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DESCRIPTION

METHOD FOR PRODUCING SECONDARY BUTANOL

5

TECHNICAL FIELD

[0001]

The invention relates to a method for producing secondary butanol (2-butanol). More particularly, the invention relates to a method for producing secondary butanol by a direct hydration method in which oxygen-containing water is used as a raw material.

BACKGROUND ART

[0002]

15 Secondary butanol is widely used as a raw material for methyl ethyl ketone (MEK) which is useful mainly as a solvent. Secondary butanol is produced by an indirect hydration method or a direct hydration method.

In the indirect hydration method, secondary butanol is obtained by esterifying n-butene with sulfuric acid, and hydrolyzing the resulting sulfate with steam. This method has such disadvantages as complicated recycling process or the like due to the use of sulfuric acid, an increased amount of energy consumed, corrosion of an apparatus, need for treating used sulfuric acid, and the like.

The applicant of the invention disclosed a method for producing secondary butanol by directly hydrating n-butene

using an aqueous heteropolyacid solution (see Patent Document 1, for example). This method enables simplification of a production process since secondary butanol can be produced without formation of a sulfate.

5 [0003]

In the direct hydration method, n-butene is required to be brought into contact with an aqueous heteropolyacid solution at high temperatures under high pressures. In addition, since the hydration reaction is conducted in a relatively strong acidic region, titanium metal which is highly resistant to corrosion by acid is used in equipment such as a reactor. Titanium metal, however, undergoes hydrogen embrittlement. To prevent corrosion of titanium metal by hydrogen, an oxide film is formed on the surface layer thereof.

15 [0004]

However, even though the equipment with a titanium oxide film being formed on the surface is used, the oxide film is gradually reduced to metal titanium with the operation of the equipment, and resistance of the equipment to corrosion by hydrogen lowers as the operation time is prolonged. Therefore, to suppress deterioration of the equipment by hydrogen embrittlement, it is required to periodically form a fresh oxide film on the surface of the equipment. As the method for forming an oxide film, heating titanium at high temperatures, treating titanium with hydrochloric acid or nitric acid, or treating titanium

with hydroperoxide water can be given (see Patent Document 2, for example). However, these methods require stopping the operation of the equipment for a long period of time as well as treating liquid waste or the like, which is time-
5 consuming or costly.

Patent Document 1: JP-A-60-149536

Patent Document 2: JP-A-63-223187

[0005]

In view of the above problems, an object of the
10 invention is to provide a method for producing secondary butanol which can suppress deterioration of a titanium oxide film by the operation of equipment.

DISCLOSURE OF THE INVENTION

15 [0006]

The inventors made extensive studies to solve the above-mentioned problems, and have found that deterioration of the oxide film can be suppressed by using water in which oxygen is dissolved. The invention has been made based on
20 this finding.

The invention provides the following method for producing secondary butanol.

1. A method for producing secondary butanol comprising directly hydrating n-butene in the presence of an aqueous
25 heteropolyacid solution as a catalyst using water in which oxygen is dissolved as a raw material.
2. The method for producing secondary butanol according

to 1, wherein the water is oxygen-saturated water.

3. The method for producing secondary butanol according to 1 or 2, wherein the water is obtained by exposing pure water to air.

5 4. The method for producing secondary butanol according to any of 1 to 3, wherein the hydration is conducted using a continuous liquid-phase direct hydration apparatus.

[0007]

In the method for producing secondary butanol of the
10 invention, life of the equipment can be prolonged since deterioration of the titanium oxide film can be suppressed. As a result, time and cost required to maintain the equipment can be reduced.

15 BEST MODE FOR CARRYING OUT THE INVENTION

[0008]

The method for producing secondary butanol of the invention comprises directly hydrating n-butene in the presence of an aqueous heteropolyacid solution as a
20 catalyst using water in which oxygen is dissolved as a raw material.

Details of the method for producing secondary butanol by directly hydrating n-butene are described in JP-A-60-149536 or JP-A-4-356434, for example. The summary of the
25 method will be described below.

[0009]

In a method where n-butene is directly hydrated, a

hydration reaction of n-butene is conducted by bringing n-butene (n-butene-1 or n-butene-2, or a mixture thereof) as a raw material into contact with an aqueous heteropolyacid solution having a pH of 2.3 or less, for example.

5 [0010]

As the heteropolyacid, silicotungstic acid, phosphotungstic acid, silicomolybdenum acid, phosphomolybdenum acid, and the like can be used. In addition, a heteropolyacid in which two or more types of
10 hetero atoms and poly atoms are combined can also be used.

