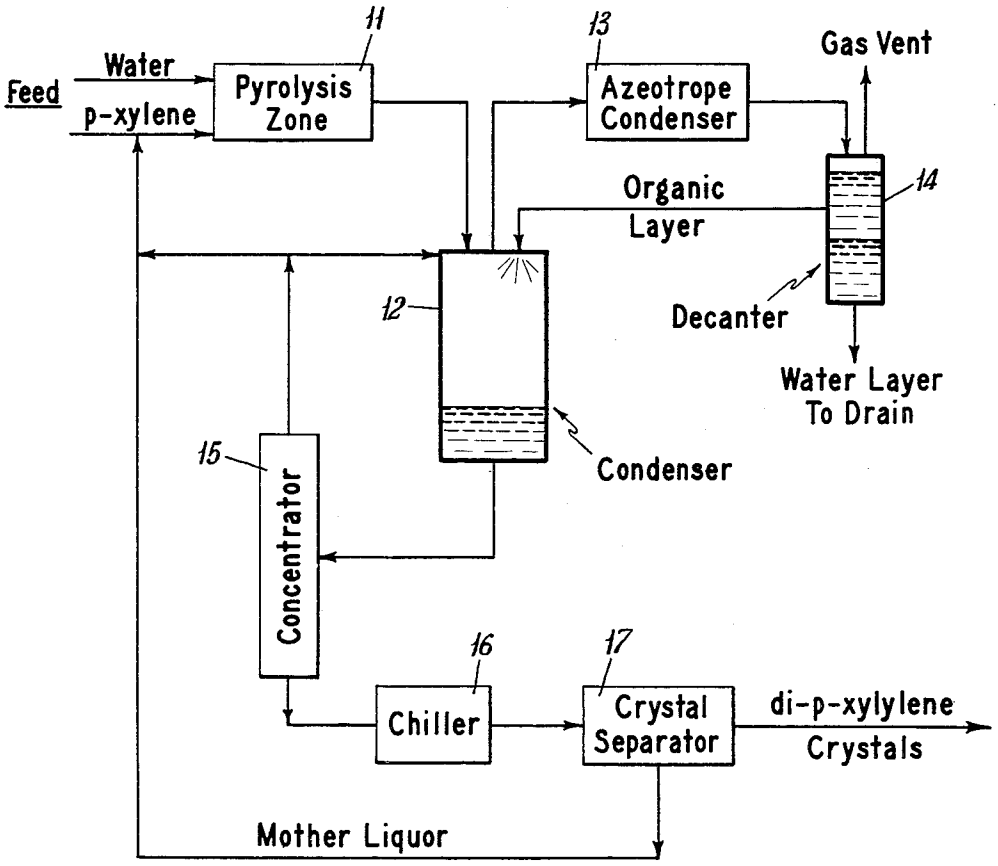
Sept. 15, 1964 D. F. POLLART 3,149,175

PREPARATION OF DI-PARA-XYLYLENES

Filed Aug. 22, 1960



INVENTOR.
DALE F. POLLART
BY
Walter A Kehm
ATTORNEY

United States Patent Office 3,149,175 Patented Sept. 15, 1964

3,149,175

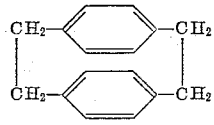
PREPARATION OF DI-PARA-XYLYLENES

Dale F. Pollart, New Brunswick, N.J., assignor to Union Carbide Corporation, a corporation of New York

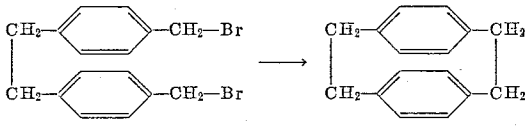
Filed Aug. 22, 1960, Ser. No. 53,574
11 Claims. (Cl. 260—670)

This invention relates to a process for the preparation of cyclic di-para-xylylene. More particularly, this invention relates to a method for the preparation of cyclic di-p-xylylene in improved yields and conversion by the pyrolysis of para-xylene and the selective condensation of pyrolysis vapors in a fluid medium.

Heretofore cyclic di-p-xylylene having the structure

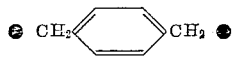


was first isolated as a by-product from the poly-p-xylylene prepared by pyrolysis of p-xylene as described by Brown et al. Nature, 164, 915 (1949) but only in trace amounts in the polymer. It has also been prepared by the following scheme



as described by Cram et al., J. Am. Chem. Soc. 93, 5691 (1951). The di-p-xylylene by such a process was secured, however, only in a 2.1% yield and a 2.5% efficiency. Such yields and low efficiencies can hardly be tolerated on commercial scale production of such a product. Thus, there remained the problem of finding a suitable and satisfactory method for producing di-p-xylylene in reasonable yields and efficiencies.

