



(51) International Patent Classification:  
**B01D 53/047** (2006.01)

(21) International Application Number:  
PCT/US2012/043474

(22) International Filing Date:  
21 June 2012 (21.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant (for all designated States except US):  
**PRAXAIR TECHNOLOGY, INC.** [US/US]; 39 Old  
Ridgebury Road, Danbury, CT 06810 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KUMAR, Ravi**  
[US/US]; 153 Wedgewood Drive, Williamsville, NY  
14221 (US). **ROSINSKI, Andrew, C.** [US/US]; 6262  
Seufert Road, Orchard Park, NY 14127 (US).

(74) Agents: **BLACK, Donald, T.** et al.; Praxair, Inc., 39 Old  
Ridgebury Road, Danbury, CT 06810 (US).

(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,

CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO,  
DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,  
HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR,  
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,  
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,  
OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD,  
SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR,  
TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,  
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,  
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,  
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,  
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

— as to applicant's entitlement to apply for and be granted a  
patent (Rule 4.17(ii))

**Published:**

— with international search report (Art. 21(3))

(54) Title: ADSORPTION PROCESS TO RECOVER CARBON DIOXIDE FROM FLUE GAS

(57) Abstract: The present invention generally relates to vacuum pressure swing adsorption (VPSA) processes and apparatus to recover carbon dioxide having a purity of approximately  $\geq 80$  mole percent from streams containing at least carbon dioxide and nitrogen, such as the gaseous products of combustion (i.e. flue gas). The feed to the CO<sub>2</sub> VPSA can be at superambient pressure. The CO<sub>2</sub> VPSA unit produces a CO<sub>2</sub> product stream. The process cycle generates a high-pressure product stream that can be used to generate power for compressing the feed stream. The recovered CO<sub>2</sub> can be further upgraded, sequestered or used in applications such as enhanced oil recovery (EOR). BACKGROUND OF THE INVENTION Many industrial operations employ combustion of fuel. Examples include kilns, incinerators, glassmaking furnaces, coal-fired power plants, and the like. Combustion of fuel produces streams of gaseous combustion products that comprise at least carbon dioxide, usually accompanied by nitrogen and one or more of oxygen, oxides of nitrogen and/or sulfur, and carbon monoxide. It would be desirable to provide economically beneficial processes and apparatus for CO<sub>2</sub> recovery. It would further be desirable for such processes and apparatus to be more efficient and easier to use relative to the prior art.



## **ADSORPTION PROCESS TO RECOVER CARBON DIOXIDE FROM FLUE GAS**

### **FIELD OF THE INVENTION**

The present invention generally relates to vacuum pressure swing adsorption (VPSA) processes and apparatus to recover carbon dioxide having a purity of approximately  $\geq 80$  mole percent from streams containing at least carbon dioxide and nitrogen, such as the gaseous products of combustion (i.e. flue gas). The feed to the CO<sub>2</sub> VPSA can be at superambient pressure. The CO<sub>2</sub> VPSA unit produces a CO<sub>2</sub> product stream. The process cycle generates a high-pressure product stream that can be used to generate power for compressing the feed stream. The recovered CO<sub>2</sub> can be further upgraded, sequestered or used in applications such as enhanced oil recovery (EOR).

### **BACKGROUND OF THE INVENTION**

Many industrial operations employ combustion of fuel. Examples include kilns, incinerators, glassmaking furnaces, coal-fired power plants, and the like. Combustion of fuel produces streams of gaseous combustion products that comprise at least carbon dioxide, usually accompanied by nitrogen and one or more of oxygen, oxides of nitrogen and/or sulfur, and carbon monoxide.

It would be desirable to provide economically beneficial processes and apparatus for CO<sub>2</sub> recovery. It would further be desirable for such processes and apparatus to be more efficient and easier to use relative to the prior art.

**SUMMARY OF THE INVENTION**

One embodiment of the present invention is a vacuum pressure swing adsorption (VPSA) process for the recovery of carbon dioxide from a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no hydrogen or no more than a trace amount of hydrogen, and which is at a pressure in a first superatmospheric pressure range, in a VPSA unit containing at least one adsorption bed containing at least one CO<sub>2</sub>-selective adsorbent, the process comprising:

feeding said multi-component gas mixture to the at least one adsorption bed at a first pressure within said first superatmospheric pressure range for a predetermined time to adsorb carbon dioxide onto said adsorbent;

depressurizing the at least one adsorption bed in a first depressurization step from the first pressure to a second pressure that is lower than said first pressure and is within a second pressure range, in a same direction as or an opposite direction to the feed flow;

depressurizing the at least one adsorption bed in a second depressurization step from the second pressure to a third pressure that is lower than said second pressure and is within a third pressure range, in a same direction as or an opposite direction to the feed flow;

depressurizing the at least one adsorption bed in a third depressurization step from the third pressure to a fourth pressure that is lower than said third

pressure and is within a fourth pressure range, in a same direction as or an opposite direction to the feed flow;

depressurizing the at least one adsorption bed in a final depressurization step from the fourth pressure to a pressure that is within a range close to ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce at least a first portion of CO<sub>2</sub> product;

evacuating the at least one adsorption bed from the pressure that is within a range close to ambient to a pressure below ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce at least a second portion of CO<sub>2</sub> product;

pressure equalizing the at least one adsorption bed in a first pressure equalization step in a same direction as the feed flow or in a direction opposite to the feed flow;

further pressure equalizing the at least one adsorption bed in a second pressure equalization step in a same direction as the feed flow or in a direction opposite to the feed flow;

further pressure equalizing the at least one adsorption bed in a third pressure equalization step in a same direction as the feed flow or in a direction opposite to the feed flow; and

repressurizing the at least one adsorption bed in a repressurization step to a pressure in the first pressure range;

wherein the process is repeated cyclically.

Another embodiment of the present invention is a vacuum pressure swing adsorption (VPSA) process for the recovery of carbon dioxide from a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no hydrogen or no more than a trace amount of hydrogen, and which is at a pressure in a first superatmospheric pressure range, in a VPSA unit containing at least one adsorption bed containing at least one CO<sub>2</sub>-selective adsorbent, the process comprising:

feeding said multi-component gas mixture to the at least one adsorption bed at a first pressure within said first superatmospheric pressure range for a predetermined time to adsorb carbon dioxide onto said adsorbent;

venting the at least one adsorption bed in a first depressurization step from the first pressure to a second pressure that is lower than said first pressure and is within a second pressure range, in a same direction as or an opposite direction to the feed flow, to produce a vent stream that can be released into the atmosphere;

depressurizing the at least one adsorption bed in a final depressurization step from the second pressure to a pressure that is within a range close to ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce at least a first portion of CO<sub>2</sub> product;

evacuating the at least one adsorption bed from the pressure that is within a range close to ambient to a pressure below ambient in a same direction as the feed flow or in a direction opposite to the feed flow

to produce at least a second portion of CO<sub>2</sub> product;  
and

repressurizing the at least one adsorption bed in  
a repressurization step to a pressure in the first  
pressure range;

wherein the process is repeated cyclically.

Yet another embodiment of the present invention is  
a vacuum pressure swing adsorption (VPSA) process for  
the recovery of carbon dioxide from a multi-component  
gas mixture which contains at least carbon dioxide and  
nitrogen and contains no hydrogen or no more than a  
trace amount of hydrogen, and which is at a pressure in  
a first superatmospheric pressure range, in a VPSA unit  
containing at least one adsorption bed containing at  
least one CO<sub>2</sub>-selective adsorbent, the process  
comprising:

feeding said multi-component gas mixture to the at  
least one adsorption bed at a first pressure within  
said first superatmospheric pressure range for a  
predetermined time to adsorb carbon dioxide onto said  
adsorbent;

depressurizing the at least one adsorption bed  
from the first pressure to a pressure that is within a  
range close to ambient in a same direction as the feed  
flow or in a direction opposite to the feed flow to  
produce a vent stream that can be released into the  
atmosphere;

evacuating the at least one adsorption bed from  
the pressure that is within a range close to ambient to  
a pressure below ambient in a same direction as the  
feed flow or in a direction opposite to the feed flow  
to produce a CO<sub>2</sub> product; and

repressurizing the at least one adsorption bed in a repressurization step to a pressure in the first pressure range;

wherein the process is repeated cyclically.

In preferred embodiments, carbon dioxide is recovered by compressing a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no more than a trace amount of hydrogen, to a pressure in a first superatmospheric pressure range, and recovering carbon dioxide from said compressed mixture in a VPSA unit by any of the processes described herein, wherein an effluent gas stream is recovered from said VPSA unit and is expanded to provide power that is used in compressing said multi-component gas mixture.

The present invention generally relates to vacuum pressure swing adsorption (VPSA) processes and apparatus to recover carbon dioxide having a purity of approximately  $\geq 80$  mole percent from streams containing at least carbon dioxide and nitrogen, and little or no hydrogen. The feed to the CO<sub>2</sub> VPSA is at superatmospheric pressure (i.e. pressure higher than atmospheric). The CO<sub>2</sub> VPSA unit produces a CO<sub>2</sub> product stream, as well as one or more other streams that can be used as described herein, such as to provide power that can be used to compress the feed to the VPSA unit.

CO<sub>2</sub> produced in accordance with the present invention may be used for any desired purpose. For example and while not to be construed as limiting, CO<sub>2</sub> produced as described herein can be further purified

and used in food-grade quality product(s), or can be used for enhanced oil recovery or other industrial processes, or can simply be sequestered to avoid addition of greenhouse gases to the atmosphere.

