

Title of the Invention

A. method for continuously producing a cyclic formal ✓

Background of the Invention

The present invention relates to a method for continuously producing a cyclic formal used as an intermediate product of solvents and drugs, a raw material of acetal resin, etc. In more detail, the present invention relates to a method for continuously producing a cyclic formal less in the contents of impurities such as unreactive formaldehyde and water, by letting an alkylene glycol and formaldehyde continuously react with each other in the presence of a catalyst.

It is known that cyclic formals such as ethylene glycol formal, diethylene glycol formal and 1,4-butanediol formal can be obtained by cyclic reaction between a corresponding alkylene glycol or alkylene oxide and aldehyde. For example, German Patent No. 191420 discloses a method for producing ethylene glycol formal, a typical cyclic formal, by letting ethylene glycol formal and formaldehyde react with each other in the presence of an acid catalyst.

Furthermore, Japanese Patent Laid-Open (Kokai) No. 49-62469 discloses a method for producing ethylene glycol formal by letting ethylene glycol and paraformaldehyde react with each other in the presence of an acid catalyst.

Moreover, Japanese Patent Laid-Open (Kokai) No. 7-224055 discloses a method for obtaining a cyclic formal by letting an

alkylene glycol and formaldehyde² react with each other at a specific molar ratio.

Any of the cyclic formals obtained in the above methods is usually obtained as a mixture consisting of a cyclic formal containing a large amount of water, and water. Methods for decreasing water from the mixture containing water, for obtaining a purified cyclic formal are also known. For example, Japanese Patent Laid-Open (Kokai) No. 49-62469 discloses a method for producing a purified cyclic formal by adding cyclohexane to the reaction distillate obtained by letting paraformaldehyde and ethylene glycol react with each other in the presence of an acid catalyst, and rectifying the mixture. Japanese Patent Laid-Open (Kokai) No. 3-24071 discloses a purification method in which a crude cyclic acetal is treated by an alkali aqueous solution and/or solid alkali hydroxide compound. Japanese Patent Laid-Open (Kokai) No. 5-241217 discloses a purification method in which the reaction distillate obtained by letting formaldehyde and ethylene glycol react with each other in the presence of an acid catalyst is brought into contact with ethylene glycol in counter current in a distillation tower. Japanese Patent Laid-Open (Kokai) No. 7-206716 discloses a purification method in which a mixture containing a cyclic formal and water is brought into contact with a hydrophilic solvent with a boiling point of 180 to 250°C in a distillation tower. Furthermore,

Japanese Patent Laid-Open (Kokai) No. 7-206717 discloses a method in which the purified cyclic formal obtained in said Japanese Patent Laid-Open (Kokai) No. 7-206716 is further treated by a dehydrating agent.

Summary of the Invention

However, the conventional methods for producing a cyclic formal still have practical problems to be solved. For example, if a cyclic formal is synthesized by letting an alkylene glycol and formaldehyde react with each other, and the product containing the cyclic formal is taken out of the reaction mixture, then the product contains unreactive formaldehyde disadvantageously. For this reason, these methods do not yet reach a practically satisfactory level as methods for producing a cyclic formal. The formaldehyde contained in the cyclic formal affects the synthesis process and the subsequent purification process. For example, formaldehyde is converted into formic acid by Cannizzaro's reaction, to pose such problems that the equipment is corroded and that the entire equipment is complicated.

Because of these problems, in the production of a cyclic formal, it is desired to obtain a cyclic formal not containing unreactive formaldehyde as far as possible.

The conventional methods for purifying a cyclic formal also have practical problems to be solved. For example, in the method of adding cyclohexane to a cyclic formal and

rectifying the mixture, the decrease of water content is not sufficient. Furthermore, in the method of bringing a cyclic formal into contact with ethylene glycol or a hydrophilic solvent with a boiling point of 180 to 250°C for distillation, though the water content of the cyclic formal decreases, water migrates into ethylene glycol or hydrophilic solvent, to require further purification of the ethylene glycol or solvent. Therefore, the number of steps increases to complicate the process disadvantageously, and problems are not solved at a practically satisfactory level.

Because of the above situation, a process for producing a cyclic formal less in the content of impurities, consistent from the synthesis to purification of the cyclic formal, is desired.

The inventors studied intensively a method for continuously producing a cyclic formal with a large water content but with a small unreactive formaldehyde content by letting an alkylene glycol and formaldehyde react with each other, and then distilling the cyclic formal with a large water content for continuously purifying it. As a result, they found that a cyclic formal with a small unreactive formaldehyde content can be easily continuously produced by continuously supplying a raw alkylene glycol to a distillation tower when unreactive formaldehyde and a cyclic formal are distilled out, and on the other hand, by continuously

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supplying raw formaldehyde to a reactor.

Furthermore, the inventors found that a cyclic formal small in the content of water, etc. can be easily continuously obtained by distilling the water-containing cyclic formal for continuously obtaining an azeotropic mixture consisting of the cyclic formal and water, and adding a specific hydrocarbon compound capable of forming another azeotropic mixture with water, to the azeotropic mixture consisting of the cyclic formal and water, for continuous distillation. Thus, the present invention has been completed.

An object of the present invention is to provide a method for continuously producing a cyclic formal with a small impurities content by a process consistent from the synthesis and purification of the cyclic formal.

Another object of the present invention is to provide a method for producing a cyclic formal with small aldehyde and water contents.

A further other object of the present invention is to provide an easy and simple method for continuously producing a purified cyclic formal small in the content of water, etc. and highly improved in rectification efficiency.

