

PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Continuous Sorption Process

5 We, UNIVERSAL OIL PRODUCTS COMPANY, a Corporation organized under the Laws of the State of Delaware, United States of America, of No. 30, Algonquin Road, Des Plaines, Illinois, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a continuous sorption process for fractionating a fluid charge mixture of components wherein one of the components of the mixture is selectively sorbed during contact with a solid sorbent having a selective sorbency for that component, unsorbed component of the charge mixture is withdrawn from contact with the sorbent, and selectively sorbed component is displaced from the sorbent by a fluid desorbent. The invention provides a method for separating a mixture of components having different degrees of sorbency on a stationary solid sorbent in a continuous manner simulating an uninterrupted countercurrent contact of the several process streams with the solid sorbent.

15 The continuous sorption process according to this invention comprises maintaining a continuous cyclic circulation of fluid successively through four serially connected processing zones of a stationary mass of the solid sorbent and from the outlet of the last zone back to the inlet of the first zone, continuously introducing the fluid charge mixture into the circulating fluid at the inlet of the first zone, continuously withdrawing unsorbed component from the circulating fluid at the outlet of the first zone, continuously introducing desorbent into the circulating fluid at the inlet of the third zone, continuously withdrawing selectively sorbed component and desorbent from the circulating fluid at the outlet of the

third zone, and periodically advancing the four zones in the stationary sorbent mass by simultaneously advancing the point of introduction of the charge mixture, the point of withdrawal of unsorbed component, the point of introduction of desorbent, and the point of withdrawal of selectively sorbed component and desorbent an equal increment along the path of flow of the continuously circulating fluid.

20 In each of the periodical advancements of the four zones in the present process the points of (1) introduction of the stream of charge mixture, (2) introduction of the stream of desorbent, (3) withdrawal of the stream of unsorbed component, and (4) withdrawal of the stream of selectively sorbed component and desorbent are simultaneously shifted an equal increment in the direction of the flow of the circulating fluid. The increment of periodical advancement of the inlet and outlet streams generally does not exceed the extent of one zone and more advantageously is equal to only a fraction thereof, such as one half, one third or a smaller fraction of one zone, preferably however, not less than one tenth of one zone. When the sum of a plurality of successive increments equals the total length of the cyclic path of the fluid circulating through the series of four zones the point of beginning is reached by completion of one cycle of periodical advancements of the four zones, and this cycle is then repeated without interruption in the flow of the inlet and outlet streams. Thereby a continuous treatment of the charge mixture with stationary sorbent is attained concomitantly with continuous desorption and removal of selectively sorbed component from the solid sorbent without removing any portion of the stationary mass of solid sorbent from the cyclic path of the circulating fluid.

It is now widely recognized that various

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- solid sorbents of specific composition and structure may be contacted with a mixture of components which differ from each other in their relative sorbency on the solid, to thereby provide a means for segregating the individual components according to their structure. This type of separation procedure has been applied to mixtures of inorganic as well as organic compounds and has found one of its most frequent applications in the field of separating hydrocarbon mixtures containing components which differ as to their structural classes. This procedure is particularly applicable to the separation of mixtures which can be separated only with difficulty by other means of separation, such as fractional distillation. One type of solid sorbent, generally characterized as having "adsorptive" properties, selectively adsorbs that component of a mixture of organic compounds which has the highest relative degree of polarity. The adsorptive capacity and retentivity of such adsorbent for the sorbate (that is, the component selectively adsorbed by the adsorbent from the charge mixture) depends upon the availability of a large superficial area on or in the adsorbent particles, the presence of a polar radical or an unsaturated bond within the structure of the sorbate, and the lack of such polar groups or bonds of unsaturation within the structure of the charge component which is less sorbed by the solid adsorbent. Adsorbents of this type are typified, for example, by such solids as silica gel (dehydrated), activated charcoal, the aluminum silicates (such as the various clays and activated silica gels, including such typical examples as Attapulgus clay, montmorillonite, and dehydrated synthetic composites of alumina and silica activated by heating to a temperature near, but somewhat below the approximate fusion point of the composite), activated alumina, particularly gamma alumina, as well as other materials of similar character which adsorb such polar or unsaturated compounds by virtue of electro-static attraction for the component of the charge mixture containing the polar or unsaturated groups and which retain a layer of sorbate component of mono-molecular thickness on the surface of the sorbent. Typical of the feed stocks which may be separated by contact with a solid, activated adsorbent include, for example: paraffinic hydrocarbon fractions (such as a gasoline fraction) containing mercaptans and/or amines, the latter polar compounds being selectively retained on the adsorbent particles; mixtures of paraffins and olefins wherein the olefinic component is the component selectively adsorbed by the solid adsorbent; mixtures of aromatic and non-aromatic hydrocarbons wherein the aromatic constituent is selectively adsorbed by the solid adsorbent; mixtures of water vapor and an inert gas, such as nitrogen or air containing moisture (the moisture being selectively adsorbed); and mixtures of phenols and/or sulfur compounds such as thiophene with liquid hydrocarbons, the phenolic or sulfur compound being selectively adsorbed.
- Another type of separation, wherein a solid adsorbent serves to separate mixtures of organic compounds by virtue of a difference in the structure of the components of the charge mixture is the so-called "clathration" method. In this method solid particles of certain amides, such as urea and thiourea, are contacted with a mixture of organic compounds to be separated and the component which has a relatively straight chain configuration selectively forms a solid adduct or "clathrate" with the sorbent, to the exclusion of the non-clathrate-forming branched chain components, when urea is utilized as the solid separating agent; or the clathrate or adduct is formed by the sorbent with the branched chain component, to the selective exclusion of the straight chain component present in the charge, when thiourea is utilized as the sorbent. Thus, a mixture of organic compounds, which differ in structure by virtue of the presence of straight chain, branched chain or cyclic components in the same mixture, may be contacted in liquid phase with solid particles of urea; it will be found that the straight chain components of the mixture are selectively retained by the urea particles in the form of an insoluble clathrate, while the branched chain components of the mixture can be separately withdrawn from the resulting crystalline clathrate. On the other hand, the same mixture of organic compounds can be contacted with thiourea and it will be found that the branched chain components of the mixture will form a clathrate with the thiourea, while the straight chain components, which fail to clathrate with thiourea, may be separately withdrawn for recovery. The method of separation utilizing urea or thiourea has a wide applicability for separating mixtures of organic compounds and is particularly useful for separating mixtures of branched chain and/or cyclic hydrocarbons from straight chain hydrocarbons.
- Still another type of separation employing a solid sorbent is the "sorption" process which utilizes solid particles of a porous sorbent which selectively occludes into the porous structure of the sorbent the straight chain components of a charge mixture of organic compounds, but which does not permit the branched chain components of the charge to enter into the pores of the sorbent. The pores present in a typical sorbent of this type are from 4 to 5 Angstroms in cross-sectional diameter and the sorbent is illustrated by a material characterized as a dehydrated metal aluminosilicate, the metal constituent of which is selected from the alkali and alkaline earth metals. Thus, a compound



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having a ~~branched~~ chain or cyclic structure, such as 2,3-dimethylbutane or cyclohexane may be readily separated as a non-sorbed raffinate from a compound having a straight chain structure, such as n-hexane (the initial mixture ordinarily being quite difficult to separate by fractional distillation) by contacting the mixture of these hexanes with solid particles of a dehydrated metal aluminosilicate sorbent; it will be found that the non-sorbed effluent or "raffinate" will be enriched with respect to the branched chain and cyclic constituents (if present in the charge mixture) when the amount of sorbent contacted with the feed stock is sufficient to occlude all or substantially all of the normal or straight chain components in the mixture. These solid sorbents, also referred to as "molecular sieves", may be prepared by coprecipitating or otherwise combining alumina, silica, and the involved metal oxide, such as an oxide or hydroxide derivative of an alkali metal (such as sodium, lithium or potassium) or of an alkaline earth metal (such as calcium, magnesium, barium, or strontium) to form a uniform and intimately dispersed mixture of silica, alumina and the metal oxide or hydroxide, removing excess water from the mixed oxides and thereafter heating the recovered dispersed mixture to a temperature at which the water of hydration will be removed by evaporation from the particles. It is often preferred to calcine the resulting dehydrated mixed oxides at a temperature of from about 200° to about 400° C. to develop structural rigidity and particle strength.

