

- 1 -

PROCESS FOR PRODUCING HIGHLY PURE PHENOL

Detailed Description of the Invention:

Industrial field of the invention

5 The present invention relates to a process
for producing a highly pure phenol, which comprises
removing impurities contained in a crude phenol
obtained from an acid-decomposition product of cumene
hydroperoxide. More specifically, it relates to a
10 process for producing a highly pure phenol, which
comprises converting impurities contained in the above
crude phenol into high-boiling compounds without
causing the substantial loss of useful substances
contained in the crude phenol, and recovering a phenol
15 by distillation.

Prior art

As an industrial process, there is known a
process for producing a phenol in which cumene
hydroperoxide obtained by oxidation of cumene is acid-
20 decomposed. The acid-decomposition product obtained by
this process contains cumene, phenol, α -methylstyrene
and acetone as main components and a small amount of
by-products. Meanwhile, a phenol is used as a raw
material for producing diphenylolpropane, poly-
25 carbonate, etc., and the phenol as a raw material for
these is required to have a high purity.

As far as the phenol for the above use is
concerned, the content of hydroxyacetone (HA) as one of
impurities is required to be 30 ppm or less, preferably
30 10 ppm or less, and the total amount of aliphatic and
aromatic carbonyl compounds (total carbonyl amount)
other than HA is required to be 100 ppm or less,
preferably 50 ppm or less.

For obtaining a highly pure phenol satisfying
35 the above-described quality, it is general practice to
carry out the following treatment for removing
impurities. That is, a crude phenol, which is obtained



- 2 -

by removing a most part of low-boiling substances such as acetone, cumene, water and α -methylstyrene and a most part of high-boiling substances such as acetophenone and α -dimethylphenylcarbinol from a
5 neutralized acid-decomposition product by fractional distillation, is further purified to remove aliphatic carbonyl compounds such as hydroxyacetone (HA) and aromatic carbonyl compound such as α -phenylpropionaldehyde.

10 In conventional methods for producing a highly pure phenol, for example, Japanese Patent Publication No. 11,664/1962 discloses a method in which a crude phenol (containing 200 ppm of hydroxyacetone) is catalytically treated with an active alumina catalyst
15 at 360° C to allow the hydroxyacetone to react with a phenol to convert it into 2-methylbenzofuran (2-MBF), and phenol and the 2-methylbenzofuran are separated from each other by steam distillation. Further, Japanese Patent Publication No. 1,289/1979 discloses a
20 method using an active alumina for purifying crude cresols.

Further, Japanese Patent Publication No. 12,250/1967 discloses a method in which a crude phenol is catalytically treated with a silica-alumina catalyst
25 at 150 to 250° C to convert carbonyl compounds into other compounds, and they are separated from a phenol by steam distillation. Furthermore, British Patent 1,231,991 discloses a method in which a crude phenol containing no water is catalytically treated with an
30 acidic ion-exchange resin catalyst at 80 to 150° C to convert carbonyl compounds to other compounds, and they are separated from a phenol by steam distillation.

The above methods are all directed to a method in which impurities are converted to other
35 compounds. The defect with these methods is that phenol and α -methyl styrene as useful components react with impurities or respectively undergo condensation to



- 3 -

form cumylphenol or dimer of olefin and thus, the useful components are wasted.

Summary of the invention

It is a first object of the present invention
5 to provide a process for producing a highly pure phenol, which permits the selective conversion of impurities to be removed to other high-boiling compounds without entailing the substantial loss of useful components contained in a crude phenol obtained by
10 acid-decomposition of cumene hydroperoxide.

It is a second object of the present invention to provide a practical process for producing a highly pure phenol satisfying the quality required as an industrial raw material from the above crude phenol.

15 Means for solving problems

According to studies of the present inventors, the above objects and advantages of the present invention are achieved by catalytically treating the above crude phenol in the presence of an
20 acidic γ -alumina having a specific surface area to be specified later and an acid strength to be specified later.

That is, according to the present invention, there is provided a process for producing a highly pure
25 phenol from a crude phenol which is obtained from an acid-decomposition product of cumene hydroperoxide and has an α -methylstyrene content of 15 % by weight or less, the process comprising:

(1) catalytically treating the above crude
30 phenol in the presence of an acidic γ -alumina catalyst having a specific surface area of 80 to 400 m²/g and an acid strength, according to Hammett's acidity function (H₀), of $3 \leq H_0 \leq 6.8$ to convert aliphatic and aromatic carbonyl compounds contained in the crude phenol into
35 high-boiling compounds without causing the substantial formation of a dimer of α -methylstyrene contained in the crude phenol, and then,



- 4 -

(2) recovering a phenol by distillation of a catalytic treatment product obtained in step (1).

