

METHOD OF PURIFYING PHENOL

This invention relates to a method of purifying phenol.

5 One method of making phenol is by oxidizing cumene to cumene hydroperoxide and decomposing the cumene hydroperoxide by a cleavage reaction to yield phenol and acetone reaction products. The phenol produced by this process may contain impurities or product contaminants that are difficult to
10 remove by conventional methods such as by distillation. These impurities are undesirable, because, they cause the formation of color products when the phenol is used in downstream processes involving chlorination or sulphonation of the phenol. Among the contaminants formed during the
15 manufacture of phenol are hydroxyketones.

U.S. Patent No. 3,454,653 discloses the use of a synthetic silica-alumina catalyst which preferably contains 5% to 30% by weight alumina and 95% to 70% by weight silica. The silica-alumina catalyst may also be modified to contain a
20 group VIA metal, such as chromium, molybdenum or tungsten, in the range of 0.01 to 5% by weight of the catalyst.

U.S. Patent No. 3,029,294 discloses the use of a number of materials, such as activated alumina, aluminum silicates, ion-exchange resins, mineral acids, strong organic acids, and
25 surface active earths, in the treatment of phenol to convert aliphatic α -hydroxy carbonyl compounds that are present in the phenol to benzofuran.

It is desirable to provide a process for purifying a phenol product that has a concentration of a contaminating
30 compound such as a hydroxyketone.

It has been surprisingly found that high purity phenol can be obtained by a purification process using a treatment

catalyst having a low silica content and further comprising alumina and a Group VIA metal.

Accordingly this invention provides a method, comprising:

- 5 purifying a phenol product, comprising phenol and a contaminating concentration of an hydroxyketone, by contacting, under suitable contacting conditions, said phenol product with a treatment catalyst having a low silica content and further comprising alumina and a Group VIA metal.

- 10 The phenol stream is contacted with a treatment catalyst under conditions suitable for converting a portion of the contaminating compound to another compound to thereby provide a treated phenol stream. The treatment catalyst is a low silica-containing catalyst comprising molybdenum supported on
15 alumina.

FIG. 1 is a schematic diagram illustrating the phenol purification reaction system and process.

- The phenol product stream to be treated, or purified, in accordance to the invention can be any phenol-containing
20 material that has a concentration of a contaminant. Thus, the phenol product stream comprises phenol and a concentration of a contaminant with the amount of phenol in the phenol product stream varying from 95 weight percent upwardly to 100 percent and, preferably, exceeding 98 weight
25 percent and, most preferably, exceeding 99 weight percent of the phenol product stream. The concentration of the contaminant in the phenol product stream is generally a contaminating concentration for the particular contaminant.

- While the contaminant component of the phenol product
30 stream may be any compound that imparts undesired properties to the phenol product stream, generally, the contaminant compounds are those compounds yielded as reaction by-products from the production of phenol by the oxidation of cumene

followed by the decomposition of the resulting cumene hydroperoxide. One such contaminant of the phenol product stream is an aliphatic hydroxy carbonyl compound, such as, for example, hydroxyketone. The concentration of the
5 contaminant of the phenol product stream to be treated or purified can be in the range of from a contaminating concentration upwardly to 1 weight percent and, more typically, from 3 parts per million by weight (ppmw) to 10,000 ppmw, or from 5 ppmw to 5000 ppmw. Most typically,
10 the concentration of contaminant will be in the range of from 10 ppmw to 2000 ppmw.

The purified phenol product, or treated phenol product stream, can have a concentration of contaminant that is reduced below the concentration thereof in the phenol product
15 stream that is treated in accordance with the invention. At least a portion, and preferably a major portion, of the contaminant contained in the phenol product stream is either removed from the phenol product stream or converted by reaction to another compound as a reaction product. The
20 reaction product is preferably one that is more easily separable from phenol by conventional distillation methods than is the contaminant. The concentration of contaminant in the purified or treated phenol product is a non-contaminating concentration that is, generally, less than or 10 ppmw. It
25 is desired, however, for the concentration of contaminant of the purified or treated phenol product stream to be less than or 5 ppmw, but preferably, less than 3 ppmw. Most preferably, the contaminant concentration in the purified or treated phenol product is less than 1 ppmw or even at a
30 concentration that is not detectable.