Another type of separation process to which the present process flow is applicable, is the type involving a chemical reaction with a solid sorbent (reactant) maintained in place as a fixed bed, with the sorbable component (the other reactant) being supplied in a fluid stream containing the same. Typical of such separations is the removal of alkaline earth metals from so-called "hard" water to thereby soften the latter and/or de-ionize the same. Thus, a stream of hard water may be charged into a so-called "softening" tank packed with a fixed bed of zeolite particles or with a sulfonated resin reactive with alkaline earth metals, the bed of softening agent selectively removing the hardness-causing alkaline earth metal ions and producing an effluent of softened, ion-free water. The introduction of a regenerating solution, such as an aqueous sodium chloride solution (for zeolite-type and sulfonated resin type water softeners), is the equivalent of the desorbent stream, hereinafter more fully characterized, and which acts as a displacing agent in the bed of softening agent. In other typical processes of this type an aqueous ion-containing stream, such as an aqueous sugar solution containing chloride- or sulfate ions in solution, is de-ionized by contact with a de-ionizing resin

such as an insoluble resin which contains amide or amino groups and is utilized as sorbent in the de-ionizer tank.

The present continuous sorption process is applicable to all of the aforementioned types of separation utilizing a solid sorbent capable of having its sorbency restored in a subsequent treatment of the "spent" sorbent, whether of the surface adsorption type, the clathration type, or the molecular sieve type. The present method, however, is particularly applicable to separations utilizing sorbents which are relatively unstable structurally and which therefore do not permit removal of the solid sorbent from one zone to the other without suffering a loss of its activity and usefulness because of attrition and other consequences of its structural instability. For purposes of this description and for expressing the generic concepts of this invention, the various methods of separation, each of which involves the use of solids which selectively combine in some form with at least one component of a fluid charge mixture of components to form a different, or "spent" solid, whether clathration, adsorption, occlusion or by chemical reaction, will be referred to herein as "sorption", and the use of the latter term herein is intended to include each and every type of separation indicated above.

The present process is characterized as a "cyclic" and "continuous" process. It is thereby intended to define a method in which the various inlet and outlet streams are charged and withdrawn, respectively, in a continuous manner while the mass of solid sorbent remains in substantially stationary position within the sorption system and the feed and desorbent inlets and the product withdrawal outlets are shifted simultaneously an equal amount at periodic intervals during the cyclic circulation of fluid through the system. Although the solid sorbent remains in stationary position, a simulated countercurrent flow arrangement is thereby established, since every portion of the mass of solid sorbent successively serves the purposes of the fourth, the third, the second, and the first zone in a cycle of operation (that is, in one complete cycle of periodical advancements of the four processing zones) whereas the general direction of flow of fluid is in the opposite direction. The charge enters the first zone (which serves as sorption zone) at a point at which the solid sorbent is relatively more spent than the sorbent at the point of withdrawal of the raffinate stream or unsorbed component from this sorption zone, and the sorption zone is periodically advanced toward a sorbent portion of restored frequency. The present process may also be visualized as being effected in a series of four interconnected zones of a single stationary mass of solid sorbent having no actual line of de-

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 5 marcation between each of the zones other than the zone boundaries defined by the points of inlet and withdrawal for the various fluid streams. The first zone which receives the charge mixture at its inlet is referred to as a "sorption" zone. The second zone in the direction of flow of fluid through the mass of solid sorbent is referred to as a "primary rectification" zone; the next adjacent or third zone is referred to as a "desorption" zone; and the fourth zone is herein designated as a "secondary rectification" zone. Although for the sake of simplicity, these zones which constitute the periodically advanced processing zones or zones of contact between fluid and sorbent are hereinafter described, in reference to a typical embodiment of the invention, as being each defined by a series of interconnected fixed beds, it is to be emphasized that the total mass of solid sorbent present in these series of beds may be considered as a single, continuous bed confined in a contacting column in which each of the processing zones is defined by the points of inlet and points of withdrawal of the various streams flowing into or out of the bed. The contacting column, when considered as confining a continuous stationary bed of solid sorbent, is of appreciably greater length than width and preferably confines a long, slender bed, such as a bed of a length which is more than four times, for example eight or ten and up to about forty times as large as the diameter of the bed. In a preferred type of contacting column, this bed is divided into a series of smaller beds by constrictions which are substantially uniformly spaced along the length of the column so that the constrictions as well as the compartments between these constrictions contain sorbent. The latter particularly preferred arrangement is shown in the accompanying drawings, hereinafter more fully described. The advantages of constricting the stationary mass of sorbent into a plurality of beds and more particularly into at least four beds or into a larger number of beds which is a multiple of four, such as eight, twelve or sixteen and up to 40 beds, and providing entry and withdrawal points for the various streams at the constrictions are: (1) prevention of convective back-mixing of fluid in a direction opposite to the general direction of fluid flow and (2) greater ease of distributing fluids flowing into and out of the contacting column because of the ability to thereby eliminate channeling and other undesirable loss of uniform distribution. By dividing a vertical sorbent bed into smaller beds by means of partitions, as illustrated in Figure 1 of the accompanying drawings, the load of solid sorbent is distributed over a plurality of intermediate supports, thereby eliminating an accumulation of the entire weight of the sorbent on a single bottom support of the sorbent bed.

Suitable charging stocks which may be utilized in the process of this invention are characterized as a fluid mixture of two or more components, one of which is sorbed with relatively greater tenacity on a solid sorbent than one or more other components present in the charge mixture. In view of the applicability of the present process to various types of sorptions, including surface adsorption, clathrate formation, and molecular occlusion, as described above, any fluid mixture of compounds containing at least one component which is subject to any of the various phenomena responsible for its selective retention by a solid sorbent may be employed herein as charge.

Typical examples of particular application of the present sorption process are those which employ a sorbent of the molecular sieve type and they include: the separation of normal alcohols such as normal butanol, from branched chain or cyclic alcohols such as tert-butyl alcohol or cyclohexanol; the separation of normal or straight chain aliphatic hydrocarbons, such as, for example, n-pentane, n-hexane, n-hexene and n-heptene from branched chain paraffins and olefins, such as, for example, 2,3-dimethylbutane and di-isobutylene, respectively, or from cyclic hydrocarbons such as, for example, cyclohexane and methylcyclopentane; the separation of the normal paraffins from a hydrocarbon fraction boiling in the gasoline range and containing naphthenes and aromatic hydrocarbons in admixture with normal and branched chain paraffins; the separation of straight chain aldehydes containing at least 4 carbon atoms per molecule from branched chain and cyclic aldehydes; the separation of straight chain ketones, such as methyl-ethyl ketone, from branched chain ketones, such as di-isopropyl ketone, or from cyclic ketones such as cyclohexanone; the separation of straight chain aliphatic acids from branched chain or cyclic acids, such as the separation of oleic acid from its branched chain isomers; and the resolution of mixtures of many other classes of organic compounds which differ in structure within the class. The choice of molecular sieve sorbent for use in the process will depend upon the molecular size (i.e., the cross-sectional diameter) of the component to be sorbed.

