View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by University of Kentucky

University of Kentucky
UKnowledge

Center for Applied Energy Research Faculty Patents

Center for Applied Energy Research

8-9-2016

Hybrid Process Using a Membrane to Enrich Flue Gas CO_2 with a Solvent-Based Post-Combustion CO_2 Capture System

Kunlei Liu
University of Kentucky, kunlei.liu@uky.edu

Reynolds A. Frimpong
University of Kentucky, reynolds.frimpong@uky.edu

Kun Liu
University of Kentucky, kun.liu@uky.edu

Right click to open a feedback form in a new tab to let us know how this document benefits you.

Follow this and additional works at: https://uknowledge.uky.edu/caer_patents

Part of the Engineering Commons

Recommended Citation

Liu, Kunlei; Frimpong, Reynolds A.; and Liu, Kun, "Hybrid Process Using a Membrane to Enrich Flue Gas CO_2 with a Solvent-Based Post-Combustion CO_2 Capture System" (2016). *Center for Applied Energy Research Faculty Patents*. 39.
https://uknowledge.uky.edu/caer_patents/39

This Patent is brought to you for free and open access by the Center for Applied Energy Research at UKnowledge. It has been accepted for inclusion in Center for Applied Energy Research Faculty Patents by an authorized administrator of UKnowledge. For more information, please contact UKnowledge@lsv.uky.edu.

US009409120B2

(12) **United States Patent**
Liu et al.

(10) **Patent No.: US 9,409,120 B2**
(45) **Date of Patent: Aug. 9, 2016**

(54) **HYBRID PROCESS USING A MEMBRANE TO ENRICH FLUE GAS CO_2 WITH A SOLVENT-BASED POST-COMBUSTION CO_2 CAPTURE SYSTEM**

(71) Applicant: **University of Kentucky Research Foundation**, Lexington, KY (US)

(72) Inventors: **Kunlei Liu**, Lexington, KY (US); **Reynolds A. Frimpong**, Lexington, KY (US); **Kun Liu**, Lexington, KY (US)

(73) Assignee: **THE UNIVERSITY OF KENTUCKY RESEARCH FOUNDATION**, Lexington, KY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **14/591,392**

(22) Filed: **Jan. 7, 2015**

(65) **Prior Publication Data**

US 2015/0190748 A1 Jul. 9, 2015

Related U.S. Application Data

(60) Provisional application No. 61/924,373, filed on Jan. 7, 2014.

(51) **Int. Cl.**

B01D 53/22	(2006.01)
B01D 53/14	(2006.01)
F01K 23/06	(2006.01)

(52) **U.S. Cl.**

CPC ..... ***B01D 53/229*** (2013.01); ***B01D 53/1425*** (2013.01); ***B01D 53/1443*** (2013.01); (Continued)

(58) **Field of Classification Search**

CPC B01D 53/1425; B01D 53/1443; B01D 53/1475; B01D 53/229; B01D 2053/221; Y02C 10/10; F01K 23/067

USPC 95/51

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,772,295	A *	9/1988	Kato	B01D 53/1443 95/50
5,520,894	A	5/1996	Heesink et al.	

(Continued)

