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(54) Title: NEARLY REVERSIBLE PROCESS FOR THE SEPARATION OF CARBON DIOXIDE FROM COMBUSTION OR PRODUCT GAS

(57) Abstract: The invention relates to a process for separating carbon dioxide from combustion or product gas. Part of the CO_2 of the combustion or product gas is dissolved in a CO_2-dissolving liquid, in a nearly reversible, dissolving process operating on the counter-flow principle, thus forming a CO_2-depleted exhaust gas and a CO_2-enriched liquid. A corresponding portion of the said CO_2 is evaporated from the said liquid to a vapour phase, thus forming a CO_2-enriched separation gas and a CO_2-depleted liquid. A mutual thermal-transfer connection is created between the dissolving and evaporation processes, from the thermal transfer taking place between them.

NEARLY REVERSIBLE PROCESS FOR THE SEPARATION OF CARBON DIOXIDE FROM COMBUSTION OR PRODUCT GAS

The present invention relates to a process for the separation of carbon dioxide from combustion or product gas, in which process:

- part of the CO_2 of the combustion or product gas is dissolved into a CO_2-dissolving liquid, in a nearly reversible dissolving process operating on the counter-flow principle, and
- a corresponding part of the said CO_2 is evaporated from the said liquid into a vapour phase.

In the following description portion and Claims, the words 'dissolution' and 'evaporation' are used in place of the more precise expressions 'dissolution or absorption' and 'evaporation or desorption'.

In the prior art, CO_2 is usually separated from process gas in a dissolution process operating on the counter-flow principle. This process is nearly reversible and produces a liquid phase with a CO_2 content corresponding to a partial pressure that is close to the partial pressure of CO_2 in the original process gas.

The CO_2 is generally evaporated from the vapour phase obtained by heating it (e.g., MEA method, publication DE 606132). The desorption of the CO_2 consumes a large amount of heat, in the MEA method of the order or 1,2 MJ per kilo of CO_2. In the heating process, considerable deviations from reversibility occur and energy is wasted.

A second solution used in the prior art is expansion evaporation, which is applied in, for example, publication DE 843545. In it, compressed blast-furnace gas at 2,5 bar, in which there is 24 % CO_2, is scrubbed with cold methanol and the CO_2 solution obtained is evaporated in two stages at pressures of 0,2 and 0,04 bar. As this type of expansion evaporation is not a reversible process, energy is wasted. In addition, large and expensive compressors are required to compress the CO_2 obtained at the pressure of 0,04 bar.

Vapour stripping is often used to transfer CO_2 from a liquid to gas phase. The publication US 4528811 discloses a 'chemical processor', in which CO_2 is absorbed from the compressed flue gas of air combustion into a solution containing a suitable absorption substance at a pressure of 11 bar and a temperature of 120 - 139 °C. Part of the CO_2 is desorbed by expanding the solution to a pressure of 1,3 bar while the remainder is 'stripped' using 50-psi (3,4-bar) steam, when one pound (0,454 kg) of steam separates 3,45 scf (0,098 Nm^3) of CO_2. 2,32 kg of stripping steam is consumed for each kilo of CO_2 separated by stripping, the enthalpy of the steam consumed being 6,3 MJ for each kilo of CO_2.

Using steam stripping, CO_2 can be separated from the solution precisely and the CO_2-depleted solution obtained can be used to separate the CO_2 almost completely from the process gas. By condensing the mixture of steam and CO_2 obtained in stripping, the latter is obtained at the pressure of the stripping steam used, thus avoiding compression of the low-pressure CO_2. The downside is the high consumption of stripping steam, in this example, 8,5 mols per mol of separated CO_2.

The desorption process can be brought close to reversibility by maintaining a constant pressure in the gas phase using a second gas with a pressure that is independent of the temperature of the column. An example of this is publication FI 111607 (WO 03/035221), in which CO_2, scrubbed from the flue gas to the solution, is transferred to a CO_2 concentrate at a lower pressure by using air scavenging. However, removing the scavenging air from the concentrate demands a complex liquidation process and increases energy consumption. Though the method of the publication is intended to achieve a nearly reversible process, the loss due to air scavenging means that the result remains half-way. On the other hand, if air scavenging is not used, energy-wasting expansion evaporation must be used. In addition, at least some of the separated CO_2 is obtained at a very low pressure, as in the aforementioned publication DE 843545, in which some of the CO_2 is obtained at a pressure of 0,04 bar, despite the fact that the pressure of the process gas is 2,5 bar. This problem is further worsened when processing combustion gas at normal pressure.