The continuous sorption process of fractionating a fluid charge mixture of inorganic or organic or mixed inorganic and organic composition as provided by the present invention is illustrated in the accompanying drawings which are described by reference to a particular charge mixture of a normal paraffin, such as n-hexane, and an isoparaffin, or cycloparaffin, such as a dimethylbutane or cyclohexane, respectively, utilizing a solid sorbent of the molecular sieve type (namely, a dehydrated calcium aluminum silicate hav-



ing pores of 5 Angstrom units internal cross-sectional diameter). It will be understood that in thus illustrating the treatment of a particular charge mixture, it is not thereby intended to limit the scope of the invention necessarily to the indicated charge mixture, sorbent, and specific process or flow conditions. Also, while the particular mode of operation, which is described below for illustrating the process of the invention, involves the contacting of fluid in substantially liquid phase with solid sorbent in a particular arrangement of multiple stationary beds, it will be understood that vapor or gaseous phase operation, other arrangements of sorbent beds, the use of upward flow of fluid through the sorbent, and the use of other types of equipment are also contemplated within the scope of the present invention.

During use of the solid sorbent in the present process in a plurality of fixed beds and in conduits of reduced cross-sectional area between each two adjacent beds a fluid pump is provided between at least one pair of adjacent beds to provide a positive, unidirectional flow of fluid. One of the essential characteristics of the process is that a continuously flowing stream of fluid (either liquid or vapor phase), which is also called carrier fluid, is circulated through the series of beds from the first to the last in the series and back to the first bed. At least two inlet streams are added to the continuously circulating fluid and at least two outlet fluid streams are withdrawn from the continuously circulating fluid, the points of outlet alternating with the points of inlet. The fluid charge enters at the inlet to one of the fixed beds of sorbent, the non-sorbed portion of the charge (that is, the residue of the fluid charge remaining after sorption of at least a portion of the selectively sorbable material in the first bed of the sorption section of the process) leaves the opposite end of the first bed in the sorption section and thereafter enters the inlet of the next adjacent bed of solid particles of sorbent. A single fixed bed of the solid sorbent or a sufficient number of such fixed beds in series is provided to constitute the sorption section or first processing zone wherein the selectively sorbable component (sorbate) is substantially completely removed from the fluid charge so that a fluid stream which contains a non-sorbed or "raffinate" component of the fluid charge and which is substantially free from sorbate component issues from the outlet of the last bed in the sorption section of the process flow. In the case of some fluid charge mixtures and some sorbents, only one bed is required to effect such separation, while in other cases, two or more beds in series and generally not more than about ten beds in series are required, the number required or the length of the series in aggregate depending upon the various factors of

the operation, notably the sorptiveness of the sorbable component of the fluid charge, the depth of sorbent, and the pressure and temperature used in the process.

The outlet from the sorption section contains an outlet port through which a portion of the non-sorbed raffinate component in admixture with a portion of the carrier fluid is withdrawn. The remaining portion of this effluent stream from the sorption section flows into a single fixed bed or a series of interconnecting fixed beds which constitutes the "primary rectifying section" or second processing zone of the process. The concentration of raffinate component in the fluid stream flowing through the primary rectifying section of the process differs at any given moment along the path of the fluid stream; this concentration is progressively less in the direction of flow and is zero near or at the outlet from this zone when sufficient sorbent is used therein.

The effluent from the primary rectifying section is joined at the outlet from this section by an inlet stream of a so-called displacing agent or desorbent flowing in the same direction as the circulating fluid, the resultant fluid mixture thus entering the sorbent bed in the desorption section or the first one of a series of beds in this section. The desorbent is a material which is capable of displacing from the solid sorbent the component of the feed stock already sorbed on the solid sorbent by virtue of a previous cycle of operation. The fluid stream thus flowing through the immediately succeeding portions or beds of the desorption section thus comprises a mixture of desorbent and sorbate previously sorbed from the fluid charge in a prior cycle of operation and released from the solid sorbent by contact thereof with the desorbent. Since the displacing action of the desorbent is primarily a mass action effect, the desorbent is charged in sufficient quantity to provide a molar ratio of desorbent to sorbate at any given point at least greater than 1 to 1, and is charged in an amount preferably sufficient to provide a molar ratio of at least 10 to 1 and up to about 30 to 1. As the mixed stream of desorbent and sorbate flows through the desorption stage of the process, it becomes progressively enriched with sorbate, the displacing agent or desorbent releasing additional sorbate in its continuing flow and taking the place of the displaced sorbate in the pores which make up the structure of the sorbent. At the outlet of the desorption section of the process flow, a stream comprising a portion of the sorbate, desorbent and circulating fluid (if different from desorbent) is withdrawn and discharged from the process as ultimate product or as intermediate feed stock for further purification, if desired. This stream may be fractionated (for example, in an auxiliary distillation unit) to



separate the desorbent from a relatively pure sorbate product.

The remaining portion of desorbent and sorbate (and carrier fluid, if different from the desorbent) not removed through the sorbate outlet continues its flow through one or more succeeding fixed beds/sorbent, serving as secondary rectification section of the process. In this section the raffinate or unadsorbed component, left in the void spaces between sorbent particles in a previous cycle of operation, is washed from the sorbent and out of the voids between the sorbent particles by the desorbent-sorbate mixture. The resultant fluid mixture issuing from the last portion or bed of the secondary rectification section thus contains sorbate and raffinate components in admixture with desorbent and is once again joined by the incoming feed stock at the inlet for the latter stream.

In a preferred embodiment of the present process the four processing zones, namely the sorption, desorption, and primary and secondary rectification sections of the process contain substantially equal quantities of the solid sorbent and a substantially equal number of stationary sorbent beds. Thus, when a single bed of solid sorbent is sufficient for effecting the sorption of sorbate component from the fluid charge mixture, a single bed of substantially the same quantity of sorbent will also be used in the primary rectification section, in the desorption section, and in the secondary rectification section, respectively. And if three connecting beds are used in the sorption sections, three connecting beds of practically the same size will also be used in each of the three succeeding processing sections. Moreover, during the course of the processing, as just described, the points of introduction of fluid charge and desorbent into the circulating fluid and the points of removing non-sorbed or raffinate component and of removing selectively sorbed component or sorbate from the circulating fluid are periodically shifted, the four points being shifted simultaneously, and each of the indicated points of entry and points of withdrawal being shifted an equal aliquot portion of the total number of beds in the direction of flow of the circulating fluid. Thus, when using three beds in each of the four processing zones or sections and advancing the processing zones each an increment equal to one bed, the point of introducing fluid charge mixture into the process flow arrives, upon a sequence of twelve shifts, at the point in the path of the circulating fluid where fluid charge mixture was introduced in the beginning of the process, one circuit in the cycle of operation then having been completed.

The process of this invention may be practiced in any suitable apparatus comprising either a series of connected fixed beds or a single continuous bed of sorbent and having

fluid-flow connecting means between the outlet of the last bed of the series and the inlet of the first bed thereof, or between the outlet and the inlet of the single bed, respectively, and also comprising suitable means, such as a valve or manifold, for shifting the points of inlet and outlet for the various feed and product streams involved in the process. The accompanying drawings illustrate diagrammatically one of the preferred apparatus designs, being particularly suitable because of its compact arrangement of the series of fixed beds.

Figure 1 of the drawings illustrates the arrangement of a series of fixed beds, stacked one upon another, within a vertical contacting column 101 containing suitably shaped partitioning means which divide the vertical column into a series of adjacent bed zones, such as zones 201 to 212. Each zone between the uppermost and lowermost zones is divided from its adjacent zones by a funnel-shaped partitioning member, such as partition 102 in zone 201, and has a downcomer 103 of restricted cross-sectional area opening into a subadjacent zone 202 through a transverse partitioning member 104 which comprises the upper boundary of the zone 202.

