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[Continued on next page]

(54) Title: IMPROVED CO2 ABSORPTION METHOD

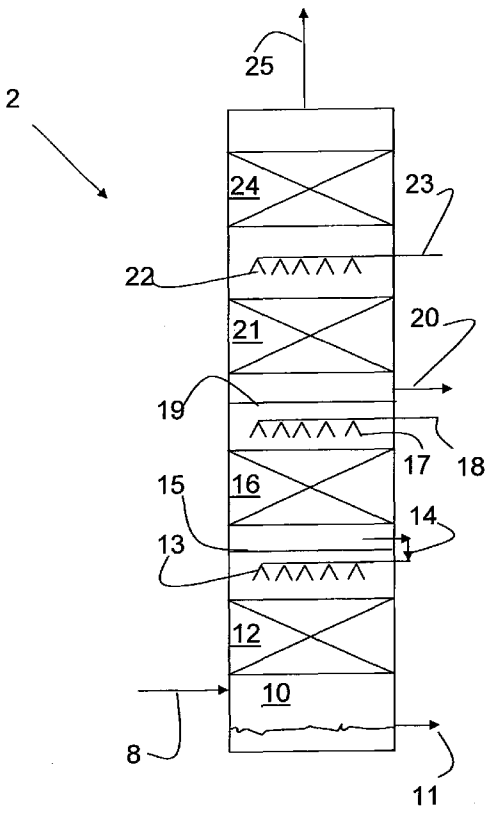


Fig. 2

(57) Abstract: A method for removing $C0_2$ in a exhaust gas from combustion of carbonaceaous meterial, in which method the exhaust gas 8 is brought in countercurrent flow with a liquid CO_2 absorbent 18 in a contact section 12, 16 of an absorption column 2, to produce a $C0_2$ depleted exhaust gas 25 that is released into the atmoshere and a $C0_2$ rich absorbent 11 that is withdrawn from the absorption column, wherein the exhaust gas is introduced into the absorption column at a temperature above about 90 and the exhaust gas is cooled in the absorption column by countercurrent flow of the liquid absorbent in the absorption column, is described.

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— *of inventorship (Rule 4.17(iv))*

Published:

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IMPROVED CO2 ABSORPTION METHOD

Technical field

The present invention relates to field of CO_2 capture from a gas mixture. More specifically the present invention relates to CO_2 capture from an exhaust gas from the combustion of carbonaceous material. Most specifically the present invention relates to an improved method and plant for cooling and absorbing CO_2 from a combustion gas.

Background

The continually increasing combustion of fossil fuel, such as coal, natural gas and oil, during the last centuries has resulted in an increase in the concentration of CO_2 in the atmosphere. The increasing concentration of CO_2 has caused concern due to the greenhouse effect caused by CO_2. The greenhouse effect is suspected already to have caused at least some of the changes in the climate that have been seen during the last decades, and is according to simulation models suspected to cause even more and potentially dramatic changes in the climate of planet earth.

This has caused a call for action from scientists, environmentalists and politicians throughout the world, to stabilize or even reduce the discharge of CO_2 from combustion of fossil fuel to the atmosphere. This may be achieved by capturing and safe depositing of CO_2 from the exhaust gas from thermal power plants and other plants where fossil fuel is combusted.

The captured CO_2 may be injected in sub terrain formations such as aquifers, oil wells for enhanced oil recovery or in depleted oil and gas wells for deposition. Tests indicate that CO_2 remains in the sub terrain formation for thousands of years and is not released into the atmosphere.

Capturing of CO_2 from a gas by means of absorption is well known and has been used for decades, e.g. for removal of CO_2 (and other acid gases) from produced natural gas at gas fields. The absorbents used or suggested in the prior art have been different aqueous alkaline solutions, such as potassium carbonate, see e.g. US5.528.811, and different amines, see e.g. US 4.112.051, US 4.397.660 and US 5.061.465. Separation of CO_2 from exhaust gas from thermal power plants by means of an amine solution, is known e.g. from US 4.942.734.

Common for these CO_2 capturing solution is that the gas mixture to be separated is introduced countercurrent to the aqueous adsorbent in an absorber column. The gas leaving the absorber column is CO_2 depleted (or acid gas depleted), whereas the CO_2 (or other acid gas) leaves the absorber column together with the absorbent. The absorbent is regenerated in the regenerator column and returned to the absorber column. Amine is regenerated by stripping the amine solution with steam in the regeneration column. The steam is generated in the reboiler at the base of the column.

As illustrated above CO_2 as such is well known in the art. However, there is a need for several improvements in the CO_2 capturing process to make CO_2 free or low CO_2 emission thermal power plants economically profitable.

The plants for capturing of CO_2 are relative large, complex and expensive constructions. It is therefore desired to reduce the size, complexity and cost of the plants.

Capturing of CO_2 is carried out at the expense of the efficiency of a thermoelectric power plant utilizing fossil fuel, so that the output of electrical power and/or medium temperature heat from a thermoelectric power plant is reduced. The reduced efficiency compared with a traditional plant makes these facilities less profitable. Improvements in the efficiency, i.e. reducing the energy cost in the CO_2 capturing process, are therefore sought.

The currently preferred absorbents are aqueous solutions of different amines. The commonly used amines are alkanol amines, such as e.g., diethanol amine, mono methyl ethanolamine, aminoethyl ethanolamine, 2-(Metylamino)etanol, MDEA as well as other amines known by skilled man in the art. The absorption of CO_2 to the amine absorbents is a reversible, exothermic reaction. Accordingly, heat has to be supplied to the regenerator column to reverse the absorption and release the CO_2.

