

CATALYST PROMOTER FOR THE MANUFACTURE OF POLYPHENOLS

5 The present invention relates to a process for the manufacture of polyphenols, and more specifically to the addition of a catalyst promoter to a reaction mixture for the manufacture of polyphenols.

10 The compound 2,2-bis(4-hydroxyphenyl)propane, also called para, para-diphenylolpropane or bisphenol-A, is generally prepared by reacting phenol and acetone in the presence of an acidic condensation catalyst along with a catalyst promoter or cocatalyst to increase the reaction rate and selectivity of the condensation catalyst. US Patent No. 2,468,982 disclosed the use of mercapto-substituted aliphatic carboxylic acids as catalyst promoters to increase the condensation reaction rate between phenols and ketones to such an extent that the reaction time could be cut to 1/10th the time previously required. Subsequently, it was discovered that the contact time of the acid-catalyzed reaction between phenol and ketones could be reduced by the use of methyl mercaptans as disclosed in US Patent No. 2,730,552. Not only was the contact time reduced, but the use of gaseous methyl mercaptan in the reaction zone allowed one to run the reaction with only minimal amounts of catalyst promoter without the formation of any substantial amounts of by-product formation or bisphenol-A product disintegration. Further, methyl mercaptan could be used as a catalyst promoter in a continuous process. It is also attractive in that its high volatility allows it to be easily separated from the reactor reaction mixture effluent containing bisphenol-A product and avoids the

presence of sulfur contaminants in the final product. Since then, the use of gaseous free methyl mercaptan has been the catalyst promoter of choice in acid-catalyzed phenol-acetone reactions.

5 However, methyl mercaptan is difficult to handle because it is gaseous at room temperature and at atmospheric pressure. This makes the shipping of methyl mercaptan inefficient because it must first be pressurized to a liquid state to economically transport
10 sufficient amounts required for the manufacture of bisphenol-A at a plant located some distance from the site producing methyl mercaptan. Moreover, since methyl mercaptan is also hazardous, in some cases shipping this material to certain locations is restricted, resulting in
15 limited availability in these areas. As a result, some bisphenol-A plants must now either produce methyl mercaptan on site, or switch to an alternative catalyst promoter which does not have the volatility of methyl mercaptan.

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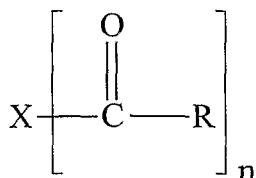
 After an extensive research we have discovered that a di-thioketal is a catalyst promoter, for the manufacture of polyphenols, which can be easily shipped and handled due to its relatively low volatility and
25 stability in liquid state during transport. This catalyst promoter has high activity and high selectivity. The amount of sulfur byproduct species produced using this catalyst promoter is low.

 There is now provided a condensation process
30 comprising introducing into a reaction zone ingredients comprising a phenolic compound reactant, a carbonyl compound reactant, and a dithioketal catalyst promoter composition, and condensing the phenolic compound and the carbonyl compound in the presence of an acid catalyst.

There is also provided a process for the manufacture of a polyphenol compound comprising introducing into a reaction zone ingredients comprising a phenolic compound reactant, a carbonyl compound reactant, and a catalyst promoter comprising a dithioketal, and reacting the ingredients within the reaction zone in the presence of an acid catalyst.

There is also provided a synthetic method comprising adding together a phenolic compound, a carbonyl compound, and a dithioketal catalyst promoter, hydrolyzing the dithioketal catalyst promoter to its dissociation products, and condensing the phenolic compound and the carbonyl compound in the presence of an acid catalyst and said dissociation products.

Accordingly the invention relates to: a process for the manufacturing of a polyphenol compound, introducing into the reaction zone ingredients comprising a phenol compound reactant, a carbonyl compound reactant, and a dithioketal catalyst promoter composition, and condensing the phenolic compound and the carbonyl compound, in the presence of an acid catalyst, and the dithioketal catalyst promoter or its dissociation products formed. Examples of carbonyl compounds are those compounds represented by the following formula:



wherein R represents hydrogen or an aliphatic, cycloaliphatic, aromatic, or heterocyclic radical, including hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, alkaryl, whether saturated or unsaturated;

n is greater than 0, preferably from 1 to 3, more preferably from 1-2, and most preferably is 1; and when n is greater than 1, X represents a bond, or a multivalent linking group having from 1 to 14 carbon atoms, preferably from 1 to 6 carbon atoms, more preferably from 1 to 4 carbon atoms; and when n is 1, X represents hydrogen or an aliphatic, cycloaliphatic, aromatic, or heterocyclic radical, including hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, alkaryl, whether saturated or unsaturated.