An essential portion of the present apparatus, essential, that is, to the realization of the type of flow provided by the process of the present invention is the provision of a suitable programming device for changing the points of inlet and outlet into and from the contacting column and for periodically advancing each of these points in equal increments and in the direction of flow of fluid through the system during the operation of the process. Any suitable form of fluid distribution center, such as a manifold arrangement of valves and incoming and outgoing lines may be provided with timed, electrically operated switches to open and close the appropriate valves. The programming may also be suitably effected by means of a plug valve of particular design, illustrated in the accompanying drawings, particularly Figure 2 thereof. Figure 2 depicts a circular valve 105 having a valve housing A and a continuously revolving plug B rotatable in the housing A in fluid sealed relationship with the housing A. The latter housing contains a number of inlet and outlet ports 1 to 12 connecting in fluid flow relationship with internal passageways inside the valve plug through which certain inlet and outlet fluid streams, hereinafter described, enter and are withdrawn from fixed beds in contacting column 101. The valve plug is arranged to provide at least 4 passageways for accommodating at least two separate inlet streams and at least two separate outlet streams, the two inlet passageways alternating with the two outlet passageways. Although it is generally preferred to arrange the inlet and outlet passageways in



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the valve plug approximately 90° apart, thereby positioning the outlets and inlets on opposite sides of the plug, it is feasible to provide any suitable arrangement of ports and passageways and thereby increase or decrease the angular relationship between the respective inlet, and outlet passageways, depending upon the relative number of fixed beds of sorbent to be assigned to the different stages of the operation.

The number of fluid inlet and outlet ports, 1 to 12, in the valve 105 corresponds to the number of contacting zones or fixed beds 201 to 212 in column 101. The ports are positioned within housing A at finite and predetermined distances apart to direct inlet and outlet streams into and from column 101 to correspond to the desired program, prearranged for the process. The ports connect the passageways through the valve plug B to lines leading to the various fixed beds within the column 101 and thus provide a means for directing the inlet and outlet streams into and from the appropriate lines connected to the contacting zones, all in accordance with the prearranged program for the process. Thus, port 1 in valve housing A provides an opening for establishing a fluid flow connection between a port in valve plug B with the top of contacting zone 201 through line 106. Similarly, port 2 in the valve housing will serve to connect any port in the valve plug with line 107 which connects with downcomer 103 between contacting zones 201 and 202 of column 101. Since, however, in the position in which the plug is illustrated in Figures 1 and 2 no internal passageway in plug B opens into zone 202 but instead, the solid portion of plug B blocks port 2 in fluid-sealed relationship thereto, no fluid flows through port 2 into line 107. In the same manner, ports 3 to 12 in the valve housing connect with their corresponding contacting zones 203 to 212 through a connecting conduit.

For the purpose of illustrating a typical embodiment of the process of the present invention, the method of utilizing the apparatus of the drawings will now be described with reference to the separation of a liquid charge mixture comprising a mixture of normal and isoparaffins such as a mixture of normal and isohexanes, that is a mixture which is particularly difficult to separate by simple fractional distillation. It is to be emphasized, however, that the process of the invention is applicable with as great or greater facility to any mixture of organic or inorganic components within the scope hereinbefore indicated. For the indicated resolution of mixed normal and branched chain hexane isomers, the solid sorbent in each of the sorption zones 201 to 212 in column 101 is a "molecular sieve" of the type comprising discrete, generally granular particles or particles of fixed

geometric shape, of a metal-aluminum silicate, as described further above. This solid sorbent is packed in the sorption beds by random distribution therein. With such distribution, there will be void spaces between the particles through a stationary mass thereof and likewise between the particles throughout each of the fixed beds.

In starting the process, the indicated charge mixture of normal and isohexanes, for the purposes of its fractionation into a stream of the normal component and a stream of the iso components, is charged into the process flow through line 108 in amounts controlled by valve 109. The charge flows through line 108 into a central axle 110 of the plug B which is divided into four compartments by a divider member 111, line 108 discharging the charge mixture through orifice 112 in the hollow axle, into internal passageway 113 which connects with outlet port 1 in housing A. The stream flowing through port 1 enters line 106, which in turn, connects with line 134 conveying circulating carrier fluid from zone 212 in the bottom of the contacting column to the upper end or inlet of zone 201. The charge mixture is supplied at sufficient pressure, relative to the pressure of the carrier fluid in line 134, in order to mix the carrier fluid with the charge mixture and cause the resultant mixed stream to flow into zone 201 and therein toward zone 202. During contact of the charge with the molecular sieve sorbent in zone 201 the sorbent selectively occludes normal paraffinic component of the charge into its pores and selectively excludes the isoparaffinic components thereof, the normal or straight chain component (n-hexane in the present example) being retained in the solid sorbent while the branched chain component (the isohexane of this example) is permitted to pass through the bed of sorbent. The latter branched chain compound is the principal component, together with carrier fluid, hereinafter defined, of the stream withdrawn from zone 201 through downcomer 103. Any remaining n-hexane component in the stream leaving zone 201 (particularly as the sorbent in zone 201 becomes spent with sorbed component) continues to flow through zone 201 into subadjacent contacting zone 202. The bed 202 of solid sorbent removes an additional quantum of residual normal paraffin, if any is present in the effluent from the preceding or superadjacent zone. In general, a series of a sufficient number of interconnecting fixed beds, each containing solid sorbent, or a continuous bed of sufficient length, is provided to supply sufficient sorbent capacity to remove all of the normal component of the charge mixture and leave only iso or branched chain charge component in the effluent stream. It is readily determined by preliminary tests whether only one bed or a number of beds in series, a shallow bed, or a bed of consider-

able depth will be required for this purpose.

In the present illustration of operation, using a normal paraffin-branched chain paraffin mixture as charge for the process, the carrier fluid is conveniently an excess of desorbent charged into the process flow and is composed entirely or at least predominantly of a normal paraffin having a lower boiling point and lower molecular weight than the normal paraffin component of the feed stock. Preferably the desorbent has a boiling point which is at least 10° C. lower than the initial boiling point of the charge mixture. Specifically, when n-hexane is the straight chain component to be separated from the charge mixture by sorption on the molecular sieve solid sorbent, the desorbent utilized is desirably a normal paraffin such as n-butane which upon its introduction into the circulating fluid displaces the n-hexane sorbate from the molecular sieve and is itself sorbed into the pores of the sorbent by virtue of its molar excess relative to the sorbate present in "spent" sorbent (that is sorbent the pores of which are filled with sorbate). As n-butane passes as the carrier fluid through line 134 and enters zone 201 with the charge, it occupies those pores of the sorbent which are not preferentially occupied by the n-hexane component present in the charge. Any excess sorbent in zone 201 and those subsequent zones (zones 202 and 203 in the present illustration) which together with zone 201 comprise the sorption section of the process at this stage of the operation, sorbs the n-butane carrier fluid, leaving iso-hexane to occupy the void spaces between the particles or sorbent and to flow through these void spaces toward the outlet of the sorption section. As more charge mixture continues to flow into zone 201, prior to the shift in the point of charge inlet to zone 202, the incoming n-hexane displaces n-butane carrier fluid from the pores of the molecular sieve sorbent in bed portions progressively nearer the outlet of the sorption section while iso-hexane is being continuously discharged together with carrier fluid from this processing zone.

