

[54] **SEPARATION PROCESS OF COMPONENTS OF FEED MIXTURE UTILIZING SOLID SORBENT**

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[51] Int. Cl. **C07c 7/12, C10g 25/04**

[58] Field of Search..... **260/674 SA; 208/310**

[56] **References Cited****UNITED STATES PATENTS**

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ABSTRACT

A process for continuously separating, in the liquid phase, the components of a feed mixture by contact with a solid sorbent utilizing a simulated countercurrent flow system wherein a liquid stream flows through serially and circularly interconnected desorption, rectification and sorption zones, in which process the flow of liquid stream is interrupted between both the desorption and rectification zones, and the first portion of effluent from the desorption zone, the portion being rich in sorbate, is directly circulated, and the second portion of the same comprising sorbate of high purity and desorbent is fed to a distillation apparatus from which one portion of the sorbate distillate is circulated, both as reflux into the rectification zone, to maximize the sorbate product purity at a reduced cost.

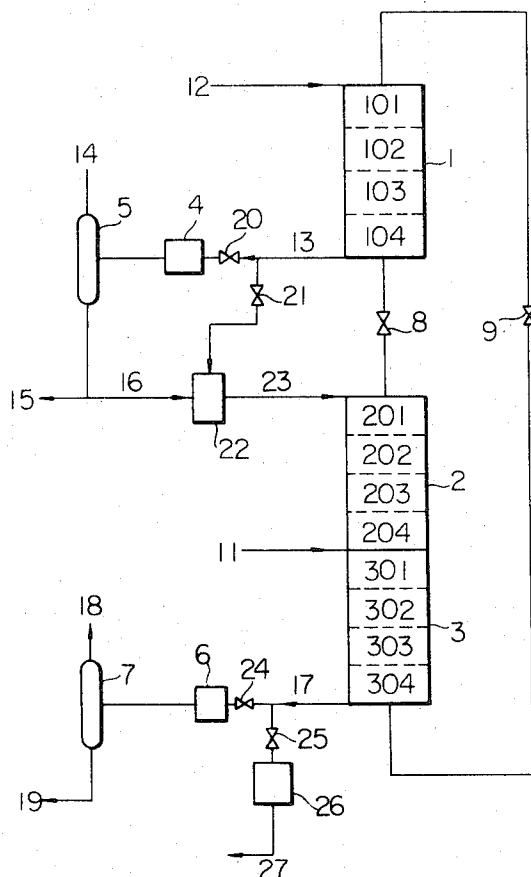
7 Claims, 8 Drawing Figures

Fig. 1

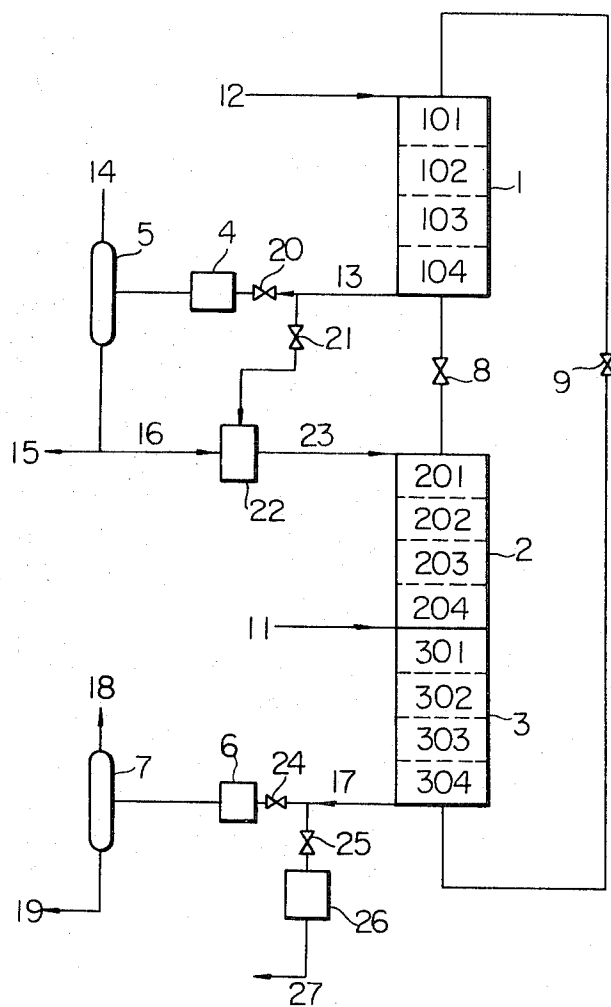
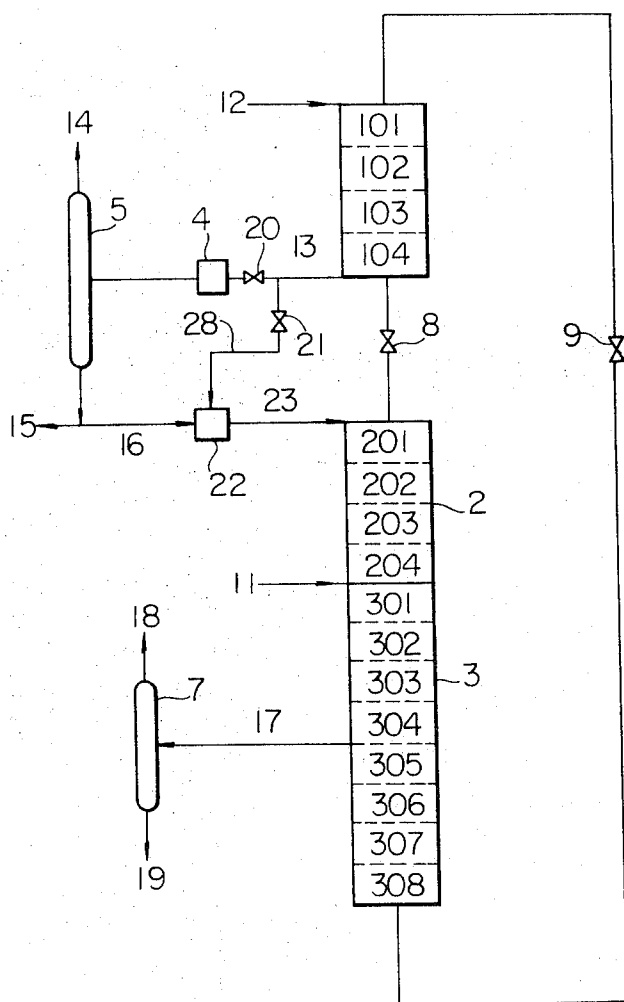