The present invention will be detailed hereinafter.

5 The crude phenol as an object to be purified in the present invention refers to a crude phenol which is obtained by acid-decomposing cumene hydroperoxide obtained by oxidation of cumene, neutralizing the acid-decomposition product and removing a most part of
10 low-boiling substances such as acetone, cumene, water and α -methylstyrene and a most part of high-boiling substances such as acetophenone and α -dimethylphenylcarbinol from the neutralized product by fractional distillation. The crude phenol contains
15 phenol as a main component and α -methylstyrene in an amount of 15 % by weight or less, preferably 0.05 to 10 % by weight.

 The above crude phenol contains, as impurities, aliphatic carbonyl compounds such as
20 hydroxyacetone (HA) and others, aromatic carbonyl compounds such as α -phenylpropionaldehyde and others, and other compounds. In the process of the present invention, not only hydroxyacetone but also other impurities such as aliphatic and aromatic carbonyl
25 compounds and others can be selectively converted to high-boiling compounds and easily removed.

 The acidic γ -alumina used as a catalyst in the present invention is an intermediate compound formed when aluminum hydroxide ($\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) is
30 decomposed under heat, and it has a tetragonal crystal structure. This acidic γ -alumina is clearly distinguishable from an α -alumina having a trigonal crystal structure.

 The acidic γ -alumina used in the present
35 invention has a specific surface area of 80 to 400 m^2/g , preferably 150 to 300 m^2/g , and an acid strength, according to Hammett's acidity function (H_0), of



- 5 -

3 $\leq$ Ho $\leq$ 6.8, preferably 3.3 $\leq$ Ho $\leq$ 6.8. The Hammett's acidity function (Ho) is an index showing the acidity (proton donation capability) of a relatively highly concentrated acid, and a greater negative value of Ho
5 shows greater proton donation capability and a higher acidity. The acidic γ -alumina used in the present invention has an acid strength of 3 $\leq$ Ho $\leq$ 6.8, i.e., has a low acidity.

The Hammett's acidity function and its
10 measurement method are explained in J. Am. Chem. Soc., 54 2721 (1932) and Physical Organic Chemistry, Chapter 9, McGrawHill Books Co., Inc., New York (1940).

In the present invention, the acidic γ -alumina having the above-specified specific surface
15 area and acid strength may be used in the form of a powder, while it may be also used in the form of any one of general solid catalysts, e.g., particles, pellets, and the like.

In the process of the present invention, the
20 aliphatic or aromatic carbonyl compounds contained in the crude phenol are converted to high-boiling compounds by bringing the crude phenol into contact with the above acidic γ -alumina. The crude phenol which is to be brought into contact, i.e.,
25 catalytically treated, with the γ -alumina may be in any one of a liquid phase and a gaseous phase. The catalytic treatment is carried out at a temperature of 40° C or higher, preferably at a temperature between 150 and 300° C, under atmospheric pressure or elevated
30 pressure. Although not specially limited, the time for the catalytic treatment is properly 1 to 60 minutes. In general, the catalytic treatment is preferably carried out at a high temperature under a high pressure for a short period of time, or at a low temperature
35 under a low pressure for a long period of time.

The method of the catalytic treatment is not specially limited, and any method such as a batch



- 6 -

method, a continuous method, etc., may be employed. However, it is industrially preferred to employ a method in which the crude phenol in a liquid or gaseous phase, particularly the vaporized crude phenol, is
5 catalytically treated by passing the crude phenol through a layer packed with the catalyst. In this case, the crude phenol may be diluted with an inert diluent such as nitrogen and cumene. The layer packed with the catalyst may be a layer of a fluidized bed or
10 fixed bed. When the crude phenol in a liquid phase or gaseous phase is flowed through the layer packed with the catalyst, the liquid hourly space velocity (LHSV) is properly 12 to 1 hr⁻¹.

Due to the contact with the catalyst, the
15 aliphatic carbonyl compounds such as hydroxyacetone, the aromatic carbonyl compounds such as α -phenylpropionaldehyde and other impurities, contained in the crude phenol, are converted to high-boiling compounds. In this catalytic treatment, the useful
20 components such as phenol and α -methylstyrene remain almost intact. This is presumably because the above γ -alumina as the catalyst has a proper specific surface area and a proper acid strength.

The impurities contained in the crude phenol
25 have been converted to high-boiling compounds due to the catalytic treatment, and can be therefore easily separated by distillation, whereby a highly pure phenol can be obtained. The distillation can be carried out by any one of steam distillation, organic solvent
30 extractive distillation and the like.

