

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 produced 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and the like; however, due to circumstances in which cracking of naphtha for a production method of ethylene has been replaced by thermal decomposition of ethane, quantities of the C4 fraction supplied have decreased.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 view of the foregoing demands, 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. Since the oxidative dehydrogenation reaction is a gas phase reaction at a high temperature, it is typically necessary to cool the obtained product gas by introducing into a cooling tower or the like so as to contact with water, or by bringing into contact with water. However, by-products such as water soluble by-products other than butadiene, as well as hardly water soluble by-products having a high boiling point, and the like are contained in the obtained product gas, leading to an inconvenience of making a continuous operation difficult since the cooling results in deposition of these by-products thereby causing clogging in the cooling tower and pipe.

[0004]

Therefore, for example: (1) a method of removing by-products using oil that dissolves the by-products, such as paraffin oil, naphthene oil and aromatic oil (see Japanese Examined Patent Application, Publication No. S49-6283); (2) a method of enabling the by-products to be separated with water by introducing the product gas having a temperature of no less than 170 °C into the cooling

tower, and maintaining the temperature on the inside wall face of the cooling tower at no less than 140 °C (see Japanese Unexamined Patent Application, Publication No. S60-115531); and (3) a method of elevating the temperature of the obtained product gas to 300 °C to 221 °C before cooling in the cooling tower such that deposition of the by-products in the product gas is avoided (see Japanese Unexamined Patent Application, Publication No. 2011-1341), and the like have been proposed.

[0005]

However, according to the method (1), since the oil content in the gas phase content is included in the cooled product gas, a step of separately recovering the oil content is required. Further, according to the method (2), although a procedure for maintaining the temperature of the product gas and on the inside wall face of the cooling tower at each specified temperature described above, the deposition of the by-products having a high boiling point occurs at the specified temperature, whereby clogging in the cooling tower and the pipe may be caused. In addition, according to the method (3) described above, at least two parallel lines for the by-products deposited are provided, thereby leading to inconveniences of needs for clogging control of the lines, switching operation and washing operation of the lines, and the like.

[0006]

It is to be noted that in PCT International Publication No. 2012/157495, use of a mixture containing an aqueous organic amine solution and an aromatic organic solvent is used as a cooling agent is proposed. However, the invention disclosed in this document is characterized in that an aqueous solution of an organic amine that is a bifunctional compound is used as the cooling solvent, whereby an acid-base reaction or aldol condensation of this organic amine with the by-products is caused to achieve the removal. In addition, as described in paragraph [0039], the document intentionally excludes use of an aqueous alkaline solution, as the cooling agent, such as an aqueous sodium hydroxide solution that causes a simple neutralizing reaction, teaching away from the scope of the presently claimed invention.

[Prior Art Documents]

[Patent Documents]

[0007]

Patent Document 1: Japanese Examined Patent Application, Publication No. S49-6283

Patent Document 2: Japanese Unexamined Patent Application, Publication No. S60-115531

Patent Document 3: Japanese Unexamined Patent Application,

Publication No. 2011-1341

Patent Document 4: PCT International Publication No. 2012/157495

[SUMMARY OF THE INVENTION]

[Problems to be Solved by the Invention]

[0008]

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 enables deposition of by-products, and clogging of the cooling tower and pipe to be inhibited, whereby a continuous operation can be stably performed.

[Means for Solving the Problems]

[0009]

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;

wherein, in the cooling step, a cooling solvent containing an organic solvent and an aqueous alkali metal compound solution is brought into contact with the gas.

[0010]

According to the production method of butadiene, since a cooling solvent containing an organic solvent in addition to an aqueous alkali metal compound solution is used in the cooling step, not only water soluble by-products that are soluble in the aqueous alkali metal compound solution but also hardly water soluble by-products having a high boiling point can be dissolved in the cooling solvent. Accordingly, clogging of the cooling tower and pipe in production of butadiene through deposition of by-products can be inhibited, whereby a continuous operation can be stably performed.