Fig. 2



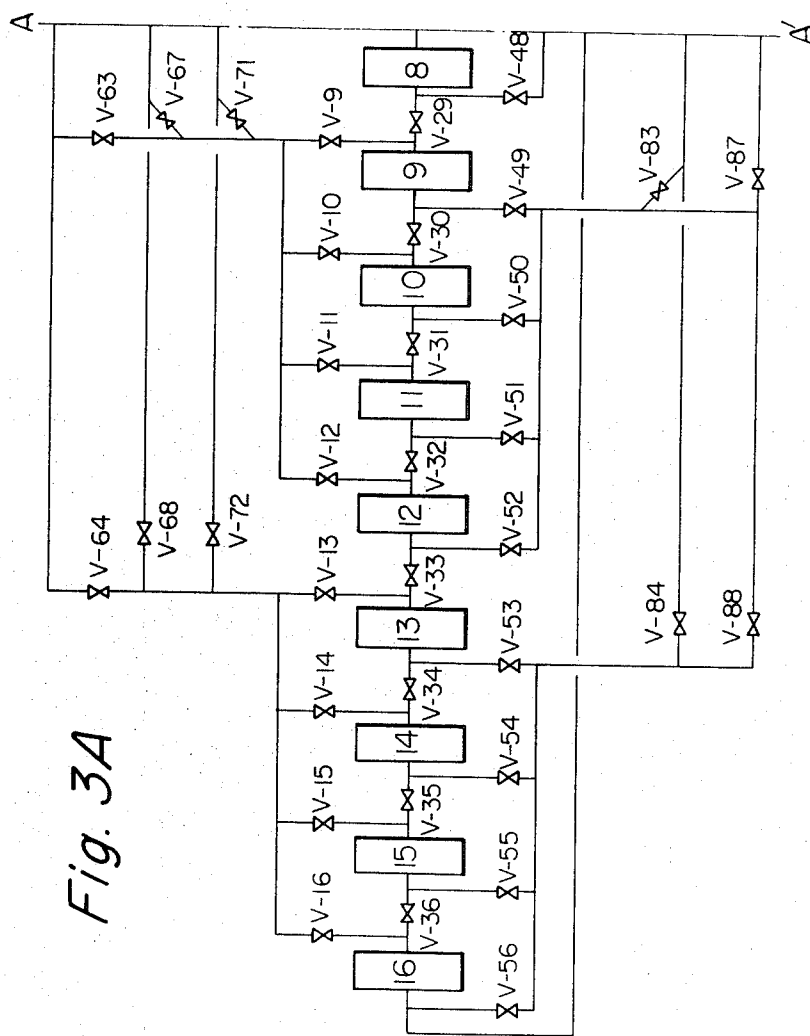


Fig. 3B

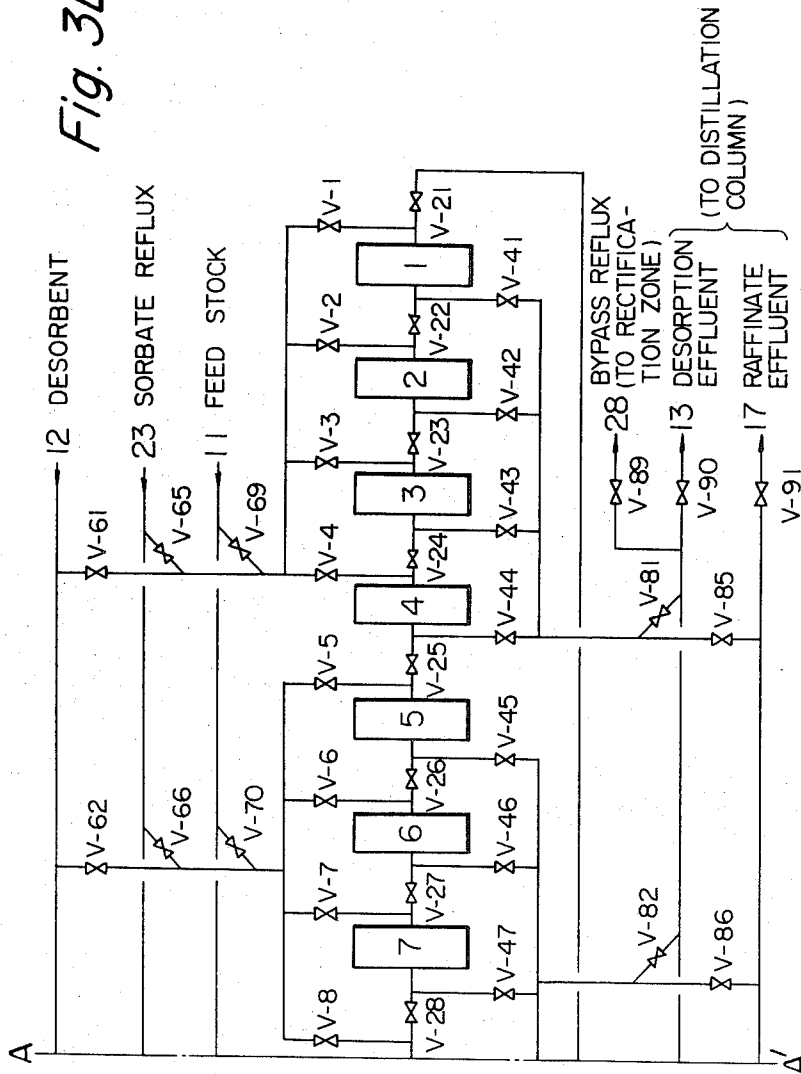


Fig. 4

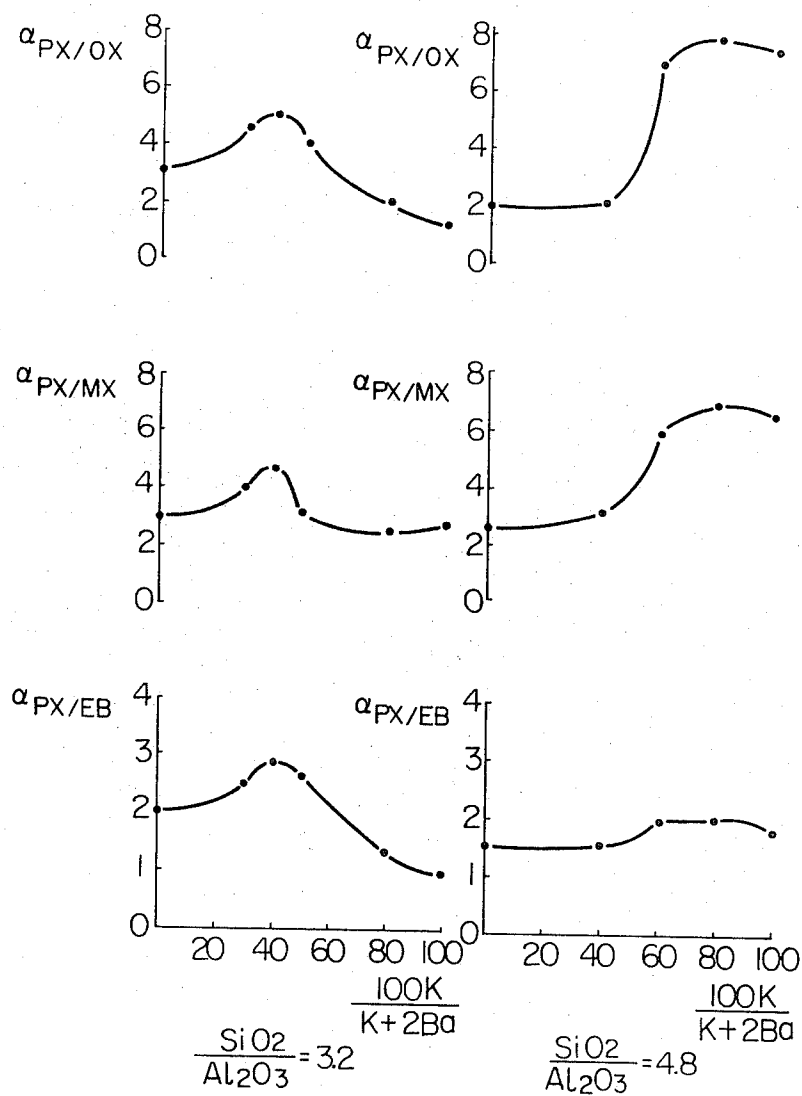


Fig. 5

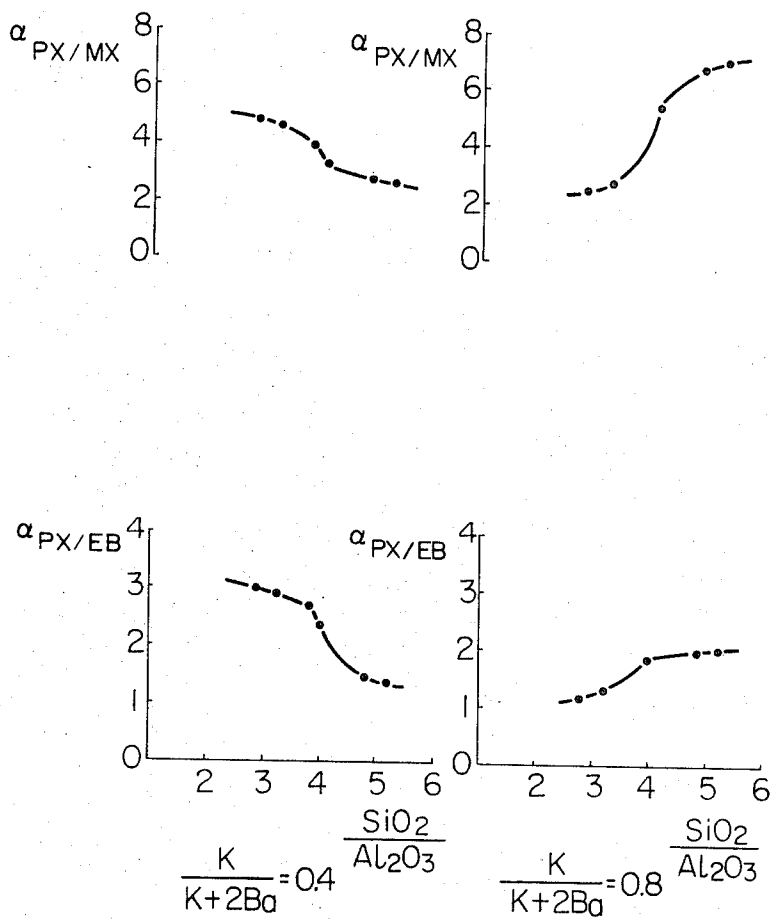


Fig. 6

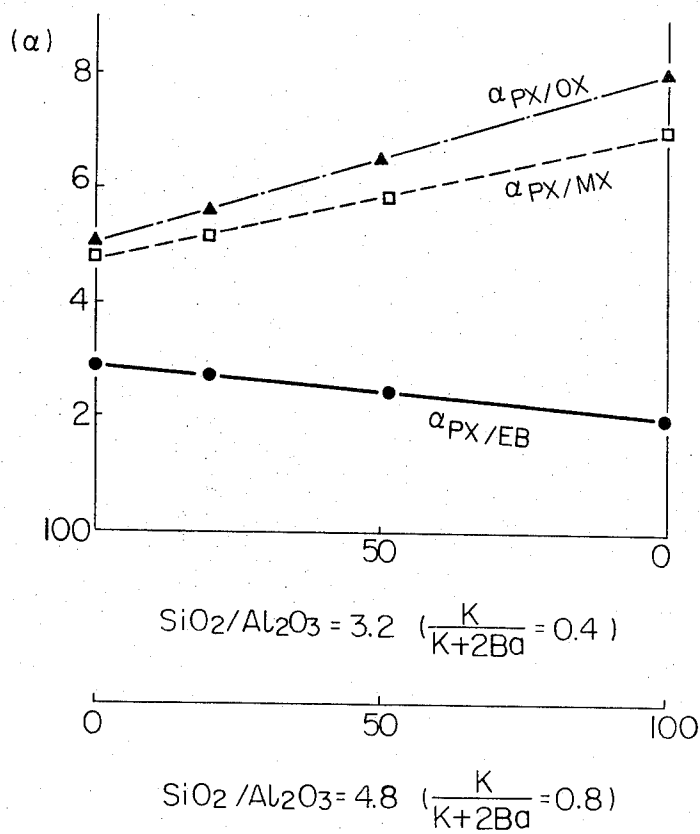
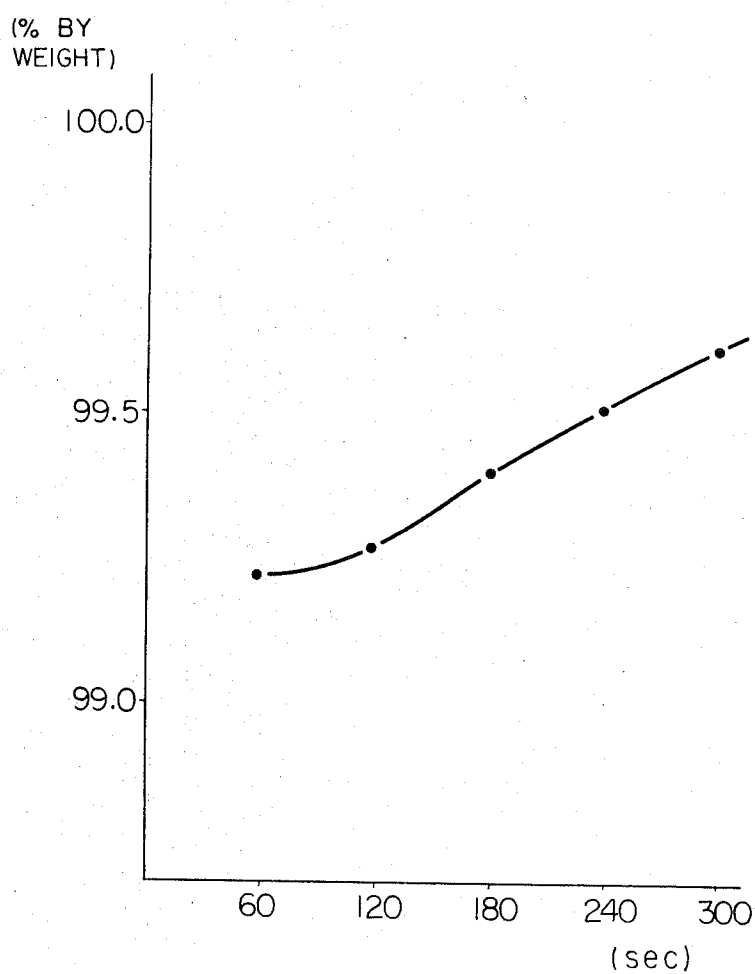


Fig. 7

SEPARATION PROCESS OF COMPONENTS OF FEED MIXTURE UTILIZING SOLID SORBENT

This invention relates to an improved process for continuously separating, in the liquid phase, two or more components of a liquid feed mixture utilizing a solid sorbent particle capable of selectively sorbing at least one component of the mixture. More particularly, it relates to certain improvements in a process for continuously separating, in liquid phase, the components of a liquid feed mixture such as xylene isomers, at least one of which is selectively sorbed by contact with solid sorbent particles such as zeolite, utilizing a simulated countercurrent flow system as hereinafter illustrated in detail, the improvement relating to discovery of process techniques which enables the separation of the selectively sorbed component having a high degree of purity at a reduced cost.

Most sorption apparatus of the type wherein a solid sorbent is employed, for example, for drying gas, adsorbing an organic substance, or separating n-paraffin in gaseous phase, involves the process technique of a type such that a number of sorption beds comprising the solid sorbent particles are used in turn to carry out sorption, desorption and regeneration in gaseous phase. However, such a process technique cannot be advantageously employed in the separation in liquid phase because, even at a stage when a sorption operation terminates, considerable amounts of a liquid feed stock remain unsorbed in the void spaces between adjacent particles of the solid sorbent, which makes it impossible to obtain a desired product of a high degree of purity with good yield.

In order to obviate this defect, it has been heretofore proposed to employ sweeping material in addition to the sorbent as disclosed in, for example, Chem. Eng. Prog. 48, 276 (1952). This is, however, disadvantageous because of complication of the operation and an increase in the cost for the distillation apparatus. In particular, such a single stage sorption-desorption process, when it is applied to adsorption-separation of a liquid feed mixture having a low separation factor, such as a mixture of xylene isomers, cannot provide the desired product, e.g., p-xylene, of high purity.

In the case of adsorption-separation of such a liquid feed mixture, the provision of a moving bed type adsorption process wherein the moving bed comprises adsorbent particles is countercurrently contacted with both streams of a liquid feed stock and desorbent apparently enhances the purifying effect, and it results in a high degree of purity of the adsorbed product. However, a problem arises; use of fragile solid sorbent particles such as zeolite is impracticable and channelling of the stream is unavoidable at the industrial scale level.

Thus, a so-called "simulated countercurrent flow system" wherein solid sorbent particles are actually stationary has been proposed to ensure the product purity, which system is disclosed in the Japanese Patent Publication 15681/67. In the known process, a sorption column is divided into four zones, i.e., a sorption zone, a secondary rectification zone, a desorption zone and a primary rectification zone, which zones are serially interconnected in order, and a continuously circulating fluid stream flowing through the four zones is maintained by circulating the effluent fluid from an outlet of the last zone to an inlet of the first zone and all the points of introducing and withdrawing the inlet and

outlet streams are simultaneously shifted at the stated intervals of time in a downstream direction to provide thereby a simulated countercurrent flow system wherein there is achieved a similar effect to that in the moving bed type adsorption process; a high degree of purity of the sorbate product can be obtained by the stream of desorbent flowing throughout all the four zones at a higher flow rate.

However, the process also has some defects; the flow of desorbent into the rectification zone and the sorption zone at a higher flow rate is rather uneconomical and decreases the separation efficiency in both the rectifying and sorbing action or sorbent. The disadvantage of the process is hereinafter described in detail in comparison with the process of the present invention.

