

Water Separation System

Background of the Invention

Field of the Invention

[0 0 0 1]

The present invention relates to a water separation system.

Background Art

[0 0 0 2]

A device for mixing fluids within microchannels (so-called microreactor), which have been manufactured by a micro-processing technology, has been recently used in fields of biotechnology, pharmaceuticals, chemical synthesis, or the like. A feature of reactions using the microreactors is, for example, a miniaturization of reaction systems. As constitutional elements of fluids (i.e. source molecules) are quickly diffused, and mixed by the miniaturization of such reaction systems, a surface area per volume (i.e. specific surface area) relatively increases. As a result, shortening of reaction time and improvement of yield can be expected, as a reaction efficiency improves, compared with a batch reaction.

[0 0 0 3]

One of chemical reactions is an equilibrium reaction. The equilibrium reaction is a reaction, in which the reaction rate for a forward reaction becomes equal to that for a backward reaction as the reaction proceeds, and composition ratio between reactants and products does not seemingly change.

[0 0 0 4]

One of the equilibrium reactions is a reaction producing water other than a target product as products. As an example, esterification reactions reacting alcohols on carboxylic acids or the like are, specifically, given. Then, the target products become carboxylate esters. As such reactions are equilibrium reactions, the generated target product (for example, carboxylate ester) is hydrolyzed by water produced at the same time and

returns to an original reactant (for example, carboxylic acid). That is, a forward reaction and a backward reaction proceed simultaneously.

[0 0 0 5]

In the case where a rate producing the target product is extremely faster than a rate hydrolyzing the target product in such an equilibrium reaction, there is no problem in view of the normal yield. In the case where the former rate is comparatively faster than the latter rate, the target product is quickly hydrolyzed, even if it is produced. As a result, it is difficult to improve the yield of the target product.

[0 0 0 6]

Accordingly, it is considered to separate (remove) water producing together with the target product outside the reaction system in order to improve the yield in such a reaction. This can improve the yield as the chemical equilibrium is shifted to produce the target product.

[0 0 0 7]

As an art separating (eliminating) water from the mixed solution containing the target product as above mentioned and water, a distillation has been generally used. In recent years, a pervaporation is drawn attentions other than the distillation. The pervaporation is a method using separation membranes with affinity for an object substance for separation (e.g. water). As a specific means applying the separation membrane, mixed solution is set (flowed) at one side (supply side) of the separation membrane and is kept under reduced pressure at an opposite side (permeation side). Thus, it facilitates a vaporization of liquid that goes through the separation membrane and reaches the opposite side, and can selectively permeate and separate an object substance for separation by permeation rate difference of each component.

[0 0 0 8]

Water separation arts using pervaporation have been various studied. For example, Japanese Patent Unexamined Publication No. 2007 - 203210 (hereinafter, referred to as Patent Literature 1) discloses a membrane

module that has a tubular separation membrane with one end closed and with the other end opened. It discloses a membrane module where the other end of the separation membrane is watertightly mounted in a tubular plate provided in a casing and a target substance is permeated in liquid mixture or in gas mixture flowing outside the separation membrane, selectively inside the separation membrane. It also discloses a membrane module filling with porous filler in a space formed between the inside of the casing and the outside of the separation membrane.

[0 0 0 9]

Japanese Patent Publication No. 4,462,884 (hereinafter, referred to as Patent literature 2) discloses a membrane separation reaction system, in which provides a reactor, a membrane module separating contaminating component generating inside the reactor and evaporating together with the reactant from the reactant, a heater heating up a mixture of the evaporated contaminating component and the ingredient, and a circulator circulating compulsively the vapor of the reactant separated in the membrane module in the liquid phase of the reactor, to configure the separation membrane of the membrane module made of zeolite membrane. The heater is configured to supply heat in such a manner that the reactant and the contaminating component exist in a state of evaporation without condensing them inside the membrane module.

[0 0 1 0]

Summary of the Invention (Problem to be solved)

[0 0 1 1]

In an art described in Patent Literature 1, a separation operation is performed in spite of a mount of water contained in solution (reaction liquid). Thus, separation efficiency is low, depending upon a mount of water contained. Then, water separation requires a lot of separation operations.

[0 0 1 2]

Furthermore, it is required to heat up the solution up to an evaporable temperature in an art described in Patent Literature 1. As a result, it results in large equipments in size.

[0 0 1 3]

In an art described in Patent Literature 2, it is configured to evaporate reactant (ethanol) and water from reaction liquid and separate water flowing through the membrane module having the separation membrane. Only a reactant after separating water returns to the reaction vessel. In such a way, in an art described in Patent Literature 2, a circulation cycle is required for water separation. Then, an equipment for forming a circulation cycle becomes larger in size and complicated. The equipment for evaporating reacting liquid may be required and also the equipment becomes large in size.

[0 0 1 4]

Reaction liquid may be unstable in temperature control by an influence of the circulated reactant (returned to the reaction vessel). Then, it is difficult to control a reaction within a reaction vessel. As a result, the yield may be low and the by-product may happen to be produced. As the time from evaporating the reactant to a time for beginning water separation is constant, the reaction time cannot be controlled only by changing the numbers of circulation. That is, a control of the reaction time may be restricted.

[0 0 1 5]

An object of the present invention is to provide a water separation system, which improves the water separation efficiency with simple equipment and is arbitrarily configurable in reaction time.

Means for solving the above problem

[0 0 1 6]

The present applicants have carefully studied to solve the above problem. As a result, they found a solution of the above problem by controlling a time to beginning water separation based on an amount of product(s), and then they have completed it.

Effect of the Invention

[0 0 1 7]

The present invention provides a water separation system, which improves the water separation efficiency with simple equipment and is arbitrarily configurable in reaction time.

Brief Description of Drawings

[0 0 1 8]

Figure 1 is a schematic view showing a configuration of the water separation system according to the first embodiment.