In the arrangement of Figure 1 the bed in zone 203 is the last bed in the series of beds comprising the sorption section, and the effluent stream leaving zone 203 is substantially pure iso-hexane in admixture with excess carrier fluid (n-butane, from which hexanes are readily separated by distillation). As the effluent stream from zone 203 passes through downcomer 114, and while fluid is prevented from leaving the sorption section through any intermediate outlet conduits, such as line 107, because of closure of outlet ports 2 and 3 by the solid portion of plug B in valve 105, at least a portion of this fluid stream flows into line 115 which is connected with port 4, the first outlet port available to this fluid stream in valves 105. The

stream thus removed from the first processing zone, that is the sorption section of the process, through line 115 is conveyed into valve 105 through port 4 connecting with internal outlet passageway 116 in plug B of valve 105, and then leaves the process by passing through orifice 117, in valve axle 110, into raffinate outlet conduit 118 in amounts controlled by valve 119. The stream thus discharged from the process may then be fractionally distilled to recover the individual components thereof, as desired.

The amount of effluent thus removed from contacting column 101 through the raffinate outlet is carefully controlled by valve 119 to provide a residue of mixed carrier fluid and iso-hexanes which flows past outlet conduit 115 into subadjacent bed 204. The quantity of non-withdrawn portion of the fluid stream thus continuing to flow through column 101, as determined by the rate of withdrawing iso-hexane raffinate through valve 119, may be any desired fixed proportion of the total fluid stream withdrawn from zone 203 into downcomer 114, but is desirably at least 20% by volume of the latter stream and preferably at least 40%, and up to about 80% by volume of the fluid stream leaving zone 203. As the stream entering zone 204 continues to flow through the sorbent in this zone and zones 205 and 206 (which at this stage of the operation constitute the second processing zone), the desorbent, or carrier fluid, n-butane occupies the internal pores of the solid sorbent and the iso-hexane raffinate components of the residual fluid stream can occupy only the spaces or voids between the particles of solid sorbent.

It will be noted that the concentration of sorbate component in the fluid flowing through the sorption section of the process at any given moment is progressively lower at successive points along the path of this fluid and the concentration of raffinate component in this fluid at the same moment is progressively greater at successive points along the path of the fluid while the effluent of the sorption section is free from sorbate component. As more charge mixture is introduced into the fluid stream entering the sorption section, however, the concentration of sorbate component in the fluid becomes greater at more advanced points within the sorption section because the pores in successive portions of the sorbent mass become progressively filled with sorbate component. If the introduction of charge mixture were continued without change of the inlet point, the fluid reaching the outlet of the sorption section would eventually contain sorbate component; but before this condition is reached the point of introduction of the charge mixture into the circulating fluid is advanced in the direction of flow of this fluid by rotation of plug B in valve 105. Prior to this advancement in the

operation of the present illustration, the iso-hexane component present in that portion of the fluid stream which by-passes raffinate withdrawal line 115 and enters the bed 204, pushes carrier fluid from the void spaces between particles in this bed. As more fluid enters the bed 204, carrier fluid will be pushed by raffinate component also from the void spaces in bed 205 and then also in bed 206. Thus the concentration of raffinate component in the fluid flowing through the primary rectification section at any given moment is progressively smaller at successive points along the path of this fluid and is zero in the fluid reaching the outlet of this processing zone. Before raffinate component shows up in the fluid at the outlet of the primary rectification section, the position of the inlet and outlet points to and from the circulating fluid is advanced by rotation of plug B in valve 105 so that the primary rectification section is shifted to include a quantity of sorbent which contains desorbent in its pores and in the void spaces between the sorbent particles, and raffinate component is thus prevented from gaining access to the desorption section of the process flow.

At a point between the second and third processing zones, and therefore in the case of the present illustration at the downcomer 120, which is the fluid outlet from bed 206 prior to the change of the inlet and outlet points to and from the circulating fluid, a stream of displacing agent (herein referred to as desorbent) is changed into contacting column 101, thereby joining the fluid stream leaving the sorbent bed 206. The stream of desorbent enters downcomer 120 through line 121 at a pressure greater than the pressure of the fluid stream in the contacting column. Desorbent which acts in the capacity of carrier fluid, as aforesaid, is supplied to the process through line 122 in amounts controlled by valve 123, the desorbent flowing from line 122 into internal passageway 125 through orifice 124 in the hollow axle of plug B of valve 105. The desorbent flows through inlet port 7 in housing A of valve 105 and thereafter into line 121 which directs the desorbent stream into the circulating fluid. The quantity of desorbent thus admitted into the process is sufficient to displace from the pores of the molecular sieve sorbent the n-hexane component previously sorbed from the charge mixture in a prior cycle of operation and, in order to effect such displacement, the n-butane desorbent must surround the spent sorbent particles and must be present in an amount sufficient to cause a transfer of sorbed n-hexane from the pores of the spent sorbent into the surrounding n-butane. The amount of n-butane required to effect this result is generally from about 2 to about 30 moles of desorbent per one mol of sorbate, and preferably, in the example at hand, is from about 5

to about 10 moles of n-butane per mole of sorbed n-hexane. In the case of other charge mixtures and for other systems of separation, utilizing other sorbents and displacing agents, the molar ratio of the compound which effects the displacement of the compound to be displaced will be in the above order of magnitude.

The mixture of desorbent (n-butane) and displaced sorbate (n-hexane) which is formed as a result of the displacement of n-hexane from the spent sorbent by n-butane and occupancy of the sorbent by the n-butane, flows from zone 207 into zones 208 and 209 in series by virtue of the positive pressure head between any given zone and a zone preceding it in the path of circulating fluid and then flows into downcomer 126 having outlet conduit 127 connected therewith. The outlet provided by conduit 127 is the first outlet through which mixed n-butane desorbent and released n-hexane sorbate can pass from the circulating fluid and from the series of beds which constitutes the third processing zone (that is the desorption section of the process), all other escape outlets of this third processing zone through the valve being blocked at this stage of the operation by the solid portions of plug B of valve 105. The fluid stream leaving bed 209 of the contacting column 101 flows through outlet port 10 in housing A of valve 105 by virtue of the pressure differential between the fluid in column 101 and the fluid in outlet port 10. The fluid consequently flows through port 10 into internal passageway 128 of valve plug B, then through orifice 129 in the hollow stem 110 of valve 105, and finally through conduit 130 and valve 131 into additional processing equipment, not illustrated, for further purification or use of the resulting mixture. Such additional equipment may comprise distillation means, for example, to separate a n-butane stream (which may be returned for further use as desorbent) from a separate fraction of n-hexane sorbate. In some instances the desired end product of the present separation process is the sorbate component of the charge mixture, whereas in other instances the object of the separation is to eliminate the sorbate component from the charge mixture and recover the raffinate component as the desired ultimate product.

In order to maintain the continuous cyclic circulation of fluid in the system, only a portion of the total stream arriving at the outlet downcomer 126 of zone 209 is withdrawn for discharge from the process through line 127 and conduits 128 and 130, the proportion thus remaining in circulation being regulated by valve 131. This portion of mixed n-butane and n-hexane continues its flow from downcomer 126 into zone 210 and succeeding zones 211 and 212. At this stage of the operation the series of sorbent beds in the

zones 210, 211 and 212 constitutes the fourth processing zone in the path of the circulating fluid and is also referred to herein as "secondary rectification" section of the process. As the stream of desorbent (n-butane, also used here as carrier fluid) and sorbate (n-hexane) progresses through zone 210 and then through zone 211 into zone 212 it comes into contact with a sorbent portion which was used in the sorption section of the preceding cycle of operation and during this contact the mixture of desorbent and sorbate pushes raffinate (iso-hexane) from the voids between particles of the sorbent in this secondary rectification section. Consequently the fluid stream issuing from bed 212 into downcomer 132 in the present example comprises n-butane, n-hexane and iso-hexane. When substantially pure sorbate is desired as a product of the process the points of introduction to and withdrawal from the circulating fluid are periodically advanced an increment which takes solely sorbent free from raffinate (non-sorbed component) into the third processing zone. Accordingly the point of withdrawal of sorbate and desorbent from the circulating fluid in the present example is advanced from the outlet of zone 209 to the outlet of zone 210 after zone 210 has been swept free from iso-hexane. In order to maintain the cyclic fluid circulation, the fluid stream must be given an incremental increase in pressure as it issues from the downcomer 132 of zone 212. For this purpose, the fluid stream issuing from downcomer 132 is pumped to a higher pressure level by means of pump (or compressor) 133 and discharged at said higher pressure into line 134 containing valve 135 which controls the flow of the continuously circulating fluid stream into the top of zone 201.