[Effects of the Invention]

[0011]

According to the production method of butadiene of the aspect of the present invention, in producing butadiene from a product gas obtained by oxidative dehydrogenation of n-butene, deposition of by-products to cause clogging of the cooling tower and pipe is inhibited, and thus a continuous operation can be stably performed.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0012]

FIG. 1 shows a flow diagram illustrating a production method of

butadiene according to an embodiment of the present invention

[Description of Embodiments]

[0013]

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

[0014]

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 no less than 200 °C and no greater than 350 °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.

[0015]

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, for example, nitrogen, argon, neon, helium, CO, CO₂ 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.

[0016]

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, CO₂ and the like, and of these, nitrogen is preferred in light of the economic aspect.

[0017]

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.

[0018]

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.

[0019]

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.

[0020]

Composition of Gas Mixture

The lower limit of the concentration of n-butene in the gas mixture is, in light of productivity of butadiene, preferably 2% by volume, more preferably 3% by volume, and still more preferably 5% by volume. On the other hand, the upper limit of the concentration of n-butene in the gas mixture is, in light of reducing the load to the metal oxide catalyst, preferably 30% by volume, more preferably 25% by volume, and still more preferably 20% by volume. In regard to the composition of the gas mixture, the lower limit of the proportion of O₂ with respect to 100 parts by volume of the raw material gas is preferably 50 parts by volume, and more preferably 70 parts by volume. The upper limit of the proportion of O₂ is preferably 150 parts by volume, and more preferably 110 parts by volume. The lower limit of the proportion of N₂ with respect to 100 parts by volume of the raw material gas is preferably 200 parts by volume, and more preferably 300 parts by volume. The upper limit of the proportion of N₂ is preferably 2,000 parts by volume, and more preferably 1,500 parts by volume. The lower limit of the proportion of H₂O with respect to 100 parts by volume of the raw material gas is preferably 0 parts by volume, and more preferably 100 parts by volume. The upper limit of the proportion of H₂O is preferably 900 parts by volume, and more preferably 300 parts by volume. When the proportion of O₂ with respect to the raw material gas departs from this range, it is likely to be difficult to adjust the O₂ concentration at the outlet of the reactor 1, even if the reaction temperature is adjusted. In addition, as the proportion of N₂ and/or H₂O 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.

[0021]

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.

[0022]

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.

[0023]

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.

[0024]

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.

[0025]

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.

[0026]

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 cooling solvent that circulates in the cooling step, 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 by-product is likely to be induced.

[0027]

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 by-product may be accumulated in the absorption solvent and the extraction solvent, and/or coking of the catalyst is likely to occur.

[0028]

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.).

[0029]

Although the lower limit of 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 typically 0.5 MPaG, preferably 0.3 MPaG, and more preferably 0.1 MPaG.

[0030]

The lower limit of the gas hourly space velocity (GHSV) in the oxidative dehydrogenation reaction is preferably 500 hr^{-1} , and more preferably 800 hr^{-1} . On the other hand, the upper limit of GHSV is preferably $5,000 \text{ hr}^{-1}$, and more preferably $3,000 \text{ hr}^{-1}$. 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).

[0031]

Concentration of Each Component in Product Gas

The lower limit of the N_2 concentration in the product gas generated by the oxidative dehydrogenation reaction is preferably 35% by volume, and more preferably 45% by volume. The upper limit of the N_2 concentration is preferably 90% by volume, and more preferably 80% by volume. The lower limit of the H_2O concentration is preferably 5% by volume, and more preferably 8% by volume. The upper limit of the H_2O concentration is preferably 60% by volume, and more preferably 40% by volume. The lower limit of the butadiene concentration is preferably 3% by volume, and more preferably 5% by volume. The upper limit of the butadiene concentration is preferably 20% by volume, and more preferably 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 accumulation of the by-product can be inhibited.

[0032]

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).

[0033]



[0034]

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.

[0035]

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.

[0036]

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.