The amine absorbents are exposed for degradation during the absorption / desorption cycle described above. The exhaust gas from the combustion of carbonaceous material

comprises oxygen which will react with the amines dependent on the type of amine, the oxygen concentration, the total contact time between oxygen and amine, temperature etc. High temperature, long contact time and high oxygen content in the gas to be treated, are factors that increase the degradation of the amine. The degradation of the amine is also a factor adding cost to the capture of CO_2. The degraded amines have to be replaced and deposited resulting in increased operational costs of the plant.

The exhaust outlet temperature from a traditional thermal power plant is normally 80 to 120 °C as the gas at lower temperatures has no value in production of electrical power, and no or limited value as a heat source in other processes.

A cooler is therefore introduced between the outlet of a thermal power plant and the absorber column. The most common cooler is a tower in which the exhaust gas is cooled by a countercurrent flow of water spray both to cool the gas and saturate the gas with water vapor. The cooled and saturated gas leaving the cooler has normally a temperature of about 50 °C and is directly introduced into the absorption column.

The cooler and absorber for a CO_2 capturing plant, constitutes a substantial part of the total investments for the plant. A decrease of the size and complexity and thus the total cost of investments for the cooler and absorber is therefore sought. Additionally, there are significant operating costs connected to the cooler. There is a pressure loss across the cooler resulting in increased power consumption. Additionally, the cooler requires large power consuming pumps.

An objective of the present invention is thus to provide solutions that makes it possible reduce to cost of investments for the cooler and absorber in a CO_2 capturing plant, without an unacceptable increase in operational costs and/or decrease in efficiency of the plant.

Short description of the invention

The present invention provides a method for removing CO_2 in a exhaust gas from combustion of carbonaceous material, in which method the exhaust gas is brought in countercurrent flow with a liquid CO_2 absorbent in a contact section of an absorption column, to produce a CO_2 depleted exhaust gas that is released into the atmosphere and a

CO_2 rich absorbent that is withdrawn from the absorption column, wherein the exhaust gas is introduced into the absorption column at a temperature above about 90 °C and the exhaust gas is cooled in the absorption column by countercurrent flow of the liquid absorbent in the absorption column. It has surprisingly been found that the inlet cooler for the absorption column may be omitted, and thus both cost of investment and cost of operation, may be reduced without a corresponding loss in absorption capacity of the absorption column. The loss of absorption capacity due to the cooling in the absorption column may be compensated by an increase of about 10% of the contact section. The omission of the inlet cooler has, however a significant positive effect on the cost of investment and the area requirement for a CO_2 capturing plant, as the inlet cooler is an expensive component requiring valuable area in the plant. The savings for the omission of the inlet cooler is far greater than the added cost for increasing either the size of or circulation rate through the contact section.

According to one embodiment, the absorbent is withdrawn from the absorption column immediately after leaving the contact section. By removing the absorbent from the absorption column immediately after leaving the contact section, the time in which the absorbent is in contact with the hot exhaust gas is reduced, thus reducing the degradation of the absorbent.

According to a second embodiment, the present invention provides an absorption column for removing CO_2 from an exhaust gas from combustion of carbonaceous material comprising an inlet section for the exhaust gas, one or more packed contact sections(s) for effecting countercurrent flow of the exhaust gas and a liquid absorbent, and means for withdrawing CO_2 depleted exhaust gas from column, and means for withdrawing CO_2 rich absorbent from the column, wherein the means for withdrawing the CO_2 rich absorbent comprises a collection tray arranged between the inlet section (10) and the contact section(s).

Short description of the figures

Figure 1 illustrates an absorption column and an inlet cooler according to the prior art,
Figure 2 illustrates an absorption column according to a first embodiment of the present invention,

Figure 3 illustrates an absorption column according to a second embodiment or the present invention,

Figure 4 illustrates an absorption column according to a third embodiment of the present invention,

Figure 5 is a graphical presentation of temperature as a function of height in a contact section for an inlet temperature of 50 °C and a saturation temperature of 47 °C,

Figure 6 is a graphical presentation of temperature as a function of height in a contact section for an inlet temperature of 90 °C, and saturation temperature of 50°C, and

Figure 7 is a graphical presentation of the absorption capacity of an absorbent at an inlet temperature of 50 °C compared to 90 °C.

Detailed description of the invention

Figure 1 illustrates an inlet cooler 1 and an absorption column 2 according to the prior art. Combustion gas, typically having a temperature of 90 – 140 °C is introduced through an exhaust line 3 into an inlet cooler chamber 4. The combustion gas is cooled in a contact zone 5 in the inlet cooler 1 by a countercurrent flow of cooling water. The cooling water is introduced through a cooling water line 6 and is sprayed by means of liquid distribution means 7 over the contact zone 5. Due to the direct countercurrent contact with the cooling water, the combustion gas is both cooled and saturated with water vapor. The cooled combustion gas is withdrawn from the top of the inlet cooler through a line 8 and introduced into the absorption column, whereas cooling water is collected in the bottom of the cooler and withdrawn through a withdrawal line 9.

