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PRODUCTION OF DIPHENYL FROM BENZENE

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The invention relates to processes for the production of diphenyl from benzene; and particularly to a process wherein the pyrolytic dehydrogenation and condensation of benzene is accomplished by intermixing therewith superheated steam as the heat carrier medium.

Several methods have been disclosed for the preparation of diphenyl from benzene. For instance, it is well known to condense benzene by exposing the vapors thereof to contact with an electrically heated metallic filament, or by passing the benzene vapor through an externally heated iron tube, or a heated mass of comminuted carbonaceous material. It has also been proposed to carry out the conversion of benzene to diphenyl in the presence of a diluent gas, such as steam. For instance, U. S. Patent No. 1,322,983 describes a method of producing diphenyl by subjecting benzene vapors in admixture with a diluent gas to a high temperature and pressure in the presence of appropriate contact substances, such as pumice, which provide cracking surfaces.

Numerous disadvantages attach to such modes of procedure. The heating filament, tube walls, or contact substances are necessarily to be maintained at a materially higher temperature than that which will be attained by the benzene vapor being contacted therewith. It is, therefore, practically impossible to avoid some overheating of the vapor layer directly adjacent to the contact surfaces if the average temperature of the vapors within the heated zone is to be maintained at the desired point. The excessive cracking due to such overheating of the vapors results in a much reduced yield of diphenyl, the loss of considerable benzene through formation of tar, and the deposition of the carbon upon the contact surfaces and/or heating zone walls, thereby causing a consequent lowering of the efficiency with which heat is transmitted therefrom to the benzene vapor. A further disadvantage accrues to methods heretofore known to the art because of the low rate of conversion of benzene to diphenyl at a single passage thereof through apparatus adapted to dehydrogenate and condense the benzene. In good commercial practice it is customary to operate at rates varying between 8 and 12 per cent of benzene converted to diphenyl at each pass. It has been found that rates of conversion materially higher than the foregoing will be accompanied by the decomposition of such high percentages of benzene to tar and free carbon, as to increase the mechanical difficulties to a point where the process cannot be worked economically.

I have found that the foregoing difficulties can be elminated by supplying the heat required to pyrolyze the benzene by mixing directly with the vapors thereof steam superheated to a temperature and in volume sufficient to produce in the reaction mixture a temperature between 800° and 950° C. I find that a high rate of conversion of benzene to diphenyl can be obtained at a single pass and that an extremely small quantity of tar and no free carbon is formed when benzene is dehydrogenated in the foregoing manner in the presence of magnetic iron oxide.

To the accomplishment of the foregoing and related ends, the invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail one mode of carrying out the invention, such disclosed mode illustrating, however, but one of various ways in which the principle of the invention may be used.

In effecting my improved process I mix the vapors of the benzene with superheated steam in amount and at a temperature sufficient to raise the temperature of the reaction mixture to a point within the range between about 800° and 950° C. In this manner I obtain practically instantaneous and uniform heating of the benzene vapors to the temperature at which dehydrogenation and condensation occurs, and avoid any overheating of the vapors and consequent excessive cracking thereof caused by contact with heating surfaces at a materially higher temperature. The temperature of the gaseous reaction product is rapidly lowered by passing the gases into a cooling system in which the diphenyl, uncracked benzene, and steam are condensed and recovered in the liquid state. The liquid mixture thus obtained may then be separated into the constituent compounds by simple distillation. The benzene which distills off may be returned to the process, while the diphenyl fraction may be obtained practically pure.

