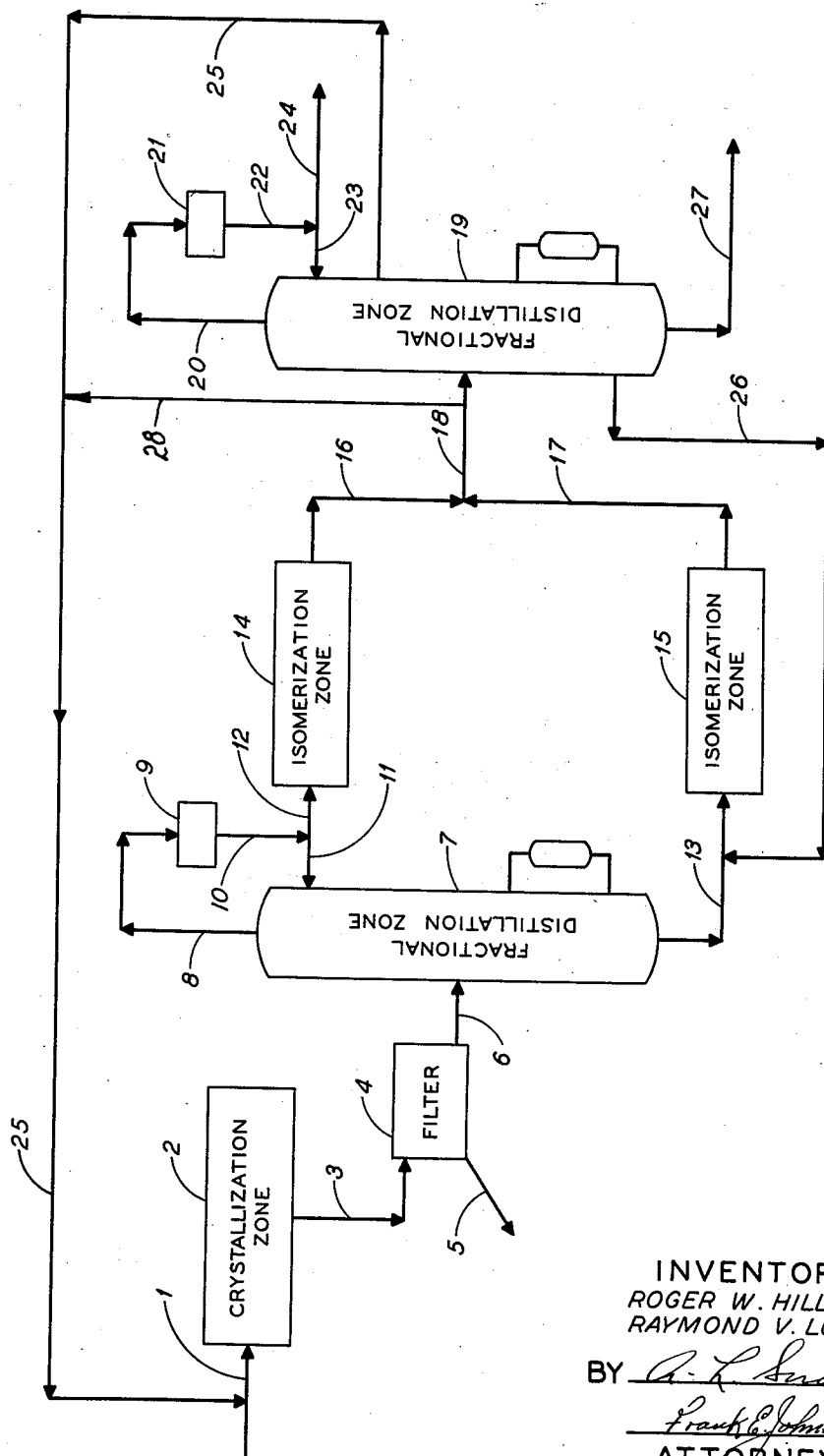


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ISOMERIZATION OF XYLENE

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ISOMERIZATION OF XYLENE

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This invention relates to the isomerization of aromatic hydrocarbons and pertains more particularly to the catalytic isomerization of xylene mixtures containing ortho-, meta-, and para-xylene.