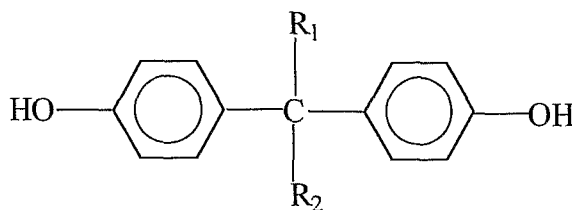
Suitable carbonyl compounds include aldehydes and ketones. These compounds generally contain from three to fourteen carbon atoms, and are preferably aliphatic ketones. Examples of suitable carbonyl compounds include ketones such as acetone, ethyl methyl ketone, diethyl ketone, dibutyl ketone, isobutyl methyl ketone, acetophenone, methyl and amyl ketone, cyclohexanone, cyclopentanone, 1,3-dichloroacetone and the like. Most preferred is acetone.

The carbonyl compounds are reacted with phenolic compounds. Suitable phenolic compounds include phenol and the homologues and substitution products of phenol containing at least one replaceable hydrogen atom directly bonded to the aromatic phenol nucleus. Such groups substituting for the hydrogen atom and directly bonded to the aromatic nucleus include the halogen radicals such as chloride and bromide, and the hydrocarbon radicals such as alkyl, cycloalkyl, aryl, alkaryl and aralkyl groups. Suitable phenolic compounds include phenol, the cresols, the xylenols, carvacrol, cumenol, 2-methyl-6-ethyl phenol, 2,4-dimethyl-3-ethylphenol, o-chlorophenol, m-chlorophenol, o-t-butylphenol, 2,5-xyleneol, 2,5-di-t-butylphenol, o-

phenylphenol, 4-ethylphenol, 2-ethyl-4-methylphenol, 2,3,6-trimethylphenol, 2-methyl-4-tertbutylphenol, 2-tert-butyl-4-methylphenol, 2,3,5,6-tetramethylphenol, 2,6-dimethylphenol, 2,6-di-tert-butylphenol, 3,5-
5 dimethylphenol, 2-methyl-3,5-diethylphenol, o-phenylphenol, p-phenylphenol, naphthols, phenanthrol, and the like. Most preferred are compositions containing phenol. Mixtures of any of the above may be used.

The above is not meant to limit the invention but to
10 illustrate representative examples of carbonyl compounds and phenolic compounds which are known in the art to make desirable polyphenol and for which those of skill in the art can substitute other similar reactants.

The polyphenol compounds obtained by the
15 condensation reaction of a phenolic compound and a carbonyl compound are compounds wherein the nuclei of at least two phenolic radicals are directly attached by carbon to carbon linkages to the same single carbon atom in the alkyl group. An illustrative non-limiting example
20 of a polyphenol compound is represented by the formula:

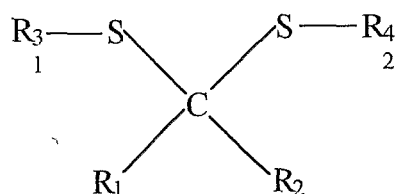


wherein R₁ and R₂ each independently represent hydrogen or a monovalent organic radical. Examples of such radicals include hydrocarbon radicals such as aliphatic,
25 cycloaliphatic, aromatic, or heterocyclic radical, more specifically hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, alkaryl, whether saturated or unsaturated. Preferably, R₁ and R₂ each independently represent hydrogen or an alkyl radical having from 1 to 2

carbon atoms. Most preferably, the polyphenol compound comprises bis(4-hydroxyphenyl)propane 9bisphenol-A) .

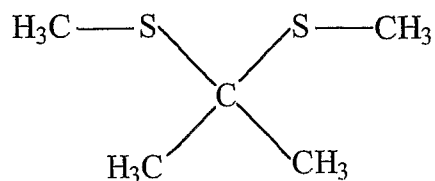
Polyphenol compounds are made by the acid-catalyzed reaction between a phenolic compound and a carbonyl
5 compound. The rate and selectivity of the reaction are promoted by introducing into the reaction zone a dithioketal catalyst promoter as such.