An object of the present invention is, in short, to provide a novel simplified process system which enables the separation of the sorbate product of high purity with an enhanced efficiency and thus, at a reduced cost.

Other objects and advantages of the present invention will be apparent from the following description.

In accordance with the present invention, there is provided an improvement in a process for continuously separating, in liquid phase, the components of a liquid feed mixture, at least one of which is selectively sorbed by contact with solid sorbent particles, utilizing a simulated countercurrent flow system wherein liquid streams are allowed to flow through three serially and circularly interconnected zones; a desorption zone, a rectification zone and a sorption zone, each zone being divided into a plural of serially interconnected sections, each section being packed with a mass of the solid sorbent particles, by introducing desorbent into the first section of the desorption zone, withdrawing a desorption effluent comprising a selectively sorbed component from the last section of the desorption zone, introducing the liquid feed mixture to the first section of the sorption zone and withdrawing a raffinate effluent comprising a less sorbed component and the desorbent from the sorption zone, and all the points of introducing and withdrawing the liquid streams into and from the sections are simultaneously shifted, one section at a time at stated intervals of time, in a downstream direction while maintaining the same order of continuity and the same spatial relationship between all the points, the improvement being characterized by interrupting the liquid streams flowing through the three zones at a point between the desorption zone and the rectification zone while the first portion of the desorption effluent flowing out from the last section of the desorption zone, which portion contains either a little or no desorbent but contains the selectively sorbed component, is directly circulated, and the second portion thereof which portion contains the selectively sorbed component of high purity, but at a lower concentration in comparison with the first portion, is introduced into a distillation apparatus from which one portion of the sorbate distillate is circulated, both as reflux into the first section of the rectification zone.

In one embodiment, the process of the present invention as disclosed above is further characterized in that the liquid streams flowing through the three zones are further interrupted at a point between the sorption zone and the desorption zone and the raffinate effluent is withdrawn from the bottom of the last section of the sorption zone while the first portion of the raffinate ef-

fluent which does not substantially contain the less sorbed component is directly circulated into the first section of the desorption zone, and the second portion thereof which contains both the less sorbed component and the desorbent is introduced into a distillation apparatus from which the desorbent fraction is circulated into the first section of the desorption zone.

In another embodiment, the process of the present invention as disclosed above is further characterized in that one portion of the raffinate effluent is withdrawn from a point such that at least one section of the sorption zone remains downstream therefrom.

The present invention relates fundamentally to a sorption-separation system involving three zones; a desorption zone, a rectification zone and a sorption zone, which system is hereinafter illustrated in detail with reference to the accompanying figures. For convenience of illustration, desorbent having a boiling point lower than that of a liquid feed mixture comprising a sorbate component (selectively sorbed component) and raffinate components (less sorbed component) is referred to herein. It is, however, to be understood that desorbent having a boiling point higher than that of the liquid feed mixture can also be used in the practice of the invention.

FIG. 1 illustrates one preferable mode of the sorption cycle of the present process,

FIG. 2 illustrates another preferable mode of the sorption cycle of the present process,

FIG. 3 schematically shows the mode as illustrated in FIG. 2, in detail,

FIGS. 4, 5 and 6 show selectivity (α) of crystalline metal aluminosilicate sorbent,

FIG. 7 shows the change of the purity of p-xylene product, separated from the desorbent, in the desorption effluent with the lapse of time.