Figure 2 is a schematic view showing a configuration of the water separation means applied in the water separation system according to the first embodiment.

Figure 3 is a view explaining a reaction rate constant concerning a reaction proceeded in the water separation means according to the first embodiment.

Figure 4 is a graph showing a change of rates relative to time.

Figure 5 is a schematic view showing a configuration of the water separation system according to the second embodiment.

Figure 6 is a schematic view showing a configuration of chemical reaction processing device applied in the water separation system according to the second embodiment.

Figure 7 is a flowchart at the time of control for the improvement of the water separation efficiency according to the second embodiment.

Figure 8 is a schematic view showing a configuration of the water separation system according to the third embodiment.

Figure 9 is a graph showing results of embodiments.

Embodiments for carrying out Invention

[0 0 1 9]

Although embodiments (the present embodiments) for carrying out the present invention will be, hereinafter, described with reference to drawings, the present embodiments are not restricted by the following matters and can be put in practice by arbitrarily changing without departing from a gist of the present invention.

[0 0 2 0]

1. First Embodiment

< Configuration >

Figure 1 is a schematic view showing a configuration of a water separation system 100 according to the first embodiment. The water separation system 100 as shown in Figure 1 is a water separation system separating water from product solution (reaction solution) obtained after a chemical reaction of oleic acid and methanol. Although oleic acid and methanol are used as an example of reactants, it is not restricted to these if it is reactants generating water by chemically reacting.

[0 0 2 1]

Although the detail will be described later, when the oleic acid and methanol are chemically reacted as reactants (specifically, an esterification reaction is proceeded), the methyl oleate and water are produced. In this embodiment, a component other than water among the produced components is called as a "product". The product used in the first embodiment is "oleic acid".

[0 0 2 2]

As shown in Figure 1, a water separation system 100 is provided with an oleic acid tank 1a, a methanol tank 1b, a pair of pumps 2a and 2b, a microreactor for mixing 3, a chemical reaction processing section 4, a temperature controller 5, a microreactor for water separation 6, a temperature controller 7, a back-pressure valve 8, a product material tank 9, a cold trap 10, a decompressor 11, and a controller 12. In Figure 1, it represents a piping as a solid line represents a piping and a dashed line represents an electrical signal line.

[0 0 2 3]

The oleic acid tank 1a is used for storing the oleic acid as a reactant. The methanol tank 1b is used for storing the methanol as the other reactant. Then, it is designed to supply the oleic acid and methanol from these tanks to the microreactor for mixing 3 by the pumps 2a and 2b.

[0 0 2 4]

The pumps 2a and 2b are configured by, for example, a syringe pump, a manual syringe, a plunger pump, a diaphragm pump, a screw pump, or the like. A solution supply device with use of a water head difference may be used in place of a pump.

[0 0 2 5]

The microreactor for mixing 3 (mixing means) is used for mixing oleic acid and methanol. The microreactor for mixing 3 is configured such that oleic acid and methanol are supplied to mix them. The specific configuration of the microreactor for mixing 3 is not particularly restricted and may be configured to mix the reactants rapidly. For example, channel structure of the microreactor for mixing 3 may be Y-shaped, T-shape, a structure forming multilayer flow, or the like, and also a commercially available microreactor.

[0 0 2 6]

Although two kinds of reactants are mixed at the microreactor for mixing 3 in the first embodiment, it may be designed to mix three or more kinds of reactants. For example, in the case where three kinds of reactants are previously mixed, it may be provided with a microreactor for mixing 3 having a flow channel mixing three kinds of reactants may be provided in place of the microreactor for mixing 3. A plurality of microreactors for mixing to mix two kinds of reactants are serially connected to mix reactants in turn, the desirable kinds (numbers) of reactants may be mixed.

[0 0 2 7]

A degree of mixture in the microreactor for mixing 3 is not particularly restricted. Reactants may be uniformly mixed or not uniformly mixed (i.e. emulsification).

[0 0 2 8]

A typical length of channel diameter of the microreactor for mixing 3 is not particularly restricted. It is desirable that the typical length may be several millimeters or less from a viewpoint of utilizing an effect based on a reaction in a space on the micrometer order. It is also desirable that the typical length may be ranged from tens of micrometers to one millimeter from a

viewpoint of mixing reactants quickly by molecular diffusion.

[0 0 2 9]

As a constitutional element of the microreactor for mixing 3, any material may be used if they are not affected by a chemical reaction. As such a material, stainless steel, silicone, gold, glass, hastelloy, silicone resin, fluorine-based resin, or the like is given as an example. Besides these materials, glass lining, coated surface of metal formed by nickel, gold, or the like, oxidized surface of silicone, and improved material in corrosion resistance may be used. From a viewpoint of thermal conductivity and strength, it is desirable to use metal as a constitutional element of the microreactor for mixing 3.

[0 0 3 0]

In order to react quickly at a chemical reaction processing section 4 as later described, it is desirable to provide a temperature controlling machine, as not shown, in the microreactor for mixing 3 and a piping connecting the microreactor for mixing 3 and pump 2a or 2b, and mix at a predetermined temperature. This causes increasing temperature width or decreasing temperature width of reaction solution to be small at the chemical reaction processing section 4. As a result, this can cause the chemical reaction to proceed more efficiently.

[0 0 3 1]

The chemical reaction processing section 4 (chemical reaction processing means) is configured to proceed the chemical reaction of reactants mixed at the microreactor for mixing 3. In the first embodiment, a piping (microchannel) flowing after discharging reaction solution from the microreactor for mixing 3 (that is, a mixture of oleic acid and methanol) functions as the chemical reaction processing section 4. Thus, the chemical reaction time can be controlled by changing a length of the piping or a sectional area of the flow channel.