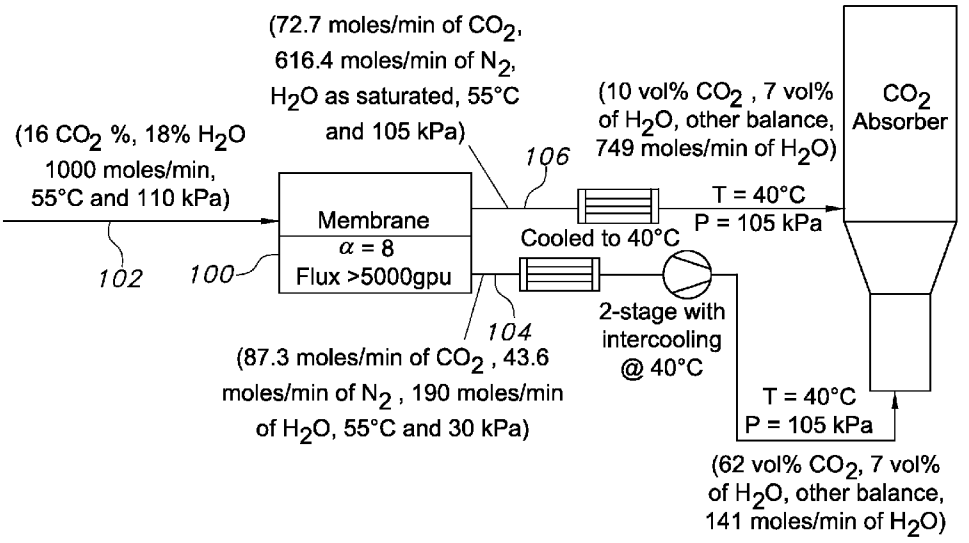
Primary Examiner — Jason M Greene

(74) *Attorney, Agent, or Firm* — King & Schickli, PLLC

(57) **ABSTRACT**

A process for recovery of CO_2 from a post-combustion gas includes pre-concentrating a CO_2 component of the post-combustion flue gas by passing the post-combustion gas through a CO_2-selective membrane module to provide a CO_2-enriched permeate stream and a CO_2-lean reject stream. Next, in a CO_2 absorber, both the CO_2-enriched permeate stream and CO_2 lean reject stream, fed to separate feed locations on the CO_2 absorber, are contacted with a scrubbing solvent to absorb CO_2 and provide a carbon-rich scrubbing solvent. Finally, absorbed CO_2 is stripped from the carbon-rich scrubbing solvent by a two-stage CO_2 stripping system. The CO_2-selective membrane may be a high flux, low pressure drop, low CO_2 selectivity membrane. The two stage stripping system includes a primary CO_2 stripping column for stripping CO_2 from the carbon-rich scrubbing solvent exiting the CO_2 absorber, and a secondary CO_2 stripping column for stripping CO_2 from a carbon-lean scrubbing solvent exiting the primary CO_2 stripping column. Apparatus for CO_2 removal from post-combustion gases in a pulverized coal power plant incorporating the described processes are described.

21 Claims, 5 Drawing Sheets



(52) **U.S. Cl.**
CPC ***B01D53/1475*** (2013.01); ***F01K 23/067*** (2013.01); *B01D 2053/221* (2013.01); *Y02C 10/06* (2013.01); *Y02C 10/10* (2013.01); *Y02E 20/18* (2013.01)

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,011,192	A *	1/2000	Baker	B01D 53/229 585/802
6,128,919	A	10/2000	Daus et al.	
6,228,145	B1	5/2001	Falk-Pedersen et al.	
6,898,936	B1	5/2005	Ochs et al.	
6,932,858	B2 *	8/2005	Nicol	B01D 3/14 95/269
7,413,595	B2	8/2008	Schmidt et al.	
7,637,984	B2	12/2009	Adamopoulos	
7,785,397	B2	8/2010	Kumar et al.	
7,815,892	B2	10/2010	Hershkowitz et al.	
7,833,328	B2	11/2010	Lackner et al.	
7,909,911	B2	3/2011	Lackner et al.	
7,947,240	B2	5/2011	Vandor	
8,007,570	B2	8/2011	Sonwane et al.	
8,163,066	B2	4/2012	Eisenberger	
8,171,718	B2	5/2012	Gulen et al.	
8,202,349	B2	6/2012	Molaison	
8,282,899	B2	10/2012	Bahr et al.	
8,328,911	B2	12/2012	Liu et al.	
8,408,006	B2	4/2013	Li et al.	
8,414,689	B2	4/2013	Tirio	
8,414,853	B2	4/2013	Liu et al.	
8,500,855	B2	8/2013	Eisenberger	
8,591,627	B2	11/2013	Jain	
8,715,393	B2	5/2014	Wright et al.	
2003/0141223	A1 *	7/2003	Wagner	B01D 53/1425 208/312
2003/0154857	A1	8/2003	Murdoch	
2006/0260189	A1	11/2006	Reddy et al.	
2006/0281960	A1 *	12/2006	Jolimaitre	B01D 53/229 585/818
2008/0011161	A1 *	1/2008	Finkenrath	B01D 53/1475 96/4
2009/0232861	A1	9/2009	Wright et al.	
2010/0205968	A1	8/2010	Graeber et al.	
2010/0242811	A1	9/2010	Court et al.	
2010/0284892	A1	11/2010	Grover et al.	
2011/0079144	A1	4/2011	Wright et al.	
2011/0203311	A1	8/2011	Wright et al.	
2011/0239700	A1 *	10/2011	Hasse	B01D 53/229 95/51
2011/0268618	A1	11/2011	Finkenrath	
2011/0290110	A1 *	12/2011	Zhou	B01D 53/1475 95/45
2011/0290111	A1 *	12/2011	Dunne	B01D 53/1443 95/51
2012/0000175	A1	1/2012	Wormser	
2012/0111192	A1 *	5/2012	Nazarko	B01D 53/1475 95/51
2012/0216547	A1	8/2012	Li et al.	
2012/0227372	A1	9/2012	Li et al.	
2012/0312020	A1	12/2012	Hume et al.	
2013/0014484	A1	1/2013	Caprile et al.	
2013/0048561	A1	2/2013	Wilson et al.	
2013/0153400	A1	6/2013	Hume et al.	
2013/0174566	A1	7/2013	Birley et al.	
2013/0239804	A1 *	9/2013	Wynn	B01D 53/229 96/4
2013/0244305	A1	9/2013	Versteeg et al.	
2013/0259781	A1	10/2013	Vitse et al.	
2013/0305925	A1	11/2013	Polak	
2013/0312606	A1	11/2013	Eisenberger	
2013/0333568	A1	12/2013	Bockman et al.	
2013/0343981	A1	12/2013	Wright et al.	
2014/0144321	A1 *	5/2014	Sawamura	B01D 53/22 96/4
2014/0357925	A1 *	12/2014	Mitariten	B01D 53/229 585/802

