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(1PDS)

PROCESS FOR PURIFYING CRUDE 1,4-BUTANEDIOL

FIELD OF THE INVENTION

This invention relates to a process for purifying crude 1,4-butanediol (hereinafter sometimes referred to simply as crude 1,4-BG). More particularly, it relates to an improvement in the purification process which comprises hydrogenating crude 1,4-BG.

BACKGROUND OF THE INVENTION

1,4-Butanediol is a compound which is useful as the starting material in synthesizing polyester resins, γ -butyrolactone, tetrahydrofuran, etc.

A known process for producing 1,4-butanediol comprises, for example, reacting butadiene, acetic acid and oxygen in the presence of a palladium catalyst to thereby give diacetoxybutene, then hydrogenating diacetoxybutene with the use of a palladium catalyst or a nickel catalyst to thereby give diacetoxybutane, and then hydrolyzing the diacetoxybutane thereby giving 1,4-butanediol (JP-A-52-7909 (published on January 21, 1977), JP-A-52-133912 (published on November 9, 1977), JP-A-7-82191 (published on March 28, 1995); the term "JP-A" as used herein means an "unexamined published Japanese patent application").

The 1,4-butanediol thus obtained is contaminated with various impurities such as 2-(4'-hydroxybutoxy)tetrahydrofuran, 2-(4'-oxobutoxy)tetrahydrofuran and 1,4-di-(2'-tetrahydrofuroxy)butane which cannot be eliminated by



distillation.

It has been found that 1,4-butanediol contaminated with these impurities is unsuitable as the starting material for producing resins, fibers, etc., since it causes the coloration of products or insufficient reactivity in the production process. Therefore, various proposals have been made to eliminate these impurities.

For example, JP-A-61-197534 (published on September 1, 1986) has proposed a process for purifying crude 1,4-butanediol which comprises hydrogenating crude 1,4-butanediol containing at least one of 2-(4'-hydroxybutoxy)tetrahydrofuran, 2-(4'-oxobutoxy)tetrahydrofuran and 1,4-di-(2'-tetrahydrofuroxy)butane in the presence of a hydrogenating catalyst. However, the activity of the hydrogenating catalyst is seriously reduced during prolonged continuous operation of this process due to the heavy impurities having high boiling point contained in the crude 1,4-butanediol, thus making it difficult to stably produce 1,4-butanediol of acceptable purity. To overcome this difficulty, JP-A-6-172235 (published on June 21, 1994) discloses a process wherein high-boiling compounds are separated by distillation and crude 1,4-butanediol obtained from the lower side stream of the distillation column is hydrogenated.

However, the improved process described in JP-A-6-172235 is not completely satisfactory, since the 1,4-butanediol produced by the process still contains about 0.2 % by



weight of 2-(4'-hydroxybutoxy)tetrahydrofuran (hereinafter sometimes referred to simply as BGTF), which is the major component of the impurities. Particularly during prolonged continuous operation of the process, there arises a problem that the content of BGTF exceeds 0.2 % by weight and is accumulated in the 1,4-butanediol product, thus making it impossible to produce 1,4-butanediol of high purity.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a purification process whereby the problem in the above-mentioned improved process described in JP-A-6-172235 is solved and highly pure 1,4-butanediol, which contains 0.2 % by weight or less of BGTF and 99.80 % by weight or more of 1,4-butanediol, can be obtained.

SUMMARY OF THE INVENTION

The present inventors have found that the crude 1,4-butanediol to be distilled according to the process of JP-A-6-172235 contains a fine powder of hydrogenating catalyst from the hydrogenation step in the process. When this hydrogenated 1,4-butanediol is supplied into the distillation column, the presence of catalyst causes BGTF to be formed from 1,4-butanediol in the distillation column, thus resulting in unacceptable levels of BGTF in the distilled product.

Accordingly, the present invention provides a process for purifying crude 1,4-butanediol obtained by hydrolyzing



diacetoxybutane which comprises the following purification steps (1) to (3):

(1) hydrogenating the crude 1,4-butanediol in the presence of a hydrogenating catalyst;

(2) removing a fine powder of the hydrogenating catalyst from the hydrogenation mixture; and

(3) distilling the hydrogenation mixture, from which the fine powder has been removed, in a distillation column to obtain 1,4-butanediol of high purity from the side stream of the distillation column.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a flow chart showing the purification steps of the present invention.