The present invention utilizes depressurizations of an adsorbent from high pressure to low pressure to increase CO<sub>2</sub> concentration in the bed(s). After CO<sub>2</sub> concentration is increased, CO<sub>2</sub> product is produced by further pressure reduction. This can be accomplished because of the recognition that for some adsorbents, depressurization from high to low pressure increases CO<sub>2</sub> concentration in the adsorbent bed(s).

Consequently, the need for rinse, purge and/or recycle steps as used in the prior art can be eliminated. This in turn allows for the elimination of certain pieces of rotating machines (e.g., rinse compressor, purge compressor, recycle compressor) and associated power requirements, thereby providing a process and apparatus which is simpler to operate and more economical than prior art systems. The proposed processes do not require steam and thus are expected to reduce the cost of CO<sub>2</sub> separation.

To increase CO<sub>2</sub> recovery, a preferred embodiment of the present invention uses the depressurized gas to build up or increase the pressure in lower-pressure beds. The bed depressurization therefore increases CO<sub>2</sub> concentration in the product and by equalizing with other beds in the unit, at the same time, increases CO<sub>2</sub> recovery.

By eliminating the hardware (i.e. rotating machinery) as mentioned hereinabove, and corresponding power requirements, the present invention is expected

to more efficiently produce CO<sub>2</sub> from flue gas and other streams containing at least carbon dioxide and nitrogen, relative to the prior art.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

For a more complete understanding of the present invention and the advantages thereof, reference should be made to the following Detailed Description taken in conjunction with the accompanying drawings in which:

Figure 1 illustrates embodiments of the present invention in which a CO<sub>2</sub> VPSA unit in accordance with the present invention is incorporated with a unit that uses a high-pressure gas stream from the VPSA unit to generate power used to compress a feed stream to the VPSA unit.

Figure 2 illustrates a cycle step chart for a CO<sub>2</sub> VPSA unit in accordance with the present invention having six beds and three pressure equalization steps.

Figure 3 shows a schematic drawing for the CO<sub>2</sub> VPSA unit of Figure 2.

Figure 4 shows the valve sequence for operation of the CO<sub>2</sub> VPSA unit shown in Figures 2 and 3.

Figure 5A and 5B illustrate cycle step charts for additional embodiments of a CO<sub>2</sub> VPSA unit in accordance with the present invention, having four beds.

Figure 6 shows a schematic drawing for the CO<sub>2</sub> VPSA unit useful in the embodiments of Figures 5A and 5B.

Figures 7A and 7B show valve sequences for operation of a CO<sub>2</sub> VPSA unit shown in Figure 6 to practice the embodiments shown in Figures 5A and 5B.

Figure 8 illustrates a cycle step chart for another embodiment of a CO<sub>2</sub> VPSA unit in accordance with the present invention, having three beds.

Figure 9 shows a schematic drawing for the CO<sub>2</sub> VPSA unit of Figure 8.

Figure 10 shows the valve sequence for operation of the CO<sub>2</sub> VPSA unit shown in Figures 8 and 9.

#### **DETAILED DESCRIPTION**

In a preferred embodiment of the present invention and as illustrated in Figure 1, stream 4 containing at least carbon dioxide and nitrogen is obtained from combustion unit 1. Examples of combustion unit 1 include kilns (such as are employed in manufacture of lime or cement), coal-fired boilers in power plants, glassmelting furnaces, and incinerators. Stream 4 is produced by combustion of carbonaceous fuel 2 (such as oil, coal, natural gas, and the like) in combustion unit 1 with oxidant 3 which can be air, oxygen-enriched air having an oxygen content higher than that of air, streams of oxygen having an oxygen of 90 vol.% or higher, or even streams containing oxygen but at a content less than that of air.

Stream 4 is cooled in heat exchanger 5, from its elevated temperature imparted by the combustion, to a temperature on the order of 30-70C. Stream 4 is then compressed, as represented by compressor 7, to a pressure in the range of 100-500 psia. The resulting high-pressure stream 6 is cooled, preferably in heat exchanger 5, to a temperature on the order of 30-70C.

The stream formed in combustion unit 1 typically contains impurities that should be removed from the stream before the stream is processed by the VPSA

process of the present invention. Impurities typically include one or more of oxides of sulfur, oxides of nitrogen, and/or water vapor. Impurities that are present may be removed before or after compression in unit 7. For instance, oxides of sulfur are preferably removed by scrubbing with an aqueous solution of soda ash, upstream of compressor 7. Oxides of nitrogen are preferably removed by scrubbing with an aqueous solution of alkali permanganate, downstream of compressor 7. Water vapor is preferably removed in dryers located downstream of compressor 7. Impurity removal, whether carried out in one stage or in more than one stage, is represented by unit 9A representing impurity removal upstream of compressor 7, and by unit 9B representing impurity removal downstream of compressor 7. Unit 9A when present generates stream 10A of removed impurities, and unit 9B when present generates stream 10B of removed impurities.

Compression, cooling and impurity removal, in any sequence, produces feed stream 8 which is fed to VPSA unit 11. Typical characteristics of stream 8 are:

|                         |                                            |
|-------------------------|--------------------------------------------|
| Oxygen content:         | 10 - 20 mole%                              |
| Carbon dioxide content: | 10 - 50 mole%                              |
| Nitrogen content:       | 50 - 90 mole%                              |
| Hydrogen:               | zero or trace (< 1 ppm)                    |
| Carbon monoxide:        | 0 - 5 mole%                                |
| Water vapor:            | Dry to saturated at the<br>feed conditions |
| Pressure:               | 100 - 500 psia                             |
| Temperature:            | 80 - 100°F                                 |

Treatment of stream 8 in VPSA unit 11, in accordance with the present invention, produces product

stream 12 that comprises at least 80 mole% carbon dioxide. Typically the pressure of this stream is 10 to 25 psia. VPSA unit 11 also produces variable-pressure waste stream 14, which typically contains carbon dioxide, nitrogen, carbon monoxide and hydrogen (if any hydrogen is in the feed and is typically at a pressure that can vary between 500 and 15 psia. Stream 14 can be vented to atmosphere, or subjected to further treatment.

VPSA unit 11 also produces high-pressure waste stream 16, which typically contains carbon dioxide, nitrogen, carbon monoxide and hydrogen (if any hydrogen is in the feed) and is typically at a pressure of 100 to 500 psia. Stream 16, to which stream 10B may be added if desired, is preferably heated such as by passage through heat exchanger 5, and is then more preferably passed through expander 13 (such as a turbine) to generate power that is used to drive compressor 7. Stream 20 emerging from expander 13 can be vented to atmosphere or processed further. Stream 20A, which can be a portion or all of stream 20, can be fed (e.g. periodically) to the dryers used for removal of water vapor, to regenerate the dryers.

The present invention recognizes that depressurizations of a CO<sub>2</sub>-selective adsorbent layer increases the CO<sub>2</sub> concentration in the adsorbent bed(s), even when the feed stream contains no hydrogen. More specifically, the present invention recognizes and utilizes depressurizations of an adsorbent from high pressure (e.g., 100-500 psia) to low pressure(s) (i.e., close to ambient and/or subambient pressures) to increase CO<sub>2</sub> concentration in the bed.

As used herein, a "feed stream" being fed to a CO<sub>2</sub> unit in accordance with the present invention is a stream containing at least carbon dioxide (CO<sub>2</sub>) and nitrogen at a pressure between about 100-500 psia (e.g., 375 psia). After the CO<sub>2</sub> concentration is increased by multiple depressurizations, it can be used to produce the CO<sub>2</sub> product by further pressure reduction. For some adsorbents, depressurization from high to low pressure increases CO<sub>2</sub> concentration in the adsorbent bed. This step in the process can be used to eliminate several process steps as described in the prior art. Consequently, several pieces of rotating machinery (e.g., rinse compressor, purge compressor, recycle compressor) and associated power requirements can be eliminated, thus providing a process and system that enhances operation and improves efficiency.

At any time during any of these processes, the beds will be in one of the following categories of steps: feed, depressurization (including a venting step), evacuation, pressure equalizations, and repressurization.

In other alternative embodiments of the present invention, the CO<sub>2</sub> VPSA processes and apparatus can be used to produce CO<sub>2</sub> having a purity of about 80 mole percent from the aforementioned feed gas, employing only one or two depressurizations followed by evacuation and repressurization, without any pressure equalization steps. At any time during any of these processes, the beds will be in one of the following categories of steps: feed, depressurization (including a venting step), evacuation, and repressurization.

In any of the embodiments, each bed is preferably packed with at least two layers of adsorbents. The type and sizing of the adsorbent layer toward the feed end (i.e. a water-selective adsorbent layer) in the bed is selected to remove moisture in the feed stream such that any residual moisture does not deteriorate the performance of the main (i.e., CO<sub>2</sub>-selective) adsorbent layer. The water-selective adsorbent layer is also preferably capable of removing impurities (e.g., trace amounts of sulfur or heavy hydrocarbon compounds) from the feed stream, to the extent such impurities are present. The main, second adsorbent layer (i.e., the CO<sub>2</sub>-selective adsorbent layer) is used for selectively adsorbing CO<sub>2</sub> from the feed stream after sufficient moisture has been removed.

