United States Patent [19]

Hayward

[11] 3,856,874

[45] Dec. 24, 1974

[54] **XYLENE ISOMERIZATION**

[75] Inventor: **Charles R. Hayward**, East Brunswick, N.J.

[73] Assignee: **Mobil Oil Corporation**, New York, N.Y.

[22] Filed: **Sept. 13, 1973**

[21] Appl. No.: **397,195**

[52] **U.S. Cl.** ..... **260/668 A**, 260/674 A

[51] **Int. Cl.** **C07c 5/24**

[58] **Field of Search** ..... 260/668 A, 674 A

[56] **References Cited**

UNITED STATES PATENTS

3,538,173	11/1970	Berger et al.	260/668 A
3,751,504	8/1973	Keown et al.	260/672 T
3,756,942	9/1973	Cattanach	208/138
3,761,389	9/1973	Rollmann	208/64
3,766,287	10/1973	Stenmark et al.	260/668 A
3,790,471	2/1974	Argauer et al.	260/672 T

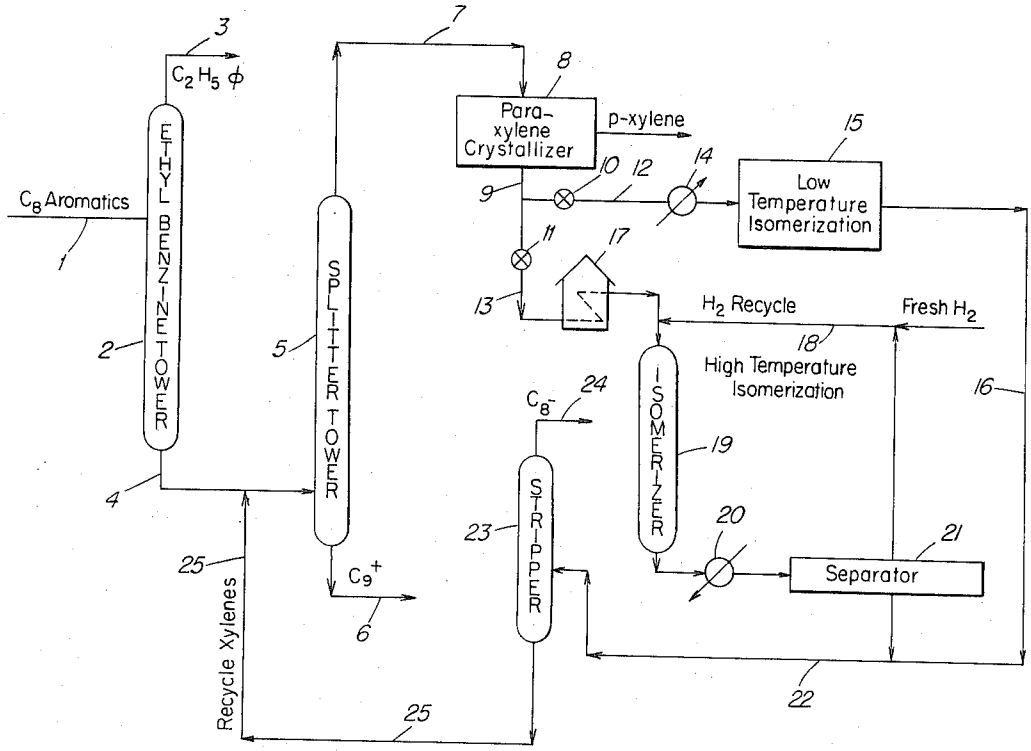
Primary Examiner—C. Davis

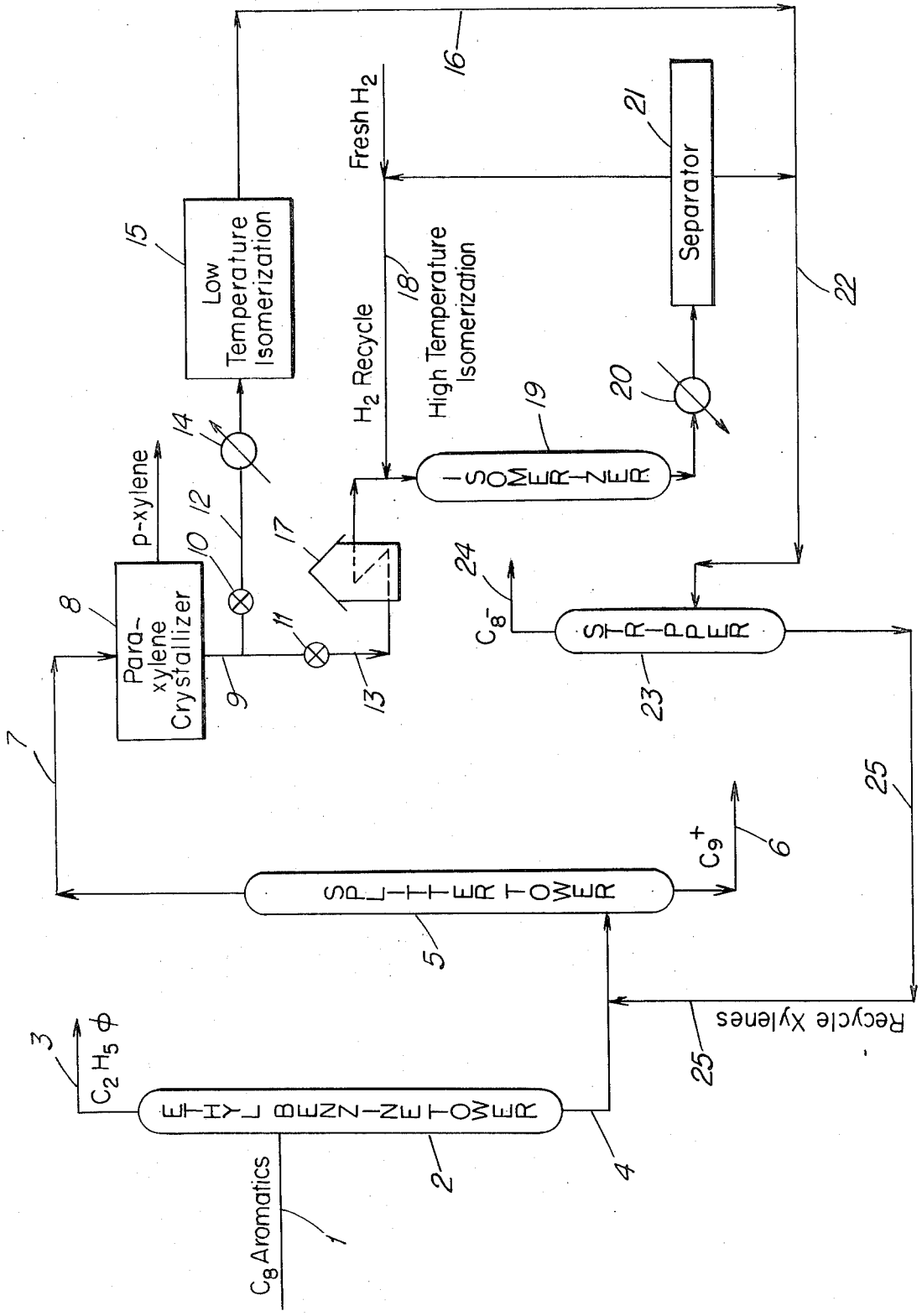
Attorney, Agent, or Firm—A. L. Gaboriault