According to the present invention, I have now discovered a method for producing the di-p-xylylene in yields of 10% or higher and at very high conversion efficiencies. This process consists of generating the reactive diradical



by the pyrolysis of para-xylene at elevated temperatures and condensing the pyrolysis vapors in a fluid medium containing an inert organic solvent. The reactive diradical vapors selectively condense in the solvent into the cyclic dimer, di-p-xylylene in much higher yields than in any other known process.

In this process, there are essentially no polymeric by-products formed. When present, they are generally less than about 0.1%. Yield of the cyclic dimer per pass through the pyrolysis zone generally averages 8–10% but under optimum conditions can be higher. The efficiency attainable at this yield level can be in the range of about 60% or higher.

The reactive diradical, p-xylylene is generated in this process by pyrolysis of para-xylene at a temperature of at least 800° C. and preferably between 850° C. and 950° C. At temperatures above 1000° C. some charring of the reactive diradical is occasioned which undesirably affects the resultant yield of product.

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 the p-xylene of about 1 to 10 mm. Hg.

While the presence of an inert diluent in this process is not critical, it is often desirable for use in this process in order to reduce the partial pressure of the p-xylene

and make it possible to operate at higher total pressures. I have found that steam is a particularly desirable inert diluent in this process in that it permits operation at atmospheric pressure and has a protective effect in preventing charring of the p-xylene, although there may also be present other inert diluents as, for example, nitrogen, argon and like inert gases. Thus, the total pressure of the system depends on the desired operating partial pressure of the p-xylene, and the amount of steam and/or other diluents employed. When no diluents are employed, the pyrolysis reaction is preferably carried out at total pressures of 0.1 to 10 mm. Hg. Thus, in this process, it is possible to operate at total pressures even up to atmospheric pressure or higher.

The amount of steam present in this process is not narrowly critical but when employed I prefer it present 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.

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 0.05 to 0.1 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.

Condensation of the p-xylene diradicals into the di-p-xylylene is accomplished in the presence of an organic solvent. In order to remove the residual heat from the pyrolysate vapors without distilling or vaporizing the organic solvent, it is preferred that the reactive diradical, p-xylylene, be cooled to about 150°–400° C. but at a temperature above the ceiling condensation temperature of the reactive diradical. Cooling to below the ceiling condensation temperature in the absence of the organic solvent causes almost spontaneous polymerization of the reactive diradical to poly-p-xylylene. This ceiling condensation temperature is generally between 25° C. and 150° C. depending somewhat on the operating pressure. However, in the vaporous state, the reactive diradical is relatively stable and does not polymerize.

The cooling of the pyrolysate vapors may be accomplished in any of several convenient means. For instance, internal or external condensers, cooling coils, tubes or the like can be employed immediately after the pyrolysis zone, or if desired, natural cooling caused by long runs of air cooled tubing or piping from the pyrolysis zone to the condensing medium can be used. It is also possible to mix the organic solvent condensing medium in the vapor state in a suitable manner or mixing chamber with the pyrolysate vapors as another method. Preferably, direct cooling means are preferred to make sure the vapors are not cooled to below the condensation temperature of the reactive diradical.

It is essential in this process that the condensation of the cooled vaporous diradical be carried out in the presence of a fluid medium of an inert organic solvent. One of the most preferred solvents for reason hereinafter discussed is p-xylene itself. However, if desired, other aromatic material such as o-xylene, m-xylene, toluene, cumene, benzene, methyl-naphthalene, o-dichlorobenzene, acetic acid, 1,2-di-p-tolylethane, mineral oil,

diphenylmethane, 1,2-diphenylethane, heptane, decahydronaphthalene, and the like and preferably those having an atmospheric boiling point between about 50° and 350° C.

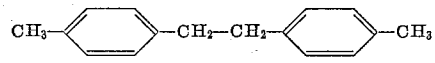
The di-p-xylylene product forms on the condensation of the vaporous diradicals in the presence of the fluid medium. It is not essential however that the fluid medium be in the liquid state. While this is most desirable, the condensation can be accomplished equally as well by mixing the pyrolysate vapors with vaporous aromatic solvent and simultaneously condensing the total mixture to the liquid state for recovery of the product.

Suitable gas scrubbers or spray tanks can be used to remove and condense the p-xylylene diradicals into the di-p-xylylene in this process. Countercurrent gas scrubbing devices are particularly desirable in continuous operation, and with the use of such very high boiling organic solvents as mineral oil where the di-p-xylylene can be recovered by distillation from the solvent.