For the first adsorbent layer (i.e. the water-selective adsorbent layer, adsorbents such as activated alumina, silica gel or zeolite molecular sieve are preferred. These adsorbents are intended to be illustrative and other adsorbents capable of removing sufficient moisture are also suitable for use in accordance with the present invention. Preferred characteristics for such adsorbent(s) include: high crush strength capabilities, high attrition resistance, large bulk density, low inter-particle void, high heat capacity, large thermal conductivity, low-pressure drop and stable in liquid water.

The main layer of adsorbent (i.e., the CO<sub>2</sub>-selective adsorbent layer) following the water-selective adsorbent layer preferably has the following characteristics: high selectivity, high working capacity, fast kinetics and low heat of adsorption.

Typical examples of such adsorbents include, but are not limited to: are NaY, HY, NaX, silica gel, and activated carbon. Other desired physical properties of the main layer adsorbent (i.e. the CO<sub>2</sub>-selective layer) include: high crush strength, high attrition resistance, large bulk density, low inter-particle void, high heat capacity, large thermal conductivity and low-pressure drop during the feed and evacuation steps.

Those skilled in the art will appreciate that a composite mixed layer containing both adsorbents could be used in the present invention so long as the characteristics of the adsorbents are satisfied.

#### 6 Bed Cycle

Referring now to Figures 2-4, a first embodiment of the present invention having six beds (A1-A6) and using ten steps to produce enriched CO<sub>2</sub> from flue gas is illustrated. The process steps include:

1. Feed Step. A feed stream 8 containing at least carbon dioxide and nitrogen gases and containing trace amounts of hydrogen or no hydrogen, at a high pressure between about 100-500 psia (for example, about 375 psia) is fed to the CO<sub>2</sub> VPSA unit 11 of the present invention. High-pressure feed effluent stream 16 is drawn off from VPSA unit 11. As noted herein, stream 16 can be passed through a turbine in which stream 16 is expanded to produce power that can be used to operate a compressor that compresses the feed. After a predetermined time based upon CO<sub>2</sub> concentration from the VPSA bed, or after CO<sub>2</sub> breakthrough from the bed, this feeding step is terminated.

2. Co-Current (CoC) Depressurization 1 (DP1). The CO<sub>2</sub> VPSA bed, which has finished the feed step is now at high feed pressure (e.g., 100-500 psia), is depressurized to a lower, medium pressure (e.g., 80-400 psia) in a direction the same as (shown in Figure 2) or opposite to (not shown in Figure 2) the feed flow.

3. Co-Current (CoC) Depressurization 2 (DP2). The CO<sub>2</sub> VPSA bed, which is now at some medium pressure (e.g., 80-400 psia), is further depressurized to a lower pressure (e.g., 60-300 psia) in a direction the same as (shown in Figure 2) or opposite to (not shown in Figure 2) the feed flow.

4. Co-Current (CoC) Depressurization 3 (DP3). The CO<sub>2</sub> VPSA bed, which is now at some medium pressure (e.g., 60-300 psia), is further depressurized to a lower pressure (e.g., 50-200 psia) in a direction the same as (shown in Figure 2) or opposite to (not shown in Figure 2) the feed flow.

5. Final Depressurization (DPf). The CO<sub>2</sub> VPSA bed, which is now at a pressure lower than at the start of step 4 (about 50-200 psia) is further depressurized to a pressure close to ambient (about 20 psia) in a direction opposite to (shown in Figure 2) and/or the same as (not shown in Figure 2) the feed flow. The stream recovered from this step constitutes a portion of the CO<sub>2</sub> product.

6. Evacuation. The CO<sub>2</sub> VPSA bed, which is now close to ambient pressure (about 20 psia), is evacuated to a predetermined low pressure, a subambient pressure (about 1-12 psia) in a direction opposite to (shown in Figure 2) or the same as (not shown in Figure 2) to the feed flow. The stream recovered from this step

constitutes another portion, preferably the remaining portion, of the CO<sub>2</sub> product.

7. Countercurrent (CcC) Pressure Equalization 3 (PE3). The evacuated bed is now pressure equalized to a pressure range of the gas produced in step 4 (DP3) (i.e., to about 50-200 psia), preferably employing the gas depressurized in the DP3 step, in a direction the same as (not shown in Figure 2) or opposite (shown in Figure 2) to the feed flow. This step increases CO<sub>2</sub> recovery by keeping the CO<sub>2</sub> from step 4 within the VPSA system. This minimizes CO<sub>2</sub> loss by eliminating the need to send the CO<sub>2</sub> to a waste stream.

8. Countercurrent (CcC) Pressure Equalization 2 (PE2). The bed pressure equalized in step 7 is now pressure equalized to a pressure range of the gas produced in step 3 (DP2) (i.e., to about 60-300 psia), preferably employing the gas depressurized in the DP2 step, in a direction the same as (not shown in Figure 2) or opposite (shown in Figure 2) to the feed flow. This step increases CO<sub>2</sub> recovery by keeping the CO<sub>2</sub> from step 3 within the VPSA system. This minimizes CO<sub>2</sub> loss by eliminating the need to send the CO<sub>2</sub> to a waste stream.

9. Countercurrent Pressure (CcC) Equalization 1 (PE1). The bed pressure equalized in step 8 is further pressure equalized to a pressure range of the gas produced in step 2 (DP1) (i.e., to about 80-400 psia), preferably employing the gas depressurized in the DP1 step, in a direction the same as (not shown in Figure 2) or opposite (shown in Figure 2) to the feed flow. This step further increases CO<sub>2</sub> recovery by keeping the CO<sub>2</sub> from step 2 within the VPSA system. This minimizes

CO<sub>2</sub> loss by eliminating the need to send the CO<sub>2</sub> to a waste stream.

10. Repressurization (FeRP). The pressure-equalized bed is repressurized to a feed pressure (100-500 psia) either by the feed gas or by part of the effluent generated from another bed in step 1 (i.e. feed effluent). Following repressurization to feed pressure, this bed is now ready to go back to step 1.

This ten-step process described is for one cycle for one bed in the CO<sub>2</sub> VPSA unit. The above ten steps are carried out in a cyclic manner with the other beds in the unit such that feed-into and feed-effluent from step 1 are continuous. In addition, the evacuation step (number 6) is designed to be continuous. This ensures that the vacuum pump operates continuously, and that there is no break in feed-into the CO<sub>2</sub> VPSA unit or to unit 13 of Figure 1. Six adsorption beds are utilized in the embodiment described above to maintain the continuity of the key process steps.

Exemplary corresponding hardware and a flow schematic of the CO<sub>2</sub> VPSA process corresponding to the cycle shown Figure 2 is depicted in Figure 3. The various valves in Figure 3 can be operated in the manner illustrated in Figure 4 to carry out the ten steps in the six-bed process as described hereinabove. It should be appreciated that pressures and step durations shown are only for illustrative purposes. Those skilled in the art will appreciate that other combinations of pressures and step durations may be used.

As can be appreciated from the above description, the present invention thus relies upon

depressurizations of at least one CO<sub>2</sub>-selective adsorbent from high pressure to low pressure to increase CO<sub>2</sub> concentration in the bed. After CO<sub>2</sub> concentration is increased, it produces the CO<sub>2</sub> product by further pressure reduction. This became possible based on the discovery that for some adsorbents, pressure reduction from high to low pressure increases CO<sub>2</sub> concentration on the adsorbent.

Alternative and additional exemplary embodiments are illustrated in Figures 5A and 5B through Figure 10. These embodiments do not employ pressure equalization.

#### 4 Bed Cycle

Referring now to Figures 5A through 7B, another embodiment of the present invention has four beds (A1-A4) and uses five steps. The process steps include:

1. Feed Step. A compressed dry flue gas feed stream at a high pressure between about 100-500 psia and purified of impurities is sent to the CO<sub>2</sub> VPSA unit of this embodiment of the present invention. High-pressure feed effluent stream 16 from the CO<sub>2</sub> VPSA unit is preferably sent to a turbine to recover part of the power needed to operate the compressor that compresses the feed stream to its feed pressure. After a predetermined time or after CO<sub>2</sub> breakthrough from the bed on the feed, the feed step is terminated.

2. Co-Current (CoC) Vent. The CO<sub>2</sub> VPSA bed, which has finished the feed step and is now at high feed pressure (e.g., 100-500 psia), is depressurized in a direction the same (shown in Figures 5A and 5B) or opposite (not shown in Figures 5A or 5B) to the feed flow direction. The pressure in the bed at the end of

this step is about 50 - 200 psia and lower than at the end of the feed step.

3. Final Depressurization (DPf). The CO<sub>2</sub> VPSA bed, which is now at the same pressure as at the end of step 2 (about 50-200 psia) is further depressurized to a pressure close to ambient (15-20 psia, preferably about 20 psia) in a direction the same as (not shown in Figures 5A or 5B) or opposite to (shown in Figures 5A and 5B) the feed flow direction. The gas from this step constitutes part of the CO<sub>2</sub> product.

4. Evacuation. The CO<sub>2</sub> VPSA bed, which is now close to ambient pressure (about 20 psia), is evacuated to a predetermined low subatmospheric pressure (about 1-12 psia) in a direction the same as (not shown in Figures 5A or 5B) or opposite to (shown in Figures 5A and 5B) the feed flow direction. The gas from the bed under evacuation constitutes part of the CO<sub>2</sub> product stream.

5. Repressurization (FeRP). The evacuated bed is repressurized to a feed pressure (100-500 psia) either by the feed gas or by part of the effluent (i.e. feed effluent) generated from implementing step 1 on another bed. Following depressurization to feed pressure, this bed is now ready to undergo step 1 again.