[57] **ABSTRACT**

Costs for commercial application of Low Temperature Isomerization (LTI) of xylenes contained in C_8 aromatic fractions are greatly reduced by diverting a portion of p-xylene separator effluent through Octafining or an equivalent isomerization over such zeolites as ZSM-5.

2 Claims, 1 Drawing Figure




C8 Aromatics
1
Ethyl Benzene Tower
2
C2 H5 Φ
3
4
Splitter Tower
5
C9+
6
7
Para-xylene Crystallizer
8
9
10
11
12
13
p-xylene
14
Low Temperature Isomerization
15
16
17
Fresh H2
H2 Recycle
18
High Temperature Isomerization
Isomerizer
19
20
Separator
21
22
C8-
24
Stripper
23
25
Recycle Xylenes

XYLENE ISOMERIZATION

BACKGROUND OF THE INVENTION

Xylenes are found in fractions from coal tar distillate, petroleum reformates and pyrolysis liquids in admixture with other compounds of like boiling point. The aromatic components are readily separated from non-aromatics by solvent extraction. Distillation provides a fraction consisting essentially of C_8 aromatics. As will appear below, o-xylene is separable from other C_8 aromatics by fractional distillation, and p-xylene is separable by fractional crystallization or selective sorption. Present demand is largely for p-xylene and it has become desirable to convert m-xylene, the principal xylene present in the feed stream, to the more desired p-xylene.

Since the announcement of the first commercial installation of Octafining in Japan in June, 1958, this process has been widely installed for the supply of p-xylene. See "Advances in Petroleum Chemistry and Refining" volume 4, page 433 (Interscience Publishers, New York 1961). That demand for p-xylene has increased at remarkable rates, particularly because of the demand for terephthalic acid to be used in the manufacture of polyesters.

Typically, p-xylene is derived from mixtures of C_8 aromatics separated from such raw materials as petroleum naphthas, particularly reformates, usually by selective solvent extraction. The C_8 aromatics in such mixtures and their properties are:

	Freezing Point °F.	Boiling Point °F.	Density Lbs./U.S. Gal.
Ethyl benzene	−139.0	277.1	7.26
P-xylene	55.9	281.0	7.21
M-xylene	−54.2	282.4	7.23
O-xylene	−13.3	292.0	7.37

Principal sources at present are catalytically reformed naphthas and pyrolysis distillates. The C_8 aromatic fractions from these sources vary quite widely in composition but will usually be in the range 10 to 32 wt. percent ethyl benzene with the balance, xylenes, being divided approximately 50 wt. percent meta, and 25 wt. percent each of para and ortho.

In turn, calculated thermodynamic equilibria for the C_8 aromatic isomers at Octafining conditions are:

Temperature	850°F.
Wt.% Ethyl benzene	8.5
Wt.% para xylene	22.0
Wt.% meta xylene	48.0
Wt.% ortho xylene	21.5
TOTAL	100.0

An increase in temperature of 50°F. will increase the equilibrium concentration of ethyl benzene by about 1 wt. percent, orthoxylene is not changed and para and meta xylenes are both decreased by about 0.5 wt. percent.

Individual isomer products may be separated from the naturally occurring mixtures by appropriate physical methods. Ethyl benzene may be separated by fractional distillation although this is a costly operation. Ortho xylene may be separated by fractional distillation

and is so produced commercially. Para xylene is separated from the mixed isomers by fractional crystallization and selective sorption.

As commercial use of para and ortho xylene has increased there has been interest in isomerizing the other C_8 aromatics toward an equilibrium mix and thus increasing yields of the desired xylenes.

The Octafining process operates in conjunction with the product xylene or xylenes separation processes. A virgin C_8 aromatics mixture is fed to such a processing combination in which the residual isomers emerging from the product separation steps are then charged to the isomerizer unit and the effluent isomerizate C_8 aromatics are recycled to the product separation steps. The composition of isomerizer feed is then a function of the virgin C_8 aromatic feed, the product separation unit performance, and the isomerizer performance.

The isomerizer unit itself is most simply described as a single reactor catalytic reformer. As in reforming, the catalyst contains a small amount of platinum and the reaction is carried out in a hydrogen atmosphere.

