

DESCRIPTION

REACTOR FOR PRODUCING SECONDARY BUTANOL

5

TECHNICAL FIELD

[0001]

The invention relates to a reactor for producing secondary butanol (2-butanol). More particularly, the invention relates to a reactor and a method for producing
10 secondary butanol by a direct hydration method without taking a catalyst solution outside the reactor.

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
20 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
25 for treating sulfuric acid used, 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]

An example of a method for producing secondary butanol by a direct hydration method will be described briefly below.

FIG. 4 is a schematic flow chart showing a
10 conventional method for producing secondary butanol.

This method has 3 main steps. In the first step, n-butene and water as raw materials, and an aqueous heteropolyacid solution as a catalyst are supplied to a reactor 1' to undergo hydration reaction, thereby
15 synthesizing secondary butanol (indicated as "SBA" in the drawing). In the second step, the resultant gas-liquid mixture containing secondary butanol, unreacted raw materials and the catalyst solution are taken out from the reactor 1' to be treated at a catalyst solution separating
20 tower 52, whereby the catalyst solution are separated from the other components. In the third step, the resultant mixture after separating the catalyst solution is purified and separated at a separating tower 50, whereby secondary butanol, which is a target material, is recovered.

25 [0004]

Since an aqueous heteropolyacid solution has strong corrosion, equipments in contact with this solution are

required for high anticorrosivity. For example, there are used equipments where a metal titanium layer is formed on a liquid-contact part and an oxide film is further formed. Since the mixture containing the catalyst solution is taken
5 from the reactor in the method, the catalyst solution separating tower 52, a pump P for circulating a catalyst solution, piping and the like as well as the reactor 1' are also required to be made of high anticorrosive materials.

Such equipments are more expensive than those made of
10 stainless steel and the like so that production costs and equipment costs are increased. Since the pressure inside the reactor is high, it is required to increase the pressure of the aqueous heteropolyacid solution with the pump P in order to circulate the solution, which has been
15 separated at the catalyst solution separating tower 52, to the reactor 1'. In this process, a large amount of energy is consumed.

Patent Document 1: JP-A-S60-149536

[0005]

20 In view of the above problems, an object of the invention is to provide a reactor and a method for more efficiently producing secondary butanol.

DISCLOSURE OF THE INVENTION

25 [0006]

The inventors made extensive studies to solve the above-mentioned problems, and have found that secondary

butanol produced in the liquid phase is extracted into the gas phase at a high concentration when an aqueous heteropolyacid solution serving as a catalyst and 2-butene form a gas-liquid interface and n-butene is present as
5 supercritical gas phase. Specifically, they have found that secondary butanol can be efficiently recovered by taking only the gas phase from the reactor without taking a catalyst solution of liquid phase.

The inventors made further studies about the
10 construction of the reactor based on the above findings. The inventors have found that by providing a circulation mechanism that can circulate the catalyst solution of liquid phase and keep the gas-liquid interface inside the reactor, secondary butanol can be produced without reducing
15 the yield while maintaining the catalyst solution inside the reactor.

[0007]

The invention provides the following reactor or method for producing secondary butanol.

- 20 1. A reactor for producing secondary butanol by directly hydrating n-butene in the presence of an aqueous heteropolyacid solution as a catalyst comprising a circulation mechanism for circulating an aqueous heteropolyacid solution inside the reactor.
- 25 2. The reactor for producing secondary butanol according to 1 wherein the circulation mechanism is an inner pipe.
3. The reactor for producing secondary butanol according

to 2 comprising a flow adjusting valve for controlling an amount of the circulated heteropolyacid solution inside the inner pipe.

4. The reactor for producing secondary butanol according to any one of 1 to 3 comprising 2 or more regions partitioned with 1 or more porous plates.

5. The reactor for producing secondary butanol according to 4 comprising 6 or more regions.

6. The reactor for producing secondary butanol according to any one of 1 to 5 wherein at least one of a gas-liquid separator and a washing tray is provided near an outlet thereof.

7. A method for producing secondary butanol comprising:
producing secondary butanol by supplying n-butene into an aqueous heteropolyacid solution which is a liquid phase in the reactor according to any one of 1 to 6;
concentrating the secondary butanol in n-butene forming a supercritical gas phase in the reactor;
taking out the secondary butanol and n-butene of a gas phase from the reactor; and then
separating the n-butene to obtain the secondary butanol.

[0008]

In the reactor for producing secondary butanol of the invention, an aqueous heteropolyacid solution is not removed outside the reactor. Therefore, recovery and circulation equipments such as a conventional catalyst

solution separating tower are not required. As a result, equipment costs and production costs can be reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

5 [0009]

FIG. 1 is a schematic cross-sectional view showing one embodiment of the reactor for producing secondary butanol of the invention.

10 FIG. 2 is a schematic view showing the inside of a reactor when producing secondary butanol.

FIG. 3 is a schematic flow chart showing the method for producing secondary butanol of the invention.

