are contacted with liquid HF at a suitable low temperature, usually in the range 60–160° F., to effect alkylation. The alkylation reaction effluent consisting of unreacted hydrocarbons, alkylate and dissolved HF is fractionated for the separation of these components and the ultimate recovery of the product alkylate.

During the alkylation reaction, particularly when H_2SO_4 is employed as the alkylation catalyst, it is desirable to maintain an isoalkane/alkene or mono-olefin mol ratio in the range 1.7–1.1 in the fresh feed to the alkylation reaction. If required to maintain this desired ratio additional isobutane and isobutene or n-butenes, propylene and C_5 and C_6 mono-olefins may be added. Desirably additional needed n-butene may be obtained from the desorbate from the adsorption operation and/or from the effluent from the dehydrogenation reaction.

Dehydrogenation of the separated straight chain C_4 hydrocarbons

The straight chain C_4 hydrocarbons comprising n-butane, and advantageously n-butenes, after desorption from the selective adsorbent are subjected to catalytic de-

hydrogenation for the production of butadiene and/or n-butenes. When the straight chain C_4 hydrocarbon stream being treated comprises a substantial or major amount of or comprises substantially only n-butane it may be catalytically dehydrogenated in a one-step operation to butadiene or, if desired, first to n-butene and then subsequently to butadiene. When, however, the straight chain C_4 hydrocarbon stream comprises a major amount of n-butenes it is preferably directly dehydrogenated to butadiene.

Various catalytic dehydrogenation processes are known and are suitable for the catalytic dehydrogenation of n-butane and n-butenes to n-butenes and/or butadiene. One suitable method is the Houdry butane dehydrogenation process, see The Petroleum Engineer, November 1954, pages C–7 through C–10, the disclosures of which are hereby incorporated and made part of this disclosure, wherein n-butane is catalytically dehydrogenated to n-butene and/or butadiene by vapor phase contact with an active chromic oxide-alumina catalyst consisting of active alumina impregnated with 18–20% by weight chromic oxide. For butadiene production the dehydrogenation reaction is carried out at a temperature of about 1125° F., at a pressure of 5 mm. Hg. absolute and at a throughput of about 1–1.5 vol. feed/vol. cat./hr. For the production of n-butene from n-butane the dehydrogenation reaction is carried out at a temperature of about 1125° F., at a pressure of 10 p.s.i.g. and at a throughput of 1.5–2.0 vol. feed/vol. cat./hr.

Another method suitable for the catalytic dehydrogenation of straight chain C_4 hydrocarbons for the manufacture of butadiene is particularly applicable to a C_4 hydrocarbon stream comprising a major amount of n-butene. In accordance with this method a C_4 hydrocarbon stream containing a major amount of n-butene (butene-1 and/or butene-2) is contacted in the presence of superheated steam at an elevated temperature in the range 1050–1300° F. with an iron oxide catalyst whereby at least a portion of the n-butenes are converted to butadiene.

In both the above-described catalytic dehydrogenation operations the resulting produced butadiene is recovered by extractive distillation from the dehydrogenation reaction effluent by contact with a suitable adsorbing medium, such as liquid furfural or cuprous ammonium acetate. Other suitable selective liquid adsorbents may be employed, e.g., aniline. The remaining dehydrogenation reaction effluent comprising n-butane and/or n-butenes is returned into the dehydrogenation reaction for the eventual conversion into butadiene. If the dehydrogenation reaction is carried out substantially only for the production of n-butenes from n-butane liquid furfural selective solvent is employed for the recovery of the n-butenes from n-butane, the n-butane being recycled to the dehydrogenation reaction and the separated n-butenes recovered as a product or passed to a second stage catalytic dehydrogenation reaction for the production of butadiene therefrom.

The following is exemplary of the practice of this invention.

EXAMPLE 1

A fresh feed C_4 hydrocarbon refinery stream having the composition set forth in Table No. II,

TABLE NO. II

Component:	Liquid vol. percent
Propane and lighter	3.6
Isobutane	28.6
Isobutene	14.1
Butene–1	11.1
Butadiene	0.2
n-Butane	22.1
Butenes-2	16.7

is combined with recycled catalytic dehydrogenator reactor effluent comprising about 49 vol. percent butene–1, 17 vol. percent butene-2, 22 vol. percent n-butane, 2 vol. percent butadiene and 8 vol. percent iso-C_4 hydrocarbons and the resulting combined stream is contacted with a solid selective adsorbent to effect substantially complete removal of the straight chain C_4 hydrocarbons from the non-straight chain C_4 hydrocarbons. The resulting treated effluent, now substantially free of straight chain C_4 hydrocarbons, has the following approximate composition in vol. percent: isobutane 67% and isobutene 33%. This admixture of isobutane and isobutene is subjected to liquid phase alkylation reaction employing H_2SO_4 or HF as the alkylation catalyst for the production of a relatively high molecular weight, high octane branched chain alkylate. The adsorbed straight chain C_4 hydrocarbons are desorbed, recovered and catalytically dehydrogenated for the production of butadiene.