The steam distillation can be carried out, for example, by the method described in Japanese Laid-Open Patent Publication No. 20,239/1984, in which the crude phenol is distilled in the presence of water to
35 separate the crude phenol into a mixture which comprises phenol containing impurities and water, and a phenol which is substantially free of impurities, and



- 7 -

the mixture and the phenol substantially free of impurities are separately recovered. The above method is employed for producing phenol according to the cumene process, and is known per se.

5 The organic solvent extractive distillation can be carried out by a method using polyalkylene glycol or its ether as is described in Japanese Patent Publication No. 1258/1975.

10 When the above steam distillation or organic solvent extractive distillation is carried out, α -methylstyrene contained in the crude phenol can be nearly entirely removed.

 According to the process of the present invention, a highly pure phenol having a remarkably
15 decreased content of impurities typified by carbonyl compounds can be obtained by catalytically treating the crude phenol with the acidic γ -alumina and then distilling the so-treated product. The so-obtained highly pure phenol can meet with the quality
20 requirements of a variety of starting materials. In particular, the contents of hydroxyacetone and other carbonyl compounds are sufficiently as low as required. The highly pure phenol obtained according to the process of the present invention may be further
25 purified by other treatment as required.

Examples

 The present invention will be explained more specifically by reference to Examples, in which various carbonyl compounds as impurities were quantitatively
30 measured by gas chromatography, etc., to determine the conversions of the impurities before and after the treatment.

Example 1

 An acid-decomposition product of cumene
35 hydroperoxide was neutralized and distilled to remove a most part of low-boiling substances such as acetone, water, cumene and α -methylstyrene and a most part of



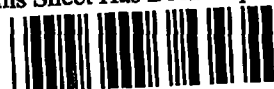
- 8 -

high-boiling substances such as acetophenone and α -dimethylcarbinol. The resultant crude phenol had a purity of 98 % by weight or less and contained 0.3 % by weight of hydroxyacetone (HA), 1 to 2 % by weight of α -methylstyrene and 0.2 % by weight (as a total carbonyl content calculated as mesityl oxide) of carbonyl compounds other than HA.

The above-obtained crude phenol in a vapor phase was allowed to pass a fixed bed packed with acidic γ -alumina catalyst having a specific surface area of $280 \text{ m}^2/\text{g}$ and an acidity function of $+3.3 \leq \text{H}_0 \leq 6.8$, at 280°C at LHSV of 2 hr^{-1} . The resultant product was analyzed to show an HA content of 5 ppm or less and a total carbonyl content of 30 ppm or less. Further, the amount of formed 2-methylbenzofuran was only 10 mol% of HA, and the formation of neither a dimer of α -methylstyrene nor cumylphenol was found.

Water in an amount of 15 % by weight was added to the crude phenol having an HA content of 15 ppm or less and a total carbonyl content of 30 ppm or less, obtained in the above, and the mixture was subjected to steam distillation under atmospheric pressure to distill off hydrocarbons such as α -methylstyrene containing 5 % by weight of a phenol from a column top. A crude phenol aqueous solution having an α -methylstyrene content of only 5 ppm or less was obtained as a column bottom product. Then, the crude phenol was subjected to batch distillation under reduced pressure to obtain water and a purified phenol as a column top product. As a result, there was obtained a purified phenol having a total impurity content of 30 ppm or less, an HA content of 2 ppm or less, a total carbonyl content of 20 ppm, a solidifying point of 40.85°C , a hue (Hasen number) of 5 or less and a sulfonation coloring value of 95 %.

The hue (Hasen number) of the phenol refers to a value determined by comparing the color of the



- 9 -

above-obtained phenol with colors of standard solutions of ASTM (American Society for Testing and Materials). The sulfonation coloring value was determined as follows. 20 Milliliters of a sample phenol was warmed
5 on a hot water bath at 45° C for 10 minutes, and 20 ml of concentrated sulfuric acid was quickly mixed. Then, the mixture was allowed to stand at room temperature for 1 minute and in water for 5 minutes. Thereafter, the mixture was charged into a 20 mm cell, and measured
10 for transmittance at 532 μ m with a photoelectric colorimeter, and the measurement value is expressed by percentage. The greater the value is, the higher the phenol quality is. The total carbonyl content was analyzed as follows. The phenol was colored by adding
15 2,4-dinitrophenylhydrazine, and the color of the colored phenol was compared with standard color hues based on mesityl oxide to determine the total carbonyl content as a mesityl oxide.