Accordingly, the dithioketal catalyst promoter composition used in the process of the invention is the
10 condensation reaction product between a carbonyl compound and at least one thiol compounds and comprises compounds having at least two sulfur atoms covalently bonded to a common carbon atom. More in particular, the dithioketal catalyst promoter composition comprises dithioketal
15 catalyst promoter compounds represented by the following structure:



wherein R_1 , R_2 , R_3 , R_4 are each independently a branched or unbranched, saturated or unsaturated monovalent organic
20 radical such as an aliphatic, cycloaliphatic, aryl, heterocyclic radical, (including hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, and alkaryl); R_1 and R_2 together may be covalently bonded to form a divalent group, and R_3 and R_4 together may be covalently bonded to
25 form a divalent group, and R_1 and/or R_2 may also represent hydrogen and preferably one of those symbols represent hydrogen. Preferably, R_1 , R_2 , R_3 , R_4 are each independently a branched or unbranched, saturated or unsaturated alkyl radical. More preferably, R_1 , R_2 , R_3 , R_4
30 are each independently a saturated alkyl radical each containing from 1 to 4 carbon atoms.

Most preferably, the dithioketal catalyst promoter composition comprises 2,2-bis(thiomethyl)propane compounds represented by the following structure:



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The particular dithioketal catalyst promoter compound chosen is preferably a type which, upon dissociation in the reaction zone, forms the same kind of carbonyl compound as the feed carbonyl compound chosen to make the polyphenol. In one embodiment, the feed carbonyl feed is acetone, and the dithioketal catalyst promoter composition comprises 2,2-bis(thiomethyl)propane, which in the presence of the acid catalyst, dissociates into acetone and methyl mercaptan catalyst promoter.

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It is also preferred to choose a particular dithioketal catalyst promoter compound which performs substantially the same as a methyl mercaptan catalyst promoter. In other words, it is desirable to select a dithioketal catalyst promoter which has the same or higher first order rate for converting the carbonyl compound as its dissociation product comprising an alkyl, aryl, alkaryl, or aralkyl mercaptan compound, and more preferably methyl mercaptan. It is also desirable to select a dithioketal catalyst promoter which has the same or higher selectivity toward formation of the polyphenol product as its dissociation product comprising an alkyl, aryl, alkaryl, or aralkyl mercaptan compound, and more preferably methyl mercaptan.

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To the reaction vessel is added the phenolic compound, the carbonyl compound, and the dithioketal

catalyst promoter composition, and optionally a solvent and water. The acid catalyst, depending upon the type used, may be charged to the reaction vessel or may be loaded into the reaction vessel prior to charging the liquid feeds. The addition sequence of reactants, catalyst promoter, catalyst and optional solvent and water to a reaction vessel is not limited. Further, the manner of introducing the dithioketal catalyst promoter to the reaction mixture is not limited and can take place by the adding the dithioketal catalyst promoter composition to a reaction mixture containing all reactants and catalyst and optional solvent, or to a reaction mixture containing only some of these ingredients, or to any feed stream containing any one of these individual ingredients or a mixture of these ingredients. Thus, the phrase "reaction mixture" when used in conjunction with the introduction of the dithioketal is not limited to the addition of the dithioketal catalyst promoter to a mixture of all the ingredients used to make the polyphenol. Rather, the introduction of the dithioketal catalyst promoter to the reaction mixture includes its addition to any one or a mixture of any one or all of the ingredients used to make the polyphenol.

The process of the invention requires introducing a dithioketal compound which has been isolated as such to the reaction mixture, in contrast to adding a mercaptan, such as methyl mercaptan, to the reaction mixture and in contrast to contacting a phenolic compound and a carbonyl compound with a dithioketal compound formed in situ by, for example, the reaction of acetone with methyl mercaptan.

When a dithioketal catalyst promoter composition such as 2,2-bis(thiomethyl)propane was added to the reaction

mixture, we have found that the reaction of 2,2-bis(thiomethyl)propane rapidly hydrolyzes and equilibrates to the formation of methyl mercaptan in situ without any induction time. The process of the invention
5 forms methyl mercaptan in situ, thus avoiding the need to isolate, ship and handle methyl mercaptan. Due to the lower volatility and stability of a dithioketal at room temperature and atmospheric conditions, it is more advantageous to isolate, ship and handle the dithioketal
10 and introduce it to the reaction mixture.

The dithioketal catalyst promoter composition can be added to the reaction mixture or to any one of the reactants in the liquid phase or in the gaseous phase. Since the dithioketal catalyst promoter composition is in
15 the liquid state during shipping and handling, it is preferred to add it to the reaction mixture or to any reactant in the liquid phase.

The dithioketal catalyst promoter composition should be liquid at room temperature and at 1 atmosphere for
20 ease of shipping and handling. For example, 2,2-bis(thiomethyl)propane is sufficient stable for transportation, it is not readily decomposed at moderate temperatures in the absence of acid catalysts and water, and its thermal decomposition half life at 120°C was
25 determined to be greater than 40 hours.