The five-step process described above is for one cycle for one bed in the CO<sub>2</sub> VPSA unit. The above five steps are carried out in a cyclic manner with other beds in the unit such that feed-into and feed-effluent from step 1 are continuous. In addition, the evacuation step (step 4) is designed to be continuous. This ensures that the vacuum pump operates

continuously, and that there is no break in feed-into the CO<sub>2</sub> VPSA unit or to unit 13. Four adsorption beds are utilized in the embodiment described above to maintain the continuity of the key process steps.

Exemplary corresponding hardware and a flow schematic of the CO<sub>2</sub> VPSA process corresponding to the cycle shown Figures 5A and 5B is depicted in Figure 6. The various valves in Figure 6 can be operated in the manner illustrated in Figures 7A and 7B to carry out the five steps in the four-bed process as described hereinabove.

### 3 Bed Cycle

Referring now to Figures 8-10, another embodiment of the present invention has three beds (A1-A3) and uses four steps to produce enriched CO<sub>2</sub> from flue gas is illustrated. The process steps include:

1. Feed Step. A compressed dry flue gas feed stream at a high pressure between about 100-500 psia and purified of impurities is sent to the CO<sub>2</sub> VPSA unit of this embodiment of the present invention. High-pressure feed effluent stream 16 from the CO<sub>2</sub> VPSA unit is preferably sent to a turbine to recover part of the power needed to operate the compressor that compresses the feed stream to its feed pressure. After a predetermined time or after CO<sub>2</sub> breakthrough from the bed on the feed, the feed step is terminated.

2. Co-Current (CoC) Vent. The CO<sub>2</sub> VPSA bed, which has finished the feed step, is now at high feed pressure (e.g., 100-500 psia), is depressurized in a direction the same (shown in Figure 8) or opposite (not shown in Figure 8) to the feed flow direction. The

pressure in the bed at the end of this step is close to ambient (15-20 psia, preferably about 20 psia).

3. Evacuation. The CO<sub>2</sub> VPSA bed, which is now close to ambient pressure (about 20 psia), is evacuated to a predetermined low pressure, to a sub-ambient pressure (about 1-12 psia) in a direction the same as (not shown in Figure 8) or opposite to (shown in Figure 8) the feed flow direction. The gas from the bed under evacuation constitutes the CO<sub>2</sub> product.

4. Repressurization (FeRP). The evacuated bed is repressurized to a feed pressure (100-500 psia) either by the feed gas or by part of the effluent (i.e. feed effluent) generated from implementing step 1 on another bed. Following depressurization to feed pressure, this bed is now ready to undergo step 1 again.

The four-step process described above is for one cycle for one bed in the CO<sub>2</sub> VPSA unit. The above four steps are carried out in a cyclic manner with the other beds in the unit such that feed-into and feed-effluent from step 1 are continuous. In addition, the evacuation step (step 3) is designed to be continuous. This ensures that the vacuum pump operates continuously, and that there is no break in feed-into the CO<sub>2</sub> VPSA unit or unit 13. Three adsorption beds are utilized in the embodiment described above to maintain the continuity of the key process steps.

Exemplary corresponding hardware and a flow schematic of the CO<sub>2</sub> VPSA process corresponding to the cycle shown Figure 8 is depicted in Figure 9. The various valves in Figure 9 can be operated in the manner illustrated in Figure 10 to carry out the four

steps in the three-bed process as described hereinabove.

In alternative embodiments of the present invention, storage tanks may be added in place of some of the adsorbent beds in the process cycle to store some of the intermediate gas streams such as the depressurized gas. The purpose of these storage tanks is to maintain flow into and out of the CO<sub>2</sub> VPSA unit as continuous.

The present invention thus provides processes and apparatus for the recovery of medium purity (e.g., approximately  $\geq 80$  mole%) carbon dioxide from flue gas. In accordance with preferred embodiments of the present invention, there is constant feed, constant product being produced and rotating machinery is preferably run continuously so as to eliminate unnecessary tank(s). If, however, there are reasons for limiting the number of adsorbent beds (e.g. high cost of the adsorbent) storage tanks instead of the adsorbent vessels may be used as explained above. While every bed the same cycle, the number of beds is to be minimized taking these factors into consideration.

**CLAIMS**

What is claimed is:

1. A vacuum pressure swing adsorption (VPSA) process for the recovery of carbon dioxide from a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no hydrogen or no more than a trace amount of hydrogen, and which is at a pressure in a first superatmospheric pressure range, in a VPSA unit containing at least one adsorption bed containing at least one CO<sub>2</sub>-selective adsorbent, the process comprising:

feeding said multi-component gas mixture to the at least one adsorption bed at a first pressure within said first superatmospheric pressure range for a predetermined time to adsorb carbon dioxide onto said adsorbent;

depressurizing the at least one adsorption bed in a first depressurization step from the first pressure to a second pressure that is lower than said first pressure and is within a second pressure range, in a same direction as or an opposite direction to the feed flow;

depressurizing the at least one adsorption bed in a second depressurization step from the second pressure to a third pressure that is lower than said second pressure and is within a third pressure range, in a same direction as or an opposite direction to the feed flow;

depressurizing the at least one adsorption bed in a third depressurization step from the third pressure to a fourth pressure that is lower than said third

pressure and is within a fourth pressure range, in a same direction as or an opposite direction to the feed flow;

depressurizing the at least one adsorption bed in a final depressurization step from the fourth pressure to a pressure that is within a range close to ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce at least a first portion of CO<sub>2</sub> product;

evacuating the at least one adsorption bed from the pressure that is within a range close to ambient to a pressure below ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce at least a second portion of CO<sub>2</sub> product;

pressure equalizing the at least one adsorption bed in a first pressure equalization step in a same direction as the feed flow or in a direction opposite to the feed flow;

further pressure equalizing the at least one adsorption bed in a second pressure equalization step in a same direction as the feed flow or in a direction opposite to the feed flow;

further pressure equalizing the at least one adsorption bed in a third pressure equalization step in a same direction as the feed flow or in a direction opposite to the feed flow; and

repressurizing the at least one adsorption bed in a repressurization step to a pressure in the first pressure range;

wherein the process is repeated cyclically.

2. The process of claim 1, carried out in a VPSA unit comprising six adsorption beds.

3. A process for the recovery of carbon dioxide, comprising compressing a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no hydrogen or no more than a trace amount of hydrogen, to a pressure in a first superatmospheric pressure range, and recovering carbon dioxide from said compressed mixture in a VPSA unit by a process according to claim 1, wherein an effluent gas stream is recovered from said VPSA unit and is expanded to provide power that is used in compressing said multi-component gas mixture.

4. The process of claim 1, wherein said first superatmospheric pressure range is between about 100-500 psia.

5. The process of claim 1, wherein the second pressure range in said first depressurization step is between about 80-400 psia.

6. The process of claim 1, wherein the third pressure range in said second depressurization step is between about 60-300 psia.

7. The process of claim 1, wherein the fourth pressure range in said third depressurization step is between about 50-200 psia.

8. The process of claim 1, wherein the first depressurization step is in a direction the same as the direction of the feed flow.

9. The process of claim 1, wherein the second depressurization step is in a direction the same as the direction of the feed flow.

10. The process of claim 1, wherein the third depressurization step is in a direction the same as the direction of the feed flow.

11. The process of claim 1, wherein the fourth depressurization step is in an opposite direction as the direction of the feed flow.

12. The process of claim 1, wherein the pressure range close to ambient in said final depressurization step is 15-20 psia.

13. The process of claim 1, wherein the pressure below ambient in said evacuating step is 1-12 psia.

14. The process of claim 1, wherein the at least first and at least second portions of the CO<sub>2</sub> product are combined to form a final CO<sub>2</sub> product.

15. The process of claim 1, wherein the CO<sub>2</sub>-selective adsorbent is selected from the group comprising: NaY, HY, NaX, silica gel, activated carbon and combinations thereof.

16. A vacuum pressure swing adsorption (VPSA) process for the recovery of carbon dioxide from a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no hydrogen or no more than a trace amount of hydrogen, and which is at a pressure in a first superatmospheric pressure range, in a VPSA unit containing at least one adsorption bed containing at least one CO<sub>2</sub>-selective adsorbent, the process comprising:

feeding said multi-component gas mixture to the at least one adsorption bed at a first pressure within said first superatmospheric pressure range for a predetermined time to adsorb carbon dioxide onto said adsorbent;

venting the at least one adsorption bed in a first depressurization step from the first pressure to a second pressure that is lower than said first pressure and is within a second pressure range, in a same direction as or an opposite direction to the feed flow, to produce a vent stream that can be released into the atmosphere;

depressurizing the at least one adsorption bed in a final depressurization step from the second pressure to a pressure that is within a range close to ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce at least a first portion of CO<sub>2</sub> product;

evacuating the at least one adsorption bed from the pressure that is within a range close to ambient to a pressure below ambient in a same direction as the feed flow or in a direction opposite to the feed flow

to produce at least a second portion of CO<sub>2</sub> product;  
and

repressurizing the at least one adsorption bed in  
a repressurization step to a pressure in the first  
pressure range;

wherein the process is repeated cyclically.