In the present invention these problems are avoided by transferring the CO_2 from a liquid phase to a gaseous phase in a nearly reversible evaporation process, the energy required for which being transferred to it from the dissolving process. The reversibility is better than in any known separation process.

In the following, the present invention is described with reference to the accompanying figures.

Figure 1 shows the pressure of CO_2 separated reversibly, without external energy, from 0,15-bar flue gas containing CO_2, as a function of the partial pressure p' of the remaining CO_2 of the flue gas,
Figure 2 shows the cycle process undergone by the liquid phase used in the scrubbing of the flue gas,
Figure 3 shows schematically one example of an application of the invention,
Figure 4 shows a schematically a second example of an application of the invention.

As is apparent from the following examination, the CO_2 separated in such a process is obtained at a substantially higher pressure than the partial pressure of the CO_2 remaining in the flue gas.

If the partial pressure of the CO_2 of the flue gas entering the process at normal pressure is p, the thermodynamic work of separation W(p) of the CO_2, per mol of flue gas, at a constant pressure T, is

$$(1)\ W(p) = -RT\ (p \ln(p) + (1 - p) \ln(1 - p)),$$

in which $R = 8{,}314\ J/(mol\ \ K)$. The term $-RT\ p \ln(p)$ is the work required to compress the separated CO_2 fraction from the pressure P to normal pressure, and the term $-RT\ (1 - p) \ln(1 - p)$ is the work of compressing the remaining flue gas fraction from the partial pressure $1 - p$ back to normal pressure.

In practice, not all of the CO_2 can be separated, as CO_2 at the partial pressure p' will remain in the flue gas. The part of the work of separation corresponding to this remains undone and reduces the value W(p) to the value

$$(2)\ W(p, p') = W(p) - (1 - p + p')W(p').$$

If the separated CO_2 is recovered at a pressure q, which is lower than normal pressure, the work of separation is then reduced to the value

$$(3)\ W(p, p', q) = W(p, p') - RT\ (p - p') \ln(q),$$

in which the last term is the work that is released in the isothermic compression of the separated CO_2 fraction from normal pressure to the pressure q.

By selecting q so that W(p, p', q) equals 0, the separation process can, in principle, be performed without external energy. Figure 1 shows the pressure of CO_2 separated reversibly, without external energy, from 0,15-bar flue gas containing CO_2, as a function of the partial pressure p' of the remaining CO_2 of the flue gas.

If $p = 0,15$ bar then $q = 0,060$ bar, in other words, if there is 0,15-bar CO_2 in the flue gas, it can be separated isothermically, in a reversible process without external energy, as a CO_2 fraction, with a pressure of 0,06 bar. When the partial pressure p' increases, W (p, p', q) increases and the pressure q correspondingly increases. For example, by leaving 0,06 bar of CO_2 in the flue gas, the pressure of the separated CO_2 increases from 0,06 bar to 0,091 bar, i.e. by 52 %. This is a substantial improvement, as the dimensions of the separation column and the CO_2 compressor are correspondingly reduced and the CO_2 compressor will require less energy. The price of this advantage is that the theoretical separation efficiency is reduced, in this example from 100 % to 60 %.

Figure 1 and this example demonstrate how, in this invention, the separation efficiency of the process and the pressure level of the separated CO_2 can be selected to achieve the best result. The method described below in application example 2, in which the pressure level of the separated CO_2 can be increased by utilizing the vapour evaporated from the scrubbing liquid, can be added to this. This shows how the conditions of the invention can be optimized to achieve the best possible economic result.

In this invention, the separation of the CO_2 does not take place isothermically, but instead in a specific temperature range. The temperature range in question is, however, small compared to the absolute temperature, being in the order of 1 - 3 %, so that the process nearly conforms to the principles described above.

Both the scrubbing of the CO_2 from the flue gas and its evaporation from the solution obtained are best performed in a column structure with a sufficient number of theoretical plates so that the deviations from reversibility caused by the mixing and heat exchange between the liquid and gas phases at different heights can be kept sufficiently small.

The present invention is described with the aid of the following examples of applications.