The cooled and saturated combustion gas in line 8 is introduced in an inlet chamber 10 at the bottom of the absorption column 2. From the inlet chamber 10, the gas flows upwards in the absorption column and countercurrent to liquid absorbent in one or more contact section(s) 12, 16. The contact section (s) is(are) preferably comprises a structural packing to increase the surface area, or the contact area between the liquid absorbent and the gas. The illustrated absorption column is provided with two serially connected contact sections 12, 16. After leaving the contact sections 12, 16, the gas is washed by a countercurrent flow of water in a washing section 21 to remove any amine in the gas flow. Washing water is introduced through a washing water line 23 and sprayed at the top

of the washing section 21, is collected at a water collection plate 19 below the washing section and is withdraw through a washing water removal line 20. Water droplets in the washed gas flow is then preferably removed in a demister section 24 before the lean exhaust gas, from which 80 to 99 % of the CO_2 has been removed by adsorption, is withdrawn through a lean exhaust gas withdrawal line 25.

Lean, or CO_2 pure, absorbent is introduced into the absorption column through a lean absorbent line 18 and is sprayed onto the top of the upper contact section 16 by means of liquid distribution means 17. The absorbent flows through the upper contact section 16 and is collected at an absorbent collection plate 15 below the contact section 16. The absorbent collection plate 15 may be a bubble cap collection plate or any other type of collection plate known by the skilled man in the art. The semi lean absorbent having absorbed CO_2 from the exhaust gas, is withdrawn in a bypass line 14 and sprayed at the top of the lower contact section 12. After flowing through the lower contact section 12, the rich absorbent having absorbed more CO_2 from the exhaust gas, is collected at the bottom of the stripper column and is withdrawn to a rich absorbent withdrawal line 11.

The rich absorbent may be regenerated in a regenerator, e.g. as described in the applicants own Norwegian patent applications NO2006 5411 NO2006 5412 or NO2006 5413, the description of which are incorporated in the present description as reference. Regenerated absorbent is then introduced as lean absorbent in line 18.

The liquid distribution means 7, 17, respectively, may be any means suitable to distribute a liquid over the contact sections. Suitable liquid distribution means 7, 17 may be nozzles, troughs or piping with small holes to allow the liquid to be distributed over the contact sections.

The embodiment illustrated in figure 2, corresponds to the above described solution according to prior art, with the difference that the cooler is omitted. By introducing exhaust gas not saturated with water and at a temperature typically from about 90 – 130 °C, the exhaust gas is cooled by evaporation of water from the absorbent to saturate the exhaust gas and results only a slight increase of temperature of the absorbent in the lowermost part of the contact section. This slight increase of temperature and the corresponding slight decrease in absorbing capacity of the absorbent, may be

compensated by an increase in the height of the contact sections(s) and/or an increased flow of absorbent. The extra costs for the increased height of the packing or increased flow of absorbent to absorb the same amount of CO_2 are, however, relatively small compared with the cost of a cooler according to the prior art.

Figures 3 and 4 illustrates two different variations of an embodiment where the rich absorbent leaving the lower contact section is collected in a collection tray 37 beneath the structured packing of the lower contact section 12, to collect the rich absorbent flowing out of the contact section. The collected rich absorbent is withdrawn from the collection tray 37 and is transferred to a rich absorbent storage tank 31, 35 through lines 30, 38, respectively. By removing the rich absorbent from the absorption column immediately after leaving contact section the exposure time of the absorbent for oxygen and high temperature is minimized. This results in a reduced degradation of the absorbent compared with the solutions according to the prior art.

To reduce the degradation of the absorbent even more, an inert gas, such as e.g. nitrogen, may be introduced into the tank 31, 35 through an inert gas line 30, 32, respectively, as a blanketing system to further reduce the contact between absorbent and oxygen. As illustrated in figure 4, the tank 35 is optionally vented into the inlet chamber of the absorbing column through a venting line 39 to avoid the need for cleaning the gas removed from the tank 35 to adjust the pressure therein.

The rich absorbent in the tank 31, 35 is carried to a regeneration plant through a rich amine return line 32, 40, respectively.

To reduce degradation of the absorbent in the tank 31, 35, respectively, by oxygen present in the absorbent, a not shown stripper column in which a stripper gas flows countercurrent to the rich absorbent, may be introduced in line 30. The stripper gas may be CO_2 from the above mentioned absorbent regenerator. The CO_2 removed from the stripper column may be dried and compressed and exported from the plant as the oxygen level even after stripping of the absorbent is sufficiently low for most applications of the CO_2.

Example

The simulation programs ProTreat and CO2Sim were used for simulation of the temperature profile in a contact section in an absorber for CO_2.

The simulated values from the simulations were compared with measured values from a test contact section having a diameter of 300 mm using MEA as absorbent amine.

Simulated values and measured values from the test absorber for gas inlet temperature of 50 °C and 90 °C are presented in figures 5 and 6, respectively. The gas entering at 50 °C corresponds to a typical cooled and humidified exhaust gas, having a dew point of about 47 °C and thus being almost saturated with water, whereas the gas entering at 90 °C corresponds to a typical exhaust gas that is released from a natural gas fired thermal power plant, having a dew point of about 44 °C.

As illustrated in the figures 5 the temperature in the contact section increases substantially linear as a function of the height, due to the exothermal absorption reaction between CO_2 and the amine. Figure 6 illustrates the fact that the gas entering the contact section at a temperature of 90 °C is effectively cooled by evaporation of water from the absorbent solution. From a height of about 0.5 m the temperature again increases due to the exothermal absorption reaction as mentioned above. From the height of 0.5 m the temperature difference between the two cases is about 2 °C.