Each of the operations of sorption, primary rectification, desorption, and secondary rectification described above occur substantially simultaneously as plug B of valve 105 is continuously rotated in a counter-clockwise direction and at any given instant of time thereafter, each bed becomes progressively a more upstream bed relative to the general direction of the flow of fluid through the beds. (The terms "upstream" and "downstream" are to be interpreted herein in their ordinary and usual definition in the chemical process arts; that is, the term "downstream" refers to an advanced point in the direction of flow relative to a point of reference, whereas "upstream" refers to a retrospective point in the direction of fluid flow). Thus, if at any given instant, the sorbent bed in zone 201 is the point which first contacts fresh charge mixture introduced into the process, at any given point of time thereafter, following a sufficient interval to permit the plug in valve 105 to complete $1/12$ of its rotation, the sorbent bed in zone 202 becomes the point of

first contact with the charge mixture and zone 201 becomes the last bed in the series of beds comprising the secondary rectification section. Thereafter, zones 203 through 212 become, successively, the bed of first contact. It will be noted that as the charge inlet is shifted in the direction of flow of the circulating fluid, the raffinate outlet, desorbent inlet and sorbate outlet also are shifted the same aliquot portion of the total cycle and in the same direction. As these points shift, the composition of the fluid stream at different points and the composition of the sorbent beds also change; the iso-hexane component (raffinate) occupies the voids between sorbent particles only in those beds which are on either side of the raffinate outlet, generally only one, two or three beds beyond the raffinate outlet. Similarly, n-hexane (sorbate) is present in the pores of the solid sorbent occupying beds in the processing zone upstream from the raffinate outlet so that the fluid stream reaching the point in the stationary mass of sorbent which is the raffinate outlet in the periodically shifting point of raffinate withdrawal is essentially pure raffinate (iso-hexane) component in admixture with n-butane desorbent and the fluid stream reaching the point in the sorbent mass which is the sorbate outlet (that is the second one of the two periodically shifting points of withdrawal), is essentially pure sorbate (n-hexane) in admixture with n-butane desorbent. These streams are contaminated only to the very small extent resulting from the residual fluid stream remaining in the lines leading from the contacting column to the valve port of a previous cycle of operation.

The flow rate of fluid in column 101 is adjusted to provide the maximum charging rate consistent with the maintenance of fixed bed conditions, which is dependent upon whether gas phase or liquid phase contacting is utilized and also upon the size of the particles of sorbent and the degree of packing the sorbent in the confines of the bed of sorbent. The size of the sorbent may vary from finely divided powders (particles down to 0.15 mm. and preferably not smaller than about 0.4 mm. size) to relatively large, granular particles, preferably not larger than about 8 mm. size. When utilizing gaseous charge mixtures and displacing agents, the charging rate is below the rate at which fluidization of the sorbent particles occurs (for example, when the contacting zones are not completely filled with solid sorbent) and preferably is not in excess of about 3 volumes of gaseous or vapour charge mixture per volume of solid sorbent per minute, more desirably in the range of from about 0.1 to about 1.5 volumes of charge per volume of solid sorbent per minute. When utilizing liquid phase contacting conditions, the charging rate of charge mixture is desirably not greater than about

1.5 volumes of liquid charge per volume of solid sorbent per minute when utilizing relatively large granular particles of sorbent and more desirably from about 0.01 to about 1.0 volumes of liquid charge per volume of solid sorbent per minute. These rates are, of course, dependent upon the size of the sorbent particles, the depth and width of the sorbent beds and other factors which are dependent upon the design of the apparatus and the process conditions. When the sorbent completely fills the beds, the limiting rate of flow of fluid through each bed is set by the free or "void" space between particles of sorbent, the space thus provided establishing a maximum accommodation flow for any given pressure differential, but which may be increased if a greater pressure differential is tolerable. The finer the particles of sorbent, the greater the pressure drop through each bed, the ultimate permissible flow rate being fixed as that rate which does not give rise to a pressure drop through all of the beds greater than the discharge pressure delivered by the circulating fluid pump.

When the desorbent is intended to be recovered from the mixed desorbent- raffinate stream or the desorbent-sorbate stream or from each of these streams upon withdrawal from the process, it is generally preferable that the boiling point of the desorbent differs sufficiently from the components of the charge mixture so that the desorbent will be readily separable from the respective component by suitable fractionation means, such as a simple distillation.

The process of this invention is operated at conditions of temperature, pressure, and under other process conditions which depend upon the particular charge mixture involved, the particular sorbent utilized in the contacting zones and the required purity of product. In general, the pressure and phase condition used in carrying out operations in accordance with the process of the present invention will depend upon the molecular weight of the components of the charge mixture. Thus, in a process for separating fluid compounds sorbable in the pores of a molecular sieve type sorbent by such sorbent, the process will more desirably be effected in gaseous phase when the components of the charge mixture contain fewer than about 5 carbon atoms per molecule, while preferably liquid phase operation is effected for compounds containing 5 or more carbon atoms per molecule; otherwise, the pressure required to maintain the fluid in liquid phase may become excessive. For gaseous phase operation a suitable process temperature may vary from about 60° to about 300° C. and pressures may be within the range of from substantially atmospheric to 10 atmospheres or more. Typical liquid phase conditions are, for example, tempera-

tures of from 0° C. to 200° C. and at pressures of from atmospheric to 30 atmospheres, or higher, depending upon the charge mixture. In the process for de-ionizing water, using a zeolite-type of sorbent, the operation is generally effected in liquid phase and at temperatures substantially below the boiling point of water. In another typical instance, for example, in the separation of aromatic hydrocarbons from aliphatic paraffins containing at least 6 carbon atoms per molecule, utilizing a silica gel adsorbent, the operation may be effected in either gas or liquid phase conditions, at temperatures of from about 30° to about 250° C. and at pressures from substantially atmospheric to 10 atmospheres or more.

This invention is further illustrated with respect to several of its specific embodiments concerning process conditions, solid sorbent, illustrative feed stock and illustrative desorbent in the following example.

EXAMPLE

The process of this invention is typically illustrated by the following operation in which a mixture of normal and cyclohexanes was fractionated into a stream of relatively pure n-hexane and a secondary product stream of substantially pure cyclohexane. In this operation a column comprising a series of 12 vertically positioned, interconnected tubular sections was used, each section having a diameter of 52.5 mm. and a length of approximately 1.2 meters. Each section contained a fixed bed of molecular sieve sorbent 1.1 meters in length. The inlet at the top and the outlet at the bottom of each of the beds was a nipple of 1.59 mm. diameter which was tapped into a cap fitted on each end of each section. The bed of sorbent was suspended in each section above the outlet by an internal screen across the section. The bottom of each bed was connected by a 1.59 mm. pipe to the top of the next lower bed, and the line connecting the bottom of the twelfth bed (lowest bed) to the top of bed No. 1 (highest bed) contained a liquid pump which delivered liquid to the top of bed No. 1 at a pressure differential between the 12th and 1st beds of about 3.33 atmospheres. The molecular sieve sorbent was composed of particles of calcium aluminosilicate (Linde Air Products Co., 5A sieves) of random sizes within a range of sizes in which 95% will pass a screen having 4.7 mm. openings and at least 98% by weight will be retained on a screen having 0.3 mm. openings. The molecular sieve sorbent, upon being packed into each section, occupied a volume of 0.762 litres per section.