Application example 1

Figure 2 shows the cycle process undergone by the liquid phase used in the scrubbing of the flue gas. The abscissa is the CO_2 content x of the liquid and the ordinate the temperature T of the liquid. At point 1, the liquid has undergone the flue-gas CO_2 dissolving process in the counter-flow column and its CO_2 content corresponds to the partial pressure of the CO_2 entering the dissolving process at the final temperature T_1 of the solution. The liquid is then cooled in part 1 - 2 to the temperature T_2, after which some of the CO_2 is evaporated at a constant pressure on the isobar 2 - 3 as the temperature rises to T_1. Next, the liquid is cooled back to the temperature T_2 in part 3 - 4, the liquid then dissolving the CO_2 from the flue gas, as its temperature rises to T_1 (part 4 - 1).

In practice, the evaporation process must be performed at a slightly lower temperature than the dissolving, to allow the heat released in the dissolving to be transferred to the evaporation. The evaporation thus takes place in practice in the range(T_2 -ΔT) - (T1 - ΔT), in which ΔT is in the order of 1...3 °C. The amount of energy transferred from the dissolving to the evaporation, per kilo of CO_2 separated is 1,2 MJ when using MEA and 0,6 MJ when using carbonate.

Figure 3 shows a diagram of the separation process. The flue gas flows upwards in a dissolving column 11 while the scrubbing liquid flows against it, until the scrubbed flue gas exhausts from the top of the column. The CO_2 enriched scrubbing liquid flows first through a heat-exchanging coil 15 in the bottom of the evaporation column 12 and then through a heat exchanger 14, which transfers most of the heat released in the dissolving to the evaporation. The liquid that has been further cooled in the cooler 17 is sprayed to the top of the evaporation column 12, where it flows downwards and warms while part of its CO_2 is simultaneously evaporated. The depleted scrubbing liquid is led from the bottom of the column 12 to the heat exchanger 13 and from there to the top of the dissolving column 11. The evaporation of a CO_2 flow of 1 mol/s requires a heat flux of 26 kW when using a carbonate solution. If this CO_2 flow is separated from a solution flow, the thermal capacity flow of which corresponds to 1 kg/s of water, the heat flux in question can then be transferred entirely from the dissolving to the evaporation in the heat exchangers 14 and 15, if $T_1 - T_2 = 6{,}2$ °C. Part of the heat flux can also be transferred, for example, by circulating the scrubbing liquid, collected in the base of the dissolving column 11, in a heat exchanger (not shown) located in the evaporation column 12, or by constructing the columns 11 and 12 with a heat-transfer connection with each other (Figure 4).

Nearly reversible evaporation of CO_2 requires the partial pressure of the CO_2 in the gas phase in the evaporation column to remain, at each height, in equilibrium with the CO_2 content of the liquid phase. In addition, the total pressure of the vapour phase must be the same at all points in the column. In this example, this is realized by the vapour phase consisting of only CO_2, the pressure of which remains constant during evaporation.

Application example 2

In this example, part 2 - 3 of the cycle process of Figure 2 is performed in such a way that the partial pressure of the CO_2 drops as the evaporation progresses, but the pressure of the water vapour evaporating from the solution correspondingly increases as the solution heats. In this example, the solvent used is a 5 N solution of MEA in water and the process is performed in the double column of Figure 4. The mixture of CO_2 and water vapour leaving the process at a temperature of $T_1 - \Delta T$ (Figure 2) is led to an additional column 16, in which the water vapour condenses and from which the CO_2 exhausts.

A good heat-transfer connection is built between the dissolving part 11 and the evaporating part 12 of the double column 10. The final temperature of the dissolving is 50 °C, at which the degree of saturation of the MEA solution in equilibrium with the partial pressure of the 0,15-bar CO_2 is 50 % (Ullmanns Encyklopädie der technische Chemie, 3. Aufl., 9. Band, s. 766). Evaporation begins at 42,5 °C, at which the partial pressure of the CO_2 of the solution is 0,075 bar and the partial pressure of the water vapour is 0,082 bar. The CO_2 content of the solution flowing downwards in the evaporating part 12 decreases simultaneously with an increase in the partial pressure of the water vapour evaporating from it, until at the bottom of the evaporating part it is 0,115 bar at a temperature of 48,50 °C. These values make no allowance for the fact that the vapour pressure of the MEA solution is slightly lower than that of pure water. A distillation column, in which the upwards flowing mixture of CO_2 and water vapour cools, while part of the water vapour simultaneously condenses, acts as the evaporating part. The mixture flow then rises in the additional column 16, in which a dephlegmator 18 condenses most of the water vapour. The energy for this distillation process is obtained form the flue gas entering the separation in a saturated state, which arrives at the process at a temperature of more than 50 °C and leaves it at about 45 °C. The total pressure of the CO_2 exhausting from the top of the additional column at 15 °C is 0,157 bar, of which 0,015 bar is water vapour. The partial pressure of the CO_2 of the CO_2-depleted solution transferring from the evaporation part to the dissolving part is 0,021 bar, so that the theoretical separation efficiency of the CO_2 is 86 %. Heat leaves the process in the coolers 17 and 18. Part of the condensate water created must also be removed.