Figure 7 illustrates the CO_2 loading of the absorbent (mole CO_2 / mole MEA) as a function of the height of the contact section for the two test and simulation cases having inlet temperatures of 50 and 90 °C, respectively. Due to the higher temperature in the lower part of the contact section, the loading is slightly lower for the higher inlet temperature than the lower temperature exhaust gas.

Discussion

The test results and simulations confirm a close agreement between the simulations and the experimental tests. The simulation model may therefore be used to predict the performance of the absorber under varying temperatures and humidity of exhaust gas.

The results confirms that the inlet cooler upstream for the absorption column in a plant for capturing of CO_2 from the exhaust gas from a thermal power plant fired by natural gas, may be omitted according to the present invention. The cost for omitting the inlet cooler is somewhat lower absorption efficiency. This lower absorption efficiency may be compensated for by increasing the circulation rate of the absorbent by about 6%, or by increasing the height of the contact section(s) by less than 10 %, or about 0.5 m.

The experimental results and the simulations also confirms that the hot (90 °C) and dry exhaust gas is cooled to a temperature that is slightly higher than the temperature of a typical cooled and humidified exhaust gas, in the lower 0.5 m or less of the contact section. This cooling effect is mostly contributed to evaporation of water from the absorbent. This evaporation will concentrate the amine solution, which may be favorable in the lower part of the absorber.

Accordingly, both the simulated values and the results from an actual test of an absorption tower confirm the present inventor's theory that the inlet cooler between a natural gas powered thermal power plant may be omitted and thus make substantial savings possible. This finding is in contradiction to the accepted view in the field that an inlet cooler is necessary for cooling the exhaust gas from a thermal power plant before introduction into an absorption column for absorption of CO_2.

Patent claims P2894PC00

1.

A method for removing CO_2 in a exhaust gas from combustion of carbonaceous material, in which method the exhaust gas is brought in countercurrent flow with a liquid CO_2 absorbent in a contact section of an absorption column, to produce a CO_2 depleted exhaust gas that is released into the atmosphere and a CO_2 rich absorbent that is withdrawn from the absorption column, wherein the exhaust gas is introduced into the absorption column at a temperature above about 90 °C and the exhaust gas is cooled in the absorption column by countercurrent flow of the liquid absorbent in the absorption column.

2.

A method according to claim 1, wherein the absorbent is withdrawn from the absorption column immediately after leaving the contact section.

3.

The method according to claim 2, wherein the rich absorbent that is withdrawn from the absorption column is introduced into a holding tank.

4.

The method according to claim 3, wherein an inert gas is introduced into the holding tank.