Octafiner unit designs recommended by licensors of Octafining usually lie within these specification ranges:

Process Conditions	
Reactor Pressure	175 to 225 PSIG
Reactor Inlet Temperature Range	830–900°F.
Heat of Reaction	Nil
Liquid Hourly Space Velocity	0.6 to 1.6 Vol/Vol/Hr.
Number of Reactors, Downflow	1
Catalyst Bed Depth, Feet	11 to 15
Catalyst Density, Lb/Cu.Ft.	38
Recycle Circulation, Mols Hydrogen/Mol Hydrocarbon Feed	7.0 to 14.0
Maximum Catalyst Pressure Drop, PSI	20

It will be apparent that under recommended design conditions, a considerable volume of hydrogen is introduced with the C_8 aromatics. In order to increase throughput, there is great incentive to reduce hydrogen circulation with consequent increase in aging rate of the catalyst. Aging of the catalyst occurs through deposition of carbonaceous materials on the catalyst with need to regenerate by burning off the coke when the activity of the catalyst has decreased to an undesirable level. Typically the recommended design operation will be started up at about 850°F. with reaction temperature being increased as needed to maintain desired level of isomerization until reaction temperature reaches about 900°F. At that point the isomerizer is taken off stream and regenerated by burning of the coke deposit.

Because of its capability to convert ethyl benzene, Octafining can accept a charge stream which contains that component. Normally, a portion of the ethyl benzene is removed by fractional distillation before the charge is processed. If no attempt is made to reduce

ethyl benzene below a few percent by weight, this can be accomplished inexpensively and the ethyl benzene recovered is in usable form as a relatively pure chemical, e.g., for dehydrogenation to styrene.

The Octafiner is in a "loop" which includes means for separation of desired xylenes; p-xylene by crystallization or selective sorption and, possibly o-xylene by distillation. The C_8 stream stripped of desired xylenes returns to the Octafiner where more of the desired xylenes are generated, for example by isomerization of m-xylene. It will be apparent that ethyl benzene will tend to build up in the loop as other components are removed. The Octafining catalyst has capability for converting ethyl benzene, thus counteracting that tendency. It, the Octafining catalyst, has the disadvantage that it is a hydrocracking catalyst due to the acid function of its silica/alumina base and its content of hydrogenation/dehydrogenation metal of the platinum group. In addition to converting ethyl benzene, this catalyst also causes net loss of xylenes.

Other catalysts have recently been identified as behaving in the same fashion as Octafining catalyst for isomerization of xylenes in C_8 aromatic fractions accompanied by conversion of ethyl benzene. These new catalysts include zeolites of the ZSM-5 type, zeolite ZSM-12 and zeolite ZSM-21. ZSM-5 type includes zeolite ZSM-5 as described in Argauer and Landolt patent No. 3,702,886, dated Nov. 14, 1972 and zeolite ZSM-11 as described in Chu patent No. 3,709,979, dated Jan. 7, 1973 and variants thereon. Zeolite ZSM-12 is described in German Offenlegungsschrift No. 2,213,109. The activity of these catalysts for the stated purpose and of ZSM-21 is described and claimed in copending application of R.A. Morrison, Ser. No. 397,039, filed Sept. 13, 1973, the disclosure of which is hereby incorporated by reference.

In general, Octafining catalyst and the zeolite catalysts referred to above behave in about the same manner, except for their aging characteristics; decline of activity with time on stream. The essentially equivalent nature of these catalysts (Octafining and the specified zeolites) with respect to activity is shown by tabulated data hereinafter.

A typical charge to the isomerizing reactor (effluent of crystallizer or selective sorption for separation of p-xylene) may contain 17 wt. percent ethyl benzene, 65 wt. percent m-xylene, 11 wt. percent p-xylene and 7 wt. percent o-xylene. The thermodynamic equilibrium varies slightly with temperature in a system in which o-xylene is separated in the loop by fractional distillation prior to the crystallizer. The objective in the isomerization reactor is to bring the charge as near to theoretical equilibrium concentrations as may be feasible consistent with reaction times which do not give extensive cracking and disproportionation.

Ethyl benzene reacts through ethyl cyclohexane to dimethyl cyclohexanes which in turn equilibrate to xylenes. Competing reactions are disproportionation of ethyl benzene to benzene and diethyl benzene, hydrocracking of ethyl benzene to ethylene and benzene and hydrocracking of the alkyl cyclohexanes.

The rate of ethyl benzene approach to equilibrium concentration in a C_8 aromatic mixture is related to effective contact time. Hydrogen partial pressure has a very significant effect on ethyl benzene approach to equilibrium. Temperature change within the range of Octafining conditions (830 to 900°F.) has but a very small effect on ethyl benzene approach to equilibrium.

Concurrent loss of ethyl benzene to other molecular weight products relates to percent approach to equilibrium. Products formed from ethyl benzene include C_6+ naphthenes, benzene from cracking, benzene and C_{10} aromatics from disproportionation, and total loss to other than C_8 molecular weight. C_5 and lighter hydrocarbon by-products are also formed.

The three xylenes isomerize much more selectively than does ethyl benzene, but they do exhibit different rates of isomerization and hence, with different feed composition situations the rates of approach to equilibrium vary considerably.

Loss of xylenes to other molecular weight products varies with contact time. By-products include naphthenes, toluene, C_9 aromatics and C_5 and lighter hydrocracking products.

Ethyl benzene has been found responsible for a relatively rapid decline in catalyst activity of Octafining catalyst and this effect is proportional to its concentration in a C_8 aromatic feed mixture. It has been possible then to relate catalyst stability (or loss in activity) to feed composition (ethyl benzene content and hydrogen recycle ratio) as that for any C_8 aromatic feed, desired xylene products can be made with a selected suitably long catalyst use cycle.