Four lines of 25.4 mm. diameter pipe (one charge supply line, one raffinate withdrawal line, one desorbent supply line and one sorbate withdrawal line) were provided for the process, the four 25.4 mm. lines serving as manifolds for distribution of the inlet and



outlet streams to and from each of the fixed beds of sorbent. Each pipe connecting two successive beds of sorbent was connected in parallel with four, separately valved 1.59 mm. diameter lines, and each one of the latter four lines was connected to one of the four manifolds so that it was possible to supply each bed with a separate stream of charge mixture of desorbent and to withdraw from each bed a separate stream of raffinate or sorbate. The valves in each of the four lines connecting each bed with each manifold were motor operated by switches activated with a program timing device which at one time would (1) open the valve connecting the charge supply manifold with the inlet to only one bed, (2) simultaneously open the valve in the line connecting the raffinate withdrawal manifold with the outlet from the third bed downstream from the charge inlet being opened, (3) also simultaneously open the valve in the line connecting the desorbent supply manifold with the inlet to the third bed downstream from the raffinate withdrawal line being opened, (4) also simultaneously open the valve in the line connecting the sorbate withdrawal manifold with the outlet from the third bed downstream from the desorbent inlet line being opened, and (5) also simultaneously close or maintain in closed position all other valves in the lines between the beds and the four manifolds.

The operation was carried out by changing a mixture of 40 weight percent n-hexane and 60 weight percent cyclohexane in liquid state at a temperature of 40° C. and at a flow rate of 3.785 litres per hour to one of the sorbent beds, simultaneously charging liquid n-butane as desorbent at a temperature of 40° C. and at a flow rate of 3.785 litres per hour to the inlet of the seventh sorbent bed downstream from the point of introduction of the charge mixture, simultaneously removing a raffinate stream from the outlet of the third bed downstream from the inlet of the charge mixture, simultaneously removing a sorbate stream from the outlet of the ninth bed downstream from the inlet of the charge mixture, maintaining a continuous circulation of liquid cyclically through the series of beds, and simultaneously advancing each of the two points of introduction of charge mixture and desorbent and each of the two points of withdrawal of raffinate and sorbate at intervals of one-half hour to the next bed in the direction of flow of the circulating liquid. This operation was preceded by a start-up procedure which assured proper functioning of the system.

In the start-up procedure the entire system, including the solid sorbent in all twelve beds, was thoroughly flushed out with vaporous normal butane and the vaporous butane was then replaced by liquid normal butane which served both as carrier fluid and as desorbent

in this operation. After all sections of the tubular column and the connecting lines between each of two of these sections were completely filled with liquid butane at 40° C. and at superatmospheric pressure sufficient to maintain the liquid phase condition, the pump in the line connecting the outlet from bed No. 12 to the inlet of bed No. 1 was started and a continuous cyclic circulation of liquid through the contacting column was established. Thereupon, the charge mixture was supplied at the aforesaid temperature and flow rate and at a pressure of 7.5 atmospheres into the bed No. 1 and simultaneously therewith the valve for raffinate withdrawal from the connection between beds Nos. 3 and 4, the valve for introduction of n-butane as desorbent into the connection between beds Nos. 6 and 7, and the valve for sorbate withdrawal from the connection between beds Nos. 9 and 10 were opened. At this time the liquid n-butane desorbent was supplied at a pressure of about 6.8 atmospheres and at the aforementioned temperature and flow rate to the inlet to bed No. 7. All other valves between the beds and the four manifolds were kept closed while the cyclic circulation through the system was maintained. After this cyclic circulation and the introduction of charge mixture and desorbent and the withdrawal of raffinate and sorbate at the points just described had been maintained for a total period of one hour, an analysis of the two withdrawal streams showed that the desired conditions of operation had been established, thus completing the initial or start-up period of operation.

In the thus established operation at the end of the start-up period, the raffinate stream was being removed from bed No. 3 at a rate of 3.785 liters per hour and was composed of 60% by weight of cyclohexane and 40% by weight of n-butane, and the sorbate stream was being withdrawn from bed No. 9 at the rate of 3.785 liters per hour and was composed of 40% by weight of n-hexane and 60% by weight of n-butane. Also at this time the liquid effluent from the bottom of bed No. 12 was being circulated to the top of bed No. 1 at the rate of 3.785 liters per hour. Upon establishment of this operation, the valve operating mechanism (which was capable of being set to program a series of operation cycles of one-half hour or shorter or longer durations and was set for one-half hour operation cycles) closed the valve controlling the line connecting the charge mixture supply manifold with the inlet to bed No. 1, simultaneously opened the valve in the line between the charge mixture supply manifold and the downcomer from bed No. 1 (inlet to bed No. 2), simultaneously closed the valve in the line connecting the downcomer from bed No. 3 to the raffinate withdrawal manifold while simultaneously opening the

valve in the line connecting the downcomer from bed No. 4 with the raffinate withdrawal manifold, simultaneously closed the valve in the line connecting the downcomer from bed No. 6 (inlet to bed No. 7) to the desorbent supply manifold while simultaneously opening the valve in the line connecting the downcomer from bed No. 7 (inlet to bed No. 8) with the desorbent supply manifold, and simultaneously closed the valve in the line connecting the downcomer from bed No. 9 to the sorbate withdrawal manifold while opening the valve in the line connecting the downcomer from bed No. 10 to the sorbate withdrawal manifold. Thereupon the above beds were retained on stream for one-half hour, followed by simultaneous shifts in the inlet and outlet streams to the next down-stream beds and this operation was thereafter continued in like manner at the same temperature, substantially uniform throughout the system, and with the same incremental advancement of the inlet and outlet streams at one-half hour intervals.

Throughout this regular operation, the valves controlling the inlet stream of charge mixture and the inlet stream of desorbent and also the valves controlling the withdrawal stream of raffinate and the withdrawal stream of sorbate were set to operate at equal volumetric flow rates and were adjusted on a volumetric basis to compensate for differences in pressure at the several points of inlet and outlet throughout the column.

The sorbate and raffinate outlet streams were each individually fractionated to separate substantially pure n-hexane and substantially pure cyclohexane as product streams while the n-butane distilled from the outlet streams in these fractionations was condensed and then recycled to the process. The above separation was operated on a continuous basis for 35 days without obvious depreciation in the activity of the molecular sieve sorbent.

WHAT WE CLAIM IS:—

1. In a continuous sorption process for fractionating a fluid charge mixture of several components wherein one of said components is selectively sorbed during contact of said charge mixture with a solid sorbent, unsorbed component of said mixture is withdrawn from contact with said sorbent and selectively sorbed component is displaced from the sorbent by a fluid desorbent, the improvement which comprises maintaining a continuous cyclic circulation of fluid successively through four serially connected processing zones of a stationary mass of said solid sorbent and from the outlet of the last zone back to the inlet of the first zone, continuously introducing said fluid charge mixture into the circulating fluid at the inlet of the first zone, continuously withdrawing unsorbed component from the circulating fluid at the outlet of the first zone, continuously introducing desorbent into the

circulating fluid at the inlet of the third zone, continuously withdrawing selectively sorbed component and desorbent from the circulating fluid at the outlet of the third zone, and periodically advancing the four zones in said stationary sorbent mass by simultaneously advancing the point of introduction of said charge mixture, the point of withdrawal of unsorbed component, the point of introduction of desorbent, and the point of withdrawal of selectively sorbed component and desorbent an equal increment along the path of flow of said circulating fluid.

