





1

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DISPROPORTIONATION OF ALKYLAROMATIC  
HYDROCARBONS

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The present invention relates to the production of aromatic hydrocarbons and is particularly concerned with disproportionation reactions of alkyl-aromatic compounds effected in the presence of catalysts, such as the conversion of toluene to desirably high yields of benzene and xylenes.

The former demand for toluene, particularly during the war years, as an intermediate for the manufacture of explosives and other organic chemicals has been well met by petroleum conversion processes, so that the increased outputs of toluene may be diverted to other outlets. There is an increasing demand for xylenes principally for use in the manufacture of benzene dicarboxylic acids as starting materials for important polymerization and condensation derivatives thereof including the new synthetic fibers known as "Dacron" and "Terylene." The demand for benzene has remained steady over many years and, because of its increasing use as an intermediate for the production of styrene as well as adipic acid used respectively in synthetic resins and synthetic fibers, has been progressively rising despite the installation of increased facilities for its production. One of the principal advantages of the present invention lies in the fact that benzene and xylene of required purity are obtained from inexpensive starting materials including crude toluene of considerably below "nitration grade" in purity.

Under conditions hitherto investigated and suggested for dealkylation of alkyl-aromatic compounds over cracking catalysts of the silica-alumina type, it was found while at about atmospheric pressure substantially complete dealkylation of C<sub>3</sub> to C<sub>5</sub> alkyl substituted benzenes to benzene and corresponding olefins could be obtained, in the case of benzene compounds having lower alkyl groups attached to the ring the reaction under the same conditions of severity was too slow and even under more severe processing conditions toluene was very resistant to dealkylation. At high pressure, however, higher alkyl benzenes also tend to produce chiefly methyl and ethyl substituted benzenes. This reported behavior of benzene is consistent with the fact that gasoline obtained by catalytic cracking is generally poor in benzene and comparatively rich in toluene and in polymethylated benzenes. Deeper catalytic cracking of aromatic hydrocarbons results in total rupture of the ring with the formation of hydrogen, coke and gaseous hydrocarbons, and even under conditions wherein dealkylation of alkyl aromatic compounds can be effected without substantial rupture of the ring, large quantities of coke are produced apparently as a result of polymerization of the olefinic radicals split off.

It has also been previously proposed to effect dealkylation of alkyl aromatic hydrocarbons by hydrogenolysis in the presence of added hydrogen and over catalysts promoting hydrogenation such as nickel. Under these conditions, however, only relatively poor yields of benzene are obtained with accompanying extensive splitting of the ring.

It has now been found that exceptionally good yields

2

of benzene and xylenes are obtained by disproportionation of toluene over a solid cracking-type catalyst at a hydrogen partial pressure above atmospheric. Only a relatively small amount of the charge is cracked to non-aromatic hydrocarbons, and coke production is comparatively small.

In accordance with the invention a charge composed of or rich in toluene is passed over siliceous cracking catalyst, such as silica-alumina, at a temperature in the order of 850–1150° F. together with added hydrogen (or recycled hydrogen-rich gas) in the ratio of at least one mol of hydrogen per mol of toluene charged, and at a total operating pressure of from about 200 to 600 pounds per square inch gauge. Space rates of the order of 0.5 to 5.0 or more volumes (as liquid) of charge per hour per volume of catalyst can be employed. Under the preferred conditions yields as high as 70% of the thermodynamic equilibrium for conversion to benzene and xylene are realized.

While coke production in the described process of the invention is quite low for the conversion level attained as compared with hitherto known disproportionation and dealkylation processes, it is nevertheless desirable to provide for the periodic regeneration of the catalyst in order to maintain more economic activity levels. To effect regeneration of the catalyst the process can be operated by known fixed catalyst bed procedures with periodic regeneration of the catalyst in situ, or by employing any of the well known moving catalyst systems wherein the catalyst is continuously recycled from the hydrocarbon conversion zone to a separate regeneration zone and returned.

In the operation of the process an equilibrium mixture of the various isomeric xylenes is produced. From the separated xylene fraction a cut consisting predominantly of meta and para-xylene can be separated from the ortho-xylene and the latter purified, if desired, to the extent required in known manner. Separation of the meta and para xylenes can be effected in various ways known to the art, such as by continuous low temperature selective crystallization of the para-isomer. The metaxylene rich cut may then be subjected to isomerization, as hereinafter described, for recovery of additional quantities of the more valuable para-xylene.

The invention will be best understood and other aspects and advantages thereof appreciated from the detailed description which follows read in connection with the accompanying drawings, wherein:

Figure 1 is a schematic flow diagram of a preferred processing technique.

