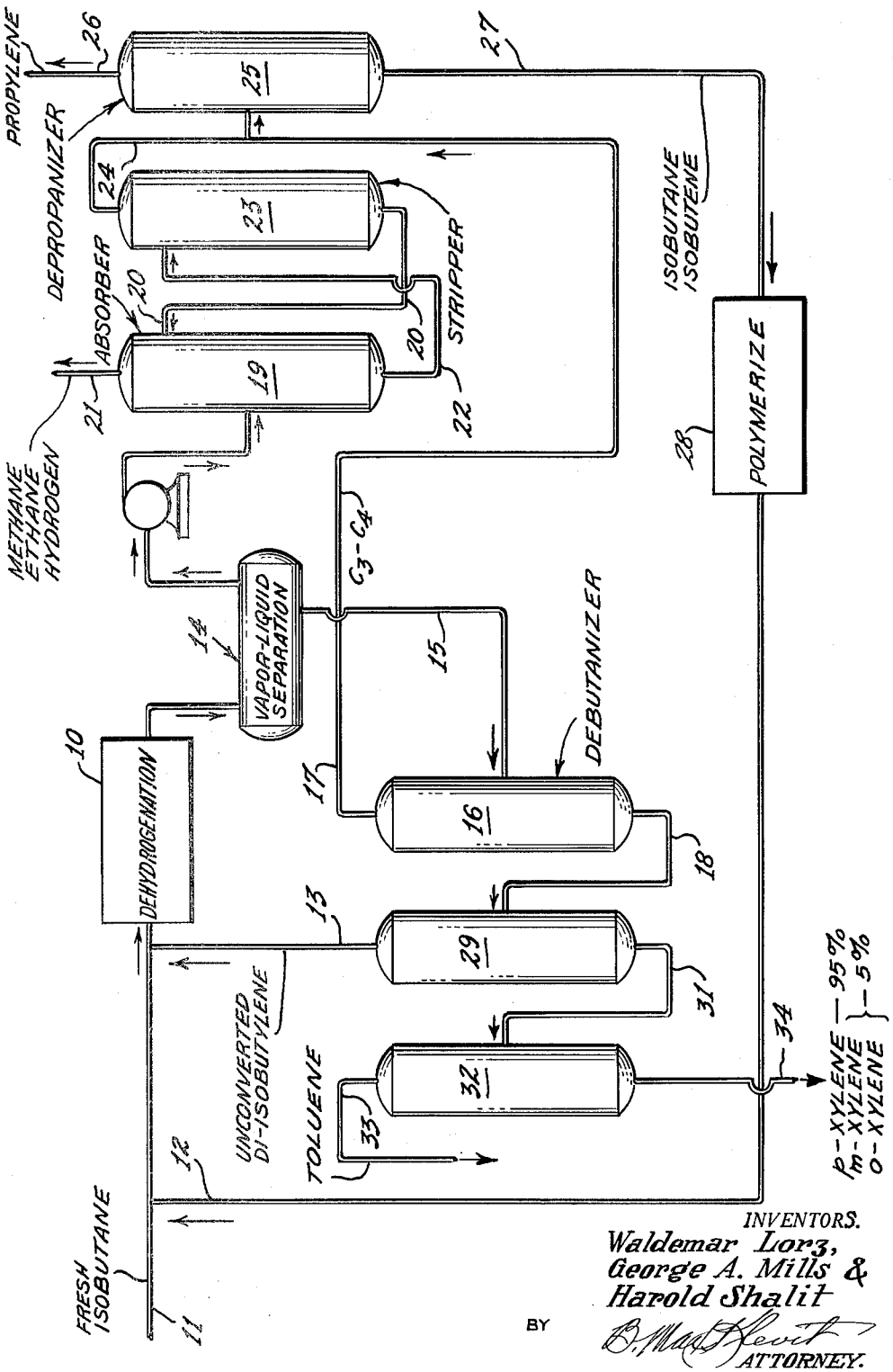
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PRODUCTION OF XYLENE

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PRODUCTION OF XYLENE

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The present invention relates to dehydrocyclization of C_8 acyclic hydrocarbons and is more particularly concerned with the production of xylene from C_8 acyclic hydrocarbons with special emphasis on the selective production of p-xylene.