The newer zeolite catalysts are characterized by very high stability as well as very high activity and selectivity in isomerization and other hydrocarbon reactions. By reason of their very high stability and selectivity, they afford longer cycle times between regenerations, even at greatly reduced hydrogen recycle ratios as compared with known Octafining catalyst. These properties result in greatly increased capacity for throughput when these new catalysts are employed instead of conventional Octafining catalyst.

Table I below compares Octafining with operation over ZSM-5 type catalyst. Since it is generally preferred to operate the ZSM-5 type catalyst at somewhat lower temperatures than those characteristic of Octafining, this comparison is, throughout these experiments, at a constant temperature of 800°F. The first column reports results with Octafining catalyst.

The Octafining data are taken from operation of a commercial Octafiner run at throughput well beyond design capacity. At this level of hydrocarbon charge, capacity of compressors limits the amount of hydrogen to that amount which, added to hydrocarbons charged, equals total capacity of the compressors. By reason of that constraint, the hydrogen to hydrocarbon mol ratio is 6.5. The data here given are "middle of cycle" yields on a cycle which started at 760°F. The second and third columns are operations at different space velocities in which the catalyst vessel is filled by a mixture of 85 vol. percent tabular alumina and 15 vol. percent of active catalyst constituted by 65 wt. percent NiHZSM-5 in 35 percent of alumina matrix. The ZSM-5 catalyst was made by ammonium and nickel exchange of ZSM-5 having a silica/alumina ratio of **70.** The total catalyst composite of ZSM-5 and alumina contained 0.68 wt. percent nickel and 0.05 wt.% sodium. This catalyst (columns 2 and 3) was in particles between **30** and **60** mesh.

The charge employed was that stated above as typical, to wit, ethyl benzene (EB) 17 wt. percent, m-xylene (M) 65 wt. percent, p-xylene (P) 11 wt. percent

and o-xylene (O) 7 wt. percent. The results of these runs are shown in the following Table I.

TABLE I

COMPARISON WITH OCTAFINING

Catalyst	Octafining $Pt/SiO_2/Al_2O_3$	15 wt. % $NiHZSM\text{-}5/Al_2O_3$ 85 wt. % Al_2O_3	
Temp.	800°F.	800°F.	800°F.
WHSV (on zeolite)	1.6	100	50
H_2/HC molar	6.5	6.5	6.5
Product			
EB	10.8	8.2	6.0
m-xylene	46.0	44.7	42.8
p-xylene	18.0	18.9	18.2
o-xylene	16.7	18.8	19.6
C_9+	1.0	1.3	1.8
Benzene & toluene	0.75	6.3	9.2
Xylene loss	3.0	1.0	3.0

Unique to catalysts of ZSM–5 type, ZSM–12 or ZSM–21, as compared with prior zeolite isomerization catalysts, is the property of converting ethyl benzene, probably by the same reaction mechanisms above discussed with respect to Octafining catalyst.

The characterizing feature of the zeolite catalyst described is ZSM–5 type of zeolite as described in said U.S. Pat. Nos. 3,702,886, Argauer et al., and 3,709,979, Chu, and ZSM–12 as described in German Offenlegungsschrift No. 2,213,109 the disclosures of which are hereby incorporated by reference. The invention also contemplates use of ZSM-21 as described in the said copending Morrison application. The most active forms for the present purpose are those in which cationic sites are occupied at least in part by protons, sometimes called the "acid form." As described in the Argauer, et al., and Chu patents, and the German Offenlegungsschrift the acid form is achieved by burning out the organic cations. Protons may also be introduced by base exchange with ammonium or amine and calcination to decompose the ammonium or substituted ammonium cation.

Preferably, the catalyst also includes a metal having hydrogenation capability such as the metals of Group VIII of the Periodic Table. A preferred metal for this purpose is nickel. These metals may be introduced by base exchange or impregnation.

The zeolite is preferably incorporated in a porous matrix to provide mechanical strength, preferably alumina. The hydrogenation metal may be added after incorporation with the zeolite in a matrix, the only essential feature being that metal sites be in the vicinity of the zeolite, preferably within the same particle.

Very high space velocities are characteristic of use of ZSM–5 type isomerization catalyst as well as ZSM-12 and ZSM–21.

Temperatures for the zeolite catalyst used according to this invention may vary depending upon design factors of the equipment. Generally these lie between 550°F. and 900°F. Pressures will also be dictated, at least in part, by design factors of the equipment and may vary from 150 to 300 lb. per square inch gauge.

In this connection, it is noted that the lower temperature limit is related to character of the hydrogenation metal, if any, on the catalyst. Octafining requires a metal of the platinum group. These are very potent hydrogenation catalysts. At temperatures much below 800°F., hydrogenation of the ring destroys greater amounts of product, the more the temperature is reduced. At the higher temperatures, thermodynamic equilibria favor the benzene ring. The zeolite catalysts are effective with such metals as nickel which give negligible ring hydrogenation at the lower temperatures here possible. In general, it is preferred to use these less potent metal catalysts in this invention to afford temperature flexibility with consequent capability for high throughput.

Space velocities for zeolite catalyst are calculated with respect to the active component of ZSM–5 type or ZSM–12 or ZSM–21 zeolite. For example a composite of 65 percent ZSM–5 and 35 percent alumina may be admixed with 5 to 10 times as much inert diluent. In a typical example 15 wt. percent of composite catalyst and 85 wt. percent of inert alumina actually involves about 10 percent of active material in the whole volume. Space velocities are calculated with respect to that 10 percent constituted by active component. So calculated, the space velocities may vary from about 1 to about 200 on a weight basis.

Severity of the reaction is a factor of both temperature and space velocity. Excessive severity will result in undue cracking of the charge and the two factors should be adjusted in relationship to each other. Thus space velocities in the lower part of the preferred range will indicate lower temperatures of reaction.