Para-xylene is currently being separated from mixed xylene isomers in commercial quantities by fractional crystallization. The feed to a crystallization unit may be a xylene fraction separated from catalytically reformed naphtha by careful fractional distillation. Such a fraction will ordinarily contain from 5-10% of non-aromatic hydrocarbons and 5-15% ethylbenzene, in addition to ortho-, meta-, and para-xylene. In some instances, the feed to the crystallization unit is prepared by a combination of extractive distillation and careful fractional distillation and is substantially free of non-aromatic hydrocarbons. In either type of feed, the C₈ aromatic isomers are present in the following proportions:

	Percent by volume
Ortho-xylene	20-27
Meta-xylene	50-54
Para-xylene	20-25
Ethylbenzene	5-12

These proportions represent the equilibrium composition of a C₈ aromatic fraction produced by dehydrogenation of naphthenic hydrocarbons, and the precise composition of a given equilibrium mixture depends upon the temperature at which the aromatic hydrocarbons are produced. The above ranges of composition hold for temperatures in the range of 600° F. to 1000° F., ortho-xylene and ethylbenzene contents increase as temperature is raised, and meta-xylene and para-xylene contents decrease as temperature is raised.

Only about one-half of the para-xylene contained in these fractions can ordinarily be separated by fractional crystallization. In order to obtain incremental production of para-xylene, it is desirable to isomerize the mother liquor produced in the fractional crystallization process.

It has now been found that these mother liquors can be advantageously isomerized to produce para-xylene with a minimum loss of xylene due to disproportionation and cracking by fractionally distilling the mother liquor to separate an overhead fraction comprising meta- and para-xylene and having an ortho-xylene content substantially less than that of the mother liquor and a bottoms fraction having an ortho-xylene content substantially higher than that of the mother liquor, contacting the overhead fraction with a silica-alumina catalyst at 700° F. to 1000° F. at a liquid space velocity in the range from 0.5-5.0, and separately contacting the ortho-xylene rich bottoms fraction with a silica-alumina catalyst at a temperature in the range from 900°-1050° F. at a liquid space velocity in the range from 0.5-5.0 v./v./hr. The

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ortho-xylene rich fraction is subjected to isomerization conditions substantially more severe than those employed in treating the overhead fraction, higher temperature or lower space velocity, or both being employed to isomerize the ortho-xylene rich fraction.

It is an object of the present invention to carry out the isomerization of a mixture of ortho-, meta-, and para-xylene to produce increased yields of para-xylene.

It is a further object of the present invention to carry out the same isomerization with a minimum xylene loss due to cracking and disproportionation.

Pursuant to this invention, a xylene feed is passed into a fractional crystallization zone where portions of the para-xylene isomer are crystallized at low temperatures. The mixture is then introduced into a centrifuge from which the crystallized para-xylene is removed as a cake, and the mother liquor is removed as the filtrate. The mother liquor, now deficient in para-xylene in respect to the xylene-isomer equilibrium, is passed into a distillation zone to remove a major proportion of the ortho-xylene and hydrocarbons with higher boiling points than ortho-xylene from the mother liquor. The separation is preferably effected by super-fractionation in a distillation column. One equivalent to at least about 35 theoretical plates appears necessary for practical operation; desirably about 45 and preferably about 60 theoretical plates are utilized. By efficient fractionation, an overhead fraction comprising meta-xylene, para-xylene, ethylbenzene, and a small proportion of ortho-xylene is separated from a bottoms fraction composed predominantly of ortho-xylene.

The overhead fraction is passed into an isomerization zone where it is contacted with a silica-alumina catalyst at a temperature in the range about 700° F. to 1000° F. The overhead fraction is contacted with the catalyst at a space velocity in the range 0.5-5.0 L. H. S. V. (liquid hourly space velocity), or 0.5 to 5.0 volumes of liquid feed per volume of catalyst per hour.

The bottoms fraction, predominantly ortho-xylene, is separately passed into another isomerization zone and contacted with a silica-alumina catalyst at a temperature in the range about 900° F. to 1050° F., and a space velocity in the range from 0.5-5.0.

The efficiency of the isomerization treatment is indicated by the para-xylene content of the product. The more closely the para-xylene content of the product approaches the para-xylene content of an equilibrium mixture of xylenes at the isomerization temperature, the more efficient is the process. A convenient numerical index of efficiency is obtained by calculating the percent approach to paraxylene equilibrium content as follows:

$$\text{Percent p-xylene equilibrium approach} = \frac{\text{percent p-xylene in product} - \text{percent p-xylene in feed}}{\text{percent p-xylene at equilibrium} - \text{percent p-xylene in feed}} \times 100$$

The percent para-xylene in the several streams is based on total xylenes, other components of the stream, if any, being excluded in the calculation. Thus, a 20% para-xylene (xylene basis) content is determined by dividing the weight of para-xylene present by the total weight of only the three isomers, ortho-, meta-, and para-xylene present. The theoretical xylene equilibrium values used herein are those reported by Rossini et al., and are given in Table 1.