The production of aromatic hydrocarbons by dehydrocyclization of appropriate C_6 and higher hydrocarbons is described in prior patents and other technical literature. It is also known to aromatize selected C_8 aliphatic hydrocarbons to produce xylenes. Thus, from n-octane there is obtained a mixture of all three isomers of xylene accompanied by ethyl benzene, which mixture predominates in o-xylene. Among the catalysts recommended for use in these dehydrocyclization processes there is chromium oxide, with or without minor quantities of other metal oxides, supported on gamma alumina.

For selective production of the desired p-xylene isomer by dehydrocyclization of acyclic C_8 hydrocarbons, with only very small quantities of the other xylene isomers in the reaction product, it is proposed by F. G. Herington and E. K. Rideal [Proc. Roy. Soc. (London) A184, p. 434 (1955)] to utilize 2,2,4-trimethylpentane as starting material. Similar processes are described in U.S. Patents 2,785,209 and 2,785,210 wherein the suggested initial charge is iso-octane (2,2,4-trimethylpentane) or di-isobutylene (2,4,4-trimethylpentenes), or mixtures of these. These patents describe various catalysts for this process, with indicated preference for catalyst comprising 5% to 40% (preferably about 12%) chromium oxide on gamma alumina and containing also minor amounts of potassium oxide and cerium oxide. While the aromatics produced in the liquid reaction product reported by these patents may contain as high as 95–98% p-xylene, the total conversion of the charge starting with isooctane does not exceed about 30% and up to about 36% in the case of the mixed trimethylpentene charge; the yield of p-xylene based on charge being at most less than about 12%.

It has now been found, in accordance with the present invention, that selective conversion of C_8 acyclic (paraffinic or olefinic) hydrocarbons can be obtained at high conversion levels by using specially prepared catalyst comprising 15% to 25% chromium oxide (Cr_2O_3) on an alumina base composed essentially of eta alumina. By the use of such catalyst in the conversion of isooctane, up to 85% or more of the charge can be converted, with p-xylene yields amounting to about 35% to 45% by weight of the charge.

The advantages of the invention can be further enhanced in accordance with another aspect thereof, by adding to the C_8 charge C_4 hydrocarbons which are simultaneously dehydrogenated. In this manner, not only is there the advantage of economically converting readily available and relatively inexpensive C_4 paraffins to xylenes, but in addition more effective temperature control is achieved inasmuch as the presence of the C_4 hydrocarbons has a dampening effect on the cyclic temperature swing otherwise encountered in the dehydrocyclization of the C_8 hydrocarbon feed under adiabatic operation, wherein periodic burning of the coke deposited in the catalyst during the on-stream period supplies at least part of the heat utilized in the succeeding endothermic hydrocarbon conversion operation. The design of an operative process for beneficial utilization of this feature to augment

production of desired C_8 aromatics is illustrated in the accompanying drawing by way of a schematic flow diagram.

Referring now to the embodiment illustrated in the drawing, there is charged to the dehydrogenation reactor system **10** a fresh feed **11** composed essentially of isobutane and recycle streams **12** and **13** containing di-isobutylenes and previously unconverted isobutane. The dehydrogenation effluent from reactor **10** is sent to a flash drum or other liquid-vapor separator system **14** wherein hydrogen and low molecular weight gases (to or through C_3) are separated as overhead, while the unvaporized products are withdrawn as liquid in line **15**.