17. The process of claim 16, carried out in a  
VPSA unit comprising four adsorption beds.

18. A process for the recovery of carbon dioxide,  
comprising compressing a multi-component gas mixture  
which contains at least carbon dioxide and nitrogen and  
contains no hydrogen or no more than a trace amount of  
hydrogen, to a pressure in a first superatmospheric  
pressure range, and recovering carbon dioxide from said  
compressed mixture in a VPSA unit by a process  
according to claim 16, wherein an effluent gas stream  
is recovered from said VPSA unit and is expanded to  
provide power that is used in compressing said multi-  
component gas mixture.

19. The process of claim 16, wherein said first  
superatmospheric pressure range is between about 100-  
500 psia.

20. The process of claim 16, wherein the second  
pressure range in said first depressurization step is  
between about 80-400 psia.

21. The process of claim 16, wherein the pressure range close to ambient in said final depressurization step is 15-20 psia.

22. The process of claim 16, wherein the pressure below ambient in said evacuating step is 1-12 psia.

23. The process of claim 16, wherein the at least first and at least second portions of the CO<sub>2</sub> product are combined to form a final CO<sub>2</sub> product.

24. The process of claim 16, wherein the CO<sub>2</sub>-selective adsorbent is selected from the group comprising: NaY, HY, NaX, silica gel, activated carbon and combinations thereof.

25. A vacuum pressure swing adsorption (VPSA) process for the recovery of carbon dioxide from a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no hydrogen or no more than a trace amount of hydrogen, and which is at a pressure in a first superatmospheric pressure range, in a VPSA unit containing at least one adsorption bed containing at least one CO<sub>2</sub>-selective adsorbent, the process comprising:

feeding said multi-component gas mixture to the at least one adsorption bed at a first pressure within said first superatmospheric pressure range for a predetermined time to adsorb carbon dioxide onto said adsorbent;

depressurizing the at least one adsorption bed from the first pressure to a pressure that is within a

range close to ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce a vent stream that can be released into the atmosphere;

evacuating the at least one adsorption bed from the pressure that is within a range close to ambient to a pressure below ambient in a same direction as the feed flow or in a direction opposite to the feed flow to produce a CO<sub>2</sub> product; and

repressurizing the at least one adsorption bed in a repressurization step to a pressure in the first pressure range;

wherein the process is repeated cyclically.

26. The process of claim 25, carried out in a VPSA unit comprising three adsorption beds.

27. A process for the recovery of carbon dioxide, comprising compressing a multi-component gas mixture which contains at least carbon dioxide and nitrogen and contains no hydrogen or no more than a trace amount of hydrogen, to a pressure in a first superatmospheric pressure range, and recovering carbon dioxide from said compressed mixture in a VPSA unit by a process according to claim 25, wherein an effluent gas stream is recovered from said VPSA unit and is expanded to provide power that is used in compressing said multi-component gas mixture.

28. The process of claim 25, wherein said first superatmospheric pressure range is between about 100-500 psia.

29. The process of claim 25, wherein the pressure range close to ambient in said depressurization step is 15-20 psia.

30. The process of claim 25, wherein the pressure below ambient in said evacuating step is about 1-12 psia.

31. The process of claim 25, wherein the CO<sub>2</sub>-selective adsorbent is selected from the group comprising: NaY, HY, NaX, silica gel, activated carbon and combinations thereof.

32. A process according to any of claims 3, 18 or 27, wherein said compressed multi-component gas mixture contains water vapor, and water vapor is removed from said multi-component gas mixture in dryers, and all or a portion of said expanded effluent gas stream is fed to said dryers to regenerate said dryers.

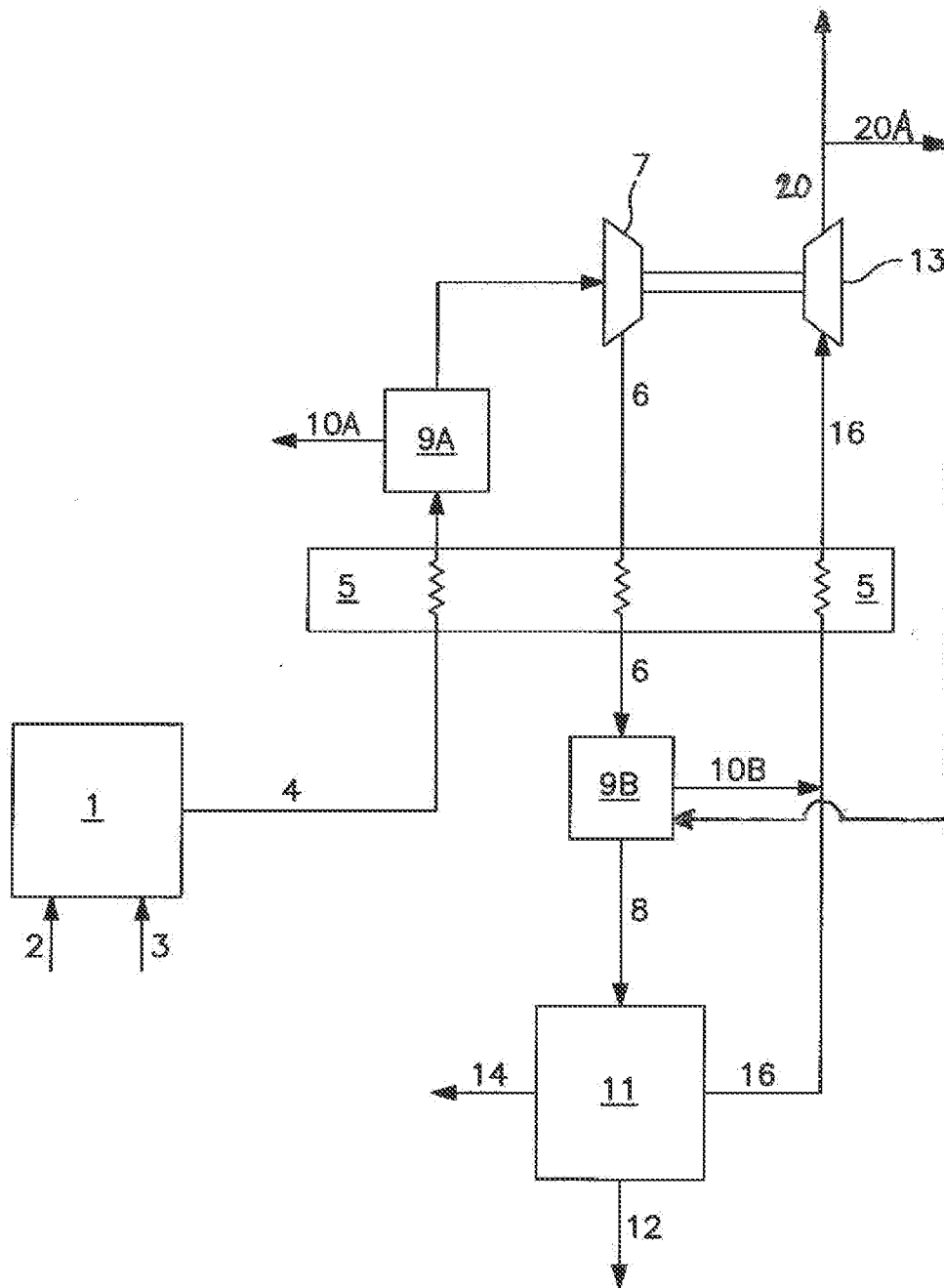


FIG. 1

|    |            |            |      |            |      |            |      |            |            |      |
|----|------------|------------|------|------------|------|------------|------|------------|------------|------|
| A1 | FEED       | DP1        | DP2  | DP3        | DPf  | Evacuation | PE3  | PE2        | PE1        | FeRP |
| A2 | FeRP       | FEED       |      | DP1        | DP2  | DP3        | DPf  | Evacuation | PE3        | PE2  |
| A3 | PE2        | PE1        | FeRP |            |      | DP1        | DP2  | DPf        | Evacuation |      |
| A4 | Evacuation | PE3        | PE2  | PE1        | FeRP | FEED       | DP1  | DP2        | DP3        | DPf  |
| A5 | DPf        | Evacuation |      | PE3        | PE2  | PE1        | FeRP | FEED       | DP1        | DP2  |
| A6 | DP1        | DP3        | DPf  | Evacuation |      | PE3        | PE2  | FeRP       |            | FEED |

Feed to CO<sub>2</sub> VPSA      →      Product as High Pressure Feed Effluent

|       |
|-------|
| Feed  |
| DP1   |
| DP2   |
| DP3   |
| DPf   |
| Evac. |
| PE3   |
| PE2   |
| PE1   |
| FeRP  |

Co-Current DP1 to PE1 with an A bed

Co-Current DP2 to PE2 with another of the A bed

Co-Current DP3 to PE3 with another of the A bed

Counter Current final DP to collect pure **CO<sub>2</sub> product** from bottom

Counter Current Evacuation to collect **CO<sub>2</sub> product** in the same **surge tank** as in the previous step.

