

## DESCRIPTION

## PRODUCTION METHOD OF 1,3-BUTADIENE

## [TECHNICAL FIELD]

[0001]

The present invention relates to a production method of 1,3-butadiene.

## [BACKGROUND ART]

[0002]

Conventionally, as a method for producing 1,3-butadiene (hereinafter, may be also referred to as “butadiene”), a method in which butadiene is prepared by separation of components other than butadiene from a fraction having 4 carbon atoms obtained by cracking of naphtha (hereinafter, may be also referred to as “C4 fraction”) through distillation has been employed. Demands for butadiene have increased as raw materials for synthetic rubbers and the like; however, due to circumstances in which cracking of naphtha for a production method of ethylene has been replaced by cracking of ethane, quantities of the C4 fraction supplied have decreased. Thus, production of butadiene without need of a C4 fraction as a raw material is desired.

[0003]

In this regard, as a production method of butadiene, a method of separating butadiene from a product gas obtained by oxidative dehydrogenation of n-butene has attracted attention. According to this method, impurities other than butadiene are included in the product gas; therefore, it is necessary to separate the impurities by using a solvent. For example, a method in which a hydrocarbon-absorptive solvent having a boiling point of 110 °C to 190 °C is used in order to separate noncondensable gases contained in the product gas at a high concentration from butadiene and other hydrocarbon having 4 carbon atoms (see Japanese Unexamined Patent Application, Publication No. S60-193931), and a method in which an absorption solvent having a boiling point of 110 °C to 210 °C is used in order to recover butadiene and other hydrocarbon predominantly having 4 carbon atoms from the product gas (see Japanese Unexamined Patent Application, Publication No. 2012-082153) have been proposed. However, these solvents have a comparatively high boiling point, and therefore, when such a solvent having a high boiling point is used, a disadvantage is involved such as a necessity of a large quantity of energy in separating components absorbed to the solvent from the solvent.

## [PRIOR ART DOCUMENTS]

## [PATENT DOCUMENTS]

[0004]

Patent Document 1: Japanese Unexamined Patent Application, Publication No. S60-193931

Patent Document 2: Japanese Unexamined Patent Application, Publication No. 2012-082153

## [SUMMARY OF THE INVENTION]

[PROBLEMS TO BE SOLVED BY THE INVENTION]

[0005]

The present invention was made in view of the foregoing circumstances, and an object of the invention is to provide a production method of butadiene that is capable of reducing energy consumption in producing butadiene from a product gas obtained by oxidative dehydrogenation of n-butene.

[MEANS FOR SOLVING THE PROBLEMS]

[0006]

According to an aspect of the invention made for solving the foregoing problems, a production method of 1,3-butadiene includes the steps of:

obtaining a product gas containing 1,3-butadiene by an oxidative dehydrogenation reaction of a raw material gas containing n-butene with a gas containing molecular oxygen in the presence of a metal oxide catalyst;

cooling the product gas; and

roughly separating the cooled product gas into: a fraction containing the molecular oxygen and an inert gas; and other gas by selective absorption to an absorption solvent,

wherein in the product gas,

the N<sub>2</sub> concentration is no less than 35% by volume and no greater than 90% by volume,

the H<sub>2</sub>O concentration is no less than 5% by volume and no greater than 60% by volume, and

the 1,3-butadiene concentration is no less than 2% by volume and no greater than 15% by volume,

and wherein the absorption solvent contains acetonitrile as a principal component.

[0007]

According to the production method of butadiene, due to the concentration of each component in the product gas falling within the above range, and use of the absorption solvent containing acetonitrile having a comparatively low boiling point as a principal component, energy consumption in preparing butadiene from a product gas obtained by oxidative dehydrogenation of n-butene can be reduced.

[0008]

In the cooled product gas, it is preferred that the N<sub>2</sub> concentration is no less than 60% by volume and no greater than 94% by volume, the H<sub>2</sub>O concentration is no less than 1% by volume and no greater than 30% by volume, and the 1,3-butadiene concentration is no less than 2% by volume and no greater than 15% by volume. When the concentration of each component in the cooled product gas falls within the above range, energy consumption in preparing butadiene from the product gas obtained by oxidative dehydrogenation of n-butene can be further reduced.

[0009]

The content of acetonitrile in the absorption solvent is preferably no less

than 55% by mass and no greater than 90% by mass. When the content of acetonitrile thus falls within the above range, energy consumption in separating components absorbed to the absorption solvent from the solvent can be efficiently reduced.

[0010]

The absorption solvent preferably further contains at least one selected from the group consisting of water and alcohols. When the absorption solvent further contains water, selectivity of the absorption solvent can be improved; however, when the content of water is too high, the hydrocarbons may fail to be dissolved in acetonitrile in the absorption solvent, thereby leading to separation into two phases. Thus, when the absorption solvent further contains at least one alcohol in addition to water, a decrease of the solubility of the hydrocarbons (other gas) in acetonitrile can be avoided even if the content of water is increased, whereby the content of water in the absorption solvent can be increased. The term “selectivity” as referred to herein means selectivity among hydrocarbons.

[0011]

The content of water in the absorption solvent is preferably no less than 5% by mass and no greater than 35% by mass. When the content of water thus falls within the above range, the selectivity of the absorption solvent can be further improved.

[0012]

The content of the alcohol in the absorption solvent is preferably no less than 5% by mass and no greater than 30% by mass. When the content of the alcohol thus falls within the above range, a decrease of the solubility of the hydrocarbons (other gas) in acetonitrile can be avoided even if the content of water is increased, whereby the content of water in the absorption solvent can be effectively increased.

[0013]

The alcohol is preferably methyl alcohol and/or ethyl alcohol. When methyl alcohol or ethyl alcohol is used as the alcohol, a decrease of the solubility of the hydrocarbons (other gas) in acetonitrile can be avoided even if the content of water is increased, whereby the content of water in the absorption solvent can be effectively increased.

[0014]

In the rough separation step, it is preferred that the amount of the absorption solvent supplied is no less than 5 times by mass and no greater than 100 times by mass with respect to the total amount of n-butene and 1,3-butadiene, and that the temperature of the absorption solvent is no less than 0 °C and no greater than 40 °C. When the amount and the temperature of the absorption solvent fall within the above range, n-butene and 1,3-butadiene can be efficiently absorbed to the absorption solvent.

