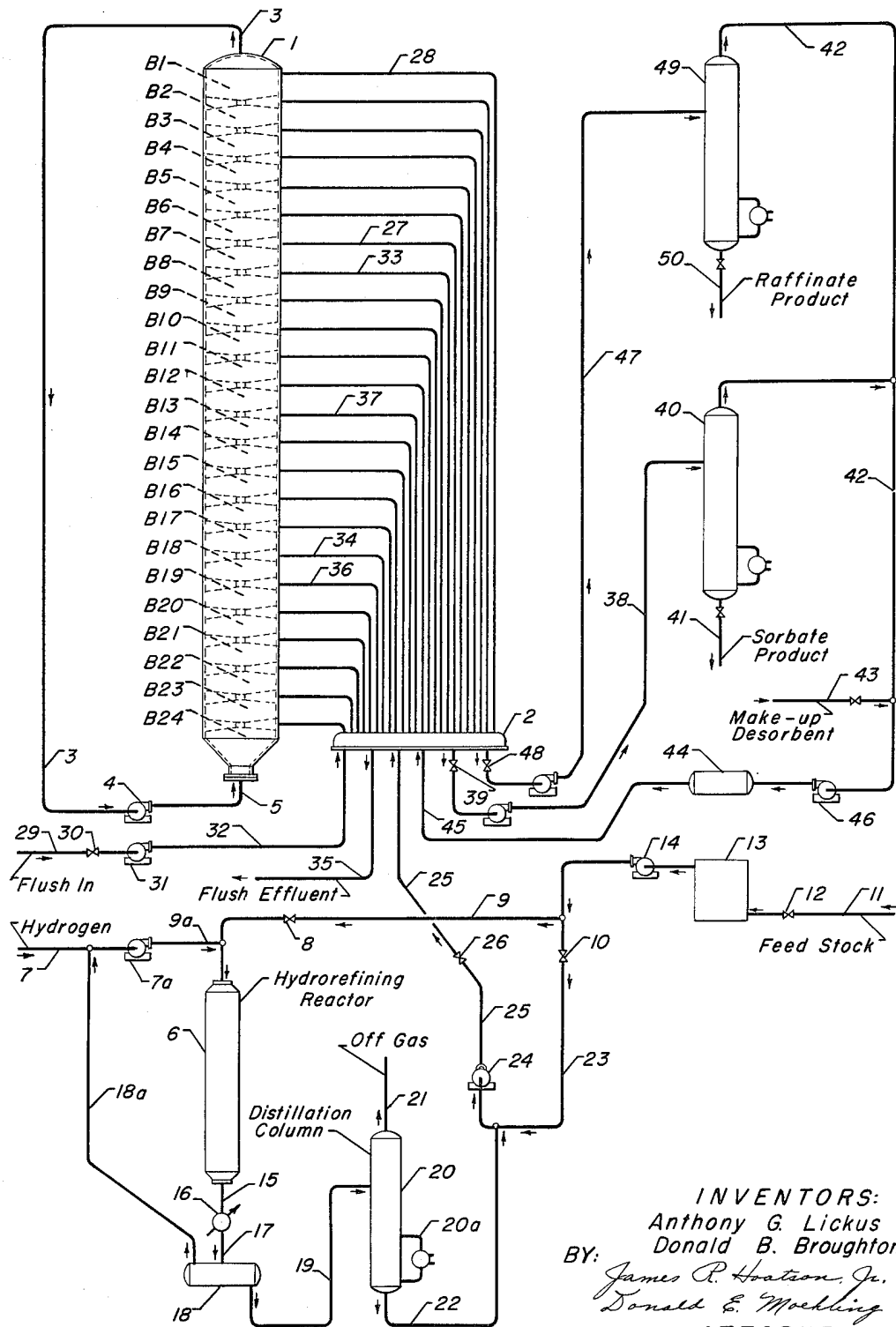


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SEPARATION OF ALIPHATIC PARAFFINS FROM NORMALLY
LIQUID HYDROCARBON MIXTURES
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3,239,455

**SEPARATION OF ALIPHATIC PARAFFINS
FROM NORMALLY LIQUID HYDROCARBON
MIXTURES**

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7 Claims. (Cl. 208—212)

This application is a continuation-in-part of our co-
pending application, Serial Number 171,205, filed Feb-
ruary 5, 1962, now abandoned.

This invention relates to a process for recovering the
relatively straight chain aliphatic hydrocarbon compo-
nents of a normally liquid hydrocarbon mixture contain-
ing the same. More specifically, this invention concerns
a process for recovering the normal aliphatic compo-
nents from a hydrocarbon mixture in which process the
feed stock is pre-hydrogenated to eliminate sulfur and
nitrogen-containing compounds and/or unsaturated hy-
drocarbons, in the separation stage of which a porous,
inorganic molecular sieve sorbent is utilized as the
separating agent. Other specific applications of the
present process, particularly preferred herein, involve the
foregoing separation in a fixed bed, simulated moving
bed, process capable of producing a raffinate product con-
sisting substantially entirely of cyclic and/or branched
chain components and a sorbate product consisting es-
sentially of normal aliphatic hydrocarbons.

Petrochemical processes are rapidly acquiring an im-
portant status as a source of many basic chemicals re-
quired by the chemical process industries and for the
manufacture of many new as well as many established
products. For example, straight chain hydrocarbons re-
covered from the kerosene boiling range fraction of
petroleum have become an important source of raw ma-
terials for the manufacture of long chain alcohols and
olefins, particularly for use in the production of de-
tergents having special properties. Thus, straight chain
alkyl groups constitute a preferred structure of the long
chain alkyl substituents in alkyl aryl sulfonate deter-
gents, as well as for the production of many other types
of detergents requiring a long chain alkyl group as the
hydrophobic portion of the detergent molecule. Such
straight chain alkyl groups yield biologically "soft" de-
tergent products which are degradable by bacterial di-
gestion and therefore do not appear in the effluent of
sewage treatment processes to contaminate natural water
supplies. In the production of jet fuels it has also been
found that the normal or relatively straight chain ali-
phatic components of kerosene and gas oil boiling range
fractions for jet fuel use are the components of great-
est economic value because these hydrocarbons produce
greater thrust per unit weight of fuel than other hy-
drocarbon types and when used as fuels in jet engines,
produce a non-luminous, non-smoky exhaust. For these
and many other reasons a substantial existing and an
accelerating potential demand for straight chain ali-
phatic hydrocarbons is developing in the petrochemical
arts. The normal components of these and other boil-
ing range cuts of normally liquid hydrocarbon mixtures
are useful for a variety of other purposes; thus, the
normal aliphatic components of naphtha boiling range
fractions, such as n-hexane, n-heptane, etc., are useful
as solvents and as a source of paraffins for conversion
to normal olefins via dehydrogenation.

The foregoing long, straight chain aliphatic paraffins,
being generally recovered as specific boiling range frac-
tions from petroleum or its conversion products as the
only readily available and not too costly source of supply,

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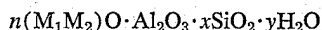
are almost without exception contaminated by sulfur
and nitrogen-containing as well as olefinic and/or aro-
matic components which interfere with the recovery
of the desired normal aliphatic components utilizing mo-
lecular sieves as the separating agent by deactivating the
molecular sieves and reducing their capacity. Although
the polar contaminants such as the nitrogen-containing
and sulfur-containing compounds present in such frac-
tions are especially detrimental to the activity and capacity
of molecular sieves, olefinic and aromatic hydrocarbons,
particularly the polycyclic aromatics are also detrimental
and constitute feed stock components desirably removed
and converted by means of the present pre-hydrogenation
treatment prior to the separation step. The present two-
stage combination process which includes a preliminary
feed stock hydrogenation step is intended to treat the feed
stock whereby such contaminants are removed therefrom
by conversion to sulfur and nitrogen-free, saturated hy-
drocarbons and thereby substantially enhance the effec-
tiveness of the molecular sieves as separating agents.