[0 0 3 2]

Strictly speaking, the above "chemical reaction time" means a time that passes after the reactants are mixed in the microreactor for mixing 3 until it

begins separating water supplied to a microreactor for water separation (as later described). A residence time inside the microreactor for mixing 3 is further shorter than a residence time inside the chemical reaction processing section 4. Although the chemical reaction actually proceeds inside the microreactor for water separation 6, the water separation process proceeds more preferentially than the chemical reaction, as an equilibrium of chemical reaction is shifted at the same time as water is separated. Thus, the "chemical reaction time" in this specification means a residence time inside the chemical reaction processing section 4.

[0 0 3 3]

The above chemical reaction time may be controlled by fixing a length of the piping and controlling an amount of oleic acid and methanol supplied to the microreactor for mixing 3. That is, as a length and an inside diameter of the piping are constant, a residence time in the chemical reaction processing section 4 shortens in the case of flowing a large amount of reaction solution. On the other hand, a residence time in the chemical reaction processing section 4 prolongs in the case of flowing a small amount of reaction solution. The chemical reaction may be controlled with the above relationships. In this case, the supply flow rates of the reactants supplied to the microreactor for mixing 3 can be controlled by the controller 12 as described later.

[0 0 3 4]

The constituent material of the chemical reaction processing section 4 is not particularly restricted. For example, the same material as the microreactor for mixing 3 may be used. For example, a material of tubes such as Teflon (Registered Trademark) or the like may be used. A flow channel diameter of the chemical reaction processing section 4 is not particularly restricted, and then a flow channel diameter explained for, for example, the microreactor for mixing 3 may be used.

[0 0 3 5]

The temperature controller 5 (controller of chemical reaction temperature) is for controlling the temperature at the time of chemical reactions in the chemical reaction processing section 4. Specific constitution of the temperature controller 5 is not particularly restricted. The thermostatic

chamber, Peltier element, mantle heater, or the like with use of fluid such as water, water-ethanol mixed solvent, or ethylene glycol may be used. In the case where the chemical reaction temperature is room temperature, the temperature controlling machine, may not be provided, depending on thermal controlling properties of reaction heat and microreactors.

[0 0 3 6]

The microreactor for water separation 6 (water separation means) is for separating water in the reaction solution flowing through the chemical reaction processing section 4. Materials or flow channel diameter constituting the microreactor for water separation 6 is not particularly restricted. For example, the matters explained in the microreactor for mixing 3 may be also applied.

[0 0 3 7]

Only one of the microreactor for water separation 6 may be provided. A plurality of the microreactors for water separation 6 may be provided to connect in series. These microreactors can be provided as required, according to the desired water separation time. The microreactor for water separation 6 has a point-symmetry configuration as later described with reference to Figure 2, a plurality of the microreactors for water separation 6 may be provided in a minimal space even in the case of serial connection of a plurality of the microreactors.

[0 0 3 8]

A specific configuration of the microreactor for water separation 6 in the first embodiment will be described with reference to Figure 2.

[0 0 3 9]

The microreactor for water separation 6 has an approximately disk shape and has a flange member at the upper and lower ends. This flange member is provided with an inlet 20d (See Figure 2B) for discharging water and an outlet 20e for discharging process liquid after separating water from the reaction solution.

[0 0 4 0]

An inside structure of the microreactor for water separation 6 is configured as shown in Figure 2B. As shown in Figure 2B, the upper and lower ends of the microreactor for water separation 6 have the same configuration. Then, a configuration of the upper end and side will be mainly described in order to simplify the explanation.

[0 0 4 1]

The microreactor for water separation 6 is mainly configured by a first disc member 20 having the inlets 20b, 20c, a second disc member 21 having a protruding portion 21a, and a microreactor body 22 made from the flange 22a and a disk member 22b. The first disc member 20, the second disc member 21 and the flange 22a are fixed by a screw 20a (6 pieces in Figure 2) penetrating therethrough.

[0 0 4 2]

The packing (O-ring) 23a, 23b for preventing leak are provided between the first disc member 20 and the second disc member 21. A packing 23c is also provided between the second disk member 21 and the flange 22a.

[0 0 4 3]

The separation membrane 24 is for separating water from the reaction solution. The separation membrane 24 is made of T-typed zeolite membrane. The separation membrane 24 is provided to surround the upper and lower protruding portions 21a through a packing as not shown. In addition, the packing may be fixed to connecting the second disc member 21 with the upper and lower ends of the separation membrane 24. This prevents leak.

[0 0 4 4]

A space formed between an outside surface of the separation membrane 24 and inside wall surface of the disk member 22b becomes a reaction solution channel 25 for sending the reaction solution. A space formed inside the separation membrane 24 kept under reduced pressure by a decompressor 11 (as later described). Thus, vaporized water permeates the separation membrane 24 and is discharged outside (the detail will be described). That

is, a space inside the separation membrane 24 forms a water vapor flow channel 26 for flowing water vapor.

[0 0 4 5]

The inlet 20b and the reaction solution channel 25, and also the reaction solution channel 25 and an outlet 20e communicate through the holes (as not shown) provided at equal intervals along a circumferential direction of the second disc member 21, respectively. Such holes cause the reaction solution to flow uniformly inside the microreactor for water separation 6. Thus, it prevents from flowing through a path of low pressure loss, i.e. so-called shortcut.

[0 0 4 6]

The water vapor flow channel 26 and the outlet 20d communicate each other, in a similar way (as shown in the figure). Thus, water contained in the reaction solution sending the reaction solution channel 25 through the inlet 20b is configured to permeate the separation membrane 24 and discharge outside through the water vapor flow channel 26 and the outlet 20d. On the other hand, the process liquid (i.e. the liquid containing methyl oleate) after water is separated from the reaction solution is configured to discharge outside through the outlet 20.