The liquid products are sent to a debutanizer **16** preferably in the form of a fractionating column operated so as to separate out an overhead vapor fraction, withdrawn through line **17**, consisting essentially of C_3 and C_4 hydrocarbons; the unvaporized higher boiling materials are discharged through line **18**. The overhead gases from the vapor separator **14** are sent to an absorber **19**, after being compressed to about 50 to 200 pounds per square inch. Absorption is effected by means of an aromatic hydrocarbon oil introduced into an upper portion of the absorber through line **20**, whereby unabsorbed hydrogen and low molecular weight gases (through C_2), which are not absorbed, are withdrawn overhead in line **21**, while the rich oil containing absorbed higher molecular weight hydrocarbons is sent by line **22** to stripper **23**, operated to separate as overhead the C_3 and C_4 hydrocarbons from the absorber oil, the lean oil being returned to the absorber **19** through line **20**. Thus, the stripper **23** may be operated under conditions to discharge as vapor overhead hydrocarbon materials boiling substantially above the initial boiling point of the absorber oil. In the typical situation, aromatic absorber oils of a boiling range from about 175° F. to about 400° F. can be conveniently employed.

The overhead streams from debutanizer **16** and stripper **23**, predominating in C_3 and C_4 hydrocarbons, are sent by lines **17** and **24**, respectively, to a depropanizer **25**, operated to separate out an overhead fraction, discharged through line **26**, composed essentially of C_3 hydrocarbons rich in propylene, while the unvaporized bottoms, composed essentially of isobutane and isobutene, are sent through line **27** to polymerization (dimerization) in any suitable reactor **28**.

Any suitable known process for dimerization of the isobutenes may be employed in reactor **28**. For example, the hydrocarbon stream introduced through line **27** may be passed over a fixed bed of silica alumina catalyst at moderate temperatures and pressures and high space rates. Typical operations involve temperatures of 300 to 400° F., pressures of 300 to 800 pounds per square inch and liquid hourly space rates of about 3 to 10. Other known dimerization processes employ either phosphoric acid catalyst or sulfuric acid catalyst at moderate temperatures designed to obtain high yields of desired dimers rich in 2,2,4-trimethyl pentene, and avoiding severity which may tend to promote excessive production of dimethyl hexenes or 2,3,4- and 2,2,3-trimethyl pentenes. The total polymerization product rich in 2,4,4-trimethyl pentene-1 and 2,4,4-trimethyl pentene-2, together with some triisobutylenes in the product, is recycled to the dehydrogenation reaction system **10** by means of line **12** as already indicated.

The bottoms fraction from the debutanizer **16** consists essentially of C_7+ hydrocarbons rich in aromatics. These are fractionated in column **29** to separate out as overhead vapors hydrocarbons boiling up to about 222° F. or slightly above, but short of the boiling point of toluene (about 230° F.). The overhead fraction, which is composed chiefly of unconverted diisobutylene together with

some higher liquid polymer, is recycled by line 13 to the dehydrogenation reactor 10 as already indicated. The buttoms fraction from column 29 is sent by line 31 to fractionating column 32 wherein toluene and lower boiling hydrocarbons are withdrawn as vapor overhead in line 33, thereby recovering at 34 the C_8 aromatic hydrocarbons, which will contain 95% or higher p-xylene, the remainder being almost entirely isomers thereof.

For the combined dehydrogenation operation carried out in reactor 10, wherein the fresh charge is composed essentially of fresh isobutane which is dehydrogenated to isobutylene while recycled dimer is simultaneously converted to xylene, preferred operating conditions include temperatures in the range of 1000 to 1100° F., and low pressures ranging from about 5 inches or mercury absolute to atmospheric (30 in. Hg). Space rates may be in the range of 0.5 to 2 volumes per hour.