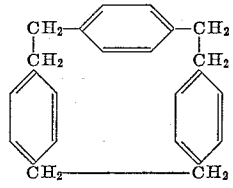
When the cooled pyrolysate vapors of the reactive diradical are collected in a liquid medium, merely bubbling or dispersing the vapors below the liquid level of the aromatic solvent is also adequite to cause the p-xylylene to dimerize to the di-p-xylylene and be recovered from the solvent solution. The bath into which these vapors are condensed can be maintained at any temperature above 50° C., and preferably from 50° to 250° C. Thus, when employed herein, the term "fluid media" is intended to cover both the liquid or gaseous state of the solvent medium in which the pyrolysate vapors are collected.

Recovery of the di-p-xylylene is relatively easy. It can, for instance, readily be recovered by distilling it from high boiling solvents such as mineral oil. Preferably, however a better method seems to be to remove a majority of a lower boiling solvent medium by distillation and then to crystallize the di-p-xylylene from the remaining solvent by cooling and filtering off the crystallized di-p-xylylene.

The product obtained by this process generally has a sharp melting point of 284°–285° C. and is free of other possible condensation products such as 1,2-di-p-tolylethane



and cyclo-tri-p-xylylene



which are contained in the filtrate of this method. These can be recycled to the pyrolysis zone with additional p-xylene inasmuch as they also are cracked back to the p-xylylene diradical in subsequent pyrolysis.

In the preferred method of operating this process, p-xylene and steam are fed to an atmospheric pressure reactor or heated tube maintained at 900° C. The p-xylene and steam flow rates are adjusted so as to give a contact time of about 0.05 to 0.1 second and a p-xylene partial pressure of 1.0 to 10 mm. Hg. The pyrolysate vapors are cooled in a condenser at the outlet of the pyrolysis zone and cooled to a temperature of about 150° C.–250° C. and then passed into a bath of gently refluxing p-xylene-water azeotrope where the condensation of the diradical to the cyclic dimer takes place.

Either continuously or in stages, the aqueous layer of the p-xylene condensation medium is removed and the solution concentrated by flashing or reduced pressure distillation to about one-tenth its original volume. On cooling the di-p-xylylene crystallizes from the p-xylene solution in high purity and is separated from the mother liquor by filtration or by centrifugation, washed and dried.

It is, of course, realized that this process can be conducted either batch-wise or continuously. The use of p-xylene as the condensation medium is highly desirable in the continuous system inasmuch as it can be recycled within the system serving not only as the reactant but also as the condensation medium and problems of handling a separate solvent are avoided.

A particularly preferred method for the operation of this process is shown in the attached drawing. In the drawing, water and p-xylene are fed to a pyrolysis zone **11** which can be a hot tube maintained at the desired pyrolysis temperature. Exit pyrolysis vapors are fed to a p-xylylene condenser **12** which is a spray chamber or scrubber for contacting the p-xylylene diradical with the organic liquid, shown here as p-xylene. Preferably the condenser **12** is operated at about the refluxing temperature of the p-xylene-water azeotrope. The vapors of the condenser **12** are then fed to an azeotrope condenser **13** for condensing the p-xylene-water azeotrope which is then fed to decanter **14**. The organic layer of the decanter is then fed back to the p-xylylene condenser **12** and the water layer is sent to the drain.

The p-xylene in condenser **12** causes the p-xylylene diradicals from the pyrolysis zone to condense with about 99% going to the di-p-xylylene. A portion of the organic liquid mixture in condenser **12** is fed to the concentrator **15** which is desirably a still column for removing a large portion of p-xylene which can be either returned to the feedstream to pyrolysis zone **11** or sent back to the p-xylylene condenser **12**. The bottoms of concentration **15** is then fed to chiller **16** for crystallizing the di-p-xylylene from the mixture. The mother liquor, mostly p-xylene and a few by-products from the crystal separator **17**, is recycled back to the feed stream. Essentially pure di-p-xylylene crystals are secured from the crystal separator **17** and need only be dried.

The following examples are illustrative of this invention but are not intended to serve as any limitation or restriction thereof.

Example I

A mixture of steam and p-xylene vapors were fed into a 12 in. reactor maintained at 900° C. at atmospheric pressure at such a rate as to give a contact time in the hot zone of 0.066 sec. at a p-xylene partial pressure of 1.3 mm. The pyrolysate vapors were passed through an air-cooled condenser for about 18 inches and then into a bath of gently refluxing p-xylene-water azeotrope fitted with an efficient reflux condenser. The temperature of the vapors entering the p-xylene bath was 145–150° C. and the temperature of the p-xylene bath was 95° C.

The reaction was continued for 4 hours during which time a total of 40.1 g. of p-xylene was passed through the furnace. The excess water which had collected in the xylene bath was separated by azeotropic distillation. The dry xylene solution then filtered and evaporated to 1/10 its volume by distillation under reduced pressure. On cooling to 20° C. 3.28 g. of di-p-xylylene, crystallized from the xylene solution in a yield of 8.20. The di-p-xylylene crystals were filtered from the mother liquor and dried. The mother liquors, which contained small amounts of other condensation products, were combined with fresh p-xylene for recycling. There was formed 0.03 g. (0.075%) of poly-p-xylylene. The di-p-xylene was in fine white crystals and had a melting point of 283°–285° C. and was of a purity of about 99.5%.