The inventive method includes contacting, under suitable contacting conditions, the phenol product stream with an alumina supported, Group VIA metal composition that

preferably has a low silica content and, thereafter, yielding or otherwise providing a treated or purified phenol product as described herein. The catalyst is an important aspect of the invention in that it provides for a treated or purified
5 phenol product having a reduced concentration of contaminants; but, moreover, it provides for the conversion of the hydroxyketone contaminants of the phenol product stream without the formation of significant quantities of undesirable benzofurans.

10 As used in this specification, the term "benzofuran" includes more than the benzene substituted heterocyclic furan compound commonly known as benzofuran but the term also includes, as well, substituted benzofuran compounds including, for example, methyl benzofuran, ethyl benzofuran,
15 dimethyl benzofuran, and diethyl benzofuran.

While benzofuran concentration in the treated phenol will generally depend upon the amount of hydroxyketones in the phenol product stream to be treated, the benzofuran concentration can be a suitably low concentration of less
20 than 5 ppmw and, preferably, less than 2 ppmw. Most preferably, the benzofuran concentration in the treated phenol is less than 1 ppmw.

The treatment catalyst of the invention comprises a Group VIA metal (Cr, Mo, or W) supported on an inorganic
25 oxide support that has a sufficiently low concentration of silica so as to provide for desired catalytic properties. As used in this specification, any references to the silica concentration as being "low" or "small" or in the "substantial absence" or the like means that the amount of
30 silica in the treatment catalyst composition is at a sufficiently low concentration so as to provide a treatment catalyst having desired catalytic properties for the inventive process. That is, to convert the hydroxyketone

contaminants of the phenol product stream without the formation of significant quantities of benzofurans. Such a concentration of silica is less than 25 weight percent of the total weight of the treatment catalyst composition, but
5 it is better for the amount of silica in the treatment catalyst to be less than 10 weight percent. Preferably, the silica content is less than 5 weight percent of the total weight of the treatment catalyst. Most preferred, however, the silica content of the treatment catalyst is less than 3
10 weight percent. Because of the practical difficulty of having a treatment catalyst with no silica, the lower concentration limit for silica in the treatment catalyst can be 0.1 weight percent, or 0.05 weight percent or even 0.01 weight percent of the total weight of the treatment catalyst.

15 The preferred inorganic support of the treatment catalyst composition is alumina and the preferred Group VIA metal is molybdenum, which is preferably in the form of an oxide. The treatment catalyst thus has a low concentration of silica, preferably having a substantial absence of silica,
20 and comprises alumina and a Group VIA metal, such as, for example, molybdenum.

The treatment catalyst of the instant invention is prepared by forming a calcined composite comprising a Group VIA metal supported on an inorganic oxide support other than
25 silica or a material having more than a low silica content. The inorganic oxide support comprises a solid usually containing a major proportion of alumina. Such materials are commonly known as refractory oxides and can include synthetic products as well as acid-treated clays. Examples of possible
30 synthetic refractory oxides include alumina, alumina-titania, alumina-magnesia, alumina-zirconia, and thoria. Preferred inorganic oxide supports are alumina refractory oxides, i.e., refractory oxides containing a substantial proportion of

alumina, e.g., at least 90 percent by weight of alumina. Any conventional catalytic grade of alumina including the beta or gamma forms can be used. Generally, the inorganic oxide support has a surface area of at least 10 m²/g and, preferably, the surface area is in the range of from 25 m²/g to 800 m²/g.

The Group VIA metal can be combined with the inorganic oxide support in any conventional method, such as, for example, by dry mixing, ion-exchange, coprecipitation, impregnation and the like. For example, a 10-100 mesh alumina can be impregnated with an aqueous solution containing a Group VIA metal salt, such as ammonium heptamolybdate or ammonium dimolybdate.

