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PREPARATION OF p-XYLYLENES

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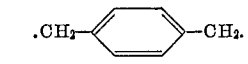
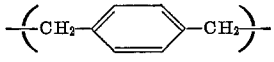
This invention relates to an improved method for the preparation of p-xylylenes from p-xylene. More particularly it relates to a method for repressing the dealkylation of the p-xylene starting material during pyrolysis to undesirable side products thereby increasing the reaction efficiency.

When p-xylene is pyrolyzed it forms p-xylylene diradicals represented by the formula



which can be condensed to p-xylylenes such as cyclic di-p-xylylene and poly-p-xylylene by known procedures. By the term "p-xylylene" as used herein is meant those compositions containing the p-xylylene unit



in their structure, for example, cyclic di-p-xylylene and p-xylylene polymers. However, during such pyrolysis hydrogen is released from p-xylene and/or the diradical which contacts the p-xylene and dealkylates considerable amounts thereof in side reactions to form by-products such as benzene and, predominantly, toluene. The amount of by-product formed represents p-xylene that, for practical purposes, is lost from the primary reaction, depleting the surplus p-xylene that can be recovered and recycled to the pyrolysis zone for further production of p-xylylene. It is therefore commercially desirable that such side reactions be suppressed whereby process efficiency and economy is much improved.

Accordingly, it is an object of the present invention to prepare p-xylylenes from p-xylene at improved process efficiency.

It is another object of the present invention to improve the pyrolysis of p-xylene to p-xylylene diradicals by repressing the dealkylation of the p-xylene, i.e., by inhibiting p-xylene consuming side-reactions which tend to occur during such pyrolysis.

These and other objects are accomplished in the present invention which provides a method for preparing p-xylylenes by pyrolysis of p-xylene to p-xylylene diradicals and thereafter condensing said diradicals to said p-xylylenes, the improvement comprising contacting the p-xylene with methane during the pyrolysis thereof, the methane being present in an amount such that the molar ratio of methane to p-xylene is between 25/1 to 100/1.

Typically, p-xylene is pyrolyzed in the presence of a suitable inert diluent such as steam at between about 800° C. and 1000° C. to form the p-xylylene diradical which can then be processed to p-xylylenes including cyclic-di-p-xylylene or poly-p-xylylene by known methods; see, for example, U.S.P. 3,149,175 to D. F. Pollart which is herein incorporated by reference.

Although other inert diluents can be employed in the pyrolysis of p-xylene, such as nitrogen, steam is generally employed as indicated above. The amount of steam present in this process is not narrowly critical but it is preferably employed in an amount of at least about 50 moles per mole of p-xylene and generally between about 100 to 200 moles per mole of p-xylene although excess steam is not detrimental to the process.

It has been found that the addition of methane to the pyrolysis of p-xylene considerably suppresses the dealkylation of p-xylene to by-products, particularly toluene. By such use of methane, the amount of p-xylene converted to toluene is considerably reduced. As indicated in Table I below, the weight ratio of poly-p-xylylene to toluene formed has been increased from 2 to 1 to about 11 to 1 resulting in a saving of p-xylene and a markedly improved process efficiency.

Low partial pressures of the p-xylene are desirable in this process, preferably such that the p-xylene partial pressure is between about 0.1 and 20 mm. Hg, with optimum conditions generally being secured at a partial pressure of about 1 to 10 mm. Hg.

Pyrolysis of the p-xylene is conveniently conducted by vaporizing the p-xylene and passing it through a pyrolysis zone preferably a heated tube or reaction vessel for a short period of time. Time of contact in the pyrolysis zone must be at least sufficient to pyrolyze or crack a portion of the p-xylene into the reactive diradical, p-xylylene, but not so long that charring or complete decomposition occurs. Contact time depends to a great degree on the particular temperature selected for pyrolysis; the lower the temperature the longer the permissible contact time and vice versa. At most desirable conditions of about 900° C. contact times are preferably between about 0.03 to 0.50 second. Seldom would it be desirable to have a contact time greater than one second. At the higher operating temperatures, contact times of 0.01 second or shorter may at times be indicated. The methane additive is preferably in contact with p-xylene during pyrolysis in the contact time range of .05 to .50 second.

In a preferred form of the invention a mixture of methane, steam and p-xylene is raised to the pyrolysis temperature of p-xylene 900–1,000° C. The preferred amount of methane is 65 moles per mole of p-xylene. The contact time is preferably about 0.10 to 0.30 sec. and the partial pressure of the p-xylene suitably about 3.3 mm. Hg. The exit vapors from the pyrolysis zone may be led to an organic quench bath to condense to di-p-xylylene or to a cold surface to condense to poly-p-xylylene. In either case, the amount of toluene is suppressed.