Fig. 2 is a flow chart showing the steps of prior art process for producing diacetoxybutane.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A preferred embodiment of the present invention will now be described in detail below.

1. Hydrolysis of Diacetoxybutane

The crude 1,4-butanediol employed as the starting material in the process of the present invention is the reaction product obtained from the hydrolysis of diacetoxybutane. Preferably, diacetoxybutane is obtained by hydrogenating diacetoxybutene, and diacetoxybutene is obtained by reacting butadiene, acetic acid and oxygen in the presence of a palladium catalyst (JP-B-55-45051 (published on



November 15, 1980), JP-B-55-16489 (published on May 2, 1980), JP-B-55-17016 (published on May 8, 1980); the term "JP-B" as used herein means an "examined Japanese patent publication").

Therefore, the diacetoxybutane to be hydrolyzed preferably comprises 1,4-diacetoxybutane as the major component, and preferably includes isomeric mixtures of 1,4-diacetoxybutane with 3,4-diacetoxybutane, 1,3-diacetoxybutane, etc. and optionally containing monohydroxyacetoxybutane, etc., depending on the production and purification processes. It may also be preferred in some cases to use a mixture of 1,4-diacetoxybutane, 1,4-monohydroxyacetoxybutane and 1,4-butanediol which is obtained by performing the hydrolysis to a certain extent and then removing water and acetic acid from the reaction mixture.

In the hydrolysis reaction of diacetoxybutane, it is preferred to use a cation exchange resin as the catalyst to achieve a high rate of hydrolysis with little formation of by-products such as tetrahydrofuran (hereinafter referred to simply as THF).

More preferably, a strongly acidic cation exchange resin of the sulfonic acid type, made of a styrene/divinylbenzene copolymer as the base, is used. The cation exchange resin may preferably be either a gel resin or a porous resin.

Particularly preferred examples of such strongly acidic cation exchange resin of the sulfonic acid type include gel type resins sold under the trade marks SK1B,



SK104, SK106, SK110 and SK112 and porous type resins sold under the trade marks PK208, PK216, PK228, RCP160H, RCP170H and RCP145H (manufactured by Mitsubishi Chemical Corporation).

The hydrolysis of diacetoxabutane is preferably performed in a temperature range of from about 30 to about 110 °C, more preferably from about 40 to about 90 °C.

The reaction pressure in the hydrolysis of diacetoxabutane is not particularly restricted. However, the reaction is preferably carried out under a pressure ranging from about atmospheric pressure to about 10 kg/cm²·G (0.1 to 1.08 MPa).

With respect to the ratio of diacetoxabutane to water, water, which serves both as a starting material and the solvent, is preferably employed in at least a stoichiometric amount. More preferably, water is used in an amount of from about 2 to about 100 mol, most preferably from about 4 to about 50 mol, per mol of diacetoxabutane.

Although the hydrolysis reaction of diacetoxabutane may be performed in various manners, it is preferred to use a system wherein diacetoxabutane and water are passed through a fixed bed packed with an acidic cation exchange resin.

2. Crude 1,4-Butanediol

Preferably, low-boiling compounds and high-boiling compounds are removed from the hydrolysis product obtained by the above process to thereby give crude 1,4-BG. These compounds can be distilled off by known methods, for example,



those described in JP-A-6-172235.

Referring to Fig. 1, it is preferred that the hydrolysis product obtained by hydrolyzing diacetoxybutane in a hydrolysis reactor (1), is supplied into a first distillation column (2) and low-boiling fractions (4) comprising water and acetic acid are substantially completely distilled off from the column top, while the bottom settlings (5) are supplied into a second distillation column (3).

The water and acetic acid (4) distilled off from the top of column (2) are preferably further distilled and purified to thereby obtain water and acetic acid of sufficient purity to be employed as the starting materials in the hydrolysis of diacetoxybutane and the acetoxylation of butadiene, respectively.

The first distillation column (2) is preferably operated at a theoretical plate number of from about 2 to about 10, under a column top pressure of from about 50 to about 200 mmHg (6.6 to 26.7 kPa), at a column bottom temperature of from about 100 to about 200 °C (more preferably from about 120 to about 180 °C) and a reflux ratio of from about 0.01 to about 1 (more preferably from about 0.1 to about 0.5).