[0015]

It is preferred that the production method of butadiene further includes

the step of:

separating the other gas obtained through the rough separation step into: 1,3-butadiene; and unreacted n-butene and butanes by selective absorption to an extraction solvent.

When this step is included, even highly pure butadiene can be obtained.

[0016]

As the extraction solvent, a solvent identical or similar to the absorption solvent described above is preferably used. When the extraction solvent is equivalent to the absorption solvent in the rough separation step in terms of the scope thereof, butadiene can be efficiently produced by a comparatively convenient process.

[0017]

It is preferred that the production method of butadiene further includes the step of

washing with water a gas not absorbed to the absorption solvent in the rough separation step or the extraction solvent in the separation step to recover the absorption solvent or the extraction solvent included in the gas.

Accordingly, the absorption solvent or the extraction solvent can be efficiently utilized.

[EFFECTS OF THE INVENTION]

[0018]

As explained in the foregoing, according to the production method of butadiene of the embodiment of the present invention, energy consumption in preparing butadiene from a product gas obtained by oxidative dehydrogenation of n-butene can be reduced.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0019]

FIG. 1 shows a flow diagram illustrating a production method of butadiene according to a first embodiment of the present invention; and

FIG. 2 shows a flow diagram illustrating a production method of butadiene according to a second embodiment of the present invention.

[DESCRIPTION OF EMBODIMENTS]

[0020]

Hereinafter, the production method of butadiene according to the embodiments of the present invention will be explained in detail with appropriate references to the drawings.

[0021]

The production method of butadiene according to an embodiment of the present invention includes the steps of:

obtaining a product gas containing 1,3-butadiene by an oxidative dehydrogenation reaction of a raw material gas containing n-butene with a gas containing molecular oxygen in the presence of a metal oxide catalyst (hereinafter, may be also merely referred to as “catalyst”) (hereinafter, may be also referred to as “reaction step”);

cooling the product gas (hereinafter, may be also referred to as “cooling step”); and

roughly separating the cooled product gas into: a fraction containing the molecular oxygen and an inert gas; and other gas by selective absorption to an absorption solvent (hereinafter, may be also referred to as “rough separation step”),

wherein in the cooled product gas,

the  $N_2$  concentration is no less than 35% by volume and no greater than 90% by volume,

the  $H_2O$  concentration is no less than 5% by volume and no greater than 60% by volume, and

the 1,3-butadiene concentration is no less than 2% by volume and no greater than 15% by volume,

and wherein the absorption solvent contains acetonitrile as a principal component.

[0022]

#### First Embodiment

The production method of butadiene according to the first embodiment of the present invention is explained with reference to FIG. 1. The production method of butadiene of this embodiment includes the reaction step, the cooling step, the rough separation step and a solvent stripping step. Each step is explained in detail below.

[0023]

#### Reaction Step

In this step, a product gas containing 1,3-butadiene is obtained by an oxidative dehydrogenation reaction of a raw material gas containing n-butene (hereinafter, may be also referred to as “raw material gas”) with a gas containing molecular oxygen in the presence of a metal oxide catalyst. First, together with the raw material gas, the air as the gas containing molecular oxygen, and as needed, an inert gas and water (water vapor) are heated with a preheater (not shown in the Figure) to about 200 °C to 300 °C, and thereafter the mixture is supplied into a reactor 1 packed with a metal oxide catalyst through a pipe 100 as shown in FIG. 1. Although the raw material gas, the inert gas, the air, and water (water vapor) may be supplied directly to the reactor 1 through each separate pipe, it is preferred that these are supplied to the reactor 1 after homogenously mixing beforehand since a trouble such as formation of a detonating gas in part from an inhomogenous gas mixture in the reactor 1 can be prevented.

[0024]

#### Gas Containing Molecular Oxygen

The gas containing molecular oxygen is a gas containing typically no less than 10% by volume of molecular oxygen, preferably no less than 15% by volume of molecular oxygen, and more preferably no less than 20% by volume of molecular oxygen. The gas containing molecular oxygen is preferably the,

air. Also, the gas containing molecular oxygen may include arbitrary impurities such as nitrogen, argon, neon, helium, CO, CO<sub>2</sub> and water within the range not leading to impairment of the effects of the present invention. The amount of the impurities is typically no greater than 90% by volume, more preferably no greater than 85% by volume, and still more preferably no greater than 80% by volume when the impurity is nitrogen. The amount of the impurities other than nitrogen is typically no greater than 10% by volume, and preferably no greater than 1% by volume. Too large amount of the impurities is likely to make supplying of oxygen required for the reaction difficult.

[0025]

#### Inert Gas

The inert gas is preferably supplied to the reactor 1 together with the raw material gas containing n-butene and the gas containing molecular oxygen. Addition of the inert gas enables the concentrations of oxygen and a flammable gas such as butene to be adjusted such that the gas mixture does not form a detonating gas in the reactor 1. Examples of the inert gas include nitrogen, argon, CO<sub>2</sub> and the like, and of these, nitrogen is preferred in light of the economic aspect.

[0026]

#### Water (Water Vapor)

It is preferred that water (water vapor) is supplied to the reactor 1. Water (water vapor) enables the concentrations of the raw material gas and oxygen to be adjusted similarly to the inert gas, and coking of the metal oxide catalyst can be inhibited.

[0027]

#### Raw Material Gas

The raw material gas is a gaseous matter provided by gasification of the raw material of 1,3-butadiene with a vaporizer (not shown in FIG. 1). The raw material involves n-butene that is a monoolefin having 4 carbon atoms. As n-butene, for example: a fraction (raffinate 2) which contains n-butene (1-butene and 2-butene) as a principal component and is obtained by separating butadiene and i-butene from a C4 fraction generated as byproducts through naphtha cracking; or a butene fraction produced by a dehydrogenation or oxidative dehydrogenation reaction of n-butane may be used. Alternatively, a gas which is obtained by dimerization of ethylene and contains highly pure 1-butene, cis-2-butene, trans-2-butene or a mixture of these may be also used. Also, a gas containing a large quantity of hydrocarbons having 4 carbon atoms (hereinafter, may be abbreviated as "FCC-C4") obtained through fluid catalytic cracking, i.e., cracking of heavy oil fraction, which is obtained in distillation of crude petroleum in a petroleum purification plant or the like, to be converted into a hydrocarbon having a low boiling point by using a powdery solid catalyst in a fluidized bed state, may be directly used as the raw material gas, or a gas obtained by eliminating impurities such as phosphorus from FCC-C4 may be used as the raw material gas. The concentration of n-butene in the raw

material gas is typically no less than 40% by volume, preferably no less than 60% by volume, more preferably no less than 75% by volume, and particularly preferably no less than 99% by volume.