TABLE 1
EQUILIBRIUM CONCENTRATIONS OF THE C₈ ALKYL BENZENES¹

Temperature, ° F.	Composition, in mole fraction, of equilibrium mixture of isomers							
	Ethylbenzene		o-Xylene		m-Xylene		p-Xylene	
	C ₈ Basis	Xylene Basis	C ₈ Basis	Xylene Basis	C ₈ Basis	Xylene Basis	C ₈ Basis	Xylene Basis
600.....	0.057	-----	0.215	0.228	0.503	0.533	0.225	0.239
700.....	0.069	-----	0.220	0.236	0.491	0.528	0.220	0.236
800.....	0.083	-----	0.224	0.244	0.478	0.522	0.215	0.234
900.....	0.097	-----	0.226	0.250	0.467	0.517	0.210	0.233
1,000.....	0.110	-----	0.228	0.256	0.457	0.513	0.205	0.231

¹ Rossini et al.; Jour. of Research Nat'l Bureau of Standards, RP 1732, vol. 37, p. 115, August 1946.

It has been found that the isomerization of a xylene mixture in which the ortho-xylene concentration is high requires drastic conditions of temperature or contact time, or both, to obtain a high percent approach to para-xylene equilibrium while xylene mixtures predominating in meta-xylene can be isomerized at relatively mild conditions to produce a product having a para-xylene content closely approaching equilibrium content. The isomerization of predominantly ortho-xylene feeds results in greater losses due to disproportionation and cracking than the isomerization of a feed predominantly meta-xylene since stock losses proceed more rapidly at severe conditions. The effects of xylene isomer concentration in the feed and the temperatures employed in the isomerization step are shown by the following examples:

Example 1

A 99% ortho-xylene feed is isomerized by contacting it with a silica-alumina catalyst at a temperature of 800° F. and a L. H. S. V. of 1. The percent approach to para-xylene equilibrium is 3.0% with a xylene loss of 5.0%.

Example 2

The Example 1 is repeated except the isomerization is carried out at a temperature of 1000° F. and an L. H. S. V. of 2. The percent approach to para-xylene equilibrium is 90% with a xylene loss of 11%.

Example 3

A 95% meta-xylene feed is isomerized by contacting it with a silica-alumina catalyst at a temperature of 800° F. and a L. H. S. V. of 2. The percent approach to para-xylene equilibrium is 95% with a xylene stock loss of less than 1%.

Example 4

Example 3 is repeated except that a temperature of 1000° F. is employed. The percent approach to para-xylene equilibrium is 95% + with a xylene loss of 11.5%.

Comparing Example 1 with Example 2, it should be noted that the increase in 200° F. increases the percentage approach to para-xylene equilibrium from 3% to 90%, but that xylene losses due to cracking and disproportionation also increase from 5% to 11%. Note that in Example 2 the xylene loss is high at the high temperature employed despite the fact the contact time is one-half that of Example 1. Examples 1 and 2 illustrate that in order to effect a large conversion of ortho-xylene to meta-xylene and para-xylene, high temperatures are required, but that large xylene losses are sustained when the requisite high temperatures and/or low space velocities are employed.

A comparison of Examples 3 and 4 shows that when the same feed (95% meta-xylene) is isomerized at 800° F. and at 1000° F. with all other conditions being identical, that at the higher temperature the xylene losses to disproportionation increase from less than 1% at 800° F. to 11.5% at 1000° F. When isomerizing predomi-

nantly meta-xylene feeds, no substantial conversion increase is realized at the higher temperature, but the xylene losses are very markedly increased.

The examples clearly illustrate that much lower temperatures may be employed to effect a high percent approach to para-xylene equilibrium with meta-xylene rich feeds than with ortho-xylene rich feeds and that xylene losses are relatively low at lower isomerization temperatures.