As is apparent from the above description and the examples of applications disclosed, the implementation variations of this invention are extremely diverse and are thus not restricted to the examples depicted above.

Compared to the prior art, the nearly reversible separation process of this invention offers the following advantages:

- the energy consumption of the process is close to the minimum value characteristic to thermodynamically reversible processes,
- even though the CO_2 is condensed using the energy obtained from its dissolving, it is obtained at a pressure substantially higher than the partial pressure of the CO_2 remaining in the flue gas,
- it is possible to utilize the thermal energy of the flue gas to increase the pressure level of the separated CO_2 (example 2).

CLAIMS

1. Process for separating carbon dioxide from combustion or product gas, in which process:

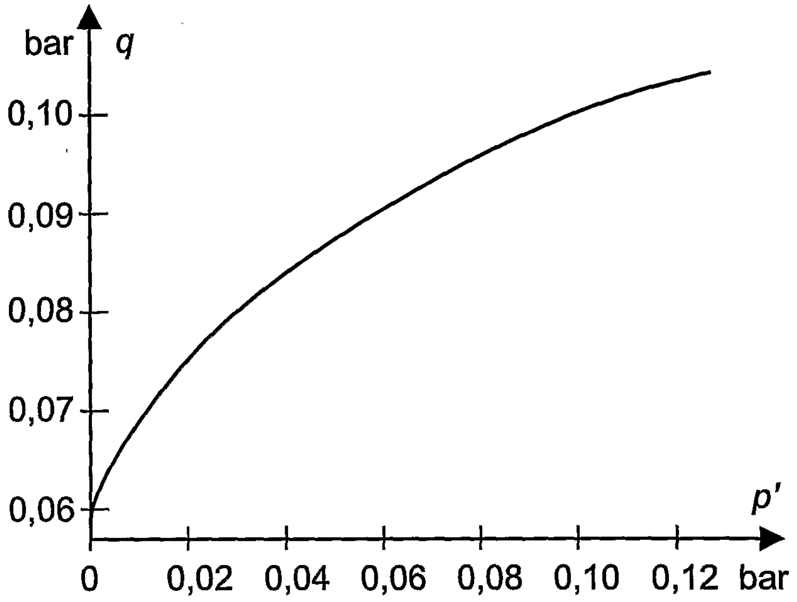
- part of the CO_2 of the combustion or product gas is dissolved in a CO_2-dissolving liquid, in a nearly reversible dissolving process operating on the counter-flow principle, thus forming a CO_2-depleted exhaust gas and a CO_2-enriched liquid, and
- a corresponding portion of the said CO_2 is evaporated from the said liquid to a gas phase, thus forming a CO_2-enriched separation gas and a CO_2-depleted liquid, and
- a mutual thermal-transfer connection is created between the dissolving and evaporation processes so that the main part of the heat transfer takes place between them, characterized in that
- the said CO_2-dissolving liquid undergoes a nearly reversible cycle process, in which cycle process:
- the CO_2-enriched liquid exiting from and heated in the said dissolving process is cooled before evaporation, in part with the aid of external cooling, to a temperature slightly lower than the initial temperature of the said dissolving process, in order to create the gradation ΔT required by the said mutual thermal transfer, and
- the said CO_2-enriched liquid is caused to flow downwards and evaporated in a thermodynamic equilibrium with an upward-flowing gas phase that is at a lower pressure than the pressure of the said combustion or product gas,
- the said downward-flowing CO_2-enriched liquid is heated as a result of the heat obtained from the said dissolving process, so that part of the CO_2 of the heating liquid transfers to the gas phase, until the temperature of the said liquid has increased to a value slightly lower than the final temperature of the said dissolving process, and

- the said depleted liquid is cooled to a temperature slightly lower than the initial temperature of the said dissolving process, and
- the said CO_2-depleted liquid is returned to the said nearly reversible dissolving process, and
- the said gas phase exhausts from the evaporation column as the said CO_2 separation gas.