[0028]

In addition, the raw material gas may contain arbitrary impurities within the range not leading to impairment of the effects of the present invention. Specific examples of the impurities include: branched monoolefins such as i-butene; saturated hydrocarbons such as propane, n-butane and i-butane; and the like. Furthermore, the raw material gas may contain as an impurity, 1,3-butadiene that is an intended reaction product. The amount of these impurities is typically no greater than 60% by volume, preferably no greater than 40% by volume, more preferably no greater than 25% by volume, and particularly preferably no greater than 1% by volume with respect to the total amount of the raw material gas. When the amount is too large, the concentration of 1-butene and/or 2-butene as a principal raw material is decreased, whereby the reaction velocity may be decreased, and/or the byproduct is likely to be increased.

[0029]

#### Composition of Gas Mixture

The concentration of n-butene in the gas mixture is, in light of productivity of butadiene, preferably no less than 2% by volume, and in light of reducing the load to the metal oxide catalyst, preferably no greater than 30% by volume. The concentration of n-butene is more preferably 3 to 25% by volume, and still more preferably 5 to 20% by volume. In regard to the composition of the gas mixture, it is preferred that with respect to 100 parts by volume of the raw material gas, O<sub>2</sub> is 50 to 120 parts by volume, N<sub>2</sub> is 400 to 1,000 parts by volume and H<sub>2</sub>O is 0 to 900 parts by volume, and it is more preferred that O<sub>2</sub> is 70 to 110 parts by volume, N<sub>2</sub> is 500 to 800 parts by volume and H<sub>2</sub>O is 100 to 300 parts by volume. When the proportion of O<sub>2</sub> with respect to the raw material gas departs from this range, it is likely to be difficult to adjust the O<sub>2</sub> concentration at the outlet of the reactor 1, even if the reaction temperature is adjusted. In addition, as the proportion of N<sub>2</sub> and/or H<sub>2</sub>O increases, the raw material gas is diluted, leading to an inferior efficiency. On the other hand, as the proportion decreases, the gas mixture may have an explosive composition, and heat removal is likely to be difficult.

[0030]

#### Explosive Range of Gas Mixture

Since the gas mixture contains oxygen and the flammable raw material gas, the composition of the gas mixture at the inlet of the reactor 1 is regulated by monitoring the flow rate of each gas (the raw material gas, the air, and as needed, the inert gas and water (water vapor)) with flow meters (not shown in the Figure) provided to the pipes for supplying each gas so as to avoid the gas mixture from falling within the explosive range, thereby adjusting to give the gas mixture composition described above.

[0031]

It is to be noted that the “explosive range” as referred to means a range in which the gas mixture has a composition that leads to an ignition in the presence of any ignition source. When the concentration of the raw material gas is lower than a certain value, it is known that the ignition does not occur even if an ignition source is present, and this certain concentration is referred to as a critical explosion lower limit. In addition, when the concentration of the raw material gas is higher than a certain value, it is known that the ignition does not also occur even if an ignition source is present, and this certain concentration is referred to as a critical explosion upper limit. Each value depends on the oxygen concentration, and in general, both these values are more approximate as the oxygen concentration is lower, and both these values become identical when the oxygen concentration attains a certain value. The oxygen concentration at which both the values become identical is referred to as a “critical oxygen concentration”, and when the oxygen concentration is lower than the critical oxygen concentration, the gas mixture does not ignite irrespective of the concentration of the raw material gas.

[0032]

When the oxidative dehydrogenation reaction of this step is to be started, it is preferred that the amount of the gas containing molecular oxygen, and the inert gas and water vapor first supplied to the reactor 1 is adjusted such that the oxygen concentration at the inlet of the reactor 1 becomes no greater than the critical oxygen concentration, and thereafter the raw material gas is began to be supplied, then the supply rate of the raw material gas and the gas containing molecular oxygen such as the air is increased such that the raw material gas concentration becomes greater than the critical explosion upper limit.

[0033]

When the supply rate of the raw material gas and the gas containing molecular oxygen is increased, the supply rate of the gas mixture may be maintained at a constant rate by decreasing the supply rate of water vapor. Accordingly, the residence time of the gas in the pipe and the reactor 1 can be maintained constant, and thus a variation of the pressure can be inhibited.

[0034]

#### Condition of Oxidative Dehydrogenation Reaction

The metal oxide catalyst described later is packed in the reactor 1, and the raw material gas reacts with oxygen in the presence of the catalyst to generate a gas containing 1,3-butadiene.

[0035]

In this oxidative dehydrogenation reaction, unsaturated carbonyl compounds having 3 to 4 carbon atoms such as acrolein, acrylic acid, methacrolein, methacrylic acid, maleic acid, fumaric acid and maleic anhydride may be produced in the product gas. When the concentration of the unsaturated carbonyl compounds is too high, the unsaturated carbonyl compounds are dissolved to be accumulated in the absorption solvent that circulates in the rough separation step described later, and the extraction

solvent that circulates in the extractive distillation step, whereby the generation of impurities is likely to be induced.

[0036]

For adjusting the concentration of the unsaturated carbonyl compounds to fall within a certain range, the reaction temperature in carrying out the oxidative dehydrogenation reaction may be adjusted. The oxidative dehydrogenation reaction is an exothermic reaction, and thus the temperature is elevated through the reaction. The lower limit of the reaction temperature is typically 300 °C, and preferably 320 °C. On the other hand, the upper limit of the reaction temperature is typically 400 °C, and preferably 380 °C. When the reaction temperature falls within the above range, coking of the catalyst can be inhibited, and also the concentration of the unsaturated carbonyl compounds having 3 to 4 carbon atoms can fall within a certain range. When the reaction temperature is less than 300 °C, the degree of conversion of n-butene may be decreased. On the other hand, when the reaction temperature is higher than 400 °C, the concentration of the unsaturated carbonyl compounds having 3 to 4 carbon atoms becomes so high that the impurities may be accumulated in the absorption solvent and the extraction solvent, and/or coking of the catalyst is likely to occur.