The dithioketal catalyst promoter composition is introduced into the reaction mixture neat or in solution. As a solution, the dithioketal may be mixed with a portion or with all the carbonyl compound used to make
30 the polyphenol. The dithioketal catalyst promoter composition may be added directly to the reaction zone, or to any of the streams feeding the reaction zone. It may be added incrementally or continuously over the course of the reaction, or all of the required catalyst

promoter may be added to the reaction zone prior to initiating the reaction.

The dithioketal catalyst promoter composition is preferably introduced as a pure composition into the reaction mixture, meaning that outside of those ingredients used to make the polyphenol which are mixed with the dithioketal catalyst promoter, the dithioketal catalyst promoter composition comprises at least 90 wt.% dithioketal, more preferably at least 95 wt.% dithioketal, most preferably at least 98 wt.% dithioketal. Whether or not a pure composition of dithioketal catalyst promoter is used, the amount of those impurities present in the dithioketal catalyst promoter composition which are a reactive species with the phenolic compound, the carbonyl compound, or the catalyst, is preferably less than 2 wt.%, more preferably less than 1 wt.%, most preferably less than 0.2 wt.%.

The exact molar amount of the dithioketal catalyst promoter composition as an fresh initial charge to the reaction zone will depend upon the particular reaction conditions employed, the species of dithioketal catalyst promoter selected, and the species of phenolic and carbonyl compounds selected, and the kind of catalyst used. Generally, however, the molar ratio of dithioketal catalyst promoter compound to the carbonyl compound used as the fresh initial charge to the reaction zone in the process of the invention ranges from 0.005:1 up to 0.5:1, preferably from 0.025:1 to 0.25:1. In one embodiment, for the manufacture of bisphenol-A using phenol and acetone as reactants, the molar ratio of dithioketal catalyst promoter compound to the carbonyl compound ranges from 0.025:1 to 0.25:1. The amount of dithioketal catalyst promoter compound added to the reaction mixture is generally about half the molar ratio of a polyphenol-A

manufacturing process equipped for the addition of methyl mercaptan since 1 mole of dithioketal catalyst promoter such as 2,2-bis(thiomethyl)propane catalyst promoter yields two moles of the corresponding mono mercaptan catalyst promoter.

Once the reaction zone is charged with the fresh initial charge of the dithioketal composition, for the following reason, the process advantageously requires only small amount of dithioketal as a fresh make-up charge to continue producing the desired yield. The feed stream(s) comprised of the phenolic compound, the carbonyl compound, and the dithioketal catalyst promoter are contacted with an acid catalyst for a period of time sufficient to effect formation of the polyphenol product.

In the reaction zone containing the phenolic compound, the carbonyl compound, the acid catalyst, and the dithioketal catalyst promoter, the dithioketal catalyst promoter almost instantly hydrolyzes to its dissociation products, one of which is a mercaptan catalyst promoter.

A mercaptan catalyst promoter is any compound having a thiol group covalently bonded to a carbon atom. Once the desired yield of polyphenol is attained by the condensation reaction between the phenolic compound and the carbonyl compound, the resulting crude reaction mixture effluent stream containing the polyphenol product is fed to a separation zone to separate the crude polyphenol compound into a crude polyphenol stream from at least a portion of other compounds such as unreacted carbonyl compounds, unreacted phenolic compounds, the dissociation products of the dithioketal catalyst promoter which include a mercaptan catalyst promoter, and excess water. These compounds may be removed as an overhead or fractionally as draws by way of, for example, distillation or fractional distillation. The method of

separation is not limited and 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

5 independently or in combination with distillation to comprise this separation process.

Any fraction containing dissociation products, one of which is the mercaptan catalyst promoter, may be recycled back to the reaction zone or to any line or
10 reactant feeding the reaction zone. This fraction may be recycled directly back to the reaction zone or may be optionally but preferably further processed to enrich the concentration of and recover the mercaptan catalyst promoter prior to recycling the mercaptan catalyst
15 promoter back to the reaction zone. Depending upon the separation means used, all the overhead may be fed to a mercaptan recovery zone, or a fraction rich in the mercaptan may be fed to a recovery zone, or multiple fractions containing the mercaptan catalyst promoter may
20 be fed to a recovery zone. The means for recovering the mercaptan catalyst promoter are not limited. For example, a stream containing the dissociation products including the mercaptan catalyst promoter compound may be fed to a catalyst promoter absorber column which
25 comprises a column filled with phenol. In the catalyst promoter absorber column, the catalyst promoter dissociation products are absorbed from the rest of the tops products of the separator. The method of recovering the dissociation product catalyst promoter is not limited
30 and can be any conventional technique, so long as the recovery zone functions to enrich the concentration of the mercaptan catalyst promoter relative to the concentration of the mercaptan catalyst promoter from the separation zone. The separated and recovered catalyst

promoter dissociation products containing the mercaptan catalyst promoter compound are generally recycled to the reaction zone by way of a return line.