[0 0 4 7]

In addition, the inlet 20c of the microreactor for water separation 6 in the first embodiment is sealed. As above mentioned, the microreactor for water separation 6 has a point-symmetry configuration about the center of the vertical (longer) direction of the microreactor as a symmetric point. Thus, in the case where a plurality of the microreactors for water separation 6 are connected, or in the case of replacing a vertical direction, it may be configured not to seal or to seal the inlet or the outlet, as needed.

[0 0 4 8]

Each of the inlet and outlet is configured to be connectable to a tube (piping). Specifically, a screw hole for fitting is formed at each of the inlet and outlet as not shown, and the tube is configured to connect to each of the inlet and outlet by using a fitting as not shown.

[0 0 4 9]

Returning to Figure 1, whole a configuration of the water separation system 100 will be subsequently described.

[0 0 5 0]

The temperature controlling machine 7 (water separation temperature control means) is used for controlling a temperature of the microreactor for water separation 6. That is, it is used for controlling a temperature at the time of separating water from the reaction solution. A specific configuration of the temperature controlling machine 7 is not particularly restricted, for example, the same as the above temperature controller 5 may be used.

[0 0 5 1]

In the first embodiment, the system may be designed such that a temperature of the chemical reaction differs from a temperature at the time of water separation each other. For example, the temperature controller 5, 7 may be designed such that a temperature of the chemical reaction increases and a temperature of water separation decreases. As the chemical reaction does not proceed without going beyond the activation energy, it is easy to proceed at a higher reaction temperature. On the other hand, it is preferable to separate water at a lower temperature, as the separation membrane 24 (See Figure 2) is generally poor in heat resistance. Thus, the temperature can be designed to differ between at the time of the chemical reaction and at the time of water separation.

[0 0 5 2]

The back-pressure valve 8 is a valve for connecting to the reaction solution channel 25 and the outlet 20e explained with reference to Figure 2. The back-pressure valve 8 applies pressure on the reaction solution channel 25 to compress and prevents from evaporating methanol having a low boiling point. As a result, a differential pressure between the reaction solution channel 25 and the water vapor flow channel 26 becomes large. Then, water separation due to the separation membrane 24 can be promoted. In the case where the desired temperatures of the temperature controller 5, 7 are set to be lower in temperature than the boiling points of oleic acid and methanol, the back-pressure valve 8 cannot be provided.

[0 0 5 3]

The product material tank 9 is a tank for storing process liquid containing methyl oleate produced by a reaction of oleic acid and methanol. Specific configuration of the product material tank 9 is not particularly restricted, and it may be the same configuration as the oleic acid tank 1a and the methanol tank 1b. A tank for separating or recovering unreacted oleic acid or methanol may be provided.

[0 0 5 4]

The cold trap 10 is configured to connect to the water vapor flow channel 26 and the outlet 20d explained with reference to Figure 2. That is, it is configured to separate in the microreactor for water separation 6 and cool down vaporized water discharged outside. Thus, the vaporized water (water vapor) changes into liquid water and then the separated water can be easily recovered.

[0 0 5 5]

The decompressor 11 is used for maintaining the water vapor flow channel 26 under reduced pressure. The decompressor 11 promotes water separation caused by the separation membrane 24. Specific configuration of the decompressor 11 is not particularly restricted and then any decompressor may be used.

[0 0 5 6]

The controller 12 is configured to control the chemical reaction time in the chemical reaction processing section 4. Specifically, it is configured to control the flow rates of the reactants into the microreactor for mixing 3 by controlling the pumps 2a and 2b by the controller 12. Thus, the chemical reaction time as above mentioned is controlled. At this time, the controller 12 controls the flow rates of the reactants based on a ratio of the product in the process liquid flowing into the product material tank 9. That is, the feedback control is made.

[0 0 5 7]

Specifically, it is configured to control the chemical reaction time such that the chemical reaction time is shortened in the case of a large amount of the

product (methyl oleate) in the process liquid and is prolonged in the case of a small amount of the product therein. In other words, it is configured to control such that the chemical reaction time in the chemical reaction processing section 4 is shortened in the case of a large amount of methyl oleate discharged from the chemical reaction processing section 4 and the chemical reaction time in the chemical reaction processing section 4 is prolonged in the case of a small amount of methyl oleate discharged from the chemical reaction processing section 4.

[0058]

A reason for controlling the above will be described. The controller can predict an amount of produced methyl oleate, as the controller controls the flow rates of the reactants as above mentioned. As compared an expected amount of the product with the actually produced amount of methyl oleate, it is judged that an increase of the chemical reaction should be further required for a case where the actually produced amount of methyl oleate is less than the expected amount of product. As a result, the chemical reaction time is prolonged. This can produce more methyl oleate and water.

[0059]

On the other hand, it is judged that an amount of produced methyl oleate does not increase even at a longer chemical reaction time, in the case where an amount of produced methyl oleate is approximately the same as the actually produced amount of methyl oleate. As a result, it is controlled to gradually shorten the chemical reaction time. This control saves the chemical reaction time.

[0060]

A measuring method of produced amount of methyl oleate is not particularly restricted. For example, the measuring method may be used with density, refractivity, FT-IR(Fourier Transform Infrared Spectroscopy), UV(Ultraviolet Infrared Spectroscopy), HPLC(High Performance Liquid Chromatography), GC(Gas Chromatography), or the like.

[0 0 6 1]

The controller 12 has a function controlling a drive of temperature controlling machine 5 and 7. That is, when a desired temperature of the temperature controlling machine 5 and 7 is inputted into the controller 12, the controller 12 is configured to control the temperature controlling machine 5 and 7 such that the desired temperature can be obtained.

[0 0 6 2]

In addition, the controller 12 is configured by CPU (Central Processing Unit), sequencer, or the like.

[0 0 6 3]

<Function and Effect>

Next, the function and effect will be described with reference to Figures 3 and 4.