* cited by examiner

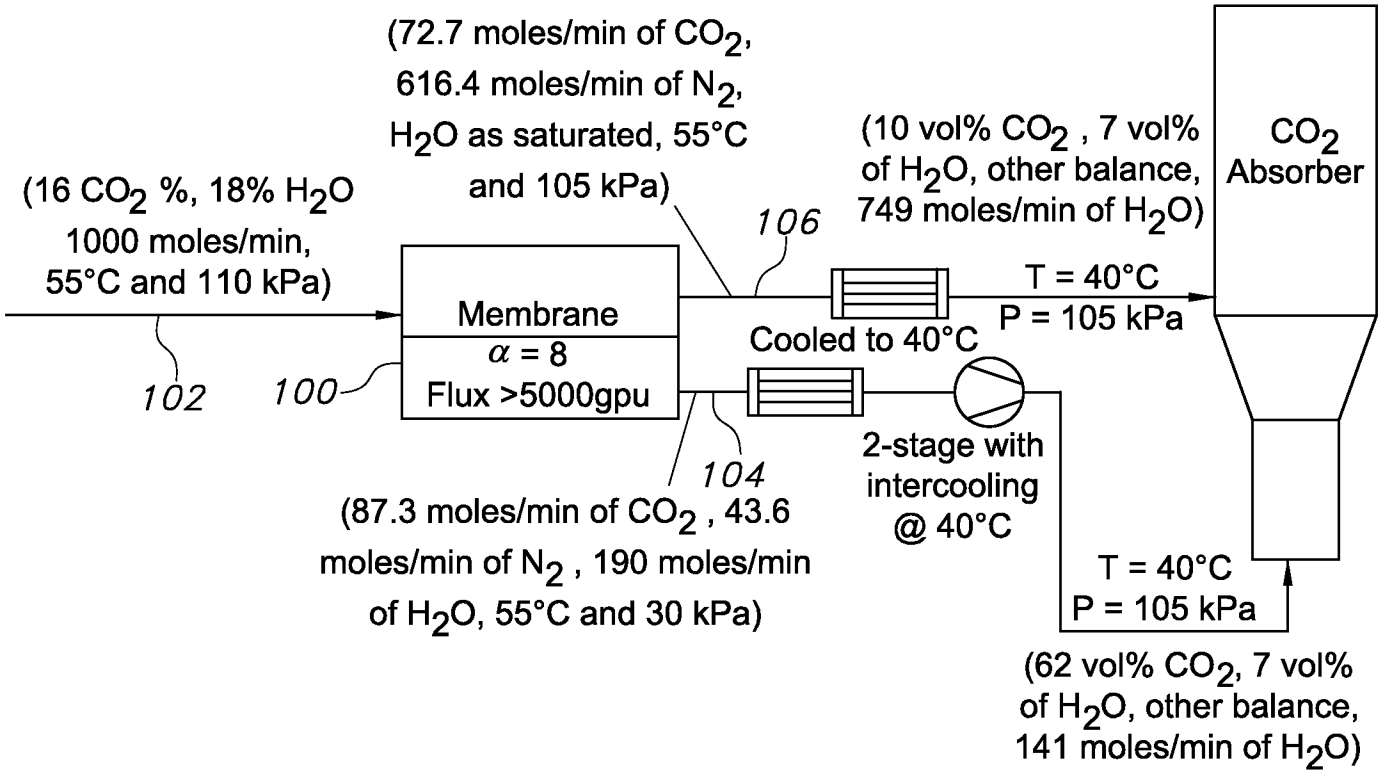

(72.7 moles/min of CO_2, 616.4 moles/min of N_2, H_2O as saturated, 55°C and 105 kPa)
(16 CO_2 %, 18% H_2O 1000 moles/min, 55°C and 110 kPa)
106
(10 vol% CO_2 , 7 vol% of H_2O, other balance, 749 moles/min of H_2O)
CO_2 Absorber
Membrane
α = 8
Flux >5000gpu
T = 40°C
P = 105 kPa
Cooled to 40°C
102
100
104
2-stage with intercooling @ 40°C
(87.3 moles/min of CO_2 , 43.6 moles/min of N_2 , 190 moles/min of H_2O, 55°C and 30 kPa)
T = 40°C
P = 105 kPa
(62 vol% CO_2, 7 vol% of H_2O, other balance, 141 moles/min of H_2O)