Still further other objects of the present invention will be seen from the following description.

The present invention is intended to achieve the above objects and has the following constitution.

The present invention is a method for continuously producing a cyclic formal, in which a reaction distillation tower equipped with a reactor and a distillation tower is used for letting an alkylene glycol and formaldehyde react with each other in the presence of a catalyst, to produce a cyclic formal, comprising the step of continuously supplying the alkylene glycol from the distillation tower to the reactor of the reaction distillation tower, while continuously supplying formaldehyde to the reactor of the reaction distillation tower, for letting both the ingredients react with each other.

The present invention is also a method for continuously producing a cyclic formal, in which said reaction distillation tower is used to let an alkylene glycol and formaldehyde react with each other in the presence of a catalyst, to produce a cyclic formal, comprising

- (1) the step of continuously supplying an alkylene glycol from the distillation tower to the reactor of the reaction distillation tower while continuously supplying formaldehyde to the reactor of the reaction distillation tower, for letting both the ingredients react with each other, to continuously obtain a reaction distillate containing water and a cyclic formal from the top of the distillation tower,
- (2) the step of continuously supplying the reaction distillate containing water and a cyclic formal obtained in said step (1) to a second distillation tower, to continuously obtain an

azeotropic mixture consisting of the cyclic formal and water, and

(3) the step of supplying the azeotropic mixture consisting of the cyclic formal and water obtained in said step (2) to an azeotropic distillation tower, while supplying a hydrocarbon compound, the azeotropic point of which with water is not higher than the boiling point of the cyclic formal, for continuous distillation, and obtaining the azeotropic mixture consisting of the hydrocarbon and water with the cyclic formal from the top of the azeotropic distillation tower while continuously obtaining the cyclic formal purified after removing water, from the tower bottom.

The present invention includes the following preferable embodiments.

- a. The alkylene glycol supplied to said distillation tower is brought into contact with the unreactive formaldehyde coming from the reactor 1 in counter current, to absorb or react with the formaldehyde, while being introduced into the reactor 1, for reaction with the formaldehyde.
- b. While the molar ratio of the alkylene glycol to formaldehyde in the reactor kept at 1 or more, the amounts of the alkylene glycol and formaldehyde continuously supplied to the distillation tower and the reactor are kept practically equimolar.
- c. The alkylene glycol is at least one selected from a group

consisting of ethylene glycol, diethylene glycol and 1,4-butanediol.

d. The reaction distillation tower used has two or more distillation stages in the distillation tower.

e. The distillation tower of the reaction distillation tower is a plate tower and/or a packed tower.

f. In said step (3), the hydrocarbon compound is at least one selected from a group consisting of cyclopentane, cyclohexene and benzene.

g. In said step (3), the azeotropic mixture consisting of a cyclic formal and water is supplied to the reflux portion or upper stage of the azeotropic distillation tower.

h. In said step (3), the distillate from the azeotropic distillation tower is at least partially refluxed to the azeotropic distillation tower, without discharging all the quantity of the distillate outside the system.

The present invention is also a method for continuously purifying a cyclic formal, in which water is removed from a water-containing cyclic formal by distillation, comprising the step of adding a hydrocarbon compound, the azeotropic point of which with water is not higher than the boiling point of the cyclic formal, to the water-containing cyclic formal, for continuous distillation. This continuous purification method includes the following preferable embodiments.

i. Said cyclic formal is at least one selected from a group

consisting of ethylene glycol formal, diethylene glycol formal and 1,4-butanediol formal.

j. Said hydrocarbon compound is at least one selected from a group consisting of cyclopentane, cyclohexene and benzene.

k. The water-containing cyclic formal is supplied to the reflux portion or upper stage of the distillation tower.

l. The distillate of the distillation tower is at least partially refluxed to the distillation tower, without discharging all the quantity of the distillate outside the system.

The present invention is described below in detail.

The alkylene glycols which can be used in the present invention include ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, (hydromethoxy)ethanol, etc. Among them, ethylene glycol, diethylene glycol and 1,4-butanediol are preferable since they are high in industrial utilization value. Ethylene glycol is especially preferable.

Formaldehyde as the other raw material of reaction can be formaldehyde gas, formaldehyde aqueous solution or paraformaldehyde, etc. In view of easy handling, the use of formaldehyde aqueous solution is preferable.

As the catalyst used in the present invention, an acid catalyst is suitable. The catalysts which can be used include mineral acids such as sulfuric acid and phosphoric acid;

strong organic acids such as sulfonic acid, phosphonic acid and trifluoroacetic acid, solid acid catalysts such as strong acid cation exchange resins, zeolite, silica-alumina and activated clay, and heteropoly-acids such as phosphorus molybdic acid and phosphorus tungstic acid. As the catalyst, an acid nonvolatile under the reaction condition can be preferably used.

As the reaction distillation tower used in the step (1) of the present invention, any ordinary publicly known reaction distillation tower can be used. For example, a reaction distillation tower with a distillation tower directly installed in a reactor can be used. Furthermore, a reaction distillation tower in which the distillate from a reactor installed separately from a distillation tower is supplied to the bottom of the distillation tower by a pipe, etc. while the condensate at the bottom of the distillation tower is returned to the reactor by a pipe, etc. can also be used. The reaction distillation tower used in the present invention is not limited to those described above.

The temperature control means for heating and cooling the reactor and the distillation tower of the reaction distillation tower can be any ordinary means such as steam, heating medium or electric heating, but is not limited to them in the present invention.

