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IMPROVED PROCESS FOR THE PRODUCTION OF BISPHENOLS

This invention relates to the production of bisphenols. More particularly, this invention relates to a process for the production of 2,2-bis(4-hydroxyphenyl) propane (also known as bisphenol A, hereafter "BPA") from acetone and phenol.

5 Bisphenols are used as raw materials in the preparation of chemical products such as epoxy resins and polycarbonates. They are commonly prepared by the condensation of phenols and ketones. BPA is among the most important of the bisphenols. It is well known that BPA can be produced by reacting acetone (also known as dimethyl ketone, hereafter "DMK") and phenol in the presence of an acid.

15 The reactants used in the production of BPA can come from a number of sources. This can introduce varying types and quantities of impurities and trace materials in bisphenol production feed. For example, DMK can be produced from the oxidation of isopropyl alcohol (IPA) or by the decomposition of cumene hydroperoxide. DMK produced from the oxidation of IPA is called "on purpose DMK" and is known to be low in methanol. It is not widely produced on a commercial basis. Most bisphenol is produced in integrated chemical manufacturing plants and utilizes DMK manufactured during the decomposition of cumene hydroperoxide. DMK produced in this manner is typically found mixed with at least about 200 ppm methanol which is an azeotrope of DMK.

25 A number of acidic catalysts can also be used in bisphenol production processes. In recent years, acidic cation exchange resins have become the overwhelming

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choice. Strongly acidic sulfonated polystyrene ion exchange resins are particularly useful in this regard.

Two different techniques for employing acidic ion exchange resins as catalysts predominate in industrial practice. In one technique (hereafter, "the free cocatalyst technique") cocatalyst is freely circulated in the reactor with the reaction feed. It is used to enhance the selectivity and/or activity of the reaction. An organic mercaptan such as methyl or ethyl mercaptan is typically used as the freely circulating cocatalyst in this technique. The acidic sites of the resin are left available, that is, largely unbound to cocatalyst. This provides flexibility in adjusting the optimal concentration of cocatalyst given the particular reaction conditions in question.

In the free cocatalyst technique, the cocatalyst can be put in the presence of reactants and catalyst in a number of ways and can be readily replenished as needed. This enables refinement of the reaction through the differential treatment of the catalyst and cocatalyst. If, for example, cocatalyst is removed from the reactor along with reactor products, it can be separated from the reaction products and recycled back into the reactor in a subsequent step. However, if a catalyst problem is encountered, the catalyst may be treated without necessarily involving any adjustments to the cocatalyst. While this is an advantage of the free cocatalyst method, it must also be acknowledged that it nevertheless introduces more variables into process control than might otherwise be encountered and makes for somewhat complex reaction dynamics.

In the second technique for employing acidic ion exchange resins in the production of bisphenols (hereafter, "the fixed modified resin technique"), the resin is modified by appending cocatalytic agents such as

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aminoalkylmercaptans to some of the acid sites on the resinous catalyst. Typically, organo mercaptan promoter groups are attached to the backbone sulfonate ion by covalent or ionic nitrogen linkages. The fixed modified resin technique requires less direct handling and treatment of cocatalysts such as the noxious mercaptans. The ability to refine the process by differential treatment of the resin and cocatalyst is greatly reduced but there are fewer possibilities for problems and reaction dynamics are less complicated than is seen in the free cocatalyst technique.

The acidic catalysts used in either technique have shown a tremendous proclivity for rapid deactivation. There are many possible reasons for this including catalyst poisoning. As noted above, any number of materials other than phenols and ketones may be present in the feed and could interfere with the catalyst. For example, metal poisoning is a possibility in large scale industrial processes of this type. Additionally, thermal perturbations can cause a loss of the acidic functional groups from the resins on which they are intended to be bound. Further, the presence of bisphenolic tars and other reaction residuals can greatly reduce mass transfer in the reaction.

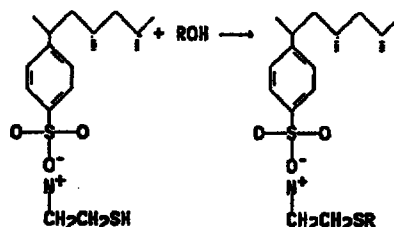
EP-A-0567857 is directed to the production of bisphenols from phenols and carbonyl compounds using a fixed modified resin technique. The catalytic exchange resin is a sulfonated polystyrene ion exchange resin modified with an aminomercaptan and without free aminomercaptan. In this patent application it was taught that catalyst life to be insufficient and proposed as a solution using a feed containing less than 1000 ppm of alkylating agent (alkyl alcohol). When feed contains more than this concentration of alkylating agent the SH group on the free end of the aminomercaptan becomes an SC

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group thereby substantially diminishing its function as a leaving group and directly poisoning the exchange resin. When the following reaction occurs, the catalyst is poisoned.



