

DESCRIPTION

GAS PURIFICATION APPARATUS

5 Technical Field

[0001] The present invention relates to a gas purification apparatus including:

an adsorption tower filled with an adsorbent that adsorbs a miscellaneous gas other than a purification target gas from a source gas;

10 a source gas supply line for supplying the source gas to the adsorption tower;

a product gas recovery line for discharging the purification target gas that has not been adsorbed on the adsorbent as a product gas; and

a miscellaneous gas discharge line for discharging the desorbed miscellaneous gas that has been adsorbed on the adsorbent,

15 the adsorption tower, the source gas supply line, the product gas recovery line, and the miscellaneous gas discharge line being connected so as to be able to perform a pressure swing operation of alternately performing

an adsorption step of receiving the source gas from the source gas supply line, adsorbing the miscellaneous gas onto the adsorbent, and recovering the product gas, and

20 a desorption step of depressurizing-desorbing the miscellaneous gas adsorbed on the adsorbent and discharging that miscellaneous gas from the miscellaneous gas discharge line.

25 Background Art

[0002] In the case of effectively using a flammable gas, it is necessary to separate a gas such as the air from a source gas containing the flammable gas, and concentrate the flammable gas into an appropriate concentration range. Various such apparatuses and methods for concentrating a flammable gas have
30 been proposed, and inventions have been proposed in which a gas (the so-called coal mine gas) generating from a coal mine containing methane as a flammable gas is used as a source gas, the air (mainly containing nitrogen, oxygen, and carbon dioxide) is separated from the source gas by using an adsorbent, and methane is concentrated for use.

35 [0003] That is, with the use of natural zeolite, which has a very slower adsorption rate for methane than for nitrogen, as an adsorbent (i.e., with the use of an

adsorbent that preferentially adsorbs nitrogen, oxygen, and carbon dioxide to methane), a coal mine gas is introduced into an adsorption tower filled with the adsorbent by a compressor or the like until a predetermined pressure is reached. Consequently, oxygen, nitrogen, and carbon dioxide that are contained in the coal mine gas are adsorbed first at the front portion (lower portion) of the adsorption tower, and methane, for which the adsorption rate is slow, is adsorbed at the back portion (upper portion) of the adsorption tower. Furthermore, inventions of apparatuses and methods for concentrating methane have been proposed in which the above-described methane is further released from the upper portion of the adsorption tower until atmospheric pressure is reached.

Thereby, the air can be separated from the coal mine gas as the source gas by using the adsorbent, methane can be concentrated, and the concentrated methane can be used as a fuel or the like.

[0004] That is, a configuration (hereinafter referred to as "PSA device") is envisaged that includes:

- an adsorption tower filled with an adsorbent that adsorbs a miscellaneous gas other than a purification target gas from a source gas;

- a source gas supply line for supplying the source gas to the adsorption tower;

- a product gas recovery line for discharging the purification target gas that has not been adsorbed on the adsorbent as a product gas; and

- a miscellaneous gas discharge line for discharging the desorbed miscellaneous gas that has been adsorbed on the adsorbent,

the adsorption tower, the source gas supply line, the product gas recovery line, and the miscellaneous gas discharge line being connected so as to be able to perform a pressure swing operation of alternately performing

- an adsorption step of receiving the source gas from the source gas supply line, adsorbing the miscellaneous gas onto the adsorbent, and recovering the product gas, and

- a desorption step of depressurizing-desorbing the miscellaneous gas adsorbed on the adsorbent and discharging that miscellaneous gas from the miscellaneous gas discharge line.

[0005] Thereby, when the source gas is supplied to the adsorption tower from the source gas supply line, the adsorption step of adsorbing the miscellaneous gas in the source gas onto the adsorbent in the adsorption tower can be performed. The purification target gas in the source gas that has not been adsorbed on the

adsorbent is recovered from the product gas recovery line, and the adsorption tower that has been saturated by adsorbing the miscellaneous gas can be regenerated by performing the desorption step of depressurizing-desorbing the miscellaneous gas adsorbed on the adsorbent. The exhaust gas generated at this time is composed mainly of the miscellaneous gas, and is discharged from the miscellaneous gas discharge line. A pressure swing operation of repeating the adsorption step and the desorption step can be performed.

[0006] Here, when the purity of the purification target gas in the product gas is to be increased to a certain level, it is necessary to suppress the amount of the miscellaneous gas passing through the adsorption tower. In that case, the purification target gas remaining in the adsorption tower is discharged as an exhaust gas, and therefore, the recovery rate of the purification target gas is reduced. On the other hand, when the recovery rate is to be increased, the purity of the product gas is reduced. Accordingly, there is a need to improve the recovery rate of the purification target gas, while maintaining the purity of the product gas.

[0007] To attain the above-described object, there have been proposed a configuration in which a membrane separator is provided in the miscellaneous gas discharge line in order to further purify the discharged exhaust and improve the recovery rate of the purification target gas (see Patent Document 1) and a configuration in which a membrane separator is provided on the upstream side of the gas purification apparatus (see Patent Document 2).

Prior Art Documents

Patent Documents

[0005] Patent Document 1: U.S. Patent Application Publication No. 2004-099138

Patent Document 2: U.S. Patent Application Publication No. 2011-094378

Disclosure of the Invention

Problem to be Solved by the Invention

[0009] However, in a configuration described in Patent Document 1 above, the purification target gas contained in an exhaust gas is subjected to membrane separation, and the purification target gas that has permeated the separation membrane is returned to the source gas supply line. Accordingly, it is necessary to secure a significant power for the membrane separation of the purification target gas, thus requiring a significant operating power for the apparatus as a whole.

Moreover, the purity of the purification target gas in the final product gas is determined by the membrane separator, and it is thus necessary to increase the amount of gas permeating the separation membrane of the membrane separator in order to maintain a high purity, as a result of which the recovery rate is inevitably reduced.

[0010] Furthermore, with the technique according to Patent Document 2 above, the product gas can be set to a high purity because the purity of the product gas can be determined by the PSA device. However, the membrane separator, which is used to increase in advance the purity of the source gas supplied to the PSA device, causes a large reduction in the recovery rate of the purification target gas, and as a result, the technique is unlikely to contribute to the increase in the recovery rate of the apparatus as a whole.

[0011] Therefore, it is an object of the present invention to improve the recovery rate of a purification target gas from a gas purification apparatus that uses a PSA device, thereby achieving both a high purity and a high recovery rate with good power efficiency.

Means for Solving Problem

[0012] (Configuration 1)

In order to achieve the above-described object, a characteristic feature of a gas purification apparatus according to the present invention is directed to a gas purification apparatus including:

- an adsorption tower filled with an adsorbent that adsorbs a miscellaneous gas other than a purification target gas from a source gas;

- a source gas supply line for supplying the source gas to the adsorption tower;

- a product gas recovery line for discharging the purification target gas that has not been adsorbed on the adsorbent as a product gas; and

- a miscellaneous gas discharge line for desorbing and discharging the miscellaneous gas that has been adsorbed on the adsorbent,

the adsorption tower, the source gas supply line, the product gas recovery line, and the miscellaneous gas discharge line being connected so as to be able to perform a pressure swing operation of alternately performing

- an adsorption step of receiving the source gas from the source gas supply line, adsorbing the miscellaneous gas onto the adsorbent, and recovering the product gas, and

a desorption step of depressurizing-desorbing the miscellaneous gas adsorbed on the adsorbent and discharging that miscellaneous gas from the miscellaneous gas discharge line,

wherein a membrane separator that includes a separation membrane impermeable to the purification target gas and permeable to the miscellaneous gas, and that separates the purification target gas and the miscellaneous gas by an exhaust gas pressure of the adsorption tower is provided in the miscellaneous gas discharge line, and

a regenerated gas return line for returning, into the source gas supply line, a regenerated gas in which the concentration of the purification target gas has been increased by the separation membrane and/or a regenerated gas recovery line for recovering that regenerated gas as the product gas is provided.

[0013] (Operation and Effect 1)

That is, when a membrane separator that includes a separation membrane impermeable to the purification target gas and permeable to the miscellaneous gas, and that separates the purification target gas and the miscellaneous gas by the exhaust gas pressure of the adsorption towers is provided in the miscellaneous gas discharge line of the PSA device, the PSA device contributes to purification of the purification target gas in a gas line for collecting the product gas from the source gas, but the membrane separator does not contribute to purification of the purification target gas. Accordingly, the purity of the purification target gas in the product gas can be set high by the PSA device. Although the recovery rate of the purification target gas from the PSA device tends to be reduced at this time, the recovery rate of the purification target gas can be increased because the exhaust gas is recovered and returned to the source gas supply line. Since the concentration of the miscellaneous gas in the gas supplied to the adsorption tower will be increased even if the whole amount of the exhaust gas is recovered, there is the possibility that the purity of the purification target gas in the product gas may be reduced. Therefore, by removing a genuine exhaust gas that does not contain the purification target gas from the returned exhaust by the membrane separator, it is possible to suppress the increase in the concentration of the miscellaneous gas in the gas supplied to the adsorption tower. Then, it is possible to suppress the reduction in the purity of the purification target gas in the product gas, thus improving the recovery rate without reducing the purity of the purification target gas in the PSA device.