Counter Current PE3 with an A Bed on DP3 to increase CO<sub>2</sub> recovery

Counter Current PE2 with an A Bed on DP2 to increase CO<sub>2</sub> recovery

Counter Current PE1 with an A bed on DP1 to increase CO<sub>2</sub> recovery

Counter Current RP by High Pressure Feed Effluent

| Typical                     | Pressure       |     |
|-----------------------------|----------------|-----|
|                             | Start          | End |
|                             | psia           |     |
| t <sub>feed</sub> = 120 sec | 350            | 350 |
| t <sub>DP1</sub> = 60 sec   | 350            | 225 |
| t <sub>DP2</sub> = 60 sec   | 225            | 132 |
| t <sub>DP3</sub> = 60 sec   | 132            | 60  |
| t <sub>cccDP</sub> = 60 sec | 60             | 20  |
| t <sub>evac</sub> = 120 sec | 20             | 4   |
| t <sub>PE3</sub> = 60 sec   | 4              | 60  |
| t <sub>PE2</sub> = 60 sec   | 60             | 132 |
| t <sub>PE1</sub> = 60 sec   | 132            | 225 |
| t <sub>RP</sub> = 60 sec    | 225            | 350 |
|                             | <u>720 sec</u> |     |

FIG. 2

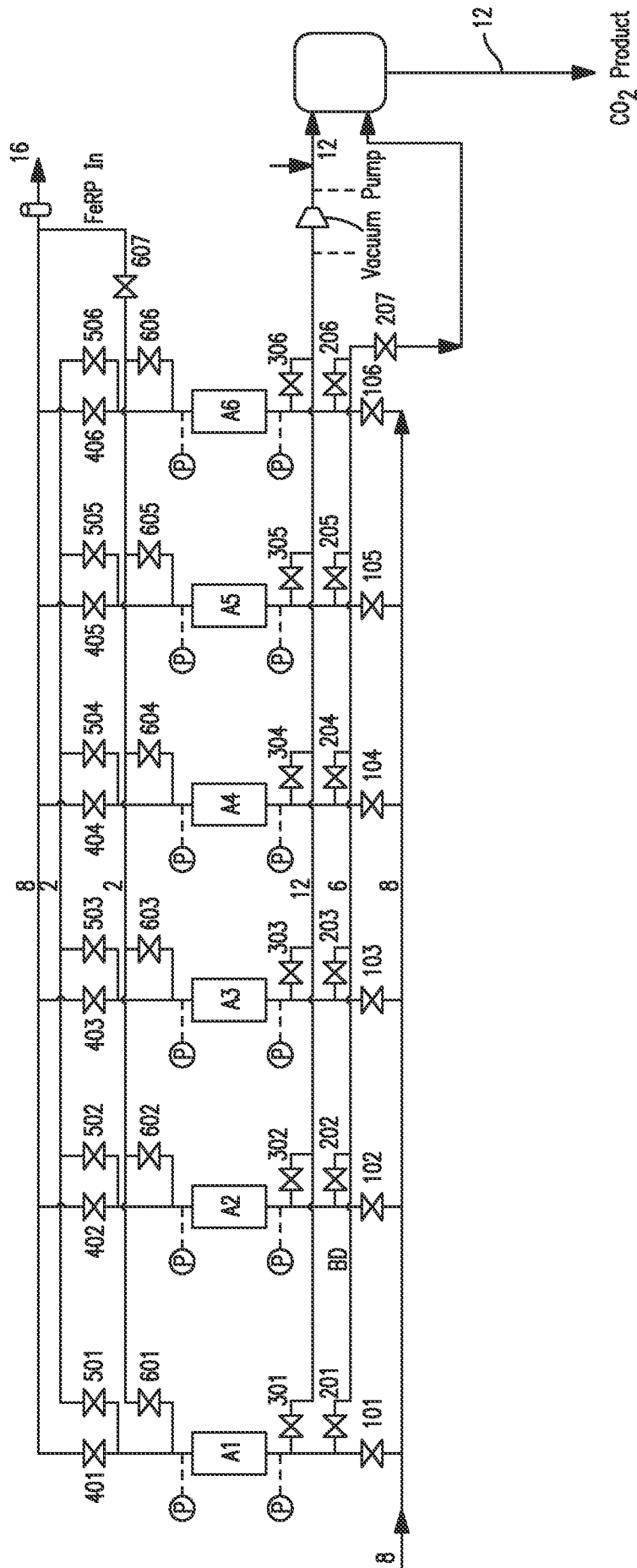


FIG. 3

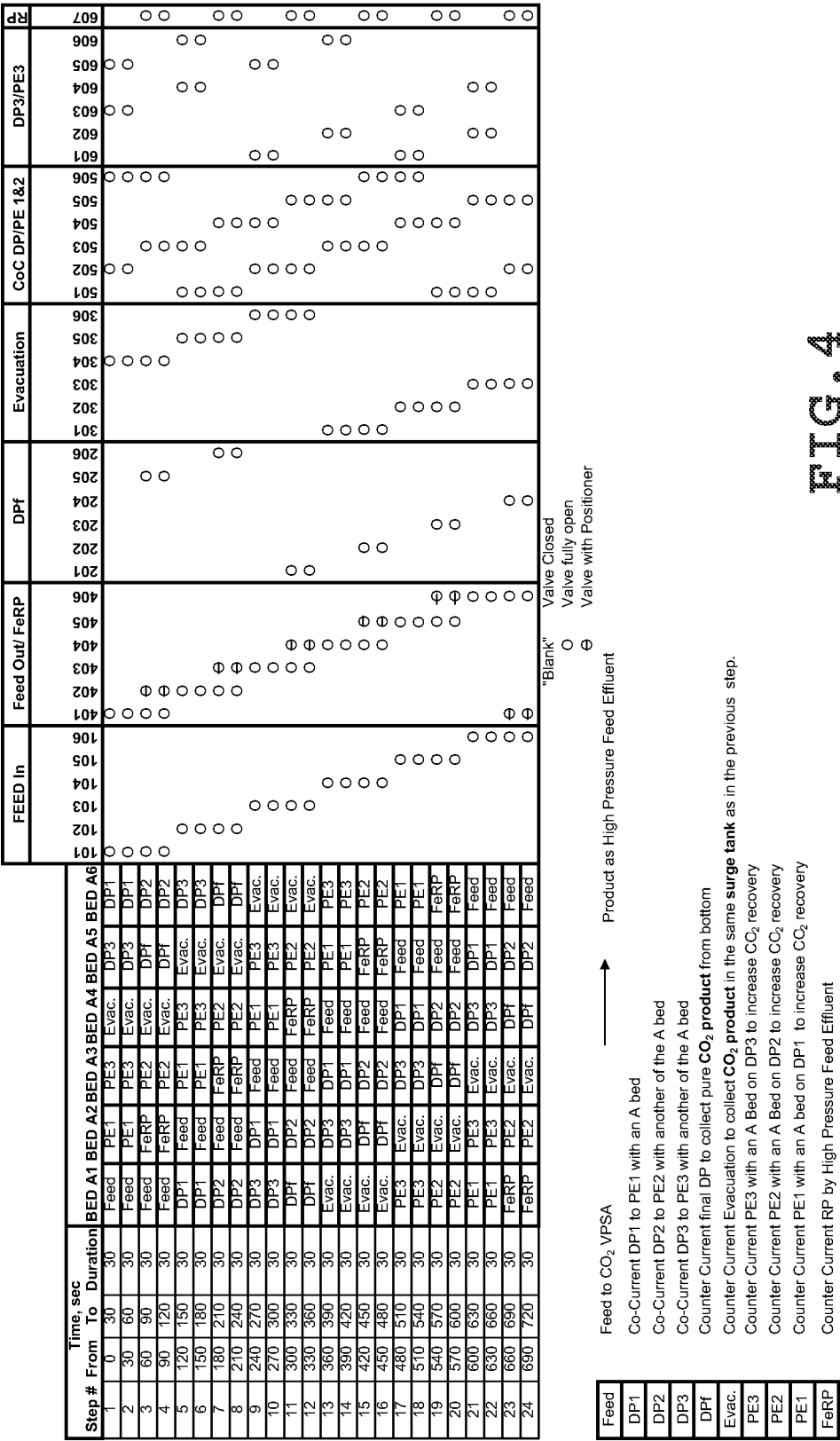


FIG. 4

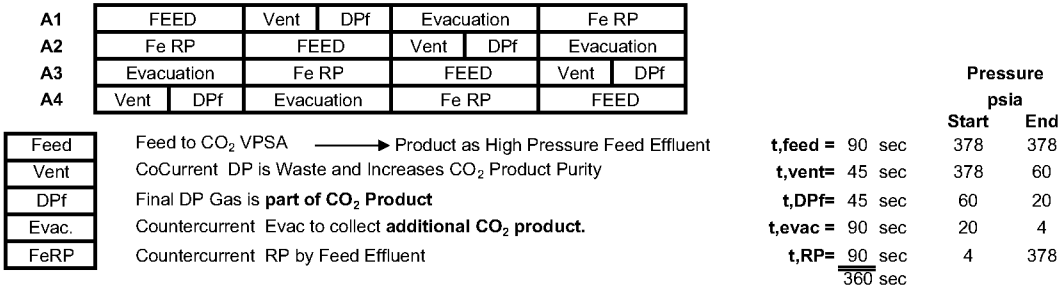


FIG. 5A

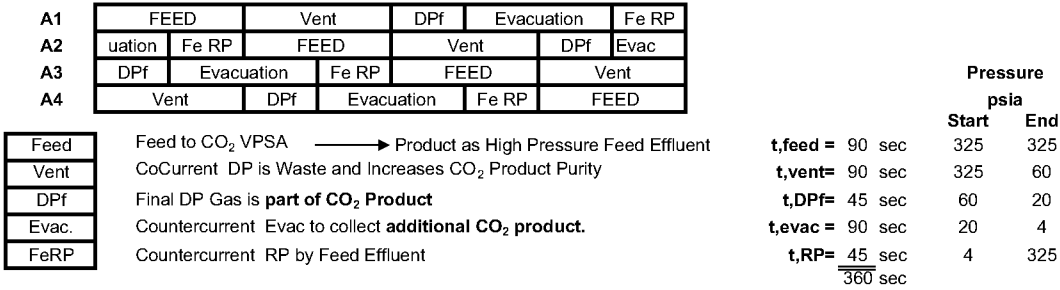


FIG. 5B

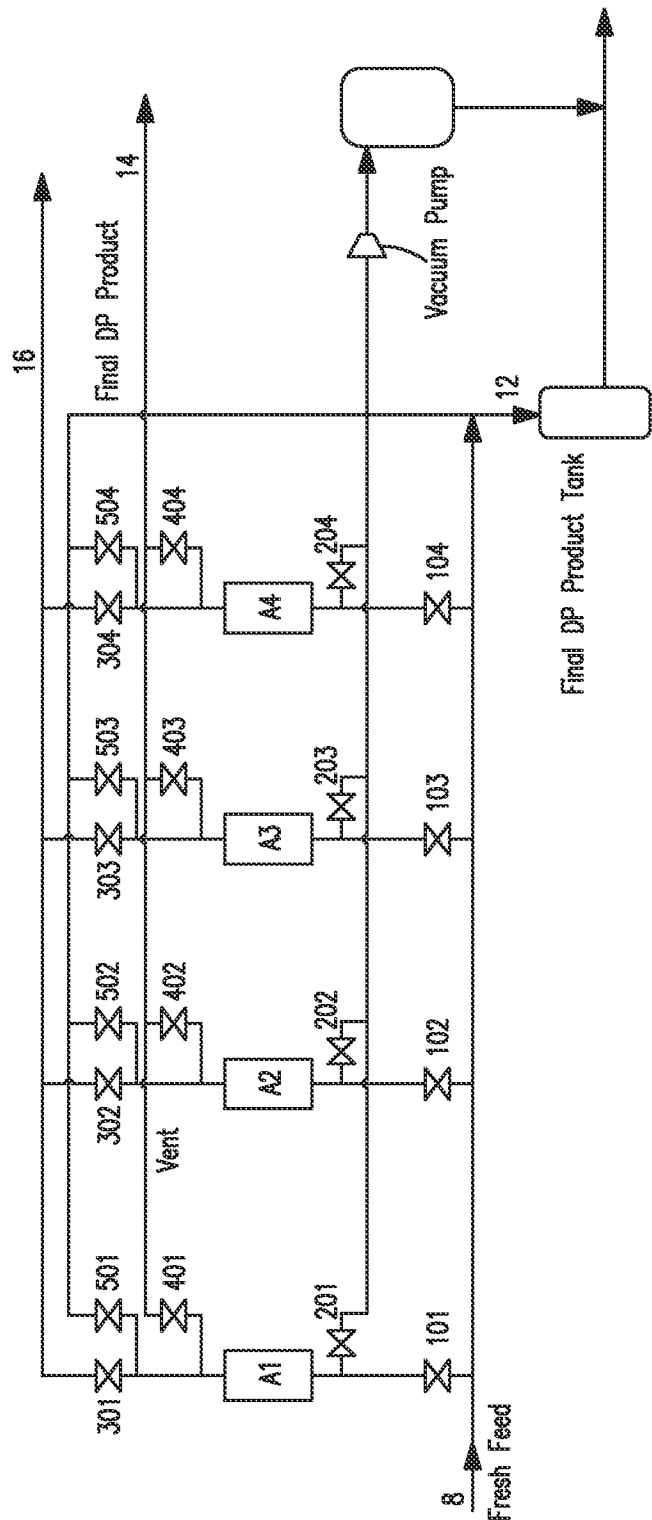


FIG. 6

|        |           |     |          |       |      |       |      |      |      |       |      |      |      |       |      |      |      |       | FEED In |      |      |       | Feed Out/ FeRP |      |      |       | Vent |  |  |  | DPf |  |  |  | Evacuation |  |  |  |
|--------|-----------|-----|----------|-------|------|-------|------|------|------|-------|------|------|------|-------|------|------|------|-------|---------|------|------|-------|----------------|------|------|-------|------|--|--|--|-----|--|--|--|------------|--|--|--|
| Step # | Time, sec |     |          | A1    |      |       |      | A2   |      |       |      | A3   |      |       |      | A4   |      |       |         |      |      |       |                |      |      |       |      |  |  |  |     |  |  |  |            |  |  |  |
|        | From      | To  | Duration | Feed  | FeRP | Evac. | Vent | Feed | FeRP | Evac. | Vent | Feed | FeRP | Evac. | Vent | Feed | FeRP | Evac. | Vent    | Feed | FeRP | Evac. | Vent           | Feed | FeRP | Evac. | Vent |  |  |  |     |  |  |  |            |  |  |  |
| 1      | 0         | 45  | 45       | Feed  | FeRP | Evac. | Vent | Feed | FeRP | Evac. | Vent | Feed | FeRP | Evac. | Vent | Feed | FeRP | Evac. | Vent    | Feed | FeRP | Evac. | Vent           | Feed | FeRP | Evac. | Vent |  |  |  |     |  |  |  |            |  |  |  |
| 2      | 45        | 90  | 45       | Feed  | FeRP | Evac. | DPf  | Feed | FeRP | Evac. | DPf  | Feed | FeRP | Evac. | DPf  | Feed | FeRP | Evac. | DPf     | Feed | FeRP | Evac. | DPf            | Feed | FeRP | Evac. | DPf  |  |  |  |     |  |  |  |            |  |  |  |
| 3      | 90        | 135 | 45       | Vent  | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP    | Feed | FeRP | Evac. | FeRP           | Feed | FeRP | Evac. | FeRP |  |  |  |     |  |  |  |            |  |  |  |
| 4      | 135       | 180 | 45       | DPf   | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP    | Feed | FeRP | Evac. | FeRP           | Feed | FeRP | Evac. | FeRP |  |  |  |     |  |  |  |            |  |  |  |