2. Process according to Claim 1, <u>characterized</u> in that, in cases where the gas phase evaporating in the said evaporation process contains a substantial amount of vapour evaporated from the said solution, the said vapour phase undergoes a nearly reversible distillation process, in which most of the said vapour condenses and from which the CO_2 is obtained in a nearly pure form, at the total pressure of the said vapour phase.

3. Process according to either of Claims 1 - 2, <u>characterized</u> in that the said dissolving and evaporation processes are performed in a double column, the dissolving and evaporation portions of which are in an efficient mutual thermal-transfer connection.

4. Process according to any of Claims 1 - 3, <u>characterized</u> in that the height, flow cross-sectional surfaces, and flow connections of the columns used in the process are matched to each other in such a way that the mass and thermal transfer between the vapour and liquid flows at different heights in them remains sufficiently small to preserve the nearly reversible nature of the separation process.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q
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0,09
0,08
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0,06
p'
0
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0,06
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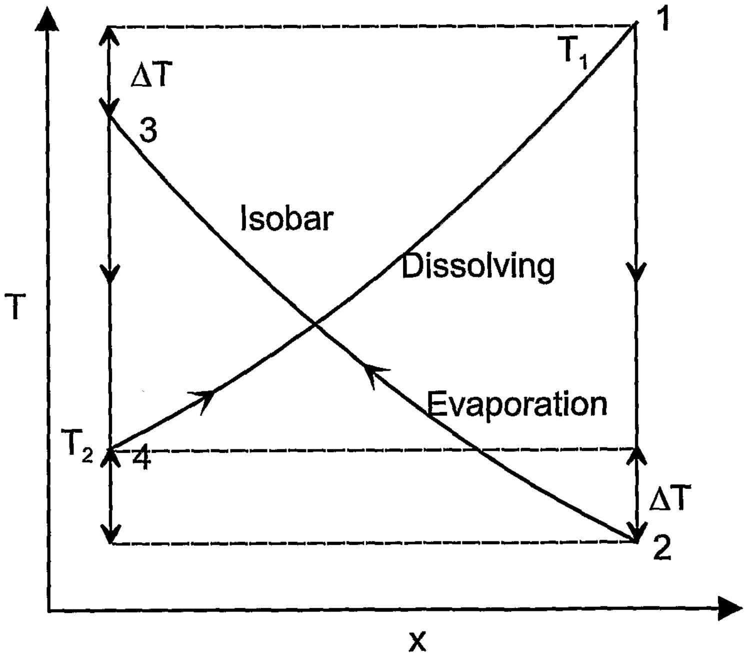
0,10
0,12
bar

Fig. 1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T1
ΔT
3
Isobar
Dissolving
T
Evaporation
T2
4
ΔT
2
x

Fig. 2

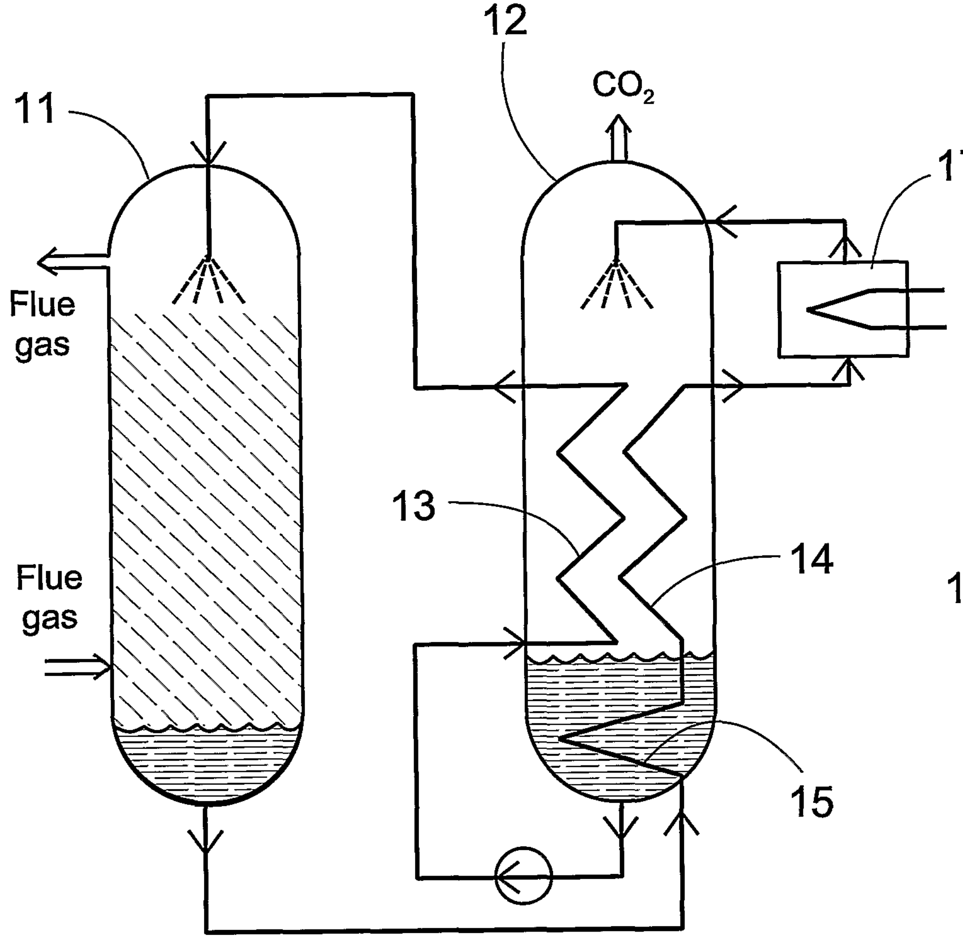
11
12
CO$_2$
17
Flue gas
Flue gas
13
14
15