In the present invention, the distillation tower of the

reaction distillation tower can be a plate tower or packed tower, etc., but is not limited to them in the present invention. The plate type of the plate tower can be any type such as bubble cap, sieve tray, Uniflux tray, Flexi tray, Natta float bubble tray, ballast tray, cascade tray, venturi tray, Kitter tray, recycling tray, chimney tray, Z tray, turbo grid tray, ripple tray, dual-flow tray or baffle tray, etc.

The packing of the packed tower can be of any type such as ring type, saddle type, Dixon ring, Magmahon packing, spray pack, Pana pack, Goodroy packing, Stedman packing or cross spiral packing, etc.

It is preferable that the number of distillation stages in the distillation tower of the reaction distillation tower is 2 or more. Simple distillation is not preferable since the distilled cyclic formal contains much unreactive formaldehyde. If the number of distillation stages of the distillation tower is sufficiently large, operation can be effected without refluxing the condensate coming from the top of the distillation tower.

At the top of the distillation tower, a condenser can also be installed. If the condenser is used to partially reflux the distillate, the distillation tower can be optimized. Of course, in the present invention, as described above, the cyclic formal can also be produced without refluxing the distillate.

In the execution of the present invention, in said step (1), the positions and timings for supplying the alkylene glycol and formaldehyde as raw materials to the reaction distillation tower are important. The alkylene glycol is supplied to the distillation tower of the reaction distillation tower and brought into contact with unreactive formaldehyde in counter current, for absorbing or reacting with the formaldehyde, to be added to the reactor. On the other hand, it is important that formaldehyde is directly supplied to the reactor for counter current contact of unreactive formaldehyde with the alkylene glycol. In this case, it is preferable that the position at which the alkylene glycol is added to the distillation tower is a middle or higher stage of the distillation tower, to enhance the effect of counter current contact with unreactive formaldehyde. However, the position is not limited to a middle or higher stage, as far as a cyclic formal with a small unreactive formaldehyde content of, say, 1 wt% or less, preferably 0.5 wt% or less can be obtained as intended in the step (1).

In the step (1), it is preferable that the molar ratio of the alkylene glycol to formaldehyde in the reactor is 1 or more, and more preferable is 2 or more. A molar ratio of less than 1 is unpreferable, since the unreactive formaldehyde content in the distilled cyclic formal is too large. On the other hand, if the molar ratio of the alkylene glycol to

formaldehyde in the reactor is larger, a larger reactor is necessary. Therefore, industrially, it is preferable that the molar ratio of the alkylene glycol to formaldehyde is 100 or less.

As for the amounts of the alkylene glycol and formaldehyde supplied to the distillation tower and the reactor in the steady continuous operation state, since they are consumed by equimolar amounts, it is preferable to supply substantially equimolar amounts of them.

For reaction between the alkylene glycol and formaldehyde, ordinary publicly known reaction conditions can be adopted. For example, in the case of ethylene glycol formal, it is preferable that the reaction temperature is 50 to 170°C, and a more preferable range is 80 to 140°C. Furthermore, it is preferable that the reaction pressure is atmospheric pressure to a pressure at which an equimolar amount of water produced in the ethylene glycol formal reaction and the water contained in the raw formalin can be evaporated.

The vapor obtained in this reaction contains a cyclic formal, water and unreactive formaldehyde. Especially as water, the reaction water equal in moles to the cyclic formal and the water in the formalin are distilled together. Thus, in the step (1), the cyclic formal is obtained as a mixture with the substantially equimolar amount of water produced in the reaction and the water in the raw formalin (reaction

distillate).

Then, the obtained reaction distillate is distilled, but since the cyclic formal and water form an azeotropic mixture, it is difficult to sufficiently separate and remove water by ordinary distillation only. So, the obtained mixture of the cyclic formal and water is transferred to the step (2) wherein the azeotropic mixture consisting of the cyclic formal and water is obtained.

The second distillation tower used in the step (2) can be an ordinary publicly known distillation tower. As in the case of the distillation tower of the step (1), if a plate tower is used, the plate type can be any type such as bubble cap, sieve tray, Uniflux tray, Flexi tray, Natta float bubble tray, ballast tray, cascade tray, venturi tray, Kitter tray, recycling tray, chimney tray, Z tray, turbo grid tray, ripple tray, dual flow tray or baffle tray, etc. If a packed tower is used, the packing can be of any type such as ring type, saddle type, Dixon ring, Magmahon packing, spray pack, Pana pack, Goodroy packing, Stedman packing or cross spiral packing, etc.

A distillation tower with a condenser installed at the top for partially refluxing the distille can also be used without any problem.

The pressure of the second distillation tower of the step (2) can be any of atmospheric pressure, higher pressure than

atmospheric pressure or reduced pressure. It is preferable that the operation temperature at the tower bottom is near the boiling point of water at the pressure concerned, and that the operation temperature at the tower top is similarly near the azeotropic point of the cyclic formal and water at the pressure concerned.

In the step (3) to further remove water from the azeotropic mixture consisting of the cyclic formal and water obtained in the step (2), the azeotropic mixture consisting of the cyclic formal and water is supplied to the reflux portion or upper stage of the azeotropic distillation tower, and separately, a hydrocarbon compound to form another azeotropic mixture with water is supplied to a middle or higher stage of the azeotropic distillation tower, for distillation. Thus, from the bottom of the azeotropic distillation tower, a purified cyclic formal can be obtained.