When the dehydrocyclization process is operated, with iso-octane or diisobutylene as fresh charge, for production of an aromatics product consisting essentially of p-xylene, somewhat lower operating severity can be employed; thus temperatures in the range of about 950 to 1050° F. can be utilized, preferably in the range of 975 to 1025° F. for best overall results from the standpoint of achieving high conversion levels without excessive production of coke and light hydrocarbon gases. While atmospheric or even slightly elevated pressure can be used, it is advantageous even here to operate at subatmospheric pressure so as to favor iC_4 olefins rather than paraffins in the by-products. The isobutane and iso C_4 olefins produced in this process can be recovered and separated, if desired, or these can be directly recycled as such, joining the fresh C_8 charge fed to dehydrocyclization. The presence of recycled isobutylene may serve to suppress splitting of the C_8 feed to some extent, and in addition thereto some part of the iC_4 paraffins and olefins may be directly converted to xylene by "a gas reversion" type mechanism taking place in the dehydrocyclization reactor, as illustrated by the reactions:

$$2iC_4H_{10} \rightarrow C_8H_{10} + 5H_2$$
$$2iC_4H_8 \rightarrow C_8H_{10} + 3H_2$$

Operating at the indicated pressure, the feed rate of the C_8 hydrocarbon may lie in the range of 0.2 to 2.0 volumes per hour per volume of catalyst (LHSV) and is preferably selected so that at the temperature and pressure employed at least 50% and preferably greater conversion of the C_8 charge is obtained. If the iC_4 hydrocarbons are recycled—as paraffins, olefins or mixtures of these—the same temperatures and pressure in general may be employed as when fresh C_8 feed only is used, but the total hydrocarbon space rate should be accordingly adjusted to obtain operating severity consistent with a minimum of 50% conversion of C_8 hydrocarbons.

As indicated above, an important feature of the invention is the particular catalyst used. Eta alumina, which constitutes the whole or major part of the support or carrier for the active catalytic component, can be produced by heating beta alumina trihydrate (Bayerite) at temperature in the range of about 600–1400° F. Alumina beta trihydrate can be obtained by various methods known to the art; one such method involves the hydrolysis of aluminum alcoholate with ammonium hydroxide. Other methods involve the controlled aging of aluminum hydroxide gels. Beta alumina trihydrate in substantially pure form (97+%) is now available commercially; also available are marketed mixtures of hydrated alumina contining 75% or more beta alumina trihydrate in association with alpha trihydrate (Gibbsite) or with alpha monohydrate (boehmite) or sometimes with both of these. Calcination (dehydration) of the alpha trihydrate leads to the production of typical gamma form of alumina, heretofore known to the art, as "activated alumina." In calcining alumina hydrate mixtures containing beta trihydrate with these alpha hydrates, there is obtained a corresponding calcined product comprising eta and gamma forms of alumina. The catalysts used in the practice of the present invention are prepared by impregnation of a dehydrated alumina base obtained from hydrated alumina containing at least 60% and preferably in excess of 75% beta trihydrate. The dehydrated alumina product is subjected to further heat treatment to adjust the surface area to the range of about 100 to 300 square meters per gram and then impregnated with chromic acid or other decomposable soluble chromium compound to incorporate 15 to 25% Cr_2O_3 by weight of the finished catalyst, after which the impregnated product is dried and calcined. The calcined chrome-alumina catalyst has a surface area of about 50–150 square meters per gram.

The preferred catalysts used in practice of the invention are those which contain at least 0.6% and preferably 0.8 to 1.5% by weight alkali metal ion calculated at Na_2O; i.e., the corresponding potassium compound used in the same molecular proportions would entail the weight range of at least 0.9% K_2O, preferably 1.2 to 2.3% K_2O by weight of the catalyst. Commercial hydrated alumina compositions composed of or predominating in beta trihydrate vary in alkali metal content from about less than 0.1% Na_2O to generally about 0.6% Na_2O. To incorporate additional alkali metal ion there may be admixed with the aqueous paste of the alumina hydrate employed in formation of granules or pellets, sodium bentonite or sodium hydroxide in an amount sufficient to provide the desired alkali metal content in the finished catalyst. On the other hand, the sodium or other alkali metal may be incorporated in the pelleted material by inclusion in the solution employed for chrome impregnation. Thus, the desired amount of Na_2O may be furnished by adding a small amount of sodium chromate to the chromic acid or the chromic acid solution may be partly neutralized by sodium hydroxide. The presence of the indicated amount of alkali metal in the catalyst is believed to enhance the selectivity of the catalyst for dehydrocyclization operations while reducing the degree of acid-catalyzed side reactions including isomerization, polymerization, and carbon-carbon scission.