[0037]

Cooling Step

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

[0038]

Cooling Tower 2

The product gas from the reactor 1 is supplied to the cooling tower 2 through a pipe 101. From the top of the cooling tower 2, a cooling solvent is introduced through a pipe 102, and the cooling solvent is brought into contact with the supplied product gas. The type of the cooling tower 2 is exemplified by a packed tower, a plate tower, a spray tower, a wetted wall tower, a bubble tower and the like, and the packed tower, and the plate tower are preferred. The packing used in the packed tower is exemplified by: nonstructured packing such as Raschig ring, Berl saddle and cascade miniring; and structured packing such as flexipack and Mellapak; and the like. The cooling procedure in the cooling tower 2 is preferably quenching by a countercurrent contact of the cooling solvent with the product gas in the packed tower using the nonstructured packing. In the countercurrent contact, the product gas is cooled to about no less 30 °C and no greater than 99 °C. As the cooling solvent, a mixture of an organic solvent and an aqueous alkali metal compound solution may be used. By using such a cooling solvent, water soluble by-products such as acrylic acid, methacrylic acid, maleic acid, fumaric acid and maleic anhydride that are generated in the aforementioned oxidative dehydrogenation reaction, as well as hardly water soluble by-products having a high boiling point such as fluorenone and anthraquinone can be dissolved in the cooling solvent and removed. In addition, by using the aqueous alkali metal solution, acids such as acrylic acid are neutralized, whereby corrosion of the apparatus can be prevented. It is to be noted that the cooling solvent may contain other solvent than the organic solvent and the aqueous alkali metal compound solution. The solvent cooled is discharged through a pipe 103. The temperature of the cooling solvent introduced may depend on the cooling temperature of the product gas of the reaction, and the lower limit is preferably 10 °C, and more preferably 20 °C. On the other hand, the upper limit of the temperature of the cooling medium is preferably 90 °C, more preferably 70 °C, and still more preferably 40 °C.

[0039]

Although the pressure in the cooling tower 2 is not particularly limited, the lower limit is preferably 0 MPaG, more preferably 0.1 MPaG, and still more preferably 0.2 MPaG. On the other hand, the upper limit of the pressure in the cooling tower 2 is preferably 1.5 MPaG, more preferably 1.0 MPaG, and still more preferably 0.5 MPaG. When the pressure in the cooling tower 2 falls within the above specified range, the by-products can be more effectively removed by the cooling solvent. The lower limit of the temperature in the cooling tower 2 is preferably 0 °C, and more preferably 20 °C. On the other hand, the upper limit of the temperature in the cooling tower 2 is preferably

100 °C, and more preferably 80 °C.

[0040]

As the organic solvent in the cooling step, an aromatic compound, an amide compound, a sulfur compound, a nitrile compound, a ketone compound, an alcohol or a combination thereof is preferred. By using the cooling solvent containing the specific organic solvent, hardly water soluble by-products having a high boiling point can be more effectively removed, and thus instability of the process resulting from accumulation of the by-products can be more prevented. It is to be noted that these organic solvents may be used alone of one type, or two or more types thereof may be used in combination.

[0041]

Examples of the aromatic compound include toluene, xylene, benzene, and the like.

[0042]

Examples of the amide compound include dimethylformamide, N-methyl-2-pyrrolidone (NMP), and the like.

[0043]

Examples of the sulfur compound include dimethyl sulfoxide (DMSO), sulfolane, and the like.

[0044]

Examples of the nitrile compound include acetonitrile, butyronitrile, and the like.

[0045]

Examples of the ketone compound include cyclohexanone, acetophenone, and the like.

[0046]

Examples of the alcohol include methyl alcohol, ethyl alcohol, allyl alcohol, crotyl alcohol, cyclopentanol, and the like.

[0047]

Of these, the organic solvent in the cooling step is preferably an aromatic compound, and more preferably toluene.

[0048]

The aqueous alkali metal compound solution in the cooling solvent is preferably an aqueous alkali metal hydroxide solution, and is exemplified by an aqueous sodium hydroxide solution, an aqueous potassium hydroxide solution, an aqueous lithium hydroxide solution and the like. Of these, the aqueous sodium hydroxide solution and the aqueous potassium hydroxide solution are more preferred, and the aqueous sodium hydroxide solution is still more preferred. Moreover, the lower limit of the concentration in terms of alkali

hydroxide of the aqueous alkali metal compound solution is preferably 1% by mass, more preferably 2% by mass, and still more preferably 3% by mass. On the other hand, the upper limit of the concentration in terms of alkali hydroxide of the aqueous alkali metal compound solution is preferably 50% by mass, more preferably 40% by mass, and still more preferably 30% by mass. It is to be noted that these aqueous alkali metal compound solutions may be used alone of one type, or two or more types thereof may be used in combination. For the purpose of neutralization and carbon dioxide-absorption, ammonia, amine, etc., may be used. However, ammonia is accompanied by a risk due to toxicity, whereas amines are less basic than alkali metals and therefore a larger amount of the amine must be used for the neutralization, and the unit prices are high, leading to an increase in the production cost of butadiene.