The process may be carried out in any suitable form of iron or steel reactor, but it will be readily apparent that a reactor of comparatively large internal cross-section is better adapted to the purpose than a small tube, such as is commonly employed for pyrolytic operations wherein the heat is supplied externally. The steel which may be used for constructing the reactor should be of the type, such as mild, chrome-vanadium, etc., which is adapted to react with steam to form magnetic iron oxide. The oxidation resistant, high chrome-nickel steels are generally not suitable. When using an iron or steel reactor it is necessary that steam be passed therethrough

for a short time prior to admitting benzene thereinto in order to heat the same to about reaction temperature and to form a coating of magnetic iron oxide on the internal surfaces of the reactor by action between the steam and iron of the reactor wall. Instead of an iron or steel reactor having a coat of magnetic iron oxide I may use a reactor constructed of or lined with a refractory material, such as silicon carbide, impregnated or coated with magnetic iron oxide. In working my process an oxidizing atmosphere in always maintained in the reactor, due to the presence of considerably more than an equivalent weight of steam relative to the benzene, so that reduction of the magnetic iron oxide does not occur. I have found that the presence of a magnetic iron oxide coating on the internal surfaces of the reactor prevents the deposition of free carbon thereon during operation of the process. If the reactor walls are not so coated, hard carbon will gradually accumulate thereon and ultimately completely fill the interior of the reactor. It is possible to carry out my process using a reactor constructed of materials other than those mentioned, provided that a body of magnetic iron oxide is present in the reactor, as in lump, granular or other form, but it will readily be seen that such a procedure would be less advantageous than that previously outlined.

My preferred mode of operation consists in vaporizing the benzene and preheating the vapors thereof to a temperature between 550° and 750° C., preferably between 650° and 700° C., which may be accomplished without the formation of decomposition products. The preheated benzene vapors are then intermixed with steam superheated to a temperature between about 950° and 1100° C., preferably between 1050° and 1100° C., in amount sufficient to produce in the reaction mixture a temperature between about 800° and 950° C., preferably between 875° and 925° C., in a reactor provided with surfaces of magnetic iron oxide. The pressure in the reactor may be slightly above atmospheric, e. g. between 0 and 5 pounds gauge. The mixing of the benzene vapor and steam may be accomplished in any well known manner. I have found it convenient to effect the mixing by causing a stream of benzene vapor and of steam to impinge at an angle of 60° or 90° to each other within the reaction chamber whereby thorough and uniform mixing thereof is obtained as well as practically instantaneous condensation of at least a portion of the benzene to diphenyl. All overheating of the benzene vapors is avoided and decomposition thereof to tar or free carbon is substantially eliminated.

While my preferred mode of operation calls for vaporizing the benzene and the preheating of the vapors thereof to a temperature between 550° and 750° C. before intermixing with the superheated steam, such procedure is not essential. If desired, the benzene may be vaporized or atomized directly by means of the superheated steam simultaneously with being heated thereby to its dehydrogenation temperature.

The proportions in which the benzene and steam are introduced into the reactor may be varied over a relatively wide range, depending upon the temperature of each of the reactants, and upon the temperature to be maintained in the reaction chamber. However, using superheated steam at a temperature of about 1050° C., and benzene vapor at about 600° C., the ratio will be about 2 pounds of steam per pound of benzene to maintain a reaction temperature of about 900° C. It is readily apparent that the quantity of steam used may be varied from this figure in accordance with well recognized principles in order to produce the general range of reaction temperature set forth in the preceding paragraph. It will be understood that if the superheated steam is used to vaporize the benzene, as well as effecting the dehydrogenation thereof, that more steam will be required than when the benzene is vaporized and preheated by other means.

The gaseous products are continuously withdrawn from the reactor and their temperature is rapidly lowered in a suitable cooling system of the usual type. The rapid withdrawal and cooling of the gaseous products further prevents the possibility of excessive cracking of the gases. The liquid condensate is removed from the cooling system and distilled to recover the uncracked benzene, and to obtain the diphenyl in a substantially pure state. The percentage of benzene converted to diphenyl at one passage through the reactor may vary somewhat with the temperature, the range in general being from about 20 per cent to as high as 30 per cent. The percentage yield of diphenyl recovered from the liquid mixture obtained in the cooling system will be in general between 90 and 95 per cent of the benzene dehydrogenated. By passing the recovered benzene repeatedly through the reactor it is possible to obtain a high degree of conversion of the benzene to diphenyl.