In a preferred embodiment, the treatment catalyst of the invention, comprising alumina and molybdenum oxide, is prepared by impregnating alumina with an aqueous molybdenum impregnation solution. The aqueous molybdenum solution consists of a water-soluble source of molybdenum oxide, such as, for example, ammonium heptamolybdate or ammonium dimolybdate, dissolved in water. Hydrogen peroxide may also be used to aid in solution preparation in some cases. For example, the molybdenum solution can be prepared by adding hydrogen peroxide to the solution in an amount in the range of from 0.1 to 1.0 mole of hydrogen peroxide per mole of molybdenum. Optionally, a suitable soluble amine compound such as monoethanolamine, propanolamine or ethylenediamine may be added to the molybdenum solution in order to aid in stabilization of the solution.

Following impregnation, the resulting material is dried and calcined. Drying is accomplished by conventional means. It may be carried out by forced draft drying, vacuum drying, air drying or similar means. Drying temperatures are not critical and depend upon the particular means utilized for

drying. Drying temperatures will typically range from 50°C to 150°C.

After drying, the material is calcined to produce the finished treatment catalyst. The material may be calcined in an oxidizing or neutral atmosphere, although air is preferred. However, if binders and/or lubricants are used, the material is heated in an oxygen-containing atmosphere, preferably air, in order to burn out the binders and lubricants. Calcining temperatures will typically range from 300°C to 600°C. Burn-out temperatures will depend on the concentration of oxygen in the burn-out atmosphere as well as the burn-out time involved. Typically, burn-out temperatures will range from 300°C to 600°C. Drying, calcining and burn-out may be combined in one or two steps. Most frequently the calcining and/or burn-out steps are combined using an oxygen-containing atmosphere.

The treatment catalyst typically contains from 1 percent by weight to 18 percent by weight, preferably from 5 percent by weight to 15 percent by weight, and more preferably from 6 percent by weight to 12 percent by weight Group VIA metal.

The process conditions under which the phenol product stream is contacted with the treatment catalyst will vary depending upon the particular contaminant contained in the phenol product stream and on such factors as the contaminant concentration and desired amount of removal. A particularly advantageous feature of the inventive method is that hydroxyketone can be efficiently removed from the phenol product stream using modest process conditions and without producing large amounts of undesirable benzofurans. The contacting temperature can be in the range of from 50°C to

250°C, preferably, from 90°C to 230°C and most preferably, from 100°C to 210°C.

While it is not a necessary feature of the invention for the phenol product stream to be in the liquid form when
5 contacted with the treatment catalyst, it can be desirable for it to be substantially in the liquid phase. Thus, the contacting pressure can be such that the phenol product stream is substantially liquid and upwardly to 100 psig. Preferably, the contacting pressure is in the range of from
10 10 psig to 60 psig.

The phenol product stream is contacted with the treatment catalyst by any suitable manner known in the art; but, preferably, the contacting occurs within a reaction zone. The contacting can be as a batch process step or,
15 preferably, as a continuous process step. In the latter operation, a solid bed of treatment catalyst, or a moving bed of treatment catalyst, or a fluidized bed of treatment catalyst can be employed. The contacting step, however, preferably is carried out within a reactor vessel which
20 defines a reaction zone and contains a fixed bed of the treatment catalyst. The reactor vessel, thus, provides means for contacting the phenol product stream with the treatment catalyst under such suitable contacting conditions as, for example, herein described, and for yielding a treated phenol
25 product stream.

The flow rate at which the phenol product stream is charged to the reaction zone is such as to provide a weight hourly space velocity ("WHSV") in the range of from greater than zero to 1000 hour⁻¹. The term "weight hourly space
30 velocity," as used herein, shall mean the numerical ratio of the rate at which the phenol product stream is charged to the reaction zone in pounds per hour divided by the pounds of

treatment catalyst contained in the reaction zone to which the phenol product stream is charged. The preferred WHSV of the phenol product stream to the reaction zone can be in the range of from 0.1 hour⁻¹ to 250 hour⁻¹, preferably, from 0.2 hour⁻¹ to 100 hours⁻¹, and most preferably, from 0.25 hour⁻¹ to 25 hours⁻¹.