[0049]

When the organic solvent in the cooling step is the aromatic compound, the lower limit of the content of the aqueous alkali metal compound solution in the cooling solvent is preferably 10% by mass, more preferably 20% by mass, and still more preferably 30% by mass. On the other hand, the upper limit of the content of the aqueous alkali metal compound solution in the cooling solvent is preferably 80% by mass, more preferably 75% by mass, and still more preferably 70% by mass. In the case where the organic solvent is thus the aromatic compound, when the content of the aqueous alkali metal compound solution in the cooling solvent falls within the above-specified range, the water soluble by-products, as well as the hardly water soluble by-products having a high boiling point can be effectively dissolved in the cooling solvent and can be removed.

[0050]

When the organic solvent in the cooling step is the amide compound, the sulfur compound, the nitrile compound, the ketone compound, the alcohol or a combination thereof, the lower limit of the content of the aqueous alkali metal compound solution in the cooling solvent is preferably 5% by mass, preferably 10% by mass, and more preferably 15% by mass. The upper limit of the content of the aqueous alkali metal compound solution in the cooling solvent is preferably 80% by mass, more preferably 70% by mass, and still more preferably 60% by mass. In the case where the organic solvent is thus the other than the aromatic compound, when the content of the aqueous alkali metal compound solution in the cooling solvent falls within the above-specified range, the by-products can be effectively dissolved in the cooling solvent and can be removed.

[0051]

Separation Step

The cooling solvent is circulated to be back into the cooling tower 2 through a pipe 122 and then used. Furthermore, a part of the cooling solvent recycled is drawn out through the pipe 103 and is separated into the organic solvent and the aqueous alkali metal compound solution in a decanter 10. The separated aqueous alkali metal compound solution containing organic acids such as maleic acid and acrylic acid is discharged through the pipe 120. On the other hand, the separated organic solvent is transferred to a regeneration vessel 11 through a pipe 121. Although the separated organic solvent contains accumulated by-products such as hardly water soluble by-products having a high boiling point, the by-products are removed in the regeneration vessel 11. The organic solvent from which the by-products were removed is recycled to the cooling tower 2 through the pipe 102. When the cooling solvent is thus recycled, drainage load through the pipe 120 can be reduced. It is to be noted that the separation step may not be necessarily included in the present invention.

[0052]

In regard to the concentration of each component in the product gas in the outlet of the cooling tower 2, the lower limit of the concentration of N_2 is preferably 30% by volume, and more preferably 40% by volume. The upper limit of the concentration of N_2 is preferably 80% by volume, and more preferably 70% by volume. The lower limit of the concentration of H_2O is preferably 5% by volume, and more preferably 10% by volume. The upper limit of the concentration of H_2O is preferably 60% by volume, and more preferably 45% by volume. The lower limit of the concentration of butadiene is preferably 3% by volume, and more preferably 5% by volume. The upper limit of the concentration of butadiene is preferably 20% by volume, and more preferably 15% by volume.

[0053]

Heat Exchanger

The product gas cooled in the cooling tower 2 is let out from the top of the cooling tower 2, and cooled to about room temperature (no less than 10 °C and no greater than 30 °C) via a heat exchanger 3 through a pipe 104, whereby a cooled product gas is obtained.

[0054]

In regard to the concentration of each component in the cooled product gas at the outlet of the heat exchanger 3, the lower limit of the concentration of N_2 is preferably 60% by volume, and more preferably 70% by volume. The upper limit of the concentration of N_2 is preferably 94% by volume, and more

preferably 85% by volume. The lower limit of the concentration of H_2O is preferably 1% by volume. The upper limit of the concentration of H_2O is preferably 20% by volume, and more preferably 10% by volume. The lower limit of the concentration of butadiene is preferably 3% by volume, and more preferably 4% by volume. The upper limit of the concentration of butadiene is preferably 20% by volume, and more preferably 15% 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.