Figure 2 is a schematic flow diagram relating particularly to the disproportionation reaction and illustrating the use of moving catalyst in a "fluidized" condition.

Figure 3 is a schematic flow diagram of an alternative modification employing a compact moving catalyst bed.

Referring now more particularly to Figure 1 there is shown a system including a fixed bed reactor 1 into which the toluene fraction coming from a preheater is pumped through a line 2, the reactor being filled with suitable catalytic material such as synthetic cracking catalyst of the silica-alumina or silica-magnesia type or with acid-activated clay or like known cracking catalyst. There is also charged to this reactor, hydrogen-rich gas by means of line 3. The hydrogen-toluene mixture is passed through the reactor under appropriate operating conditions hereinafter described for an on-stream period determined by the conversion level sought to be maintained, and when the catalyst activity falls below this level the catalyst is regenerated in suitable manner. In practical operation, to maintain continuity, several of such reactors 1 operating in parallel will be provided so that

3

during the regeneration period of one of said reactors the charge to be converted will be passed to the other reactor for the appropriate on-stream period.

The products leaving reactor 1 through line 4 are passed through a condenser (not shown) and the liquid product introduced into a receiver 5 where it is degassed. The off gas then passes through line 6 to a vessel 7, wherein the gas is subjected to countercurrent scrubbing, such as by means of a suitable hydrocarbon liquid, to remove hydrocarbon gases from the hydrogen. The thus enriched hydrogen is then recycled to the reactor 1 by line 8 and the hydrocarbon scrubbing liquid passed to vessel 9 by means of line 10. In vessel 9 the scrubbing liquid is degassed; the gases being vented overhead at 11 and the hydrocarbon liquid being recycled for further use in scrubbing through line 12.

The degassed mixture from vessel 5, containing benzene, toluene and xylenes is passed by line 13 to a fractionating column 14 wherein a benzene cut is separated out overhead and passed to storage or other treatment through line 15. The bottoms fraction from the column is passed by line 16 to a second column 17 wherein a toluene cut is taken overhead and recycled, by line 18, to reactor 1. The xylene containing bottoms fraction from column 17 is passed through line 19 to a third fractionator 20 to separate out any ethyl benzene, which is withdrawn overhead through a line 21. A middle cut consisting predominantly of meta-xylene and para-xylene is withdrawn through line 22 close to the top of the fractionator, while the bottoms, which consist mostly of ortho-xylene, are removed through line 23, and sent to further fractionation or other desired purification.

The xylenes fraction withdrawn through line 22 is subjected to low temperature crystallization in vessel 24 from which the para-xylene fraction is removed by line 25 and sent to storage.

If desired, particularly if the mixture from vessel 5 contains significant quantities of paraffins forming azeotropes with the aromatics present, paraffins may be removed from the mixture by chromatographic adsorption, selective extraction or other known techniques, before it is sent to fractionator 14.

The meta-xylene fraction from the crystallizer is passed by line 26 to a low pressure reactor 27 containing catalytic material, which may be the same as that in reactor 1 or other catalytic material effective in promoting isomerization. In reactor 27 the meta-xylene is isomerized under conditions to produce para-xylene, which product contains other isomers. Hydrogen is charged to vessel 27 by means of line 28 and the conversion products withdrawn through line 29.

If desired all or a portion of the ethylbenzene and ortho-xylene may be charged to the isomerization reactor 27.

The product withdrawn through line 29 is passed to fractionator 20, after intermediate degassing, if necessary. In some instances, if substantial amounts of toluene are formed, the isomerized product in line 29 may be passed to fractionator 17 for separation. As in the case of reactor 1, regeneration of the catalyst in reactor 27 may be effected by the provision of a similar parallel reactor, to maintain the continuity of the process.

Instead of employing a fixed catalyst bed, as illustrated in Figure 1, a moving catalyst system may be substituted. Thus, as illustrated in Figure 2, the fresh toluene feed including recycle feed from the fractionators is passed by line 50 through a preheater and into a "fluidized" catalyst reactor 51, in which reactor finely divided or powdered catalyst of suitable particle size is maintained in fluidized condition by the addition of hydrogen-rich gas through line 52. A light phase region of materially reduced solid particle concentration is maintained in the upper portion of the reactor. The mixture of fluid conversion products and suspended solid particles passes from the light phase to suitable solid particle separating

4

equipment, such as the cyclone separator 53, wherein entrained solid particles are removed from the outgoing stream of fluid conversion products; the separated solid particles being returned through a standpipe 54 while the fluid conversion products pass overhead through line 55.