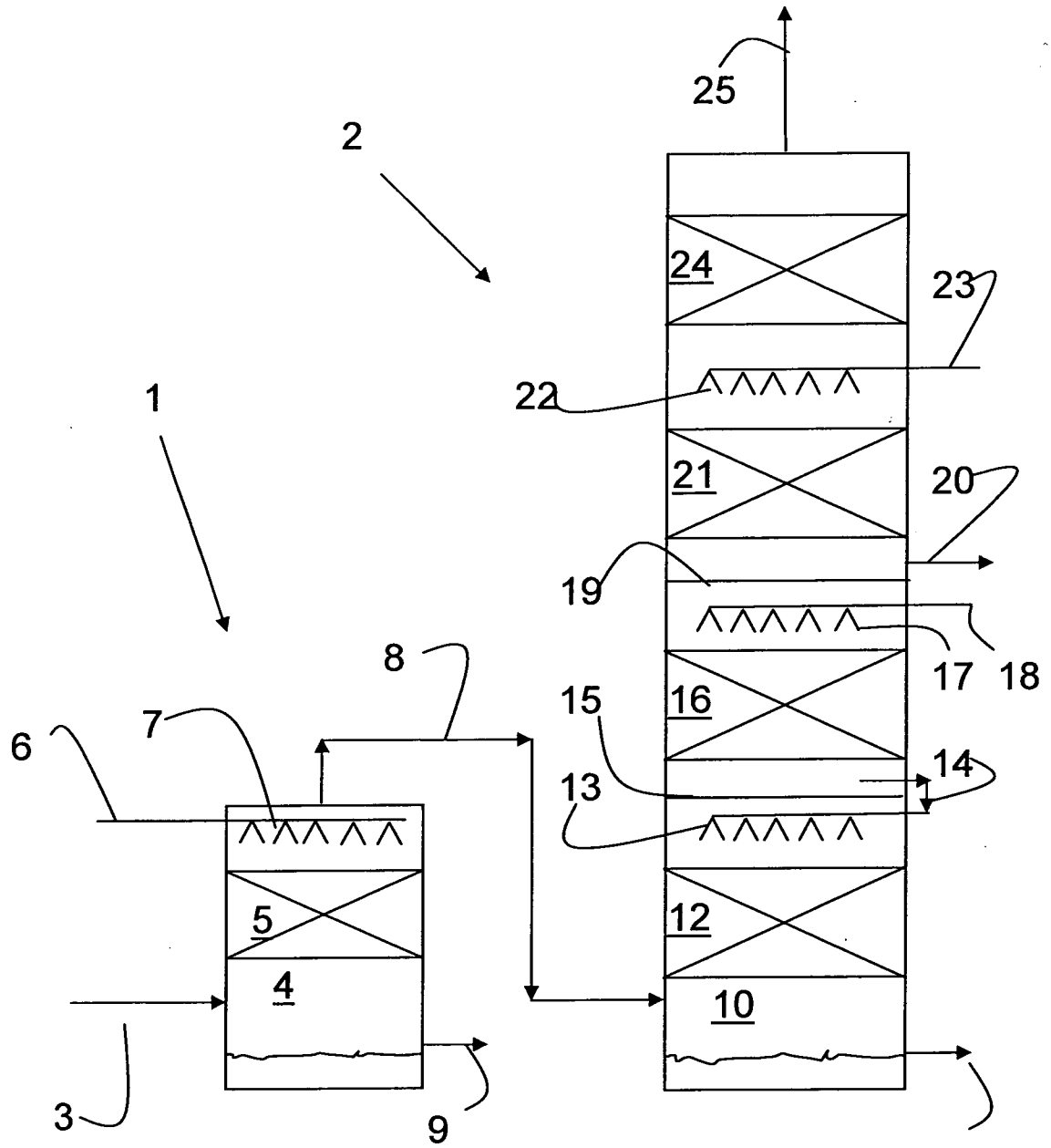


Fig. 1

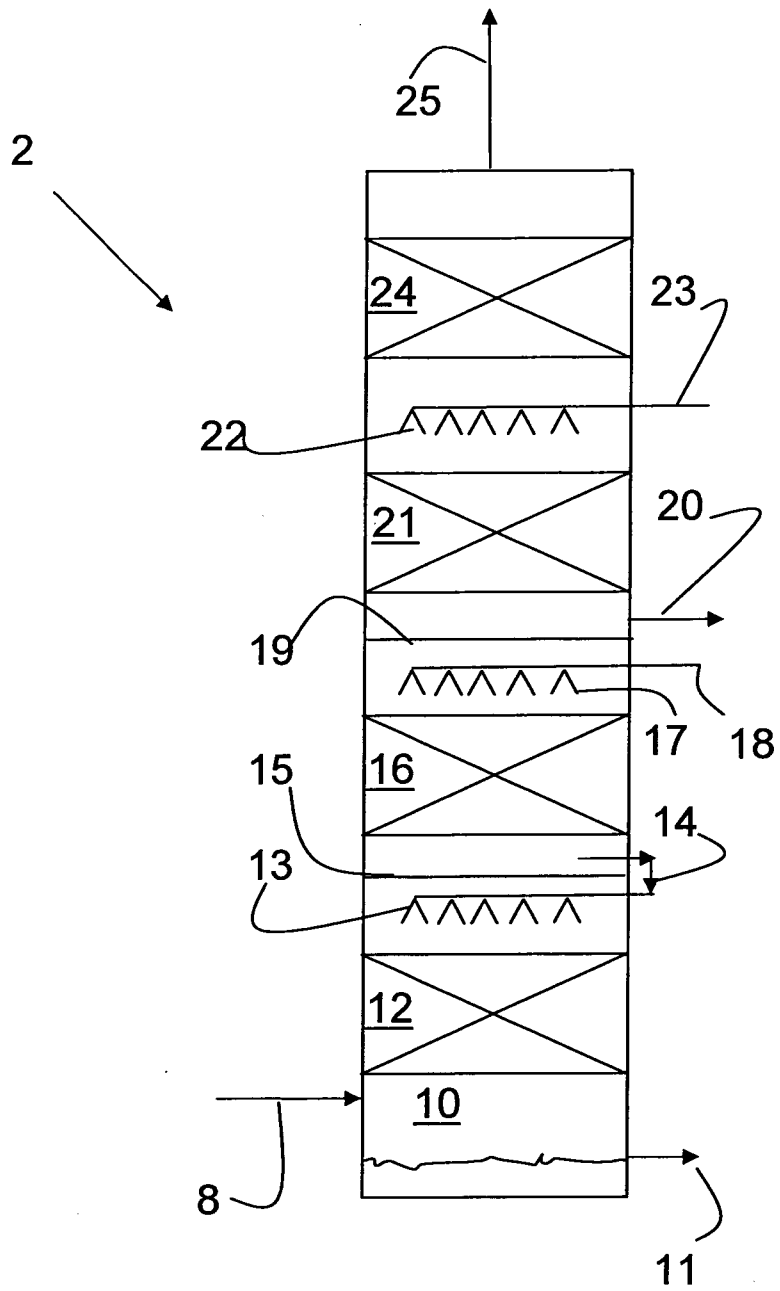


Fig. 2

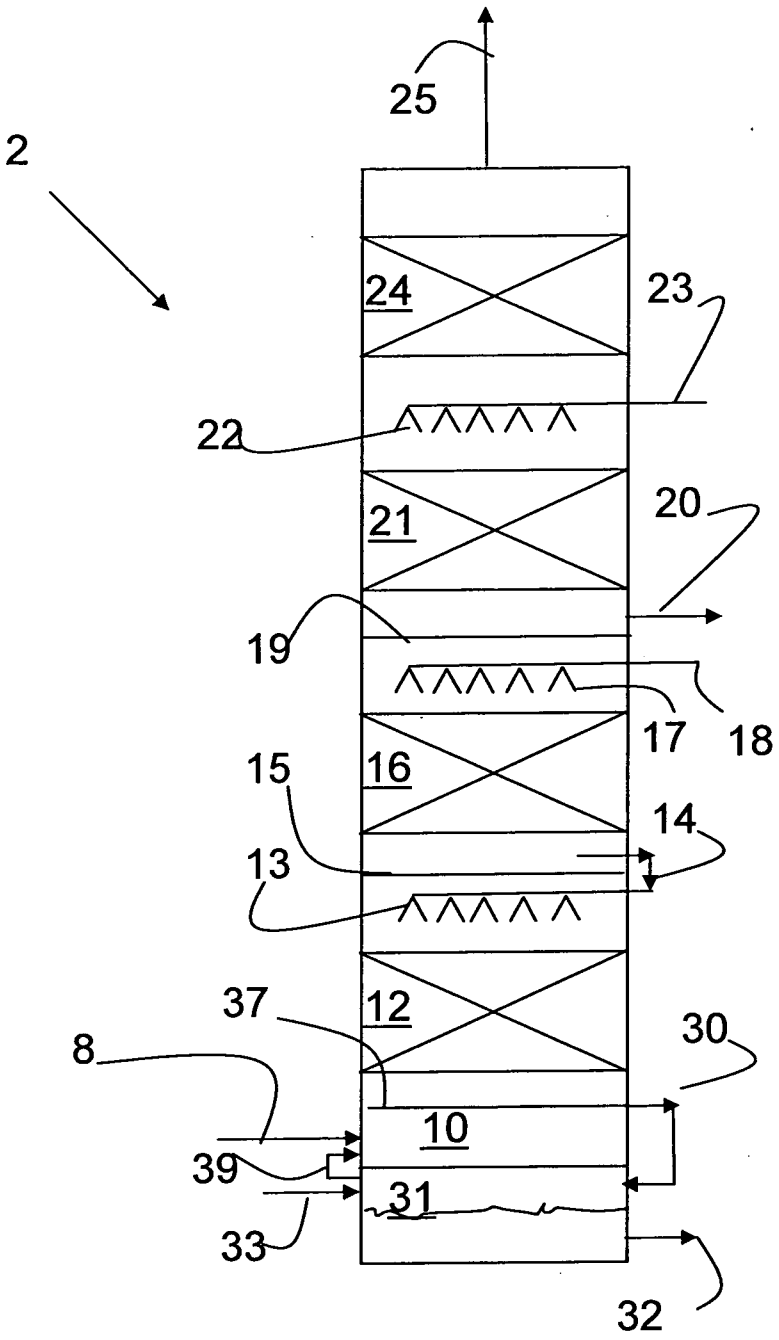