5 In the present invention, the inventors address the premature deactivation of catalyst in a free cocatalyst process for the production of bisphenol. According to the rationale of EP-A-567857 to the free cocatalyst method, it would be expected that catalyst deactivation is the result of the production of esters due to the
10 reaction of sulfonic acid groups on the resin with alkyl alcohols. However, the inventors have found that catalyst deactivation is not appreciably attributable to ester formation. Moreover, conducting the process at the alkyl alcohol concentration proposed in EP-A-567857 would
15 still result in substantial catalyst deactivation. Clearly, the catalyst deactivation mechanism experienced in the free cocatalyst method differs from that of the fixed modified resin method. Thus, in the present
20 invention, different process parameters and methods for reducing or eliminating the premature deactivation of catalyst are presented.

Japanese Patent Publication 6-92889 of April 5, 1994 proposes a process for producing BPA by the condensation
25 of DMK and phenol in which the concentration of methanol in the DMK feed is kept below 10,000 ppm. This is done by recirculating unreacted DMK back to the feed after some of the methanol in the unreacted DMK is purged out of the reactor product stream. The mixture of fresh DMK

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and DMK obtained through the separation tower apparently will never contain less than about 400 ppm methanol. The purpose of this process is to directly control the acidity of the catalyst. While they describe their invention as ameliorating the "deterioration" of the catalyst, no information is presented regarding the effect of lowering methanol concentration over time. Rather, a higher one pass conversion to useful products is presented. This makes it clear that Nakawa et. al. were not addressing a catalyst poisoning mechanism but were instead maintaining the effective acidity of the reaction/catalyst at the more optimal level with respect to catalyst activity. Adding excess water would have the same type of effect.

It has now been found that the free cocatalyst method for producing bisphenols could be further improved through the amelioration of the catalyst poisoning reaction. Since the free cocatalyst and fixed modified resin techniques deactivate catalyst differently, new process steps, parameters, and conditions are necessary to provide such an improvement.

An improved process for the production of bisphenols has been found. The process is a free cocatalyst process in which the primary alkyl alcohols, having from 1 to 8 carbon atoms and in particular from 1-3 carbon atoms, content in the feed is reduced to less than 50 ppm and in which cocatalyst conversion to harmful sulfidic derivatives is ameliorated through the use of purges or other withdrawal means.

In one aspect of this invention, a process for the production of bisphenols and in particular BPA is presented comprising the steps of:

- a) removing any primary alkyl alcohol having from 1 to 8 carbon atoms from a feed stream of DMK and

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phenol to a concentration of less than 50 ppm and preferably less than 10 ppm;

- 5 b) reacting a said feed stream in a reactor in the presence of a acidic ion exchange resin catalyst and a free cocatalyst comprising an alkylmercaptan to form a product mixture comprising BPA, phenol, DMK, water, methanol, and cocatalyst and cocatalyst derivatives;
- 10 c) separating the components of said product mixture;
- d) returning cocatalyst separated from said product mixture to said reactor;
- e) returning DMK and phenol separated from said product mixture to said feed stream; and
- f) recovering BPA.

15 According to a more specific embodiment of the present invention the alkyl alcohol is methanol the removal of which provides a feed stream comprising DMK and phenol with a concentration of methanol of less than 10 ppm.

20 In yet another embodiment of this invention, the lower alkyl alcohol removal step comprises distillation.

 In yet another embodiment of this invention, the lower alkyl alcohol removal step comprises adsorption by passage through a molecular sieve.

25 In yet another preferred embodiment of this invention, the process is conducted as part of an integrated chemical manufacturing process wherein phenol and DMK reactants are produced from the decomposition of cumene hydroperoxide.