From the bottom settlings (5) supplied into the second distillation column (3), a fraction containing diacetoxybutane and mainly 1,2- or 1,3-isomers of hydroxy-acetoxybutane is distilled off from the column top (7), a



fraction primarily containing the 1,4-monomer of hydroxy-acetoxabutane is distilled off from the upper side stream (6) and is recirculated into the hydrolysis reactor (1), while crude 1,4-BG is removed as a vapor phase from the lower side stream (8).

The upper side stream (6) is preferably located above the inlet through which the liquid (5) is supplied from the first distillation column (2), while the lower side stream (8) is preferably located below the inlet.

The bottom settlings (9) of the second distillation column (3), which contain a large amount of high-boiling compounds, may preferably be purged from the reaction system. Alternatively, bottom settlings (9), usually containing 1,4-butanediol as the major component, may preferably be supplied into a fourth distillation column (10). The vapor distillate (11) from column (10) is then preferably circulated into the second distillation column (3) to thereby improve the yield of 1,4-butanediol.

The second distillation column (3) is preferably operated at a theoretical plate number of from about 50 to about 150, under a column top pressure of from about 50 to about 200 mmHg (6.6 to 26.7 kPa), at a column bottom temperature of from about 150 to about 220 °C and a reflux ratio of from about 0.1 to about 10. From distillation column (3), the crude 1,4-BG fraction (8) is supplied into hydrogenation reactors (12, 12').



3. Purifying Treatment

The crude 1,4-BG (8) obtained from distillation column (3) preferably contains from about 97 to about 98 % of 1,4-butanediol together with 2 to 3 % of impurities such as 4-hydroxy-1-butanal and 1,4-butanediol which are mono- and dialdehydes respectively of 1,4-butanediol; 2-(4'-hydroxy-butoxy)tetrahydrofuran (BGTF), 2-(4'-oxobutoxy)tetrahydrofuran (BDTF) and 1,4-di-(2'-tetrahydrofuroxy)butane (BGDTF) which are adducts of dihydrofuran (i.e., the dehydration/cyclization products of the above-mentioned aldehydes) and 1,4-butanediol and high-boiling compounds. These impurities are converted into 1,4-butanediol or compounds easily separated from 1,4-butanediol by distillation (tetrahydrofuran, butanol and ditetramethylene glycol) by step (1) of the present invention wherein the crude 1,4-butanediol is hydrogenated.

As the hydrogenating catalyst in the hydrolysis of crude 1,4-butanediol according to the invention, use can be made of catalysts commonly employed in hydrogenation. Preferred examples of these catalysts include precious metals such as Pd, Pt, Ru and Rh, with Pd and Ru being particularly preferred.

It is not necessary that hydrogen (13, 13') used in the hydrogenation of crude 1,4-BG be pure. The hydrogen may be diluted with an inert gas and a saturated hydrocarbon.

The hydrogenation of crude 1,4-BG is preferably



performed under a hydrogen pressure of from about 5 to about 20 kg/cm² and at a reaction temperature of from about 40 to about 250 °C, more preferably from about 80 to about 180 °C.

It may be preferred that the hydrogenation step (1) of the process of the invention is performed by a multistage system, as shown in Fig. 1, in which the hydrogenation of crude 1,4-BG is performed in first and second hydrogenation reactors 12 and 12' connected in series.

In step (2) of the process of the invention, the hydrogenation product (14) obtained from reactors 12 and 12' is subjected to gas/liquid separation with the use of a gas/liquid separator (15).

The liquid phase (16) obtained from gas/liquid separator (15) is then treated to remove the finely powdered hydrogenating catalyst.

In order to remove the fine powder of the hydrogenating catalyst from the hydrogenation product, the liquid phase (16) is preferably filtered through a porous plate or filter (17) packed with a filtering medium, etc.

It is preferred that the filtering medium is chemically resistant to 1,4-butanediol and is heat resistant to temperatures exceeding the hydrogenation temperature. The filter (17) is preferably selected from the group comprising porous plates made of sintered metals, porous plates made of carbon or graphite, filters made from alundum, silica, ceramics, etc., or filters packed with glass wool or



asbestos. It is particularly preferred that the filter comprise a glass wool filter or a porous sintered metal plate.

The pore size of the filter is preferably about 10 μm or less, more preferably from about 1 to about 5 μm .