[0055]

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. It is to be noted that the rough separation step may be omitted.

[0056]

As needed, the cooled product gas is compressed with a compressor 4 and further cooled with a heat exchanger 5. The cooled product gas is supplied to an absorption tower 6 through a pipe 107. From the top of the absorption tower 6, the absorption solvent the temperature of which has been adjusted via a heat exchanger 123 is introduced through a pipe 108, and the absorption solvent is brought into countercurrent contact with the 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 are roughly separated from the other gas.

[0057]

The pressure in the absorption tower 6 is not particularly limited, and the lower limit of the pressure is preferably 0.1 MPaG, and more preferably 0.2 MPaG. The upper limit of the pressure is preferably 1.5 MPaG, and more preferably 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.

[0058]

Also, the temperature in the absorption tower 6 is not particularly limited, and the lower limit of the temperature is preferably 0 °C, and more

preferably 10 °C. The upper limit of the temperature is preferably 60 °C, and more preferably 50 °C. An increase in the temperature results in an advantage that the oxygen, nitrogen and the like are less likely to be absorbed to the solvent, whereas a decrease in the temperature results in an advantage that an absorption efficiency of hydrocarbons such as butadiene is improved.

[0059]

Absorption Solvent

The absorption solvent used in this step is exemplified by solvents containing as a principal component the organic solvent similar to those exemplified as the organic solvent in the cooling step, and the like. The principal component is preferably the same organic solvent as one used in the cooling step, more preferably toluene or acetonitrile, and still more preferably toluene. The “principal component” as referred to herein means a component contained at a content in the organic solvent of no less than 50% by mass in the absorption solvent during the supplying. The lower limit of the content of the organic solvent in the absorption solvent is preferably 55% by mass, and more preferably 60% by mass. The upper limit of the content of the organic solvent in the absorption solvent is preferably 100% by mass.

[0060]

When the absorption solvent contains toluene as a principal component, the content of toluene in the absorption solvent is preferably no less than 80% by mass, more preferably no less than 90% by mass, and still more preferably 100% by mass.

[0061]

When the absorption solvent contains acetonitrile as a principal component, 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.

[0062]

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.

[0063]

When the absorption solvent contains acetonitrile as a principal component, the lower limit of the content of water in the absorption solvent is preferably 5% by mass, and more preferably 10% by mass. The upper limit of the content of water in the absorption solvent is preferably 35% by mass, and more preferably 25% by mass. When the content of water falls within the above range, selectivity of the absorption solvent can be effectively increased.

[0064]

When the absorption solvent contains acetonitrile as a principal component, the lower limit of the content of the alcohol in the absorption solvent is preferably 5% by mass. The upper limit of the content of the alcohol in the absorption solvent is preferably 30% by mass, and more preferably 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.

[0065]

When the absorption solvent contains acetonitrile as a principal component, the absorption solvent may contain other solvent than acetonitrile, alcohol and water.

[0066]

The amount of the absorption solvent used in the rough separation step is not particularly limited. With respect to the total flow rate of butadiene and unreacted n-butene in the product gas supplied from the reactor 1, the lower limit of the amount of the absorption solvent is preferably 1 time by mass and more preferably 5 times by mass. On the other hand, the upper limit of the amount of the absorption solvent is preferably 100 times by mass, and more preferably 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.

[0067]

The lower limit of the temperature of the absorption solvent is preferably 0 °C. The upper limit of the temperature of the absorption solvent is preferably 60 °C, and more preferably 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 123.

[0068]

Components (the molecular oxygen and the inert gas) that failed to be absorbed by the absorption solvent are discharged from the top of the absorption tower 6, and supplied to a washing tower 7 through a pipe 110. The molecular oxygen and the inert gas are washed with oil (when the absorption solvent contains toluene as a principal component) or water (when the absorption solvent contains acetonitrile as a principal component) supplied through a pipe 118 of the 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 via a pipe 117. The washed molecular oxygen and inert gas may be recycled by transferring to the reaction step through a pipe 119.