Preferably, when treating a combined C_4 hydrocarbon stream, as indicated above, or a C_4 refinery stream containing less than 50 mol or vol. percent iso-C_4 hydrocarbons, such as a C_4 stream having a composition substantially the same as that set forth in Table No. II, the C_4 stream is prefractionated to produce an overhead fraction containing substantially all the branched chain or iso-C_4 hydrocarbons in the C_4 stream, such as an overhead fraction having the composition set forth in Table No. III,

TABLE NO. III

Component:	Liquid vol. percent
Propane and lighter	5.1
Isobutane	38.8
Isobutene	19.6
Butene-1	18.5
Butadiene	0.3
n-Butane	10.7
Butene-2	7
Pentane and heavier	----

and containing more than 50 vol. or mol percent iso-C_4 hydrocarbons, substantially all of the iso-C_4 hydrocarbons in the stream so fractionated, and to produce a bottoms fraction containing substantially all of the straight chain C_4 hydrocarbons stream so fractionated, such as a bottoms fraction containing more than 50 vol. or mol percent straight chain C_4 hydrocarbons, e.g., a bottoms fraction having the composition set forth in Table No. IV.

TABLE NO. IV

Component:	Vol. percent
Propane and lighter	---
Isobutane	1.1
Isobutene	2.2
Butene-1	8.8
Butadiene	---
n-Butane	39.2
Butene-2	38.3
Pentanes and heavier	10.4

The overhead fraction is then contacted with the selective adsorbent to remove substantially all of the straight chain hydrocarbons therefrom, followed by desorption of the straight chain hydrocarbons and separation of the propane and lighter hydrocarbons therefrom to produce a straight chain C_4 stream comprising predominantly n-butane and n-butenes. If desired this stream may be further treated, as by selective adsorption and/or fractionation or by extractive distillation in the presence of liquid furfural, to yield an effluent or raffinate stream comprising substantially only n-butane and an extract stream comprising substantially only n-butene.

The bottoms fraction, after removal of the pentanes and heavier therefrom, may be admixed with the above-described straight chain C_4 stream, or the above-described raffinate or extract stream, preferably the extract stream, and passed to the catalytic dehydrogenator. By operating in the above manner the total amount of hydro-

carbons treated by selective adsorption for the separation of isobutane and isobutene is substantially and significantly reduced and is the preferred embodiment of the practice of this invention. The iso-C_4 hydrocarbons separated during the above-described operation are sent to the alkylation reactor and the n-C_4 hydrocarbons, comprising substantially all of the above-indicated admixture, together with minor amount of unseparated iso-C_4 hydrocarbons present in the above-indicated bottoms fraction, are sent to the catalytic dehydrogenator.

The resulting admixture comprised predominantly of straight chain C_4 hydrocarbons, principally butene-1 and butene-2, together with a minor amount of n-butane, preferably less than 10 liquid vol. or mol percent n-butane (based on C_4 hydrocarbon content) by separating substantially all of the n-butane from the aforesaid bottoms fraction, is subjected to catalytic dehydrogenation by contact with an iron oxide catalyst (major amount Fe_2O_3 promoted with minor amounts of potassia and chromia) at a temperature in the range 1100–1200° F. for the production of butadiene. A feed admixture of straight chain C_4 hydrocarbons to the dehydrogenation reactor might have the following composition in liquid volume percent: butene-1 31.5%, butadiene 1.1%, n-butane 6.6%, butene-2 56.6%, iso-C_4 hydrocarbons 4.2%. The hydrocarbons issuing from the dehydrogenation reactor might have the following composition in mol percent: propane and lighter 41.0, isobutane 0.3, isobutene 2.0, butene-1 13.9, butadiene 13.1, n-butane 3.9, butenes-2 25.3, pentane and heavier 0.5. After the dehydrogenation reactor effluent has been subjected to suitable fractionation and solvent extraction for the separation and recovery of butadiene therefrom there is recovered a separate butadiene stream containing at least about 97 mol percent butadiene and about 2% butene-1. The remaining n-butane and n-butene in the dehydrogenation reactor effluent are recycled to the dehydrogenation reactor.

This application is a continuation of copending patent application Serial No. 489,232, filed February 18, 1955, now abandoned.

As will be apparent to those skilled in the art in the light of the foregoing disclosure many modifications, substitutions and changes are possible without departing from the spirit or scope of this invention.

We claim:

1. A method of treating a C_4 hydrocarbon stream consisting essentially of n-butane, isobutane, isobutene and n-butene which comprises contacting said hydrocarbon stream with a selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, recovering from the aforesaid adsorption operation a first stream comprising isobutane and isobutene, desorbing the adsorbed straight chain hydrocarbons from said adsorbent under conditions to effect the selective desorption of n-butane followed by the selective desorption of n-butene, the selective desorption of n-butane being effected at a temperature not greater than the critical temperature of n-butene, subjecting the resulting selectively desorbed n-butene to catalytic dehydrogenation for the resulting production of butadiene and separating butadiene from the effluent issuing from the aforesaid dehydrogenation reaction.

2. A method of treating a C_4 hydrocarbon stream consisting essentially of n-butane, isobutane, isobutene and n-butene which comprises contacting said hydrocarbon stream with a selective adsorbent which selectively adsorbs straight chain hydrocarbons to the substantial exclusion of non-straight chain hydrocarbons to adsorb straight chain hydrocarbons therefrom, recovering from the aforesaid adsorption operation a first stream comprising isobutane and isobutene, desorbing the adsorbed straight chain hydrocarbons from said adsorbent under conditions to effect the selective desorption of n-butane followed by the selective desorption of n-butene, the selective desorption of n-butane being effected at a temperature not greater than the critical temperature of n-butene, subjecting the resulting selectively desorbed n-butane to catalytic dehydrogenation for the resulting production of butadiene and separating butadiene from the effluent issuing from the aforesaid dehydrogenation reaction.

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