It is important that the hydrocarbon compound used here has an azeotropic temperature with water of not higher than the boiling point of the cyclic formal, and can be concretely, cyclopentane, cyclohexene or benzene, etc. An especially preferable hydrocarbon compound is benzene in view of the separation efficiency between the cyclic formal and water.

As the hydrocarbon compound used to form an azeotropic mixture with water, the hydrocarbon compound obtained by condensing by a condenser, the hydrocarbon compound vapor

containing water, etc. distilled from the top of the azeotropic distillation tower, and separating from the water phase of the condensate by a liquid-liquid separator can be refluxed to the azeotropic distillation tower.

Since the rectification in the step (3) is intended to separate water, the condensed and separated water phase is of course discharged outside the azeotropic distillation tower. In this case, if the water phase discharged outside the azeotropic distillation tower is at least partially returned to the azeotropic distillation tower, the rectification efficiency can be remarkably improved.

As for the quantity of the distillate to be refluxed, it is only required that the molar ratio of the total quantity of the hydrocarbon compound used in circulation in the azeotropic distillation tower and newly supplied to it, to the total quantity of water used in circulation in the azeotropic distillation tower and newly supplied to it is kept preferably at 0.8 to 1.2. As a result, while the water content of the residue from the azeotropic distillation tower is sufficiently kept low, the accompanying hydrocarbon compound can be stably controlled.

It is preferable that the distillate is refluxed to a stage higher than the stage to which the hydrocarbon compound to form an azeotropic mixture with water is supplied, or that both are supplied to the reflux portion. As a result, the

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azeotropic composition can be easily formed, and it can be prevented that the water re-supplied as the distillate separated from the azeotropic distillation tower is contained in the residue.

In the present invention, it is preferable that the added amount of the hydrocarbon compound to form an azeotropic mixture with water is 0.1 to 10 as a ratio by weight to the amount of the azeotropic mixture consisting of the cyclic formal and water. A more preferable range is 0.5 to 5. Since the hydrocarbon compound accompanies the distillate coming from the top of the azeotropic distillation tower and the residue, the amount of the hydrocarbon compound to be newly supplied from outside corresponds to the amount to make up for the shortage in the distillation tower. The amount of the hydrocarbon compound to be newly supplied from outside is usually 0.001 to 1 as a ratio by weight to the amount of the azeotropic mixture consisting of the cyclic formal and water.

The pressure of the azeotropic distillation tower for purifying the cyclic formal is any of atmospheric pressure, higher pressure than atmospheric pressure or reduced pressure. It is preferable that the operation temperature at the tower bottom is about the boiling point of the cyclic formal at the pressure concerned, and that the operation temperature at the tower top is similarly about the azeotropic point of the hydrocarbon compound, cyclic formal and water at the pressure

concerned.

The azeotropic distillation tower used for purification in the step (3) is any ordinary publicly known distillation tower like the second distillation tower. If a plate tower is used, the plate type can be any type such as bubble cap, sieve tray, Uniflux tray, Flexi tray, Natta float bubble tray, ballast tray, cascade tray, venturi tray, Kitter tray, recycling tray, chimney tray, Z tray, turbo grid tray, ripple tray, dual flow tray or baffle tray, etc. If a packed tower is used, the packing can be of any type such as ring type, saddle type, Dixon ring, Magmahon packing, spray pack, Pana pack, Goodroy packing, Stedman packing or cross spiral packing, etc.

In the method of the present invention for continuously producing a purified cyclic formal, raw formaldehyde is supplied to the reactor of a reaction distillation tower, and an alkylene glycol is supplied to the distillation tower of the reaction distillation tower, to produce a cyclic formal with a small unreactive formaldehyde content. Furthermore, the cyclic formal with a small unreactive formaldehyde content is distilled, and rectified with a hydrocarbon solvent to form an azeotropic mixture with water. Thus, a cyclic formal with a small water content can be easily produced at a high yield. The method for continuously producing a cyclic formal of the present invention is economical and can be simplified in operation industrially very significantly.

Brief Description of the Drawings

Fig. 1 is a schematic process drawing for illustrating a cyclic formal production process of the present invention.

Fig. 2 is a schematic process drawing for illustrating another cyclic formal production process of the present invention.

Fig. 3 is a schematic process drawing for illustrating a further other purification process of the present invention.

Fig. 4 is a schematic process drawing for illustrating a still further other purification process of the present invention.

Description of the Preferred Embodiments

In Fig. 1, a reaction distillation tower (not numbered) consists of a reactor 1 and a distillation tower 2. As indicated by arrows, the reactor 1 is connected with the distillation tower 2, and an alkylene glycol is supplied from the bottom of the distillation tower 2 to the reactor 1. Furthermore, from the reactor 1, a product and an unreactive mixture are supplied to the distillation tower 2.

In the present invention, at first, predetermined amounts of an alkylene glycol, formalin and catalyst are initially supplied into the reactor 1, and the temperature in the reactor 1 is heated to a predetermined level.

Then, formalin is continuously supplied from a formalin supply portion 7 into the reactor 1, and the alkylene glycol

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is continuously supplied from an alkylene glycol supply portion 6 into the distillation tower 2.

The alkylene glycol supplied into the distillation tower 2 contacts the unreactive formaldehyde coming from the reactor 1 in counter current, to absorb or react with it, while entering the reactor 1. On the other hand, formaldehyde is directly supplied into the reactor 1, to let unreactive formaldehyde contact the alkylene glycol in counter current. In this case, for better counter current contact of both, it is preferable that the alkylene glycol is added to a middle or higher stage of the distillation tower 2. Thus, a distillate mainly consisting of the alkylene glycol formal and water and small in formaldehyde content (reaction distillate) can be obtained. Furthermore, at the top of the distillation tower 2, a condenser (not illustrated) can also be installed to partially reflux the distillate.