[0069]

Solvent Stripping Step

In this step, the solvent is separated from the absorption solvent containing butadiene to obtain a gas stream containing butadiene. More specifically, the absorption solvent containing butadiene obtained from the bottom of the absorption tower 6 is supplied to a solvent stripper 8 through a pipe 109. In the solvent stripper 8, separation by distillation is carried out to obtain a gas stream containing butadiene from the top of the tower via a pipe 113. The solvent thus separated is drawn out from the tower bottom, and recycled as the absorption solvent in the absorption tower 6 through a pipe 111, whereas a part of the separated solvent is supplied to a solvent regeneration tower 9 through a pipe 112, and recycled in the absorption tower 6 through a pipe 116 after the separation of impurities in the solvent. Thus separated impurities are discharged through pipes 114, 115 connected to the top and bottom of the solvent regeneration tower 9.

[0070]

The pressure in the solvent-stripping tower 8 is not particularly limited, and the lower limit is preferably 0.03 MPaG, and more preferably 0.2 MPaG. The upper limit of the pressure in the solvent-stripping tower 8 is preferably 1.0

MPaG, and more preferably 0.6 MPaG.

[0071]

Further, the lower limit of the tower bottom temperature of the solvent-stripping tower 8 is preferably 80 °C, and more preferably 100 °C. On the other hand, the upper limit of the tower bottom temperature of the solvent-stripping tower 8 is preferably 200 °C, and more preferably 180 °C.

[0072]

The pressure in the solvent regeneration tower 9 is not particularly limited, and the lower limit is preferably 0 MPaG. The upper limit of the pressure in the solvent regeneration tower 9 is preferably 0.8 MPaG, and more preferably 0.5 MPaG.

EXAMPLES

[0073]

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. 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. H₂O was calculated through adding the moisture content obtained by ice cold trap in gas sampling.

[0074]

Table 1

Summary of Gas Composition Analysis		
Gas species	1,3-butadiene, n-butene	N ₂ , O ₂ , CO _x , H ₂ O
Model of gas chromatograph	GC-14B (Shimadzu Corporation)	GC-14B (Shimadzu Corporation)
Detector	FID	TCD
Column	TC-BOND Alumina/ Na ₂ SO ₄ 0.53 mm I.D. x 30 m df = 10 μm (GL Sciences, Inc.)	WG-100 6.35 mm I.D. x 1.8 m (GL Sciences, Inc.)
Carrier gas	N ₂ 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) → 185 °C (15 °C/min)	50 °C

[0075]

Example 1

Example 1 demonstrates the production method of butadiene according to the embodiment of the present invention. In the following, Example 1 will be described with reference to FIG. 1.

[0076]

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.

[0077]

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 hr^{-1} , and a reaction was allowed at 320 °C to 330 °C to obtain a product gas containing 1,3-butadiene.

[0078]

Cooling Step

The product gas taken out from the reactor 1 was introduced into the cooling tower 2 having an external diameter 1·1/4 inches and a height of 1,600 mm, made of a SUS 316L material, and having Raschig rings of $\phi 5 \times 5$ mm provided inside thereof. In the cooling tower 2, the product gas introduced was brought into contact with a cooling solvent containing toluene and a 5% by mass aqueous sodium hydroxide solution at a ratio of 1: 1 under a condition involving a pressure of 0.01 MPaG to cool the gas to 67 °C, and then to room temperature (30 °C) with the heat exchanger 3. The ratio of each gas component in the product gas at the outlet of the cooling tower 2, 1,3-butadiene/ unreacted n-butene/ N_2 / H_2O / O_2 / CO_x , was 8.5/1.0/66/19/4.1/1.4 by volume. Ten days later, the operation was stopped and as a result of a visual inspection of the filter provided downstream the cooling tower 2, the presence of attached matter was not found. The cooling solvent was recycled, and a part thereof was drawn out and introduced into the decanter 10 so as to separate toluene and the aqueous sodium hydroxide solution. Thus separated toluene contained by-products such as fluorenone and anthraquinone, which were introduced into the regeneration vessel 11. After the by-products were removed, toluene was reused. The separated aqueous sodium hydroxide solution contained organic acids such as maleic acid and acrylic acid.