[0037]

It is to be noted that the reactor 1 is preferably cooled appropriately to regulate the temperature of the catalyst layer so as to be constant by, for example, removing the heat with a heating medium (dibenzyltoluene, nitrite salt, etc.).

[0038]

Although the pressure in the reactor 1 is not particularly limited, the lower limit is typically 0 MPaG, preferably 0.02 MPaG, and more preferably 0.05 MPaG. On the other hand, the upper limit is preferably 0.5 MPaG, and more preferably 0.3 MPaG.

[0039]

The gas hourly space velocity (GHSV) in the oxidative dehydrogenation reaction is preferably no less than 500 hr<sup>-1</sup> and no greater than 5,000 hr<sup>-1</sup>, more preferably no less than 800 hr<sup>-1</sup> and no greater than 3,000 hr<sup>-1</sup>, and still more preferably no less than 1000 hr<sup>-1</sup> and no greater than 2,500 hr<sup>-1</sup>. When the gas hourly space velocity falls within such a range, an efficient reaction is allowed to proceed. The gas hourly space velocity (GHSV) can be derived according to the following formula:

$$\text{GHSV (hr}^{-1}\text{)} = [\text{gas flow rate (Nm}^3\text{/hr)}] / [\text{catalyst layer volume (m}^3\text{)}].$$

In the above formula, the term “catalyst layer volume” as referred to means the total volume including voids (apparent volume).

[0040]

#### Concentration of Each Component in Product Gas

In the product gas generated by the oxidative dehydrogenation reaction, the N<sub>2</sub> concentration is no less than 35% by volume and no greater than 90% by

volume, the H<sub>2</sub>O concentration is no less than 5% by volume and no greater than 60% by volume, and the butadiene concentration is no less than 2% by volume and no greater than 15% by volume. When the concentration of each component in the product gas falls within the above range, the efficiency of the butadiene purification process can be improved, and a side reaction of butadiene which may occur in the purification process can be inhibited, whereby the energy consumption in preparing butadiene can be reduced. In the product gas, the N<sub>2</sub> concentration is preferably no less than 45% by volume and no greater than 80% by volume, the H<sub>2</sub>O concentration is preferably no less than 8% by volume and no greater than 40% by volume, the n-butene concentration is preferably no less than 0% by volume and no greater than 2% by volume, and the butadiene concentration is preferably no less than 3% by volume and no greater than 10% by volume.

[0041]

#### Metal Oxide Catalyst

Next, the metal oxide catalyst used in this step is explained. The catalyst is not particularly limited as long as it functions as a catalyst for oxidative dehydrogenation of the raw material gas, and a well-known catalyst may be used, which is exemplified by a metal oxide catalyst containing metal oxide that includes at least molybdenum (Mo), bismuth (Bi), and iron (Fe). The metal oxide is preferably a composite metal oxide represented by the following formula (1).

[0042]



[0043]

It is to be noted that in the formula (1): X represents at least one or more elements selected from Ni and Co; Y represents at least one element selected from the group consisting of Li, Na, K, Rb, Cs, and Tl; Z represents at least one element selected from the group consisting of Mg, Ca, Ce, Zn, Cr, Sb, As, B, P, and W; a, b, c, d, e, f and g represent the proportion of atoms of each element, wherein provided that “a” is 12, b = 0.1 to 8, c = 0.1 to 20, d = 0 to 20, e = 0 to 4, f = 0 to 2, and g is the number of atoms of oxygen required for satisfying the atomic valence of each component described above.

[0044]

The metal oxide catalyst is highly active and highly selective in the production method of butadiene through oxidative dehydrogenation using molecular oxygen, and further is superior in lifetime stability.

[0045]

Although a preparation method of the catalyst is not particularly limited, a well-known method such as an evaporation to dryness method, a spray-drying method, an oxide mixing method carried out using a raw material substance of each element may be employed. The raw material substance of each element is not particularly limited, and is exemplified by an oxide, a nitrate salt, a carbonate, an ammonium salt, a hydroxide, a carboxylate salt, a carboxylic acid

ammonium salt, a halogenated ammonium salt, a hydrogen acid, an alkoxide and the like of the component element, and the like. The catalyst may be carried by an inert carrier, and the carrier species is exemplified by silica, alumina, silicon carbide, and the like.

[0046]

#### Cooling Step

In this step, the product gas from the reactor 1 is cooled. This cooling step includes cooling in a quench tower 2, and cooling with a heat exchanger 3.

[0047]

#### Quench Tower 2

The product gas from the reactor 1 is supplied to the quench tower 2 through a pipe 101. From the top of the quench tower 2, a cooling solvent is introduced through a pipe 102, and the cooling solvent is brought into countercurrent contact with the supplied product gas. Thus, the product gas is cooled to about 30 °C to 99 °C by the countercurrent contact. The cooling solvent is exemplified by water, an aqueous alkaline solution and the like. The cooling solvent after the cooling is discharged through a pipe 103. The temperature of the cooling solvent introduced may depend on the cooling temperature of the reaction product gas, and is typically 10 °C to 90 °C, preferably 20 °C to 70 °C, and more preferably 20 °C to 40 °C.

[0048]

The pressure in the quench tower 2 is not particularly limited, and is typically 0 MPaG to 0.5 MPaG, and preferably 0 MPaG to 0.2 MPaG. The temperature in the quench tower 2 is typically 0 °C to 100 °C, and preferably 20 °C to 80 °C.

[0049]

In regard to the concentration of each component in the product gas in the outlet of the quench tower 2, N<sub>2</sub> is preferably no less than 30% by volume and no greater than 80% by volume, and more preferably no less than 40% by volume and no greater than 70% by volume. H<sub>2</sub>O is preferably no less than 5% by volume and no greater than 60% by volume, and more preferably no less than 10% by volume and no greater than 45% by volume. Butadiene is preferably no less than 2% by volume and no greater than 15% by volume, and more preferably no less than 3% by volume and no greater than 10% by volume.