| 5      | 180       | 225 | 45       | Evac. | Vent | FeRP  | FeRP | Feed | Vent | FeRP  | FeRP | Feed | Vent | FeRP  | FeRP | Feed | Vent | FeRP  | FeRP    | Feed | Vent | FeRP  | FeRP           | Feed | Vent | FeRP  | FeRP |  |  |  |     |  |  |  |            |  |  |  |
| 6      | 225       | 270 | 45       | Evac. | DPf  | Evac. | FeRP | Feed | DPf  | Evac. | FeRP | Feed | DPf  | Evac. | FeRP | Feed | DPf  | Evac. | FeRP    | Feed | DPf  | Evac. | FeRP           | Feed | DPf  | Evac. | FeRP |  |  |  |     |  |  |  |            |  |  |  |
| 7      | 270       | 315 | 45       | FeRP  | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP | Feed | FeRP | Evac. | FeRP    | Feed | FeRP | Evac. | FeRP           | Feed | FeRP | Evac. | FeRP |  |  |  |     |  |  |  |            |  |  |  |
| 8      | 315       | 360 | 45       | FeRP  | FeRP | Evac. | DPf  | Feed | FeRP | Evac. | DPf  | Feed | FeRP | Evac. | DPf  | Feed | FeRP | Evac. | DPf     | Feed | FeRP | Evac. | DPf            | Feed | FeRP | Evac. | DPf  |  |  |  |     |  |  |  |            |  |  |  |

FIG. 7A

|        |  |           |     |          |       |      |       |       |      |       |     |      |      |      |       |     |      |      | FEED In |       |     |      | Feed Out/ FeRP |      |       |     | Vent |  |  |  | DPf |  |  |  | Evacuation |  |  |  |
|--------|--|-----------|-----|----------|-------|------|-------|-------|------|-------|-----|------|------|------|-------|-----|------|------|---------|-------|-----|------|----------------|------|-------|-----|------|--|--|--|-----|--|--|--|------------|--|--|--|
| Step # |  | Time, sec |     |          | A1    |      |       |       | A2   |       |     |      | A3   |      |       |     | A4   |      |         |       |     |      |                |      |       |     |      |  |  |  |     |  |  |  |            |  |  |  |
|        |  | From      | To  | Duration | Feed  | FeRP | Evac. | Feed  | FeRP | Evac. | DPf | Vent | Feed | FeRP | Evac. | DPf | Vent | Feed | FeRP    | Evac. | DPf | Vent | Feed           | FeRP | Evac. | DPf | Vent |  |  |  |     |  |  |  |            |  |  |  |
| 1      |  | 0         | 45  | 45       | Feed  | FeRP | Evac. | Feed  | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |
| 2      |  | 45        | 90  | 45       | Vent  | FeRP | Evac. | Vent  | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |
| 3      |  | 90        | 135 | 45       | Vent  | FeRP | Evac. | Vent  | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |
| 4      |  | 135       | 180 | 45       | Vent  | FeRP | Evac. | Vent  | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |
| 5      |  | 180       | 225 | 45       | DPf   | FeRP | Evac. | DPf   | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |
| 6      |  | 225       | 270 | 45       | Evac. | FeRP | Evac. | Evac. | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |
| 7      |  | 270       | 315 | 45       | Evac. | FeRP | Evac. | DPf   | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |
| 8      |  | 315       | 360 | 45       | FeRP  | FeRP | Evac. | FeRP  | FeRP | Evac. | DPf | Vent | ○    | ○    | ○     | ○   | ○    | ○    | ○       | ○     | ○   | ○    | ○              | ○    | ○     | ○   | ○    |  |  |  |     |  |  |  |            |  |  |  |

FIG. 7B

Feed

Vent

DPf

Evac.