[0 0 6 4]

As shown in Figure 3, the equilibrium reaction in the supply side of the separation membrane 24 (e.g. reaction solution channel 25), an equilibrium reaction proceeds with a reaction rate constant k_1 for a forward reaction, and a reaction rate constant k_2 for a rearward reaction. Strictly speaking, the reaction proceeds just after starting a mixture of the reactants until the methyl oleate is isolated. This figure shows, for convenience of explanation, by restricting to a reaction inside the microreactor for water separation 6. The liquid water in the supply side permeates the separation membrane 24 by being decompressed to water vapor, and reaches a permeation side (i.e. water vapor channel 26). The permeation rate constant (i.e. separation rate constant) for permeating the separation membrane 24 or water vapor is set as k_2 .

[0 0 6 5]

As shown in Figure 4, when the reaction time becomes longer, the reaction rate for the forward reaction (forward reaction rate) decreases according to the residues of reactants. When the reaction rate becomes faster, an amount of water existing in the reaction system also results in increasing as the reaction proceeds. On the other hand, in the water separation due to

the separation membrane 24, as an amount of water in the reaction solution becomes larger, the separation rate becomes faster. In consideration of the above matter, as a longer reaction time makes an amount of water existing in the reaction system larger, the water separation rate becomes faster.

[0 0 6 6]

In the case of equilibrium reaction, the backward reaction, however, proceeds as well as the forward reaction. The reaction rate for the backward reaction increases, as the reaction time becomes longer. When the reaction time becomes enough, even if the reaction time is longer, the forward reaction rate becomes equal to the backward reaction rate in some time. Then, the chemical reaction is hard to proceed. In other word, the water production rate decreases gradually, and an amount of water existing in the reaction system does not change. High separation efficiency of water (i.e. high yield) and a cut of the waste time until a beginning of water separation can be, therefore, obtained by appropriately setting the reaction time according to an amount of the product as performed by the water separation system 100. Complication and increasing the size of the equipment can be also prevented in order not to circulate the reaction liquid. Furthermore, as a temperature of the reaction liquid is stably controlled, the by-product can be restricted to produce.

[0 0 6 7]

2. Embodiment 2

Next, referring to Figure 5, a water separation system 200 according to Embodiment 2 will be described in detail. Here, the same units (members) as the water separation system 100 in Figure 1 are denoted by the same numerals, and the detailed explanations will be omitted.

[0 0 6 8]

<Configuration>

As shown in Figure 5, in the water separation system 200, a chemical reaction processing section 4 is provided with three chemical reaction processing devices 131, 132 and 133 and three channel controlling units 141, 142 and 143. A configuration of the chemical reaction processing device 13 is shown in Figure 6A.

[0 0 6 9]

The chemical reaction processing device 13 has a microchannel 13b of a typical length that is embedded inside a substrate 13d. As shown in Figure 6A, the microchannel 13b has one open end as an inlet 13a on the front side, and the other open end as an outlet 13c on the rear side. As a result, the reaction solution entered from the inlet 13a is designed to flow through the microchannel 13b and go out from the outlet 13c.

[0 0 7 0]

The constituent material of the chemical reaction processing device 13 is not particularly restricted. For example, the same material as that of the microreactor for mixing 3 as described above may be used. A flow channel diameter of the chemical reaction processing device 13 is not particularly restricted, and can be, for example, the same as a flow channel diameter for the microreactor for mixing 3.

[0 0 7 1]

Further, the structure of the microchannel 13b may not be limited to the structure shown in Figure 6A, and may be linear or spiral. In addition, each of the chemical reaction processing devices 13 may have a different channel structure from the rest of the devices, or only some of the devices may have an identical channel structure and the other devices may have different channels. Preferably, all of the microchannels in the chemical reaction processing devices 13 may have an identical structure in view of uniforming heat removal performance of each the chemical reaction processing device 13 and making chemical reaction control easy. Further, the chemical reaction processing device 13 may be formed in one piece or may be disassembled.

[0 0 7 2]

Further, the inlet 13a and the outlet 13c are disposed to be point symmetric about the center of the vertical (longer) direction of the chemical reaction processing device 13. In such an arrangement of the inlet 13a and the outlet 13c, a length of the microchannel 13b can be easily changed by only making a pile of the devices, as shown in Figure 6B. Furthermore, a plurality of the chemical reaction processing devices 13 can be connected

with a minimum dead volume.

[0 0 7 3]

Further, each of the inlet 13a and the outlet 13c has a screw hole for fitting (not shown). With the unillustrated fittings, the tube can be connected to either of the inlet 13a and the outlet 13c.

[0 0 7 4]

In the water separation system 200 shown in Figure 5, a plurality of the chemical reaction processing devices 13 are mutually connected through the channel controlling units 14. The controller 12 is designed to change the number of the chemical reaction processing devices 13 that the reaction solution flows through by switching over the channel controlling unit 14. A length of the microchannel 13b can be easily changed by a configuration of the chemical reaction processing section 4 to control the chemical reaction time easily.

[0 0 7 5]

Specifically, when, for example, the mixture is meant to flow through the single chemical reaction processing device 13(131), the channel controlling units 141 and 143 may be controlled so that the mixture reaches neither the chemical reaction processing devices 132 or 133. Furthermore, when the mixture is meant to flow through the two chemical reaction processing devices 13 (any two of the devices 131, 132 and 133), or through the three chemical reaction processing devices 13 (131, 132 and 133), the chemical control units 14 may be controlled likewise to easily change the channels. That is, the channel control units 14 may be controlled in order to easily change the length of the microchannels 13b that the solution flows through.

[0 0 7 6]

In addition, as the channel controlling unit 14, a valve may be provided in each of the channels. A control of the valve can control the channels that the solution flows through. Although, in Figure 5, a plurality of the chemical reaction processing devices 13 is connected in series, only one of the chemical reaction processing device 13 may be connected.