FIG. 4 is a schematic flow chart showing a conventional method for producing secondary butanol.

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BEST MODE FOR CARRYING OUT THE INVENTION

[0010]

20 FIG. 1 is a schematic cross-sectional view showing one embodiment of the reactor for producing secondary butanol of the invention. FIG. 2 is a schematic view showing the inside of the reactor when producing secondary butanol.

25 A reactor 1 comprises an inlet 12 for supplying n-butene provided at a lower part of a cylinder-shaped body 11. An outlet 13 for taking n-butene gas containing secondary butanol produced therefrom is provided at an upper part of the body 11. A gas distributing plate 14

through which butene gas can pass and liquid cannot pass is provided above the inlet 12 to prevent the leakage of liquid phase from the reactor through the inlet 12.

An inlet 15 for supplying water for hydrating n-butene is provided above the gas distributing plate 14 in the lower part of the body 11.

[0011]

An inner pipe 20 is provided along the longitudinal center line of the body 11. An end of the inner pipe 20 is positioned near the inlet 12. The other end of the inner pipe 20 is present in the liquid phase 42 near a liquid-gas interface (refer to FIG. 2). Such arrangement of the inner pipe 20 allows the following; The gas component in the liquid phase moves to the gas phase, thereby causing the difference in relative density in the liquid phase. This circulates the liquid phase inside and outside the inner pipe 20. Specifically, since the solution on the lower side of the reactor 1 contains a relatively large amount of butene gas and secondary butanol produced, the solution has a small relative density and moves upward. Since butene gas and secondary butanol move from the liquid phase 42 to the gas phase 44 in the vicinity of gas-liquid interface 40, the solution has a larger relative density and moves downward. As a result, an upward flow is caused outside the inner pipe 20 and a downward flow is caused inside the pipe. The arrows indicate the circulation of the liquid phase in FIG. 2.

[0012]

It is preferable that the ratio of the inner diameter of the inner pipe to the diameter of the reactor be 0.05 to 0.20 in order to give appropriate circulation of the liquid phase (downward flow) and ensure a reaction volume (upward flow).

[0013]

Since a liquid phase can be appropriately circulated in the reactor of the invention, the secondary butanol produced in the liquid phase can be diffused throughout the liquid phase, maintaining a gas-liquid interface. Since hydration reaction caused in the liquid phase is equilibrium reaction biased toward raw material system, the hydration reaction can be more efficiently conducted by diffusing secondary butanol in the liquid phase.

[0014]

In the reactor of the invention, it is preferable that a flow adjusting valve 22 for controlling the amount of circulating heteropolyacid solution be provided inside the inner pipe to control circulation from the outside using a manipulating valve 22a. Hydration reaction can be easily optimized by controlling the circulation rate of liquid phase with the flow adjusting valve. It is preferable that a flow indicator 24 be further provided inside the inner pipe.

As examples of the flow adjusting valve, a general butterfly valve, gate valve, groove valve and the like can

be used.

[0015]

In the reactor, it is preferable to form 2 or more regions (vessels) 28 by partitioning the part where a liquid phase is circulated with one or more porous plates 26. The porous plate 26 has functions of enhancing contact efficiency of gas phase and liquid phase by re-distributing butene gas bubbles. The provision of porous plate 26 gives the same effects as those of a plurality of vessels formed in the reactor 1. The circulation of liquid phase can approximate plug flow (piston flow), thereby enhancing the yield of secondary butanol. In FIG.1, five ring-shaped porous plates 26 are provided around the outer circumference of the inner pipe 20 across the body 11 (six vessels). In the invention, the reactor preferably has 6 or more regions (vessels) 28, more preferably 10 to 20 regions.

It is preferable that the porous plates have an aperture ratio of 0.06 to 0.10 and aperture diameter of 3 to 10 mm to efficiently distribute the butene gas of the gas phase, to keep the plug flow and to suppress back mixing (reverse-flow of liquid).

[0016]

It is preferable that a gas-liquid separator 30 (demister) and/or a washing tray 32 be provided near the outlet 13 of the reactor 1. Since they prevent the leakage of the aqueous heteropolyacid solution from the outlet 13

to the outside of the reactor, corrosion of the equipments connected to the reactor can be suppressed.

When a washing tray is provided, an inlet 34 for supplying washing water is provided above the washing tray
5 32 in the body 11.

[0017]

The method for producing secondary butanol of the invention will be described below.

FIG. 3 is a schematic flow chart showing the method
10 for producing secondary butanol of the invention. The method of the invention comprises blowing n-butene into a liquid phase of an aqueous heteropolyacid solution in the above-mentioned reactor to produce secondary butanol in the liquid phase. Thereafter, the secondary butanol is
15 concentrated in the n-butene, and taken as gas from the reactor.

[0018]

In the method of the invention, an aqueous heteropolyacid solution is added into the reactor in
20 advance. The liquid level of the solution is adjusted to be at a specific position. For example, as shown in FIG. 2, the liquid level is at the position where the aqueous heteropolyacid solution does not leak from the outlet 13 and the whole inner pipe 20 welters in the liquid phase 42.