[0079]

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 1·1/2 inches, a height of 1,000 mm, made of a SUS304 material, and having a structured packing provided inside thereof, whereas toluene (absorption solvent) was supplied at 10 °C from the upper area of the tower. The amount of supplied toluene was 16 times by mass the 1,3-butadiene and unreacted n-butene which were intended to be absorbed to toluene.

[0080]

The gas not absorbed to toluene, and taken out from the top of the tower contained 91% by volume of N₂, 5% by volume of O₂, and 4% by volume of impurities such as CO_x. The gas obtained from the top of the tower was transferred to the washing tower 7, and after a small amount of the solvent contained in the gas was removed with oil, a part thereof was transferred to the reaction step to allow for recycling.

[0081]

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 1·1/2 inches, a height of 1,000 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 75% by volume of 1,3-butadiene, 8% by volume of n-butene, and 17% by volume of impurities such as CO_x and the solvent.

[0082]

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.

[0083]

Example 2

Butadiene was produced by a similar operation to Example 1 except that a 25% by mass aqueous sodium hydroxide solution was used as the cooling solvent for the cooling tower 2 in Example 1. The substances contained and the concentrations thereof in the part of toluene and sodium hydroxide drawn out were not altered. As a result of a visual inspection of the filter provided downstream the cooling tower 2, the presence of attached matter was not found.

As the amount of sodium hydroxide used is smaller, the production cost of butadiene is reduced.

[0084]

Comparative Example 1

Butadiene was produced by a similar operation to Example 1 except that a 5% by mass aqueous sodium hydroxide solution was used as the cooling solvent for the cooling tower 2 in Example 1. As a result of a visual inspection of the filter provided downstream the cooling tower 2, the presence of attached matter was found.

[INDUSTRIAL APPLICABILITY]

[0085]

According to the production method of butadiene of the embodiment of the present invention, in producing butadiene from a product gas obtained by oxidative dehydrogenation of n-butene, deposition of by-products, and clogging of the cooling tower and pipe can be inhibited, whereby a continuous operation can be stably performed.

[Explanation of the Reference Symbols]

[0086]

- 1 reactor
- 2 cooling tower
- 3 heat exchanger
- 4 compressor
- 5 heat exchanger
- 6 absorption tower
- 7 washing tower
- 8 solvent-stripping tower
- 9 solvent regeneration tower
- 10 decanter
- 11 regeneration vessel
- 100 to 122 pipe
- 123 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; and
cooling the product gas,
wherein, in the cooling, a cooling solvent containing an organic solvent and an aqueous alkali metal compound solution is brought into contact with the gas.
2. The production method of 1,3-butadiene according to claim 1, wherein the organic solvent in the cooling is an aromatic compound, an amide compound, a sulfur compound, a nitrile compound, a ketone compound, an alcohol or a combination thereof.
3. The production method of 1,3-butadiene according to claim 2, wherein the organic solvent in the cooling is the aromatic compound,
a content of the aqueous alkali metal compound solution in the cooling solvent is no less than 10% by mass and no greater than 80% by mass.
4. The production method of 1,3-butadiene according to claim 2, wherein
the organic solvent in the cooling is an amide compound, a sulfur compound, a nitrile compound, an alcohol or a combination thereof,
and a content of the aqueous alkali metal compound solution in the cooling solvent is no less than 5% by mass and no greater than 80% by mass.
5. The production method of 1,3-butadiene according to any one of claims 1 to 4, wherein the cooling solvent is recycled in the cooling.
6. The production method of 1,3-butadiene according to claim 5, further comprising: drawing out a part of the recycled cooling solvent; and separating into the organic solvent and the aqueous alkali metal compound solution.
7. The production method of 1,3-butadiene according to claim 6, further comprising separating by-products accumulated in the organic solvent obtained by the separating.

8. The production method of 1,3-butadiene according to any one of claims 1 to 7, wherein the cooling is carried out under a pressure of no less than 0 MPaG and no greater than 0.5 MPaG.