A standpipe 56 is provided within the reactor terminating at a level beneath the upper extremity of the dense phase, through which pipe a column of solid particles is continuously withdrawn and passed through the flow control valve 57 into the transfer line 58. In this line the solid particles are contacted with a stream of regenerating gas supplied thereto through line 59. A sufficient pressure drop is maintained across valve 57 to prevent upward passage of the regenerating gas into the standpipe, and the regenerating gas serves to transport the solid particles through line 58 into the lower portion of the regenerator 60. In known manner the regenerator 60 as well as the reactor 56 is provided near the bottom thereof with suitable perforated plates or distributing grids (not shown) through which the fluidizing gas passes upwardly at required velocity to maintain the solid particles in turbulent fluidized condition or in a state of hindered settling.

In the regenerator 60 the finely divided catalyst particles are subjected to combustion of coke therein by the oxygen content of the regenerating gas. If required for control of temperature within the regenerator, a portion of the catalyst may be withdrawn from the upper portion of the vessel and returned through a suitable side arm cooler to the lower portion thereof in conventional manner.

Steam or other stripping or sealing gas is supplied by a line 62 to the lower part of standpipe 56 just above the valve 57 to help prevent the passage of light products and occluded hydrocarbon vapors into the transfer line 58.

As in the reactor 51 there is also provided in the regenerator 60 a cyclone separator 63 associated with a solid particle return line 64 and a vapor withdrawal line 65 operating in similar manner to that described for the like parts in reactor 51. A standpipe 66 terminates at an appropriate level within the regenerator, through which pipe a column of catalyst is withdrawn and passed into line 52, being transported therethrough into the reactor 51 by the hydrogen rich gas admitted through line 67. Standpipe 66 is provided with a flow control valve 68 and a gas line 69 operating similarly to analogous parts in standpipe 56. By adjustment of the density and/or height of the dense phase portion of the catalyst in these vessels respectively, in known manner, the regenerator 60 may be operated at any desired pressure equal to or below that of reactor 51.

The vapor products from line 55 after suitable cooling are passed into a flash drum 70 from which gas is withdrawn through line 71 and the major portion thereof recompressed and recycled by line 72 through the heater for return to the reactor through line 67. The liquid product withdrawn from the bottom of drum 70 is sent to fractionation in a manner already described in connection with Figure 1.

The process can also be operated in a system employing granular or pelleted catalyst as a compact moving bed. Thus as shown in Figure 3, the toluene charge together with hydrogen or hydrogen-rich recycle gas, having been suitably heated, is passed into a compact moving bed reactor 80 and passed therethrough in concurrent relation to the catalyst, as illustrated; if desired, the hydrocarbon charge may be passed upwardly through the gravitating catalyst bed. The vapor products are separated from the gravitating catalyst near the bottom of the reactor by known gas disengaging devices or arrangements (not shown) and withdrawn through line 81, by which line the products are sent to suitable means for separation of hydrogen-rich gas and subsequent fractionation of the liquid product, as already above de-

5

scribed. Below the gas disengaging level in reactor 80 the catalyst is stripped by gas or vapor introduced through line 82 and passed by a conduit 83 into a gas lift engager 84 forming a bed of catalyst therein. Lift gas enters the lift engager through a line 85 and together with catalyst engaged thereby passes upwardly into the lift pipe 86 discharging into a vessel 87. In the particular system herein illustrated, regeneration of the catalyst is effected partly in the lift 86 and completed within the vessel 87. For this purpose the lift gas employed is composed of or comprises air or other oxygen-containing gas suitable for effecting combustion of the coke contained in the catalyst during its passage through the lift.

The lift gas together with the catalyst discharge upwardly into the vessel 87 and, after the momentum velocity of the catalyst has been spent as a result of the expanded area of the vessel, the catalyst falls downward to form a compact moving bed within the vessel supported by a tube sheet or other suitable means 88. The regenerating gas still containing combustion supporting oxygen passes downwardly through the bed of catalyst in vessel 87 and is disengaged at an intermediate level therein by a series of inverted channel members 89, the spent flue gas being withdrawn through a line 90 communicating with a discharge beam into which the gases collected by the channel members flow. Below the level of channel members 89 a similar series of inlet channels 91 are provided for the introduction of air or other fresh oxygen containing gas by means of line 92, a portion of which gas passes upwardly through the bed of catalyst above channel members 91 to discharge through line 90 and the remaining portion passing downwardly through the bed together with the gravitating catalyst discharging through a series of downcomers 93 arranged in the tube sheet 88. The downcomers 93 discharge catalyst and gas within the vessel 87 at an appropriate level above the bottom thereof to form a layer providing a gas disengaging and collecting space between the surface of the layer and the bottom of tube sheet 88. The gas is collected in this space and withdrawn by means of a line 94 communicating therewith, while the regenerated catalyst continues its downward movement through a conduit or leg 95 returning the catalyst to the top of reactor 80.