EXAMPLE I

The preferred catalyst employed in practice of the invention is prepared in the manner described below:

Commercial alumina beta trihydrate (96+% bayerite) was thoroughly admixed by mulling with aqueous nitric acid employing 0.09 part nitric acid (1.42 S.G.) and 0.108 water by weight of the alumina trihydrate. The acid mix after standing overnight was extruded through a die plate and the strands cut to form 2.4 mm. pellets. The pellets were dried at 240° F. and dehydrated in air at about 800–900° F. (surface area=367 $m.^2/g.$). The dehydrated pellets were then subjected to surface area adjustment by steaming (100% H_2O) for 2 hours at 900° F. (surface area=170–190 $m.^2/g.$).

The area-adjusted pellets were impregnated by soaking in a chromic acid solution, employing 1 liter of the solution for each kilogram of pellets. The chromic acid solution was prepared by dissolving CrO_3 in water to form a solution of 1.420 specific gravity (60/60° F.) containing about 550 grams CrO_3 per liter of solution, in which there was also dissolved solid sodium hydroxide furnishing 41.8 grams NaOH per liter. After 2 hours soaking, the excess liquid was decanted from the pellets. The drained pellets were dried in air at 250° F., then heat treated for 4 hours at 1400° F., in an atmosphere of 20% steam and 80% air. The finished pellets analyzed 1.09% Na_2O by weight.

The catalyst pellets had the following approximate composition:

	P.b.w.
Cr_2O_3	20
Al_2O_3 (~100% eta)	78.9
Na_2O	1.1

EXAMPLE II

Catalyst prepared as described in Example I above was utilized in dehydrocyclization of isooctane and of diisobutylene, respectively, in a number of runs at atmospheric pressure with the yields and under the operating conditions reported in Tables 1 and 2 below:

Table 1

ISOOCTANE RUNS

Run No.	1	2	3	4	5	6
Oper. Cond.:						
Temp., ° F.	950	1,000	1,000	1,000	1,000	1,000
LHSV	0.25	0.25	1.0	1.0	1.5	0.5
H_2/oil mol	3	3	-------	-------	-------	-------
Products wt. percent chg. (no loss basis):						
Liquid	77.4	63.3	86.9	79.4	65.8	69.1
Gas	22.4	36.4	11.4	18.7	31.7	28.6
Coke	0.2	0.3	1.7	1.9	2.5	2.3
Conversion, wt. percent chg.[1]	35.7	75.2	53.9	69.1	83.7	81.7
Selec., wt. percent chg.	34	38.5	71	64.7	53.1	56.1
Yield/pass, wt. percent chg.	12.2	28.9	38.3	44.7	44.4	45.8
Liquid anal., wt. percent:						
Isooctane	77.4	28.6	36	26.1	17.4	18.6
Diisobutylene	5.7	10.0	17.1	12.9	7.3	7.9
p-Xylene	15.7	45.7	43.7	56.3	67.6	66.0
Gas Analysis, wt. percent:						
Hydrogen	4.7	5.4	20.5	14.3	8.8	9.4
Isobutane	60.8	63.8	44.7	48.4	45.2	49.2
Total butenes [2]	16.7	19.5	17.7	24.4	23.0	23.3

[1] Conversion is based on products in the effluent other than isooctane and diisobutylene.

[2] Utilization of at least a portion of the butenes as recycle material after suitable processing as by dimerization will increase the selectivity value.