Pursuant to the invention, the desired high percentage of para-xylene approach to equilibrium with a minimum of xylene losses is attained by isomerizing the meta- and para-xylene overhead fraction by contacting it with a silica-alumina catalyst at temperature in the range 700°–1000° F. and a space velocity in the range of 0.5–5.0, and separately isomerizing the ortho-xylene rich bottoms fraction by contacting it with the same catalyst at a temperature in the range about 900°–1050° F. and at a space velocity in the range 0.5–5.0. The space velocity is increased within the specified range as temperatures are increased within the temperature ranges set forth for use in isomerizing the two xylene fractions. Thus, in isomerizing the meta-xylene rich overhead fraction a space velocity of 0.5 to 1.5 is employed when the temperature is 700° F. and a space velocity of 3 to 5 is employed when the temperature used is toward 1000° F. Similarly, a space velocity of 0.5 to 1.5 is employed in isomerizing the ortho-xylene rich fraction at 900° F., while a space velocity of 3 to 5 is employed when the temperature of isomerization is toward the upper limit of the described range.

From the two isomerization zones, the two isomerized mixtures are further processed by any one or combination of the following alternative methods:

(1) All, or a substantial part of the isomerized product from both fractions, is returned to the crystallization zone where portions of the para-xylene produced in the two isomerization zones is crystallized out of the mixture and then separated by filtration.

(2) The product from the isomerization of the overhead is returned to the crystallization zone and the product from the isomerization of the bottoms is fractionally distilled to separate three fractions; an overhead fraction comprising predominantly of ethylbenzene and lighter materials, a side cut fraction comprising meta-xylene and para-xylene which is returned to the crystallization zone, and a bottoms fraction of predominantly ortho-xylene.

(3) The total product from both isomerization zones is passed into a distillation zone where a separation of ethylbenzene and lighter materials as an overhead, meta-xylene and para-xylene together as a side cut, and ortho-xylene as a bottoms fraction is attained by fractional distillation. The meta-, para-xylene side cut is returned to the crystallization zone to remove portions of the para-xylene, and the ortho-xylene bottoms fraction is returned to the bottoms isomerization zone.

In a modification of the present invention the original xylene feed is passed into a distillation zone, the over-

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head fraction, comprised substantially of meta-xylene and para-xylene, is passed into the crystallization zone, the ortho-xylene rich bottoms fraction is passed into an isomerization zone, and the isomerized product is returned to the distillation zone with the original feed.

The following examples of feeds to the noted various zones are merely illustrative and the process of the present invention is not confined to the compositions shown.

(1) Illustrative feed to the crystallization zone with no prior fractional distillation.

Compound	Weight Percent	Weight Percent (Xylene basis)
Ethylbenzene.....	5.8	-----
Para-xylene.....	18.6	22.4
Meta-xylene.....	38.4	46.3
Ortho-xylene.....	26.0	31.3
Or-C ₈ and Paraffins.....	11.2	-----
	100.0	100.0

(2) Representative composition of a meta-para-xylene rich fraction separately subjected to isomerization at a temperature in the range 700° F.-1000° F.

Compound	Weight Percent	Weight Percent (Xylene basis)
Ethylbenzene.....	8.4	-----
Para-xylene.....	9.5	11.9
Meta-xylene.....	56.6	70.8
Ortho-xylene.....	13.8	17.3
Or-C ₈ and Paraffins.....	11.7	-----
	100.0	100.0

(3) Representative composition of an ortho-xylene rich fraction separately subjected to isomerization at a temperature in the range 900° F.-1100° F.

Compound	Weight Percent	Weight Percent (Xylene basis)
Ethylbenzene.....	0.4	-----
Para-xylene.....	5.2	5.5
Meta-xylene.....	16.1	17.1
Ortho-xylene.....	72.8	77.4
Or-C ₈ and Paraffins.....	5.5	-----
	100.0	100.0

The appended drawing is a diagrammatic illustration of apparatus and process flow suitable for the practice of the invention.

A xylene-containing feed as described above is passed through line 1 into crystallization zone 2, where a portion of the para-xylene present in the feed is crystallized at a temperature in the range -75° F. to -120° F. The mixture containing para-xylene crystals is removed from crystallization zone 2 by line 3 and is passed into centrifugal filter 4 where the cooled mixture is centrifugally filtered to separate the crystalline phase and a mother liquor. The crystal phase, containing para-xylene at a substantially greater concentration than that of the mother liquor, is removed from centrifuge 4 by line 5 and the mother liquor, deficient in para-xylene, is removed from centrifuge 4 by line 6. The crystallization is desirably conducted in the manner described in U. S. Patent No. 2,541,682.