Instead of particular system shown in Figure 3 wherein initial combustion is effected in the lift, inert gas might be employed for circulating the catalyst with the provision of a suitable separate regeneration vessel as is generally known in the art. To avoid excess temperatures, suitable provision is made for heat removal during regeneration of catalyst vessel 87.

In the initial conversion reactor, such as vessel 1 in Figure 1, or the corresponding vessels 51 and 80 respectively is Figures 2 and 3, reaction temperatures are in the range of 850–1150° F. preferably at 950–1050° F., and the vessels are operated at a pressure of from about 200–600 pounds per square inch. While regeneration of the catalyst can be effected at such pressure, it is generally preferred to carry out regeneration at lower pressure, as at about 50–100 or more pounds below the pressure in the reaction vessel. Regeneration at as low as atmospheric pressure is possible, but introduces greater complexity of equipment and operation from the standpoint of the extent of depressuring and repressuring thereby required.

The following examples illustrate, without limitation thereto, various conditions that may be employed in operation of the invention and typical yields.

#### EXAMPLE I

A fixed bed reactor capable of being pressurized was charged with a silica-alumina catalyst (87.5% SiO<sub>2</sub>, 12.5% Al<sub>2</sub>O<sub>3</sub>) having a CAT-A activity of 45 (see Laboratory Method for Determining the Activity of Cracking Catalyst by J. Alexander and H. G. Schimp, National Petroleum News, Technical Section, August 2, 1944,

6

page R-537), the catalyst being in the form of cylindrical pellets of approximately 4 mm. size. The reactor was brought up to operating temperature and pressurized with hydrogen after flushing the system with inert gas. A charge of toluene together with the stated molar quantity of hydrogen was simultaneously passed into the reactor at the indicated charging rates shown below. The several runs made under the listed operating conditions produced the following yields.

Table I

Run.....	A	B
Temperature, ° F.....	1,050	1,000
Pressure, p. s. i. g.....	400	400
Space rate (as liquid) Vol./hr./vol. Cat.....	3.0	1.5
H <sub>2</sub> /toluene ratio.....	1.0	1.0
	Mol Percent of Charge	
Products:		
Benzene.....	17.8	16.7
Xylenes.....	12.9	13.7
Toluene.....	64.9	65.6
Loss.....	4.4	4.0
	100.0	100.0

Under the conditions of the above runs the amount of toluene demethanation occurring is quite small, the effluent gas containing 90–95% H<sub>2</sub>. Since it would be possible to employ recirculated hydrogen in the process of even as low as 80–85% purity, enrichment of the effluent gas as by scrubbing is not always necessary; a portion of recycled gas can be vented and replaced by fresh hydrogen to maintain desired purity.

While other processes are available for the purpose, the isomerization of the meta-xylene concentrate obtained by fractionation and separation of the products, can be carried out over the same type of catalyst employed in the disproportionation reaction. The meta-xylene concentrate was passed over this catalyst at 950° F. at a pressure of 90 mm. of mercury at a rate providing a contact time of approximately two seconds, with the resulting conversion of approximately 30% of the meta-xylenes in the charge to predominantly para-xylene with the formation of lesser quantities of ortho-xylene and ethyl-benzene.

It is important to maintain subatmospheric pressure during isomerization, since at about atmospheric pressure and particularly above, in the presence of hydrogen, a larger portion of the xylene is reconverted by dealkylation, and/or by disproportionation to toluene and higher alkyl benzenes.

Suitable conditions for isomerization of meta-xylene over silica-alumina or other siliceous cracking catalyst include temperatures of from about 850°–1200° F., pressures of from about 0.1 to 0.5 atmosphere, and space rates of from about 0.1 to 3 volumes of charge (as liquid) per hour per volume of catalyst. Coke production is comparatively low in these operations.

#### EXAMPLE II

Following generally the procedure described in Example I another run was carried out by passing toluene over the same type catalyst at 1100° F., at a pressure of 300 pounds per square inch gauge and at a space rate of 0.75 (vol./hr./vol. cat.), with addition of 3 mols hydrogen per mol of toluene charged. Under these conditions 29.6 mol percent of the toluene was converted to benzene.

By continuously running under the above conditions over a 4-hour period the respective amounts of benzene and xylene produced, tended to become equalized; with the production during this period of 20.2 mol percent benzene and 16.6 mol percent xylenes per mol of toluene charged.