Accordingly, one object of this invention is to pro-
vide a non-contaminated source of normally liquid,
straight chain hydrocarbons initially supplied from readily
available sources. Another object of this invention is
to provide a process for the recovery of a substantially
pure straight chain, paraffinic hydrocarbon from a hydro-
carbon mixture containing said hydrocarbon by means of
an efficient, low cost process. Still another object of
this invention is to provide a means for converting un-
saturated and the nitrogen and sulfur-containing compo-
nents present in a normal paraffin-containing hydro-
carbon mixtures to saturated hydrocarbons, thereby elimi-
nating such contaminants from the feed stock which have
an undesired effect on the activity of the absorbent used
in the process to separate the straight chain components.

In one of its embodiments this invention relates to a
process for separating a relatively straight chain aliphatic
hydrocarbon from a normally liquid hydrocarbon mixture
which comprises catalytically hydrogenating said mixture
at hydrogenation reaction conditions sufficient to reduce
at least the olefinic unsaturation in the hydrocarbons com-
prising said mixture, thereafter contacting the resulting
hydrogenated mixture with a porous, inorganic sorbent
of the molecular sieve type in which the pores are of a
size capable of admitting a normal aliphatic hydrocarbon
into the porous structure of the sorbent and of rejecting
branched chain and cyclic hydrocarbons, withdrawing
raffinate comprising a non-sorbed, non-straight chain
hydrocarbon from the sorbent particles and thereafter
contacting the sorbent containing the adsorbed, relatively
straight chain aliphatic component of said mixture with
a desorbent comprising a straight chain hydrocarbon hav-
ing a boiling point at least 20° F. outside of the boiling
range of the adsorbed component of the mixture.

The use of molecular sieves as a separating agent for
the recovery of the straight chain or normal aliphatic
components of hydrocarbon mixtures has become recog-
nized as one of the most effective means for segregating
straight chain compounds from their close-boiling
branched chain aliphatic and cyclic structural isomers.
This method of separation which is referred to as a
"sorption" process, depends upon the existence of pores
in the structure of the molecular sieve sorbent particles
having cross-sectional diameters slightly greater than the
mean effective, transverse diameter of the normal ali-
phatic hydrocarbons present in the feed stock (i.e., about
4.9 Angstrom units), but less than the transverse diam-
eter of the branched chain aliphatic and cyclic compo-
nents, or less than about 5.6 Angstrom units. A variety
of solid substances of both natural and synthetic origin,
contain pores within the foregoing selective pore size

range and accordingly are useful sorptive separating agents for segregating the long, straight chain or normal hydrocarbons from the branched chain or cyclic components of the hydrocarbon mixture comprising the feed stock. In the process of this invention the preferred molecular sieve sorbents which act as the separating agent for recovering the normal and relatively straight chain aliphatic components of the hydrocarbon feed stock are the dehydrated metal aluminosilicates. These sorbents are prepared by removing the water of crystallization from certain zeolitic aluminosilicates having compositions corresponding to the following empirical formula:



in which M_1 and M_2 are selected from the alkali and alkaline earth metals, such as sodium, potassium and lithium of the former group and calcium, magnesium, strontium, and barium of the latter group, n is a number having a value in the range: 1 ± 0.2 , x is a number having a value in the range: 1.85 ± 0.5 , and y is a number having a value in the range of 4 to 6. The properties and structure of these sorbents are described in papers of D. W. Breck et al., published in: Scientific American, January 1959, pages 85-94 and in United States patents issued to R. M. Milton et al.: 2,882,243 and 2,882,244. The members of this group of sorbents which contain pores having mean cross-sectional diameters of from about 5 to about 6 Angstrom units are capable of admitting into the porous structure of the sorbent the normal or straight chain aliphatic components of hydrocarbon mixtures made up of hydrocarbons having at least four carbon atoms per molecule and of rejecting (i.e., not admitting) the components of the mixture having a branched chain and cyclic structure.

The dehydrated metal aluminosilicates in which a major proportion of the M_2 metal is an alkaline earth metal contain pores having cross-sectional diameters of from about 5 to about 6 Angstrom units, making these sorbents especially suitable for use in the present process for separating the desired normal components of a hydrocarbon feed stock boiling in the specified range. These inorganic compositions are preferably prepared by synthetic means, for example, by the process of United States Patent 2,882,243, issued to Robert M. Milton. Other suitable molecular sieve sorbents are the alkaline earth metal-exchanged, naturally occurring zeolites such as chabazite, analcite, phacolite and others, dehydrated by calcination to develop the porous structure of the particles. In order to provide particulate solid sorbents which can be used in fluid flow contacting processes without large pressure drops through the beds of sorbent particles, the finely divided crystals of metal aluminosilicates (the form in which these zeolites inherently and naturally occur) are preferably composited with binding clays and pilled into larger particles such as short cylinders, spheres, etc. prior to use in the present fluid-flow contacting process.

A suitable source of mixed structural isomers of aliphatic hydrocarbons comprising normal and relatively straight chain components of C_4 to C_{20} chain length, utilized herein as the primary feed stock to the process of this invention, are available as fractions from various natural and synthetic sources. Thus, the hydrocarbon products formed in the Fischer-Tropsch process may be fractionated to separate a cut boiling up to about 650° F., including any narrower boiling range fraction within such range, may be utilized as feed stock in this process. A generally more convenient source of feed stocks are the middle and upper boiling range fractions of petroleum or portions thereof having boiling points corresponding to the middle boiling range naphthas, kerosene, gas oil and/or diesel fuel cuts of petroleum and more preferably, fractions of petroleum boiling from about 60° to about 650° F. These fractions or cuts may be separated from crude petroleum itself or from certain conversion

products thereof, such as the gasoline, kerosene and diesel oil fractions of thermally or catalytically cracked gas oil products, preferably hydrocracked oils, reformed naphthas and gas oils, and especially, the foregoing cuts separated from catalytically reformed naphthas and kerosene fractions converted in the presence of hydrogen. All of the foregoing sources of feed stock, as well as other synthetically prepared and naturally-occurring hydrocarbon fractions, are mixtures of isomers and structural types, including branched chain aliphatic isomers and their cyclic analogues, such as the naphthenic and aromatic species. The segregation and recovery of the normal and relatively straight chain aliphatic components of these feed stocks is the special objective to which the process of this invention is directed.

Most primary sources of the feed stock to the present process which may contain components of from C_4 to C_{20} carbon atom content or any mixture of straight chain and branched chain hydrocarbons within the foregoing range, such as a mixture of C_4 to C_{10} hydrocarbons present in a gasoline boiling range fraction of petroleum contain varying proportions of olefinic and/or aromatic components, as indicated by the adsorption of bromine when the fraction is mixed with the elemental form of this reagent. These fractions, when derived from petroleum also contain various polar nitrogen and sulfur-containing compounds such as the mercaptans and pyrroles which adversely affect the present molecular sieve sorbents when the feed stock fraction is contacted therewith. In some instances, depending upon the source of the petroleum fraction which may be derived from a conversion product of a hydrocarbon initially separated from petroleum, the fraction may contain significant proportions of polyolefinic hydrocarbons as well as monoolefins in the same molecular weight range.