In step (3) of the process of the invention, the hydrolysis mixture (18), from which the fine powder of the hydrogenating catalyst has been removed by filter (17), is supplied into a third distillation column (19) and 1,4-butanediol of high purity is obtained from the side stream (20) thereof.

The third distillation column (19) is operated at a theoretical plate number of from about 10 to about 100, under a column top pressure of from about 10 to about 100 mmHg, at a column top temperature of from about 100 to about 200 $^{\circ}\text{C}$ and a reflux ratio of from about 0.1 to about 10.

The 1,4-butanediol product is preferably distilled out from the lower side stream (20) of third distillation column (19), while low-boiling compounds (22) such as water, tetrahydrofuran and butanol are distilled off from the top of column (19). The high-boiling compounds (21) are drawn from the bottom of column (19). In some cases it may be preferred that the distillation is performed using a plurality of third distillation columns.

When oxygen enters third distillation column (19) during the above-mentioned distillation process, 2-hydroxy-



tetrahydrofuran, 4-hydroxybutylaldehyde, etc. are formed as by-products and are difficult to separate from 1,4-butanediol by distillation. Thus, the entry of oxygen into column (19) should preferably be minimized by regulating the oxygen pressure at the top of third distillation column (19) to about 10 mmHg or below, more preferably from about 0 to about 5 mmHg.

The following examples further illustrate preferred aspects of the present invention in greater detail. However, it is to be understood that the present invention is not restricted to the embodiments described therein. In the following examples, all "parts" and "%" are by weight.

Unless otherwise noted, the values given below are analytical data obtained by gas chromatography carried out 5 days after the initiation of the process, i.e., during steady operation of the process.

REFERENCE EXAMPLE

Into an acetoxylation reactor (101) were supplied 170 part/hr of butadiene, 3,000 part/hr of acetic acid which was contaminated with 0.8 % of 1,4-hydroxyacetoxybutane and 0.6 % of 1,2-hydroxyacetoxybutane, and 530 part/hr of oxygen as shown in Fig. 2. In the presence of a catalyst comprising 3 % of palladium and 0.6 % of tellurium supported on active carbon, the mixture was reacted under 9 MPa at 100 °C and degassed by gas-liquid separator (102) to thereby give a reaction product containing 12.5 % of 1,4-diacetoxybutene.

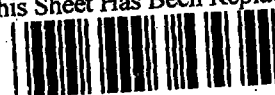


This reaction product was supplied into a first distillation column (103) at a rate of 3,100 part/hr. Water and portion of the acetic acid were distilled off from the column top at a rate of 250 part/hr, while the bottom settlings containing 74.8 % of 1,4-diacetoxybutene were drawn off at a rate of 580 part/hr.

The bottom settlings from the first column were supplied into a second distillation column (104) (practical plate number: 20) at a rate of 580 part/hr and distilled therein under the column top pressure of 2.7 kPa at a reflux ratio of 0.5. Thus, a solution containing 75.5 % of 1,4-diacetoxybutene was distilled off from the column top at a rate of 550 part/hr.

The diacetoxybutene fraction thus obtained was supplied into a hydrogenation reactor (105) packed with a palladium catalyst and a ruthenium catalyst and hydrogenation was performed under a hydrogen gas stream and a reaction pressure of 5 MPa and a temperature of 70 °C to thereby give a reaction mixture containing 75.6 % of 1,4-diacetoxybutane.

This reaction mixture was subjected to gas/liquid separation and then supplied into a third distillation column (106) (practical plate number: 20) at a rate of 550 part/hr. The mixture was then distilled therein under a column top pressure of 2.0 kPa at a reflux ratio of 0.25. Thus a solution containing 75.9 % of 1,4-diacetoxybutane as shown in Table 1 was distilled off from the column top at a rate of



520 part/hr.

EXAMPLE 1

The 1,4-diacetoxybutane-containing solution obtained above, having the composition shown in the first column of Table 1, was supplied into a hydrolysis reactor (1) packed with 100 l of a cation exchange resin SK1B (manufactured by Mitsubishi Chemical Corporation) at a rate of 520 part/hr together with 250 part/hr of a 28 % aqueous solution of acetic acid. Hydrolysis was then carried out at a temperature of 50 °C. The second column of Table 1 shows the composition of the hydrolysis product thus obtained, excluding water.