As shown in FIG. 1, the present sorption-separation system fundamentally involves solid sorbent particles-charged columns which are divided into three zones; 1 desorption zone, 2 rectification zone and 3 sorption zone. These zones are serially and circularly interconnected in order. Each zone is composed of a plural of serially interconnected sections in the flow direction of liquid streams.

In the desorption zone 1, a sorbate component selectively sorbed onto solid sorbent particles is desorbed by contact with a desorbent stream. In the rectification zone 2, countercurrent contact between the stream of a sorbate product and a simulated flow of the solid sorbent particles is effected to maximize thereby the purity of the product. In the sorption zone 3, separation of a liquid feed mixture takes place by selective sorption of a sorbate component of the mixture by solid sorbent particles.

Flows of the various liquids are illustrated with reference to FIG. 1. Desorbent 12 flows into the desorption zone 1 through an inlet of the first section 101 of the zone while a liquid mixture 13 of desorbent and sorbate (the mixture is hereinafter referred to as "desorption effluent") is withdrawn through an outlet of the last section 104 of the desorption zone 1 and flows through a mixing equipment 4 into a distillation column 5 wherein the desorption effluent is separated into both desorbent 14 and sorbate components. The desorbent 14 is circulated for re-use, as hereinafter more specifically illustrated. One portion of the sorbate component 15 is withdrawn from the system as a product and the

other portion flows 16 into the top section 201 of the rectification zone 2 as a reflux stream. A liquid feed mixture 11 comprising at least one sorbate component flows through an inlet positioned between both the rectification and sorption zones into the sorption zone 3. A mixture 17 of desorbent and raffinate components, i.e., less sorbed components (which mixture is hereinafter referred to as "raffinate effluent") is withdrawn from the bottom section 304 of the sorption zone 3 and flows through a mixing equipment 6 into a distillation column 7 wherein the raffinate effluent is separated into desorbent 18 and raffinate 19. The desorbent 18 is circulated for re-use and the raffinate 19 is withdrawn from the system. The liquid streams flowing through the three zones are interrupted at two points between both the desorption and rectification zones and both the sorption and desorption zones, respectively, by suitable interrupting means such as valves 8, 9.

The top sections 101, 201, 301 of the desorption, rectification and sorption zones are simultaneously transferred to the bottoms of the sorption, desorption and rectification zones, respectively, at stated intervals, of time. The transfer is effected by shifting all the points of introducing and withdrawing of all the liquid streams (12, 13, 23, 11 and 17) into and from the sorption column one step (i.e., one section) simultaneously in a downstream direction. Thus, a simulated countercurrent flow system is provided whereby the effects are obtainable similar to that achieved by a moving bed type sorption process wherein reflux streams come countercurrently into contact with fluid occupying the void spaces between sorbent particles, and the rectification action, going hand in hand with desorption action effected in the desorption zone, ensures the continuous preparation of the sorbate product of high purity.

In the above described system wherein sorbate products flow back to the adsorption column so as to maximize the purity of product to be prepared, a stream of solid sorbent particles seemingly flows in the opposite direction to the reflux stream of the products by shifting the points of introducing and withdrawing of the liquid streams into and from the adsorption column. Accompanying the simulated shift of solid sorbent particles, fluid occupying the void spaces between the sorbent particles also flows in the opposite direction to the reflux stream of the product. Therefore, the rectification effect due to the reflux stream in an adsorption column substantially corresponds to the difference in flow rate between an actual reflux stream and the stream flowing in the opposite direction to the reflux stream. The volume of the fluid occupying the void spaces is extremely large in the liquid phase and accordingly, it is of no advantage from an economical point of view to apply the above illustrated system as it is, to liquid phase separation.

Thus, the present invention has been completed, based upon the following technical ideas:

It is preferable to utilize solid sorbent particles having a relatively small size for increasing the sorption rate in the sorption-separation process. It was found that, if uniform distribution of the liquid feed flow is attained successfully at an entrance portion of the sorption column, streams of the liquid flowing through beds of solid sorbent particles are quite similar to a piston flow. Consequently, it is observed that desorption effluent flow-

ing out from the bottom of the desorption zone varies in composition with the lapse of time; at the time immediately after shifting the points of outlet and inlet, the desorption effluent contains sorbate product (selectively sorbed component) at an approximately 100 percent concentration because only the liquid occupying the void spaces between the sorbent particles is pushed out in accordance with piston flow, but at the time when the liquid occupying the void spaces is completely removed, a desorption effluent containing both the product selectively sorbed on the sorbent particle and desorbent begins to flow out and the concentration of desorbent in the effluent increases with the lapse of time.

Based upon the above observation, the process of the present invention involves the following procedures; a stream 13 of the desorption effluent flowing out from the bottom of the last section 104 of the desorption zone 1 during the first part of the time interval between shifts, which effluent contains sorbate product at an extremely high concentration, is introduced, not into a fractionation means such as distillation column 5, but directly into a reservoir 22 through a valve 21, in which reservoir 22 the effluent is mixed with a reflux stream 16 of a portion of sorbate product fraction separated at a distillation column 5 and the mixture is allowed to flow into the rectification zone 2 as a reflux stream 23, as shown in FIG. 1. When desorbent begins to increase in the desorption effluent 13 removed from the desorption zone 1 at the end of a certain period of time from the shift in inlets and outlets, the valve 21 is shut simultaneously with the valve 20 being opened, thereby the desorption effluent 13 is allowed to be introduced into a distillation column 5 and the sorbate fraction from the distillation column 5 is divided into two portions; one portion being withdrawn 15 as a product and the other being circulated 16 to the top of the rectification zone 2 as a reflux stream (the latter reflux flowing from the distillation column 5 to the rectification zone 2 is hereinafter referred to as "substantial reflux" and the former reflux flowing, not through the distillation column, but directly to the rectification zone 2 is hereinafter referred to as "bypass reflux").

In accordance with the above process, a flow rate of the substantial reflux flowing by way of a fractionation means can be considerably reduced, and thus, in the case where an ideal piston flow is realized through the sorption column, a the flow rate of the substantial reflux can be reduced to the degree equal to or less than that in gaseous phase separation.

Concerning the handling of raffinate effluent removed from the sorption zone 3, two processes are provided in accordance with the present invention.

The first process is illustrated with reference to FIG.

1. A stream 17 of the entire effluent flowing out from the bottom of the last section 304 in the sorption zone 3 is divided into two portions; a first portion of the effluent removed during the first part of the time interval between shifts of inlets and outlets, which portion has occupied the void spaces between sorbent particles and does not substantially contain the raffinate component (less sorbed component), i.e., consisting substantially of desorbent, is directly circulated 27 through a valve 25 and a reservoir 26, without going by way of a fractionation means, to the first section 101 of the desorption zone 1. The other portion of the effluent removed during the second part of the cycle, which contains

both raffinates and desorbent, is introduced through a valve 24 and a reservoir 6 into a fractionation means such as a distillation column 7, from which desorbent the fraction 18 is circulated to the first section 101 in the desorption zone 1 and the raffinate fraction is removed 19 from the system. Thus, the process reduces heat loads and consumption of utilities in comparison with the conventional process wherein heating of the entire effluent is required for the distillation.

The second process for the handling of the raffinate effluent removed from the sorption zone, which is illustrated with reference to FIG. 2, is characterized as follows:

1. The sorption zone 3 has an increased number of sections. Raffinate effluent 17 is withdrawn from a point such that at least one section (which total number is four in the example illustrated in FIGS. 2 and 3) remains downstream thereof.

2. In operation, the entire liquid stream flowing through the sorption zone 3 is divided into two portions, one portion being withdrawn 17 from the zone 3 as a raffinate effluent and the other portion allowed to flow directly down into the remaining sections (305, 306, 307, 308).

3. The former portion of raffinate effluent 17 is introduced into a distillation column 7, from which desorbent fraction 18 is circulated to the top of the desorption zone. This flow system is not provided with the bypass flow conduit shown in FIG. 1 by the numerical reference 27.

4. The number of the sections existing downstream from the withdrawal point of raffinate effluent 17 in the sorption zone 3 are determined as follows; the entire length of the sections from the withdrawal point to the bottom of the last section 308 in the sorption zone is such that a concentration of raffinate contained in the stream flowing down through these sections reaches approximately zero at the bottom of the last section 308.

5. Thus, the stream substantially containing no raffinate components is directly and continuously introduced through a valve 9 into the desorption zone.

The second process achieves the same effect as that of the first process by the arrangement of an increased number of the sections in the sorption zone without providing a bypass flow conduit as illustrated in FIG. 1.

A preferred embodiment of the invention is summarized as listed below.

1. A sorption-separation column involving solid sorbent particles consists of three zones; a desorption zone, a rectification zone and a sorption zone.

2. Each zone is divided into a plurality of serially interconnected adjacent sections each being packed with a mass of the solid sorbent particles, and all the points of introducing and withdrawing liquid streams are simultaneously shifted, one section at a time at stated intervals of time in a downstream direction while maintaining the same order of continuity and the same spatial relationship between the points whereby the liquid streams contact the mass of solid sorbent particles in a simulated countercurrent manner.

3. A portion of sorbate products is circulated as a reflux stream to the top section in the rectification zone to thereby maximize the purity of sorbate products.