The mother liquor is removed from centrifuge 4 by line 6 and is introduced into fractional distillation zone 7 where a major proportion of the ortho-xylene and hydrocarbons with higher boiling points than ortho-xylene is removed from the mother liquor. The separation is accomplished by efficient fractional distillation resulting in an overhead fraction of meta- and para-xylene and

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ethylbenzene and a bottoms fraction substantially composed of ortho-xylene. The overhead product is removed from distillation zone 7 by line 8, reflux condenser 9, line 10, reflux line 11, and line 12. Reflux ratios on distillates of from about 2:1 to about 12:1 have been found satisfactory. The ortho-xylene rich bottoms fraction is removed from distillation zone 7 by line 13.

The overhead fraction is introduced into isomerization zone 14 by line 12 where it is isomerized by contacting it with a silica-alumina catalyst in the range about 700° F.-1000° F. as heretofore described. The predominantly ortho-xylene bottoms fraction from distillation zone 7 is passed by line 13 into isomerization zone 15 where it is isomerized with a silica-alumina catalyst at a temperature in the range about 900°-1050° F.

The isomerized overhead fraction is removed from isomerization zone 14 by line 16 and the isomerized bottoms fraction is removed from isomerization zone 15 by line 17 and the two isomerized mixtures are passed into line 18 and are introduced into distillation zone 19. In distillation zone 19, the following separations are made by efficient fractionation:

Ethylbenzene and lighter components are passed through line 20 into reflux condenser 21, and portions of the ethylbenzene and lighter components are returned to distillation zone 19 as reflux by lines 22 and 23, and the remaining portion is passed to storage facilities by line 24. A fraction of predominantly meta- and para-xylene is removed from line 25. A fraction predominantly ortho-xylene is removed from distillation zone 19 by line 26. A heavy bottoms product is removed by line 27.

The meta- and para-xylene stream is passed from distillation zone 19 by lines 25 and 1 into the crystallization zone 2 and the ortho-xylene rich fraction from distillation zone 19 is passed through lines 26 and 13 into isomerization zone 15.

As noted hereinbefore, the above-described process can be modified by passing all, or a substantial part, of the isomerized products from isomerization zones 14 and 15 to crystallization zone 2 by lines 16, 17, 18, 28, 25 and 1. By operating in this manner, portions of the para-xylene produced in the two isomerization zones can be crystallized out of the isomerized products.

It is readily apparent from the foregoing description that various modifications of the process can be made within the spirit of the present invention and the scope of the appended claims. For the sake of simplicity and clarity, apparatus has not been shown in detail in the drawings but is illustrated only as to major unit operation in the process. Many detailed pumps, valves, condensers, heat exchangers, temperature controls, and the like have been omitted, since any suitable form of apparatus incorporating these features can be supplied in obvious manner by those skilled in the art.

We claim:

1. A process for producing para-xylene which comprises cooling a xylene feed to a temperature in the range -75° F. to -120° F. to cause crystallization of a portion of the para-xylene, separating the para-xylene crystals and a mother liquor, fractionally distilling the mother liquor to separate an overhead fraction comprising meta-xylene and para-xylene and having an ortho-xylene content substantially less than that of the mother liquor and a bottoms fraction having an ortho-xylene content substantially higher than that of the mother liquor, isomerizing the overhead fraction by contacting it with a silica-alumina catalyst at 700° F. to 1000° F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., separately isomerizing the bottoms fraction by contacting it with a silica-alumina catalyst at conditions of temperature and space velocity substantially more severe than those employed in isomerizing the overhead fractions, the temperature being in the range from 900° F. to 1050° F. and the space velocity being in the range from 0.5 to 5.0 v./v./hr., passing the isomerizing product mixture

into a fractional distillation zone to separate an overhead fraction comprising meta-xylene and para-xylene and having an ortho-xylene content substantially less than that of joined isomerizing product mixtures and a bottom fraction having an ortho-xylene content substantially higher than that of the joined isomerizing product mixtures, and fractionally crystallizing the overhead mixture to recover para-xylene.