The presence of olefinic hydrocarbons and particularly diolefins, or aromatic or sulfur and nitrogen-containing compounds in the feed stock to the separation stage of the present process in which the hydrocarbon mixture is contacted with the aluminosilicate molecular sieve sorbent is the cause of direct and immediate loss in the activity of the molecular sieve adsorbent, presumably because of blocking of the pore openings in the structure of the molecular sieve adsorbent with the preferentially adsorbed polar and unsaturated compounds. Although the pore openings in the molecular sieve sorbents are not of sufficient size to admit aromatic hydrocarbons (which are cyclic and have cross-sectional diameters greater than the pore openings), at least some of the aromatics are adsorbed on the surface of the sorbent, tending to block the pore openings by virtue of the size of the aromatic molecule. This effect is minimized by operating the separation stage of the process at a sufficiently elevated temperature to reduce the adsorptivity of the aromatics on the sorbent; however, the preferred method of operating the present process is to prehydrogenate the feed stock at hydrogenation conditions sufficiently severe to reduce a large proportion of the aromatic components to naphthenes which are not sorbed in the pores or adsorbed on the surface of the molecular sieves.

Metal aluminosilicates of the type present in the composition of molecular sieve adsorbents are known to be slightly acidic and capable of causing the polymerization of mono-olefinic hydrocarbons and particularly diolefins which may be present in the hydrocarbon feed stock. Even though the proportion of mono- and/or diolefins in the feed stock is relatively minute, the acidic aluminosilicates are active polymerization sites at any concentration of the olefin or diolefin in the feed stock and thus are believed to become the sites of the formation of high molecular weight resinous materials capable of clogging the pore openings into the pores of the molecular sieve particles. As the pore openings become filled with high molecular weight materials of resinous character, deactivation of the molecular sieve particles progresses as long as olefins or diolefins are present in the feed stock;

the rate of such deactivation would be expected to, and in fact does increase as the concentration of olefin and/or diolefin components in the feed stock increases. Whether polymerization of the olefinic components of the feed stock is the actual cause of such deactivation, it is noted, nevertheless, that the rate of deactivation is directly proportional to the olefin and/or diolefin content of the feed stock and that a major cause of such deactivation ceases to be evident when the pre-hydrogenation step of the present process (accompanied by the disappearance of mono- and diolefin hydrocarbons) is incorporated into the process flow. Such prolongation of the activity of molecular sieve sorbents is also evident as the concentration of nitrogen and sulfur-containing compounds in the feed decreases via pre-hydrogenation of the hydrocarbon mixture.

Still another effect realized by the pre-hydrogenation step of the present combination of the process is the removal of adsorptive aromatic hydrocarbons from the feed stock. Although the presence of aromatic hydrocarbons in the feed stock is not as significant a factor involved in the declining activity of molecular sieves accompanying the use of these adsorbents, aluminosilicates, including the present molecular sieves, are known to have surface adsorptive capacity and are thus capable of retaining aromatic hydrocarbons by electrostatic forces of attraction on the surface of the molecular sieve particles. Although aromatic hydrocarbons adsorbed on the surface of molecular sieve particles are displaced therefrom by feed stock as adsorption continues and the adsorbent gradually becomes "spent" with respect to the retention of normal hydrocarbons within the internal pore structure of the adsorbent, the presence of aromatics adsorbed on the surface of the molecular sieve particles during the initial activated stage of the process cycle following regeneration of the molecular sieves tends to reduce the over-all capacity and activity of the molecular sieves during such initial stages of the process flow. The hydrogenation stage of the present process in which the feed stock is contacted with an active hydrogenation catalyst of the type hereinafter characterized may be operated, if desired, to reduce aromatic components, if present in the feed stock, to naphthenic hydrocarbons and in a preferred method of operating the pre-hydrogenation stage of the process, hydrogenation reaction conditions are specifically provided to accomplish the saturation or reduction of most of the aromatic components if these are present in the feed stock.

Hydrogenation of the present mixed hydrocarbon feed stock which precedes the adsorptive separation stage of the present combination process is effected at sufficiently severe hydrogenation reaction conditions to saturate at least substantially all of the olefinic hydrocarbons, including polyolefins, and more preferably at reaction conditions sufficiently severe to simultaneously saturate any aromatic compounds, if any are present in the feed stock, thereby converting the aromatics to naphthenes or cycloparaffins. During the hydrogenation reaction, the feed stock is contacted with hydrogen and in the presence of a hydrogenation catalyst which enhances the speed of the reaction and promotes specific conversions not otherwise occurring in the absence of a catalyst, such as ring saturation. Typical useful hydrogenation catalysts for this purpose include the Group VIII metals of the Periodic Table, their oxides or sulfides, generally composited with a suitable refractory support, such as alumina, silica, silica-alumina, silica-magnesia, silica-zirconia, and other metal oxides or metal oxide mixtures calcined or otherwise heat treated to form a physically stable, refractory support. Of the Group VIII metals, metal oxides and metal sulfides, the iron group metals, particularly nickel and cobalt, and the so-called "noble" metals: platinum and palladium, are the preferred members of this group. The metal is composited with the support by methods well-known in the art and in some cases certain modifying components may be added to the catalyst composi-

tion, as in the case of nickel or cobalt sulfide, which when combined with molybdenum oxide, forms a nickel or cobalt thiomolybdate. The elemental metal is generally converted to its sulfide or oxide derivative after the metal has been composited with the refractory support, for example, by heating the composite in the presence of hydrogen sulfide or air. Alternatively, the metal sulfide or oxide may be mixed with the oxide support prior to forming the composite into discrete particles, in which form the catalyst is finally used in the process. The nickel and cobalt thiomolybdate derivatives are especially active hydrogenation catalysts when composited with a refractory metal oxide carrier or support such as alumina. The most active, and therefore, the preferred hydrogenation catalysts are the supported nickel and platinum or palladium catalysts composited with refractory metal oxide supports such as alumina, silica or an aluminosilicate which may be prepared synthetically with various proportions of alumina and silica or may be derived from naturally occurring mineral sources, such as kieselguhr clay, bauxite, attapulgus clay, cracking catalyst composites, etc. In the case of the nickel and cobalt supported catalysts, the active metallic component is present in the composites in amounts up to about 20 percent by weight, and more preferably, from about 0.5 to about 10 percent by weight of the catalyst composition. Platinum and palladium supported catalysts generally contain from 0.01 to about 1 percent by weight of the active, noble metal component which is preferably composited with the refractory support in a finely divided crystalline form (generally as a reduced sulfide precipitate) of enhanced activity for hydrogenation purposes.

The feed stock is hydrogenated by contacting the feed stock mixture of hydrocarbons with the hydrogenation catalyst in the presence of a molar excess of hydrogen, sufficient to saturate all of the unsaturated double bonds in the olefinic and/or aromatic (if any) components present in the feed stock. The hydrogenation catalyst simultaneously reduces any sulfur or nitrogen-containing compounds present in the feed stock to hydrogen sulfide and ammonia which are withdrawn from the process in the excess hydrogen.

Although the catalyst may be conveniently stirred into the oil in the presence of an atmosphere of hydrogen above the oil surface, the preferred procedure comprises passing a flowing stream of the oil at the conversion temperature over a fixed bed of the hydrogenation catalyst particles in the presence of hydrogen supplied at the required pressure. For this purpose the feed stock contacted with the catalyst in liquid phase is supplied at a temperature of from about 80° to about 350° C. and more preferably, at a temperature of from about 125° to about 200° C. and at a superatmospheric pressure, preferably within the range of from about 5 to about 50 atmospheres. Hydrogenation proceeds at a relatively rapid rate, particularly at the above-specified elevated temperatures and pressures and particularly in the presence of one of the foregoing hydrogenation catalysts. Reaction periods of from 5 minutes to 1 hour or liquid hourly space velocities (in the presence of a solid catalyst) of from 0.1 to 2.5 volumes of feed stock per volume of catalyst per hour are generally sufficient to hydrogenate all of the olefinic and in most cases, all of the aromatic double bonds in the feed stock and to convert the nitrogenous and sulfur-containing compounds to paraffins and naphthenes as well.