4. Flow of the liquid stream flowing through the three zones is interrupted at a point between the desorption zone and the rectification zone whereby a flow rate of

desorbent flowing into both the rectification and sorption zones is advantageously controlled to thereby enhance the efficiency of solid sorbent particles in both zones.

5. Desorption effluent containing a selectively sorbed component at a high concentration, which is removed from the last section of the desorption zone during the first part of the time interval between shifts of all the introduction and withdrawal points is allowed to flow back as a bypass reflux to the top section in the rectification zone, together with a substantial reflux, without passing by way of a distillation apparatus, because the desorption effluent has a similar composition to that of the substantial reflux allowed to flow back to the rectification zone. The reason for the above is that, accompanying the simulated shift of sorbent particles, there is a simulated shift of the liquid occupying the void spaces between the sorbent particles also and therefore, immediately after the shift, the liquid occupying the void spaces in the last section of the desorption zone, which has just shifted from the top section of the rectification, has the same composition as that of the substantial reflux.

6. The entire liquid stream flowing through the sorption zone is divided into two portions; one portion being continuously withdrawn as a raffinate effluent from a point so that at least one section of the sorption zone remains downstream thereof and the other portion being allowed to flow down directly through the remaining sections of the zone as illustrated above with reference to FIG. 2. The flow rates of both streams and the number of the sections existing downstream from the withdrawal point of the raffinate effluent are suitably determined whereby the concentration of raffinate component in the liquid stream, which concentration decreases with a descent of the stream through the sections, reaches approximately zero at the bottom of the last section in the sorption zone and thus, a liquid stream free of raffinate component is allowed to flow into the desorption zone.

In order to realize a piston flow in the sorption columns, it is effective to utilize sorbent particles of a smaller size and a column of a smaller diameter and to increase the linear velocity of the liquid stream. It is particularly important for the objective that the liquid stream is uniformly dispersed in the inlet portion of the sorption columns, and this may be achieved by a suitable distributing means such as a distributing plate and a distributing pipe. It may also be achieved by for example, dividing the sorption column lengthwise.

In accordance with the process of the present invention, all the points of the introduction and withdrawal of liquid streams are shifted at the same time and at a predetermined interval of time. The shift may be effected by opening and shutting valves arranged in pipes connecting all the sections with each other and with liquid streams flowing into and out of the column. The valves used in the process include two or threeway valves of a type operated for example by oil pressure, air pressure or electric power.

A liquid feed stock supply pipe 11, a reflux pipe 23 and a desorbent supply pipe 12; and a desorption effluent pipe 13 and a raffinate effluent pipe 17 may be arranged in such a manner that they are in common between the valves and the sorption column as shown in FIG. 3 which is hereinafter illustrated.

The process conditions of the invention are illustrated below.

1. The process is carried out in a liquid phase.

The process of the present invention is effective particularly for liquid phase separation; although the sorption rate in liquid phase separation is lower than that in gaseous phase separation, the process possesses the following advantages in liquid phase;

A. The life of the sorbent is prolonged because firstly the separation process may be carried out at a relatively low temperature and secondly, impurities having a high boiling point produced on sorbent particles are continuously washed off thus preventing deterioration of the sorbent.

15 B. Consumption of utilities is small.

C. The apparatus to be used in the process is of small size.

20 D. The liquid phase separation is particularly advantageous in the case where a desorbent having a high boiling point is used. On the contrary, in gaseous phase separation wherein the desorbent is utilized, a high temperature operation is required, which results in lowering of sorption capacity, undesirable side-reactions and shortening of the life of sorbent.

25 2. Temperature and linear velocity in the column.

In order to minimize the pressure drop of the stream through the sorption column, it is most desirable effective to utilize sorbent particles having a large size or to reduce the linear velocity of liquid. A preferred size (diameter) of sorbent particles is within the range from 0.05 to 5 mm. With a decrease in the linear velocity of the liquid flow, uniformity of the liquid stream tends to be decreased, although the pressure drop is minimized. A preferred linear velocity thereof based on the empty column is within the range from 0.5 to 20 cm/sec. With an increase of temperature, the sorption rate also increases, but the sorption capacity decreases. Further, a high temperature causes undesirable side-reactions. Suitable temperatures vary depending upon the particular process but may be easily determined by considering the above factors.

3. Reflux ratio, required amount of solid sorbent, interval from the shift of all the introduction and withdrawal points to the next shift and number of sections:

35 In order to ensure high degree of purity of sorbate product in accordance with the process of the present invention the sorbate component is allowed to flow back as a reflux stream with a flow rate exceeding the minimum reflux ratio to the rectification zone whereby the component contacts countercurrently with the sorbent particles simultaneously flowing upstream in the rectification zone, as is carried out in a distillation column. The term "reflux ratio" as used herein means the ratio of the flow rate of the sorbate product allowed to flow back to the rectification zone to the entire sorbate product with drawn from the The minimum reflux ratio varies depending upon the composition of the liquid feed stock, purity of the product, the particular sorbent, etc. An increased reflux ratio is obviously disadvantageous from an economical viewpoint. From our experiments, it has been found that the reflux ratio is preferably 1.01 to 2.0 times the minimum reflux ratio.

40 In general, a change wherein the number of sections is increased and the volume of sorbent charged in each section is decreased so as to keep the sorption capacity constant, and the interval of time between the shifts of the introduction and withdrawal points is shortened,

has the advantage that total amounts of sorbent required may be reduced, but the disadvantage that the number of valves required increases with the increased number of the sections. Further, the shortening of the interval raises a problem of mechanical structure of valves for smooth shifting. On the other hand, another modification wherein the volume of sorbent to be charged into each section is increased and the interval is prolonged requires a greater amount of sorbent. Taking the above facts into consideration, these process conditions should be suitably determined.

From our experiments, it has been found that an interval of 0.5 to 10 minutes between the shifts is generally preferred. The number of the sections should be determined depending upon absorption equilibrium, reflux ratio, flow rate of desorbent, the interval of time between the shifts, etc., and, in general, is preferably 9 to 40. In general, a liquid phase sorption process is far more affected by the shift of points of introducing and withdrawing of the inlet and outlet streams and therefore, a larger number of the sections is required in comparison with a gaseous phase sorption process.

The amount of sorbent to be required in the present process is indicated by the following formula:

$$\text{Amount of sorbent to be required } T = N \cdot W \cdot \theta / 60$$

wherein

N is the number of the sections,

W is the apparent flow rate of sorbent (T/Hr),

θ is the interval of time between the shifts (min).

It has been found from our extensive experiments that the amount of sorbent is preferably within the range from 5 to 100 tons per ton of sorbate product per hour.

4. Bypass reflux

As the flow rate of the bypass reflux varies depending upon the degree of the undesirable mixing between both sorbate and the desorbent in the sorption column, void in a sorption column, the separation factor between sorbate and desorbent, etc., the real flow rate of the bypass flow should be determined based upon a model experiment wherein a sorption column analogous to that used for the mass production is utilized. In the case where an ideal distribution of liquid is effected in the sorption column, the flow rate of bypass reflux corresponds to the product of fractional void in a sorption column and the apparent flow rate of sorbent.

The bypass reflux does not cause any particular trouble in the operation of the sorption column even if the reflux contains a small amount of desorbent. In general, a concentration of desorbent in the bypass reflux is preferably at most 40 or 50 percent. When the concentration exceeds the upper limit, the amount of desorbent, which is sorbed onto and shifts together with sorbent particles, inevitably increases.

5. Raffinate effluent

The process of the present invention is further characterized, as illustrated above, in that one portion of the raffinate-containing liquid flowing down through the sorption zone is withdrawn as a raffinate effluent from a point such that at least one section of the sorption zone remains downstream thereof. A suitable flow rate of the raffinate effluent varies depending upon operation conditions, composition of liquid feed stock, adsorption selectivity, the number of the sections, etc. It has been found that a suitable flow rate, in general, falls within the range defined by the following inequality.

$$[R + F - 0.6WV] \geq y \geq [R + F - (WV + 0.7WC)]$$

wherein

Y is the flow rate of raffinate effluent (m^3/Hr),

R is the flow rate of reflux (m^3/Hr),

F is the flow rate of liquid feed stock (m^3/Hr),

W is the flow rate of sorbent (T/Hr),

V is the void fraction per unit weight of sorbent (m^3/T),

C is the sorption capacity per the unit weight of sorbent (m^3/T).

From an economical viewpoint, it is preferable to lower the flow rate as far as possible while still satisfying the inequality.

The process of the present invention is applicable to all methods of sorption-separation relying upon solid sorbent particles having a capacity to selectively sorb at least one of the components of a feed stock in liquid phase, such as the separation of an olefin and paraffin; and separation of an aromatic hydrocarbon and a non-aromatic hydrocarbon, both by sorbents such as silica gel or active charcoal as well as separation of alkyl-substituted aromatic compounds by the zeolite adsorbent, and separation of n-paraffins from their isomers relying upon molecular sieve sorbent. In particular, a separation process relying upon solid sorbent particles of a type too fragile to be utilized in moving beds or fluidized beds may preferably be performed by the present invention.

Among others, the present process may be most preferably applied to separation of p-xylene from xylene isomers particularly relying upon a particular crystalline metal aluminosilicate sorbent.

The separation of p-xylene from xylene isomers is hereinafter illustrated in greater detail.