From the above described runs and numerous others made under various operating conditions, it appears that with increasing severity resulting from raising the temperature and/or lowering the space rate, while keeping other process variables constant, the production of increased yields of benzene and xylene is favored, but simultaneously there is also an increase in the extent of cracking to gas and coke. From overall considerations temperatures generally in the range of 850–1150° F. are advocated, at space rates of 1–3 volumes hydrocarbon charge per hour per volume of catalyst. The presence of added hydrogen is highly effective in reducing the production of compounds below C<sub>6</sub>, thereby significantly increasing the yields of desired benzene and xylene. With high molar ratios of hydrogen to toluene the production of benzene is favored over that of xylenes, indicating that some hydrogenation of hydrocarbon fragments is occurring at the higher hydrogen partial pressure.

At low operating pressures in the order of less than about 3 atmospheres, the yields of benzene and xylene are quite low; at 1100° F. and atmospheric pressure conversion to benzene was only 2.4%. The best yields of benzene and xylene are obtained at pressures of about 300–400 pounds per square inch; at higher pressures above about 600 pounds per square inch the extent of cracking becomes excessive.

While the invention has been described with particular reference to disproportionation of toluene, it will be understood that the principles thereof are also applicable in similar conversion of other alkyl-aromatic compounds, particularly methylated and ethylated benzene and naphthalene.

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 process of converting toluene to benzene and xylenes which comprises contacting a toluene-rich hydrocarbon feed material in a reaction zone with a silica-alumina cracking catalyst at 850 to 1150° F., from 200 to 600 pounds per square inch, at space rates of from 0.3 to 5 volumes of toluene per volume of catalyst per hour and in the presence of from one to three mols of added hydrogen per mol of toluene.

2. The process of converting toluene to benzene and xylenes which comprises contacting a toluene-rich hydrocarbon feed material in a reaction zone with a silica-alumina cracking catalyst at a temperature of about 850° to 1100° F., a pressure of about 200 to 600 pounds per square inch, at space rates of from about 0.3 to 1.0 volume of toluene per volume of catalyst per hour and in the presence of from one to three mols of added hydrogen per mol of toluene.

3. The process of converting toluene to benzene and xylenes which comprises contacting a toluene-rich hydrocarbon charge in a reaction zone with siliceous cracking catalyst at a temperature of 850 to 1150° F. under a total pressure of 200 to 600 pounds per square inch gauge in an atmosphere of hydrogen providing at least one mol hydrogen per mol of toluene charged, separating from the effluent products hydrogen-rich gas and recycling such gas to the reaction zone, condensing the normally liquid hydrocarbons in the product and fractionating the same to produce at least cuts predominating respectively in benzene, toluene and xylenes, recycling toluenes to said reaction zone for further conversion to benzene and xylenes, separating said xylenes into ortho, meta and para fractions, and isomerizing the meta xylene fraction over solid cracking catalyst in the presence of hydrogen and under sub-atmospheric pressure to produce further quantities of para xylene.

4. In the production of high yields of para xylene from toluene the method which comprises contacting toluene with siliceous cracking catalyst at elevated temperature and under a total pressure of 300–400 pounds per square inch in the presence of at least one mol hydrogen per mol of toluene, recycling hydrogen-rich gas separated from the effluent products, separating a para-xylene fraction and a meta-xylene fraction from the normally liquid products in the effluent, isomerizing the meta-xylene fraction over siliceous cracking catalyst in the presence of hydrogen at subatmospheric pressure, separating para xylene from the isomerate product formed, and recycling at least a portion of the remaining isomerate to further isomerization.

5. The method of producing high yields of para xylene from a converted naphtha fraction containing aromatic hydrocarbons boiling over the range from benzene through ortho xylene, which comprises the steps of fractionating said naphtha fraction to separate out benzene from toluene and xylenes, further separating the toluene and subjecting the same to disproportionation to produce further quantities of benzene and xylenes, collecting the xylene fractions obtained from the naphtha fractionation and from the toluene disproportionation, and subjecting the same to fractional distillation to separate the same into a mixed cut composed predominantly of meta and para xylene and a separate cut of orthoxylene, any ethyl benzene present being also thus separated out, subjecting the mixed cut to low temperature selective crystallization to crystallize out the para xylene, collecting the remaining liquid rich in meta xylene and subjecting such liquid to isomerization at sub-atmospheric pressure over a cracking type solid catalyst in the presence of hydrogen to form an isomerate containing para xylene, and recycling said isomerate to said fractional distillation to separate therefrom further quantities of para xylene.

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