2. A process for producing para-xylene which comprises cooling a hydrocarbon fraction consisting predominantly of xylenes including ortho-xylene, meta-xylene, and para-xylene in a crystallization zone to a temperature in the range from -75°F. to -120°F. to produce a slurry containing para-xylene crystals, filtering the slurry to separate solid para-xylene crystals and a liquid filtrate, fractionally distilling the filtrate to separate an overhead fraction rich in meta-xylene and having an ortho-xylene content substantially lower than that of the filtrate and a bottoms fraction rich in ortho-xylene and having a substantially higher content of ortho-xylene than the filtrate, contacting the overhead fraction with a silica-alumina catalyst at a temperature in the range from 700°F. to 1000°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., separately contacting the bottoms fraction with a silica-alumina catalyst at a temperature in the range from about 850°F. to 1050°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., said bottoms fraction being contacted with said catalyst at a higher temperature than the catalyst contacting step of said overhead fraction, the space velocities within the defined ranges being coordinated with the temperatures within the defined ranges by employing lower space velocities within the space velocity ranges in conjunction with lower temperatures within the defined temperature ranges, and returning a substantial proportion of the isomerization products to the crystallization zone.

3. A process for isomerizing a xylene feed consisting predominantly of ortho-xylene and meta-xylene and containing para-xylene in less than equilibrium amount which comprises fractionally distilling the xylene feed to separate an overhead fraction comprising meta-xylene and para-xylene and having an ortho-xylene content substantially less than that of the feed and a bottoms fraction having an ortho-xylene content substantially higher than that of the feed, contacting the overhead fraction with a silica-alumina catalyst at a temperature in the range from 700°F. to 1000°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., separately contacting the bottoms fraction with a silica-alumina catalyst at a temperature in the range from about 850°F. to 1050°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., said bottoms fraction being contacted with said catalyst at a higher temperature than the catalyst contacting step of said overhead fraction, the space velocities within the defined ranges being coordinated with the temperatures within the defined ranges by employing lower space velocities within the space velocity ranges in conjunction with lower temperatures within the defined temperature ranges.

4. A process for isomerizing a xylene feed consisting predominantly of ortho-xylene and meta-xylene and containing para-xylene in less than equilibrium amount which comprises fractionally distilling the xylene feed to separate an overhead fraction comprising meta-xylene and para-xylene and having an ortho-xylene content sub-

stantially less than that of the feed and a bottoms fraction having an ortho-xylene content substantially higher than that of the feed, contacting the overhead fraction with a silica-alumina catalyst at a temperature in the range from 700°F. to 1000°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., separately contacting the bottoms fraction with a silica-alumina catalyst at a temperature in the range from about 850°F. to 1050°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., said bottoms fraction being contacted with said catalyst at a higher temperature than the catalyst contacting step of said overhead fraction, the space velocities within the defined ranges being coordinated with the temperatures within the defined ranges by employing lower space velocities within the space velocity ranges in conjunction with lower temperatures within the defined temperature ranges, passing the two isomerized product mixtures into a distillation zone, separating a meta-xylene and para-xylene rich overhead fraction from an ortho-xylene rich bottoms fraction, passing the overhead fraction into a fractional crystallization zone and recovering para-xylene crystals from said crystallization zone.

5. A process for isomerizing a xylene feed consisting predominantly of ortho-xylene and meta-xylene and containing para-xylene in less than equilibrium amount which comprises fractionally distilling the xylene feed to separate an overhead fraction comprising meta-xylene and para-xylene and having an ortho-xylene content substantially less than that of the feed and a bottoms fraction having an ortho-xylene content substantially higher than that of the feed, contacting the overhead fraction with a silica-alumina catalyst at a temperature in the range from 700°F. to 1000°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., separately contacting the bottoms fraction with a silica-alumina catalyst at a temperature in the range from about 850°F. to 1050°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr., said bottoms fraction being contacted with said catalyst at a higher temperature than the catalyst contacting step of said overhead fraction, the space velocities within the defined ranges being coordinated with the temperatures within the defined ranges by employing lower space velocities within the space velocity ranges in conjunction with lower temperatures within the defined temperature ranges, passing the two isomerized product mixtures into a distillation zone, separating a meta-xylene and para-xylene rich overhead fraction from an ortho-xylene rich bottoms fraction, passing the overhead fraction into a fractional crystallization zone and recovering para-xylene crystals from said crystallization zone, and returning the ortho-xylene rich bottoms fraction to an isomerization zone and contacting the bottoms fraction with a silica-alumina catalyst at a temperature in the range from about 850°F. to 1050°F. and at a space velocity in the range from 0.5 to 5.0 v./v./hr.

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