When p-xylene was intended to be selectively separated from a mixed xylene, i.e., xylene isomers ordinarily comprising p-xylene, m-xylene, o-xylene and ethylbenzene, a high degree of selectivity was, in the past, not obtainable for all the kinds of xylene feed stocks because the selectivity varies too much with the particular xylene isomers. Even the sorbent which possessed a greater capacity to selectively sorb p-xylene from the particular xylene feed stock could not be successfully applied to all other xylene feed stock, the composition of which inevitably varies with the stock situation. It has been, therefore, eagerly desired to solve the problem.

The following crystalline metal aluminosilicate sorbents are rather preferably utilized for the separation of xylene;

A. Potassium-substituted zeolite-X or -Y, represented by the formula, $\text{K}_x\text{OA}1_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ wherein m is a positive real number and x is a real number.

B. Barium-substituted zeolite-X or -Y, represented by the formula, $\text{BaOA}1_2\text{O}_3 \cdot m\text{SiO}_2 \cdot x\text{H}_2\text{O}$ wherein m and x are the same as defined above.

C. Barium and potassium-substituted zeolite-X or -Y.

It has been surprisingly found that a selectivity of a faujasite-type crystalline aluminosilicate sorbent, a part of cations contained therein having been substituted with (a) barium, (b) potassium and/or (c) at least one metal selected from the group consisting of zirconium, yttrium, neodymium, lead, uranium and mercury (which group is referred to hereinafter as "group A"), greatly varies depending upon both the silica/alumina ratio and the proportion of the metals, i.e., barium, po-

tassium and group A metal, introduced therein, and that faujasite-type crystalline aluminosilicate sorbent exhibits an extremely improved selectivity by suitably selecting both the silica/alumina ratio and the proportion of the metals; sorption characteristics of the sorbent particles vary too much with the silica/alumina ratio; and the sorbent particles having desirable sorption characteristics may be prepared by blending two sorbents, the sorption characteristics of which differ from each other.

More particularly, the preferable sorbents for the separation of p-xylene are the specific crystalline metal aluminosilicate, which is classified into the three types;

1. Crystalline metal aluminosilicate in the form of faujasite-type, characterized as having a silica/alumina ratio of less than 4.0 and containing (a) barium, (b) potassium and (c) at least one metal (hereinafter referred to as *M* for brevity) selected from A group in the proportion satisfying the following atomic ratios;

$$K/(K + 2Ba) = 0.0 \sim 0.5$$

$$M/(K + 2Ba) = 0.0 \sim 0.5$$

2. Crystalline metal aluminosilicate in the form of faujasite-type, characterized as having a silica/alumina ratio of not less than 4.0 and containing (a) barium, (b) potassium and (c) *M*, defined above, in the proportion satisfying the following atomic ratio;

$$K/(K + 2Ba) = 0.6 \sim 1.0$$

$$M/(K + 2Ba) = 0.0 \sim 0.5$$

3. A mixed metal aluminosilicate comprising both the crystalline metal aluminosilicates defined in the preceding items (1) and (2).

It should be noted that the sorbent characteristics of the preferable aluminosilicate, i.e., ordinarily referred to as zeolite, in the form of faujasite-type crystalline material greatly depends upon both the silica/alumina ratio and the content of the metals. In other words, in the case of the silica/alumina ratio being less than 4, the proportion of metals indicated by both formulae $K/(K + 2Ba)$ and $M/(K + 2Ba)$ preferably falls within the range of 0.0 ~ 0.5. On the contrary, in the case of the ratio being not less than 4.0, the proportion of the metals indicated by both $K/(K + 2Ba)$ and $M/(K + 2Ba)$ preferably falls within the range of 0.6 to 1.0 and 0.0 to 0.5, respectively. The numerical value of 0.0 in both equations means that potassium and/or *M* is not contained in the aluminosilicate sorbent and the value of 1.0 in the former formula means that barium is not contained therein.

The metal aluminosilicates defined above exhibit an extremely high selectivity to p-xylene among xylene isomers, but an extremely weak affinity for other xylene isomers, i.e., o-xylene, m-xylene and ethylbenzene. In other words, the crystalline metal aluminosilicate sorbent has excellent selectivity with respect to p-xylene and thus, facilitates the separation of a p-xylene product of high purity at a reduced cost.

The crystalline metal aluminosilicate in the form of faujasite-type to be preferably utilized in the present process may be prepared by substituting barium, potassium and the metal *M* ions for a cation, for example, sodium ion of a faujasite-type crystalline zeolite, which zeolite is ordinarily commercially available and may be prepared by the hydrothermal reaction wherein a silica source such as sodium silicate, silica gel, etc. it reacted

with alumina source such as sodium aluminate, etc., sodium hydroxide and water. The synthesis is disclosed in detail in, for example, Japanese Patent Publications No. 124/1963, 1639/1961, 20121/1965, 19180/1966, 16941/1967, 8527/1967, 6712/1957, 5722/1968, 12016/1969, 23986/1969, 20387/1967, 5054/1965, 845/1967, 746/1965, 5806/1963, 30611/1969, 3659/1963 and 12016/1969.

The substitution of barium, potassium and the metal *M* defined above for the sodium ion of the faujasite-type crystalline zeolite may be effected by conventional methods known as ion exchange of such zeolites. Usually, aqueous solutions of salts of the metal to be substituted are utilized for the substitution. The aqueous solutions may be applied separately, or as a mixed solution.

Preferably, compounds to be used for the substitution include, for example, a metal salt of inorganic acids such as nitric acid, carbonic acid and hydrochloric acid, metal hydroxide and other inorganic compounds. Organic salts such as acetate may also be used. Amongst others, nitrate and carbonate are most preferable. These salts may be utilized as a solution in any concentrations, but in the case of an aqueous solution, the concentration is preferably 1 to 20 percent and most preferably 5 to 10 percent, both by weight.

The ion exchange may be satisfactorily effected even at room temperature, but preferably at an elevated temperature, for example, at 100°C or more, to raise the reaction rate. It may be performed continuously or batchwise. The degree of the substitution of barium, potassium and the metal *M* for the cation such as sodium ion is preferably not less than 60 percent and most preferably not less than 80 percent based on the total cations present.

Zeolite, thus prepared by the ion exchange, contains a large amount of water therein and therefore, ordinarily must be subjected to a dehydration treatment so as to be activated. The treatment may be effected by heating the zeolite at temperatures higher than 100°C but lower than the decomposition temperature thereof, e.g., preferably 150° to 600°C and most preferably 200°C to 500°C, and for a period of scores of minutes to several hours. The zeolite to be utilized in the present process may further contain therein any other cations in addition to barium, potassium and the metal *M* unless they counteract the inventive effect.

The relation between the composition of zeolite sorbent and the selectivity to p-xylene will be hereinafter illustrated.

FIG. 4 shows the selectivity (α), which is defined by the following formula:

$$\alpha A/B = C_{SA}/C_{SB} \cdot C_{LB}/C_{LA}$$

wherein C_{SA} and C_{SB} are concentrations of components A and B in the sorbed phase, respectively and C_{LA} and C_{LB} are concentrations of components A and B in the liquid phase which are in equilibrium with the sorbed phase, respectively, of various aluminosilicate sorbents differing in silica/alumina ratio and the proportion of the metals Ba, K and *M*. In FIG. 4, PX, MX, OX and EB indicate p-xylene, m-xylene, o-xylene and ethylbenzene, respectively.

As is evident from FIG. 4, the sorbent having a silica/alumina ratio of 3.2 exhibits a high selectivity at a $K/(K + 2Ba)$ ratio ranging from 0.0 to 0.5, particularly from 0.3 to 0.5, but a low selectivity at both the ratios falling

outside the ranges. On the contrary, the sorbent having a silica/alumina ratio of 4.8 exhibits a high selectivity at a $k/(K + 2Ba)$ ratio ranging from 0.6 to 1.0, but a low selectivity at both the ratios falling outside the ranges. The sorbent having a silica/alumina ratio of less than 4.0 is effective particularly for the separation of p-xylene from ethylbenzene in comparison with the sorbent having the ratio of not less than 4.0. On the contrary, the latter sorbent having the ratio of not less than 4.0 is effective particularly for the separation of p-xylene from o- and m-xylenes in comparison with the former sorbent.

FIG. 5 shows dependence of selectivity (α) upon silica/alumina ratio, which was tested under the conditions of the $K/(K + 2Ba)$ ratio being constant and the silica/alumina ratio being varied. As is evident from FIG. 5, with respect to the sorbent having a $K/(K + 2Ba)$ ratio of 0.4, it exhibits a high selectivity at a silica/alumina ratio of less than 4.0. But, the sorbent having a $K/(K + 2Ba)$ ratio of 0.8 exhibits this at a silica/alumina ratio of not less than 4.0.

It should be noted that the sorbent having a silica/alumina ratio of less than 4.0, when $K/(K + 2Ba)$ ratio falls within the range from 0.0 to 0.5, is effective particularly for the separation of p-xylene from ethylbenzene, and the sorbent having a silica/alumina ratio of not less than 4.0, when $K/(K + 2Ba)$ ratio falls within the range from 0.6 to 1.0, is effective particularly for the separation of p-xylene from o- and m-xylenes and that selectivity may be varied at will by blending both the sorbents, as illustrated in FIG. 6. FIG. 6 shows the dependence of selectivity (α) upon the mixed proportion of both the aluminosilicates, one being $SiO_2/Al_2O_3 = 3.2$, $K/(K + 2Ba) = 0.4$ and the other being $SiO_2/Al_2O_3 = 4.8$, $K/(K + 2Ba) = 0.8$, wherein the ordinate indicates the selectivity (α) and abscissa indicates the mixed proportion (percent).