The hydrogenated feed stock, now substantially free of contaminants which interfere with the use of molecular sieve sorbents, such as the olefinic, sulfur and nitrogen-containing components and preferably free of aromatic hydrocarbons as well (components present in the untreated feed stock), is then contacted in liquid phase with the molecular sieve sorbent to recover the normal components of the mixture, in accordance with the objectives of the process. The temperature, pressure, flow rate and other process conditions required to provide an operable

process of separation are determined and selected on the basis of the boiling range of the feed stock, the higher boiling, more viscous hydrocarbon mixtures being separated at optimum rates and with maximum effectiveness at higher temperatures than feed stocks of lower boiling points. The operating temperature and pressure, for any given feed stock is selected to provide essentially liquid phase in the separation zone, generally at temperatures of from about 20° to about 250° C. and at pressures from atmospheric to 100 or more atmospheres. For feed stocks having relatively low boiling points, such as a light naphtha, the preferred operating temperature for the separation stage is within the range of from about 30° to about 150° C., with pressures sufficient to maintain the feed stock in substantially liquid phase. Using a feed stock in the upper boiling range of the naphthas, a middle distillate oil or a kerosene or gas oil boiling range fraction, temperatures of from 100° to about 250° C. are preferred and pressures sufficient to maintain a feed stock of this boiling range in substantially liquid phase are generally from atmospheric to about 10 atmospheres (150 lbs./in.² gage). Substantial advantages in economy of operation, simplification and reduction in the number of pieces of equipment and other advantages such as increased yields of product, products of greater purity, etc., are realized by operating the entire process, including both the sorption and desorption stages at essentially isobaric, isothermal conditions.

Fluid feed stock rates of flow are primarily dependent upon viscosity of the feed stock, although the use of higher temperatures enable the use of higher feed stock flow rates. Since the present process involves contacting a fluid feed stock with a particulate solid, generally maintained in fixed bed relationship to the flowing feed stream, a convenient means of expressing feed rates in the process is by the use of the term: "liquid hourly space velocity" which designates the volume of feed stock in liquid form contacted with a specified volume of solid sorbent particles per hour. For the present process, the flow rate of feed stock is within the range of from about 0.01 to about 2.5 volumes of fluid per volume of sorbent per hour.

Following completion of the sorption stage of the separation process, generally marked (although not necessarily) by the saturation of the molecular sieve particles with the desired straight chain or normal aliphatic component of the feed stock, at which point the molecular sieve particles are substantially "spent" with respect to having further or additional capacity to sorb normal components of the feed stock, the sorbate (normal aliphatic hydrocarbons) is recovered by contacting the spent sorbent with a fluid desorbent which displaces the sorbate component from the spent molecular sieves at the same or at a different set of process temperatures and/or pressures, although preferably at the same or essentially the same conditions, as aforementioned. The desorption of sorbate from the molecular sieves simultaneously regenerates, or reactivates the sorbent particles to a "regenerated" condition suitable for recycle to the sorption zone of the process flow.

The desorbent utilized herein to effect displacement of the previously sorbed, straight chain hydrocarbon sorbate from the molecular sieve particles is preferably a hydrocarbon of the straight chain aliphatic type having a boiling point at least 20° F. above or below (i.e., outside of) the boiling range of the sorbate product which occupies the pores of the sorbent after contact with the feed stock. The preferred desorbents are the normal aliphatic hydrocarbons having two or more carbon atoms fewer than the lowest boiling sorbate component in the feed stock, or from one to two carbon atoms more than the highest boiling sorbate component of the feed stock. The choice of a normal aliphatic hydrocarbon for use as desorbent is dictated by the process conditions and must, in general, be separable by means of fractional distillation from the desired sorbate-containing effluent stream (mixed sorbate-

desorbent) withdrawn from the process. When utilizing a desorbent comprising a relatively straight chain aliphatic hydrocarbon boiling above the sorbate product component, an additional factor controlling the choice of specific desorbent is that the desorbent must generally be distillable from the mixed desorbent-sorbate stream at temperatures below the level at which thermal cracking of the desorbent residue takes place; alternatively, the desorbent could be recovered from the mixture by means of vacuum distillation to reduce the pot temperature of the still.

Desorption is effected at any temperature within the range of from about 20° to about 300° C., although preferably, the temperature at which desorption takes place is substantially the same as the temperature at which the sorption stage is effected, whereby an isothermal sorption-desorption process is provided, as aforesaid. The pressure variable is fixed at a sufficiently elevated level to maintain the fluids in the system in essentially liquid phase.

The mechanism of desorption utilizing a relatively straight chain aliphatic hydrocarbon as a component of the desorbent stream is essentially that of displacement of the sorbate component within the pores of the molecular sieve particles by another sorbate-type hydrocarbon. The driving force of desorption which takes place even in the case of a desorbent of lower molecular weight than the sorbate is essentially a Mass Action effect whereby the number of molecules of desorbent supplied to the desorption zone and surrounding the pores of the spent molecular sieve particle containing the sorbate component is greater than the number of sorbate molecules within the pores of the sorbent particle, the rate of desorption increasing as the molar ratio of desorbent to sorbate in the interstitial fluid increases. The desorption of the last traces of sorbate from the molecular sieve particles by displacement with desorbent goes to completion as long as the desorbent pervades the mass of sorbent and the molar ratio of desorbent to sorbate in the interstitial fluid phase surrounding the particles of sorbent is greater upstream than it is downstream, where upstream refers to a retrospective point in the path of fluid flow and a downstream point is a point ahead of the point of reference, further along the path of flow, a point in the bed of sorbent yet to be contacted with the fluid currently at the point of reference. Although, theoretically, any ratio of desorbent to sorbate sufficient to provide a molar ratio in any portion of the desorption zone contacted with desorbent, greater than 1 to 1, accomplishes a significant degree of desorption, the preferred molar ratios are above 1 to 1, particularly when a desorbent boiling below the sorbate component of the feed stock is utilized. Suitable ratios may vary from 2 to 1 to 30 to 1, and more preferably from 3 to 1 to 15 to 1 moles of desorbent per mole of sorbate in the desorption zone at the particular stage of the process.

The preferred desorbents for use in displacing sorbate hydrocarbons derived from feed stocks boiling in the kerosene and gas oil boiling range, as specified herein, for example, are mixtures of straight chain and branched chain or cyclic hydrocarbons which boil from 20° to 50° F. below the boiling point of the lowest molecular weight sorbate component of the feed mixture. For feed stocks which boil in the naphtha (gasoline, for example) boiling range, a desorbent which boils from 10° to 50° F. above the end boiling point of the feed stock may be preferred.