[0 0 7 7]

<Controlling Method>

Hereinafter, referring to Figure 7, the control method used in the water separation system 200 shown in Figure 5 will be described. The controller 12 performs the control operations shown in the flowchart of Figure 7. Further, an enhancement of the water separation efficiency is judged based on a change of the amount of produced methyl oleate. That is, since the stoichiometric ratio between the methyl oleate and water produced in the reaction is 1:1, an increased amount of produced methyl oleate means the increased water separation efficiency (more specifically, the enhanced production efficiency of water).

[0 0 7 8]

After Step S102, a study for improving the water separation starts (Step S101). In the beginning, oleic acid and methanol are mixed at the predetermined flow rate (i.e. a certain reaction time) (Step S101), and then the chemical reaction starts to produce methyl oleate and water. The water separation efficiency is calculated based on an amount of the presently produced methyl oleate and compared with the theoretical efficiency. If the water separation efficiency is judged to be enhanced (i.e. good) (Yes in Step S103), the reaction time is regarded as being optimized and the optimization study is terminated (Steps S110 and S111), and the operation continues under the condition.

[0 0 7 9]

On the contrary, in Step S103, this is the case that the water separation efficiency is judged not to be enhanced (No in Step S103). If the flow rates of oleic acid and methanol are changeable (Yes in Step S104), the flow rates are changed by controlling the pumps 2a and 2b to repeat Steps S102 and S103. If the flow rates are not changeable (No in Step S104, for example, the pumps 2a and 2b are already operated at the maximum output, although the flow rates are meant to be changed), the chemical reaction processing device 13 will be studied (Step S105).

[0 0 8 0]

Specifically, the number of the chemical reaction processing devices 13,

through which the reaction solution flows, is determined by controlling the channel control unit 14. That is, the chemical reaction time is set again. After the setting for the chemical reaction processing devices 13 is completed, if the water separation efficiency is judged to be good (Yes in Step S106) like Step S103, the reaction time is regarded as being optimized and the optimization study is terminated (Steps S110 and S111), and the operation continues under the conditions.

[0 0 8 1]

In Step S106, if the water separation efficiency is judged not to be good (No in Step S106), the number of the flown chemical reaction processing devices 13 is changed (Yes in Step S107) and then Steps S105 and S106 are repeated. On the contrary, in Step S107, if the number of the chemical reaction processing devices 13 is unchangeable (No in Step S107, for example, when all the chemical reaction processing devices 13 are already used, although the chemical reaction time is meant to be prolonged), the water separation temperature is changed by controlling the temperature controller 7 (Step S108). Then, the water separation efficiency is judged (Step S109). The enhanced efficiency terminates an optimization study (Yes in Step S109, Steps S110 and S111).

[0 0 8 2]

In Step S109, if no enhanced water separation efficiency is recognized (No in Step S109), the changeability of the water separation temperature is studied (Step S112). If changeable, Steps S108 and S109 are repeated. On the contrary, if unchangeable, — the temperature controlling machine 7 may be already operated at maximum output or the operation temperature may have reached the thermal resistance temperature limit of the separation membrane 24, although the separation temperature is meant to be raised— the unattainable optimization of the chemical reaction time terminates the study (No in Step S112, Steps S113 and S111).

[0 0 8 3]

[3. Embodiment 3]

Hereinafter, a water separation system 300 according to Embodiment 3 will be described referring to Figure 8. Here, the same units (members) as the

water separation systems 100 and 200 in Figures 1 and 5 are denoted by the same numerals, and the detailed description will be omitted.

[0 0 8 4]

<Configuration>

The water separation system 300 has the measurement device 15 (in-line measuring device) for automatically measuring an amount of the product (methyl oleate). In the embodiment, the measurement device 15 is provided between the back-pressure valve 8 and the product material tank 9. The measurement device 15 may be provided between the microreactor for water separation 6 and the back-pressure valve 8.

[0 0 8 5]

The specific configuration of the measurement device 15 is free from particular limitation, and any automated measurement device, to which the above-mentioned method is applicable, may be employed. Accordingly, providing such measurement device 15 can avoid a complicated controlling operation by exempting the operator from manually measuring an amount of the product in the processing solution. Moreover, the immediate input of the measured amount of product into the controller 12 can significantly reduce the time lag occurring in the above feedback control. As a result, the water separation efficiency is enhanced more accurately.

Examples

[0 0 8 6]

Hereinafter, the embodiments of the present invention are described in more detail referring to Examples. However, Examples should not be construed as limiting the scope of the embodiment of the present invention.

[0 0 8 7]

The water separation efficiency was investigated. Water was produced together with methyl oleate from oleic acid and methanol. The water separation system 100, as shown in Figure 1, was used in the reaction system. Hereinafter, the detailed conditions were described.

[0 0 8 8]

Example 1

<Configuration>

Methanol used in Examples was the special grade chemical of methanol manufactured by Wako Pure Chemical Industries, Ltd. The methanol used in Examples was mixed with the special grade chemical of concentrated sulfuric acid as a catalyst manufactured by Wako Pure Chemical Industries, Ltd. as a catalyst. The obtained methanol solution was used. The mixed amount of the concentrated sulfuric acid was 1.6 mass percent to the entire methanol solution.

[0 0 8 9]

Oleic acid used in Examples was the Wako grade chemical of oleic acid manufactured by Wako Pure Chemical Industries, Ltd. Oleic acid used in Examples was sieved using a 25 μ m mesh stainless sieve manufactured by As One Corporation for removing the possible impurities. This treatment prevented various pores such as pores of a separation membrane 24 from being clogged.

[0 0 9 0]

The mixing ratio between oleic acid and methanol solution was 7.18:1. The excess amount of methanol was used to accelerate the chemical reaction. The flow rate to the microreactor for mixing 3 of oleic acid was 0.898 mL/min, and the flow rates of methanol was 0.125 mL/min. That is, the total supply flow rate of the pumps 2a and 2b combined was set to 1.023 mL/min.