Thus a sorbent having desirable selectivity, which depends upon a composition of the xylene feed stock used in the present process, may easily be prepared merely by blending both the sorbents in a suitable proportion, one of which sorbents has a silica/alumina ratio of less than 4.0 and $K/(K + 2Ba)$ ratio of 0.0 to 0.5 and is suitable for treating a xylene feed stock which is poor in o- and/or m-xylene, and the other of which sorbents has a silica/alumina ratio of not less than 4.0 and $K/(K + 2Ba)$ ratio of 0.6 to 1.0 and is suitable for treating a xylene feed stock being poor in ethylbenzene.

Further, the introduction of at least one metal, hereinafter referred to as M, improves the selectivity to p-xylene, but weakens the affinity for other xylene isomers, particularly ethylbenzene.

The optimum amount of the metal M to be substituted for sodium depends upon the particular metal. Generally the metal should be preferably present in the amount satisfying the following atomic ratio;

$$M/(K + 2Ba) = 0.0 \sim 0.5$$

Table 1 shows selectivity (α) of various sorbents prepared by the introduction of the metal M into potassium- and barium-substituted aluminosilicates differing in the silica/alumina ratio and the $K/(K + 2Ba)$ ratio from each other.

Table 1

No.	SiO_2/Al_2O_3	$K/(K + 2Ba)$	$M/(K + 2Ba)$	PX/EB α	PX/MX
1	3.2	0.3	0	2.0	4.6

2	3.2	0.3	Zr 0.1	2.3	4.6
3	4.8	0.7	0	2.0	6.5
4	4.8	0.7	Y 0.05	2.2	6.4
5	4.8	0.7	Nd 0.05	2.3	6.4
6	4.8	1.0	0	1.8	6.6
7	4.8	1.0	Pb 0.03	2.3	6.6
8	4.8	1.0	Th 0.03	2.0	6.5
9	4.8	1.0	U 0.04	2.1	6.7
10	4.8	1.0	Hg 0.04	2.2	6.6

As is evident from Table 1, lead and mercury are particularly preferable among the metals listed above.

Selection of a suitable desorbent is also important because it affects the cost of separation. Suitable desorbents are those which are capable of being sorbed onto sorbent particles at a high sorption rate and of desorbing sorbate from the sorbent and satisfy the following equation in sorbate-desorbent system;

$$\text{Selectivity } (\alpha) = Y(1 - X)/(1 - Y)X = 0.2 - 5$$

wherein X and Y are fractions by weight of sorbate in the liquid phase and in the sorbed phase, respectively. When a weak desorbent (which exhibits a selectivity exceeding 5) is utilized, a large amount of desorbent is needed for the desorption, which leads to an increase of the desorbent concentration in the sorbate product and therefore, an increase in the cost of separation. On the contrary, strong desorbent (which exhibits a selectivity of less than 0.2), has a tendency to remain in the sorbent in a greater amount, which also leads to an increase of the desorbent concentration in the product. Further, the desorbent remaining undersorbed in sorbent causes reduction of the sorption capacity of the sorbate and accordingly, an increase in the amount of sorbent to be used.

The desorbent should preferably have a boiling point differing from those of the sorbate product and the raffinate by 5°C or more. A desorbent having an extremely low boiling point is not preferred because there is a need to maintain the pressure high enough to ensure the liquid phase.

Suitable desorbents should be chosen in consideration of the above matters. Preferred desorbents to be used particularly for the separation of p-xylene from other xylene isomers includes, for example, alkyl-substituted aromatic hydrocarbons having seven to 12 carbon atoms such as toluene, o-ethyltoluene, m-ethyltoluene, p-ethyltoluene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 1,2,3-trimethylbenzene, n-propylbenzene any isomers or a mixture of o-, m- and p-diethylbenzene; and ethylidene chloride, dichloropropane, chloroform, thiophene, and the like.

Features and advantages of the present invention are summarized as follows;

1. The present process involves a sorption-separation system wherein the beds of solid sorbent particles are divided into serially and circularly interconnected three zones; a desorption zone, a rectification zone and a sorption zone, through which zones liquid streams flow, but, the flow thereof is interrupted between the desorption zone and the rectification zone, whereby there exists no desorbent in the rectification zone or, even if it exists therein, is far less in comparison with the known separation system as disclosed in the Japanese Patent Publication 15681/1967, which fact leads to an improvement in the efficiency of rectification.
2. The present process involves the interruption of the liquid streams at a point between the desorption zone and the rectification zone and a first portion of the desorption effluent flowing out from the desorption zone,

which portion contains either a little or no desorbent but contains a sorbate component, is directly circulated and the second portion thereof which contains both a sorbate component of high purity at a low concentration in comparison with the first portion and desorbent, is introduced into a fractionation apparatus from which a portion of the sorbate fraction is circulated, both into the rectification zone as a reflux stream.

Thus, the reflux of sorbate rather than desorbent enables not only a high degree of purity of the product being obtained, but also increases the concentration of sorbate at the upper part of the rectification zone, that is, it increases the concentration of the sorbate product in the liquid sorbed onto sorbent particles, which conduces to the reduction of the apparent flow rate of sorbent.

3. Because of the absence of the cyclic flow of the desorbent stream through all the desorption, rectification and sorption zones in the present process, the concentration of desorbent in both desorption effluent and raffinate effluent is low and thereby, substantial economies for the fractionation of desorbent are ensured.

4. The known process as disclosed in Japanese Patent Publication 15681/1967, wherein liquid stream circulates through all the beds of sorbent particles, requires programming facilities for controlling, more particularly, varying the flow rate of the cyclic flow each time all the valves are changed over. On the contrary, the process of the invention does not require such auxiliary facilities as the complicated programming facilities for controlling the cyclic flow rate and pumps because of the absence of such a cyclic flow.

The process of the present invention is further illustrated in the following examples which exemplify the separation of p-xylene from xylene isomers.

EXAMPLE 1

Such an arrangement as shown in FIG. 3 involves piping including 71 valves and 16 vertical columns serially interconnected all the columns being divided into three zones; desorption, rectification and sorption zones and each zone being comprised of 4, 4 and 8 columns, respectively. Each column had an inner diameter of 25 mm and a height of 2.0 m and was packed with potassium zeolite Y particles having a silica/alumina ratio of 4.7 to a height of 1.8 m from the bottom, which spherical particles, are of a particle size of 1 mm, and copper particles have a particle size of 1 mm in the remaining vacant space, i.e., to a height of 0.2 m from the top of the zeolite layer. The total amount of the zeolite particles packed in the columns was 10.5 kg. Thus, a flow rate of flow of sorbent (W) was $10.5/16 \times 60/5 = 7.9$ (Kg/Hr) at the shift interval of 5 minutes. Sorption capacity (C) and fractional void (V) of the sorbent were 0.26 l/Kg and 1.10 l/Kg, respectively. All the pipes and the valves had an inner diameter of 2 mm and the distance between the column and the valve for shifting the points of introducing and withdrawing of the liquid streams into and from the columns was determined short enough to prevent contamination of the liquid stream. Opening and shutting of all the valves was effected by a program timing apparatus, time required for opening and shutting being less than 1 second.

A feed stock consisting of 20 percent by weight of p-xylene, 40 percent by weight of m-xylene, 20 percent by weight of ethylbenzene and 20 percent by weight of o-xylene, after being heated to 140°C, was continu-

ously fed through a pipe 11 at a flow rate of 2.1 l/Hr and a pressure of 8 Kg/cm²G. P-xylene having a purity of 99.3 percent by weight, after being heated to 140°C, was continuously fed as reflux through a pipe 23 at a flow rate of 9.5 l/Hr and a pressure of 10 Kg/cm²G. Diethylbenzene, after being heated to 140°C was continuously fed through a pipe 12 at a flow rate of 5 l/Hr and a pressure of 12 kg/cm²G.

Prior to the feeding of the three liquids, 27 valves, indicated by the numerical references V-1, 5, 9, 21, 22, 23, 24, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 44, 52, 61, 66, 71, 81, 87, 90 and 91 in FIG. 3, were opened and the other 44 valves were shut. Five minutes after the feeding commenced. These valves were simultaneously changed over; 27 valves of the references V-2, 6, 10, 21, 22, 23, 24, 25, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 45, 53, 61, 66, 71, 82, 88, 90 and 91 were opened and the other 44 valves were shut whereby all the points of introduction and withdrawal of the liquid streams were shifted by one section (i.e., one column). Similarly, all the introduction and withdrawal points were simultaneously shifted at intervals of five minutes.

Raffinate effluent was continuously withdrawn at a constant flow rate of 2.8 l/Hr, in which effluent diethylbenzene desorbent was present at a concentration of 38 percent by weight based on the effluent, and p-xylene was present at a concentration of 2 percent by weight based on the entire xylene fraction contained therein. Desorption effluent was withdrawn at a flow rate of 13.8 l/Hr. The entire amount was fed into a distillation column to be thereby separated into diethylbenzene and p-xylene. The p-xylene fraction had a purity of 99.3 percent by weight.