Substantially all of the mercaptan catalyst promoter
5 can be recycled back to the reaction zone with only minimal losses. Once recycled to the reaction zone, the mercaptan catalyst promoter is just as effective to increase the activity of the acid catalyst and selectively convert the carbonyl compound to the
10 polyphenol product as it was when formed from the dissociation of the dithioketal catalyst promoter compound charged as an fresh initial charge to the reaction zone. Accordingly, after the fresh initial charge of dithioketal to the reaction zone, only a fresh
15 make-up charge of dithioketal catalyst promoter composition is necessary to continue feeding the reaction zone in order to make up for the amount of losses in the course of recovering and recycling the mercaptan catalyst promoter.

20 Thus, after the fresh initial charge of the dithioketal catalyst promoter composition to the reaction zone, make up charges of the dithioketal catalyst promoter compound may be added to the reaction zone commensurate with the loss rate experienced by the
25 process of separating and recycling the corresponding dissociation products of the dithioketal catalyst promoter back to the reaction zone. Generally, more than 99% of the dissociation product catalyst promoter is recycled, meaning that only 1 wt. % per hour of the
30 dithioketal needs to be charged as a makeup based on the total weight of mercaptan compounds in the reaction system. Higher or lower amounts of the dithioketal catalyst promoter may be introduced as needed.

Accordingly, an additional advantage to using the dithioketal catalyst promoter is that once charged as an fresh initial charge, the catalyst promoter does not have to flow through the process and be discarded or converted
5 or neutralized. The dissociation products of the dithioketal catalyst promoter are easily volatilized, completely separated, and can be recycled back to the reaction zone and used as a catalyst promoter.

The phenolic compounds and the carbonyl compounds
10 are reacted in a reaction vessel, whether in the batch or continuous mode, at a temperature ranging from 20°C to 130°C, preferably from 50°C to 130°C.

The pressure and temperature should be set under conditions to retain the reactants in the liquid phase in
15 the reaction zone.

The reactants are introduced into the reaction zone under conditions to assure a molar excess of the phenolic compound over the carbonyl compound. Preferably, the phenolic compound is reacted in a substantial molar
20 excess over the carbonyl compound, wherein the molar ratio of the phenolic compound to the carbonyl compound is preferably at least 2:1, more preferably at least 5:1, and up to 25:1.

Along with the dithioketal catalyst promoter charged
25 into the reaction zone, a small of water is required, or may be produced in situ by the condensation reaction between the carbonyl compound and the phenolic compound. A molar ratio of water to dithioketal catalyst promoter ranging from 1:1 to 5:1 is sufficient

30 The reaction is normally conducted in an acidic medium at a pH ranging less than 5. The condensation catalysts used in the process of the invention are any acidic catalysts known for condensing a phenolic compound with a carbonyl compound to make a polyphenol. The acid

catalysts may be homogeneous catalysts or heterogeneous catalysts. Acid homogeneous catalysts include the hydrogen halides such as hydrogen chloride, preferably in the anhydrous state, sulfuric acid, hydrochloric acid, phosphoric acid, hydrobromic acid, hydrofluoric acid, nitric acid, acetyl chloride dimethylsulfate, sulfur dioxide, p-toluene sulfonic acid, boron trifluoride, boron trifluoride complexes, a. and any other acids which have a dissociation constant greater than 10^{-3} .

The condensation of carbonyl compound and phenolic compound can be conducted using a heterogeneous acid catalyst. These catalysts include the organo polysiloxanes containing sulfonic acid groups, solid perfluorinated polymer catalyst having pendant sulfonic acid groups, acidic clays, or acidic ion exchange resins having a plurality of pendant sulfonic acid groups.

The acidic ion exchange resins are often mercaptan modified resins of the type conventionally known in the art which include any compound which will react with the acidic groups of the cation exchange resin to introduce a mercapto substituent into the resin. Suitable mercaptan modifying agents to be bound onto the acid sites of the exchange resin include alkyl mercapto amines such as propylaminopropyl mercaptan, bis-(2-mercaptoethyl)amine, thiazolidine and the like.