Although the normal component of such mixed desorbents is the component of the mixture which effects the actual desorption via displacement of the sorbate component occupying the pores of the "spent" molecular sieve particles, the isoparaffinic component of the mixed desorbent serves a significant function in the desorption. Such mixtures are preferred over normal paraffins exclusively for the reason that the branched chain or cyclic component of the desorbent mixture reduces the propor-

tion of normal component in the secondary reflux entering the secondary rectification zone and results in a higher ultimate recovery of normal sorbate product from the process. Since the volumetric flow rate of secondary reflux is preferably greater than balanced reflux (balanced reflux being equal to the rate which will just replace interstitial fluid in the first bed of the primary rectification zone between shifts of inlets and outlets to the next succeeding downstream bed), desorption in the primary rectification zone (where desorption would be undesirable) is reduced if the primary reflux is made up in part of a raffinate-type hydrocarbon. The preferred branched chain and cyclic hydrocarbons for mixing with the normal hydrocarbon desorbent are those which boil at the same or nearly the same temperature as the normal component of the desorbent, so that in the subsequent fractionation of the desorbent from the desorbate product (the effluent mixture of the desorption stage of the process) the desorbent mixture is recovered directly for recycling purposes as a fraction of constant composition and boiling point, either as overhead (if the desorbent boils below the feed stock initial boiling point) or as a residue (if the desorbent composition boils above the end boiling point of the feed stock). Paraffinic desorbents which boil below the lowest boiling sorbate component of the feed stock are further preferred over their unsaturated analogs and higher boiling desorbents. Thus, for example, in the desorption of n-dodecane from a mass of molecular sieves previously contacted with a feed stock containing n-dodecane, a mixture of normal and branched chain paraffins, such as normal and isoheptanes are preferred over a mixture of normal and iso-tetradecanes as desorbent. Although the proportion of normal to non-normal components in the desorbent mixture is not critical, at least 10 percent, preferably not exceeding 95 percent of the mixture is a normal hydrocarbon.

Any suitable method of contacting the liquid feed stock with a fixed bed of the solid sorbent may be utilized in the present process. For continuous methods of operation, desorption must generally be effected in a separate and different portion of the process flow at essentially the same time that sorption takes place, either in the same or in different portions of the apparatus. Thus, the swing-reactor principle may be employed in the present process to provide a sorption zone which operates at the same time that a fixed bed of the sorbent, maintained in a separate desorption zone, undergoes regeneration and after a fixed period of time (determined by the period required for regeneration of the sorbent in the desorption zone or the appearance of straight chain feed stock components in the effluent of the sorption chamber) the feed stock and desorbent inlets are switched, desorbent thereafter entering the zone into which feed stock was charged in the prior cycle and vice versa. Thereafter, the two chambers are alternately switched to provide substantially continuous flow.

A particularly preferred method of continuously and countercurrently contacting the feed stock with a fixed bed of solid molecular sieve sorbent, while simultaneously contacting (also under continuous, countercurrent flow conditions) the desorbent with the resulting spent molecular sieve particles (i.e., sorbent containing the sorbed normal aliphatic components of the feed stock) is provided in the apparatus and process described in U.S. Patent 2,985,589, issued to Donald B. Broughton et al. The latter process and apparatus are especially adapted for use in a sorption-type separation process in which the solid sorbent is porous and fragile and which, when subjected to the forces of attrition, as in a moving bed process, is rapidly reduced to a mass of fines. Typical of such fragile sorbents are the aforementioned molecular sieves which are fabricated into uniformly sized particles by pilling a mixture of porous clay with the fine crystals which characterize the zeolitic metal aluminosilicates. The use of the aforementioned fixed bed, simulated mov-

ing bed process enables the production of both the sorbate and raffinate products in an exceptionally pure form.

Although fixed bed systems of contacting fluid feed stocks with solid sorbent particles of the type contemplated herein are usually preferred because of the structural fragility of porous adsorbents of the molecular sieve type or of the surface adsorption type, such as silica gel, nevertheless when the adsorbent is a solid material of sufficient structural strength to resist pulverization under conditions of attrition, a moving bed system for countercurrently contacting the fluid feed stock with the solid adsorbent may also be utilized in the present process.

The present process flow, applied to the treatment of normally liquid hydrocarbon feed stocks boiling in the gasoline and kerosene ranges and the effects of the hydrogenation pretreatment of the feed stock, in accordance with the process of the present invention will be further described and illustrated in the following examples. In thus specifying particular process conditions, feed stocks, etc., it is not thereby intended to limit the generally broad scope of this invention necessarily in accordance therewith.

EXAMPLE I

Experiments designed to separate a normal paraffin product from a mixture of hydrocarbons containing normal, branched chain and cyclic components at various process conditions were performed to determine the effect of the presence of olefinic and/or aromatic components, as well as nitrogen and sulfur-containing compounds, in the feed stock on the purities of both the raffinate and sorbate products, as well as the effect of these components on the rate and extent of recovery of both products from the feed stock. In the following runs, utilizing the same feed stock (a middle distillate kerosene fraction) and otherwise similar process conditions, sorbate and raffinate products were separated from the feed stock before and after pre-hydrogenation, the hydrogenation stage of the process being effected at reaction conditions sufficiently severe to hydrogenate the olefinic components present in the feed stock to paraffins and some or all of the aromatics, if present, to naphthenes, simultaneously eliminating the sulfur and nitrogen-containing contaminants from the feed stock by converting the nitrogen to ammonia and the sulfur to hydrogen sulfide. The runs in the following examples were selected from a large number of experiments in which it was established that optimum recovery of n-paraffins is obtained when using feed stocks in the middle distillate and kerosene boiling range at about 450° F. process temperature.

In each run the feed stock is a fraction of petroleum boiling from 382° to about 454° F. The fractions contain normal paraffins, naphthenes and aromatics of from C₉ to C₁₄ chain length and contains 3.1 p.p.m. of total nitrogen and 1800 p.p.m. of sulfur. In Run 1 the sorbent is contacted with the feed stock in its as-received form; that is, without prior treatment. In other runs the pre-hydrogenation reaction conditions were varied to obtain selective removal of the nitrogenous, sulfur-containing, olefinic and aromatic components. Thus, the feed stock was contacted with the sorbent at separation conditions substantially similar in all respects in each of the runs, thereby, on a comparative basis, demonstrating the effect on the capacity and activity of the sorbent of eliminating the sulfur and nitrogen-containing impurities and also the effect of converting the olefinic and aromatic components contained in the feed stock to their paraffinic and naphthenic analogs.

The separation stage of the process was effected in a continuous-flow, multiple, fixed bed system, utilizing essentially the process and apparatus described in U.S. Patent 2,985,589, issued to Donald B. Broughton, et al. and illustrated in its adaptation to the present process in the sole figure of the accompanying diagram. Make-up desorbent is a mixture of 45% by weight of iso-octane and 55% by weight of normal heptane.

The sorbent packed into each of the fixed beds of the contacting column are molecular sieve particles comprising a mixture of clay and crystals of dehydrated calcium aluminosilicate (Linde Co. 5A molecular sieves), piled into cylinders of from 30 to 50 mesh in size. Contacting column 1, illustrated in the accompanying sole figure, contained 24 stacked fixed beds, each having a uniform size and each containing 44 cc. of the above 5A molecular sieve particles, or an aggregate volume of 1056 cc. for the entire column. At any particular stage of the cycle, six of the beds in series comprise the sorption zone, the next downstream six beds in series comprise the primary rectification zone, the next six downstream beds of the series make up the desorption zone and the furthest downstream six beds comprise the so-called secondary rectification zone. The fluid outlet of the secondary rectification zone connects with the inlet of the sorption zone, thereby establishing a complete, continuous-flow cycle. The inlet and outlet boundaries for each functional zone shift simultaneously after each 2.5 minute interval to the next downstream bed, providing a continuously operating cyclic process. Although six beds are assigned to each functional zone in the process flow of this example, the number of beds in each zone may be varied to meet special conditions of the process, for example, when charging other feed stocks or other desorbents requiring a different proportion of beds for the various functional zones of the cycle. Each of these beds is connected by a pipe to a fluid distribution center, shown in the sole figure as a flat-plate rotary valve 2 which distributes the fluids flowing into and out of the process in accordance with a prearranged program, determined by channels and ports constructed into the rotating plates of valve 2, more fully described in U.S. Patent 3,040,777, issued to D. B. Carson et al.