EXAMPLE 2

Utilizing the same apparatus as that of Example 1, procedures of Example 1 were repeated wherein a mixed liquid consisting of 20 percent by weight of p-xylene having a purity of 99.3 and 80 percent by weight of diethylbenzene, after being heated to 140°C, was continuously circulated through the pipe 23 as reflux at a flow rate of 9.5 l/Hr and a pressure of 10Kg/cm²G.

The concentration of p-xylene in the entire xylene fraction contained in the effluent flowing through the pipe 17 was 2 percent by weight. The entire desorption effluent flowing out at a flow rate of 13.8 l/Hr was fed into a distillation column to be thereby separated into p-xylene and ethylbenzene. The p-xylene fraction exhibited a purity of 98.5 percent, which is lower by 0.8 percent compared with that of Example 1.

EXAMPLE 3

Utilizing the same apparatus as that of Example 1, the procedures of Example 1 were repeated wherein desorption effluent flowing out at a flow rate of 13.8 l/Hr was divided into two portions; the first portion thereof, withdrawn for a period of 118 seconds after the shift of the withdrawal point was recycled through a pipe 23 as reflux (herein referred to as bypass reflux), which portion was mainly composed of sorbate product, and therefore not required to be separated by distillation, and the second portion withdrawn after the lapse of 118 seconds from the shift was fed into a distillation column to be separated into p-xylene and diethylbenzene. The p-xylene fraction exhibited a purity of 99.5 percent by weight, which is higher by 0.2 percent

by weight compared with that of Example 1. One portion of the p-xylene fraction was withdrawn at a flow rate of 0.39 l/Hr from the system as a product and the other portion was recycled as reflux (herein referred to as substantial reflux). An average purity of p-xylene in both the bypass reflux and the substantial reflux was 99.3 percent by weight.

Raffinate effluent flowing through a pipe 17 contained desorbent at a concentration of 38 percent by weight and p-xylene at a concentration of 2 percent by weight based on the entire xylene fraction contained therein.

The change in the purity of p-xylene product, separated from desorbent, in the desorption effluent with the lapse of time during the interval between shifts is shown in FIG. 7 wherein the ordinate indicates purity of p-xylene product (percent by weight) and the abscissa indicates the lapse of time after the shift (sec). It is evident from FIG. 7 that the p-xylene purity increases with the lapse of time and therefore, p-xylene product of high purity is obtainable by distilling the second portion of the desorption effluent.

Another advantage obtained by the process wherein the first portion of desorption effluent flowing out for a period of 118 seconds after the shift was recycled as bypass reflux is as follows; the substantial reflux ratio, i.e., the flow rate ratio between the substantial reflux stream to be recycled from a distillation apparatus and the sorbate product to be withdrawn from the system, could be sharply reduced as compared with that of the process wherein the entire desorption effluent is introduced into a distillation apparatus, that is, the ratio was reduced from $9.5/0.39 \approx 24$ to $4.07/0.39 \approx 10$ in the present example, leading to reduction of the distillation cost.

EXAMPLE 4

Utilizing the same apparatus as that of Example 1, the procedures of Example 1 were repeated wherein both the flow rates of the raffinate effluent withdrawn through a pipe 17 and the desorbent feed introduced through a pipe 12 were 2.2 l/Hr and 4.4 l/Hr, respectively, with all other conditions remaining substantially same.

The concentration of desorbent in raffinate effluent was 23 percent by weight and the concentration of p-xylene in the entire xylene contained in the effluent was 2 percent by weight. The p-xylene purity of the entire xylene contained in the desorption effluent was 98.2 percent by weight, showing that, in the case where the flow rate of the raffinate effluent is lower than that defined by the formula, $R + F - (WV + 0.7WC)$, at least one portion of the xylene isomer components other than p-xylene, which components are not completely separated in a sorption zone and thus, enter a desorption zone, is incorporated into the desorption effluent.

In this example, the entire amount of p-xylene having a purity of 98.2 percent was withdrawn from the system as a product and another p-xylene having a purity of 99.3 percent was circulated as a reflux stream.

EXAMPLE 5

Utilizing the same apparatus as that of Example 1, the procedures of Example 1 were repeated wherein spherically molded sorbent particles having a diameter of 1 mm and comprising faujasite-type crystalline zeolite characterized as having a silica/alumina ratio of 4.7

and containing Ba, K and Pb in the proportions satisfying the following atomic ratio;

$$K/(K + 2Ba) = 0.7$$

$$Pb/(K + 2Ba) = 0.05$$

were substituted for the potassium zeolite Y particle with all other conditions remaining substantially same.

The concentration of desorbent in raffinate was 38 percent by weight and the concentration of p-xylene in the entire xylene components contained in the raffinate effluent was 1.8 percent by weight. The purity of p-xylene in the desorption effluent was 99.5 percent.

Example 6

The procedures of Example 5 were repeated wherein faujasite-type crystalline zeolite characterized as having a silica/alumina ratio of 3.0 and containing Ba, K and Pb in the proportion satisfying the following atomic ratio;

$$K/(K + 2Ba) = 0.40$$

was substituted with all other conditions remaining substantially same.

The concentration of desorbent in raffinate effluent was 38 percent by weight and the concentration of p-xylene in the entire xylene components contained in the raffinate effluent was 1.9 percent by weight. The purity of p-xylene in the desorption effluent was 99.5 percent.

What we claim is:

1. In a process for continuously separating, in liquid phase, the components of a liquid feed mixture, at least one of which is selectively sorbed by contact with solid sorbent particles, utilizing a simulated countercurrent flow system wherein liquid streams are allowed to flow through three serially and circularly interconnected zones; a desorption zone, a rectification zone and a sorption zone, each zone being divided into a plurality of serially interconnected sections, each section being packed with a mass of said solid sorbent particles, by introducing desorbent into the first section of said desorption zone, withdrawing a desorption effluent comprising a selectively sorbed component from the last section of said desorption zone, introducing said liquid feed mixture into the first section of said sorption zone and withdrawing a raffinate effluent comprising a less sorbed component and said desorbent from said sorption zone, and all the points of introducing and withdrawing said liquid streams into and from said sections are simultaneously shifted, one section at a time at stated intervals of time, in a downstream direction while maintaining the same order of continuity and the same spatial relationship between said points, an improvement characterized by interrupting said liquid streams flowing through said three zones at a point between said desorption zone and said rectification zone while the first portion of said desorption effluent flowing out from said last section of said desorption zone, which portion contains either a little or no desorbent but contains said selectively sorbed component, is directly circulated, and the second portion thereof which portion contains said selectively sorbed component of high purity, but at a lower concentration in comparison with the first portion, is introduced into a distillation apparatus from which one portion of the sorbate fraction is circulated, both as reflux into the first section of said rectification zone.

2. The process according to claim 1 further characterized in that said liquid streams flowing through said three zones are further interrupted at a point between said sorption zone and said desorption zone and said raffinate effluent is withdrawn from the bottom of the last section of said sorption zone while the first portion of said raffinate effluent which portion substantially consists of said desorbent is directly circulated into the first section of the desorption zone and the second portion thereof which contains both said less sorbed component and said desorbent is introduced into a distillation apparatus from which the desorbent fraction is circulated, into the first section of said desorption zone.

3. The process according to claim 1 further characterized in that one portion of said raffinate effluent is withdrawn from a point such that at least one section of said sorption zone remains downstream therefrom.

4. The process according to claim 1 further characterized in that said solid sorbent is a crystalline metal alumino-silicate and said liquid feed mixture is a mixture of xylene isomers.

5. The process according to claim 4 further characterized in that said crystalline metal alumino-silicate is a faujasite-type crystalline metal alumino-silicate having a silica/alumina ratio of less than 4.0 and containing (a) barium (b) potassium and (c) at least one metal selected from the group consisting of zirconium, yttrium, neodymium, lead, uranium and mercury (herein referred to as *M*) in the proportion satisfying the following atomic ratios;

$$K/(K + 2Ba) = 0.0 \sim 0.5$$

$$M/(K + 2Ba) = 0.0 \sim 0.5$$

6. The process according to claim 4 further characterized

terized in that said crystalline metal alumino-silicate is a faujasite-type crystalline metal alumino-silicate having a silica/alumina ratio of not less than 4.0 and containing (a) barium, (b) potassium and (c) at least one metal *M* selected from the group consisting of zirconium, yttrium, neodymium, lead, uranium and mercury in the proportion satisfying the following atomic ratios;

$$K/(K + 2Ba) = 0.6 \sim 1.0$$

$$M/(K + 2Ba) = 0.0 \sim 0.5$$

7. The process according to claim 4 further characterized in that said crystalline metal alumino-silicate is a mixture of both the faujasite-type crystalline metal alumino-silicates, one having a silica/alumina ratio of less than 4.0 and containing (a) barium, (b) potassium and (c) at least one metal selected from the group consisting of zirconium, yttrium, neodymium, lead, uranium and mercury in the proportion satisfying the following ratios;

$$K/(K + 2Ba) = 0.0 \sim 0.5$$

$M/(K + 2Ba) = 0.0 \sim 0.5$ and the other having a silica/alumina ratio of not less than 4.0 and containing (a) barium, (b) potassium and (c) at least one metal *M* selected from the group consisting of zirconium, yttrium, neodymium, lead, uranium and mercury in the proportion satisfying the following atomic ratios;

$$K/(K + 2Ba) = 0.6 \sim 1.0$$

$$M/(K + 2Ba) = 0.0 \sim 0.5$$

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