The effects of the several variables will be apparent from examples presented below in tabular form.

Table II reports a number of examples in which the catalyst was 65 percent nickel acid ZSM–5 in an alumina matrix. This was admixed in the proportion of 15 wt. percent of the composite and 85 wt. percent of tabular alumina. Space velocities are reported with respect to the zeolite only in each case. The specified charge was admixed with hydrogen in the molar proportions shown by the value given for "H_2/HC". Yields of products and by-products are shown in the Table. In each case, yields are supplied for products on two bases. The yield on total charge is reported. Also each product is reported as a percentage of C_8 aromatics in the product, thus permitting comparison against the equilibrium mixture.

TABLE II

C_8 Aromatics Isomerization NiHZSM-5 Catalyst
Charge, wt.%: 17.1 EB, 11.0 p-xyl, 65.4 m-xyl, 6.8 o-xyl

Run No.	1	2	3	4	5	6
Temp., °F.	801	800	797	800	700	725
Pressure, PSIG	205	210	210	200	200	200
WHSV(on zeolite)	100	200	200	50	50	50
H_2/HC	6.5	6.5	6.5	6.5	6.5	6.5
Time On Stream hrs.	18.3	22.3	45.8	50.1	4.2	23.1
Material Balance	94.7	96.6	100.3	100.5	99.9	99.6

TABLE II – Continued

C_8 Aromatics Isomerization NiHZSM-5 Catalyst
Charge, wt.%: 17.1 EB, 11.0 p-xyl, 65.4 m-xyl, 6.8 o-xyl

Run No.	1		2		3		4		5		6	
Product Distribution wt.%												
C_2	1.5		1.0		0.7		2.0		0.2		0.3	
C_2=	0.2		0.3		0.4		0.1		0.1		0.2	
C_3	0.1		0.1		0.1		0.3		0.1		0.1	
i-C_4	0.01		—		—		—		—		—	
n-C_4	0.01		0.005		—		—		—		—	
C_6H_6	5.7		4.3		3.6		7.6		2.3		4.0	
Toluene	0.6		0.3		0.3		1.6		0.1		0.7	
C_8 Aromatics on total and on C_8 aromatics	Total	C_8 Ar	Total	C_8 Ar	Total	C_8 Ar	Total	C_8 Ar	Total	C_8 Ar	Total	C_8 Ar
EB	8.2	9.1	10.0	10.8	10.6	11.3	6.0	7.0	12.4	12.9	10.7	11.4
m-xylene	44.7	49.3	46.5	50.1	42.2	50.2	42.8	49.4	45.5	47.5	45.5	48.1
p-xylene	18.9	20.9	19.6	21.1	19.9	21.1	18.2	21.0	19.2	20.0	18.8	19.9
o-xylene	12.2	20.7	16.7	18.0	16.4	17.4	19.6	22.6	18.9	19.7	19.5	20.6
C_9 Aromatics	1.3		1.1		0.8		1.8		1.6		4.4	
Wt.% conversion to non-aromatics	1.8		1.4		1.2		2.4		0.4		0.6	
Wt.% loss C_8 aromatics	9.4		7.2		5.9		13.4		4.5		5.5	

Zeolite ZSM-12 impregnated with 0.5 wt. percent platinum shows similar activity and selectivity. This catalyst was prepared from ZSM-12 of 97.5 silica/alumina ratio by base exchanged with ammonium nitrate. The zeolite was contacted with 1N ammonium nitrate solution at room temperature for 1 hour. The zeolite was then drained and contacted with a fresh solution of ammonium nitrate at room temperature for 1 hour. This ammonium form of zeolite ZSM-12 was dried at 230°F., pelleted and sized to 30–60 mesh. The pellets were calcined in air at 1,000°F.

A portion of the calcined pellets in the amount of 5.34 grams was then impregnated with platinum by emersion in a solution of 0.75 grams of chloroplatinic acid in 25 grams of water. The zeolite was allowed to remain in contact with the solution for 5 minutes then drained by vacuum on a Buchner funnel. The impregnated pellets were calcined at 1,000°F., for 8 hours.

A charge consisting of 17.2 wt. percent ethyl benzene, 10.7 wt. percent p-xylene, 65.6 wt. percent m-xylene and 6.5 wt. percent o-xylene was reacted over a mixture of 3.1 wt. percent of the PtZSM-12 catalyst mixed with 96.9 wt. percent of tabular alumina at 700°F. and 200 p.s.i.g. pressure. Hydrogen was admixed with the charge in a molar ratio of 6.5 H_2 per mol of hydrocarbon. Space velocity was 50 unit weights of hydrocarbon per unit weight of PtZSM-12. In a run of 4 hours duration, products were collected and analyzed. Material balance was 99.5 percent.

The product of reaction included traces of propane, isobutane and n-butane. Other components of the effluent were:

TABLE IV

COMPONENT	WT.% OF TOTAL	WT.% OF C_8 AROMATICS
Benzene	0.1	—
Cyclohexane	0.1	—
Toluene	3.7	—
C_8 Alkanes	4.0	—
Ethyl benzene	10.2	11.5
m-xylene	41.9	47.6

TABLE IV – Continued

COMPONENT	WT.% OF TOTAL	WT.% OF C_8 AROMATICS
p-xylene	18.6	21.1
o-xylene	17.4	19.7
C_9 Aromatics	3.9	—

The results show 11.8 wt. percent loss of C_8 aromatics; 4.1 wt. percent conversion to non-aromatic products.

A catalyst NiHZSM-21 was prepared by mixing in the manner hereinafter described of 3 separate ingredients designated A, B and C:

A.	$NaAlO_2$	33.0	gm.
	50% NaOH soln.	3.4	gm.
	H_2O	870	gm.
B.	Colloidal SiO_2	824	gm.
C.	Pyrrolidine	182	gm.

Ingredient C was added to solution A. Ingredient B was added to that composite and the whole was stirred for 20 minutes. The mixture was allowed to crystallize in a stirred autoclave at 270°F. for 17 days. Solids were separated by filtration and dried at 230°F., then calcined at 1,000°F. in air.