Line 3 connects the outlet of the top bed of column 1 (bed B1) through pump 4 and line 5 with the inlet of bed B24 at the bottom of the contacting column, raising the pressure of the fluid on the outlet side of the pump to thereby provide a pump-around fluid stream from the outlet of the top bed (B1) to the inlet of the bottom bed (B24) and continuous recycle of fluid through the series of contacting beds B24 through B1. Downflow of fluid through each of the beds could be provided in an alternative flow arrangement by withdrawing fluid from the bottom of bed B24 through line 5 and transferring the stream by means of pump 4 into line 3 and thence into the top of bed B1.

Fluid distribution center 2 directs the influent and effluent streams into the lines leading to the fixed beds of solid sorbent and by channels in the plates of the valve re-align themselves and advance the inlet and outlet points equidistantly to the next adjacent, downstream beds at intervals of 2.5 minutes each. Each bed during a cycle of 60 minutes thereby becomes successively: the first bed of a series of six beds comprising the sorption zone in which feed stock is first contacted with the sorbent, then the outlet for the raffinate stream six beds downstream from the feed stock inlet, then the first bed of the desorption zone (12 beds downstream from the feed stock inlet) in which desorbent is first contacted with the sorbent containing sorbed normal paraffins and thereafter, the outlet through which sorbate product is removed. After the completion of each cycle, the feed stock inlet again arrives at the inlet to the bed receiving feed stock at the beginning of the cycle. Thus, after one complete rotation of the rotary plate of valve 2 the inlets and outlets for the various influent and effluent streams have been shifted in 24 successive increments through the 24 beds in series to the points of beginning, completing one cycle of operation.

An integral portion of the improved process flow comprising the present invention is the hydrogenation reaction zone which is indicated in the accompanying diagram as a tubular hydrorefining reactor 6 in which pretreatment of the charge stock is effected in the presence of a hydro-

genation catalyst packed in the reactor, hereinafter more fully described.

Feed stock enters the process flow through line 11 at a rate controlled by valve 12 through furnace 13 which raises the temperature of the feed stock to the temperature required in the hydrorefining reaction to effect the present pretreatment of the feed stock and by means of pump 14 is thereafter transferred at the pressure required in the downstream portions of the process flow into line 23. In those runs in which the feed stock is subjected to pretreatment in hydrorefining reactor 6 the feed stock is shunted into line 9 by closing valve 10 in line 23, but if charged directly into the separation stage of the process flow, valve 10 is opened, valve 8 in line 9 is closed and the untreated feed stock flows directly from line 23 into central distributing valve 2 which directs the feed stock mixture at the temperature acquired in furnace 13 and at the pressure provided by pump 14 into the feed stock inlet line of column 1, as hereinafter more fully described.

In Runs 2 to 4 of the series comprising this example the middle distillate feed stock (in liquid phase) is charged into the pre-hydrogenation reactor at various flow rates from 5 to 30 volumes of liquid feed stock per volume of catalyst per hour, at 675° F. and at 4000 lbs./in.² pressure. The catalyst is a nickel-cobalt molybdate composite containing 11.3 percent by weight of nickel and 0.09 percent by weight of cobalt supported on an alumina-silica base containing 10 percent by weight of silica in the form of pills 1/8" x 1/8", the catalyst particles being packed in reactor 6 through which the feed stock and hydrogen flows as a mixed phase downwardly through the catalyst. Hydrogen is charged into feed stock supply line 9 from sources hereinafter described, through line 9a at a flow rate of 1500 ft.³ per barrel of hydrocarbon feed stock, line 9a connecting with line 9 above the inlet to hydrorefining reactor 6. The flow rate of the hydrocarbon stock through the hydrorefining reactor containing the catalyst determines the residence time of the stock with the catalyst at the aforementioned conditions and thereby determines the extent of aromatic and olefin conversion to saturates. The removal of nitrogen and sulfur-containing contaminants is complete even at the highest flow rates utilized.

The conversion of the hydrocarbon stock effected in reactor 6 by contact with the aforementioned hydrorefining catalyst at the above reaction conditions not only saturates the olefins and usually a part of the aromatics, if present in the feed stock, but also produces hydrogen sulfide and ammonia from the nitrogen and sulfur-containing components of the feed stock. The entire reaction mixture is removed from reactor 6 through line 15 and cooler 16 which liquefies the condensable hydrocarbon components of the products. The resulting mixture of gases and liquids flows through line 17 into receiver vessel 18 where the portion of the product which liquefies at the pressure maintained on the product stream from hydrorefining reactor 6 separates from the gaseous portion of the product. The latter gases, consisting mostly of excess hydrogen are removed from vessel 18 through line 18a and charged into line 7 for recycle by mixing with make-up hydrogen supplied from outside sources, pump 7a transfers the combined hydrogen into line 9a which conveys the hydrogen into mixed hydrogen-hydrocarbon feed supply line 9.

The liquid portion of the hydrorefining reaction product, including ammonia and hydrogen sulfide produced by hydrorefining the sulfur and nitrogen-containing contaminants of the feed stock is withdrawn from the bottom of receiver vessel 18 through line 19 and charged into distillation column 20 which separates the low boiling ends from the desired liquid hydrorefined product recovered as bottoms from column 20. Heat for distillation purposes is supplied by reboiler 20a. The light ends, including dissolved ammonia and hydrogen sulfide, as well as light hydrocarbon components are distilled overhead as off gas through line 21 and are withdrawn

from the process flow. The bottoms, consisting of the desired hydrotreated C₉ to C₁₄ normally liquid hydrocarbons, now free of olefins and nitrogen and sulfur contaminants, as well as aromatics (depending upon the feed stock flow rate), leaves reactor 6 via line 22 and enters feed stock supply line 23 for the separation stage of the present process. Pump 24 adjusts the pressure on the feed stock to the level existing in column 1 and discharges the feed stock through line 25 at a rate controlled by valve 26 into the fluid distribution center, illustrated on the accompanying diagram as valve 2. By means of the internal channels and ports of valve 2, the feed stock (at the stage of the cycle illustrated in the diagram) is directed into line 27 connecting to the inlet of bed B6, currently the first bed in the series B6 to B1 constituting the 6-bed sorption zone.

As the feed stock, comprising the aforementioned mixture of normal and non-normal aliphatic and cyclic hydrocarbons, flows through the series of fixed beds containing 5A molecular sieves, the latter sorbent particles retain the normal or straight chain components of the feed stock by sorption into the porous structure of the sorbent particles and permits the non-normal, branched chain and cyclic hydrocarbon components to pass over and around the particles of sorbent in the contacting beds. The ports and channels of valve 2 which connect with the ports of the contacting beds are so arranged that the fluid stream in the contacting beds: B6 to B1 is not permitted to leave the column until the downstream outlet of bed B1 is reached.

At the flow rate of feed stock provided in this run and with the volume of sorbent in beds B6 to B1, the sorbent provides sufficient capacity to retain substantially all of the normal components of the feed stock and the composition of the fluid stream flowing out of bed B1 is substantially free of sorbate component (indicated by the composition of the raffinate stream in Table I, hereinbelow). In accordance with the continuous process provided by present process flow, the effluent stream flowing from bed B1 through the outlet end of the sorption zone is divided into two streams: (1) a net raffinate product which is withdrawn from the process flow, and (2) a primary reflux portion which flows continuously downstream into the inlet of the primary rectification zone consisting of the next 6 beds in series. The provision of a primary reflux stream in the present process maintains a continuously cyclic stream which replaces the interstitial fluid residing in the void spaces between the particles of sorbent in bed (B24), the next adjacent bed downstream from the raffinate outlet with fluid of raffinate composition and prepares this bed for withdrawal of raffinate product therefrom after the next succeeding shift in inlets and outlets into and from the column.