Methane can be used to suppress toluene formation during pyrolysis of p-xylene with such inert diluents as steam, nitrogen, carbon dioxide, argon and any of the noble gases or it can be used without any inert diluent i.e., serve itself as the diluent. In any event, for the purpose of the present invention sufficient methane is added so that the molar ratio of methane to p-xylene is between 25 to 1 and 100 to 1.

The following example is intended as an illustration of the invention and should not be construed in limitation thereof. All parts and percentages given are by weight unless otherwise specified.

Example 1.—Pyrolysis of p-xylene in the presence of steam and CH_4

Liquid p-xylene pumped at 8.6 cc./hr., total 0.28 mole, was delivered to a gas inlet mixer where methane was added at 28 cc./sec., total 18 moles. This zone was maintained at 210–220° C. Vaporized deionized water (steam) was added to the xylene-methane mixture at a rate of 202 g./hr., total 45 moles, and together they were passed into a preheater section at 750° C. This zone was packed with ¼" Berl saddles. The mixture then passed into the pyrolysis zone which was at 950° C. and pyrolysis of p-xylene to p-xylylene diradical took place. A quartz rod insert was used to control the volume of this zone, so that the contact time was about 0.17 second. These heated zones were controlled by two electric furnaces which completely encased the one-inch diameter quartz reaction tube.

The p-xylylene diradicals were condensed on the cold surfaces of cold finger condensers as poly-p-xylylene 2.6 g. or 8.8% conversion per pass. The liquid products which were condensed were washed together with Decalin and distilled. They were quantitatively determined by vapor phase chromatographic analysis. Recovered p-xylene was 22.7 g .or 76.9%, toluene 0.23 g. or 0.8% and benzene, a trace. The efficiency was 38.3% (weight of poly-p-xylylene recovered divided by weight of p-xylene used times 100).

Further examples were conducted with several different diluents as indicated in the following table. The temperature of the runs was between 940° C. and 1000° C. and the contact times were about 0.17 second i.e., in a range of .15 to .20 second.

TABLE I.—EFFECT OF METHANE ON PPX-TOLUENE RATIO

Diluents	Mole Ratio of CH_4/p-Xylene	Weight Ratio of Poly-p-Xylylene/Toluene
Steam		1.8–1
Do		2.1–1
Steam-CH_4	8–1	2.8–1
N_2-CH_4	12–1	2.9–1
N_2-CH_4	23–1	5.5–1
N_2-CH_4	27–1	8.6–1
N_2-CH_4	50–1	11.6–1
CH_4	76–1	11.6–1
Steam/CH_4	65–1	11.3–1

Thus it is readily apparent that the addition of methane to the pyrolysis of p-xylene considerably represses the dealkylation of p-xylene, lowering toluene formation, as evidenced by the increased weight ratio of poly-p-xylylene to toluene. A saving of p-xylene is thus realized, making possible higher yields of di-p-xylylene and poly-p-xylylene from a given amount of p-xylene starting material and improved process efficiency.

For the process of the present invention chemically pure methane (99.99% CH_4) should be used rather than natural gas (90.0% CH_4) which has proved unsatisfactory. Natural gas contains many aliphatic hydrocarbons, ethane, propane and the like, which pyrolize to give large quantities of hydrogen. Hydrogen, as previously indicated, promotes toluene formation and thus impairs the efficiency of the primary reaction.

What is claimed is:

1. In a method for preparing p-xylylenes by pyrolysis of p-xylene generating p-xylylene diradicals and thereafter condensing said diradicals to said p-xylylenes, the improvement which comprises contacting said p-xylene with methane during the pyrolysis thereof, said methane being present in an amount such that the molar ratio of methane to p-xylene is between 25/1 to 100/1 whereby the process efficiency is improved.

2. The process of claim **1** wherein said p-xylene contacts said methane during said pyrolysis for at least 0.1 second.

3. The process of claim **1** wherein said p-xylene is pyrolyzed at a temperature between 800° C. and 1000° C.

4. The process of claim **1** wherein an inert diluent selected from the group consisting of stream and nitrogen is contacted with said mixture during pyrolysis.

5. The process of claim **4** wherein said diluent is steam.

6. The process of claim **4** wherein the p-xylylene diradicals are condensed to di-p-xylylene in an organic quench bath.

7. The process of claim **4** wherein the p-xylylene diradicals are condensed to poly-p-xylylene on a cool surface maintained at a temperature below the condensation temperature of said diradicals.

No references cited.

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