[0014] Here, since the membrane separator is configured to obtain the membrane

separation pressure in the separation membrane from the exhaust gas pressure of the adsorption tower and to separate the purification target gas and the miscellaneous gas, it is possible to perform membrane separation without providing a gas supply device such as a compressor in the membrane separator itself. That is, the exhaust gas pressure from the adsorption towers is applied to the miscellaneous gas discharge line in a state in which the desorption step is performed in the PSA device. By using this exhaust gas pressure to perform the membrane separation, the power required for gas supply can be reduced, thus making it possible to perform gas separation with low energy and high power efficiency.

[0015] Accordingly, by effectively using the membrane separator, it is possible to improve the recovery rate with high power efficiency, without reducing the purity of the purification target gas.

[0016] Since the membrane separator requires a lower cost of equipment than the PSA device, it is possible to configure the gas purification apparatus at a lower cost than when the purification target gas in the product gas or the exhaust gas that has undergone purification in the PSA device is further purified by the PSA device.

[0017] When an exhaust gas having a high product gas concentration generates from the gas purification apparatus, passing the exhaust gas through the membrane separator may result in a very high product gas purity in the regenerated gas flowing through the regenerated gas return line, and the regenerated gas may be recoverable as a product. It seems to be very wasteful in terms of efficiency to mix such a gas with a regenerated gas in which the purity of the product gas has been merely increased to the same level as that of the source gas, and to purify the mixed gas as the source gas again.

[0018] Therefore, even in such a case, the provision of the regenerated gas recovery line makes it possible to return the regenerated gas having an increased concentration of the purification target gas to the product gas recovery line, thus efficiently recovering a gas having a high product gas purity.

[0019] Note that one of the regenerated gas return line for returning the regenerated gas in which the concentration of the purification target gas has been increased by the separation membrane to the source gas supply line and the regenerated gas recovery line for recovering the regenerated gas as the product gas may be provided, or both of them may be provided.

[0020] (Configuration 2)

Further, a membrane separator that includes a separation membrane impermeable to the purification target gas and permeable to the miscellaneous gas, and that separates the purification target gas and the miscellaneous gas by an exhaust gas pressure of the adsorption tower may be provided in the miscellaneous gas discharge line,

a regenerated gas return line for returning a regenerated gas in which the concentration of the purification target gas has been increased by the separation membrane into the source gas supply line may be provided, and

a bypass line for causing the miscellaneous gas flowing through the miscellaneous gas discharge line to bypass the membrane separator so as to be guided to the regenerated gas return line may be provided.

[0021] (Operation and Effect 2)

Depending on the steps of PSA, an exhaust gas having a high product gas concentration may generate from the gas purification apparatus. Such an exhaust gas may cause a significant loss of the product gas in the membrane separator if it is supplied to the membrane separator as with a miscellaneous gas having a low product gas purity, and it may be preferable to directly reuse the gas as the source gas.

[0022] Therefore, when the above-described configuration includes the regenerated gas return line, the provision of the bypass line enables the exhaust gas to bypass the membrane separator so as to be guided to the regenerated gas return line, thereby making it possible to reuse the product gas as the source gas without any loss.

[0023] (Configuration 3)

A buffer tank may be provided upstream of the membrane separator in the miscellaneous gas discharge line.

[0024] (Operation and Effect 3)

The buffer tank can temporarily store the miscellaneous gas discharged by the desorption step before it is supplied to the membrane separator. At this time, a high-pressure miscellaneous gas containing a relatively high concentration of the purification target gas can be accumulated in the buffer tank by a pressure equalization operation using the difference in pressure between the adsorption tower and the buffer tank.

[0025] Thereafter, the miscellaneous gas in the buffer tank can be supplied to the membrane separator, and a high-pressure miscellaneous gas initially discharged from the adsorption tower can be subjected to pressure relaxation and be supplied

to the membrane separator, thus making it possible to purify the purification target gas from the miscellaneous gas with high precision, while performing a membrane separation operation at a high recovery rate by using the pressure of the high-pressure miscellaneous gas. That is, it is possible to avoid a situation where the miscellaneous gas does not sufficiently permeate the separation membrane because of an excessively high flow velocity of the high-pressure miscellaneous gas initially discharged from the adsorption tower, and a part of the miscellaneous gas flows into the regenerated gas side to reduce the purification precision.

(Configuration 4)

Further, a vacuum pump may be provided on a miscellaneous gas permeable side of the membrane separator in the miscellaneous gas discharge line.

[0026] (Operation and Effect 4)

The provision of the vacuum pump enables a necessary minimum power for continuing the membrane separation of the purification target gas when the membrane separation pressure of the membrane separator is insufficient, and it is therefore possible to continue the membrane separation operation in a more stable manner.

[0027] Also, in a case where the exhaust gas pressure of the PSA device fluctuates or a case where it is desired to maintain the membrane separation pressure constant as necessary, suitable membrane separation conditions of the membrane separator can be easily set and maintained by adjusting the output of the vacuum pump.

[0028] (Configuration 5)

Further, a regenerated gas tank may be provided in the regenerated gas return line.

[0029] (Operation and Effect 5)

The gas obtained as a result of removal of the miscellaneous gas in the exhaust gas from the PSA device by the membrane separator has an increased concentration of the purification target gas, and serves as a regenerated gas that can be used as the source gas. However, the concentration of the purification target gas in this regenerated gas fluctuates during the steps of the PSA device. Therefore, temporarily storing the regenerated gas in the regenerated gas tank makes it possible to relax the concentration fluctuation over time of the regenerated gas, contributing to stable supply of the regenerated gas to the source gas.

[0030] (Configuration 6)

Further, a regeneration pressure control valve may be provided in the regenerated gas return line, and a regeneration controller that controls a membrane separation pressure of the separation membrane by the regeneration pressure control valve may be provided.

[0031] (Operation and Effect 6)

With the above-described configuration, the settings for the pressure applied to the regenerated gas tank and the separation membrane of the membrane separator can be changed by the regeneration pressure control valve.

This makes it possible to stably remove the miscellaneous gas from the exhaust gas in the membrane separator, and also balance the above-described pressure and the source gas supply pressure on the source gas supply line side, thus inhibiting instability of supply of the source gas.

[0032] Even if the regenerated gas pressure fluctuates during the steps of the PSA device, the provision of the regeneration controller that controls the membrane separation pressure of the separation membrane by the regeneration pressure control valve contributes to stable supply of the regenerated gas into the source gas according to the fluctuation.

[0033] (Configuration 7)

Further, a product gas tank may be provided in the product gas recovery line.

[0034] (Operation and Effect 7)

When the product gas tank is provided also in the product gas recovery line, it is possible to stabilize the concentration of the purification target gas in the product gas. Further, by providing the product gas tank in such a configuration, the inside of the product gas tank is pressurized, and therefore, the product gas can be flowed into the adsorption tower as a washing gas when the miscellaneous gas is desorbed from the adsorbent in the adsorption tower and the adsorbent is regenerated so as to be resorbable.

[0035] (Configuration 8)

Furthermore, in the above-described configuration, a product gas washing line for flowing the product gas from the product gas tank into the adsorption tower may be provided, a product pressure control valve may be provided between the product gas tank and the adsorption tower in the product gas washing line, and a washing controller for washing the adsorption tower by flowing the product gas into the adsorption tower from the product gas tank may be provided.

[0036] (Operation and Effect 8)

When the washing line for flowing the product gas into the adsorption tower from the product gas tank is provided in addition to the product gas tank, and the product pressure control valve is provided between the product gas tank and the adsorption tower in the washing line, it is possible to supply the product gas from the product gas tank to the PSA device via the washing line. This makes it possible to directly use the product gas as the washing gas when the miscellaneous gas is desorbed from the adsorbent in the adsorption tower and the adsorbent is regenerated so as to be resorbable. Further, the pressure at this time is also applied to the exhaust gas when a wash exhaust gas is discharged to the miscellaneous gas discharge line. Therefore, the apparatus is operated such that the purification target gas contained in the wash exhaust gas can be also recovered by the membrane separator. Also, it is not necessary to separately supply the applied pressure, and therefore, the supply of power to the membrane separator can be reduced.

[0037] Note that the membrane separator can also be continuously operated when the miscellaneous gas is desorbed from the adsorbent in the adsorption tower and the adsorbent is regenerated so as to be resorbable, and it is therefore possible to stably operate the apparatus without causing any problem in the operation of the membrane separator.

[0038] (Configuration 9)

Further, the source gas may be a methane-containing gas, the purification target gas may be methane, and the miscellaneous gas may be a gas composed mainly of carbon dioxide.

[0039] (Operation and Effect 9)

For example, methane having a purity sufficient to be directly used as a fuel gas can be supplied from a gas source such as biogas that has a methane content that is too low to be directly used as a fuel gas, thus achieving an effective use of unused fuel gas. Further, when mainly containing carbon dioxide as the miscellaneous gas, such a source gas can be used particularly preferably because it is suitable for separation using the membrane separator because of the difference in chemical properties between methane and carbon dioxide.

[0040] (Configuration 10)

Further, the source gas may be a methane-containing gas containing at least 40% methane as the purification target gas, and a product gas containing at least 90% methane may be obtained.

[0041] (Operation and Effect 10)

A typical biogas composition contains about 40 to 60% methane and about 60 to 40% carbon dioxide. In the case of obtaining a product gas containing at least 90% methane by using a conventional gas purification apparatus for such biogas, the recovery rate cannot be increased very much, and the concentration of methane contained in the exhaust gas tends to be high.