The acidic ion exchange resin's effectiveness in the condensation step of the process of the invention is to some extent influenced by its exchange capacities such that the greater the exchange capacity, the more desirable the resin. Preferably, the cation exchange capacity is at least about 0.5 and, preferably, greater than 4.0 meq/g dry weight. Also, those cation exchange resins having bound cationic exchange groups of the stronger exchange potential acids are preferred for use

in the condensation step of the process of the present invention. Acidic cation exchange resins suitable (for optional modification with a mercapto modifying agent) for use in the condensation step of the process of the invention include sulfonated styrene-divinyl-benzene copolymers, sulfonated cross-linked styrene polymers, phenol-formaldehyde-sulfonic acid resins, benzene-formaldehyde-sulfonic acid resins, perfluorinated sulfonic acid resins and the like. These include resins under such tradenames as Amberlites (Rohm and Haas Co.), DOWEX.RTM. (Dow Chemical Co.), Permutit QH (Permutit CO.), Chempro (Chemical Process Co.), catalysts from Purolite, Lewatit (Bayer A. G.), NAFION (DuPont) and the like. Strong acid sulfonated styrene-divinylbenzene copolymer resins are preferred.

Commercially available aromatic sulfonic acid resins are generally obtained as sodium salts and are converted to the acid form prior to use. Both macroreticular resins and gel resins are useful in the condensation process of the present invention. The choice of resin will of course depend on the starting materials, the reaction conditions and the effect of an individual resin under the conditions selected, which determination and selection is within the skill of the art.

The precise amount of acidic cation exchange resin to be used will vary to some degree depending on the specific resin, feed and conditions used for the process. By way of illustration, sufficient catalyst is loaded into the reaction zone to afford a contact time equivalent to a weight hourly space velocity of 0.1 to 10 hr^{-1} . The feed stream comprised of the phenolic compound, the carbonyl compound, and the dithioketal catalyst promoter passes through the resin catalyst for a period of time sufficient to effect formation of the polyphenol

depending on the feed rate, size of the resin bed, the particular resin and dithioketal catalyst promoter used and the like as can readily be determined by those of skill in the art.

5 Any suitable reactor may be used as the reaction zone. The reaction can occur in a single reactor, or in a plurality of reactors connected in series or in parallel. The reactor can be a back mixed or plug flow reactor, and the reaction can be conducted in a
10 continuous or batch mode, and the reactor can be oriented to produce an up-flow or down-flow stream.

The invention is not limited to a particular method for recovering the polyphenol compound, and any method known to those of skill in the art is suitable.

15 Generally, however, the crude reaction mixture effluent from the reaction zone is fed to a separator as mentioned above. The polyphenol product, polyphenol isomers, unreacted phenolic compound, and a small amount of various impurities are removed from the separator as a
20 bottoms product. This bottoms product may be fed to a further separator. While crystallization is a common method of polyphenol separation but any method which can be used to separate polyphenol from the mother liquor can be used depending upon the desired degree of purity of
25 the polyphenol product. Once separated, the mother liquor comprising phenol and polyphenol isomers may be returned to the reaction zone as reactant.

Polyphenol separated from mother liquor in separator can then be sent to yet further separations and purifiers
30 such as the polyphenol recovery process. This can be particularly important where very pure product is required as where BPA is produced for use in the subsequent production of polycarbonates. Generally, such

further separations can be beneficially conducted using techniques such as recrystallization.

The invention is illustrated by the following example, which is not meant to limit other examples within the spirit and scope of the invention as described herein.

Examples

This example demonstrates that the rate, selectivity, and distribution of sulfur species for the acidic resin-catalyzed manufacture of bisphenol-A by the introduction of free 2,2-bis(thiomethyl)propane as a catalyst promoter behaves substantially the same as with the use of methyl mercaptan (MeSH) added as a catalyst promoter.

Preparation of 2,2-bis(thiomethyl)propane.

To a three-neck round bottom flask equipped with a mechanical stirrer and a dry ice cold finger condenser was added 100 g of acetone, 5 g of CT-122, a strongly acidic 2% crosslinked sulfonated styrene divinylbenzene cationic gel exchange resin commercially available from Purolite, and 96 g of methyl mercaptan. After stirring at ambient temperature for 3h and 40°C for 1 h, the liquid phase was decanted into 200 ml of methylene chloride and the combined washed mixture washed with 100 ml of water three times, dried over anhydrous magnesium sulfate, and concentrated by rotavap. The residue was fractionally distilled to yield 26 g of 2,2-bis(thiomethyl)propane having a boiling point of 64-66°C at 27 torr. Analysis of the sample by C13 NMR peaked at δ 12.35 corresponding to the presence of the CH₃S group, and at δ 29.63 corresponding to a CH₃ group, and at δ 54.47, corresponding to the presence of a quaternary carbon atom.