Table 2

DIISOBUTYLENE RUNS

Run No.	7	8	9	10
Oper. Cond.:				
Temp., ° F.	1,000	1,000	1,000	1,000
LHSV	0.25	0.25	0.5	0.5
H_2/oil mol	3	3	1.5	-------
Products, wt. percent chg. (no loss basis):				
Liquid	60	66.7	61.3	66.7
Gas	35.6	32.9	87.3	31.3
Coke	4.4	0.8	1.4	2.0
Conversion, wt. percent chg	94	92.4	92	89.4
Selectivity, wt. percent chg	35.7	41	37.2	45.7
Yield/pass, wt. percent chg	33.6	37.9	34.2	40.9
Liquid anal., wt. percent:				
Diisobutylene	11.3	11.4	13.1	15.9
p-Xylene	56	56.8	55.9	61.2
Gas analysis, wt. percent:				
Hydrogen	0.5	1.6	1.6	4.7
Isobutane	76.2	73.4	64.1	50.8
Total butenes	14.9	11.8	22.7	29.8

It will be seen from the foregoing tables that under conditions of sufficient severity to obtain 50% or greater conversion of the charge, once-through yields of 30–45% p-xylene are obtained by weight of charge. Moreover, the aromatics fraction in the liquid effluent is of high purity in p-xylene and relatively free of the other C_8 aromatic isomers. The isooctane and diisobutylene in the liquid product can, of course, be recycled to dehydrocyclization for conversion to additional p-xylene. Considering such recycle operation, the highest ultimate yields would be obtained under conditions of Runs 3 and 4, carried out at a severity level giving about 50–70% per pass conversion of C_8 charge. At higher conversion level, there is a corresponding loss in selectivity. The addition of hydrogen appears to lower the once-through yield to some extent, but on the other hand may tend to reduce the quantity of coke deposited.

EXAMPLE III

A series of runs were made over catalyst similar to that of the previous example at the conditions given below to determine the effect of varying the ratio of isobutane/diisobutylene in the feed. The results are reported in the table below:

Table 3

Run No.	1	2	3	4	5	6
Temp., ° F.	1,050	1,050	1,050	1,100	1,100	1,100
Pressure, mm. Hg	400	400	400	400	120	120
Space rate (GHSV [1])	200	300	400	400	800	400
Isobutane to DIB mol ratio	0.9	1.9	2.8	2.8	6.4	2.8
Data Based On: Isobutane and DIB→Isobutylene and p-Xylene						
Wt. percent chg.:						
Conversion	74.2	66.7	62.4	74.8	44.3	60.7
Selectivity	80.3	85.8	83.3	77.3	79.9	76.9
Yield/pass	59.6	57.2	52	57.8	35.4	46.7
Data Based On: Isobutane→p-Xylene						
Wt. percent chg.:						
Conversion	37.8	26.7	23.9	29.4	16.8	25.4
Selectivity	61.6	64.4	56.6	42.2	47	44.9
Yield/pass	23.3	17.2	13.5	12.4	7.9	11.4

[1] GHSV=Volume vapor per hour per volume catalyst.

From these runs it appears that desired product balance is obtained at isobutane/DIB mol ratios of 2 to 3; approximate equilibrium conditions are obtained when the mol ratio of isobutane/isobutylene in the charge lies in the range of 2 to 4.