Subsequently, the distillate is supplied to a second distillation tower 3 for continuous distillation. From the bottom of the second distillation tower 3, water is taken out, and from the tower top, an azeotropic mixture consisting of the alkylene glycol formal and water can be obtained.

The azeotropic mixture is continuously supplied to an azeotropic distillation tower 4 for purification shown in Fig. 1, and separately, a hydrocarbon compound is continuously supplied to the top of the azeotropic distillation tower 4,

for distillation in the azeotropic distillation tower 4.

In this case, a vapor is taken out from the top of the azeotropic distillation tower 4. The taken out vapor is condensed by a condenser (not illustrated), and separated into hydrocarbon compound phase and water phase in a liquid-liquid separator 5. The hydrocarbon compound is continuously supplied to the top of the azeotropic distillation tower 4 through a reflux pipe 10. From the bottom of the liquid-liquid separator 5, distillation drain 9 is taken out. From the residue portion 8 at the bottom of the azeotropic distillation tower 4, the purified alkylene glycol formal is taken out.

Fig. 2 shows another embodiment slightly different from Fig. 1. The azeotropic mixture obtained in the second distillation tower of Fig. 1 is continuously supplied to the reflux line of the azeotropic distillation tower 4 for purification shown in Fig. 2. Separately, the hydrocarbon compound is also continuously supplied through the reflux line to the azeotropic distillation tower 4. The vapor taken out of the top of the azeotropic distillation tower 4 is condensed by a condenser (not illustrated) and separated into hydrocarbon compound phase and water phase in the liquid-liquid separator 5. The obtained hydrocarbon compound is continuously supplied through the reflux pipe 10 to the top of the azeotropic distillation tower 4.

From the bottom of the liquid-liquid separator 5, distillation drain 9 is taken out. The condensed and separated water phase is of course discharged outside the system, but as illustrated, the water phase discharged outside the system is at least partially returned to the azeotropic distillation tower 4. Thus, the rectification efficiency can be significantly improved. From the residue portion 8 at the bottom of the azeotropic distillation tower 4, the purified alkylene glycol formal is taken out.

Fig. 3 shows a further other embodiment of the azeotropic distillation tower 4.

The azeotropic mixture consisting of the alkylene glycol formal and water is continuously supplied to the reflux line of the azeotropic distillation tower 4 shown in Fig. 3, and separately the hydrocarbon compound is also continuously supplied through the reflux line to the azeotropic distillation tower 4. Subsequently, the vapor taken out of the top of the azeotropic distillation tower 4 is condensed by a condenser 11, and separated into hydrocarbon compound phase and water phase in the liquid-liquid separator 5. The obtained hydrocarbon compound is continuously supplied to the top of the azeotropic distillation tower 4 through the reflux pipe 10.

In this case, to make up for the hydrocarbon compound decreased in the azeotropic distillation tower 4, the

hydrocarbon compound can be additionally supplied through the reflux pipe 10 to a hydrocarbon compound supply port 12. From the residue portion 8 at the bottom of the azeotropic distillation tower 4, the purified alkylene glycol formal is taken out.

Fig. 4 shows a still further other embodiment of the azeotropic distillation tower 4. The azeotropic mixture consisting of the alkylene glycol formal and water is continuously supplied to the azeotropic distillation tower 4 through the reflux line of the azeotropic distillation tower 4 shown in Fig. 4. Furthermore, the hydrocarbon compound is also continuously supplied to the azeotropic distillation tower 4 through the reflux line. Subsequently, the vapor taken out of the top of the azeotropic distillation tower 4 is condensed by the condenser 11, and separated into hydrocarbon compound phase and water phase in the liquid-liquid separator 5. The hydrocarbon compound obtained like this is continuously supplied to the top of the azeotropic distillation tower through the reflux pipe 10. In this case, to make up for the hydrocarbon compound decreased in the azeotropic distillation tower 4, the hydrocarbon compound can be additionally supplied through the reflux pipe 10 to the hydrocarbon compound supply port 12. Furthermore, the water phase condensed and separated in the liquid-liquid separator 5 is discharged outside the system, but as illustrated, the

water phase can be returned at ²⁴ least partially to the azeotropic distillation tower 4, for significantly improve the rectification efficiency. From the residue portion 8 at the bottom of the azeotropic distillation tower 4, the purified alkylene glycol formal is taken out.

Examples

Examples of the present invention are described below. The present invention is not limited thereto or thereby, and can be properly modified within the scope of the gist of the present invention.

Example 1

In this example, a reaction distillation tower consisting of a reactor 1 (with a capacity of 800 ml) and a distillation tower 2 (Older Shaw plate tower with a diameter of 30 mm and 20 sieve trays installed) was used.

At first, 270 g (4.4 moles) of ethylene glycol, 130 g of 60% formalin (2.6 moles of formaldehyde) and 4 g of sulfuric acid were initially supplied into the reactor 1, and the reactor 1 was heated till the inside temperature reached 120°C. When the inside temperature reached 120°C, 60% formalin was continuously supplied to the reactor 1 from the formalin supply port 7 at a rate of 85 g/hr (1.7 moles of formaldehyde per hour). Separately, ethylene glycol was continuously supplied from the hydrocarbon compound supply port 6 at the 10th stage from the bottom of the distillation tower 2 at a

flow rate of 106 g/hr (1.7 moles/hr).