30 The attached figure is a schematic diagram of the process of the invention.

 It has been found now that the production of certain sulphides formed from the mercaptan cocatalysts used in the free cocatalyst technique can result in rapid

35 deactivation of acidic ion exchange resins used in the

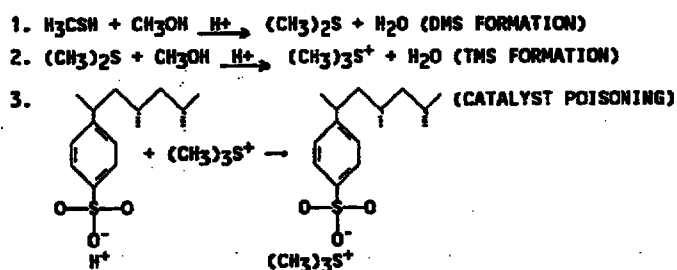
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production of bisphenols. Removal of intermediates that lead to the production of these sulphides and reduction or elimination of feed impurities greatly improves catalyst activity over time. This is best exemplified when the catalyst is a sulfonated polystyrene catalyst and the co-catalyst is methylmercaptan (MeSH). In such cases it has been found by convincing experimental evidence that if an ordinary feed, containing e.g. 200 ppm methanol, is used, the methanol reacts with the MeSH to form dimethylsulphide (DMS) and water. The DMS then reacts again with additional methanol to form a trimethylsulfonium cation (TMS). It is the TMS ion which quantitatively ties up the proton on the acid site on the resin. This process can be depicted as follows:



It has also been found that in the fixed modified resin technique, the catalyst deactivation results from the direct alkylation of the catalyst modifier attached to the resin. That is, the hydroxyl group of an alkyl alcohol condenses with the terminal hydrogen of the modifier to form water. The alkyl group then directly alkylates the modifier interfering with the subsequent synthesis of BPA. Thus, alkylation poisons the resin directly and cannot be ameliorated by adjustment or treatment of a cocatalyst or cocatalyst derivatives.

In the process of this invention, bisphenols are produced by the condensation of a ketone with stoichiometric excess of a phenol or a phenolic derivative. Reactants are supplied to a reactor in two

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feed streams comprising a ketone stream and a phenolic stream respectively. Alkyl alcohol, typically methanol, is removed from the ketone stream. Mercaptan cocatalyst is also added to the reactor as a feed stream. The reactants are introduced into a reactor wherein the temperature is from 40°C to 95°C. Catalyst and cocatalyst are, of course, also present in the reactor. The pressure within the reactor may be ambient or within the range of 1-5 atmospheres. Within the reactor, bisphenols are then formed and are discharged as part of a product stream. The product stream comprising a bisphenol, unreacted ketone, water, mercaptan cocatalyst, alkyl alcohol (and in particular methanol in case of preparation of BPA), and unreacted phenol is then sent to a separator. Bisphenol and unreacted phenol is removed as a bottoms product while water and any residual alkyl alcohol, e.g. methanol, that may be present is withdrawn as a side draw. Ketone and in particular acetone and mercaptan cocatalyst are withdrawn as tops products and are recirculated back to the reactant/feed stream.

Extension of catalyst life or reduction in catalyst deactivation is achieved by the practice of the following steps. Alkyl alcohols are removed from the feed stream prior to the reaction. Cocatalyst and cocatalyst derivatives are removed from the reactor with reactor products and subsequently separated; harmful cocatalyst derivatives such as dimethylsulphide can then be purged from the process. This allows cocatalyst without harmful derivatives to be returned to the reactor. Alternatively, cocatalyst and cocatalyst derivatives can simply be replaced by fresh cocatalyst. Unreacted alkyl alcohol is also removed as a side draw (along with water) from the separated product mixture so that recycle streams do not add any significant quantity of alkyl alcohols to the reactor. Including these steps can, and

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typically will, lengthen the life of the catalyst fourfold. That is, the catalyst can be left on stream and without a significant loss in activity or selectivity four times as long as a bisphenol production process in which these steps are not followed.

5 A typical ketone feed contains between 2000-3000 ppm water and 150-300 ppm alkyl alcohol (e.g. methanol). Up to 40,000 lbs per hour are typically processed in this manner. Alkyl alcohol (e.g. methanol) is removed from the feed stream by any of the well known methods such as distillation. In the typical case of an integrated chemical manufacturing facility, the alkyl alcohol is found only in the ketone feed. Usually this will require an azeotrope separation. This is the case when the ketone is DMK and the alkyl alcohol is methanol. Such azeotrope separations are well understood and easily achieved with techniques known in the art. Use of distillation as the separation technique can readily reduce the methanol concentration in the DMK feed to less than 50 ppm.

10 15 20 Ketone feeds having less than 50 ppm methanol are substantially methanol free for the purpose of practising this invention.