25 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 hetero atoms and poly atoms are combined can also be used.

The concentration of the aqueous heteropolyacid solution is adjusted appropriately depending on the type of a heteropolyacid or the like, normally 0.001 mol/l to 0.2 mol/l. The aqueous heteropolyacid solution has a pH of 2.3 or less.

[0019]

Then, n-butene gas (n-butene-1, n-butene-2, or a mixture thereof) is supplied from the inlet 12 and water is supplied from the inlet 15. The n-butene gas becomes bubbles 46 and the bubbles 46 move upward in the reactor (as shown by outline arrows in FIG.2). A part of the n-butene is dissolved into the catalyst solution to produce secondary butanol in the liquid phase 42. A major part of the n-butene does not react and pass through the liquid phase 42 to form the gas phase 44 in the upper part of the reactor 1. N-butene is supplied such that the interface 40 between the aqueous heteropolyacid solution (liquid phase) 42 and n-butene (gas phase) 44 stays at the above-mentioned specific position.

[0020]

In the invention, n-butene forming the gas phase 44 in the reactor 1 is present in a supercritical state. The hydration reaction has a low equilibrium inversion rate of secondary butanol and the concentration of secondary butanol in the liquid phase 42 is dilute. Since secondary

butanol is distributed in the supercritical n-butene of the gas phase 44 at a high concentration, secondary butanol can be efficiently recovered by taking only the gas phase 44 to the outside of the reactor 1.

5 The reaction temperature and the reaction pressure are 140°C to 300°C and 6 MPa or more to bring n-butene forming the gas phase into a supercritical state. It is preferable that the reaction temperature and the reaction pressure be 180°C to 230°C and 18 MPa to 22 MPa.

10 [0021]

Then, the gas phase 44 is taken out from the outlet 13. Since the liquid phase 42 and gas phase 44 are present in the reactor 1 while forming the interface 40 in the method of the invention, only the gas phase 44 can be
15 easily taken out from the reactor. The secondary butanol and n-butene, forming the gas phase 44, can be selectively taken out while maintaining the catalyst solution inside the reactor 1. Unlike the flow chart shown in FIG. 4, equipments for circulating a catalyst solution such as the
20 catalyst solution separating tower 52 are not required, whereby equipment costs and production costs can be reduced.

The rate of taking out the gas phase 44 is adjusted such that the interface between the catalyst solution phase 42 and the gas phase 44 is at a specific position, taking
25 the amount of supplied n-butene and water into account.

[0022]

The gas phase 44 is a mixture mainly composed of

secondary butanol and n-butene. The mixture is sent to a separating tower 50 for separation thereof. A method for the separation includes a method in which a mixture taken as gas is cooled to be liquefied. The separated n-butene
5 is circulated as a raw material to the reactor again. The separated secondary butanol is sent to a purification process, if necessary.

[0023]

Details of the method for producing secondary butanol
10 by directly hydrating n-butene are described in JP-A-60-149536 or JP-A-4-356434, for example.

INDUSTRIAL APPLICABILITY

[0024]

15 The reactor for producing secondary butanol of the invention can be used not only as an equipment for producing secondary butanol but also as an equipment for producing methyl ethyl ketone.

Since the method for producing secondary butanol of
20 the invention can reduce equipment costs and production costs, it is suitable for producing secondary butanol. In addition, the method of the invention can improve the efficiency of MEK production when a MEK production process involves the method of the invention as a part thereof.

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CLAIMS

1. A reactor for producing secondary butanol by directly hydrating n-butene in the presence of an aqueous
5 heteropolyacid solution as a catalyst comprising a circulation mechanism for circulating an aqueous heteropolyacid solution inside the reactor.
2. The reactor for producing secondary butanol according
10 to claim 1 wherein the circulation mechanism is an inner pipe.
3. The reactor for producing secondary butanol according to claim 2 comprising a flow adjusting valve for
15 controlling an amount of the circulated heteropolyacid solution inside the inner pipe.
4. The reactor for producing secondary butanol according to any one of claims 1 to 3 comprising 2 or more regions
20 partitioned with 1 or more porous plates.
5. The reactor for producing secondary butanol according to claim 4 comprising 6 or more regions.
- 25 6. The reactor for producing secondary butanol according to any one of claims 1 to 5 wherein at least one of a gas-liquid separator and a washing tray is provided near an

outlet thereof.

7. A method for producing secondary butanol comprising:
producing secondary butanol by supplying n-butene
5 into an aqueous heteropolyacid solution which is a liquid
phase in the reactor according to any one of claims 1 to 6;
concentrating the secondary butanol in n-butene
forming a supercritical gas phase in the reactor;
taking out the secondary butanol and n-butene of a
10 gas phase from the reactor; and then
separating the n-butene to obtain the secondary
butanol.