[0 0 9 1]

Hitachi Microreactor System Micro Process Server (MPS-a200) manufactured by Hitachi Plant Technologies, Ltd. was used to feed the reactants. Micro Process Server (MPS-a200) was a system using syringe pumps for feeding. During feeding, Micro Process Server (MPS-a200) program flow mode was used to operate two syringe pumps (corresponding to pumps 2a and 2b) repeatedly taking turns in performing introduction and feed. The operation could feed without interruption the reactants of the volume larger than the syringe pump capacity.

[0 0 9 2]

The microreactor Micro Process Server (CMPS-a04) manufactured by Hitachi Plant Technologies, Ltd. was used as the microreactor for mixing 3.

[0 0 9 3]

Further, the chemical reaction processing section 4 was provided with a fluorine-based resin tube (manufactured by GL Sciences, Inc.) having an outer diameter of 3mm, an inner diameter of 2mm and a length of 10m.

[0 0 9 4]

The microreactor for water separation 6 shown in Figure 2 was provided with a tube having an inner diameter of 16 mm, and a separation membrane 24 of T-type zeolites membrane (manufactured by Mitsui Engineering & Shipbuilding Co., Ltd.), as the separation membrane 24, disposed inside the tube. The microreactor for water separation 6 has a total length of 331mm. The diameters of the first disc member 20, of the second disc member 21 and of the flange 22a were all 40mm. The measured outer diameter of the T-type zeolite membrane was measured 12.3 mm, and the measured length of the T-type zeolite membrane was 300 mm. As a result, the width of the reaction solution channel 25 was 2mm or smaller (1.85mm).

[0 0 9 5]

To connect the inlet 20b with the outlet 20e through the reaction solution channel 25, the second disc member 21 was provided with four holes of a diameter of 0.2mm along the circumference at equal intervals. In this manner, the time taken by the reaction solution to flow from the inlet 20b of the microreactor for water separation 6 to the outlet 20e was nearly equal to the theoretical value. The holes provided the proper solution flow.

[0 0 9 6]

The quantitative analysis of the product (methyl oleate) and the residue of oleic acid was performed using High Performance Liquid Chromatography (HPLC).

[0 0 9 7]

<Operation Conditions>

At first, the microreactor for mixing 3 was immersed in a thermostatic bath of a temperature of 60 °C. Into the reactor 3, the oleic acid and the methanol solution were supplied at a total supply flow rate of 1.023mL/min to obtain the reaction solution. The reaction solution flew through the chemical reaction processing section 4 immersed in a thermostatic bath of a temperature of 60 °C. (i.e. the set temperature of the temperature controller 5 corresponded to 60 °C.) Subsequently, the solution flew at the same supply flow rate through the microreactor for water separation 6 immersed in a thermostatic bath of 60 °C (i.e. the set temperature of the temperature controller 7 corresponded to 60°C.). The solution flew through the reaction solution channel 25. The decompression device 11 decompressed the vapor flow channel 26 to 0.085 MPa. and water in the channel was vaporized and separated. The separated water was collected in a cold trap 10 cooled with ice.

[0 0 9 8]

The starting point of the water separation was set to 31 minutes after mixing the oleic acid and the methanol solution. That is, at 31 minutes after the mixing, the reaction solution began to be supplied to the microreactor for water separation 6. Further, the so-called "stopped flow method" was applied to make the water separation time longer. That is, the supply flow was halted for 30 minutes from 56 minutes after the mixing and then it was resumed.

[0 0 9 9]

Further, the preset temperatures of the temperature controller (not shown) mounted on the microreactor for mixing 3 and of the temperature controllers 5 and 7 were all set to 60°C. The temperature was a little lower than the boiling point of methanol (64.7°C.).

Even small amount of the vaporized methanol in the reactants may reduce the contact areas among the reactants, lowering the reaction rate. To avoid such a problem, the pressure of the reaction system was maintained at 138 kPa (20 psi) or more by controlling the back-pressure valve 8.

[0 1 0 0]

Comparative Example 1

A study was conducted in the same procedures as the above Examples except that the chemical reaction processing section 4 was provided with a fluororesin tube (manufactured by GL Sciences, Inc.) of an outer diameter of about 1.6 mm, an inner diameter of 1 mm, and a length of 0.1 m. In this case, the chemical reaction processing section 4 was very short. The reaction solution discharged from the microreactor for mixing 3 was immediately supplied to the microreactor for water separation 6.

[0 1 0 1]

Comparative Example 2

A batch method was studied in Comparative Example 2. In the batch method, a T-type zeolite membrane, which can be decompressed, was prepared by sandwiching the membrane between silicone rubber stoppers. A tube was inserted into one of the stoppers and the T-type zeolite membrane can be decompressed. 100 mL of oleic acid was stirred in a 200-mL round-bottom flask immersed in a thermostatic bath of a temperature of 60°C. While stirring, 13.9 mL of the methanol solution containing concentrated sulfuric acid by 1.6 mass percent was poured into the flask in three portions for 1 minute to obtain the reaction solution. The stirring was continued while the chemical reaction proceeded.

[0 1 0 2]

The length of the membrane sandwiched between the upper and lower silicone rubber stoppers was set to 20 mm. The membrane's sandwiched part was constantly immersed in the reaction solution. A decompressor kept the internal pressure the membrane at -0.085 MPa. In this manner, the water in the system permeated the membrane to be evaporated and separated. The separated water was collected in a cold trap cooled with ice. At 3 hours after the water separation, the produced amount of methyl oleate in the reaction solution was measured.