Now referring to FIG. 1 is a schematic representation of the phenol purification reaction system 10 which includes Reactor 12. Reactor 12 defines a reaction zone that contains a treatment catalyst 14. Reactor 12 is equipped with an inlet 16 and an outlet 18 and provides means for contacting a phenol stream, having a contaminating concentration of hydroxyketone, with treatment catalyst 14 under such suitable contacting conditions as to convert a portion of the hydroxyketone to another compound. The phenol stream is introduced into the reaction zone defined by reactor 12 by way of conduit 20 which is operably connected to inlet 16 so as to provide fluid flow communication with the reaction zone. A purified phenol stream is yielded as a reactor effluent through outlet 18 and conduit 22. Conduit 22 is operably connected to outlet 18 so as to provide for fluid flow communication with the reaction zone.

EXAMPLES

Examples 1-4 describe the experimental procedure used to measure the effectiveness of a low silica content alumina material, especially when such a material is used as a support in combination with molybdenum, in treating a phenol product that contains a contaminating concentration of hydroxyketones. These Examples show that alumina having a low silica content can be effectively used to convert the hydroxyketones contained in the phenol product without an excess production of benzofuran by-products.

In the following Examples 1-4 a pure, anhydrous phenol was used which was collected from a side-draw product stream of a phenol distillation column of a commercial process for manufacturing phenol from cumene. Feeds for each of the
5 examples were prepared by adding small amounts of hydroxyketone impurities using available reagents. The phenol feed was then contacted in the liquid phase by stirring with a catalyst in the amount of 2 percent based on phenol weight for a period of time and at temperatures in the
10 range of 50-150°C. The reaction product mixture was then cooled, filtered, and analyzed by gas chromatography for the individual hydroxyketones and the corresponding benzofuran derivatives. The alumina used for the catalyst contained less than 3 weight percent silica.

15

Example 1 (8% Mo on alumina γ -alumina containing 1-2% dispersed silica)

A feed containing 990 ppm hydroacetone (HA or acetol), 520 ppm of 1-hydroxy-2-butanone (1HB), and 490 ppm of 3-
20 hydroxy-2-butanone (3HB or acetoin), was prepared from pure phenol and contacted for 2 hours at 145°C with an alumina catalyst containing approximately 8 percent molybdenum. The catalyst was previously activated and dried. Conversion of hydroxyketones averaged 98, 98, and 100 percent for HA, 1HB,
25 and 3HB, respectively, for three separate experiments. Approximately 6 percent of the HA was converted to 2-methyl benzofuran, 3 percent of the 1-HB was converted to 2-ethyl benzofuran, and 3 percent of 3-HB was converted to 1,3-dimethyl benzofuran.

30

Example 2 (4% Mo on γ -alumina containing 1-2% dispersed silica)

A feed containing 990 ppm hydroacetone (HA or acetol),
5 520 ppm of 1-hydroxy-2-butanone (1HB), and 490 ppm 3-hydroxy-
2-butanone (3HB or acetoin), was prepared from pure phenol
and contacted for 2 hours at 145°C with an alumina catalyst
containing approximately 4 percent molybdenum. The catalyst
was previously activated and dried. Conversion of
10 hydroxyketones averaged 84, 87 and 98 percent for HA, 1HB,
and 3HB, respectively, for three separate experiments. The
corresponding benzofuran selectivities averaged approximately
6, 3, and 2.5 percent.

15 Example 3 (alumina only)

A feed containing 990 ppm HA, 520 ppm of 1HB, and 490
ppm of 3HB was prepared from pure phenol and contacted for 2
hours at 145°C with an alumina catalyst containing no
molybdenum and which had been previously activated and dried.
20 Conversion of hydroxyketones were 18, 15, and 8 percent for
HA, 1HB, and 3HB, respectively. The corresponding benzofuran
selectivities were approximately 2, 0.5, and 2 percent.