The ethylene glycol supplied to the distillation tower was introduced into the reactor 1 while being brought into contact with the unreactive formaldehyde coming from the reactor in counter current, for reaction with formaldehyde.

In the reaction distillation tower, it took 120 minutes to obtain a distillate with a stable composition (reaction distillate). The distillate was analyzed by gas chromatography and found to contain 65.4 wt% of ethylene glycol formal, 33.7 wt% of water and 0.1 wt% of formaldehyde.

Example 2

Ethylene glycol formal was produced as described in Example 1, except that the amounts of ethylene glycol and 60% formalin initially supplied into the reactor 1 were 140 g (2.3 moles) of ethylene glycol and 200 g of 60% formalin (4 moles of formaldehyde). The obtained distillate (reaction distillate) was analyzed by gas chromatography and found to contain 62.8 wt% of ethylene glycol formal, 33.1 wt% of water and 1.0 wt% of formaldehyde.

It can be seen that if the molar ratio of ethylene glycol to formaldehyde in the reactor 1 is larger than 1, the amount of formaldehyde as impurity in ethylene glycol formal is obviously small.

Example 3

A reaction distillation tower of the same type as that of

Example 1 except that the distillation tower 2 was a packed tower with a diameter of 30 mm, two distillation stages and ring type packing.

Two hundred and seventy grams (4.4 moles) of ethylene glycol, 130 g of 60% formalin (2.6 moles of formaldehyde) and 4 g of sulfuric acid were initially supplied into the reactor, and the reactor was heated till the inside temperature reached 110°C. When the inside temperature of the reactor 1 reached 120°C, 60% formalin was continuously supplied into the reactor 1 at a flow rate of 85 g/hr (1.7 moles of formaldehyde per hour), and ethylene glycol was continuously supplied to the 1st stage from the bottom of the distillation tower 2 at a flow rate of 106 g/hr (1.7 moles/hr).

In the reaction distribution tower, it took 120 minutes to obtain a distillate with a stable composition (reaction distillate). The distillate was analyzed by gas chromatography and found to contain 64.3 wt% of ethylene glycol formal, 33.4 wt% of water and 0.5 wt% of formaldehyde.

Example 4

A reaction distillation tower consisting of a reactor 1 (with a capacity of 800 ml) and a distillation tower (Older Shaw plate tower with a diameter of 30 mm and 20 sieve trays installed) shown in Fig. 1 was used.

Two hundred and seventy grams (4.4 moles) of ethylene glycol, 130 g of 60% formalin (2.6 moles of formaldehyde) and

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4 g of sulfuric acid were initially supplied into the reactor 1, and the reactor 1 was heated till the inside temperature reached 120°C. When the inside temperature of the reactor 1 reached 120°C, 60% formalin was continuously supplied from the formalin supply port 7 into the reactor 1 at a flow rate of 85 g/hr (1.7 moles of formaldehyde per hour), and ethylene glycol was continuously supplied from the ethylene glycol supply port 6 at the 10th stage from the bottom of the distillation tower 2 at a flow rate of 106 g/hr (1.7 moles/hr).

It took 120 minutes to obtain a distillate with a stable composition (reaction distillate). The distillate was analyzed by gas chromatography and found to contain 65.4 wt% of ethylene glycol formal, 33.7 wt% of water and 0.1 wt% of formaldehyde.

In succession, the distillate was supplied into the distillation tower 3 (plate tower with a diameter of 30 mm and 20 sieve trays) at the 10th stage from the bottom of the distillation tower at a flow rate of 191 g/hr, for continuous distillation at a tower bottom temperature of 103°C. It took 120 minutes to obtain a distillate with a stable composition. From the top of the second distillation tower 3, an azeotropic mixture containing 91.8 wt% of ethylene glycol formal and 7.6 wt% of water was obtained.

The azeotropic mixture was continuously supplied to the 10th stage from the bottom of the azeotropic distillation

tower 4 (plate tower with a diameter of 30 mm and 40 sieve trays) for purification shown in Fig. 1 at a flow rate of 136 /hr, and benzene was continuously supplied to the 3rd stage from the top of the azeotropic distillation tower 4 at a flow rate of 16 g/hr. The distillation operation in the azeotropic distillation tower 4 was conducted at atmospheric pressure at a tower bottom temperature of 77°C. Subsequently, the vapor from the tower top was condensed and separated into benzene phase and water phase in the liquid-liquid separator 5, and the benzene phase was continuously supplied to the 1st stage from the top of the azeotropic distillation tower 4 at a flow rate of 367 g/hr.

From the residue portion 8 at the tower bottom, purified ethylene glycol formal containing 11 wt% of benzene was obtained at 135 g/hr. The yield of ethylene glycol formal to the initially supplied ethylene glycol and formaldehyde was 97.5%. The water content was measured according to the Karl Fischer method and found to be 44 ppm.