Fig. 3

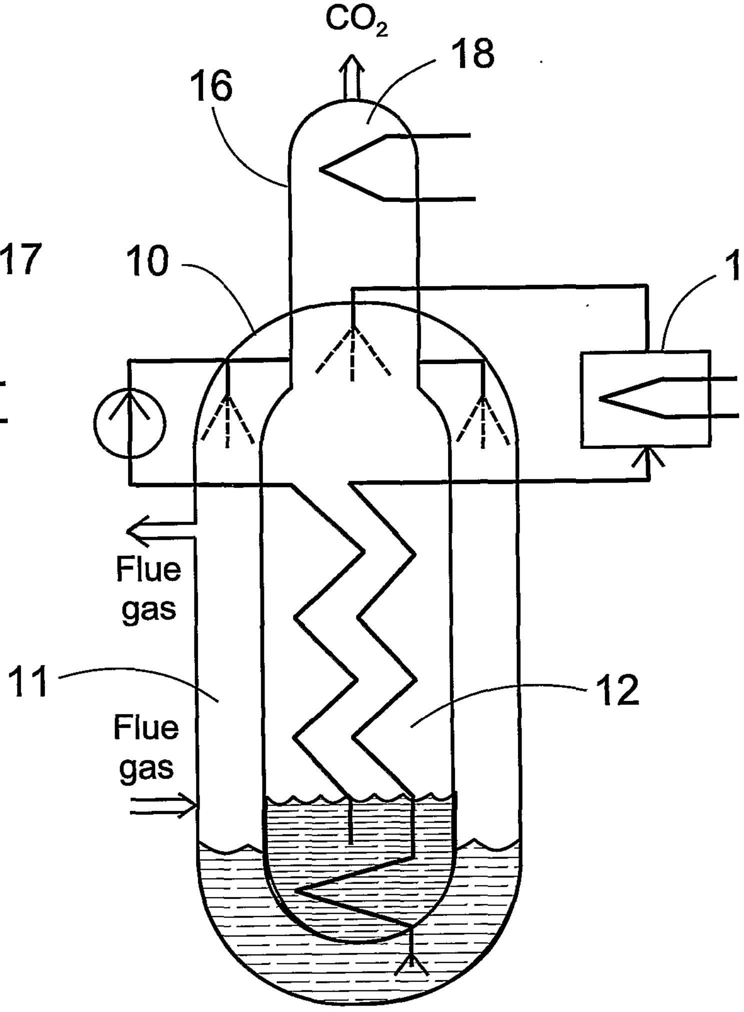
CO$_2$
18
16
10
17
Flue gas
11
Flue gas
12

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 2005/050075

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B01D 53/62, B01D 53/14
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)

IPC7: B01D

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

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 0204098 A1 (NURMIA, WENDIE), 17 January 2002 (17.01.2002) --	1-4
A	WO 03035221 A1 (NURMIA, WENDIE), 1 May 2003 (01.05.2003) -- --------	1-4

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

30/04/2005

International application No.
PCT/FI 2005/050075

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