However, a product gas containing at least 90% methane can be obtained by the gas purification apparatus including the membrane separator and having an improved recovery rate, it is possible to effectively use methane contained in the biogas, and reduce methane as a global warming gas that is diffused into the air, thus contributing to the preservation of the environment.

[0042] (Configuration 11)

The adsorbent may be composed mainly of at least one material selected from the group consisting of an activated carbon, a molecular sieve carbon, zeolite, and a porous metal complex.

[0043] (Operation and Effect 11)

Adsorbents composed mainly of at least one material selected from the group consisting of an activated carbon, a molecular sieve carbon, zeolite, and a porous metal complex are widely used as the adsorbents of PSA devices, and those having a high efficiency of gas adsorptive separation are known. In particular, an activated carbon and a molecular sieve carbon have excellent properties of separating a methane gas and carbon dioxide, and can perform efficient adsorptive separation of carbon dioxide during concentration of biogas and coal mine gas. A molecular sieve carbon, zeolite, and a porous metal complex are suitable for separation of a gas having a small molecular diameter, and can be suitable for use in concentrating methane from a gas containing hydrogen, helium, or the like.

[0044] (Configuration 12)

The adsorbent may be a molecular sieve carbon having a pore volume ($V_{0.38}$), at a pore diameter of 0.38 nm or more, of not exceeding $0.01 \text{ cm}^3/\text{g}$, and a pore volume ($V_{0.34}$), at a pore diameter of 0.34 nm, of $0.20 \text{ cm}^3/\text{g}$ or more, as measured by the MP method.

[0045] (Operation and Effect 12)

Such a molecular sieve carbon has very high methane-air separation properties, and can be preferably used for concentrating methane as a purification target gas from a source gas such as biogas.

[0046] (Configuration 13)

Further, the separation membrane may be composed mainly of at least one material selected from the group consisting of cellulose acetate, polyamide, polyimide, polysulfone, polytetrafluoroethylene, polyether sulfone, a carbon film, a microporous glass composite film, DDR-type zeolite, multibranched polyimide silica, and polydimethylsiloxane.

[0047] (Operation and Effect 13)

A membrane separator including a separation membrane composed of any of these materials is useful because it is known to be able to perform the membrane separation efficiently and also to have a high durability. Further, these materials have a high separation factor especially for methane and carbon dioxide, and are effective in concentrating methane from biogas.

[0048] (Configuration 14)

Further, a booster pump may be provided in the source gas supply line, and a pressure of supply of the source gas to the adsorption tower by the booster pump may be 0.5 MPaG to 2 MPaG.

Note that "PaG" as used in the present application is a gauge pressure expressed in Pa, and denotes a relative pressure with respect to atmospheric pressure.

[0049] (Operation and Effect 14)

Such a pressure is preferable because the source gas supplied at normal pressure can be supplied to the adsorption tower of the PSA device with the use of a relatively low power, and a sufficient adsorptive separation performance is readily exerted in the PSA device. An excessively high pressure poses the problem of a reduced recovery rate of methane.

Therefore, the pressure is set to be 0.5 MPaG or more so as to be able to maintain a high gas separation capability in the PSA device, and the pressure is also set to be 2 MPaG or less so as to be able to set a power that provides a high energy efficiency as the apparatus as a whole, and also to maintain a high recovery rate of methane.

[0050] Note that the exhaust gas pressure of the PSA device fluctuates in accordance with the gas desorption pressure during the desorption step and the gas washing pressure during washing of the adsorbent. The membrane separation pressure is, at most, a differential pressure with normal pressure (if a vacuum pump is provided on the miscellaneous gas permeable side of the membrane separator, the vacuum degree thereof). Therefore, the exhaust gas

pressure fluctuates to a certain degree depending on the state of progress of the steps in the PSA device, and the membrane separation pressure also fluctuates accordingly. When a vacuum pump is provided on the miscellaneous gas permeable side of the membrane separator, it is possible to set and maintain the drive power of the vacuum pump at a low level and in the range that allows efficient membrane separation.

Advantageous Effects of Invention

[0051] Accordingly, it is possible to recover methane having a higher purity, and to effectively use biogas and the like that have been conventionally difficult to reuse, with a high recovery rate of methane.

Brief Description of the Drawings

[0052] FIG. 1 is a schematic diagram of a gas purification apparatus.

FIG. 2 is a step diagram showing a methane concentration method.

FIG. 3 is a diagram illustrating a gas flow operation in the case of performing the methane concentration method of FIG. 2.

FIG. 4 is a diagram showing the transition of pressure in adsorption towers in the case of performing the methane concentration method of FIG. 2.

FIG. 5 is a schematic diagram of a gas purification apparatus according to Alternative Embodiment (2).

FIG. 6 is a schematic diagram of a gas purification apparatus according to Alternative Embodiment (5).

FIG. 7 is a schematic diagram of a gas purification apparatus according to Alternative Embodiment (6).

FIG. 8 is a step diagram showing a methane concentration method using a gas purification apparatus according to Alternative Embodiment (7).

FIG. 9 is a schematic diagram of a gas purification apparatus according to Alternative Embodiment (10).

FIG. 10 is a step diagram showing a methane concentration method according to Alternative Embodiment (11).

FIG. 11 is a diagram illustrating a gas flow operation in the case of performing the methane concentration method of FIG. 10.

FIG. 12 is a diagram showing the transition of pressure in adsorption towers in the case of performing the methane concentration method of FIG. 10.

FIG. 13 is a schematic diagram of a variation of the gas purification

apparatus according to Alternative Embodiment (5).

Best Mode for Carrying out the Invention

[0053] Hereinafter, a gas purification apparatus according to the present invention will be described. Although preferred embodiments will be described below, each of these embodiments is described for more specifically illustrating the present invention. Various modifications may be made without departing from the scope and spirit of the invention, and the present invention is not limited to the following description.

[0054] (Gas Purification Apparatus)

As shown in FIG. 1, a gas purification apparatus includes adsorption towers A1 to A4 that are filled with adsorbents A11 to A41. Each adsorption tower is provided with a source gas supply line L1 for supplying, for example, a biogas from a source gas tank T1, a product gas recovery line L2 and a product gas tank T2 for recovering, as a product gas, methane as a purification target gas that has not been adsorbed on the adsorbents A11 to A41, and a miscellaneous gas discharge line L3 for desorbing and discharging carbon dioxide as a miscellaneous gas that has been adsorbed on the adsorbents A11 to A41. Although the configuration in the present embodiment includes four adsorption towers A1 to A4, the number of towers is not limited as long as there are a plurality of towers, and three, five or any other number may be appropriately selected as needed.

[0055] The supply of gas from the source gas tank T1 to the source gas supply line L1 is carried out using a supply pump P1, and a bypass line L10 that bypasses the supply pump P1 is provided with a pressure control valve Vc1 so as to be able to stably control the pressure at the time of increasing the pressure in the adsorption towers A1 to A4. The source gas supplied to the source gas supply line L1 is supplied to the adsorption towers A1 to A4 via supply lines L11 to L41 including switching valves V11 to V41.

[0056] The product gas discharged from the adsorption towers A1 to A4 flow into a product gas recovery line L2 through recovery lines L12 to L42 including switching valves V12 to V42. A pressure control valve Vc2 is provided in the product gas recovery line L2. By using the pressure control valve Vc2 to control the pressure of the product gas recovered from the adsorption towers A1 to A4 into the product gas tank T2, the pressure of recovery of the product gas from the adsorption towers A1 to A4 can be controlled based on the relationship with the pressure of supply of the source gas in the adsorption towers A1 to A4.

[0057] The miscellaneous gas adsorbed in the adsorption towers A1 to A4 is desorbed from the adsorbents A11 to A41 by being decompressed, and is discharged from the miscellaneous gas discharge line L3 through exhaust gas lines L13 to L43 including switching valves V13 to V43. The miscellaneous gas discharge line L3 includes a separation membrane M1 that is impermeable to methane as a purification target gas and permeable to carbon dioxide as the miscellaneous gas. Further, a membrane separator M that separates the purification target gas and the miscellaneous gas by the exhaust gas pressure in the adsorption towers A1 to A4 is provided, and a regenerated gas return line L5 that returns, to the source gas supply line L1, a regenerated gas in which the concentration of the purification target gas has been increased by the separation membrane M1 is provided, and an exhaust line L6 is provided on the miscellaneous gas permeable side of the membrane separator M in the miscellaneous gas discharge line L3.

[0058] In the product gas recovery line L2, a product gas washing line L4 for flowing the product gas as a washing gas into the adsorption towers A1 to A4 from the product gas tank T2 is provided on the upstream side (the adsorption towers A1 to A4 side) with respect to the pressure control valve Vc2. That is, the washing gas flows into the product gas washing line L4 from the product gas tank T2, and is supplied to the adsorption towers through washing lines L14 to L44 including switching valves V14 to V44. Also, the gas in the adsorption towers A1 to A4 is replaced with the product gas, and discharged as the miscellaneous gas from the miscellaneous gas discharge line L3 through exhaust gas lines L13 to L43 including switching valves V13 to V43. Furthermore, a pressure reducing valve Vr4, an open/close valve Vo4, and a needle valve Vn4 are provided between the product gas recovery line L2 and the adsorption towers A1 to A4 in the product gas washing line L4. This allows the product gas from the product gas tank T2 to flow as a washing gas into the adsorption towers A1 to A4 from the gas washing line L4 via the washing lines L14 to L44 including the switching valves V14 to V44, thus performing the operation of washing the adsorption towers A1 to A4. Accordingly, the pressure for washing the adsorption towers A1 to A4 is controlled with the pressure reducing valve Vr4, and is adjusted with the needle valve Vn4 so as to prevent a rapid pressure change, and is easily switched by the open/close valve Vo4.

[0059] A regenerated gas tank T5 and a pressure control valve Vc5 are provided in the regenerated gas return line L5. That is, any miscellaneous gas that has not

permeated through the separation membrane M1 in the membrane separator M is recovered and stored in T5 through L5, and is re-supplied to L1 from the regenerated gas tank T5. Accordingly, the membrane separation pressure of the membrane separator M is controlled based on the exhaust gas pressures of the adsorption towers A1 to A4, and the regenerated gas that is stored in the regenerated gas tank T5 and returned to the regenerated gas return line L5 is returned to the source gas supply line L1 at a constant pressure and reused.

[0060] Further, a bypass line L30 is provided that bypasses the miscellaneous gas from the miscellaneous gas discharge line L3 to the downstream side (the regenerated gas tank T5 side) with respect to the pressure control valve Vc5 of the regenerated gas return line L5 without via the membrane separator M. Open/close valves Vo3 and Vo5 are provided in the miscellaneous gas discharge line L3 on the membrane separator M side with respect to the bypass line L30 and the bypass line L30 so as to be able to recover a miscellaneous gas having a high methane purity directly into the regenerated gas tank T5 without via the membrane separator M.

[0061] A vacuum pump P6 is provided in the exhaust line L6 on the miscellaneous gas permeable side of the membrane separator M. The vacuum pump P6 is operated in a steady state, and serves to maintain the membrane separation pressure at a predetermined pressure or higher based on the pressure of the adsorption towers A1 to A4 on the miscellaneous gas discharge line L3 side.

[0062] Further, an inter-tower pressure equalization line L7 is provided for the adsorption towers A1 to A4 such that the gas discharged from the upper portion of the adsorption towers A1 to A4 during pressure equalization (pressure lowering) steps can be transferred via L4 to the upper portion of the adsorption towers A1 to A4 in which pressure equalization (pressure increasing) steps are performed. That is, the gas discharged from the upper portion of the adsorption towers A1 to A4 in the pressure equalization (pressure lowering) steps flows into the inter-tower pressure equalization line L7 via pressure equalization lines L17 to L47 including switching valves V17 to V47, and flows via the washing lines L14 to L44 including the switching valves V14 to V44 into the adsorption towers A1 to A4 in which the pressure equalization (pressure increasing) steps are performed. A needle valve Vn7 and an open/close valve Vo7 are provided in the inter-tower pressure equalization line L7, and thereby, the gas discharged from the upper portion of each adsorption tower via the corresponding pressure equalization line at this time is gradually transferred via the needle valve Vn7, and flows into a different one of

the adsorption towers A1 to A4 via the product gas washing line L4. Although the pressure equalization line in the present embodiment has a configuration in which the upper portions of the adsorption towers are connected with each other to achieve pressure equalization as shown in FIG. 1, the present invention is not limited thereto. For example, this configuration may be modified as appropriate, for example, so as to connect the upper portion and the lower portion of the adsorption towers, or to connect the lower portions or the intermediate portions of the adsorption towers with each other.

[0063] Further, a product gas pressure increasing line L8 for supplying a product gas as a gas for increasing the pressure inside the adsorption towers A1 to A4 is provided for the adsorption towers A1 to A4. That is, in the pressure increasing step, the product gas supplied from T2 flows into the adsorption towers from the product gas pressure increasing line L8 via pressure increasing lines L18 to L48 including switching valves V18 to V48. An open/close valve Vo8 and a pressure control valve Vc8 is provided in the product gas pressure increasing line L8, and the pressure in the adsorption towers A1 to A4 can be increased by transferring the product gas into the adsorption towers based on the retaining pressure of the product gas tank T2 at this time.

[0064] Further, a controller C is provided in the gas purification apparatus. The controller C controls the opening and closing of the switching valves V11 to V48 and the like provided in the adsorption towers A1 to A4, and the piping of the source gas supply line L1, the product gas recovery line L2, the miscellaneous gas discharge line L3, the product gas washing line L4, L5 described above, L6 described above, L7 described above, and L8 described above. Accordingly, the controller C serves as an adsorption/desorption controller that performs the adsorption steps in the adsorption towers A1 to A4 by using P1 and P6, and also functions as a regeneration controller that controls the membrane separation pressure of the separation membrane M1 by using the pressure control valve Vc5, and a washing controller for washing the adsorption towers A1 to A4 by flowing the product gas into the adsorption towers A1 to A4 from the product gas tank T2.

[0065] Here, adsorbents A11 to A41 capable of selectively adsorbing the miscellaneous gas composed mainly of carbon dioxide in a biogas are preferably used as the adsorbents A11 to A41. As such adsorbents A11 to A41, an adsorbent composed mainly of at least one material selected from the group consisting of an activated carbon, a molecular sieve carbon, zeolite, and a porous metal complex. Specifically, it is possible to use, for example, a molecular sieve

carbon having a pore volume ($V_{0.38}$), at a pore diameter of 0.38 nm or more, of not exceeding 0.01 cm³/g, and a pore volume ($V_{0.34}$), at a pore diameter of 0.34 nm, of 0.20 cm³/g or more, as measured by the MP method.

[0066] As the separation membrane M1, it is preferable to use a material permeable to the miscellaneous gas composed mainly of carbon dioxide in the exhaust gas, and impermeable to methane as the purification target gas. As such a separation membrane, it is possible to use a separation membrane composed mainly of at least one material selected from the group consisting of cellulose acetate, polyamide, polyimide, polysulfone, polytetrafluoroethylene, polyether sulfone, a carbon film, a microporous glass composite film, DDR-type zeolite, multibranched polyimide silica, and polydimethylsiloxane.

[0067] Note that the biogas as the source gas used here is a biogas composed mainly of methane and carbon dioxide and having a methane content of about 60%, and gas purification for obtaining a product gas containing at least 98% methane is performed.

[0068] (Adsorption Towers)

The adsorption towers A1 to A4 are filled with the adsorbents A11 to A41, respectively. Below the adsorption towers A1 to A4, the supply lines L11 to L41 for supplying a biogas from the source gas tank T1 by the supply pump P1 are provided to form the source gas supply line L1. Above the adsorption towers A1 to A4, the recovery lines L12 to L42 for recovering methane as the purification target gas that has not been adsorbed on the adsorbents A11 to A41 from the biogas supplied to the adsorption towers A1 to A4 are provided to form the product gas recovery line L2. This provides a configuration capable of supplying the biogas from the source gas supply line L1 to the adsorption towers A1 to A4, and discharging any methane that has not been adsorbed on the adsorbents A11 to A41 from the product gas recovery line L2, thus adsorbing the miscellaneous gas onto the adsorbents A11 to A41 and separating the miscellaneous gas from methane. Further, in the adsorption towers A1 to A4, the exhaust gas lines L13 to L43 for discharging the miscellaneous gas adsorbed on the adsorbents A11 to A41 are provided below the adsorption towers A1 to A4 to form the miscellaneous gas discharge line L3, providing a configuration capable of collecting, from the biogas supplied to the source gas supply line L1, a high-concentration carbon dioxide that has been adsorbed on the adsorbents A11 to A41 and concentrated.

[0069] Note that switching valves V11 to V48 are provided in the gas lines L11 to L48, thus providing a configuration that enables the controller C to perform overall

control of the switching between supply, discharge, and suspension of the gas to the adsorption towers A1 to A4 by the operation of the pumps P1 and P6.

[0070] (Membrane Separator)

The membrane separator M includes the separation membrane M1 in the form of a module, and is configured to be able to perform membrane separation of the miscellaneous gas supplied via the miscellaneous gas discharge line L3 and to recover the purification target gas contained in the miscellaneous gas. Specifically, in the case of purifying methane as the purification target gas by using a biogas as the source gas, a methane-containing gas composed mainly of carbon dioxide is supplied as a miscellaneous gas to the membrane separator M. The miscellaneous gas supplied to the membrane separator M comes into contact with the separation membrane M1 in the membrane separator M, and carbon dioxide is removed as a result of permeating the separation membrane M1 by the membrane separation properties of the separation membrane M1, and a regenerated gas in which methane is more highly concentrated than in the supplied miscellaneous gas is obtained as non-permeated gas. While this regenerated gas is discharged to the regenerated gas return line L5 and is returned to the source gas supply line L1, the gas composed mainly of carbon dioxide that has permeated the membrane is discharged to the outside from the exhaust line L6.

[0071] Further, the regenerated gas tank T5 is provided in the the regenerated gas return line L5, and the regenerated gas that has been subjected to membrane separation is stored in the regenerated gas tank T5, and subsequently returned to the source gas supply line L1 at a predetermined pressure.

[0072] (Methane Concentration Method)

As shown in FIG. 3, the controller C controls the switching valves V11 to V47 and the pumps P1 and P6 to perform a pressure swing operation of alternately performing, in the adsorption towers A1 to A4 according to FIG. 2,

an adsorption step of receiving the source gas from the source gas supply line L1, adsorbing the miscellaneous gas onto the adsorbents A11 to A41, and recovering the product gas, and

a desorption step of depressurizing-desorbing the miscellaneous gas composed mainly of carbon dioxide that has been adsorbed on the adsorbents A11 to A41 and discharging the miscellaneous gas from the miscellaneous gas discharge line L3.

[0073] To perform the pressure swing operation, as specifically shown in FIG. 2, the operation is controlled so as to perform in order:

a parallel adsorption step in which the adsorption step simultaneously proceeds in two of the adsorption towers A1 to A4 is performed before and after the adsorption step of receiving a biogas near atmospheric pressure from the lower portion of the adsorption towers A1 to A4 and supplying the biogas to the adsorbents A11 to A41 by using the supply pump P1, adsorbing the miscellaneous gas composed mainly of carbon dioxide, and releasing the product gas composed mainly of methane as the purification target gas from the upper portion of the adsorption towers A1 to A4 (a pre-parallel adsorption step, an adsorption step, and a post-parallel adsorption step are performed in order);

after the post-parallel adsorption step, an initial pressure equalization (pressure lowering) step of transferring a gas having a relatively low miscellaneous gas concentration in one of the adsorption towers A1 to A4 that is in a high pressure state to another one of the adsorption towers A1 to A4 that is in an intermediate pressure state at a pressure lower than that in the one of the adsorption towers A1 to A4 so as to bring the pressure in the one of the adsorption towers A1 to A4 into a high pressure-side intermediate pressure state;

a standby step of not performing the operation of the adsorption towers A1 to A4;

a final pressure equalization (pressure lowering) step of transferring a gas in which the methane concentration has been slightly increased than that in the initial pressure equalization (pressure lowering) step in one of the adsorption towers A1 to A4 that is in an intermediate pressure state at a pressure higher than that of the low pressure state to another one of the adsorption towers A1 to A4 that is in a low pressure state so as to bring the pressure in the one of the adsorption towers A1 to A4 into a low pressure-side intermediate pressure state;

after the tower pressure has been reduced by the pressure equalization (pressure lowering) step, a desorption step of further reducing the pressure in the one of the adsorbents A11 to A41 into a low pressure state to desorb the miscellaneous gas adsorbed on the one of the adsorbents A11 to A41 and recovering the miscellaneous gas from the lower portion of the one of the adsorption towers A1 to A4;

a washing step of displacement washing, with a product gas, the miscellaneous gas remaining in the one of the adsorption towers A1 to A4 in which the corresponding one of the adsorbents A11 to A41 has been regenerated by the desorption step;

an initial pressure equalization (pressure increasing) step of receiving, into

the one of the adsorption towers A1 to A4 in the low pressure state, the gas in the other one of the adsorption towers A1 to A4 in the high pressure-side intermediate pressure state so as to bring the pressure in the one of the adsorption towers A1 to A4 into the low pressure-side intermediate pressure state;

5 the standby step;

 a final pressure equalization (pressure increasing) step of receiving, into the one of the adsorption towers A1 to A4 that is in the low pressure-side intermediate pressure state, the gas in another one of the adsorption towers A1 to A4 that is in the high pressure state so as to bring the pressure in the one of the
10 adsorption towers A1 to A4 into the high pressure-side intermediate pressure state; and

 after the tower pressure has been increased by the pressure equalization (pressure increasing) step, a pressure increasing step of further supplying a pressure increasing air into the one of the adsorption towers A1 to A4 from the
15 upper portion of another one of the adsorption towers A1 to A4 so as to restore the corresponding one of the adsorbents A11 to A41 into the high pressure state in which methane can be selectively adsorbed.

[0074] By such a control, the internal pressures of the adsorption towers A1 to A4 transition as shown in FIG. 4. That is, by successively reducing the tower
20 pressure by the pressure equalization steps, the desorption step can be performed from a state in which the tower pressure has been significantly reduced, and therefore, the miscellaneous gas adsorbed on the adsorbent can be desorbed with a little power, and the adsorbent can be easily regenerated.

[0075] More specifically, the adsorption tower A1 is controlled according to the
25 following steps. Although the same operation is also performed for the other adsorption towers A2 to A4 in a phase shifting manner, the detailed description thereof has been omitted and replaced by the description with reference to FIGS. 2 to 4 to avoid redundancy. Note that the adsorption towers A1 to A4 are referred to as first to fourth adsorption towers A1 to A4 in this order. FIG. 3 show the
30 operating state of the open/close valves and the like in the steps. The number written in < > denotes the step number in FIGS. 2 to 4. The operating conditions specifically described below are merely illustrative, and the present invention is not limited by the following specific examples.

[0076] <1> Pre-parallel adsorption step

35 As shown in FIGS. 2 and 3, a biogas as the source gas is introduced into the first adsorption tower A1 from the source gas tank T1. At this time, the

pressure in the first adsorption tower A1 is increased by the supply pressure of the source gas. Further, while carbon dioxide as the miscellaneous gas in the biogas supplied from the source gas tank T1 via the switching valve V11 of the supply line L11 is adsorbed onto the adsorbent A11, any non-adsorbed methane is recovered as the product gas into the product gas tank T2 via the switching valve V12 of the recovery line L12.

Here, in the initial stage of the adsorption step, the adsorption step of the first adsorption tower A1 is started to gradually increase the internal pressure of the first adsorption tower A1, concurrently with a gradually reduction of the internal pressure of the fourth adsorption tower A4 in the final stage of the adsorption step of the fourth adsorption tower A4. That is, prior to the start of the adsorption step of the first adsorption tower A1, the pre-parallel adsorption step for the first adsorption tower A1 is performed together with the post-parallel adsorption step of the fourth adsorption tower A4.

[0077] At this time, the second adsorption tower A2 is in the standby step, and the desorption step has been started in the third adsorption tower A3.

[0078] The pre-parallel adsorption step is performed for about five seconds, and the adsorptive separation of methane and carbon dioxide in the source gas is started in the first adsorption tower A1.

[0079] <2 to 4> Adsorption step

As shown in FIGS. 2 and 3, following the pre-parallel adsorption step, the biogas is introduced into the first adsorption tower A1 from the source gas tank T1. At this time, the pressure in the first adsorption tower A1 is further increased by the supply pressure of the source gas. Also, while carbon dioxide is adsorbed onto the adsorbent A11 via the switching valve V11 of the supply line L11, methane is recovered into the product gas tank T2.

[0080] At this time, the second adsorption tower A2 performs <1> the final pressure equalization (pressure increasing) step, and transitions to <2 to 3> the pressure increasing step.

Also, the third adsorption tower A3 performs the washing step and the initial pressure equalization (pressure increasing) step, following the desorption step.

Furthermore, the fourth adsorption tower A4 performs the initial pressure equalization (pressure lowering), and transitions to the final pressure equalization (pressure lowering) step, with the standby step in between.

[0081] The methane purity in the product gas at this time can be set by setting

the time or the like of the adsorption step, and can be set to 90% or more.

For example, in the case of using a cylindrical (inside diameter: 54 mm, volume: 4.597 L) adsorption tower A1, and

using, as the adsorbent A11, a molecular sieve carbon having a pore volume ($V_{0.38}$), at a pore diameter of 0.38 nm or more, of about 0.05 cm³/g, and a pore volume ($V_{0.34}$), at a pore diameter of 0.34 nm, of 0.20 to 0.23 cm³/g, in the pore diameter distribution as measured by the MP method, and

treating a biogas containing about 60% methane and about 40% carbon dioxide at 10 L/min,

a product gas having a methane concentration of 96 to 98%, a carbon dioxide concentration of 2%, and a pressure of about 0.7 to 0.75 MPaG was successfully recovered into the product gas tank T2 when the adsorption step was performed for about 90 seconds with the supply pressure by the supply pump P1 set at about 0.8 MPaG.

[0082] <5> Post-parallel adsorption step

In the final stage of the adsorption step of the first adsorption tower A1, the post-parallel adsorption step of performing the adsorption step in parallel with the second adsorption tower A2 in the initial stage of the adsorption step is performed. That is, the supply amount of the biogas in the adsorption step and the supply amount of the biogas to the first and second adsorption towers A1 and A2 in the present step are the same, and therefore, in the present step, each of the supply amounts of the biogas to the first and second adsorption towers A1 and A2 is set to be smaller than the supply amount of biogas in the adsorption step. Accordingly, as shown in FIGS. 2 and 3, in the present step, by reducing the adsorption flow rate in the final stage of the adsorption step, the environmental change in the adsorption tower can be suppressed so as to proceed gradually, and it is possible to stabilize the biogas flow in the adsorption tower A1, inhibit the generation of a turbulent flow in the adsorption tower A1, and cause the adsorbent A11 to act in a stable manner.

[0083] Note that at this time, the third adsorption tower A3 performs the standby step, and the fourth adsorption tower A4 performs the desorption step.

[0084] The post-parallel adsorption step is performed for five seconds immediately after the above-described adsorption step.

[0085] <6> Initial pressure equalization (pressure lowering) step

The first adsorption tower A1 that has finished the adsorption step performs the initial pressure equalization (pressure lowering) step between itself

and the third adsorption tower A3 that performs the final pressure equalization (pressure increasing) step. That is, as shown in FIGS. 2 and 3, non-adsorbed gas in the tower is discharged via the switching valve V17 of the pressure equalization line L17, and is transferred to the third adsorption tower A3 via a switching valve V34 of a washing line L34. Consequently, as shown in FIG. 3, pressure equalization is performed between the first adsorption tower A1 and the third adsorption tower A3 in the low pressure-side intermediate pressure state.

[0086] Note that at this time, the second adsorption tower A2 performs the adsorption step, and the fourth adsorption tower A4 performs the desorption step.

[0087] The initial pressure equalization (pressure lowering) step is performed for five seconds, and the first adsorption tower A1 transitions to the high pressure-side intermediate pressure state at about 0.5 MPaG.

[0088] <7> Standby step

Next, the first adsorption tower A1 enters the standby state, and the high pressure-side intermediate pressure state is maintained.

[0089] At this time, the second adsorption tower A2 performs the adsorption step, the third adsorption tower A3 transitions to the pressure increasing step, and the fourth adsorption tower A4 transitions to the washing step.

[0090] The standby step is performed for 90 seconds, and the above-described high pressure-side intermediate pressure state is maintained.

[0091] <8> Final pressure equalization (pressure lowering) step

Next, as shown in FIGS. 2 and 3, the first adsorption tower A1 performs a final pressure equalization (pressure lowering) step between itself and the fourth adsorption tower A4 that has finished the desorption step and performs the initial pressure equalization (pressure increasing) step. That is, any non-adsorbed gas in the tower and the miscellaneous gas that starts to desorb initially from the adsorbent A11 are discharged via the switching valve V17 of the pressure equalization line L17, and are transferred to the fourth adsorption tower A4 via a switching valve V44 of a washing line L44. Consequently, pressure equalization is performed between the first adsorption tower A1 and the fourth adsorption tower A4 that has finished the desorption step and is in the low pressure state.

[0092] Note that at this time, the second adsorption tower A2 performs the adsorption step, and the third adsorption tower A3 performs the pressure increasing step.

[0093] The final pressure equalization (pressure lowering) step is performed for five seconds, and the first adsorption tower A1 transitions to an intermediate

pressure state on the low pressure-side at about 0.25 MPaG.

[0094] <9 to 10> Desorption step

As shown in FIGS. 2 and 3, the first adsorption tower A1 that has reached the low pressure-side intermediate pressure state is in a state in which a high-concentration miscellaneous gas is adsorbed on the adsorbent A11 in the tower, and the high-concentration miscellaneous gas adsorbed on the adsorbent A11 is recovered by performing a desorption step of decompressing the inside of the tower from the low pressure-side intermediate pressure state to the low pressure state. That is, the concentrated miscellaneous gas is supplied to the membrane separator M via the switching valve V13 of the exhaust gas line L13 by the internal pressure of the first adsorption tower A1.

The operating state of the membrane separator M at this time will be described later.

[0095] Note that at this time, after performing the post-parallel adsorption step in parallel with the third adsorption tower A3, the second adsorption tower A2 performs the initial pressure equalization (pressure lowering) step between itself and the fourth adsorption tower A4.

In the third adsorption tower A3, after the pre-parallel adsorption step is performed in parallel with the second adsorption tower A2, the adsorption step is performed.

After the standby step, the fourth adsorption tower A4 performs the final pressure equalization (pressure increasing) step between itself and the second adsorption tower A2.

[0096] The desorption step is performed for 365 seconds, and the first adsorption tower A1 transitions from the intermediate pressure state on the low pressure-side to a near-atmospheric low pressure state, as shown in FIG. 4.

[0097] <11> Washing step

As shown in FIGS. 2 and 3, the first adsorption tower A1 that has transitioned to the low pressure displacement washes the gas in the tower into a gas composed mainly of methane by causing the product gas to flow into the tower. That is, the open/close valve Vo4 of the product gas washing line L4 is opened, and the needle valve Vn4 is adjusted, the product gas is flowed into the first adsorption tower A1 from the product gas tank T2 through the switching valve V14 of the washing line L14 so as to cause the internal pressure of the product gas tank T2 to act gently on the adsorption tower A1, thereby replacing the atmosphere in the first adsorption tower A1 with methane, and the gas remaining in the first

adsorption tower A1 is released as an exhaust gas into the miscellaneous gas discharge line L3 via the switching valve V13 of the exhaust gas line L13.

At this time, by opening the open/close valve Vo5 and closing the open/close valve Vo3, the washing gas composed mainly of the product gas is caused to bypass the membrane separator M so as to be transitioned to the regenerated gas return line L5 and directly recover into the regenerated gas tank T5.

[0098] Note that at this time, the second adsorption tower A2 is in the standby step, and the third adsorption tower A3 continues the adsorption step. In addition, the fourth adsorption tower A4 performs the pressure increasing step.

[0099] The washing step is performed for about 90 seconds, and the inside of the first adsorption tower A1 is transitioned to a near-atmospheric low pressure state.

[0100] <12> Initial pressure equalization (pressure increasing) step

As shown in FIGS. 2 and 3, the first adsorption tower A1, which has entered the low pressure state and has released the adsorbed methane and in which the adsorbent A11 has been regenerated, performs an initial pressure equalization (pressure increasing) step between itself and the second adsorption tower A2, thereby restoring the pressure in the tower and receiving an exhaust gas discharged in the final pressure equalization (pressure lowering) step in the second adsorption tower A2, the exhaust gas containing a relatively high concentration of methane due to the initially desorbed gas from the adsorbent A11. That is, the tower gas discharged from the second adsorption tower A2 in the high pressure-side intermediate pressure state via the switching valve V27 in the pressure equalization line L27 is received in the inter-tower pressure equalization line L7 via the switching valve V14 in the washing line L14. Consequently, as shown in FIG. 4, the first adsorption tower A1 restores its pressure from the low pressure state to the low pressure-side intermediate pressure state.

[0101] Note that at this time, the third adsorption tower A3 continues the adsorption step, and the fourth adsorption tower A4 performs the pressure increasing step.

[0102] The initial pressure equalization (pressure increasing) step is performed for about 10 seconds, and the first adsorption tower A1 restores its pressure to about 0.25 MPaG.

[0103] <13> Standby step

Next, as shown in FIGS. 2 and 3, the first adsorption tower A1 enters the standby state, and the high pressure-side intermediate pressure state is

maintained.

[0104] At this time, the second adsorption tower A2 performs the desorption step, and the third adsorption tower A3 and the fourth adsorption tower A4 has transitioned the post-parallel adsorption step and the pre-parallel adsorption step.

5 [0105] The standby step is performed for about five seconds, and the first adsorption tower A1 is maintained at about 0.25 MPaG.

[0106] <14> Final pressure equalization (pressure increasing) step

As shown in FIGS. 2 and 3, the first adsorption tower A1 that has restored its pressure to the low pressure-side intermediate pressure state attempts to
10 further restore the pressure in the tower by subsequently performing a final pressure equalization (pressure increasing) step between itself and the third adsorption tower A3 that performs the adsorption step immediately after finishing the initial pressure equalization (pressure lowering) step. That is, the tower in the gas discharged from the third adsorption tower A3 in the high pressure state is
15 received in the pressure equalization lines L17 to L37 of the inter-tower pressure equalization line L7 via the switching valves V17 and V37. Consequently, as shown in FIG. 3, the first adsorption tower A1 restores its pressure from the low pressure-side intermediate pressure state to the high pressure-side intermediate pressure state.

20 [0107] Note that at this time, the second adsorption tower A2 performs the desorption step, and the fourth adsorption tower A4 performs the adsorption step.

[0108] The final pressure equalization (pressure increasing) step is performed for about 10 seconds, and the pressure inside the first adsorption tower A1 is increased to about 0.5 MPaG.

25 [0109] <15 to 16> Pressure increasing step

As shown in FIG. 4, the pressure of the first adsorption tower A1 that has restored its pressure to the high pressure-side intermediate pressure state is restored to the high pressure state by injection of the product gas. That is, the product gas is flowed into the first adsorption tower A1 via the switching valve V14
30 of the product gas washing line L4. Consequently, the inside of the first adsorption tower A1 is restored to the high pressure state, and regenerated by supply of biogas into a high pressure state capable of adsorbing carbon dioxide contained in the biogas.

[0110] Note that at this time, the second adsorption tower A2 performs the initial
35 pressure equalization (pressure increasing) step between itself and the third adsorption tower A3, following the washing step. The third adsorption tower A3

performs, after the standby step, the final pressure equalization (pressure lowering) step between itself and the second adsorption tower A2. The fourth adsorption tower A4 performs the adsorption step.

[0111] The pressure increasing step is performed for about 50 seconds, and the pressure in the first adsorption tower A1 is increased to 0.8 MPaG at which methane and carbon dioxide contained in the biogas can be separated.

[0112] (Operating State of Membrane Separator)

The membrane separator M including the separation membrane M1 is provided in the miscellaneous gas discharge line L3, and the membrane separator M is connected so as to be able to separate methane by allowing permeation of the carbon dioxide contained in the miscellaneous gas that is discharged from the miscellaneous gas discharge line L3 and composed mainly of carbon dioxide. The membrane separator M is configured such that the gas that has not permeated the separation membrane M1 and thus contains methane having an increased concentration is discharged as the regenerated gas into the regenerated gas return line L5 and the gas that has permeated the separation membrane M1 and thus is composed mainly of carbon dioxide is released into the exhaust line L6 by the vacuum pump P6.

[0113] During the desorption step, the pressure on the primary side of the separation membrane M1 provided by the membrane separator M serves as the exhaust gas pressures of the adsorption towers A1 to A4 and therefore fluctuates from about 0.25 MPaG to 0 MPaG. However, the pressure on the secondary side is constantly maintained at -0.1 MPaG (corresponding to vacuum) by the vacuum pump P6, and the membrane separation pressure is maintained at 0.35 MPaG to 0.1 MPaG at which a continuous membrane separation operation can be performed.

[0114] During the washing step, the pressure on the primary side provided by the membrane separator M serves as the washing pressure for the adsorption towers A1 to A4 and is thus constant at about 0 MPaG, and the membrane separation pressure is maintained at 0.1 MPaG at which a continuous membrane separation operation can be performed. However, in the case of basically using the product gas as the washing gas, the gas supplied to the membrane separator M contains little carbon dioxide gas, and therefore a sufficient gas separation is continued.

[0115] With such a configuration, the exhaust gas released from the exhaust line L6 can be an exhaust gas containing about 2 to 6% methane and about 94 to 98% carbon dioxide. The gas composition of the gas returned to the regenerated gas

return line L5 is a methane-containing gas containing about 60% methane and about 40% carbon dioxide.

[0116] The pressure control valve Vc5 is provided in the regenerated gas return line L5, the regenerated gas tank T5 is provided between the membrane separator M and the pressure control valve Vc5, and the regenerated gas return line L5 is connected on the upstream side of the supply pump P1 in the source gas supply line L1, and therefore, the regenerated gas can be mixed with the source gas, and be separated and purified again.

[0117] With the methane concentration method of the above-described embodiment, a product gas containing 96 to 98% methane and an exhaust gas containing 2 to 5% methane were obtained when treating a biogas containing 60% methane at 10 L/min, and the methane recovery rate was 95%. When the flow rate was increased to 17 L/min, a product gas containing 96 to 98% methane and an exhaust gas containing 2 to 5% methane were also obtained, resulting in a methane recovery rate of 95%, and it was confirmed that methane can be concentrated at the same concentration efficiency and recovery rate.

In contrast, as a result of concentrating methane by performing the pressure swing operation of the adsorption towers without using the above-described membrane separator, when a product gas containing 96 to 98% methane was obtained in the case of treating a biogas containing 60% methane at 10 L/min, the exhaust gas contained 15 to 20% methane, and the methane recovery rate was 83%.

That is, it was experimentally clarified that the methane concentration method according to the present invention can achieve both a high concentration efficiency and a high recovery rate.

[0118] (Alternative Embodiments)

(1)

The above-described gas purification apparatus may be provided with a pressure sensor, a temperature sensor, and the like, as appropriate. Specifically, a pressure sensor and a gas sensor for monitoring the supply pressure of the source gas and the methane concentration of the product gas are usually provided, but the detailed description thereof has been omitted in the above-described embodiment.

[0119] (2)

The arrangement of the supply pump P1 and the vacuum pump P6 for flowing gases through various pipes is not limited to the one described above, and

may be modified in various ways as long as it is configured to be able to flow gases. Specifically, although the above-described gas purification apparatus has a minimum necessary configuration, it is possible to adopt a configuration in which the supply pump P1 is provided in the source gas supply line L1 on the upstream side (source gas tank T1 side) relative to the connection portion with the regenerated gas return line L5. Apart from this, for example, the supply pump P1 may be omitted, and a compression pump P5 for providing the supply pressure for the source gas to the source gas supply line L1 may be provided in the regenerated gas return line L5. In such a case, the gas purification apparatus is configured as shown in FIG. 5, for example, and the pressure of supply to the source gas supply line L1 is maintained properly by a pressure control valve Vc51 provided in a bypass line that is bypassed to a compression pump P5.

[0120] (3)

It is evident from the description of the above embodiment that the exhaust line L6 is operable without being provided with the vacuum pump P6. It is preferable to omit the vacuum pump P6 from the viewpoint of simplification of the facility, and it is preferable to provide the vacuum pump P6 from the viewpoint of stabilization of the membrane separation pressure. In the case of providing the vacuum pump P6, it is preferable to operate the vacuum pump P6 in a steady state from the viewpoint of safety operation. However, the vacuum pump P6 may be operated under a low load or suspended during the steps 3, 7, 11, and 15 in which the washing step proceeds in FIG. 2, and the steps 4, 8, 12, and 16 until which the desorption step is subsequently started. In such a case, the pressure control valve Vc5 may be fixed in a state in which its opening is reduced or in the closed state.

[0121] That is, during the desorption step, it is necessary to subject the gas in the miscellaneous gas discharge line L3 to membrane separation so as to obtain a regenerated gas, and therefore, the membrane separation pressure needs to be exerted sufficiently. However, in the case of using the product gas during the steps in which no gas flows out into the miscellaneous gas discharge line L3, or during the washing step, the need to perform membrane separation is low, and the pressure of gas supply to the membrane separator M is inherently low in the washing step. Accordingly, the output of the vacuum pump P6 may be lowered during a time period in which the membrane separation pressure is not required. In the case of lowering the output of the vacuum pump P6 in accordance with the required membrane separation pressure, the vacuum pump P6 may be subjected

to inverter control.

[0122] (4)

In view of achieving a balanced gas composition, a situation is conceivable in which the amount of gas recovered from the membrane separator M is greater than the amount of gas re-supplied to the source gas supply line L1 in the regenerated gas return line L5 in the above-described embodiment. In such a case, the gas stored in the regenerated gas tank T5 continues to increase, and therefore, a disposal line for disposing of an excess regenerated gas may be provided in the regenerated gas tank T5.

[0123] (5)

As previously stated, the gas flowing through the miscellaneous gas discharge line L3 during the washing step is composed mainly of the product gas and thus may have a purity sufficient to be directly recovered as the product gas after the membrane separation step. Similarly, a regenerated gas in a normal desorption step may have a sufficient purity. In such a case, as shown in FIG. 6, a regenerated gas recovery line L9 for recovering the regenerated gas as the product gas may be provided in the regenerated gas return line L5 so as to bypass the regenerated gas to the product gas recovery line L2 via an injection pump P9. In such a case, branch control of the flow destination of the regenerated gas may be performed so as to flow the regenerated gas from the regenerated gas return line L5 to the source gas supply line L1 or from the regenerated gas recovery line L9 to the product gas tank T2, in accordance with the composition of the gas flowing through the miscellaneous gas discharge line L3. That is, it is possible to adopt a configuration in which the regenerated gas is recovered into the product gas tank T2 via the regenerated gas recovery line L9 if the product gas purity of the regenerated gas is high, and the regenerated gas is returned to the source gas supply line L1 via the regenerated gas return line L5 if the product gas purity of the regenerated gas is low.

Note that, for example, if (1) the gas purity of the regenerated gas can be constantly maintained at a purity sufficient to be recovered as the product gas, or if (2) the regenerated gas has a high purity than that of the source gas, or if (3) the regenerated gas has a purity sufficient to be used as a power generation fuel by adding an appropriate amount of the source gas thereto, the regenerated gas return line L5 may be omitted and only the regenerated gas recovery line L9 may be provided (see FIG. 13).

[0124] (6)

Although the gas purification apparatus includes four adsorption towers A1 to A4 in the above-described embodiment, the present invention is not limited thereto. It is possible to adopt a configuration in which two or three adsorption towers alternately perform processing as long as a plurality of adsorption towers are provided so as to be able to perform a continuous PSA. For example, when three adsorption towers are provided, it is possible to adopt a configuration as shown in FIG. 7.

[0125] (7)

The PSA cycle is not limited to the one described above as long as it is configured such that the adsorption towers can be continuously used in an effective manner, and various modifications may be made. For example, in the case of the gas purification apparatus having the above-described configuration shown in FIG. 7, it is possible to perform an operation method in accordance with FIG. 8.

[0126] (8)

Although the product gas is supplied to the adsorption towers at static pressure (with no pressure applied) during the washing step in the previous embodiment, it is also possible to perform the washing step in a pressurized state. In this case, the washing efficiency can be improved.

[0127] (9)

Although an example is shown in which the gas purification apparatus according to the present invention is used for purification of biogas, the gas purification apparatus can be used when methane contained in gases other than biogas, such as a coal mine gas, is concentrated into a high concentration as with biogas, and also for uses in which a miscellaneous gas other than a purification target gas is adsorbed from the source gas. At this time, the adsorbent and the material of the separation membrane may be changed as appropriate, depending on the type and the concentration of the purification target gas and the miscellaneous gas.

[0128] (10)

In addition to the configuration of the previous embodiment, a buffer tank T3 may be provided upstream of the membrane separator M in the miscellaneous gas discharge line L3, as shown in FIG. 9. Note that Vc52 is a pressure control valve for maintaining the pressure in the buffer tank T3 at a pressure lower than the internal pressures of the adsorption towers A1 to A4 as needed. In FIG. 9, L9 denotes a pipe line for recovering a regenerated gas into the product gas recovery

line L2 via the injection pump P9, and a similar reference numeral is assigned to indicate that this line is similar to the regenerated gas recovery line L9 in FIG. 6.