[0050]

#### Heat Exchanger 3

The product gas cooled in the quench tower 2 is let out from the top of the quench tower 2, and cooled to about room temperature (10 °C to 30 °C) via a heat exchanger 3 through a pipe 104, whereby a cooled product gas is obtained.

[0051]

In regard to the concentration of each component in the cooled product gas at the outlet of the heat exchanger 3, N<sub>2</sub> is preferably no less than 60% by volume and no greater than 94% by volume, and more preferably no less than

70% by volume and no greater than 85% by volume. H<sub>2</sub>O is preferably no less than 1% by volume and no greater than 30% by volume, and more preferably no less than 1% by volume and no greater than 3% by volume. Butadiene is preferably no less than 2% by volume and no greater than 15% by volume, and more preferably no less than 3% by volume and no greater than 10% by volume. When the concentration of each component of the cooled product gas falls within the above range, the concentration of butadiene in the cooled product gas can be adjusted to fall within the above range, whereby an absorption efficiency to the absorption solvent in the following step can be improved.

[0052]

#### Rough Separation Step (Absorption Step)

In this step, the cooled product gas is roughly separated into: a fraction containing the molecular oxygen and an inert gas; and other gas by selective absorption to the absorption solvent. The “other gas” as referred to herein means a gas containing at least butadiene and unreacted n-butene absorbed to the absorption solvent.

[0053]

The cooled product gas obtained in the cooling step is, as needed, subjected to compression with a compressor 4, and/or cooling with a heat exchanger 5. The cooled product gas is supplied to an absorption tower 6 through a pipe 105. From the top of the absorption tower 6, the absorption solvent the temperature of which has been adjusted via a heat exchanger 112 is introduced through a pipe 106, and the absorption solvent is brought into countercurrent contact with the supplied cooled product gas. Accordingly, the other gas (gas containing butadiene and unreacted n-butene) in the cooled product gas is absorbed to the absorption solvent, whereby the fraction containing the molecular oxygen and the inert gas, and the other gas are roughly separated.

[0054]

The pressure in the absorption tower 6 is not particularly limited, and is typically 0.1 MPaG to 1.5 MPaG, and preferably 0.2 MPaG to 1.0 MPaG. As the pressure increases, the absorption efficiency can be improved, whereas as the pressure decreases, the energy required for raising the pressure in introducing the gas into the absorption tower 6 can be reduced.

[0055]

Also, the temperature in the absorption tower 6 is not particularly limited, and is typically 0 °C to 60 °C, and more preferably 10 °C to 50 °C. A higher temperature results in an advantage that the oxygen, nitrogen and the like are less likely to be absorbed to the solvent, whereas a lower temperature results in an advantage that an absorption efficiency of hydrocarbons such as butadiene is improved.

[0056]

#### Absorption Solvent

The absorption solvent used in this step contains acetonitrile as a principal component. The term "principal component" as referred to herein means a component contained at the content of acetonitrile in the absorption solvent in supplying the same of no less than 50% by mass. Since the absorption solvent contains acetonitrile having a comparatively low boiling point as a principal component, the energy consumption in separating components absorbed to the absorption solvent from the solvent can be reduced in the solvent stripping step and the separation step (extractive distillation step) described later. The content of acetonitrile in the absorption solvent is preferably no less than 55% by mass and no greater than 90% by mass, and more preferably no less than 60% by mass and no greater than 85% by mass. When the content of acetonitrile having a comparatively low boiling point falls within the above range, energy consumption in separating components absorbed to the absorption solvent from the solvent can be further efficiently reduced.

[0057]

It is preferred that the absorption solvent further contains at least one selected from the group consisting of water and alcohols. When the absorption solvent further contains water, the selectivity of the absorption solvent can be improved; however, when the content of water is too high, the hydrocarbons may fail to be dissolved in acetonitrile in the absorption solvent, thereby leading to separation into two phases. Thus, when the absorption solvent further contains at least one alcohol in addition to water, a decrease of the solubility of the hydrocarbons (other gas) in acetonitrile can be avoided even if the content of water is increased, whereby the content of water in the absorption solvent can be increased.

[0058]

The alcohol is exemplified by those having no greater than 8 carbon atoms in light of the affinity to the hydrocarbons and to water. Among these, alcohols having no greater than 5 carbon atoms having a boiling point that is approximate to the boiling point of acetonitrile is preferred. The alcohol is more preferably an aliphatic saturated alcohol such as methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol and n-pentyl alcohol, an aliphatic unsaturated alcohol such as allyl alcohol and crotyl alcohol, or an alicyclic alcohol such as cyclopentanol, and particularly preferably ethyl alcohol.

[0059]

The content of water in the absorption solvent is preferably no less than 5% by mass and no greater than 35% by mass, and more preferably no less than 10% by mass and no greater than 25% by mass. When the content of water falls within the above range, selectivity of the absorption solvent can be effectively increased.

[0060]

The content of the alcohol in the absorption solvent is preferably no less

than 5% by mass and no greater than 30% by mass, and more preferably no less than 5% by mass and no greater than 15% by mass. When the content of the alcohol falls within the above range, a decrease of the solubility of the hydrocarbons (other gas) in acetonitrile can be avoided even if the content of water is increased, whereby the content of water in the absorption solvent can be increased.

[0061]

The absorption solvent may contain other solvent except for acetonitrile, alcohol and water.

[0062]

The amount of the absorption solvent used in the rough separation step is not particularly limited, and with respect to the total flow rate of butadiene and unreacted n-butene in the product gas supplied from the reactor 1, the amount of the absorption solvent is typically no less than 1 time by mass and no greater than 100 times by mass, and preferably no less than 5 times by mass and no greater than 50 times by mass. When the amount of the absorption solvent falls within the above range, the absorption efficiency of butadiene, etc., can be improved. A too large amount of the absorption solvent is likely to lead to a disadvantage in an economical aspect, whereas when amount of the absorption solvent is too small, the absorption efficiency of butadiene, etc., is likely to be inferior.