Fig. 3

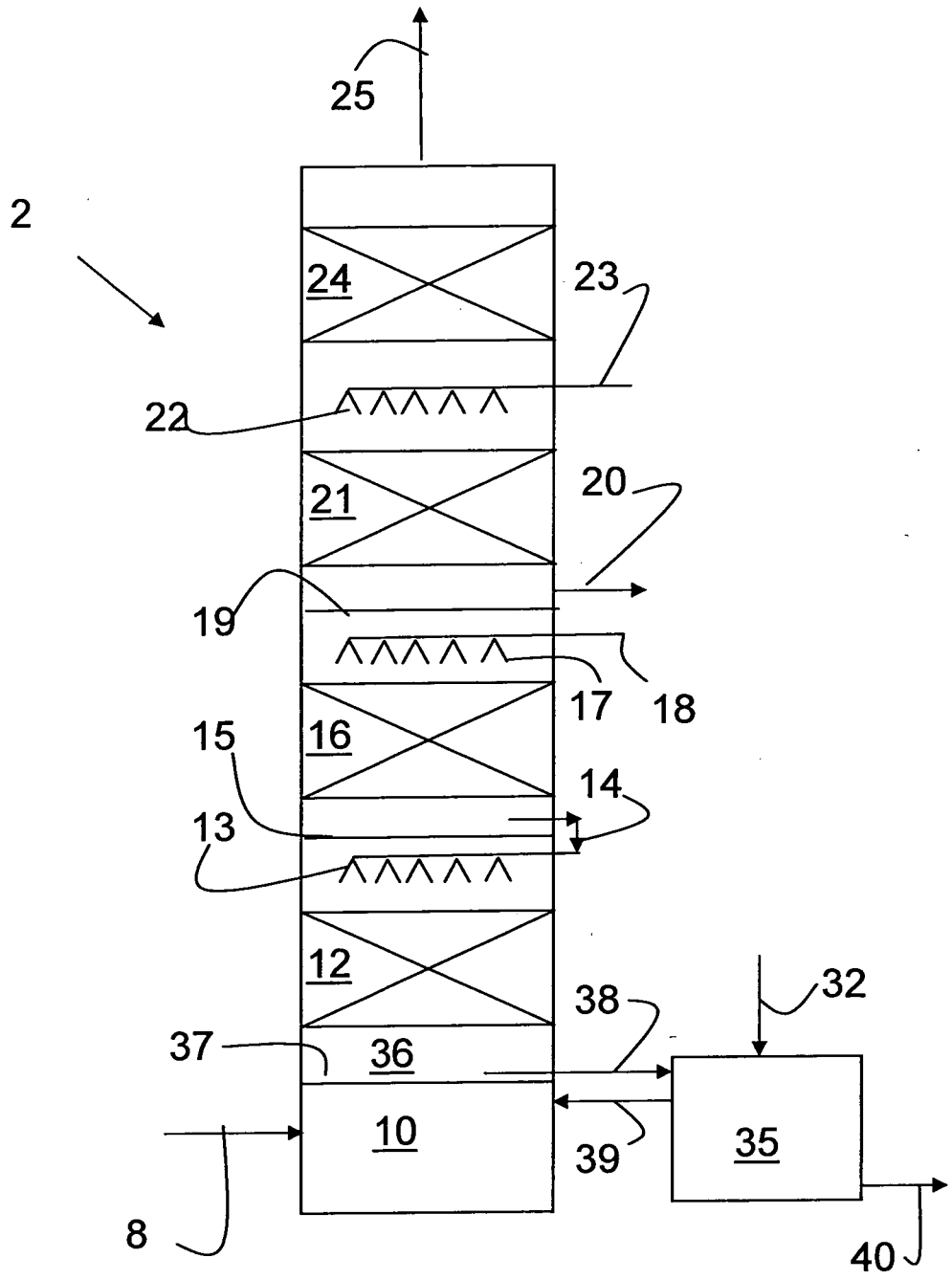


Fig. 4

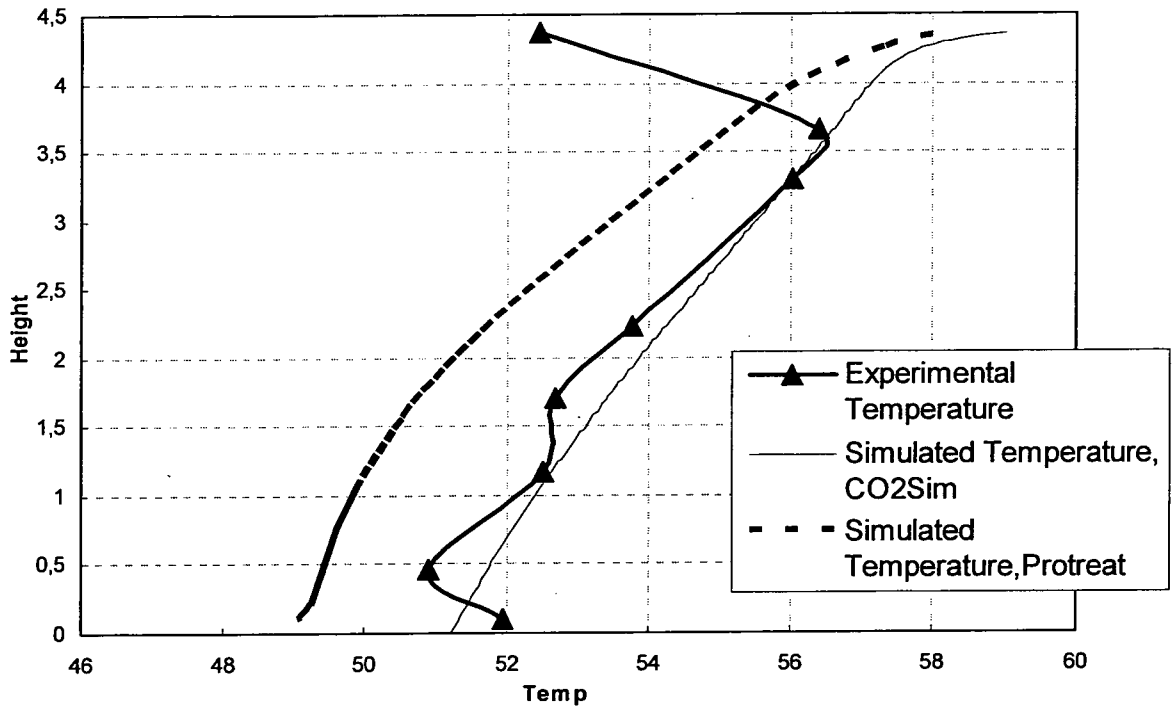

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Temp
Experimental Temperature
Simulated Temperature, CO2Sim
Simulated Temperature,Protreat