TABLE 1

<u>Component</u>	<u>Initial content (%)</u>	<u>Content in hydrolyzed product (%)</u>
1,4-diacetoxybutane	75.9	8.0
1,4-hydroxyacetoxybutane	5.2	32.5
1,4-butanediol	0.5	27.8
1,2-diacetoxybutane	8.3	0.7
1,2-hydroxyacetoxybutane	4.3	1.8
1,2-butanediol	0.2	4.7
acetic acid	2.2	20.4
others	3.4	4.1

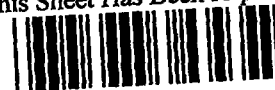
This hydrolysis product mixture in a hydrolysis reactor (1) was supplied into the first distillation column



(2) as shown in Fig. 1 and distilled therein. The first distillation column (2) was made of SUS 316 and had an inner diameter of 200 mm. This column was packed with a Raschig ring made of SUS 316 at a height of 3000 mm. A liquid inlet was provided 500 mm below the top of the pack layer. The first distillation column (2) was operated under a column top pressure of 70 mmHg, a column bottom temperature of 160 °C and a reflux ratio of 0.5. From the column top, water, acetic acid and a small amount of other low-boiling compounds were distilled off and the bottom settlings were supplied into the second distillation column (3).

The second distillation column (3) was made of SUS 304 and had an inner diameter of 100 mm. This column was packed with a McMahon Packing at a height of 5000 mm. A side stream outlet (6) was provided 1000 mm below the top of the pack layer and a liquid inlet was provided 1000 mm therebelow. Further, a vapor outlet (8) was provided 1000 mm below the liquid inlet. The bottom settlings from first distillation column (2) were distilled in second distillation column (3) under a column top pressure of 300 mmHg, a reflux ratio of 80 and a column bottom temperature of 210 °C.

From the column top, a fraction comprising 9.5 % of 1,2-diacetoxybutane, 25.2 % of 1,2-hydroxyacetoxybutane and 65.3 % of 1,2-butanediol was distilled off. From the side stream, another fraction comprising 0.4 % of 1,2-diacetoxybutane, 0.9 % of 1,2-hydroxyacetoxybutane, 2.4 % of 1,2-



butanediol, 15.9 % of 1,4-diacetoxybutane, 64.1 % of 1,4-hydroxyacetoxybutane and 11.4 % of 1,4-BG was taken out. This fraction was recirculated as a part of the starting materials into the above-mentioned hydrolysis reactor (1).

Further, crude 1,4-butanediol was taken out as a vapor phase (8) from the vapor outlet.

The above-mentioned crude 1,4-butanediol, which contained 2.05 % of BGTF and 0.1 % of impurities including BDTF, BGDTF and other high-boiling compounds, and had a carbonyl value of 6.2 mg·KOH/g and a purity of 97.5 %, was supplied at a rate of 1874 part/hr together with 0.5 part/hr of hydrogen into two hydrogenation reactors (12, 12') connected in series. Hydrogenation reactors (12, 12') were each 500 mm in inner diameter and 1300 mm in height and packed with a catalyst comprising 0.5 % of ruthenium supported on active carbon in the first hydrogenation reactor (12) and another catalyst comprising 1.0 % of palladium supported on active carbon in the second hydrogenation reactor (12'). The hydrogenation was conducted under a pressure of 9.5 kg/cm² and a temperature of 100 °C.

The hydrogenation reaction product mixture was then supplied into a gas/liquid separator (15) where excess hydrogen was separated from the reaction mixture. Next, the reaction mixture was filtered through a glass wool filter (17) of 5 µm pore size to thereby remove the fine powder of the catalyst. Then the reaction mixture was distilled in



third distillation column (19).

The third distillation column (19) was made of carbon steel and had an inner diameter of 100 mm. This column was packed with a McMahon Packing at a height of 2000 mm. The line (20) for drawing the side stream was exclusively made of SUS 304.

A side stream outlet (20) was provided 300 mm below the top of the pack layer and a liquid inlet (18) was provided 700 mm therebelow. Distillation was then performed under a column top pressure of 200 mmHg, a column top oxygen pressure of 0 mmHg, a reflux ratio of 90 and a column bottom temperature of 215 °C. After continuously operating the process for 100 hours and 1,000 hours, the 1,4-butanediol taken out from the side stream of third distillation column (19) contained 0.11 % and 0.12 % of BGTF, respectively. The purity of the obtained 1,4-butanediol was 99.8 % in each case.