[0063]

The temperature of the absorption solvent is typically no less than 0 °C and no greater than 60 °C, and preferably no less than 0 °C and no greater than 40 °C. When the temperature of the absorption solvent falls within the above range, the absorption efficiency of hydrocarbons such as butadiene can be further improved. Therefore, it is preferred that the temperature is adjusted with a device such as the heat exchanger 112.

[0064]

Components (the molecular oxygen and the inert gas) that failed to be absorbed to the absorption solvent are discharged from the top of the absorption tower 6, and supplied to a water-washing tower 7 through a pipe 107. The molecular oxygen and the inert gas are washed with water supplied through a pipe 110 of the water-washing tower 7, whereby the absorption solvent admixed (i.e., entrained) with the molecular oxygen and the inert gas are removed, and the removed absorption solvent is recovered through a pipe 108. The washed molecular oxygen and inert gas may be recycled by transferring to the reaction step through the pipe 109.

[0065]

The pressure in the water-washing tower 7 is not particularly limited, and is typically 0.05 MPaG to 1.5 MPaG, and preferably 0.05 MPaG to 1.0 MPaG. The temperature in the water-washing tower 7 is not particularly limited, and is typically 0 °C to 80 °C, and preferably 10 °C to 60 °C.

[0066]

### Solvent Stripping Step

In this step, the solvent is separated from the absorption solvent containing butadiene to obtain a gas stream containing butadiene. The absorption solvent containing butadiene obtained from the bottom of the absorption tower 6 is supplied to a solvent stripper 8 through a pipe 111. In the solvent stripper 8, separation by distillation is carried out to obtain a gas stream containing butadiene from the top of the tower. The solvent thus separated is drawn out from the tower bottom, and recycled as the absorption solvent in the absorption tower 6, whereas a part of the separated solvent is supplied to a solvent regeneration tower 9, and recycled in the absorption tower 6 after the separation of impurities in the solvent.

[0067]

The pressure in the solvent stripper 8 is not particularly limited, and is typically 0.03 MPaG to 1.0 MPaG, and preferably 0.2 MPaG to 0.6 MPaG.

[0068]

Furthermore, the tower bottom temperature in the solvent stripper 8 is preferably 80 °C to 160 °C, and more preferably 100 °C to 140 °C. Since the absorption solvent used in the embodiment of the present invention contains acetonitrile having a comparatively low boiling point as a principal component, even if the temperature in the solvent stripper 8 is lowered to a comparatively low level as in the range described above, separation of the absorption solvent into the solvent, and the gas stream containing butadiene is enabled, whereby the energy consumption can be reduced.

[0069]

The pressure in the solvent regeneration tower 9 is not particularly limited, and is typically 0 MPaG to 0.5 MPaG, and preferably 0 MPaG to 0.3 MPaG.

[0070]

In this step, although comparatively highly pure butadiene can be obtained, distillation of this butadiene (for example, in a separation step described later) enables further highly pure butadiene to be obtained.

[0071]

### Second Embodiment

The production method of butadiene according to the second embodiment of the present invention further includes a separation (extractive distillation) step after the rough separation step and before the solvent stripping step in the method according to the first embodiment. The production method of butadiene according to the second embodiment is explained with reference to FIG. 2. In regard to the reaction step, the cooling step, the rough separation step and the solvent stripping step, explanations are omitted since similar steps to those in the first embodiment shown in FIG. 1 as described above may be adopted. The separation (extractive distillation) step is explained below.

[0072]

### Separation Step (Extractive Distillation Step)

The other gas (gas containing butadiene) obtained through the reaction step, the cooling step and the rough separation step in a similar manner to the production method of butadiene according to the first embodiment is separated into: 1,3-butadiene; and unreacted n-butene and butanes by selective absorption to an extraction solvent in this step.

[0073]

The absorption solvent containing the other gas obtained from the bottom of the absorption tower 36 is supplied to an extractive distillation tower 38 through pipe 201. Since the bottom of the extractive distillation tower 38 is heated with a reboiler, a part of the absorption solvent, and the gas absorbed to the absorption solvent may be gasified. The gas is brought into countercurrent contact with the extraction solvent supplied through the pipe 202 into the upper area of the extractive distillation tower 38, and a liquid condensed with a condenser at the top of the tower. Accordingly, 1,3-butadiene is selectively absorbed to the extraction solvent. The selective absorption to the extraction solvent as referred to indicates a concept including an embodiment in which the absorption solvent containing the other gas is subjected to repeated evaporation and absorption to the solvent in the extractive distillation tower 38, and as a result, butadiene is selectively absorbed to the extraction solvent. The unreacted n-butene and butanes failed to be absorbed are discharged through a pipe 203 from the top of the tower; however, a part of the unreacted n-butene and butanes may be recycled through transferring to the reaction step.

[0074]

As the extraction solvent, illustrative examples of the absorption solvent in the rough separation step (absorption step) described above may be employed. Accordingly, a solvent regeneration step, the solvent stripper and the like for each of the absorption solvent and the extraction solvent are not necessary, and thus butadiene can be efficiently produced by a comparatively simple process.

[0075]

The pressure in the extractive distillation tower 38 is not particularly limited, and is typically 0.1 MPaG to 1.0 MPaG, and preferably 0.2 MPaG to 0.8 MPaG.

[0076]

Furthermore, the tower bottom temperature of the extractive distillation tower 38 is preferably 60 °C to 160 °C, and more preferably 80 °C to 140 °C.

[0077]

The extraction solvent containing butadiene obtained from the bottom of the extractive distillation tower 38 is supplied to a solvent stripper 39 through a pipe 204. Following the Solvent Stripping Step carried out in the solvent stripper 39, the explanations on the subsequent Solvent Stripping Step of the first embodiment described above may be adopted.

[EXAMPLES]

[0078]

Hereinafter, specific Examples of the production method of butadiene are explained, but it should be construed that the present invention is not limited to the following Examples.

[0079]

It is to be noted that the gas composition analyses described in the following Examples were conducted with gas chromatography under the conditions shown in Table 1 below. H<sub>2</sub>O was calculated through adding the moisture content obtained by ice cold trap in gas sampling.