Rate of reaction for the preparation of Bisphenol-A

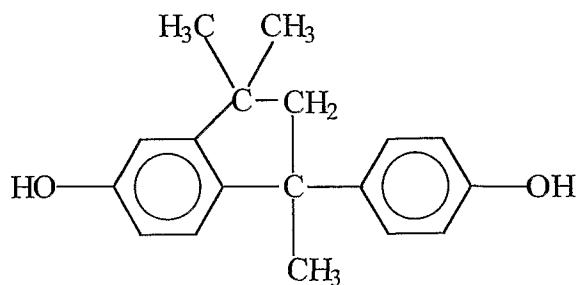
The rates of the acetone/phenol condensation catalyzed by the strongly acidic cationic exchange resin CT122 (Purolite), and promoted with MeSH and 2,2-bis(thiomethyl)propane ("DMA"), respectively, were measured by in-situ IR. A mixture of phenol, water, and CT122 was preheated to 75°C in an autoclave at autogeneous pressure, followed by injection with a solution of acetone and a promoter. The relative molar composition of the feed in the MeSH-promoted reaction was 100 moles of phenol, 8.1 moles of acetone, 2.8 moles of water, and 1.04 moles of MeSH. The relative molar composition of the feed in the DMA-promoted reaction was the same except that MeSH was replaced with half the molar amount of DMA. The weight ratio of phenol to CT122 was 100 to 3.17 in both reactions. The mixture was reacted over a period of about 3 hours, during which time the reaction rate was measured. The results are graphically depicted in Figure 1. The kinetic plot shown in the Figure demonstrates that there is no induction period in the DMA-promoted reaction and its first order rate for conversion of acetone is substantially identical to that of a MeSH-promoted reaction.

Selectivity Analysis

The selectivity of the catalyst promoter solutions to the formation of p,p-BPA were measured by HPLC. The following product distribution data show that replacing MeSH with 2,2-bis(thiomethyl)propane (DMA) has no effect on the selectivity of BPA formation. All numbers are in relative units.

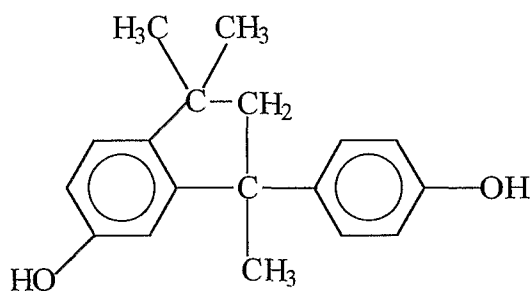
Promoter	% Acetone conversion	p,p-BPA	o,p-BPA	o,o-BPA	CDA*	CDB**	BPX***	Unk. H****
MeSH	90	100	3.58	0.094	0.39	0.092	1.13	0.094
DMA	90	100	3.52	0.091	0.4	0.1	1.2	0.11

*Cyclic Dimer A:

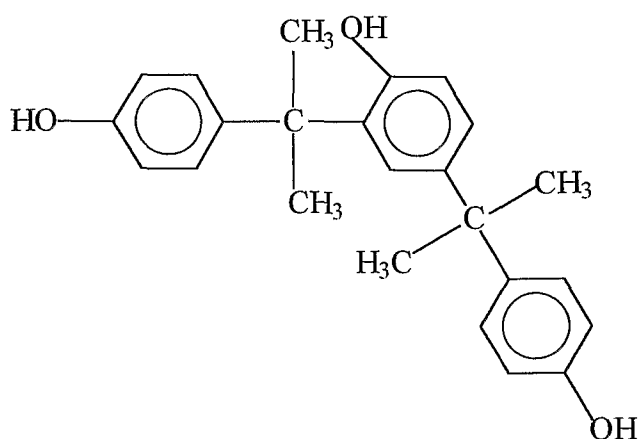


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**Cyclic Dimer B:

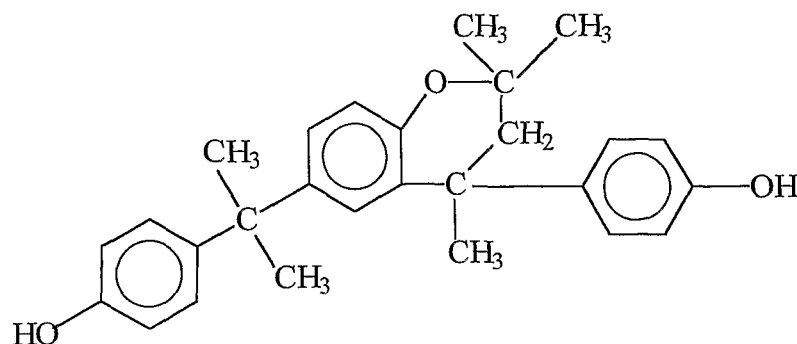


***Trisphenol:



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****Hydroxy Cumyl Codimers:



Sulfur Species Analysis

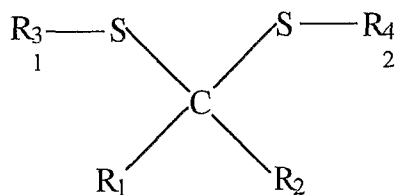
The presence of sulfur by-products in the MeSH and the DMA promoted reaction were measured by GC-MS of the reaction mixtures. Analysis showed the presence of three sulfur species in each case: methyl mercaptan (MeSH), DMA, and 4-thiomethyl-4-methyl-2-pentanone (TMP). The relative concentrations of the three sulfur species are virtually the same in both the MeSH and DMA promoted reactions. This is consistent with rapid equilibration of DMA and MeSH leading to the same distribution of sulfur species under reaction conditions. The small amount of dimethyl disulfide found in the MeSH-promoted reaction was shown to be impurity in MeSH. All numbers are relative areas.

Promoter	% Acetone conversion	MeSH	DMA	TMP	Dimethyl Disulfide
MeSH	90	32.2	54.6	11.7	1.5
DMA	90	37.8	51.8	10.4	0

These results are showed in Figure 1, which is the graphical plot of the first order rates for converting acetone in a methyl mercaptan promoted reaction and a 2,2-bis (thiomethyl)propane (DMA) promoted reaction.

C L A I M S

1. A process for the manufacturing of a polyphenol compound, introducing into the reaction zone ingredients comprising a phenol compound reactant, a carbonyl compound reactant, and a dithioketal catalyst promoter composition, and condensing the phenolic compound and the carbonyl compound, in the presence of an acid catalyst, and the dithioketal catalyst promoter or its dissociation products formed.
2. The process according to Claim 1, wherein the dithioketal catalyst promoter has the structure:

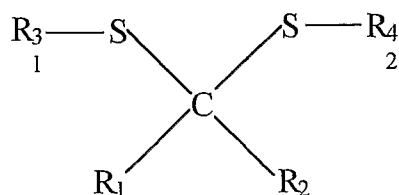


wherein R_1 , R_2 , R_3 , R_4 are each independently a branched or unbranched, saturated or unsaturated monovalent organic radical such as an aliphatic, cycloaliphatic, aryl, heterocyclic radical, (including hydrocarbon radicals such as alkyl, cycloalkyl, aryl, aralkyl, and alkaryl); R_1 and R_2 together may be covalently bonded to form a divalent group, and R_3 and R_4 together may be covalently bonded to form a divalent group, and one of R_1 and or R_2 may also both represent hydrogen and preferably one of those symbols represent hydrogen. Preferably, R_1 , R_2 , R_3 , R_4 are each independently a branched or unbranched, saturated or unsaturated alkyl radical.

3. The process according to claim 2, wherein R_1 , R_2 , R_3 , R_4 are each independently a saturated alkyl radical each containing from 1 to 4 carbon atoms.
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4. The process of Claims 1-3, wherein the dithioketal catalyst promoter composition is a type which dissociates in the reaction zone into the same carbonyl compound as introduced into the reaction zone, wherein the carbonyl compound comprises acetone, the phenolic compound comprises phenol, wherein the dithioketal catalyst promoter composition is liquid at room temperature and at atmospheric pressure and has a thermal decomposition half life at 120°C greater than 40 hours.
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5. The process of claim 1, wherein the amount of impurities present in the dithioketal catalyst promoter composition which are a reactive species with the phenolic compound reactant, the carbonyl compound reactant, or the acid catalyst, is less than 2 wt.%.
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6. The process of claim 1, wherein the molar ratio of dithioketal catalyst promoter to the carbonyl compound used as an fresh initial charge to the reaction zone ranges from 0.025:1 to 0.25:1.
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7. The process of claim 1, wherein the acid catalyst comprises an acidic cation exchange resin having a cation exchange capacity of greater than 4.0 meq/g dry weight.
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8. The process of claim 1, wherein the contact time of the reactants over the acidic catalyst

is equivalent to a weight hourly space velocity of 0.1 to 10 hr⁻¹.

9. Dithioketal catalyst promotor composition, obtainable by condensation reaction product between a carbonyl compopund and at least one thiol compound.
10. Dithioketal catalyst promotor composition according to Claim 9 of formula:



11. Dithioketal catalyst promotor composition according to Claim 10, wherein R₁, R₂, R₃, R₄ are each independently a saturated alkyl radical each containing from 1 to 4 carbon atoms.
12. Dithioketal catalyst promotor composition according to Claims 9-11 comprising 2,2-bis (thiomethyl)propane (DMA) of the struture:

