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An Amine Solution for Capturing and Absorbing Carbon Dioxide and a Method for Capturing and Absorbing Carbon Dioxide in Gas

Field of the Invention

5 The present invention pertains to the technical field of capturing carbon dioxide in gas, and relates to an amine solution for capturing and absorbing carbon dioxide and a method for capturing and absorbing carbon dioxide in gas.

Background of the Invention

10 The enormous emission of CO₂ results in global warming, intensification of the greenhouse effect and frequent occurrence of extreme weathers. The countries in the world are all paying increasing attention to the control of carbon dioxide emission. Following the conclusion of the Kyoto Protocol and the convention of Global Climate Summit in Copenhagen, all countries have attached more importance to the Research
15 and Development and industrialization of carbon dioxide emission reduction technology. On November 26, 2009, Chinese government officially released the control target of greenhouse gas emission by 2020——by 2020, the emission of unit GPD shall decrease by 40%-45% over 2005. This indicates that the capture and utilization technology of carbon dioxide is a matter with extreme significance to the society and environment and
20 has a very broad application prospect.

The CO₂ emitted from the combustion of fossil fuel accounts for about 80% of the total emission amount. The flue gas generated by fossil fuel-fired power plants is a



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lasting, stable and concentrated emission source of CO₂ and the amount of CO₂ emitted by them accounts for 30% of the total emission amount. It is predicted that by 2050, about 20-40% of CO₂ emission generated fossil fuel in the world is technically suitable for capture, including 30-60% of CO₂ emission from coal-fired power plants and 30-40% of CO₂ emission from other industries. Therefore, realizing mass capture of CO₂ in the flue gas of coal-fired power plants will become a major way to reduce emission of greenhouse gas and is one of the methods with great potential to cope with global climate changes.

The process of the membrane absorption method combines the selectivity of the chemical absorption method and the compactness of membrane separation method. It is a rather promising CO₂ capture process. The membrane absorption method may overcome the shortcoming of conventional gas-liquid contact equipment and raise carbon dioxide capture efficiency and meanwhile may use the alkanolamines with desirable absorption and regeneration performance and high degradability, such as monoethanolamine and N-methyldiethanolamine to greatly reduce the energy consumption in the capture process. The gas treated in the membrane absorption method does not directly contact the absorption solution. The two fluids flow on the two sides of the membrane respectively. The membrane per se has not selectivity to gas and only plays a role of isolating the gas from the absorption solution. The micropores on the membrane may allow the separated gas molecules on one side of the membrane to pass through the micropores and reach to the other side of the membrane under certain pressure. Through selective absorption of the absorption solution on the other side of the membrane, the purpose of separating a certain component in the gas is realized.

The gas contacts the absorption solution through the micropores of the hollow fiber membrane, the CO_2 in which quickly reacts with the absorption solution to realize capture and absorption of CO_2 . When the membrane contactor is used to capture and absorb CO_2 , the gas passes by one side of the hollow fiber membrane module, while the absorption solution passes by the other side of the membrane module, and the two fluids contact reversely. Gas is diffused through the micropores of the membrane from the gaseous phase to the membrane-liquid interface. The CO_2 in the gas reacts with the absorption solution. As a result, the concentration of CO_2 on the membrane-liquid interface is close to zero. Under the drive of a concentration difference, CO_2 is diffused continuously to the side of the absorption solution, and reacts with the absorption solution so as to realize capture and absorption of CO_2 . Other components (such as N_2 and O_2) in the gas have a very low solubility in the absorption solution and can not react with the absorption solution, so there is no drive of a concentration difference to make them go through the microporous membrane, as a result the other components are kept in the feed gas.

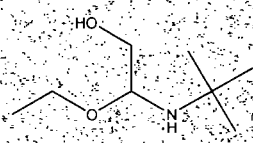
It is found in the research process that in the existing method for absorbing carbon dioxide in the gas by the membrane absorption method, the absorption ratio and absorption velocity of carbon dioxide for the absorption solution and the handling capacity for the equipment need to be improved.

Summary of the Invention

The present invention aims to overcome the deficiency of the prior art in carbon dioxide capture and absorption, and to provide an amine solution for capturing and

absorbing carbon dioxide and a method for capturing and absorbing carbon dioxide in gas.

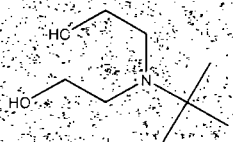
The present invention provides an amine solution for capturing and absorbing carbon dioxide, which comprises a monoethanolamine and at least one first activator selecting from the group consisting of 2-(*tert*-butylamino)-2-ethoxy ethanol (i.e.,



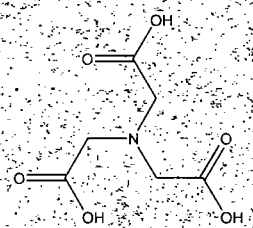
), N-methyl monoethanolamine (i.e.,



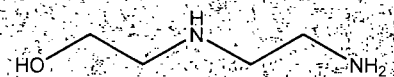
N-*tert*-butyl diethanolamine (i.e.,



), nitrilotriacetic acid (i.e.,



) and N-hydroxyethyl-ethylenediamine (i.e.,



), based on the total amount of the amine solution, the content of monoethanolamine is in a range of 5-40% by weight and the total content of the first activators is in a range of 5-10% by weight.

The solvent of the amine solution according to the present invention may be a conventional selection. In consideration of environmental protection, the preferred solvent of the amine solution is water. The content of the solvent in the amine solution may be a conventional selection in the art. Usually, based on the total amount of the amine solution, the content of the solvent may be in a range of 50-90% by weight.

The amine solution according to the present invention may optionally contain other common activator as a second activator. For example, the second activator may be at least one selected from the group consisting of diethanolamine, 2-amino-2-methyl-1-propanol, piperazine and piperidine. Based on the total amount of the amine solution, the content of the second activator may be in a range of 1-8% by weight.

The amine solution according to the present invention can not only obtain a higher absorption ratio of carbon dioxide but also achieve a higher absorption velocity of carbon dioxide. Therefore, the amine solution of the present application is particularly applicable to the occasion where the membrane absorption method is used to capture and absorb carbon dioxide in gas.

The present invention further provides a method for capturing and absorbing carbon dioxide in gas, which uses an amine solution as absorption solution through a hydrophobic hollow fiber module to capture and absorb carbon dioxide in gas; amine solution absorbed with carbon dioxide is regenerated in a desorber, and regenerated amine solution is circularly used as the absorption solution; the method comprises the following steps:

- (1) a flow of gas to be treated passes through a system for dust-removing and cooling and enters tube pass or shell pass of the hydrophobic hollow fiber membrane module via a compressor or an air blower and subsequently via a gas flow control system;

(2) a flow of amine solution passes through a filtration system and a cooling system successively and is pumped into tube pass or shell pass of the hydrophobic hollow fiber membrane module via a flow regulating system;

(3) the flow of gas to be treated and the flow of amine solution are on inner side and outer side of the hydrophobic hollow fiber membrane respectively so as not to directly contact each other; carbon dioxide in the flow of the gas to be treated passes through the surface micropores of the hydrophobic hollow fiber membrane to react with amine in the flow of amine solution, as a result, the carbon dioxide in the flow of the gas to be treated is captured and absorbed, wherein by use of a gas flow regulating system, a gas pressure control and an amine solution flow regulating system and an amine solution pressure regulating system, a pressure difference in a range of 0.05-0.25MPa is maintained between the flow of gas to be treated and the flow of amine solution to realize absorption; and

(4) a flow of amine solution absorbed with carbon dioxide is output from the hydrophobic hollow fiber membrane module, the flow of amine solution absorbed with carbon dioxide passes through a lean-rich liquid heat exchanger to recover energy, and then enters a desorber from the top of the desorber to regenerate, the desorber is provided with a steam boiling unit for heating at the bottom, a flow of product gas of carbon dioxide is obtained by condensing a flow of desorbed carbon dioxide to separate water;

wherein, the amine solution is the amine solution provided by the present invention.

According to the method provided by the present invention, the flow of gas to be treated and the flow of amine solution are on the inner side and the outer side of the

hydrophobic hollow fiber membrane respectively so as not to directly contact each other.

In other words, the flow of gas to be treated enters the tube pass of the hydrophobic hollow fiber membrane module, while the flow of amine solution enters the shell pass

of the hydrophobic hollow fiber membrane module; or the flow of gas to be treated

enters the shell pass of the hydrophobic hollow fiber membrane module, while the flow of amine solution enters the tube pass of the hydrophobic hollow fiber membrane module.

According to the method provided by the present invention, the pressure difference between the flow of gas to be treated and the flow of amine solution on the inner side

and the outer side of the hydrophobic hollow fiber membrane is in a range of

0.05-0.25MPa, so a good balance can be achieved between absorption ratio of carbon dioxide and efficiency of production.

According to the method provided by the present invention, the material for making the hydrophobic hollow fiber membrane may be any of the common hydrophobic

membrane materials those can react with neither the gas to be treated nor the amine solution, for example, the material can be polypropylene, polytetrafluoroethylene or

poly(vinylidene fluoride). The micropores in the hydrophobic hollow fiber membrane

may have a pore size in a range of 0.02-2 μ m, preferably in a range of 0.02-1 μ m, more,

preferably in a range of 0.02-0.5 μ m. The hydrophobic hollow fiber membrane may

have a porosity in a range of 30-50%. The filling ratio of membrane may be in a range

of 30-60%. In the present application, the pore size of the micropores is measured

with a JCM-5000 NeoScope table-type scanning electron microscope commercially

purchased from Nikon Co.; the porosity is measured with a V-Sorb 2800P specific

surface area and porosity analyzer commercially purchased from Beijing App-one

Technology Co., Ltd. according to the method prescribed in Chinese national standard GB/T 19587-2004; the filling ratio of membrane refers to the percentage by volume of the hollow fiber membrane in the cavity of the membrane module.

According to the method provided by the present invention, the amine solution is same as the above-mentioned amine solution. In the view of brief, the amine solution is not described in detail herein.

According to the method provided by the present invention, the desorber may be any of the desorbers commonly used in the art which can regenerate the amine solution absorbed with carbon dioxide (i.e., rich liquid), preferably packed column. According to the method provided by the present invention, a steam boiling unit for heating is provided at the bottom of the desorber. The present invention has no particular limitation to the concrete conditions of desorption, which may be a conventional selection in the art provided that carbon dioxide in the amine solution absorbed with carbon dioxide can be released, thereby regenerating the amine solution absorbed with carbon dioxide.

According to the method provided by the present invention, the regenerated amine solution (i.e., lean liquid) output from the desorber may pass through a filtration system and a cooling system successively and be pumped into the tube pass or shell pass of the hollow fiber membrane module via a flow regulating system to absorb the carbon dioxide in the gas to be treated again.

According to the method provided by the present invention, the gas to be treated may be any of the common gases containing carbon dioxide need to be captured and absorbed. For example, the gas to be treated may be the flue gas from any source.

According to the method provided by the present invention, the hydrophobic hollow fiber membrane module has a large specific surface area and can raise the removal ratio of carbon dioxide, which overcomes the problems of conventional absorbers, such as flooding, entrainment and bias flow, effectively reduces the possibility of contacting the amine solution with the oxygen in the flue gas so that the degradation consumption of the amine solution is lowered. Furthermore, the amine solution provided by the present invention is used as absorption solution in the method provided by the present invention; consequently, even under high flow of gas and flow of liquid, the method provided by the present invention can still maintain a high carbon dioxide removal ratio and meanwhile can obtain high-purity carbon dioxide product gas.

Brief Description of the Drawings

The accompanying drawings are intended to provide further understanding on the present invention and constitute a part of the specification, together with the embodiments below are intended to explain the present invention and not to limit the present invention. Among the accompanying drawings:

Figure 1 is a flow diagram for showing the method for capturing and absorbing carbon dioxide in gas according to the present invention.

Figure 2 is a structural diagram of a hollow fiber membrane module used in the examples of the present invention.

Figure 3 is used to explain the residual ratio of amines in the amine solution in example 6 and comparative example 4.

Description to the reference signs in the drawings:

1: gas compressor; 2: dust-removing and cooling system for flue gas;
 3: gas flow control system; 4: hydrophobic hollow fiber membrane module;
 5: desorber; 6: heat exchange system for amine solution;
 7: pump for amine solution; 8: flow control system for amine solution;
 9: filtration system for amine solution; 10: cooling system for amine solution;
 11: steam boiling unit; 12: cooling and separation system for carbon dioxide;
 13: inlet of amine solution; 14: outlet of amine solution;
 15: gas inlet; 16: gas outlet;
 17: hydrophobic hollow fiber membrane; 18: shell pass.

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Detailed Description of the Embodiments

Below the present invention is further described in detail by referring to the examples and accompanying drawings.

In the examples and comparative examples, the flue gas to be treated and obtained
 15 product gas of carbon dioxide are analyzed with KM9106E flue gas analyzer
 commercially purchased from British Kane Co. by the method prescribed in JJG
 968-2002.

Example 1

20 In this Example, the content of CO₂ in the flue gas is 15% by volume and the flow
 rate of the flue gas is 3Nm³/h. In the amine solution, the total content of amines is

30% by weight, wherein the content of monoethanolamine is 25% by weight, the content of 2-(*tert*-butylamino)-2-ethoxy ethanol (TBEE) used as the first activator is 5% by weight, and the rest is water. The flow rate of the amine solution is 15L/h.

In this Example, the hollow fiber membrane used in the hydrophobic hollow fiber membrane module is made from polypropylene. The hollow fiber membrane has a pore size of 0.02-0.1 μ m and a porosity of 40%. The filling ratio of membrane is 45%, and the volume of the cavity of the membrane module is 0.012m³. The hollow fiber membrane tube has an inner diameter of 0.38mm, an outer diameter of 0.50mm and an effective length of 0.6m. The structure of the hydrophobic hollow fiber membrane module is as shown in Figure 2.

As shown in Figure 1, a flow of the fuel gas successively passes through a dust-removing and cooling system for flue gas 2 and a gas flow control system 3 and is sent into the tube pass of the hydrophobic hollow fiber membrane module 4 through gas inlet 15 by air blower. The amine solution is cooled in a cooling system for amine solution 10, and enters the shell pass of the hydrophobic hollow fiber membrane module 4 through inlet of amine solution 13 via a flow control system for amine solution 8. The pressure difference between the two sides of the hydrophobic hollow fiber membrane is 0.08MPa. The CO₂ in the flue gas is captured and absorbed by the amine solution.

The rich liquid absorbed with CO₂ exchanges heat with the lean liquid coming out from the desorber 5 to recover heat in the lean-rich liquid heat exchanger (i.e., heat exchange system for amine solution 6), and then enters the desorber 5 from the top of the desorber 5.

A steam boiling unit 11 for heating is provided at the bottom of the desorber 5. Product gas of CO₂ with a purity of 99.5% by mole is obtained by separating water from CO₂ obtained by regeneration in cooling and separation system for carbon dioxide 12. The lean liquid coming out from the bottom of the desorber 5 passes through the lean-rich liquid heat exchanger (i.e., heat exchange system for amine solution 6) followed by pumped via pump for amine solution 7 into filtration system for amine solution 9, and passes through cooling system for amine solution 10, then enters the hydrophobic hollow fiber membrane module 4 to perform absorption again.

By analyzing, it is determined that in the treated flue gas, the removal ratio of carbon dioxide may be maintained stably at 90% by mole, and the purity of the obtained product gas of carbon dioxide reaches 99.5% by mole.

Example 2

The carbon dioxide in flue gas is captured and absorbed by a method same as the method of Example 1, the difference is that the first activator is *N-tert*-butyl diethanolamine.

By analyzing, it is determined that in the treated flue gas, the removal ratio of carbon dioxide may be maintained stably at 98% by mole, and the purity of the obtained product gas of carbon dioxide reaches 99.8% by mole.

Example 3

The carbon dioxide in flue gas is captured and absorbed by a method same as the method of Example 1, the difference is that the first activator is nitrilotriacetic acid.

By analyzing, it is determined that in the treated flue gas, the removal ratio of carbon dioxide may be maintained stably at 97% by mole, and the purity of the obtained product gas of carbon dioxide reaches 99.8% by mole.

5 Comparative Example 1

The carbon dioxide in flue gas is captured and absorbed by a method same as the method of Example 1, the difference is that an absorption tower with the same size is used to replace the hydrophobic hollow fiber membrane module, wherein the flue gas enters the absorption tower from bottom of the tower, and the amine solution enters the absorption tower from top of the tower, to make the flue gas and the amine solution contact each other reversely in the tower, the temperature in the tower is in a range of 40-65°C and the pressure is 1 standard atmospheric pressure.

By analyzing, it is determined that in the treated flue gas, the removal ratio of carbon dioxide is 75% by mole, and the purity of the obtained product gas of carbon dioxide is 97.5% by mole.

By comparing Examples 1-3 with Comparative Example 1, it can be seen that by using the method provided by the present invention to capture and absorb carbon dioxide in flue gas, the removal ratio of carbon dioxide is raised by about 20% at the same time, product gas of carbon dioxide can be obtained with a higher purity, thereby alleviating the burden of the post-treatment and even eliminating the need for the post-treatment.

Example 4

The carbon dioxide in flue gas is captured and absorbed by a method same as the method of Example 1, the difference is as flows.

The content of CO₂ in the flue gas is 17% by volume. In the amine solution, the total content of amines is 25% by weight, wherein the content of monoethanolamine is 15% by weight, the content of N-hydroxyethyl-ethylenediamine used as the first activator is 7% by weight, the content of diethanolamine used as the second activator is 3% by weight, and the rest is water. The flow rate of the amine solution is 8L/h.

The hollow fiber membrane used in the hydrophobic hollow fiber membrane module is made from polytetrafluoroethylene. The hollow fiber membrane has a pore size of 0.02-0.1μm and a porosity of 50%. The filling ratio of membrane is 45%.

The flow rate of the flue gas is 0.2Nm³/h, 0.4Nm³/h, 0.6Nm³/h, 0.8Nm³/h and 1.2Nm³/h, respectively.

The removal ratio of carbon dioxide is shown in Table 1.

Comparative Example 2

The carbon dioxide in flue gas is captured and absorbed by a method same as the method of Example 4, the difference is that the amine solution contains neither the first activator nor the second activator. The removal ratio of carbon dioxide is shown in

Table 1.

Comparative Example 3

The carbon dioxide in flue gas is captured and absorbed by a method same as the method of Example 4, the difference is that in the amine solution, there is no N-hydroxyethyl-ethylenediamine and the content of diethanolamine is 10% by weight. The removal ratio of carbon dioxide is shown in Table 1.

Table 1

Flow rate of flue gas	Removal ratio of carbon dioxide (%)		
	Example 4	Comparative Example 2	Comparative Example 3
0.2Nm ³ /h	100.00	93.96	95.85
0.4Nm ³ /h	99.60	92.67	93.53
0.6Nm ³ /h	99.20	91.00	92.11
0.8Nm ³ /h	98.80	87.63	90.05
1.2Nm ³ /h	82.46	76.15	78.06

It can be seen from Table 1 that by using the method according to the present invention, a higher removal ratio of carbon dioxide can be obtained even at a high flow rate of flue gas.

Example 5

The carbon dioxide in flue gas is captured and absorbed by a method same as the method of Example 1, the difference is as follows:

In the flue gas, the content of CO₂ is 12% by volume, the content of oxygen is 6% by volume, and the flow rate of the flue gas is 0.8Nm³/h. In the amine solution, the total content of amines is 20% by weight, wherein the content of monoethanolamine is 12% by weight, the content of N-methyl monoethanolamine as the first activator is 8% by weight, and the rest is water. The flow rate of the amine solution is 6L/h.

The hydrophobic hollow fiber membrane of the hydrophobic hollow fiber membrane module is made from polypropylene. The hydrophobic hollow fiber membrane has a pore size of 0.02-0.1μm and a porosity of 50%. The membrane filling ratio is 45%.

The operation is carried out continuously for 80 days.

By analyzing, it is determined that the removal ratio of carbon dioxide may be maintained stably at 98% by mole, and the purity of the obtained product gas of carbon dioxide reaches 99.8% by mole.

In the process of the operation, the total content (which is denoted as c_1) of monoethanolamine and N-methyl monoethanolamine (i.e., amines) in the amine solution is analyzed by gas chromatography, and the percentage (i.e., $\frac{C_1}{C_0} \times 100\%$) of c_1 to the initial total content (which is denoted as c_0) of monoethanolamine and N-methyl monoethanolamine in the amine solution is calculated; and then the residual ratio of amines in the amine solution is obtained. The result is shown in Figure 3.

Comparative Example 4

The carbon dioxide in flue gas is captured and absorbed and the residual ratio of amine is calculated by methods same as the methods of Example 5, the difference is that an absorption tower with the same size is used to replace the hydrophobic hollow fiber membrane module, wherein the flue gas enters the absorption tower from bottom of the tower, and the amine solution enters the absorption tower from top of the tower, to make the flue gas and the amine solution contact each other reversely in the tower; the temperature in the tower is in a range of 40-65°C and the pressure is 1 standard atmospheric pressure.

By analyzing, it is determined that the removal ratio of carbon dioxide is 92% by mole; and the purity of the obtained product gas of carbon dioxide is 98% by mole. The residual ratio of amines in the amine solution is shown in Figure 3.

It can be seen from Figure 3 that by using the method provided by the present invention, the dissolution and entrainment of the amine solution to the oxygen in the gas to be treated can be effectively avoided, so as to effectively reduce the oxidative degradation of amine in the absorption solution during the process of the operation, lengthen the life of amine in the absorption solution and lower operating cost.

Above the preferred Examples of the present invention are described in details, but the present invention is not limited to the details of the foregoing Examples. Within the technical conception of the present invention, the technical solution of the present invention may have various modifications within the protective scope of the present invention.

It should be noted that the concrete technical characteristics described in the foregoing examples can be combined in any appropriate way under the condition of no conflict. In order to avoid unnecessary repetition, the present invention does not describe the possible combinations.

5 Further, the examples of the present invention may be combined freely as long as the combinations do not disobey the thought of the present invention. They shall also be deemed as the content disclosed by the present invention.

Claims

- 1 An amine solution for capturing and absorbing carbon dioxide, which comprises
monoethanolamine and at least one first activator selected from the group consisting of
2-(*tert*-butylamino)-2-ethoxy ethanol, N-methyl monoethanolamine, N-*tert*-butyl
5 diethanolamine, nitrilotriacetic acid and N-hydroxyethyl-ethylenediamine, and based on the
total amount of the amine solution, the content of monoethanolamine is in a range of 5-40%
by weight, and the total content of the first activators is in a range of 5-10% by weight.
- 2 The amine solution as described in claim 1, wherein the amine solution further comprises a
10 second activator selected from the group consisting of diethanolamine,
2-amino-2-methyl-1-propanol, piperazine and piperidine, and based on the total amount of
the amine solution, the content of the second activator is in a range of 1-8% by weight.
- 3 A method for capturing and absorbing carbon dioxide in gas, which uses an amine solution
15 as absorption solution through a hydrophobic hollow fiber module to capture and absorb the
carbon dioxide in gas; amine solution absorbed with carbon dioxide is regenerated in a
desorber, and regenerated amine solution is circularly used as the absorption solution, the
method comprises the following steps:
(1) a flow of gas to be treated passes through a system for dust-removing and cooling and
20 enters tube pass or shell pass of the hydrophobic hollow fiber membrane module via a
compressor or an air blower and subsequently via a gas flow control system;

(2) a flow of amine solution passes through a filtration system and a cooling system successively and is pumped into tube pass or shell pass of the hydrophobic hollow fiber membrane module via a flow regulating system;

(3) the flow of gas to be treated and the flow of amine solution are on inner side and outer side of the hydrophobic hollow fiber membrane respectively so as not to directly contact each other; carbon dioxide in the flow of the gas to be treated passes through the surface micropores of the hydrophobic hollow fiber membrane to reacts with amine in the flow of amine solution, as a result, the carbon dioxide in the flow of the gas to be treated is captured and absorbed, wherein by use of a gas flow regulating system, a gas pressure control and an amine solution flow regulating system and an amine solution pressure regulating system, a pressure difference in a range of 0.05-0.25MPa is maintained between the flow of gas to be treated and the flow of amine solution to realize absorption; and

(4) a flow of amine solution absorbed with carbon dioxide is output from the hydrophobic hollow fiber membrane module, the flow of amine solution absorbed with carbon dioxide passes through a lean-rich liquid heat exchanger to recover energy, and then enters a desorber from the top of the desorber to regenerate, the desorber is provided with a steam boiling unit for heating at the bottom, a flow of product gas of carbon dioxide is obtained by condensing a flow of desorbed carbon dioxide to separate water;

wherein the amine solution is the amine solution as described in claim 1 or 2.

4 The method as described in claim 3, wherein the material for making the hydrophobic hollow fiber membrane is polypropylene, polytetrafluoroethylene or poly(vinylidene fluoride).

5 5 The method as described in claim 3 or 4, wherein micropores in the hydrophobic hollow fiber membrane has a pore size in a range of 0.02-2 μ m, and a porosity in a range of 30-50%; filling ratio of membrane is in a range of 30-60%.

6 The method as described in claim 3, wherein the desorber is a packed tower.