Fig. 5

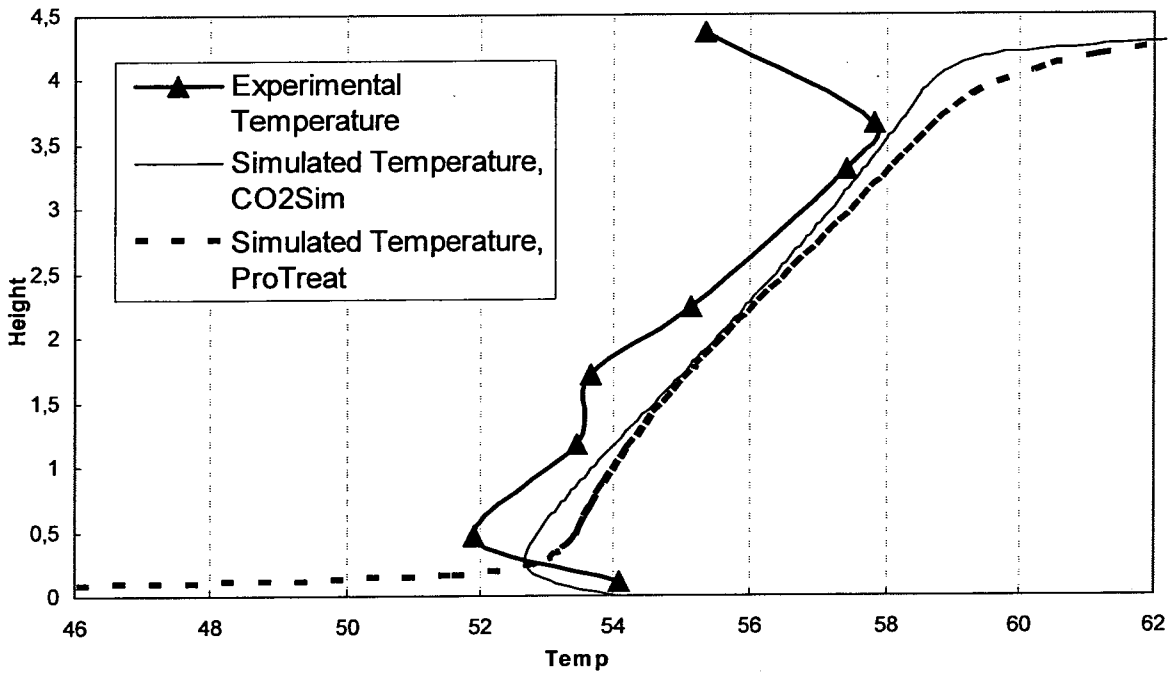

Experimental Temperature
Simulated Temperature, CO2Sim
Simulated Temperature, ProTreat
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Fig. 6

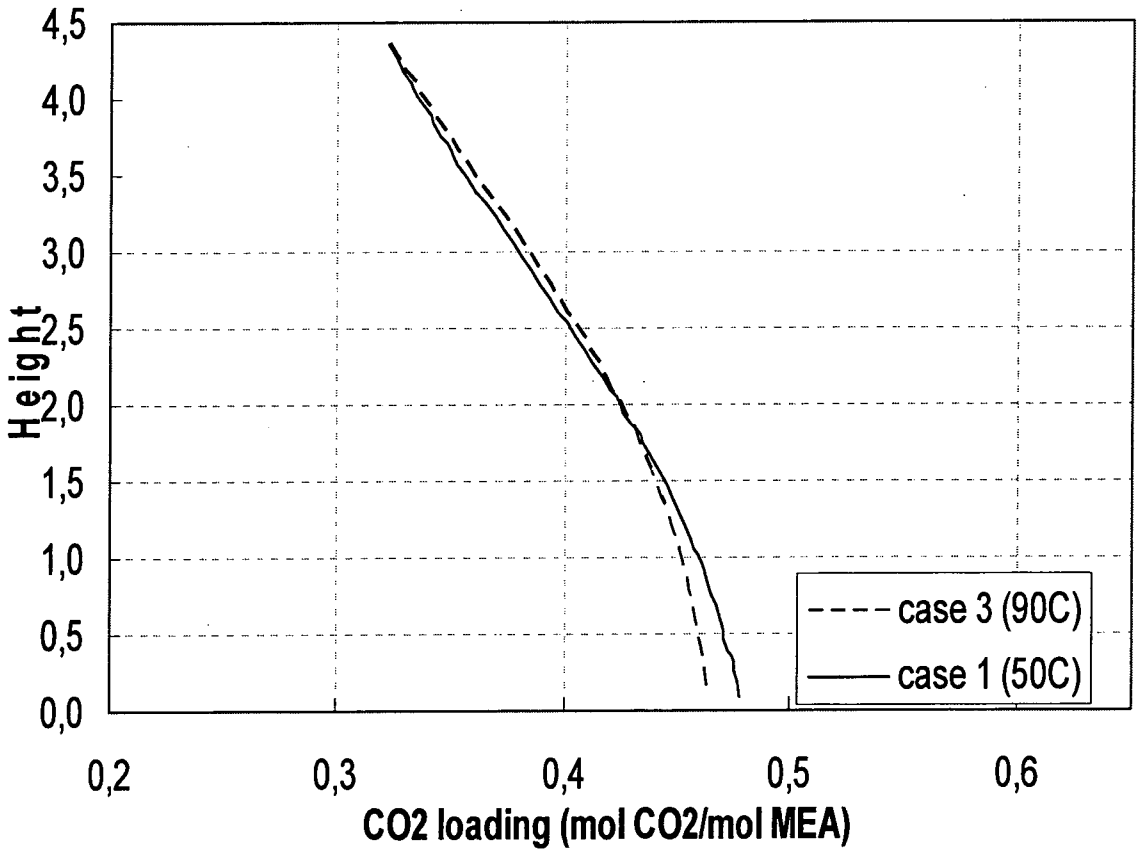

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Height
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0,5
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CO2 loading (mol CO2/mol MEA)
case 3 (90C)
case 1 (50C)

Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/NO2008/000078

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 725 529 A (GIAMMARCO G ET AL) 3 April 1973 (1973-04-03) column 2, line 46 - column 3, line 14 column 11, line 34 - column 12, line 14 figures; example 1	1-4
X	US 4 079 117 A (BUTWELL KENNETH FRANCIS) 14 March 1978 (1978-03-14) column 1, lines 5-18 column 6, lines 9-39	1-4
X	US 3 563 695 A (BENSON HOMER E) 16 February 1971 (1971-02-16) column 3, line 71 - column 4, line 56 column 6, line 62 - column 7, line 2; figures	1-4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
20 June 2008	01/07/2008

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Persichini, Carlo

INTERNATIONAL SEARCH REPORT

International application No
PCT/NO2008/000078

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 331 526 A (INST FRANCAIS DU PETROLE [FR]) 26 May 1999 (1999-05-26) pages 1,2; figures	1-4
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