The following results were obtained from a specific run in apparatus adapted to carry out my process. Superheated steam at a temperature of about 1045° C. was introduced at the rate of about 450 pounds per hour into a steel reactor coated on the interior surfaces with a film of magnetic iron oxide. Benzene, vaporized and preheated to about 585° C., was fed to the reactor at the rate of about 235 pounds per hour. The relative proportions of steam and benzene therefore were 1.9 pounds of steam per pound of benzene. The gaseous products were continuously withdrawn from the reactor so that the pressure therein was maintained at about 2 pounds gauge. A total of 2570 pounds of benzene was treated, of which 1877 pounds or 73.1 per cent was recovered for further use by distillation of the liquid mixture condensed from the gaseous reaction products by the cooling thereof to about 20° C. A total of 632 pounds of diphenyl, and 16 pounds of phenol were obtained by further distilling the said liquid mixture. The amount of benzene converted to diphenyl at a single pass was accordingly 24.6 per cent of the total benzene treated. The balance of the mixture, 38 pounds or only 1.4 per cent of the benzene treated, was a tarry decomposition product. The amount of benzene decomposed to fixed gases was 7 pounds, i. e. less than 0.3 per cent of the benzene used.

Among the advantages which inure to my novel process for the production of diphenyl from benzene are:—(1) a high percentage of benzene is converted to diphenyl at a single pass; (2) a high over-all conversion of benzene to diphenyl is obtained because of the low percentage decomposed to tar, carbon, or fixed gases; (3) the thermal efficiency of the process is high because the heat is supplied to the benzene directly without having to pass through reactor walls; (4) and, the magnetic iron oxide coating on the internal surfaces of the reactor

prevents the deposition of carbon thereon and consequent plugging of the reactor.

Other modes of applying the principle of my invention may be employed instead of the one explained, change being made as regards the process herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. The process for producing diphenyl from benzene which comprises intermixing benzene vapors with a volume of steam superheated to a temperature sufficient to produce in the mixture a temperature between 800° and 950° C., in the presence of magnetic iron oxide.

2. The process for producing diphenyl from benzene which comprises intermixing benzene vapors with sufficient steam superheated to a temperature between about 950° and 1100° C. to produce in the mixture a temperature of 800° to 950° C., in the presence of magnetic iron oxide.

3. The process for producing diphenyl from benzene which comprises vaporizing benzene, preheating the vapors thereof to a temperature between 550° and 750° C., and intimately mixing the same with sufficient superheated steam at a temperature between about 950° and 1100° C. to produce in the mixture a temperature between 800° and 950° C., in the presence of magnetic iron oxide.

4. The process for producing diphenyl from benzene which comprises simultaneously vaporizing and heating benzene to a temperature between 800° and 950° C. by intermixing superheated steam therewith in the presence of magnetic iron oxide.

5. In a process for the production of diphenyl from benzene, the steps which consist in vaporizing benzene, preheating the vapors thereof to a temperature between 650° and 700° C., intermixing therewith steam superheated to a temperature between about 1050° and 1100° C. in the ratio of about 2 pounds of steam per pound of benzene vapor, while in contact with surfaces of magnetic iron oxide, cooling the reaction product to condense liquefiable materials therefrom, and distilling the condensate for the separate recovery of diphenyl and unreacted benzene.

6. In a process for the production of diphenyl from benzene, the steps which consist in vaporizing benzene, preheating the vapors thereof to a temperature between 650° and 700° C., intermixing therewith steam superheated to a temperature between about 1050° and 1100° C. in the ratio of about 2 pounds of steam per pound of benzene vapor, while in contact with surfaces of magnetic iron oxide, cooling the reaction product to condense liquefiable materials therefrom, distilling the condensate for the separate recovery of diphenyl and unreacted benzene, and returning the unreacted benzene to the first step.

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