Example 5

The azeotropic mixture obtained in Example 4 (containing 91.8 wt% of ethylene glycol formal and 7.6 wt% of water) was continuously supplied into the reflux line of the azeotropic distillation tower 4 (plate tower with a diameter of 30 mm and 40 sieve trays) for purification shown in Fig. 2 at a flow rate of 136 g/hr, and benzene was also continuously supplied

into the reflux line at a flow rate of 16 g/hr. The azeotropic distillation tower 4 was operated at atmospheric pressure at a tower bottom temperature of 77°C. Subsequently, the vapor taken out of the top of the azeotropic distillation tower 4 was condensed and separated into benzene phase and water phase in the liquid-liquid separator 5, and the benzene was continuously supplied to the 1st stage from the tower top at a flow rate of 367 g/hr. Furthermore, supply of water was gradually started, and finally water was continuously supplied to the top of the azeotropic distillation tower 4 at a flow rate of 9 g/hr. From the residue portion 8 at the tower bottom, purified ethylene glycol formal containing 0.7 wt% of benzene was obtained at 135 g/hr. The yield of ethylene glycol formal to the initially supplied ethylene glycol and formaldehyde was 97.5%. The water content was measured according to the Karl Fischer method and found to be 22 ppm.

Comparative Example 1

Ethylene glycol formal was produced as described in Example 4, except that ethylene glycol was supplied together with formaldehyde into the reactor, instead of supplying ethylene glycol to the 10th stage from the bottom of the distillation tower 2. It was analyzed as described in Example 4 and found to contain 63.4 wt% of ethylene glycol formal, 33.8 wt% of water and 1.8 wt% of formaldehyde. It can be seen that the product of the present invention is obviously smaller

in the content of aldehyde as impurity in ethylene glycol formal.

The distillate was purified by the azeotropic distillation tower 4 after distillation in the second distillation tower as described in Example 4. The yield of ethylene glycol formal was 91.4%, and the water content measured according to the Karl Fischer method was 46 ppm.

Comparative Example 2

Ethylene glycol formal was obtained as described in Example 1, except that methanol was added to the azeotropic distillation tower 4 instead of benzene. In this case, the yield of ethylene glycol formal was 97.0%. The water content was measured by gas chromatography and found to be 6.5 wt%.

Example 6

A reaction distillation tower consisting of a reactor with a capacity of 800 ml and a distillation tower 2 (plate tower with a diameter of 30 mm and 20 sieve trays) shown in Fig. 1 was used.

Two hundred and seventy grams (4.4 moles) of ethylene glycol, 130 g of 60% formalin (2.6 moles of formaldehyde) and 4 g of sulfuric acid were initially supplied into the reactor, and the reactor 1 was heated till the inside temperature reached 120°C. When the inside temperature of the reactor 1 reached 120°C, 60% formalin was continuously supplied into the reactor 1 at a flow rate of 85 g/hr (1.7 moles of formaldehyde

per hour), and ethylene glycol was continuously supplied into the distillation tower 2 at a flow rate of 106 g/hr (1.7 moles/hr), for operation at a reflux ratio of 0.5. It took 120 minutes to obtain a distillate with a stable composition (reaction distillate). The distillate was analyzed by gas chromatography and found to contain 65.4 wt% of ethylene glycol, 33.7 wt% of water and 0.1 wt% of formaldehyde. The distillate was supplied into the second distillation tower 3 (plate tower with a diameter of 30 mm and 20 sieve trays), heated to 74°C at atmospheric pressure, and distilled at a reflux ratio of 0.6, to obtain an azeotropic mixture containing 91.8 wt% of ethylene glycol formal and 7.6 wt% of water from the top of the second distillation tower.

The azeotropic mixture containing ethylene glycol formal and water was continuously supplied to the 10th stage from the bottom of the azeotropic distillation tower (plate tower with diameter of 30 mm and 40 sieve trays) shown in Fig. 1 at a flow rate of 211 g/hr, and benzene was continuously supplied to the 3rd stage from the tower top at a flow rate of 24 g/hr, for operation at atmospheric pressure at a tower bottom temperature of 77°C. Then, the vapor from the tower top was condensed and separated into benzene phase and water phase in the liquid-liquid separator, and the benzene phase was continuously supplied to the tower top at a flow rate of 570 g/hr. Purified ethylene glycol formal was obtained from the

tower bottom. When measured according to the Karl Fischer method, the water content was found to be 40 ppm and the benzene content was found to be 12 wt%.

Example 7

The azeotropic mixture containing 91.8 wt% of ethylene glycol formal and 7.6 wt% of water obtained in Example 6 was continuously supplied into the reflux line of the azeotropic distillation tower 4 (plate tower with a diameter of 30 mm and 40 sieve trays) shown in Fig. 3 at a flow rate of 211 g/hr, and benzene was also continuously supplied to the reflux line at a flow rate of 24 g/hr, for operation at atmospheric pressure at a tower bottom temperature of 77°C. Subsequently, the vapor from the top of the azeotropic distillation tower 4 was condensed and separated into benzene phase and water phase in the liquid-liquid separator 5, and the benzene phase was continuously supplied to the top of the azeotropic distillation tower 4 at a flow rate of 570 g/hr. From the bottom of the azeotropic distillation tower 4, purified ethylene glycol formal was obtained. When measured according to the Karl Fischer method, the water content was found to be 20 ppm and the benzene content was found to be 12 wt% as before.

Example 8

The azeotropic mixture containing 91.8 wt% of ethylene glycol formal and 7.6 wt% of water obtained in Example 6 was

continuously supplied into the reflux line of the azeotropic distillation tower 4 (plate tower with a diameter of 30 mm and 40 sieve trays) shown in Fig. 4 at a flow rate of 211 g/hr, and benzene was also continuously supplied into the reflux line at a flow rate of 24 g/hr, for operation at atmospheric pressure at a tower bottom temperature of 77°C. Subsequently, the vapor from the tower top was condensed by the condenser 11 and separated into benzene phase and water phase in the liquid-liquid separator 5, and the benzene phase was continuously supplied to the top of the azeotropic distillation tower 4 at a flow rate of 570 g/hr. Furthermore, supply of water phase was gradually started, and finally water was continuously supplied to the tower top at a flow rate of 14 g/hr. When the distillate and the residue of the azeotropic distillation tower 4 became stable in composition, purified ethylene glycol formal was obtained from the bottom of the azeotropic distillation tower 4. When measured according to the Karl Fischer method, the water content was found to be 20 ppm and the benzene content was found to be 0.8 wt%.