The concentration of the aqueous heteropolyacid solution is required to be adjusted appropriately depending on the type of a heteropolyacid or the like, but normally, 0.001 mol/l to 0.2 mol/l.

15 [0011]

It is preferred that the reaction temperature and the reaction pressure be 140°C to 300°C, and 6 MPa or more, respectively. Since the reaction is conducted at such high temperatures and high pressures, as well as in a strong
20 acidity, it is necessary to take measures to suppress corrosion of the equipment. Specifically, the inner surface of the equipment such as a reactor is subjected to lining (explosion-bonded clad lining) with metal titanium and an oxide film is further formed on the lined equipment.
25 An oxide film can be formed by a known method (the above-mentioned Patent Document 2, for example). It is preferred that the thickness of the oxide film be 150Å to 5,000Å.

[0012]

As the production equipment, known equipment such as a batch liquid-phase direct hydration reactor or a continuous liquid-phase direct hydration apparatus can be
5 used.

In the continuous liquid-phase hydration reactor, since secondary butanol is continuously produced, n-butene and water as raw materials are supplied at a predetermined rate to a reactor for hydration reaction, and secondary
10 butanol as a reaction product and by-products are removed at a predetermined rate. As a result, the concentration of the aqueous heteropolyacid solution in the reaction system can be maintained in a predetermined range.

[0013]

15 In the invention, water in which oxygen is dissolved is used as a raw material to be supplied to the reactor. As a result, oxygen deficiency of an oxide film caused by the reduction of n-butene can be suppressed. The reason therefor is considered as follows. Oxygen dissolved in
20 water oxidizes the inner surface of the reactor to form an oxide film by exposure to high temperatures and high pressures in the reactor. The oxide film-forming action by the dissolved oxygen and the reduction action by n-butene are compensated, whereby a decrease in the amount of an
25 oxide film formed in the reactor can be suppressed.

[0014]

Heretofore, water which is degassed after being

deionized (so-called pure water) has been used as a raw material to be supplied to a reactor in order to minimize entering of impurities to a reaction system.

In the industrial equipment, for ensuring efficient
5 water treatment, the same water which is subjected to the same treatment is generally used for a reaction system and for steam used as a power source or a driving source or the like. In addition, it is essential that the pure water be used in a steam supply system such as a boiler to suppress
10 oxidization of an apparatus. For these reasons, pure water has been used as the water to be supplied to a reaction system.

[0015]

In spite of the above-mentioned state, the invention
15 has been made based on a finding that supplying water in which oxygen is dissolved to a reaction system maintains an oxide film in a reactor.

Depending on reaction conditions, water in which oxygen is dissolved may form an oxide film inside the
20 reactor. In such a case, corrosion of the equipment can be suppressed even when an oxide film is not formed prior to use of the equipment.

[0016]

As the water in which oxygen is dissolved used in the
25 invention, water in which oxygen is dissolved and from which impurities such as ions which affect adversely on the reaction system are removed may be used. Specific examples

include water which is not degassed after being deionized, water obtained by exposing pure water to air so that oxygen in the air is absorbed in the pure water, and water obtained by bubbling pure water with air or oxygen so that
5 oxygen is dissolved in the pure water.

For deionizing or other treatments, known methods such as using an ion exchange resin may be used.

[0017]

In the above-mentioned industrial equipment, if the
10 same water is used in the reaction system and for the steam, the following water may be used; pure water to be used in the reaction system is placed in an air-opened tank or the like so as to allow oxygen to be dissolved in the pure water, and then supplied to a reactor. As a result, pure
15 water can be supplied to a steam supply system, while water in which oxygen is dissolved can be supplied to a reaction system, with a common water-treating equipment.

[0018]

Since the amount of oxygen in water is usually very
20 small, in the invention, it is preferable to use water saturated with oxygen at 5°C to 30°C under atmospheric pressure.

To enhance the effect of suppressing deterioration of an oxide film attained by the oxygen dissolved in water, it
25 is preferred that the reaction be performed at a temperature of 150°C to 220°C, and at a pressure of 6 MPa to 25 MPa.

EXAMPLES

[0019]

The invention will be described in more detail
5 referring to the examples.