A sample of 50 grams of the solid so obtained was contacted with 950 ml of 5 percent ammonium chloride at 210°F. for 1 hour. That contact was repeated for a total of 5 times with fresh ammonium chloride solution without stirring. Thirty grams of the resultant NH_4 ZSM-21 were placed in 30 ml of 0.5N nickel nitrate for 1 contact of 4 hours at 190°F. with stirring. The resultant material was dried at 230°F. for 17 hours sized to 30–60 mesh and calcined 10 hours at 1,000°F.

The same charge as that described for ZSM-12 was reacted over a mixture of 3.1 wt. percent NiHZSM-21 and 96.9 wt. percent tabular alumina at 700°F., 200 p.s.i.g., 50 WHSV and hydrogen to hydrocarbon ratio of 6.5. A 4 hour run was made at a material balance of 99.4 percent. Gaseous products included 0.3 wt. percent ethane, 0.01 wt. percent ethylene and 0.05 wt. percent propane. Other products are shown in Table V.

TABLE V

	WT.% OF TOTAL	WT.% OF C_8 AROMATICS
Benzene	1.1	—
Toluene	0.5	—
Ethyl benzene	14.7	15.1
m-xylene	44.0	45.1
p-xylene	20.9	21.2
o-xylene	18.0	18.4
C_9 Aromatics	0.6	—

Weight percent conversion to non-aromatics was 0.4; loss of C_8 aromatics was 2.5 wt. percent.

A more recent development than Octafining is Low Temperature Isomerization (LTI), conducted under pressure adequate to maintain the C_8 aromatics in the liquid phase. That technique is described in Wise Pat. No. 3,377,400, dated Apr. 9, 1968. A particularly effective catalyst for the purpose is zeolite ZSM–4 which provides unusual capabilities in aromatics processing. See Bowes et al. 3,578,723, May 11, 1971. This catalyst is highly effective for positional isomerization — moving methyl groups around aromatic rings. A process using ZSM–4 catalyst for low-temperature, liquid-phase isomerization of xylenes over a fixed bed provided yields of xylenes at 98+ percent with essentially no losses to gases and non-aromatics. Small quantities of benzene, toluene and C_9+ aromatics are formed. Approaches of 95–98 percent to isomer equilibrium are achieved. Ethyl benzene does not enter into the C_8 aromatic equilibrium; none is produced or lost.

The low-temperature isomerization process can be incorporated into a C_8 aromatics complex for recovery of either purity p-xylene, o-xylene or combinations of both. Catalyst life is at least two years with two regenerations.

Low-temperature liquid-phase positional isomerization of xylenes over homogeneous acidic catalysts such as $AlCl_3$ and $HF.BF_3$ had been extensively studied. High-temperature vaporphase isomerization of xylenes over heterogeneous catalysts, both acidic (SiAl) and dual functional (Pt/SiAl), is also well known, e.g., the Octafining Process discussed above.

With the development of very highly active acidic zeolite catalysts such as rare-earth-exchanged zeolite X (REX) the discovery was made of feasibility for isomerization of xylenes at temperatures below their critical points. This discovery opened up the potential for the development of a highly selective heterogeneously catalyzed liquid-phase process for xylene isomerization. One feature of zeolite catalyzed isomerization of xylenes is that unlike dual functional catalyzed isomerization ethyl benzene is not coupled into the reaction. For all practical purposes, ethyl benzene is not converted into xylenes nor are xylenes converted to ethyl benzene. The basic reaction mechanism is believed to be a 1–2 shift through m-xylene as an intermediate.

Two desirable characteristics of a xylene isomerization process are long catalyst life and high efficiency for isomerization as compared to disproportionation or cracking side reactions. Catalyst life can be greatly extended by operation under liquidphase conditions. Vapor-phase isomerization of o-xylene over a rare-earth-exchanged zeolite X results in rapid aging while in liquid-phase operation over the same catalyst the aging rate is greatly reduced.

In addition to a low aging rate it is desirable to have high efficiency for conversion of xylene to other xylene isomers rather than for disproportionation or cracking to less desirable products. The ZSM–4 catalysts are intrinsically more selective for isomerization than is REX. The efficiency for isomerization of xylenes is substantially higher with ZSM–4 catalysts than with the rare-earth exchanged zeolite X.

Discovery and development of ZSM–4 catalysts coupled with special processing techniques provide unusual capabilities for commercial aromatics processing. Yields of better than 99% aromatic products are obtained during the entire life of the catalyst regardless of the o-xylene/p-xylene production ratio. Zeolite catalysts are extremely active, allowing operations to be carried out in the liquid phase at low temperatures (400°F.–500°F.). The relatively low temperatures compatible with the process are bases for the terminology Low Temperature Isomerization (LTI).

For processing purposes, xylene isomerization can be defined as "the conversion of nonequilibrium mixture of xylenes to a composition closer to that of equilibrium by movement of methyl groups around the aromatic ring." The approach to equilibrium depends on the efficiency of the catalyst and the severity of reaction conditions. At LTI temperatures (400°F.–500°F.) the equilibrium mix contains about 24 wt. percent p-xylene, 55 wt. percent m-xylene and 21 wt. percent o-xylene. The basic reaction is accompanied by formation of small quantities of benzene, toluene, and C_9+ aromatics. There are essentially no losses to gas or non-aromatics.