What is claimed is:

1. A method for continuously producing a cyclic formal, in which a reaction distillation tower equipped with a reactor and a distillation tower is used for letting an alkylene glycol and formaldehyde react with each other in the presence of a catalyst, to produce a cyclic formal, comprising the step of continuously supplying the alkylene glycol from the distillation tower to the reactor of the reaction distillation tower, while continuously supplying formaldehyde to the reactor of the reaction distillation tower, for letting both the ingredients react with each other.



2. A method for continuously producing a cyclic formal, according to claim 1, wherein the alkylene glycol supplied to the distillation tower is brought into contact with the unreactive formaldehyde coming from the reactor in counter current, to absorb or react with the formaldehyde, while being introduced into the reactor 1, for reaction with the formaldehyde.

3. A method for continuously producing a cyclic formal, according to claim 1 or 2, wherein the molar ratio of the alkylene glycol to formaldehyde in the reactor is kept at 1 or more, while the amounts of the alkylene glycol and the formaldehyde continuously supplied into the distillation tower and the reactor are substantially equimolar.

4. A method for continuously producing a cyclic formal, according to any one of claims 1 through 3, wherein the alkylene glycol is at least one selected from a group consisting of ethylene glycol, diethylene glycol and 1,4-butanediol.

5. A method for continuously producing a cyclic formal,



according to any one of claims 1 through 4, wherein the reaction distillation tower used has two or more distillation stages in the distillation tower.

6. A method for continuously producing a cyclic formal, according to any one of claims 1 through 5, wherein the distillation tower used in the reaction distillation tower is a plate tower and/or a packed tower.

7. A method for continuously producing a cyclic formal, in which a reaction distillation tower equipped with a reactor and a distillation tower is used to let an alkylene glycol and formaldehyde react with each other in the presence of a catalyst, to produce a cyclic formal, comprising

(1) the step of continuously supplying an alkylene glycol from the distillation tower to the reactor of the reaction distillation tower while continuously supplying formaldehyde to the reactor of the reaction distillation tower, for letting both the ingredients react with each other, to continuously obtain a reaction distillate containing water and a cyclic formal from the top of the distillation tower,

(2) the step of continuously supplying the reaction distillate containing water and a cyclic formal obtained in said step (1) to a second distillation tower, to continuously obtain an azeotropic mixture consisting of the cyclic formal and water, and

(3) the step of supplying the azeotropic mixture consisting of



the cyclic formal and water obtained in said step (2) to an azeotropic distillation tower, while supplying a hydrocarbon compound, the azeotropic point of which with water is not higher than the boiling point of the cyclic formal, for continuous distillation, and obtaining the azeotropic mixture consisting of the hydrocarbon and water from the top of the azeotropic distillation tower while continuously obtaining the cyclic formal purified after removing water, from the tower bottom.

8. A method for continuously producing a cyclic formal, according to claim 7, wherein the molar ratio of the alkylene glycol to formaldehyde in the reactor is kept at 1 or more, while the amounts of the alkylene glycol and the formaldehyde continuously supplied into the distillation tower and the reactor are substantially equimolar.
9. A method for continuously producing a cyclic formal, according to claim 7 or 8, wherein the alkylene glycol is at least one selected from a group consisting of ethylene glycol, diethylene glycol and 1,4-butanediol.
10. A method for continuously producing a cyclic formal, according to any one of claims 7 through 9, wherein in said step (3), the hydrocarbon compound is at least one selected from a group consisting of cyclopentane, cyclohexene and benzene.
11. A method for continuously producing a cyclic formal,



according to any one of claims 7 through 10, wherein in said step (3), the azeotropic mixture consisting of a cyclic formal and water is supplied to the reflux portion or upper stage of the azeotropic distillation tower.

12. A method for continuously producing a cyclic formal, according to any one of claims 7 through 11, wherein in the step (3), the distillate from the azeotropic distillation tower is refluxed at least partially to the azeotropic distillation tower, without discharging all the quantity of the distillate outside the system.

13. A method for continuously purifying a cyclic formal, in which water is removed from a cyclic formal containing water by distillation, comprising the step of adding a hydrocarbon compound, the azeotropic point of which with water is not higher than the boiling point of the cyclic formal, to the cyclic formal containing water, for continuous distillation.

14. A method for continuously purifying a cyclic formal, according to claim 13, wherein the cyclic formal is at least one selected from a group consisting of ethylene glycol formal, diethylene glycol formal and 1,4-butanediol formal.

15. A method for continuously purifying a cyclic formal, according to claim 13 or 14, wherein the hydrocarbon compound is at least one selected from cyclopentane, cyclohexene and benzene.

16. A method for continuously purifying a cyclic formal,



according to any one of claims 13 through 15, wherein the cyclic formal containing water is supplied to the reflux portion or upper stage of the distillation tower.

17. A method for continuously purifying a cyclic formal, according to any one of claims 13 through 16, wherein the distillate of said distillation tower is refluxed at least partially to the distillation tower, without discharging all the quantity of the distillate outside the system.