COMPARATIVE EXAMPLE 1

The procedure of Example 1 was repeated but filtration through a filter was omitted. After continuously operating the process for 100 hours and 1,000 hours, the 1,4-butanediol taken out from the side stream of the third distillation column contained 0.21 % and 0.25 % of BGTF, respectively. The purity of the obtained 1,4-butanediol was 99.7 % in each case.

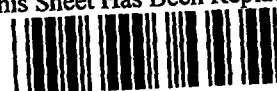


TABLE 2

	<u>Purity of 1,4- butanediol</u>	<u>BGTF (impurity) content</u>	
		<u>after 100 hr</u>	<u>after 1,000 hr</u>
Ex. 1	99.8 wt. %	0.11 wt. %	0.12 wt. %
Comp. Ex. 1	99.7 wt. %	0.21 wt. %	0.25 wt. %

APPLICATION EXAMPLE

To 73.7 parts of BGTF-containing 1,4-butanediol obtained after continuously operating the process of Example 1 for 1,000 hours, and to 73.7 parts of BGTF-containing 1,4-butanediol obtained after continuously operating the process of Comparative Example 1 for 100 hours, in combination with 132.4 parts of dimethyl phthalate, was added 37 ppm (in terms of metallic titanium) of tetrabutyl titanate to prepare two mixtures. Each mixture was subjected to esterification at 150 to 215 °C for 3 hours. 15 minutes before the completion of the esterification, 600 ppm of a hindered phenol anti-oxidant (Irganox 1010[™] manufactured by Ciba-Geigy) was added to the reaction mixture. Successively, 69 ppm (in terms of metallic titanium) of tetrabutyl titanate was added thereto and polycondensation was performed while slowly reducing the pressure from atmospheric pressure to 3 Torr over 85 minutes and, at the same time, elevating the temperature from 215 to 245 °C. Subsequently, the polycondensation was continued at 245 °C and 3 Torr. When a predetermined stirring torque was attained, the reaction was stopped and the PBT polymer was



taken out. Table 3 summarizes the polymerization time and the intrinsic viscosity and colour of the obtained polymer.

TABLE 3

<u>Origin of 1,4-</u> <u>butanediol</u>	<u>Polymerization</u> <u>time (hr:min)</u>	<u>Intrinsic</u> <u>viscosity (dl/g)</u>	<u>Colour</u>
Ex. 1	2:54	0.946	white
Comp. Ex. 1	3:05	0.943	yellowish

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

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WHAT IS CLAIMED IS:

1. A process for purifying crude 1,4-butanediol obtained by hydrolyzing diacetoxymethane to produce 1,4-butanediol having high purity, said process comprising:

(1) hydrogenating the crude 1,4-butanediol in the presence of a hydrogenating catalyst;

(2) removing a fine powder of the hydrogenating catalyst from the hydrogenation mixture; and

(3) distilling the mixture, from which the fine powder has been removed, in a distillation column and thereby obtaining the 1,4-butanediol having high purity from a side stream of distillation column.

2. The purification process as claimed in claim 1, wherein said hydrogenation step (1) is performed in the presence of a palladium catalyst and a ruthenium catalyst.

3. The purification process as claimed in claim 1, wherein said fine powder of the hydrogenating catalyst is removed with the use of a filter in the step (2).

4. The purification process as claimed in claim 3, wherein said filter has a pore size of about 10 μm or less.

5. The purification process as claimed in claim 1, wherein said crude 1,4-butanediol is 1,4-butanediol contaminated with 2-(4'-hydroxybutoxy)tetrahydrofuran and separated by distillation from a reaction product obtained by hydrolyzing diacetoxymethane.





6. The purification process as claimed in claim 5, wherein said separation by distillation is performed by separating water and acetic acid from said hydrolysis product by a low-boiling distillation column and then taking out the crude 1,4-butanediol as a vapor phase from the lower side flow of a high-boiling distillation column.

7. The purification process as claimed in claim 5, wherein the purified 1,4-butanediol is contaminated by about 0.1 % by weight or less of 2-(4'-hydroxybutoxy)tetrahydrofuran.

8. The purification process as claimed in claim 1, wherein the oxygen pressure at the column top in the step (3) is about 10 mmHg or lower.

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