Example 2

20 The same acidic γ -alumina as that used in Example 1 was impregnated with an aqueous solution containing 5 % by weight of ammonium fluoride, and dried under a nitrogen current to obtain an acidic γ -alumina having a fluorine content of 1.5 % by weight.
25 The so-obtained γ -alumina had a specific surface area of 240 m²/g and an acidity function of $+4.0 \leq H_0 \leq 6.8$. Then, the procedures of Example 1 were repeated except that the γ -alumina was replaced with the above-obtained acidic γ -alumina and that the LHSV was
30 changed to 1 hr⁻¹. The resultant product was analyzed to show an HA content of 5 ppm or less and a total carbonyl content of 20 ppm or less. Further, the amount of formed 2-methylbenzofuran was 5 mol% of HA, and α -methylstyrene remained intact.
35 Then, diethylene glycol in the same amount as that of the crude phenol was added to the crude phenol, and the mixture was subjected to batch distillation



- 10 -

under reduced pressure to obtain hydrocarbons and a purified phenol as a column top product. As a result, there was obtained a highly pure phenol having a total impurity content of 20 ppm, an HA content of 2 ppm or less and a total carbonyl content of 15 ppm. The so-obtained phenol had a solidifying point of 40.85° C, a hue (Hasen number) of 5 or less and a sulfonation coloring value of 98%.

Comparative Example 1

10 Example 1 was repeated except that the γ -alumina was replaced with a hydrogen-exchange mordenite type zeolite having an acidity function of $\text{H}_0 \leq -8.2$. As a result, the amount of formed 2-methylbenzofuran was 70 mol% of HA, and 90 % of α -methylstyrene was
15 polycondensed or polymerized.

Comparative Example 2

 Example 1 was repeated except that the γ -alumina was replaced with cation-exchange resin (Amberlyst-15R) and that the treatment temperature was
20 changed to 120° C. As a result, the amount of formed 2-methylbenzofuran was 90 mol% of HA, and the total amount of α -methylstyrene was polycondensed or polymerized.

Comparative Example 3

25 Example 1 was repeated except that the γ -alumina was replaced with a γ -alumina catalyst having a specific surface area of 92 m²/g and an acidity function of $-3.0 \leq \text{H}_0 \leq +1.5$. As a result, 90 mol% of hydroxyacetone was converted to 2-methylbenzofuran, or
30 phenol was consumed. Further, 50 % of α -methylstyrene was dimerized or converted to cumylphenol.

Comparative Example 4

 The crude phenol having an HA content of 0.3% by weight and a total carbonyl content of 0.2% by
35 weight which was obtained in Example 1, was subjected to the same distillation as that of Example 2. As a result, the so-obtained phenol had a total impurity



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- 11 -

content of 2,100 ppm, an HA content of 1,800 ppm, a total carbonyl content of 1,500 ppm and a solidifying point of 40.7° C.

Effect of the invention

5 According to the present invention, aliphatic and aromatic carbonyl compounds can be converted to high-boiling compounds, while inhibiting the substantial loss of phenol and α -methylstyrene as useful components, by catalytically treating the crude phenol
10 with an acidic γ -alumina catalyst having the specified specific surface area and the specified acid strength. As a result, phenol can be easily separated, and a highly pure phenol can be produced.

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- 12 -

WHAT IS CLAIMED IS:

1. A process for producing a highly pure phenol from a crude phenol which is obtained from an acid-decomposition product of cumene hydroperoxide and has
5 an α -methylstyrene content of 15 % by weight or less, the process comprising:
 - (1) catalytically treating the above crude phenol in the presence of an acidic γ -alumina catalyst having a specific surface area of 80 to 400 m²/g and an
10 acid strength, according to Hammett's acidity function (Ho), of $3 \leq \text{Ho} \leq 6.8$ to convert aliphatic and aromatic carbonyl compounds contained in the crude phenol into high-boiling compounds without causing the substantial formation of a dimer of α -methylstyrene contained in
15 the crude phenol, and then,
 - (2) recovering a phenol by distillation of a catalytic treatment product obtained in step (1).
2. A process according to claim 1, wherein the crude phenol is catalytically treated at a temperature
20 between 150 and 300° C.
3. A process according to claim 1, wherein the crude phenol is catalytically treated for 1 to 60 minutes.
4. A process according to claim 1, wherein the
25 acidic γ -alumina has an acid strength of $3.3 \leq \text{Ho} \leq 6.8$ according to acidity function Ho.
5. A process according to claim 1, wherein the acidic γ -alumina has a specific surface area of 150 to 300 m²/g.
- 30 6. A process according to claim 1, wherein the crude phenol is in a gaseous phase and catalytically treated with the acidic γ -alumina.
7. A process according to claim 1, wherein the crude phenol is in a liquid phase and catalytically
35 treated with the acidic γ -alumina.
8. A process according to claim 1, wherein the catalytic treatment product is recovered by steam

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- 13 -

distillation or organic solvent extractive
distillation.

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