A typical LTI process loop consists of (1) liquid-phase catalytic isomerization of C_8 aromatics to 95–98% approach to equilibrium, (2) distillation to recover benzene, ethyl benzene, C_9+, and xylenes for subsequent processing, (3) separation of p-xylene from m-xylene, and (4) catalyst regeneration. Alternatively, an additional stage of distillation can be incorporated for separate recovery of o-xylenes.

LTI reactor feed is p-xylene-lean xylene-separator effluent. The feed stream is passed through a heater which heats it to LTI reaction temperature.

The initial reactor temperature is 400°F. The reactor temperature is incrementally increased during the on-cycle to maintain 95 percent – 98 percent approach to equilibrium. Total pressure is 300 p.s.i.g., and the weight hourly space velocity is 3.0 lb. oil/hr-lb catalyst. Catalyst regeneration is required when reactor temperatures reach 500°F. after about 8 months of operation. Catalyst life is at least 2 years.

The cooled reactor effluent is fed to a dexylenizer. Benzene and toluene are separated from the C_8 fraction in this column.

Toluene and benzene are removed as column overhead. Dexylenizer bottoms are sent to the ethyl benzene column as a secondary feed. Primary feed to the ethyl benzene column is C_8+ aromatics extracted from refinery reformate or hydrotreated pyrolysis gasoline. Ethyl benzene column bottoms containing 3–5% ethyl benzene are fed to the xylenes splitter where most of the o-xylene and all of the C_9+ aromatics are separated from p-xylene and m-xylene. The p-xylene-rich overhead is processed to recover purity p-xylene. Splitter column bottoms are fractionated to produce purity o-xylene. C_9+ aromatics are removed from the system as o-xylene column bottoms.

Processes utilizing dual functional catalysts can be represented by a C_8 equilibrium system in which ethyl benzene is an integral part of the system. In the LTI Process ethyl benzene does not enter into the C_8 equilibrium nor is it destroyed when present in low concentrations. When operating in the 400°F. to 500°F. temperature range, LTI can be represented by a model concerned only with the reversible reaction of isomerization between m-xylene and p-xylene and the reversible isomerization between m-xylene and o-xylene. This characteristic allows LTI to operate with small quantities (less than **10** percent) or no ethyl benzene in the xylene loop, effecting a reduction in equipment size and more efficient p-xylene removal. (If dual-functional isomerizer feed contains less than **10–12** percent ethyl benzenes (equilibrium level) xylene will be isomerized to ethyl benzene).

Since ethyl benzene is not converted by xylene in the LTI reactor, most ehtyl benzene is removed by fractionation of the feed. Small amounts of ethyl benzene are circulated without loss over the AP catalyst. To avoid build-up the recycle stream is circulated through the ethyl benzene column stripping section.

There are two general classes of isomerization reactor feedstocks: (1) o-xylene and p-xylene production (o-xylene in isomerization reactor feed is below equilibrium), and (2) p-xylene production only (o-xylene in isomerization reactor feed is above equilibrium). Since the isomerization mechanism proceeds via the route o-xylene → m-xylene → p-xylene, it is more difficult to isomerize feeds containing high concentrations of o-xylene. The higher the o-xylene content the more difficult the isomerization. LTI can maintain 98+ percent efficiency to xylenes with both types of feedstock.

An efficiency of xylenes of 98+ percent can be maintained with LTI at 95–98 percent approach to equilibrium during the entire life of the zeolite catalyst by utilizing toluene as a feed diluent. Essentially no feed is lost as non-aromatics. The amount of toluene preferred varies from 10 to 20 wt.% of the LTI reactor feed. The diluent is removed immediately downstream from the reactor and recycled. The toluene apparently inhibits the xylene disproportionation reaction.

THE INVENTION

Utilization of high temperature vapor phase isomerization with a catalyst capable of converting ethyl benzene in parallel with LTI, provides process economics of major significance if proper relationships are maintained between the parallel reactors. Losses incident to the use of Octafining catalyst or other high temperature catalyst are minimized as is the quantity of expensive platinum catalyst. Instead a small Octafiner or equivalent serves to convert ethyl benzene to an extent which keeps the system in balance without circulating large quantities of that compound.

The combined process of this invention takes major advantage of LTI economics without need for ethyl benzene fractionation of material in the conversion/-separation loop.

Operation according to the invention is advantageously conducted at levels of ethyl benzene in the isomerizer feed somewhat higher than that conventional for Octafiners and much above that characteristic of prior LTI practice. As will be seen from the example below, isomerizer feed according to this invention may contain 25 wt. percent of ethyl benzene as compared with 17 percent normal feed to Octafining. At reasonably moderate Octafiner conditions, very substantial conversion of ethyl benzene occurs because of the spread between concentration in the feed and the equilibrium concentration. Preferably, the system is operated to provide at least 20 percent ethyl benzene in the isomerizer feed.

These effects are achieved with the quantity of the feed to the Octafiner less than that supplied to the LTI reactor, but at least equal to 20 wt. percent of the feed to LTI. Stated differently, the isomerizer feed stream is divided such that 10 to 50 wt. percent passes to Octafining and the balance to LTI. A preferred ratio is three parts of isomerizer feed to LTI for each part directed to Octafining or equivalent.

EXAMPLE

In this example of operation according to the invention, the high temperature isomerization phase is Octafining and that term has been used above in general discussion of the high temperature in the interest of simplicity. It will be understood that, as demonstrated hereinabove, zeolites of the ZSM-5 type and zeolites ZSM-12 and ZSM-21 are full equivalents of Octafining catalyst for the present purpose and reference to Octafining contemplates substitution of the said zeolites for platinum on silica/alumina Octafining catalyst.

The annexed drawing is a diagrammatic representation of equipment for practice of the specific embodiment described in this example.