Example II

Vaporized p-xylene at a total pressure of 3.0 mm. was metered into a 12-inch reactor heated to 1,000° C. at such a rate as to give a contact time of 0.05 sec. The pyrolysate vapors from the pyrolysis zone were passed through an air-cooled condenser for about 8 inches to lower the temperature to about 250° C. and then into the bottom of a vertical 1" x 20" Vigreaux scrubber through which was being recirculated about 1,250 ml. of

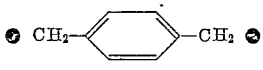
mineral oil countercurrently to the upwardly rising vapors at a rate of about 2 liters per minute. The oil and scrubber column were maintained at a temperature of 100° C. The vapors emerging from the top of the scrubber column were led through a series of two Dry-Ice cooled traps to remove all condensable gases and finally to a high vacuum mechanical fore-pump.

The reaction was continued for 3½ hours during which time 51 g. of p-xylene was fed to the reactor. At the end of the reaction, the mineral oil solution was transferred to a distillation flask fitted with a phase-separating trap under an efficient reflux condenser. This entire system was placed under about 0.1 mm. of pressure and the solution refluxed until all of the product di-p-xylpylene had distilled from solution and collected as a crystalline solid in the bottom of the phase separator. The solid was collected by filtering, washed free of mineral oil with ethyl ether and dried. There was obtained 3.0 g. of di-p-xylylene, M.P. 283–285° C.; yield 5.9%.

From the Dry-Ice-cooled traps of the reactor was recovered 40 g. (78%) of unreacted p-xylene and less than 0.5 g. of poly-p-xylylene.

I claim:

1. A process for the preparation of cyclic di-p-xylylene substantially free of poly-p-xylylene which includes the steps of pyrolyzing a mixture of steam and p-xylene at a temperature between about 800° C. and 1000° C. to generate the reactive diradical



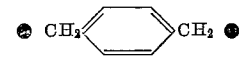
and condensing the reactive diradical in intimate mixture with a fluid medium containing an inert organic solvent and being maintained at a temperature between 50° C. and 250° C., and recovering the cyclic di-p-xylylene from the said fluid medium.

2. A process according to claim 1 wherein the partial pressure of the p-xylene is between about 0.1 and 20 mm. Hg.

3. A process according to claim 2 wherein the temperature is between 850° C. and 950° C.

4. A process according to claim 3 wherein the steam is present in an amount of at least 50 moles per mole of p-xylene.

5. A process for the preparation of cyclic di-p-xylylene substantially free of poly-p-xylylene which includes the steps of pyrolyzing p-xylene at a temperature between about 800° C. to 1000° C. at a p-xylene partial pressure of between about 0.1 to 20 mm. Hg to generate the reactive diradical



cooling the pyrolysis vapors to a temperature of about 150°–400° C. but at a temperature above the ceiling condensation temperature of the reactive diradical, and thereafter condensing the reactive diradical in intimate mixture with a fluid medium containing an inert organic solvent, said medium maintained at a temperature between 50° C. and 250° C. and thereafter recovering the cyclic di-p-xylylene from the fluid medium.

6. A process according to claim 5 wherein steam is employed as an inert diluent in the pyrolysis of the p-xylene.

7. A process according to claim 6 wherein p-xylene is employed as the inert organic solvent for condensing the reactive diradical.

8. A continuous process for the preparation of cyclic di-p-xylylene substantially free of poly-p-xylylene which comprises continuously feeding p-xylene to a pyrolysis zone maintained at a temperature between about 800° C. and 1000° C., at a p-xylene partial pressure between about 0.1 to 20 mm. Hg, feeding the vapors from said pyrolysis zone to a condensing zone wherein said vapors are contacted with a fluid medium containing an inert organic liquid solvent, maintained at a temperature between 50° C. and 250° C. but low enough to cause p-xylylene diradicals to condense therein, and continuously removing from the said condensing zone, at least a portion of said fluid medium containing the condensed p-xylylene diradicals and thereafter separating from the fluid media, di-p-xylylene.

9. A continuous process according to claim 8 wherein steam is employed as an inert diluent in the pyrolysis of the p-xylene.

10. A continuous process according to claim 9 wherein p-xylene is employed as the inert organic solvent.

11. A continuous process according to claim 10 wherein the temperature of the fluid medium is maintained at a temperature between 90° C. and 100° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,719,131	Hall	Sept. 27, 1955
2,769,786	Szwarc et al.	Nov. 6, 1956

OTHER REFERENCES

Farthing: "lin-poly-p-xylylene," J. Chem. Soc., October 1953, pages 3261–2.