Example 4 (blank - heat but no catalyst)

25 A feed containing 990 ppm HA, 520 ppm of 1HB and 490 ppm
of 3HB was prepared from pure phenol and heated for 2 hours
at 145°C without addition of a catalyst. Conversion of
hydroxyketones averaged 5, 5, and 7 percent for HA, 1HB, and
3HB, respectively, for three separate experiments. The
30 corresponding benzofuran selectivities averaged approximately
3, 0.1, and 3 percent.

The following table summarizes the results from the above tests.

Table I: Conversion of the Hydroxyketone Contained in a Phenol Product Using Different Catalysts

	% Conversion of hydroxyketones			% Selectivity to benzofuran		
	HA	1HB	3HB	HA	1HB	3HB
8% Mo on alumina	98	98	100	6	3	3
4% Mo on alumina	84	87	98	6	3	2.5
alumina only	18	15	8	2	0.5	2
no catalyst	5	5	7	3	0.1	3

The conversion data presented in Table I above show the advantages from using either a low silica content alumina or molybdenum supported on a low silica content alumina in the treatment of a phenol product that contains a concentration of hydroxyketone when compared to the use of no treatment catalyst. As can be observed, the conversion of hydroxyketones using the catalyst was better than using no catalyst. Also, the selectivity to benzofuran was very low and, in most cases, 3 percent or less. The molybdenum/alumina catalysts provided significantly better conversion of hydroxyketones than the alumina only catalyst, and the molybdenum/alumina catalysts still provided for low selectivity to benzofuran.

C L A I M S

1. A method, comprising:
purifying a phenol product, comprising phenol and a
contaminating concentration of an hydroxyketone, by
contacting, under suitable contacting conditions, said
phenol product with a treatment catalyst having a low
silica content and further comprising alumina and a
Group VIA metal.
2. A method according to claim 1 wherein the amount of
phenol in said phenol product is in the range of from 95
weight percent upwardly to 100 weight percent and said
contaminating concentration is in the range exceeding 3
ppmw.
3. A method according to claim 1 or 2 wherein said
contacting conditions include a contacting temperature
in the range of from 50°C to 250°C and a contacting
pressure upwardly to 100 psig.
4. A method according any of claims 1 to 3 wherein said
treatment catalyst has a concentration of silica less
than 25 weight percent of the treatment catalyst.
5. A method according to any of claims 1 to 4 wherein said
Group VIA metal is molybdenum which is present in the
treatment catalyst in an amount in the range of from 1
percent by weight to 18 percent by weight of the
treatment catalyst.
6. A method according to any of claims 1 to 5 further
comprising yielding a treated phenol product having a
concentration of said hydroxyketone that is reduced
below the concentration thereof in said phenol product.
7. A method according to claim 6 wherein said concentration
of said hydroxyketone in said treated phenol product is
less than 3 ppmw.

8. A method according to any of claims 1 to 7 wherein said treatment catalyst consists essentially of alumina and a Group VIA metal.
9. A method of purifying a phenol stream according to claim 1 comprising:
5 providing a reactor having an inlet and an outlet and which defines a reaction zone containing a low silica-containing treatment catalyst comprising alumina and a Group VIA metal;
10 introducing said phenol stream into said reaction zone through said inlet;
operating said reaction zone under suitable reaction conditions to convert at least a portion of said hydroxyketone in said phenol stream to another compound;
15 and
removing a purified phenol stream from said reaction zone as a reactor effluent through said outlet.
10. A reactor system useful for the method according to claim 1 said reactor system comprises:
20 a reactor having an inlet and an outlet and which defines a reaction zone containing phenol and a low silica-containing catalyst comprising alumina and a Group VIA metal.
11. A high purity phenol composition prepared according to the method of claim 1, comprising:
25 at least 95 weight percent phenol and less than 5 ppmw benzofuran.
12. A high purity phenol composition according to claim 11 wherein said phenol is present in said high purity
30 phenol composition in an amount of at least 98 weight percent, preferably 99 weight percent, of the total weight of said high purity phenol composition, and wherein said benzofuran is present in said high purity

phenol composition in an amount of less than 2 ppmw,
preferably less than 1 ppmw.