As shown in that drawing a stream of C_8 aromatics derived from reforming a petroleum naphtha, solvent extraction of aromatics and distillation is supplied by line **1** to ethyl benzene tower **2.** A portion of the ethyl benzene is taken overhead from tower **2** by line **3.** Bottoms from tower **2** is withdrawn by line **4** to constitute fresh feed to the isomerized/separator loop for production of para-xylene. That fresh feed is constituted by 14.2 wt. percent ethyl benzene, **18.0** wt. percent p-xylene, 44.5 wt. percent m-xylene and 23.3 wt. percent o-xylene. The fresh feed is blended with a recycle stream shortly to be described and the combined feed passed to splitter tower **5** from which components of the combined stream heavier than C_8 are withdrawn as bottoms by line **6.**

A variation can be introduced when it is desired to also produce o-xylene. In such case, splitter **5** will be operated to include o-xylene in the bottoms which then will be passed to fractionation to take o-xylene as overhead and C_9+ as bottoms.

In the present example concerned, for simplicity, only with p-xylene production; overhead from tower **5** passing by line **7** to p-xylene separation is the sum of the streams fed to tower **5** less the small amount of C_9+ components there separated. As shown in the drawing, p-xylene separation is accomplished by fractional crystallization in crystallizer **8** to yield p-xylene. Crystallizer **8** operates in the manner described by Machell et al. Pat. No. 3,662,013 dated May 9, 1972. It will be understood that other systems for p-xylene separation can be used in a plant for practice of this invention, e.g., selective sorption as described in Cattanach patent No. 3,699,182 dated Oct. **17, 1972.**

An aromatic stream lean in p-xylene passes by line **9** to parallel LTI and Octafining isomerizers. This stream is constituted by 25.0 wt. percent ethyl benzene, 7.7 wt. percent p-xylene, 45.8 wt. percent m-xylene and 21.5

wt. percent o-xylene. The isomerizer feed stream is split by any suitable means, such as proportioning valves **10** and **11** to provide a desired ratio between flows in lines **12** and **13** to LTI and Octafining, respectively. In this example, 75 percent of the flow to isomerization passes by line **12** through heater **14** to Low Temperature Isomerization indicated generally at **15.**

The catalyst is isomerizer is HZSM-4 as described in Bowes, et al. U.S. patent No. 3,578,723, the disclosure of which is hereby incorporated by reference. Conditions of reaction are 430°F., 300 p.s.i.g. and weight hourly space velocity (WHSV) of 3 pounds of hydrocarbon per pound of catalyst per hour. The effluent of LTI reactor **15,** withdrawn by line **16,** is constituted by 24.2 wt. percent ethyl benzene, 16.0 wt. percent p-xylene, 38.7 wt. percent m-xylene, 18.9 wt. percent o-xylene and 2.2 wt. percent by-products. The by-products break down to 0.5 wt. percent benzene, 0.6 wt. percent toluene and 1.1 wt. percent C_9+ aromatics.

The remainder of isomerizer feed, 25 percent of the total, passes through heater **17,** is mixed with recycle hydrogen, from line **18,** and introduced to Octafiner containing conventional platinum on silica/alumina catalyst. The Octafiner is operated at 850°F., 225 p.s.i.g., a WHSV of 2 pounds of hydrocarbon per pound of catalyst per hour, and a hydrogen to hydrocarbon mol ratio of 10:1. Effluent of Octafiner 19 is cooled in heat exchanger **20** and passed to high pressure separator **21,** wherein hydrogen is separated for recycle through line **18.** The liquid product from separator **21** is mingled with LTI product from line **16** to provide a total isomerizer product flowing in line **22** to stripper **23.**

The Octafiner product is constituted by 18.8 wt. percent ethyl benzene, 21.9 wt. percent p-xylene, 39.8 wt. percent m-xylene, 15.0 wt. percent o-xylene and **4.5** wt.% by-product. The by-products break down to 1.4 wt. percent C_5 and lighter paraffins, 0.45 wt. percent naphthenes, 0.95 wt. percent benzene, 0.5 wt. percent toluene and 1.2 wt. percent C_9+ aromatics.

In stripper **23,** by-products lighter than C_8 are removed as an overhead stream and the stripped combined isomerizate is returned to splitter tower **5** as recycle of which the C_8 portion is 23.5 wt. percent ethyl benzene, 18.0 wt. percent p-xylene, 40.1 wt. percent m-xylene and 18.4 wt. percent o-xylene.

For ease of comparison the composition of important streams are set out in Table VI.

TABLE VI

	STREAM COMPOSITION, % WT.				
COMPONENT	FRESH FEED LINE 4	C_8 RECYCLE LINE 25	ISOMERIZER FEED-LINE 9	OCTAFINER PRODUCT SEPARATOR 21	LTI PRODUCT LINE 16
Ethyl benzene	14.2	23.5	25.0	18.8	24.2
p-xylene	18.0	18.0	7.7	21.9	16.0
m-xylene	44.5	40.1	45.8	39.8	39.7
o-xylene	23.3	18.4	21.5	15.0	18.9
Loss, C_8 Aromatics	—	—	—	4.5	2.2

I claim:

1. In a process of selectively recovering one or more eight carbon atom aromatic isomer from a mixture of such isomers isomerizing a mixture of unrecovered isomers and recycling isomerizate to the selective recovery step; the improvement which comprises contacting a portion of said unrecovered isomers greater than half but less than 90 percent of the total with a crystalline aluminosilicate catalyst under isomerizing conditions at a temperature less than 600°F. and under pressure sufficient to maintain said unrecovered isomers in the liquid phase and contacting hydrogen and the remainder of said unrecovered isomers in vapor phase with platinum on silica-alumina, a zeolite of the ZSM-5 type, zeolite-12 or zeolite 21 at a temperature of 550 to 900°F. and a pressure of 150 to 300 pounds per square inch; and thereafter blending the products of said contacting together for recycle as aforesaid.

2. A process as defined in claim **1** wherein p-xylene is selectively recovered.

* * * * *