[0 1 0 3]

<Results>

Figure 9 illustrates the relationships between the yields and the elapsed time from the start of the mixing, i.e. the chemical reaction time. Here, the yields means the yields of the methyl oleate calculated by Formula 1 described below. In Formula 1, [oleic acid] means the molar concentration of the oleic acid in the reaction solution, and [methyl oleate] means the molar concentration of the methyl oleate in the reaction solution.

$$\text{Yield [\%]} = \{[\text{methyl oleate}] / ([\text{oleic acid}] + [\text{methyl oleate}])\} \times 100 \quad 1$$

[0 1 0 4]

In Example 1, as shown in Figure 9A, before the water separation started, an equilibrium state was attained with the yield of 52%. Starting the water separation increased the yield. The increased yield was much higher than that of the Comparative Example 2 of the conventional method. Particularly, at the reaction time of 85 minutes, the yield reached 63 %, 7 % higher than that of Comparative Example 2.

[0 1 0 5]

Further, as shown in Figure 9B comparing the conventional methods, Comparative Examples 1 and 2 revealed almost identical behaviors to each other. Here, Comparative Example 1 had no chemical reaction processing section 4, and Comparative Example 2 was a conventional batch method. In addition, no water separation was observed within the reaction time of 55 minutes in Comparative Example 1 (not shown in figures).

[0 1 0 6]

Further, the rate constants k_1 , k_{-1} and k_2 in Example 1, Comparative Examples 1 and 2 are calculated by Formula 2 described below (See Figure 3.). The specific formulae for computation are shown as follows.

$$\begin{aligned} d[\text{oleic acid}] / dt &= -k_1[\text{oleic acid}][\text{methanol}] + k_{-1}[\text{methyl oleate}][\text{water (I)}] \\ d[\text{methyl oleate}] / dt &= k_1[\text{oleic acid}][\text{methanol}] - k_{-1}[\text{methyl oleate}][\text{water (I)}] \\ d[\text{water (I)}] / dt &= k_1[\text{oleic acid}][\text{methanol}] - k_{-1}[\text{methyl oleate}][\text{water (I)}] - k_2[\text{water(I)}] \end{aligned} \quad 2$$

[0 1 0 7]

Table 1 shows the summary of the above results.

TABLE.1

	Reaction Time [min]	Yield [%]	Rate Constant		
			k_1 [1/(mol·s)]	k_{-1} [(mol·s)]	k_2 [1/s]
Example 1 (with Chemical Reaction Processing Section 4)	31	52	2.0×10^{-3}	3.9×10^{-3}	※
	85	63	3.9×10^{-5}	7.5×10^{-5}	1.9×10^3
Comparative Example 1 (without Chemical Reaction Processing Section 4)	55	52	4.0×10^{-4}	7.9×10^{-4}	※
Comparative Example 2 (Batch Method)	180	56	3.5×10^{-4}	6.9×10^{-4}	1.6×10^{-5}

"*" in Table 1 indicates no calculation made because of no measurement of the water separation.

[0 1 0 8]

Hereinafter, the comparison of Example 1 with Comparative Examples 1 or 2 is discussed referring to the rate constants. In Example 1, the water separation started at 31 minute of the reaction time. In Comparative Example, the water separation started at the starting point of the reaction. In Comparative Example 2, the batch method was performed. A direct comparison between Example 1 and Comparative Example 1 or 2 may carry some risk of oversimplification. Nevertheless, the water separation rate constant k_2 of Example 1 is 10^3 times larger than that of Comparative Example 1 and 10^8 times larger than that of Comparative Example 2. The result clearly shows that a microreactor for water separation used with a chemical reaction processing section 4 can achieve a highly efficient water separation.

[0 1 0 9]

In addition, the forward reaction rate constant k_1 before starting the water separation (i.e. before 31 minutes) in Example 1 is larger than that of either Comparative Example 1 or 2. The comparison clearly shows that a chemical reaction processing section 4 can shorten the chemical reaction time.

[0 1 1 0]

The above-mentioned results show that the embodiments of the present invention can effectively separate water and achieve the higher yields at a shorter chemical reaction time.

[0 1 1 1]

Reference Numeral List

- 3 microreactor for mixing (mixing unit)
- 4 chemical reaction processing section (chemical reaction processing unit)
- 5 temperature controller (controller of chemical reaction temperature)
- 6 microreactor for water separation
- 7 water separation temperature controller
- 12 controller (controlling unit)
- 13 chemical reaction processing device
- 15 measurement device (in-line measuring device)

CLAIM (S)

1 A water separation system separating water from product solution obtained after chemical reaction of reactants, comprising:

a mixer mixed by a supply of the reactants,

a chemical reaction processing means connected below the mixer to proceed a chemical reaction of the mixed reactants,

a water separation means connected below the chemical reaction processing means to separate the produced water at the chemical reaction processing means, and

a controller controlling a chemical reaction time in the chemical reaction processing means,

wherein

the controller is controlled to shorten a chemical reaction time in the chemical reaction processing means, in the case of a large amount of product material in a solution discharged from the chemical reaction processing means, and

to prolong the chemical reaction time in the chemical reaction processing means, in the case of a small amount of product material in a solution discharged from the chemical reaction processing means

2. The water separation system according to Claim 1,

wherein

the controller is provided with a function controlling a flow rate of reactants supplied to the mixer, and

a chemical reaction is controlled by controlling the supply flow rate of reactants.

3. The water separation system according to Claim 1,

wherein

the chemical reaction processing means has a microchannel to control the chemical reaction time by changing a length of the microchannel.

4. The water separation system according to Claim 3,
wherein
the chemical reaction processing means is configured by a device having the
microchannel with a predetermined length, and
the length of the microchannel is set by serially connecting one device or a
plurality of the devices.

5. The water separation system according to any one of Claims 1 to 4,
further comprising
the chemical reaction temperature control means controlling a temperature
at the time of chemical reaction, and
a water separation temperature control means controlling a temperature at
the time of water separation,
to set mutually different temperatures for between chemical reaction and
water separation.

6. The water separation system according to any one of Claims 1 to 5,
further comprising
an in-line measuring means measuring an amount of product material.