[0080]

[Table 1]

| Summary of Gas Composition Analysis |                                                                                                                          |                                                                       |
|-------------------------------------|--------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------|
| Gas species                         | 1,3-butadiene, n-butene                                                                                                  | N <sub>2</sub> , O <sub>2</sub> , CO <sub>x</sub> , H <sub>2</sub> O  |
| Model                               | GC-14B<br>(manufactured by Shimadzu Corporation)                                                                         | GC-14B<br>(manufactured by Shimadzu Corporation)                      |
| Detector                            | FID                                                                                                                      | TCD                                                                   |
| Column                              | TC-BOND Alumina/Na <sub>2</sub> SO <sub>4</sub><br>0.53 mm I.D. x 30 m df = 10 μm<br>(manufactured by GL Sciences, Inc.) | WG-100<br>6.35 mm I.D. x 1.8 m<br>(manufactured by GL Sciences, Inc.) |
| Carrier gas                         | N <sub>2</sub> 40 ml/min                                                                                                 | He 50 ml/min                                                          |
| Temperature                         |                                                                                                                          |                                                                       |
| Injection                           | 200 °C                                                                                                                   | 60 °C                                                                 |
| Detector                            | 250 °C                                                                                                                   | 80 °C                                                                 |
| Column                              | 60 °C 5 min → 135 °C (5 °C/min)<br>→ 185 °C (15 °C/min)                                                                  | 50 °C                                                                 |

[0081]

In addition, the solution composition analyses described in the following Examples were conducted with gas chromatography under the conditions shown in Table 2 below.

[0082]

[Table 2]

|             |                                                                                                         |
|-------------|---------------------------------------------------------------------------------------------------------|
| Gas species | Acetonitrile, Water, Ethanol                                                                            |
| Model       | GC-14B<br>(manufactured by Shimadzu Corporation)                                                        |
| Detector    | TCD                                                                                                     |
| Column      | Polyethylene glycol 1500 20% ON Shimalite<br>2 mm I.D. x 3 m<br>(manufactured by Shimadzu Science Inc.) |
| Carrier gas | He 250 kPa                                                                                              |
| Temperature |                                                                                                         |
| injection   | 120 °C                                                                                                  |
| detector    | 150 °C                                                                                                  |
| column      | 100 °C                                                                                                  |

[0083]

## Example 1

Example 1 is the production method of butadiene according to the first embodiment described above. In the following, Example 1 is explained with reference to FIG. 1.

[0084]

## Reaction Step

## (a) Catalyst

A catalyst in which an oxide represented by the composition formula of:  $\text{Mo}_{12}\text{Bi}_5\text{Fe}_{0.5}\text{Ni}_2\text{Co}_3\text{K}_{0.1}\text{Cs}_{0.1}\text{Sb}_{0.2}$  was carried by spherical silica at a proportion of 20% of the total volume of the catalyst was used.

[0085]

To a reactor 1 (internal diameter: 21.2 mm, external diameter: 25.4 mm) shown in FIG. 1 packed with the catalyst (a) described above to give a catalyst length of 4,000 mm, a gas mixture prepared by mixing: a raw material gas containing n-butene; air; water vapor; and nitrogen, at a volume ratio of 1.0:4.3:1.2:3.4 was supplied with a gas hourly space velocity (GHSV) of 1,000  $\text{hr}^{-1}$ , and a reaction was allowed at 320 °C to 330 °C to obtain a product gas

containing 1,3-butadiene.

[0086]

#### Cooling Step

The product gas taken out from the reactor 1 was quenched to 76 °C through bringing into contact with water in the quench tower 2, and then cooled with the heat exchanger 3 to room temperature (30 °C). The ratio of each gas component in the product gas at the outlet of the quench tower 2, 1,3-butadiene/ unreacted n-butene/ N<sub>2</sub>/ H<sub>2</sub>O/ O<sub>2</sub>/ CO<sub>x</sub>, was 6.8:1.4:59:29:2.2:1.6 by volume. In addition, the composition of the cooled product gas at the outlet of the heat exchanger 3, 1,3-butadiene/ unreacted n-butene/ N<sub>2</sub>/ H<sub>2</sub>O/ O<sub>2</sub>/ CO<sub>x</sub>, was 9.3:1.9:81:2.8:3.1:2.1 by volume.

[0087]

#### Rough Separation Step (Absorption Step)

The cooled product gas obtained in the above cooling step was compressed to 0.4 MPaG with a compressor 4, and cooled to 50 °C with the heat exchanger 5. The gas after cooling was supplied from the bottom of the absorption tower 6 having an external diameter of 6 inch, a height of 7,800 mm, made of a SUS304 material, and having a structured packing provided inside thereof, whereas the absorption solvent containing acetonitrile, water and ethanol at a ratio of 75:15:10 (% by mass) was supplied at 10 °C from the upper area of the tower. The amount of the supplied absorption solvent was 15 times by mass the 1,3-butadiene and unreacted n-butene which were intended to be absorbed to the absorption solvent.

[0088]

The gas not absorbed to the absorption solvent, and taken out from the top of the tower contained 93% by volume of N<sub>2</sub>, 4% by volume of O<sub>2</sub>, and 3% by volume of impurities such as CO<sub>x</sub>. The gas obtained from the top of the tower was transferred to the water-washing tower 7, and after a small amount of the solvent contained in the gas was removed, a part thereof was transferred to the reaction step to allow for recycling.

[0089]

#### Solvent Stripping Step

The solvent containing 1,3-butadiene obtained from the bottom of the absorption tower 6 was supplied to the solvent stripper 8 having an external diameter of 8 inch, a height of 6,600 mm, made of a SS400 material, and having a packing provided inside thereof, and thus a gas stream not substantially containing the solvent was obtained from the top of the tower. The gas obtained from the top of the tower of the solvent stripper 8 contained 80% by volume of 1,3-butadiene, 17% by volume of n-butene, and 3% by volume of impurities such as CO<sub>x</sub> and the solvent.

[0090]

The solvent taken out from the bottom of the solvent stripper 8 and not substantially containing 1,3-butadiene was cooled with the heat exchanger, and thereafter supplied to the absorption tower 6 to allow for recycling. Whereas,

a part thereof was supplied to the solvent regeneration tower 9, and after separating the impurities, it was recycled to the absorption tower 6.