The portion of raffinate effluent from bed B1 withdrawn as raffinate product is diverted into line 28 which conveys the stream into fluid distributing valve 2 and thereafter into product receivers, as hereinafter more fully described. The primary reflux portion of the sorption zone effluent flows into line 3 connected to the inlet of pump 4 which discharges the primary reflux through line 5 into the bottom of bed B24, the first bed of the series: B24-B19 comprising the primary rectification zone. The quantity of primary reflux in the pump-around stream is a critical process variable which must be controlled in volume to prevent the raffinate components present in the primary reflux from entering the downstream desorption zone where the raffinate would tend to contaminate the sorbate product desorbed from the molecular sieve sorbent in the downstream desorption zone in the event that the flow rate of primary reflux exceeds the critical maximum rate.

The aggregate volume of void space between the particles of sorbent in any particular bed is equal for all of the beds and the volume of fluid required to replace the

interstitial fluid in each bed (i.e., the aggregate volume of void space) in the interval of time between successive shifts in the outlets and inlets of the fixed beds is referred to herein as "balanced reflux." Since the volume of primary reflux entering bed B24 of the primary rectification zone must not exceed the critical maximum volume required to displace the interstitial fluid in bed B24 prior to the next shift in inlets and outlets (for each 2.5 minute interval and, further, if maximum purity of the sorbate product is to be maintained) the primary rectification zone is necessarily "under-reflexed" with a volume of primary reflux (i.e., pump-around fluid in the stage of the cycle shown in FIGURE 1) less than the aggregate void space volume in the first bed of the primary rectification zone. Thus, the flow rate of the primary reflux stream flowing into the first bed of the primary rectification zone is set to provide a total volume of primary reflux which is less than the volume required to completely displace all of the interstitial fluid from the void spaces in the first bed during the 2.5 minute interval that the bed receives primary reflux and as the zone boundaries of the primary rectification zone are shifted upwardly through the series of superadjacent beds in the column; this zone is accordingly said to be "under-refluxed." In the run herein described, the primary reflux volume rate of flow is maintained at about 90 percent of balanced reflux, although satisfactory operation of the process is obtained at rates of from 60 to 95 percent of balanced reflux.

A flush stream of the same composition as the desorbent which thereby simplifies its recovery from the process effluent streams is charged into the process flow through line 29 at a rate controlled by valve 30 and raised to the ambient pressure in the process by means of pump 31. The flush stream is discharged from pump 31 through line 32 into the fluid distribution center (rotary valve 2), being thereafter directed through the internal channels of valve 2 into line 33 which last previously carried feed stock into column 1, thereby replacing the feed stock in these lines with the flush stream (which is readily fractionated from the sorbate product stream later removed through line 33 during a subsequent stage of the process when the inlets and outlets into and from the column have advanced through the cycle to the point that the sorbate product stream is withdrawn from bed B8 through line 33). When the cycle advances to this stage, it is advantageous to have had line 33 preflushed of any feed stock remaining in the line because of its prior use to carry feed stock into bed B7 when the latter bed was the first bed in the series of beds comprising the sorption zone. The flush stream flowing through valve 2 and line 33 carries the feed stock residue in line 33 into column 1, joining the stream of fluid flowing into the downstream contacting beds. A similar volume of fluid is withdrawn from a downstream bed of column 1 (bed B18) through line 34 (thereby equalizing the volume of desorbent flow) connected to the outlet of bed B18, through valve 2, and from the process flow through line 35.

At the stage of the operation illustrated in the accompanying diagram in which feed stock enters column 1 through line 27 into bed B6, desorbent enters downstream bed B18 through line 36 from fluid distribution center 2 and enters the latter valve mostly from recycle sources, hereafter described. The desorbent displaces the normal paraffins contained in the porous structure of the molecular sieve particles retained thereby during a preceding stage of the cycle of operation when feed stock entered bed B18. The desorbent mixture (normal heptane and iso-octane) flows upwardly through the series of beds (B18 to B13), part of the effluent stream of bed B13 being withdrawn from the outlet of bed B13 through line 37 as the sorbate product stream (a mixture of desorbent and desorbed feed stock normal paraffins), and the remainder, herein designated as "second-

ary reflux," enters bed B12 which is the first bed in the series: B12 to B7 comprising the secondary rectification zone. The volume of secondary reflux entering bed B12 is maintained at about 120 percent of balanced reflux in order to provide complete replacement of interstitial fluid in bed B12 prior to the shift of the sorbate product outlet from bed B13 to the outlet of bed B12. The mixture of sorbate and desorbent leaving bed B13 through line 37 is withdrawn from the fluid distribution center (valve 2) through line 38 at a rate controlled by valve 39 into distillation column 40 wherein desorbent (mixed n-C₇ and iso-C₈) is separated as overhead from a less volatile residue comprising the normal paraffin sorbate product recovered from the feed stock as the sorbate stream. Valve 39, by controlling the withdrawal rate of the sorbate stream to product take off, also thereby determines the amount of sorbate stream which continues to flow downstream into bed B12 as secondary reflux. The ultimate yield of sorbate product, set forth in Table I hereinbelow, is withdrawn from the bottom of column 40 through line 41 and transferred to product storage.

The desorbent overhead of distillation column 40, enters line 42 for recycle to the process. Make-up desorbent to replace losses from the process is introduced into the process flow through line 43. In order to remove possible contaminants in the make-up desorbent, some of which (such as moisture) deactivates the molecular sieves, the recycled desorbent stream is preferably passed through guard chamber 44, packed with a mixture of activated alumina and 5A molecular sieves, before entering the fluid distribution center through line 45 and thence into column 1 through line 36. Pump 46 in line 42 raises the pressure on the desorbent stream to the pressure maintained in column 1.

The portion of raffinate effluent withdrawn as raffinate product from the process flow through line 28 is directed by the fluid distribution center (valve 2) into raffinate product withdrawal line 47 at a rate controlled by valve 48. The setting on valve 48 also controls the amount of raffinate which continues to flow downstream from the outlet of bed B1 into bed B24 as primary reflux (that is, pump-around fluid transferred from the outlet of the sorption zone to the inlet of the primary rectification zone). The mixture withdrawn as raffinate effluent consists of raffinate and desorbent and to separate the mixture, the raffinate stream withdrawn from the process flow through the fluid distribution center and line 47 enters distillation column 49 to separate an overhead comprising desorbent which is recycled in the process flow through line 42 from a non-volatilized residue comprising raffinate product (branched chain aliphatic and cyclic hydrocarbons) which is withdrawn from the bottom of distillation column 49 through line 50 as primary product.

The process conditions and compositions of the sorbate and raffinate products are indicated in the following Table I, Runs 1 to 4. In Run 1, the feed stock (middle distillate kerosene) is used directly as feed stock to the aforementioned separation process in which the molecular sieve particles are used, the feed stock containing all of the olefinic and aromatic components present in the initial kerosene fraction, as well as the sulfur-containing and nitrogen-containing components also present in the feed stock prior to prehydrogenation. In Runs 2, 3 and 4, the feed stock of Run 1 containing the sulfur-containing and nitrogenous impurities is subjected to progressively more severe prehydrogenation conditions to determine the effect of the aforementioned components and classes of contaminants in the charge stock on the yield and total recovery of the sorbate and raffinate products. Previous comparative runs utilizing other similar conditions, indicated that for a kerosene boiling range feed stock, an operating temperature of about 450° F. was more preferable insofar as yield and quality of the raffinate and sorbate products was concerned than lower operating temperatures for the separation process.