The most preferred method for this removal of alkyl alcohols is through adsorption on a molecular sieve. In this method, a column is filled zeolite such that one bed volume of zeolite is used to treat up to 25 volumes of DMK. Molecular sieves useful for this purpose have pore sizes of about 4-5 Å. The "Type A" molecular sieve commercially available from Zeochem Inc. is the presently preferred molecular sieve. When alkyl alcohol is removed by the use of a molecular sieve, its concentration in the feed can be readily reduced to less than 10 ppm.

30 In general, the catalytic agents employed in this invention are sulfonated aromatic resins comprising hydrocarbon polymers having a plurality of pendant

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sulfonic acid groups. These are typically 2 or 4% divinyl benzene crosslinked. Sulfonated polystyrene, poly(styrenedivinyl-benzene) copolymer, and sulfonated phenolformaldehyde resins have utility in this regard.

5 Sulfonated polystyrene resin catalysts commercially available as "A-32" brand catalyst from Rohm and Haas Chemical Company, Inc. and "K1131" brand catalyst from Bayer Chemical Company are the most preferred ion exchange resin for this purpose. The exchange capacity
10 of the acidic resin is preferably at least 2.0 meq. H⁺/gram of dry resin. Ranges from 3.0 to 5.5 meq H⁺/gram of dry resin are most preferred.

Cocatalysts useful in this invention are comprised of alkyl mercaptans such as methyl mercaptan, ethyl
15 mercaptan, propyl mercaptan. Methyl mercaptan is presently the preferred cocatalyst.

Turning now to the figure, upstream process 1 produces ketones and phenols (such as DMK and phenol) along with other minor components including alkyl alcohol
20 such as methanol. One such upstream process is the cleavage of cumene hydroperoxide. Upstream process 1 is also understood to be the bisphenol reactant source.

Two different streams of reactants, a ketone stream 1a, and a phenol stream 13 are withdrawn from upstream
25 process 1. The phenol stream is fed into reactor 4. The ketone stream is fed into alkyl alcohol removal vessel 2 where alkyl alcohol is removed from the stream. As noted above this can be done through distillation, zeolitic adsorption, or any other means known in the art provided
30 that the method reduces the alkyl alcohol concentration below 50 ppm and preferably below 10 ppm.

Having had the alkyl alcohol concentration reduced to below 50 ppm, the ketone stream is, together with phenol
stream 13, fed into reactor 4. Feed stream volumes
35 flowing into reactor 4 can be up to 200,000 lbs per hour

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although, as one skilled in the art will readily appreciate, the feed rate is dependent upon the conditions in which the reaction is carried out. Reactor 4 can be a single reactor or can be a series of reactors and can be run in the up or downflow configuration.

Preferably reactor 4 is operated at temperatures between 40°C and 95°C and pressures between 1 and 5 atmospheres.

Reactor 4 is also charged with an acidic ion exchange resin catalyst of the type discussed above. Finally,

reactor 4 is also charged with free mercaptan cocatalyst of the type discussed above. This cocatalyst is

originally fed into the reactor from a cocatalyst source 12. Cocatalyst concentration is also controlled by the

return (to either the reactor or the cocatalyst source

12) of cocatalyst which has been withdrawn from the

product stream and dealkylated. The cocatalyst return

is shown as stream 10 in the figure.

The reactants in reactor 4 react to form bisphenol (BPA when the reactants are DMK and phenol) and leave the

reactor 4 as a product stream comprising the bisphenol, unreacted reactants, cocatalyst, cocatalyst derivatives,

comprising primary alkylated mercaptans such as dimethyl sulphide, water, and a small amount of unreacted alkyl

alcohol such as methanol. The product stream is fed into

the separator 5 which can be any conventional method for separating such materials. Distillation is generally the

simplest and most preferred method. However, other well

known methods can be used independently or in combination with distillation to comprise this separation process.

When the separation is done as a distillation, the tops products will comprise the cocatalyst, cocatalyst derivatives, alkyl alcohol, and a small amount of other

impurities. These tops products are fed to the cocatalyst absorber column 8 which comprises a column

filled with phenol. In the cocatalyst absorber column 8,

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cocatalyst is absorbed from the rest of the tops products of separator 5 and is returned to the reactor via a cocatalyst return line 10. Cocatalyst derivatives such as dimethyl sulphide can simply be purged from the cocatalyst absorber along with other impurities such as alkyl alcohols. Those skilled in the art will appreciate that this purge can also be separated into constituents which can also find subsequent utility. These are withdrawn from the process in purge 9. This purge of cocatalyst derivatives such as DMS and methanol enable a fine sense of refinement by which the life of the catalyst in reactor 4 is further preserved.