Example 1

As the aqueous heteropolyacid solution, a 17 wt%
aqueous silicotungustic acid solution was used. About five
10 cc (liquid height: about 40 cm) of the aqueous
heteropolyacid solution was placed in a tube made of
titanium with an inner diameter of 4 mm (not treated),
followed by pressurization with hydrogen to 2 MPa. To
maintain the hydrogen partial pressure inside the reaction
15 system at a constant level, the pressure was controlled
using a back pressure valve while supplying a slight amount
of hydrogen. The concentration of the hydrogen in this
evaluation example was about 1,000 times higher than the
concentration in the actual production for controlling
20 hydrogen differential pressure.

Subsequently, the aqueous solution portion was heated
to 220°C. Since hydrogen was supplied (at a rate of 1
cc/min or less), the liquid level was lowered and the
concentration of the heteropolyacid was increased.
25 Therefore, pure water in which air is absorbed by exposing
to air was replenished appropriately at an amount of about
1 cc/day.

After continuing the condition for 12 days, one cm of the heated portion of the titanium tube was cut, and the hydrogen concentration of the titanium material was measured. An increase in hydrogen concentration in the heated portion of the titanium material was not observed.

The hydrogen concentration was measured according to JIS H 1619.

[0020]

Comparative Example 1

The hydrogen concentration of the titanium material was measured in the same manner as in Example 1, except that water obtained by degassing pure water was used as the replenishing water. It was revealed that the hydrogen concentration of the titanium material was increased by 23 wt ppm.

[0021]

Example 2

The same procedures as in Example 1 were performed, except that the heating time was changed to 34 days. It was revealed that the hydrogen concentration of the heated portion of the titanium material was not increased.

[0022]

Comparative Example 2

The same procedures as in Comparative Example 1 were performed, except that the heating time was changed to 34 days. It was revealed that the hydrogen concentration of the heated portion of the titanium material was increased

by 48 wt ppm.

[0023]

Example 3

The same procedures as in Comparative Example 1 were
5 performed, except that a 30 wt% aqueous silicotungstic
acid solution was used as the aqueous heteropolyacid
solution. It was revealed that the hydrogen concentration
of the heated portion of the titanium material was not
increased.

10 [0024]

Comparative Example 3

The same procedures as in Comparative Example 1 were
performed, except that a 30 wt% aqueous silicotungstic
acid solution was used as the aqueous heteropolyacid
15 solution. It was revealed that the hydrogen concentration
of the heated portion of the titanium material was
increased by 76 wt ppm.

[0025]

Example 4

20 Secondary butanol was prepared under a condition
where a plurality of sheet-like titanium test pieces (45 mm
x 25 mm x 5 mm (thickness)) were placed in a hydration
reactor with a volume of about 30 m³. The amount of
hydrogen absorbed in the titanium material was evaluated.

25 As the catalyst, an aqueous silicotungstic acid
solution was used, and the concentration of the solution in
the hydration reactor was adjusted to 2.1 wt%. The

temperature and the pressure of the reactor were 200°C to 220°C, and 19 to 22 MPa, respectively. To the apparatus, water saturated with oxygen at 5°C to 30°C at an atmospheric pressure was supplied at 5°C to 30°C at a rate of 25 l/min. Also, an n-butene gas was supplied at a rate of 2,150 l/min. The n-butene gas contained about 90 mol ppm of hydrogen as an impurity.

After continuing the operation for three years under the above condition, two test pieces were taken out of the hydration reactor, and the amount of hydrogen absorbed in the titanium material was measured. It was revealed that the amount of hydrogen in the two pieces was 13 wt ppm and 14 wt ppm, respectively. For comparison, the amount of hydrogen absorbed in an unused titanium material was measured, and found to be 17 wt ppm. The results confirmed that the hydrogen was not absorbed in the titanium material in the reactor.

INDUSTRIAL APPLICABILITY

[0026]

The method for producing secondary butanol of the invention leads to reduction in time and cost needed in maintenance of equipment since life of the equipment can be prolonged. Therefore, the method of the invention is suitable for producing secondary butanol. In addition, the method of the invention can improve the efficiency of production of MEK when a MEK production process includes

the method of the invention as a part thereof.

CLAIMS

1. A method for producing secondary butanol comprising directly hydrating n-butene in the presence of an aqueous
5 heteropolyacid solution as a catalyst using water in which oxygen is dissolved as a raw material.
2. The method for producing secondary butanol according to claim 1, wherein the water is oxygen-saturated water.
10
3. The method for producing secondary butanol according to claim 1 or 2, wherein the water is obtained by exposing pure water to air.
- 15 4. The method for producing secondary butanol according to any of any one of claims 1 to 3, wherein the hydration is conducted using a continuous liquid-phase direct hydration apparatus.