Table I

SEPARATION OF C₉-C₁₄ n-PARAFFINS FROM A KEROSENE FEED STOCK AND FROM THE SAME STOCK PREHYDROGENATED

	Run 1 ¹	Run 2 ²	Run 3 ³	Run 4 ⁴
Feed Stock:				
Olefins, Wt. Percent.....	1.8.....	Nil	Nil	Nil
Nitrogen, p.p.m.....	3.1.....	Nil	Nil	Nil
Sulfur, p.p.m.....	1,800.....	Nil	Nil	Nil
Aromatics, Wt. Percent.....	14.1.....	14.1	8.2	1.1
Product Recoveries, Wt. Percent of Feed:				
Sorbate Fraction.....	29 to 11 ⁵	26.5	26	26
Normal Paraffin Content, ⁵	94.5 to 58 ⁵	96.8	97.9	99
Olefin Content ⁵	2.3.....			
Aromatic Content ⁵	3.1.....	2.8	1.5	Nil
Raffinate Fraction.....	71 to 88 ⁵	73.5	74	74
Normal Paraffin Content, ⁵	0.3 to 17 ⁵	0.3	0.1	Nil
Isoparaffin Content ⁵	73 to 56 ⁵	73	73	73.5
Naphthene Content ⁵	10 to 7 ²	10.6	17	25.1
Aromatic Content.....	16.....	16	9.7	1.2
Capacity of Molecular Sieve Sorbent:				
Feed Rate, Gals. of Feed Stock/Hr./Ft. ³ of Sorbent.....	2.4 ⁶ to 0.6 ⁶	1.4	2.1	2.6
Sorbent Usefulness Gals. of Feed. ⁷	11.....	61	71	239

¹ Middle distillate fraction (B.P. 382-454° F.); specific gravity at 60° F.: .8835; contains 3.1 p.p.m. nitrogen, 1,800 p.p.m. sulfur, 14.1% aromatics, 0.4% olefins, 85.5% paraffins + naphthenes of which 22.4% are normal paraffins.

² Feed stock of Run 1 catalytically pre-hydrogenated at foregoing reaction conditions and in the presence of the above indicated catalyst at a space velocity of feed stock through the catalyst bed of 29.9 volumes of liquid per volume of catalyst per hour; pre-hydrogenated feed contains 0.0% olefins, sulfur: nil, nitrogen: nil and 14.5% aromatics.

³ Feed stock of Run 1 catalytically pre-hydrogenated at foregoing reaction conditions, except that the conversion of aromatics to naphthenes was increased by reducing the space velocity of the feed stock flowing over the catalyst, which increases the residence time of the feed stock with the hydrogen and catalyst, to 5.3 volumes of liquid per volume of catalyst per hour.

⁴ Feed stock of Run 1 and pre-hydrogenation at conditions of Run 1, except space velocity reduced to 1.0 vol. of liquid feed stock per volume of catalyst per hour.

⁵ By infra-red analysis.

⁶ By adsorption on activated silica gel and bromine number index.

⁷ Sorbent usefulness determined by the number of gallons of feed stock separated until sorbent reduced to 75 percent of its initial capacity; a measure of deactivation rate.

⁸ Determined after 6 hours of use.

⁹ Input of feed stock at beginning of run.

The data for these runs (i.e., Runs 1 and 4) demonstrate that the yield and quality of both the sorbate and raffinate products are enhanced when the feed stock is subjected to pre-hydrogenation prior to separation, presumably by eliminating the components of the feed stock which became adsorbed on the surface of the molecular sieve particles and prevent adsorption of the normal sorbate components of the feed stock. Thus, by eliminating the polar nitrogen and sulfur-containing components from the feed stock to the separation unit, the rapid decline in the activity of the molecular sieve particles and the appearance of non-normal components in the sorbate fraction are eliminated. The purity of the sorbate product was increased from 94.5 weight percent (Run 1) to 99 percent by weight (Run 4). Simultaneously, the normal paraffin content of the raffinate stream was reduced to nil and the deactivation rate of the molecular sieves was greatly reduced.

After being on stream as indicated above for approximately 2.5 minutes, the feed stock, desorbent and flush stream inlets are each moved to the inlets of the next adjacent downstream beds, respectively (feed stock point of entry) being shifted from the inlet of bed B6 to the inlet bed B5; desorbent entry from the inlet of bed B18 to the inlet of bed B17; and the flush stream inlet from bed B7 to the inlet of bed B6). Simultaneously, all product and flush stream outlets are also moved to the outlets of the downstream bed next adjacent downstream to the bed from which these streams were last withdrawn. These shifts in the inlets and outlets were effected by the rotation of one of the plates comprising the fluid distribution center

whereby each of the inlet and outlet streams enter the appropriate lines into and from the next adjacent downstream beds. Thus, after 2.5 minutes on stream, the sorbate product effluent stream has been shifted from the outlet of bed B12 to the outlet of bed B11; the raffinate effluent stream has been shifted from the outlet of bed B1 to the outlet of bed B24 and the flush stream effluent from bed B17 to bed B16. Thereafter, following each succeeding 2.5 minute interval, the inlet and outlet ports for the above influent and effluent streams are shifted to the next adjacent downstream beds, relative to the bed into and from which these streams were previously charged and withdrawn preceding the shift.

These results indicate that polar organic compounds such as nitrogen-containing or sulfur-containing compounds, and olefinic and aromatic hydrocarbons usually present in feed stocks of petroleum origin cause a rapid reduction in the capacity and the activity of the molecular sieves, although the effect of aromatic hydrocarbons (believed to be surface-adsorbed and not pore adsorbed) is somewhat less at elevated desorption temperatures than at lower operating temperatures.

What is claimed is:

1. A process for separating a relatively straight chain aliphatic hydrocarbon from a normally liquid hydrocarbon mixture containing sulfurous, nitrogenous and olefinic contaminants which interfere with the action of the separating agent, hereinafter specified, said hydrocarbon mixture having a boiling range not in excess of the boiling range of the gas oil fraction of petroleum, which comprises catalytically hydrogenating said mixture at hydrogenation reaction conditions sufficient to reduce at least the major portion of said contaminants to hydrogen sulfide, ammonia and paraffin hydrocarbon, separating the hydrogen sulfide and ammonia from the hydrocarbon mixture, thereafter contacting the hydrocarbon mixture with a porous, inorganic sorbent of the molecular sieve type in which the pore openings are of a size sufficient to admit a normal aliphatic hydrocarbon into the molecular sieve, but not of sufficient size to admit branched chain and cyclic hydrocarbons, withdrawing a raffinate comprising nonsorbed, non-straight chain hydrocarbons from

the sorbent particles and thereafter contacting the sorbent containing sorbed, relatively straight chain aliphatic components of said mixture with a desorbent comprising a straight chain hydrocarbon having a boiling point of at least 20° F. outside of the boiling range of the adsorbed component of the mixture.

2. The process of claim 1 further characterized in that the catalyst contacted with said mixture at said hydrogenation reaction conditions is a composite of a refractory metal oxide and a hydrogenation catalyst selected from the metals of Group VIII of the Periodic Table and a sulfur-containing derivative of said metal.

3. The process of claim 2 further characterized in that said hydrogenation catalyst component is thiomolybdate of a metal selected from the group consisting of nickel and cobalt, supported on alumina.

4. The process of claim 1 further characterized in that said porous, inorganic sorbent of molecular sieve type is a metal alumino-silicate containing calcium, dehydrated to form pores in the sorbent having openings of about 5 Angstrom units in cross-sectional diameter.

5. The process of claim 1 further characterized in that said hydrocarbon mixture is a fraction of petroleum boiling in the kerosene boiling range.

6. The process of claim 5 further characterized in that said mixture is contacted with said sorbent at a temperature of from about 350° to about 450° F. and at sufficient pressure to maintain said mixture in substantially liquid phase.

7. The process of claim 1 further characterized in that said hydrocarbon mixture is a middle distillate of petroleum containing aliphatic hydrocarbons having from about 9 to about 14 carbon atoms.

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