In the illustrated embodiment of the invention diisobutylene is recycled to the reactor in which dehydrogenation of isobutane is also effected. If desired, alternatively, separate reactors may be provided, respectively, for dehydrogenation of the isobutane and for cyclization of the diisobutylene, wherein the latter may be operated at somewhat lower severity including lower temperature and higher pressure approaching atmospheric. In such operation, any isobutylene that is not polymerized at 28 would be returned to the dehydrogenation reactor with the unconverted isobutane.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. The method for production of p-xylene which comprises: feeding to a catalytic dehydrogenation zone mixed hydrocarbon streams, including at least one recycled products stream comprising diisobutylene, and isoC$_4$ hydrocarbons comprising isobutane, the ratio of isoC$_4$ hydrocarbons to diisobutylene being within the range from about 2:1 to about 3:1; contacting said mixed hydrocarbon streams in said dehydrogenation zone with chrome-alumina catalyst comprising 15 to 25% chromium oxide, determined as Cr_2O_3, and alkali metal in an amount equivalent to at least 0.6% by weight Na_2O on alumina carrier, said catalyst having been obtained by dehydrating beta alumina trihydrate to produce sorptive alumina having a large surface area, lowering the surface area to within the range from 100 to 300 m.^{2}/g. by treatment with hot steam, impregnating the surface reduced alumina, and heating the impregnated eta alumina, said contacting being effected at a temperature in the range of 1000 to 1100° F. and pressure in the range of 5–30 inches Hg absolute, and at a space rate correlated therewith to obtain at least 50% conversion of C_8 hydrocarbons in the charge with resulting production of products including p-xylene and isobutylene; separating from the resulting products hydrogen and hydrocarbons up to C_3; further separating from the reaction products isoC$_4$ hydrocarbons to provide an aromatic residual fraction; subjecting said separated isoC$_4$ hydrocarbons to dimerization in a separate reaction zone to obtain diisobutylene; admixing the obtained diisobutylene with the fresh isobutane charged

to said dehydrogenation zone; and recovering from said aromatic residual fraction a xylene cut highly concentrated in p-xylene.

2. The method producing a hydrocarbon product of high p-xylene content which comprises feeding to a dehydrogenation zone a hydrocarbon mixture of isobutane and diisobutylene under conditions effecting simultaneous cyclization of said diisobutylene and dehydrogenation of said isobutane, said conditions including contact of said hydrocarbon mixture to obtain at least 50% conversion of C_8 hydrocarbons and the contacting of said hydrocarbon mixture with catalyst prepared by dehydrating an alumina hydrate composition containing at least 60% beta trihydrate, adjusting the surface area by treatment with hot steam to a surface area in the range of 100 to 300 $m.^2/g.$, impregnating the surface reduced alumina, and heating the impregnated alumina to prepare a chromia on eta alumina comprising 15 to 25% Cr_2O_3, and said conditions including temperature in the range of 1000 to 1100° F., and at a pressure in the range of from about 5 inches of mercury absolute pressure to about 30 inches of mercury absolute pressure.

3. The method for preparation of p-xylene which comprises the following steps:

(a) feeding to a catalytic dehydrogenation zone a fresh hydrocarbon charge consisting essentially of isobutane,

(b) feeding to said dehydrogenation zone diisobutylene,

(c) dehydrogenating said fresh hydrocarbon charge in the presence of said diisobutylene to produce isobutylene therefrom while converting part of said diisobutylene to xylene, said dehydrogenation zone being at temperature in the range of 1000 to 1100° F. and at subatmospheric pressure within the range from about 5 inches of mercury absolute to about 30 inches of mercury absolute and containing a bed of catalyst comprising 15 to 25% Cr_2O_3 on an alumina base comprising eta alumina, said base having been obtained by dehydration of a hydrated alumina consisting essentially of beta alumina trihydrate,

(d) withdrawing the reaction products from said dehydrogenation zone and removing therefrom hydrogen and light hydrocarbons through C_3 leaving a C_4+ hydrocarbon product,

(e) removing from said C_4+ hydrocarbon product a fraction concentrated in iC_4 hydrocarbons, including isobutylene, leaving an aromatics-containing hydrocarbon fraction,

(f) separating unconverted diisobutylene from said aromatics-containing fraction and recycling said diisobutylene to said dehydrogenation zone,

(g) further fractionating the aromatics-containing fraction, after removal of diisobutylene therefrom, to separate out toluene and lower boiling hydrocarbons, thereby recovering a C_8 aromatic fraction concentrated in p-xylene,

(h) polymerizing the isobutylene from step (e) to produce additional diisobutylene, and

(i) feeding the polymerization product from step (h) to the dehydrogenation zone.

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