Another purge can also be taken from separator 5 as middle distillate components comprising methanol and water. This occurs at purge 7 and can result in the removal of between 10 and 25 %wt of the total alkyl alcohol in the process at any one time.

The bisphenol product, bisphenol isomers, phenol, and a small amount of various impurities are removed from separator 5 as a bottoms product. This bottoms product is fed to a further separator 6. Crystallization is the preferred method of bisphenol separation but any method which can be used to separate bisphenol from the mother liquor can be used depending upon the desired degree of purity of the bisphenol product. Once separated, the mother liquor comprising phenol and bisphenol isomers is returned to the reactor 4 as reactant. It can thus be seen that recirculated phenol is free of alkyl alcohols and thus further enhances the life of the catalyst in the free cocatalyst method.

Bisphenol separated from mother liquor in separator 6 can then be sent to yet further separations and purifiers such as the bisphenol recovery process 11. This can be particularly important where very pure product is required as where BPA is produced for use in the

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subsequent production of polycarbonates or epoxy resins. Generally, such further separations can be beneficially conducted using techniques such as recrystallization.

5 Thus it can be seen that by removing alkyl alcohols from the feed, removing and adjusting cocatalyst concentration and the presence of harmful derivatives of
10 cocatalyst, removing alkyl alcohol from downstream steps of the reaction, and controlling cocatalyst use, this free cocatalyst method of bisphenol production provides a number of flexible means for eliminating or reducing
catalyst poisoning and thereby extending the life of the catalyst up to fourfold relative to processes which do not employ these steps.

15 It will be appreciated that the overall costs for operation of the process of the present invention will be significantly decreased, as this process does not use the more expensive aminoalkyl mercaptans as used according to
EP-A-0567857, in spite of the additional costs of the separation of cocatalyst or its derivative from the
20 product.

CLAIMS

1. A method for making bisphenols comprising:
 - a) removing alkyl alcohol having from 1 to 8 carbon atoms from a reactant stream comprising a ketone and a phenol,
 - 5 b) reacting said reactant stream in the presence of a cation exchange resin and a free sulphur-containing cocatalyst to produce a reaction production comprising cocatalyst, cocatalyst derivatives, and a bisphenol liquor comprising bisphenol and phenol,
 - 10 c) separating said bisphenol and phenol from said reaction products,
 - d) removing cocatalyst and cocatalyst derivatives from said reaction products,
 - e) returning cocatalyst to said reactor, and
 - 15 f) recovering bisphenol.
2. The method of claim 1 wherein said cocatalyst is a mercaptan.
3. The method of claims 1 and 2 further comprising the steps of removing the alkyl alcohol from said reactions products.
- 20 4. The method of claims 1-3 wherein said alkyl alcohol is present in said stream at a concentration of less than 50 ppm based relative to the weight of the ketone after said alkyl alcohol removal step.
- 25 5. The method of claim 4 wherein said alkyl alcohol is present in a said stream at a concentration of less than 10 ppm after the alkyl alcohol removal step.
6. The method of claim 2 wherein said cocatalyst is methyl mercaptan.

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7. A method for making bisphenol A comprising:

a) feeding acetone produced as a product of a cumene production process to a methanol removal process to produce substantially methanol free acetone feed,

5 b) reacting said acetone feed with phenol in the presence of an acidic cation exchange resin and a free sulphur containing cocatalyst to produce BPA and effluent,

c) separating BPA from the reaction products,

10 d) separation of cocatalyst and cocatalyst derivatives from the reaction products,

e) returning only the cocatalyst obtained from step c) to said reaction, and

f) recovering BPA.

15 8. The method of claims 1-7 wherein said cation exchange resin is selected from the group consisting of sulfonated polystyrene, poly(styrenedivinyl-benzene) copolymer, and sulfonated phenolformaldehyde resins.

20 9. In a method for producing bisphenol A by reacting an acetone stream comprising methanol with a phenol stream in the presence of an acidic cation exchange resin and a sulphur containing cocatalyst, the improvement which consists of removing substantially all of the methanol from said acetone stream and eliminating alkylated
25 cocatalyst derivatives from said reaction such that the acidic cation exchange resin is not poisoned.

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