[0129] In this case, the buffer tank can temporarily store the miscellaneous gas discharged by the desorption step before the miscellaneous gas is supplied to the membrane separator. At this time, a high-pressure miscellaneous gas containing a purification target gas having a relatively high concentration can be accumulated in the buffer tank by a pressure equalization using the pressure difference between the adsorption tower and the buffer tank. Of the miscellaneous gas, a miscellaneous gas at a relatively low pressure can be supplied to the regenerated gas tank via Vo5, and the miscellaneous gas in the buffer tank and the regenerated gas tank can be supplied to the membrane separator as necessary even during a period in which the adsorption towers do not perform the desorption step.

[0130] When the miscellaneous gas in the buffer tank is subsequently supplied to the membrane separator, a high-pressure miscellaneous gas that is initially discharged from the inside of the adsorption towers can be subjected to pressure relaxation and supplied to the membrane separator, and it is possible to purify the purification target gas from the miscellaneous gas with high precision, while performing a membrane separation operation with a high recovery rate by using the pressure of the high-pressure miscellaneous gas.

[0131] As in the configuration of FIG. 6, in the configuration of FIG. 9 as well, branch control of the flow destination of the regenerated gas may be performed so as to, for example, flow the regenerated gas from the regenerated gas return line L5 to the source gas supply line L1 or from the regenerated gas recovery line L9 to the product gas tank T2, or use the regenerated gas from the regenerated gas recovery line L9 directly as the product gas, in accordance with the composition or the like of the gas flowing through the miscellaneous gas discharge line L3. That is, when the product gas purity of the regenerated gas is high, the regenerated gas can be recovered into the product gas tank T2 via the regenerated gas recovery line L9, or used as a different product gas for a use different from that of the product gas in the product gas tank T2, without being recovered into the product gas tank T2. When the product gas purity of the regenerated gas is low, the regenerated gas can be returned into the source gas supply line L1 via the regenerated gas return line L5.

Note that when the regenerated gas can be constantly maintained at a product gas purity sufficient to be recovered as the product gas, the regenerated

gas return line L5 may not be provided and only the regenerated gas recovery line L9 may be provided.

[0132] (11)

5 By simplifying the configuration of the pipes and the valves of the gas purification apparatus having the configuration shown in FIGS. 2 to 4 in the previous embodiment, it is possible to perform an operation method in accordance with FIGS. 10 to 12.

10 That is, according to the configuration shown in FIGS. 10 to 12, it is possible to eliminate the need for the product gas pressure increasing line L8 and also the washing step by omitting the pressure increase of the adsorption towers by using the product gas and performing the pressure increase by using the source gas, and therefore, the product gas washing line L4 is not necessary. At this time, it is possible to reduce a loss of the product gas caused by the pressure increase, thus improving the product gas recovery rate. Although the pressure
15 fluctuates in three steps from a maximum pressure to a minimum pressure in FIG. 4, the pressure fluctuates more gradually in four steps in FIG. 12 by temporarily stopping the pressure fluctuation by providing the standby step after the post-parallel adsorption step, and therefore a sudden pressure fluctuation will not occur in the adsorption towers, contributing to a stable operation of the gas
20 purification apparatus.

Industrial Applicability

[0133] A gas purification apparatus according to the present invention can recover methane having a higher purity, and can be used as a gas purification
25 apparatus capable of using biogas and the like, which have been conventionally difficult to reuse, efficiently and with a high methane recovery rate.

Description of Reference Signs

[0134] A1 to A4: First to fourth adsorption towers
30 A11 to A41: Adsorbents
C: Controller
L1: Source gas supply line
L2: Product gas recovery line
L3: Miscellaneous gas discharge line
35 L4: Product gas washing line
L5: Regenerated gas return line

	L6:	Exhaust line
	L7:	Inter-tower pressure equalization line
	L8:	Product gas pressure increasing line
	L9:	Regenerated gas recovery line
5	L10, L30:	Bypass lines
	L11 to L41:	Supply lines
	L12 to L42:	Recovery lines
	L13 to L43:	Exhaust gas lines
	L14 to L44:	Washing lines
10	L17 to L47:	Pressure equalization lines
	L18 to L48:	Pressure increasing lines
	M:	Membrane separator
	M1:	Separation membrane
	P1:	Supply pump
15	P5:	Compression pump
	P6:	Vacuum pump
	P9:	Injection pump
	T1:	Source gas tank
	T2:	Product gas tank
20	T5:	Regenerated gas tank
	V11 to V44:	Switching valves
	Vc1 to Vc8:	Pressure control valves
	Vn4, Vn7:	Needle valves
	Vo3 to Vo8:	Open/close valves
25	Vr4:	Pressure reducing valve

CLAIMS

1. A gas purification apparatus comprising:

an adsorption tower filled with an adsorbent that adsorbs a miscellaneous gas other than a purification target gas from a source gas;

a source gas supply line for supplying the source gas to the adsorption tower;

a product gas recovery line for discharging the purification target gas that has not been adsorbed on the adsorbent as a product gas; and

a miscellaneous gas discharge line for discharging the desorbed miscellaneous gas that has been adsorbed on the adsorbent,

the adsorption tower, the source gas supply line, the product gas recovery line, and the miscellaneous gas discharge line being connected so as to be able to perform a pressure swing operation of alternately performing

an adsorption step of receiving the source gas from the source gas supply line, adsorbing the miscellaneous gas onto the adsorbent, and recovering the product gas, and

a desorption step of depressurizing-desorbing the miscellaneous gas adsorbed on the adsorbent and discharging said miscellaneous gas from the miscellaneous gas discharge line,

wherein a membrane separator that includes a separation membrane impermeable to the purification target gas and permeable to the miscellaneous gas, and that separates the purification target gas and the miscellaneous gas by an exhaust gas pressure of the adsorption tower is provided in the miscellaneous gas discharge line,

a regenerated gas return line for returning, into the source gas supply line, a regenerated gas in which the concentration of the purification target gas has been increased by the separation membrane is provided, and

a regeneration pressure control valve is provided in the regenerated gas return line,

opening degree of said regeneration pressure control valve being adjusted so as to control the pressure for reducing gradually the exhaust gas pressure of the adsorption tower in the desorption step, a regeneration controller that controls a membrane separation pressure of the separation membrane by the regeneration pressure control valve is provided, and the membrane separation pressure of the separation membrane is controlled by the exhaust gas pressure of the adsorption tower with the regeneration pressure control valve.

2. The gas purification apparatus according to claim 1,

wherein a regenerated gas recovery line for recovering a regenerated gas in which the concentration of the purification target gas has been increased by the separation membrane as the product gas is provided.

3. The gas purification apparatus according to claim 1 or 2,

wherein a bypass line for causing the miscellaneous gas flowing through the miscellaneous gas discharge line to bypass the membrane separator so as to be guided to the regenerated gas return line is provided.

4. The gas purification apparatus according to any one of claims 1 to 3,

wherein a buffer tank is provided upstream of the membrane separator in the miscellaneous gas discharge line.

5. The gas purification apparatus according to any one of claims 1 to 4, wherein a vacuum pump is provided on a miscellaneous gas permeable side of the membrane separator in the miscellaneous gas discharge line so as to be operated in a steady state.

6. The gas purification apparatus according to any one of claims 1 to 5,
wherein a regenerated gas tank is provided in the regenerated gas return line.
7. The gas purification apparatus according to any one of claims 1 to 6,
wherein a product gas tank is provided in the product gas recovery line.
8. The gas purification apparatus according to claim 7,
wherein a product gas washing line for flowing the product gas into the adsorption tower from the product gas tank is provided, a product pressure control valve is provided between the product gas tank and the adsorption tower in the product gas washing line, and a washing controller for washing the adsorption tower by flowing the product gas into the adsorption tower from the product gas tank is provided.
9. The gas purification apparatus according to any one of claims 1 to 8,
wherein the source gas is a methane-containing gas, the purification target gas is methane, and the miscellaneous gas is a gas composed mainly of carbon dioxide.
10. The gas purification apparatus according to any one of claims 1 to 9,
wherein the source gas is a methane-containing gas containing at least 40% methane as the purification target gas, and a product gas containing at least 90% methane is obtained.
11. The gas purification apparatus according to any one of claims 1 to 10,
wherein the adsorbent is composed mainly of at least one material selected from the group consisting of an activated carbon, a molecular sieve carbon, zeolite, and a porous metal complex.

12. The gas purification apparatus according to claim 11,

wherein the adsorbent is a molecular sieve carbon having a pore volume ($V_{0.40}$), at a pore diameter of 0.38 nm or more, of not exceeding $0.01 \text{ cm}^3/\text{g}$, and a pore volume ($V_{0.34}$), at a pore diameter of 0.34 nm, of $0.20 \text{ cm}^3/\text{g}$ or more, as measured by the MP method.

13. The gas purification apparatus according to any one of claims 1 to 12,

wherein the separation membrane is composed mainly of at least one material selected from the group consisting of cellulose acetate, polyamide, polyimide, polysulfone, polytetrafluoroethylene, polyether sulfone, a carbon film, a microporous glass composite film, DDR-type zeolite, multibranched polyimide silica, and polydimethylsiloxane.

14. The gas purification apparatus according to any one of claims 1 to 13,

wherein a booster pump is provided in the source gas supply line, and a pressure of supply of the source gas to the adsorption tower by the booster pump is 0.5 MPaG to 2 MPaG.