FeRP

Feed to CO<sub>2</sub> VPSA

→

Feed Effluent is Waste

CoC DP is Waste and Increases CO<sub>2</sub> Product Purity

Final DP Gas is **part of CO<sub>2</sub> Product**

CoC Evac to collect **additional CO<sub>2</sub> product**.

CoC RP by Feed Effluent

"Blank"

○

⊖

Valve Closed

Valve fully open

Valve with Positioner

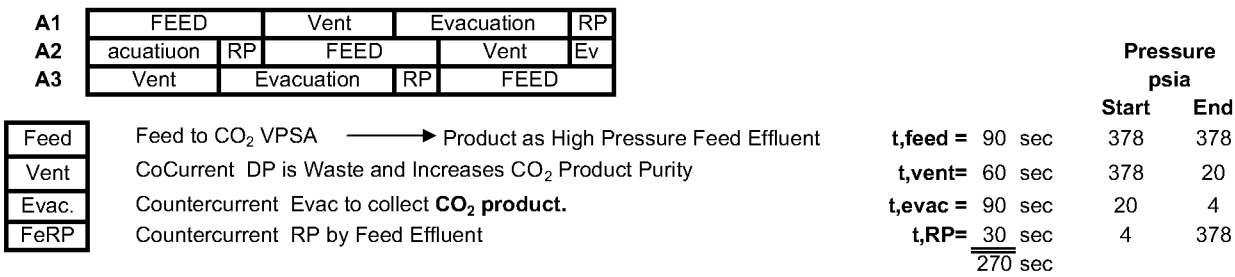


FIG. 8

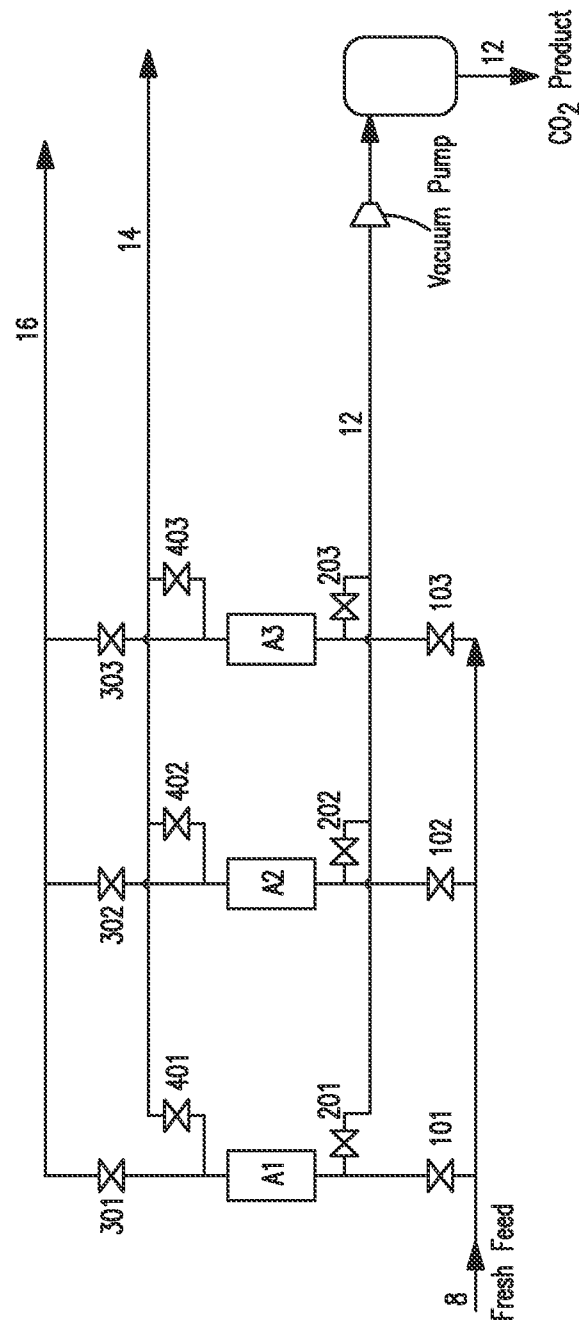


FIG. 9

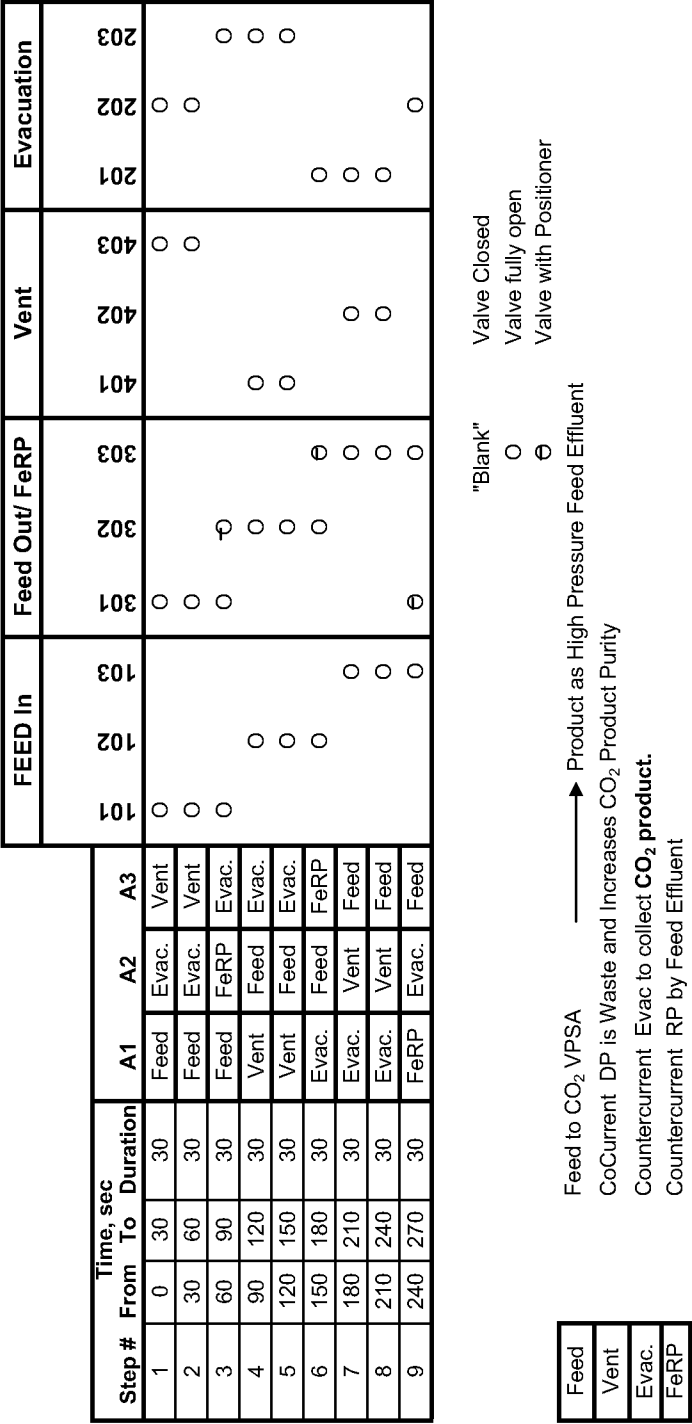


FIG. 10

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/043474

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. B01D53/047  
 ADD.

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 practicable, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                | Relevant to claim No.            |
|-----------|-------------------------------------------------------------------------------------------------------------------|----------------------------------|
| X         | US 5 248 322 A (KUMAR RAVI [US])<br>28 September 1993 (1993-09-28)                                                | 1,2,<br>4-17,<br>19-26,<br>28-31 |
| Y         | column 9, lines 25-44; claims; figure                                                                             | 3,18,27,<br>32                   |
| X         | -----<br>US 2008/072752 A1 (KUMAR RAVI [US])<br>27 March 2008 (2008-03-27)                                        | 1,2,<br>4-17,<br>19-26,<br>28-31 |
| Y         | claims; figures                                                                                                   | 3,18,27,<br>32                   |
| Y         | -----<br>GB 2 090 160 A (MITSUBISHI HEAVY IND LTD)<br>7 July 1982 (1982-07-07)<br>claims; figures<br>-----<br>-/- | 3,18,27,<br>32                   |



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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

2 April 2013

Date of mailing of the international search report

09/04/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040,  
 Fax: (+31-70) 340-3016

Authorized officer

Persichini, Carlo

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2012/043474

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-24

Vacuum pressure swing adsorption for recovery of carbon dioxide wherein product gas is recovered during a final depressurization section and during evacuation

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2. claims: 25-32

Vacuum pressure swing adsorption for recovery of carbon dioxide wherein product gas is recovered during during evacuation and gas recovered during depressurization is vented

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/043474

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                              |                       |
|------------------------------------------------------|----------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages           | Relevant to claim No. |
| Y                                                    | FR 2 890 575 A1 (AIR LIQUIDE [FR])<br>16 March 2007 (2007-03-16)<br>claims; figures<br>----- | 3,18,27,<br>32        |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/043474

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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|                                           |    |                     | WO 2008039771 A2           | 03-04-2008          |
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|                                           |    |                     | GB 2090160 A               | 07-07-1982          |
| -----                                     |    |                     |                            |                     |
| FR 2890575                                | A1 | 16-03-2007          | NONE                       |                     |
| -----                                     |    |                     |                            |                     |