[0091]

#### Example 2

Example 2 is the production method of butadiene according to the second embodiment described above. More specifically, in Example 2, 1,3-butadiene was obtained by a similar operation to Example 1 (i.e., the reaction step, the cooling step and the rough separation step being carried out under identical conditions to those of Example 1), except that an additional Separation Step (Extractive Distillation Step) was carried out after the Rough Separation Step (Absorption Step) and before the Solvent Stripping Step in Example 1 described above. The Separation Step (Extractive Distillation Step) and the subsequent step of Example 2 are explained below with reference to FIG. 2.

[0092]

#### Separation Step (Extractive Distillation Step)

The solvent containing 1,3-butadiene obtained from the bottom of the absorption tower 36 was supplied to the extractive distillation tower 38 having an external diameter of 12 inch, a height of 8,200 mm, made of a SUS304 material, and having a structured packing provided inside thereof, whereas the extraction solvent containing acetonitrile, water and ethanol at a ratio of 75:15:10 by mass was supplied at 30 °C from the upper area of the tower. The amount of the supplied extraction solvent was 3 times by mass the target components which were intended to be absorbed to the solvent.

[0093]

The gas not absorbed to the extraction solvent, and taken out from the top of the tower contained 80% by volume of n-butene, 1% by volume of butanes, 9% by volume of N<sub>2</sub>, and 10% by volume of impurities such as the solvent. The gas taken out was subjected to a purification step of n-butene to further increase the n-butene concentration, and thereafter transferred to the reaction step and used as a part of the raw material gas.

[0094]

#### Solvent Stripping Step

The solvent containing 1,3-butadiene obtained from the bottom of the extractive distillation tower 38 was supplied to the solvent stripper 39 having an external diameter of 8 inch, a height of 6,600 mm, made of a SS400 material, and having a structured packing provided inside thereof, and thus a gas stream containing 1,3-butadiene as a principal component and containing the solvent drastically decreased was obtained from the top of the tower. The gas obtained from the top of the tower of the solvent stripper 39 contained 90% by volume of 1,3-butadiene, 9% by volume of the solvent and the like, and 1% by volume of the impurities such as CO<sub>x</sub>.

[0095]

The solvent taken out from the bottom of the solvent stripper 39 and not

substantially containing 1,3-butadiene was cooled with the heat exchanger 205 or the heat exchanger 206, and thereafter supplied to the absorption tower 36 and the extractive distillation tower 38 to allow for recycling. Whereas, a part thereof was supplied to the solvent regeneration tower 40, and after separating the impurities, it was recycled to the absorption tower 36 and the extractive distillation tower 38.

[INDUSTRIAL APPLICABILITY]

[0096]

The production method of butadiene according to the embodiment of the present invention can achieve a reduction of energy consumption in preparing butadiene from a product gas obtained by oxidative dehydrogenation of n-butene.

[EXPLANATION OF THE REFERENCE SYMBOLS]

[0097]

1 reactor

2 quench tower

3 heat exchanger

4 compressor

5 heat exchanger

6 absorption tower

7 water-washing tower

8 solvent stripper

9 solvent regeneration tower

100 to 111 pipe

112 heat exchanger

31 reactor

32 quench tower

33 heat exchanger

34 compressor

35 heat exchanger

36 absorption tower

37 water-washing tower

38 extractive distillation tower

39 solvent stripper

40 solvent regeneration tower

201 to 204 pipe

205 heat exchanger

206 heat exchanger

## CLAIMS

1. A production method of 1,3-butadiene comprising:  
obtaining a product gas containing 1,3-butadiene by an oxidative dehydrogenation reaction of a raw material gas containing n-butene with a gas containing molecular oxygen in the presence of a metal oxide catalyst;  
cooling the product gas; and  
separating the cooled product gas into: a fraction containing the molecular oxygen and an inert gas; and other gas comprising n-butene and 1,3-butadiene by selective absorption to an absorption solvent,  
wherein in the product gas, a N<sub>2</sub> concentration is no less than 35% by volume and no greater than 90% by volume, a H<sub>2</sub>O concentration is no less than 5% by volume and no greater than 60% by volume, and a 1,3-butadiene concentration is no less than 2% by volume and no greater than 15% by volume,  
wherein the absorption solvent comprises acetonitrile as a principal component,  
and wherein the absorption solvent further comprises water and an alcohol, and the alcohol is methyl alcohol or ethyl alcohol.
2. The production method of 1,3-butadiene according to claim 1, wherein in the cooled product gas, the N<sub>2</sub> concentration is no less than 60% by volume and no greater than 94% by volume, the H<sub>2</sub>O concentration is no less than 1% by volume and no greater than 30% by volume, and the 1,3-butadiene concentration is no less than 2% by volume and no greater than 15% by volume.
3. The production method of 1,3-butadiene according to claim 1 or 2, wherein a content of acetonitrile in the absorption solvent is no less than 55% by mass and no greater than 90% by mass.
4. The production method of 1,3-butadiene according to any one of claims 1 to 3, wherein a content of water in the absorption solvent is no less than 5% by mass and no greater than 35% by mass.
5. The production method of 1,3-butadiene according to any one of claims 1 to 4, wherein a content of the alcohol in the absorption solvent is no less than 5% by mass and no greater than 30% by mass.
6. The production method of 1,3-butadiene according to any one of claims 1 to 5, wherein an amount of the absorption solvent supplied in separating the cooled product gas is no less than 5 times by mass and no greater than 100 times by mass with respect to a total amount of n-butene and 1,3-butadiene, and a temperature of the absorption solvent is no less than 0 °C and no greater than

40 °C.

7. The production method of 1,3-butadiene according to any one of claims 1 to 6, further comprising washing with water a gas not absorbed to the absorption solvent in separating the cooled product gas to recover the absorption solvent included in the gas.

8. The production method of 1,3-butadiene according to any one of claims 1 to 7, further comprising:  
separating the other gas into: 1,3-butadiene; and unreacted n-butene and butanes by selective absorption to an extraction solvent.

9. The production method of 1,3-butadiene according to claim 8, wherein a solvent identical or similar to the absorption solvent is used as the extraction solvent.

10. The production method of 1,3-butadiene according to claim 8 or 9, further comprising  
washing with water a gas not absorbed to the extraction solvent in separating the other gas to recover the extraction solvent included in the gas.