2. Process as claimed in Claim 1 wherein the points of introduction to and withdrawal from the circulating fluid are simultaneously advanced along the path of the circulating fluid periodically before the capacity of the sorbent for sorbing sorbable component in the first processing zone has been completely spent and before unsorbed component is carried in the circulating fluid from the second into the third processing zone.

3. Process as claimed in Claim 1 or 2 wherein the points of introduction to and withdrawal from the circulating fluid at each periodic interval are simultaneously advanced an increment which is a fraction of one processing zone but is not less than one-tenth of one processing zone.

4. Process as claimed in any of the Claims 1 to 3 wherein the points of introduction to and withdrawal from the circulating fluid are periodically advanced an increment which takes into the third processing zone solely sorbent free from unsorbed component of the charge mixture.

5. Process as claimed in any of the Claims 1 to 4 wherein the circulating fluid is passed successively through four processing zones containing substantially equal quantities of sorbent.

6. Process as claimed in any of the Claims 1 to 5 wherein a fluid charge mixture comprising at least one straight chain organic compound and at least one non-straight chain organic compound is introduced continuously into the circulating fluid at the inlet of the first processing zone, a straight chain organic compound boiling below the initial boiling point of the charge mixture is maintained in circulation cyclically through the series of four processing zones and also is introduced continuously as desorbent into the circulating fluid at the inlet of the third processing zone while each of the four processing zones contains a sorbent of the molecular sieve type having pores sufficiently large for selectively sorbing the straight chain compound of said charge mixture and sufficiently small to preclude sorption of said non-straight chain compound in said pores, unsorbed non-straight chain compound is continuously withdrawn from the circulating fluid at the outlet of the first processing zone, selectively sorbed



valve in the line connecting the downcomer from bed No. 4 with the raffinate withdrawal manifold, simultaneously closed the valve in the line connecting the downcomer from bed No. 6 (inlet to bed No. 7) to the desorbent supply manifold while simultaneously opening the valve in the line connecting the downcomer from bed No. 7 (inlet to bed No. 8) with the desorbent supply manifold, and simultaneously closed the valve in the line connecting the downcomer from bed No. 9 to the sorbate withdrawal manifold while opening the valve in the line connecting the downcomer from bed No. 10 to the sorbate withdrawal manifold. Thereupon the above beds were retained on stream for one-half hour, followed by simultaneous shifts in the inlet and outlet streams to the next down-stream beds and this operation was thereafter continued in like manner at the same temperature, substantially uniform throughout the system, and with the same incremental advancement of the inlet and outlet streams at one-half hour intervals.

Throughout this regular operation, the valves controlling the inlet stream of charge mixture and the inlet stream of desorbent and also the valves controlling the withdrawal stream of raffinate and the withdrawal stream of sorbate were set to operate at equal volumetric flow rates and were adjusted on a volumetric basis to compensate for differences in pressure at the several points of inlet and outlet throughout the column.

The sorbate and raffinate outlet streams were each individually fractionated to separate substantially pure n-hexane and substantially pure cyclohexane as product streams while the n-butane distilled from the outlet streams in these fractionations was condensed and then recycled to the process. The above separation was operated on a continuous basis for 35 days without obvious depreciation in the activity of the molecular sieve sorbent.

WHAT WE CLAIM IS:—

1. In a continuous sorption process for fractionating a fluid charge mixture of several components wherein one of said components is selectively sorbed during contact of said charge mixture with a solid sorbent, unsorbed component of said mixture is withdrawn from contact with said sorbent and selectively sorbed component is displaced from the sorbent by a fluid desorbent, the improvement which comprises maintaining a continuous cyclic circulation of fluid successively through four serially connected processing zones of a stationary mass of said solid sorbent and from the outlet of the last zone back to the inlet of the first zone, continuously introducing said fluid charge mixture into the circulating fluid at the inlet of the first zone, continuously withdrawing unsorbed component from the circulating fluid at the outlet of the first zone, continuously introducing desorbent into the

circulating fluid at the inlet of the third zone, continuously withdrawing selectively sorbed component and desorbent from the circulating fluid at the outlet of the third zone, and periodically advancing the four zones in said stationary sorbent mass by simultaneously advancing the point of introduction of said charge mixture, the point of withdrawal of unsorbed component, the point of introduction of desorbent, and the point of withdrawal of selectively sorbed component and desorbent an equal increment along the path of flow of said circulating fluid.

2. Process as claimed in Claim 1 wherein the points of introduction to and withdrawal from the circulating fluid are simultaneously advanced along the path of the circulating fluid periodically before the capacity of the sorbent for sorbing sorbable component in the first processing zone has been completely spent and before unsorbed component is carried in the circulating fluid from the second into the third processing zone.

3. Process as claimed in Claim 1 or 2 wherein the points of introduction to and withdrawal from the circulating fluid at each periodic interval are simultaneously advanced an increment which is a fraction of one processing zone but is not less than one-tenth of one processing zone.

4. Process as claimed in any of the Claims 1 to 3 wherein the points of introduction to and withdrawal from the circulating fluid are periodically advanced an increment which takes into the third processing zone solely sorbent free from unsorbed component of the charge mixture.

5. Process as claimed in any of the Claims 1 to 4 wherein the circulating fluid is passed successively through four processing zones containing substantially equal quantities of sorbent.

6. Process as claimed in any of the Claims 1 to 5 wherein a fluid charge mixture comprising at least one straight chain organic compound and at least one non-straight chain organic compound is introduced continuously into the circulating fluid at the inlet of the first processing zone, a straight chain organic compound boiling below the initial boiling point of the charge mixture is maintained in circulation cyclically through the series of four processing zones and also is introduced continuously as desorbent into the circulating fluid at the inlet of the third processing zone while each of the four processing zones contains a sorbent of the molecular sieve type having pores sufficiently large for selectively sorbing the straight chain compound of said charge mixture and sufficiently small to preclude sorption of said non-straight chain compound in said pores, unsorbed non-straight chain compound is continuously withdrawn from the circulating fluid at the outlet of the first processing zone, selectively sorbed

5 straight chain compound is continuously withdrawn from the third processing zone, and both unsorbable compound and sorbable compound of the charge mixture are continuously carried in the circulating fluid from the fourth processing zone into the first processing zone.

10 7. Process as claimed in Claim 6 wherein a normally liquid charge mixture comprising at least one straight chain hydrocarbon and at least one hydrocarbon of the group of branched chain and cyclic hydrocarbons is introduced in liquid phase into the circulating fluid at the inlet of the first processing zone, a straight chain hydrocarbon boiling at least 15 10° C. below the initial boiling point of the charge mixture is maintained in circulation cyclically through the series of four processing zones and also is introduced as desorbent into the circulating fluid at the inlet of the third processing zone, and the hydrocarbons are maintained in liquid phase and at substantially uniform temperature throughout the 20 four processing zones and in the circulating fluid stream.

8. Process as claimed in any of the Claims 1 to 7 wherein the circulating fluid is passed through four processing zones in each of which the sorbent is substantially uniformly distributed among not more than ten serially connected fixed beds, and the points of introduction to and withdrawal from the circulating fluid are simultaneously advanced an increment equal to one fixed bed at each of the periodic intervals. 25 30

9. Process as claimed in Claim 8 wherein the circulating fluid is passed in each processing zone through an equal number of from 2 to 4 serially connected fixed sorbent beds of greater length than diameter, the length of each bed being not more than 10 times as large as its diameter. 35 40

10. The continuous sorption process substantially as described with reference to the accompanying drawings.

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