FIG. 1

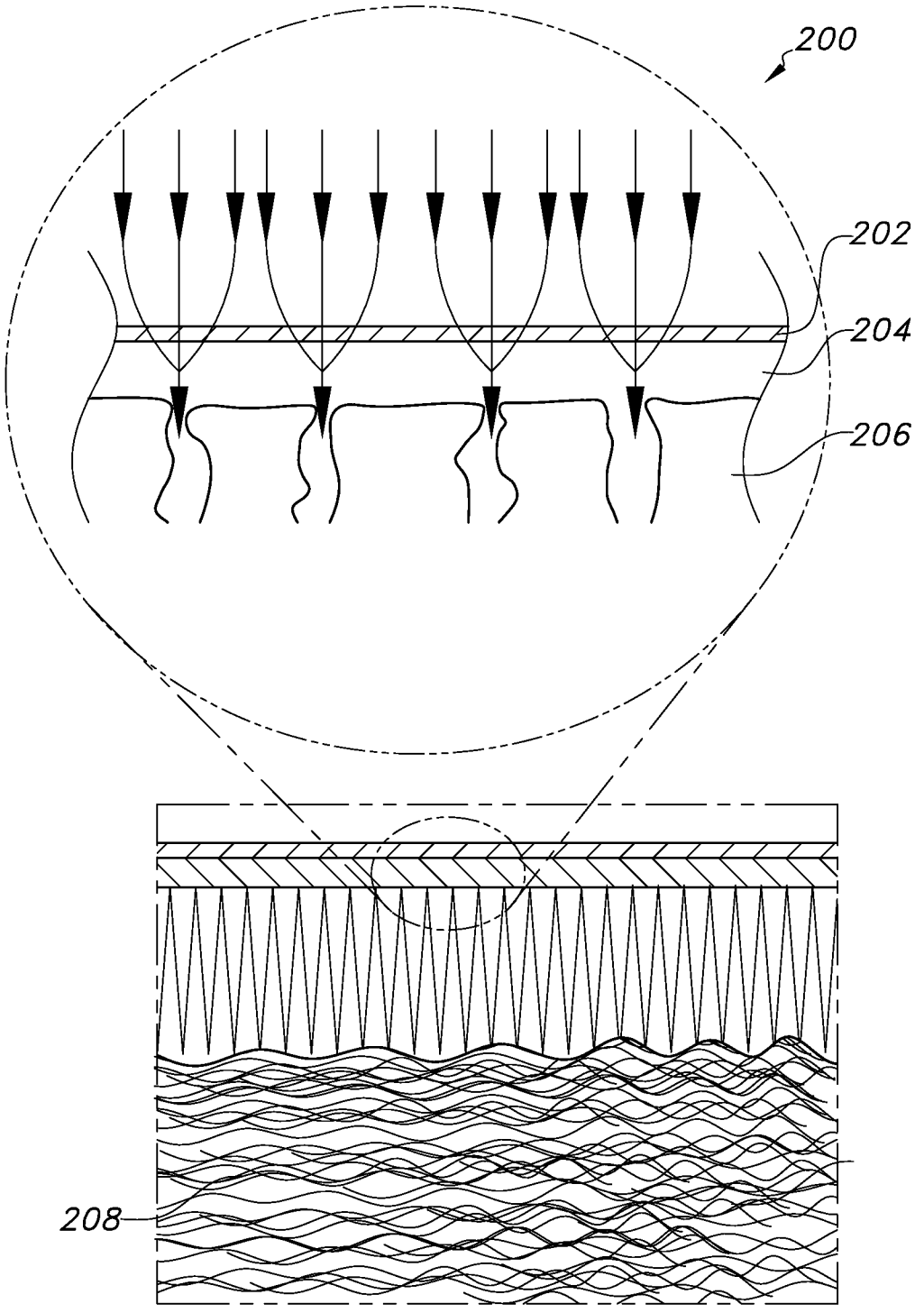


FIG. 2

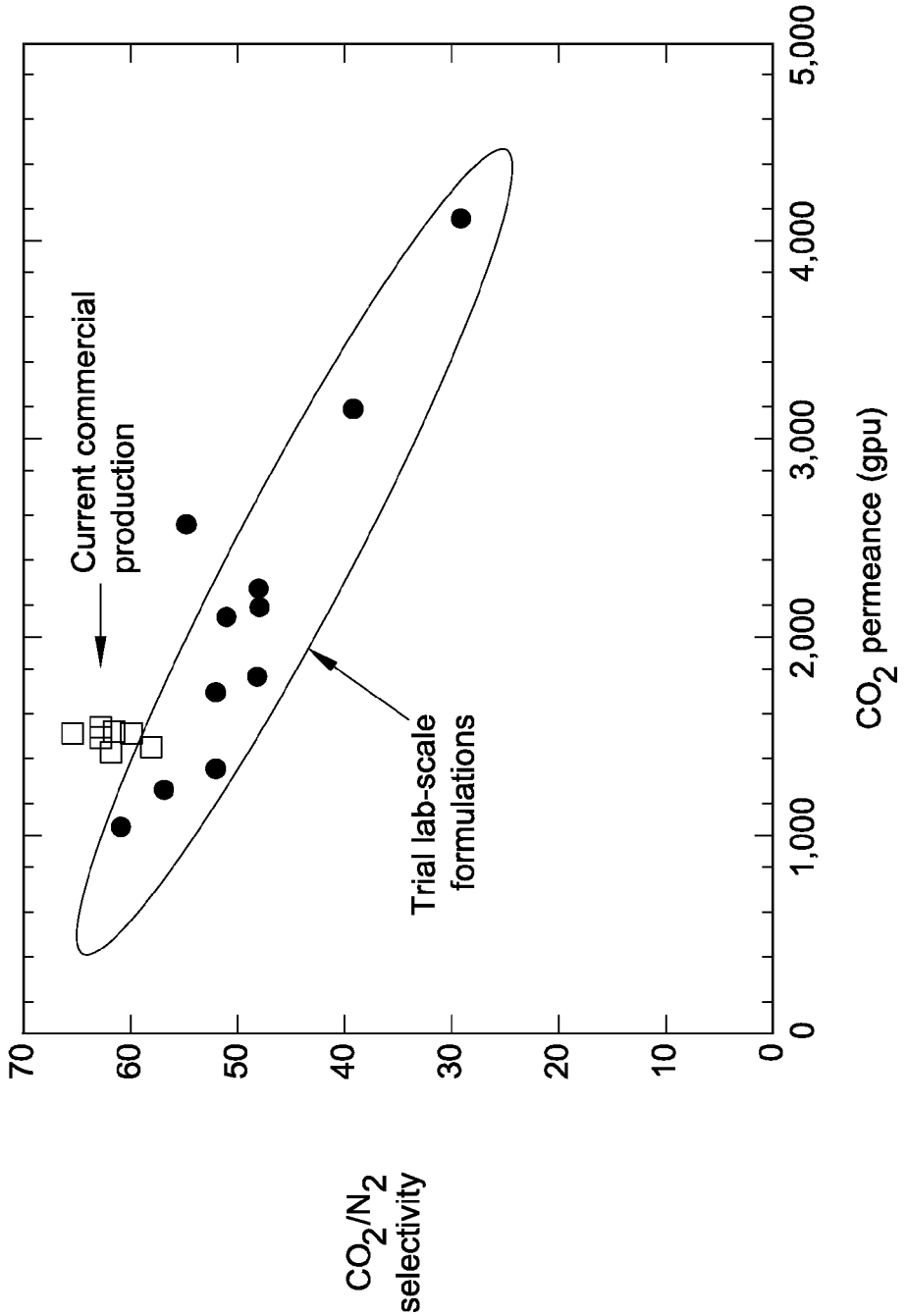

Current commercial production
Trial lab-scale formulations
CO_2 permeance (gpu)
CO_2/N_2 selectivity
0
1,000
2,000
3,000
4,000
5,000
10
20
30
40
50
60
70

FIG. 3

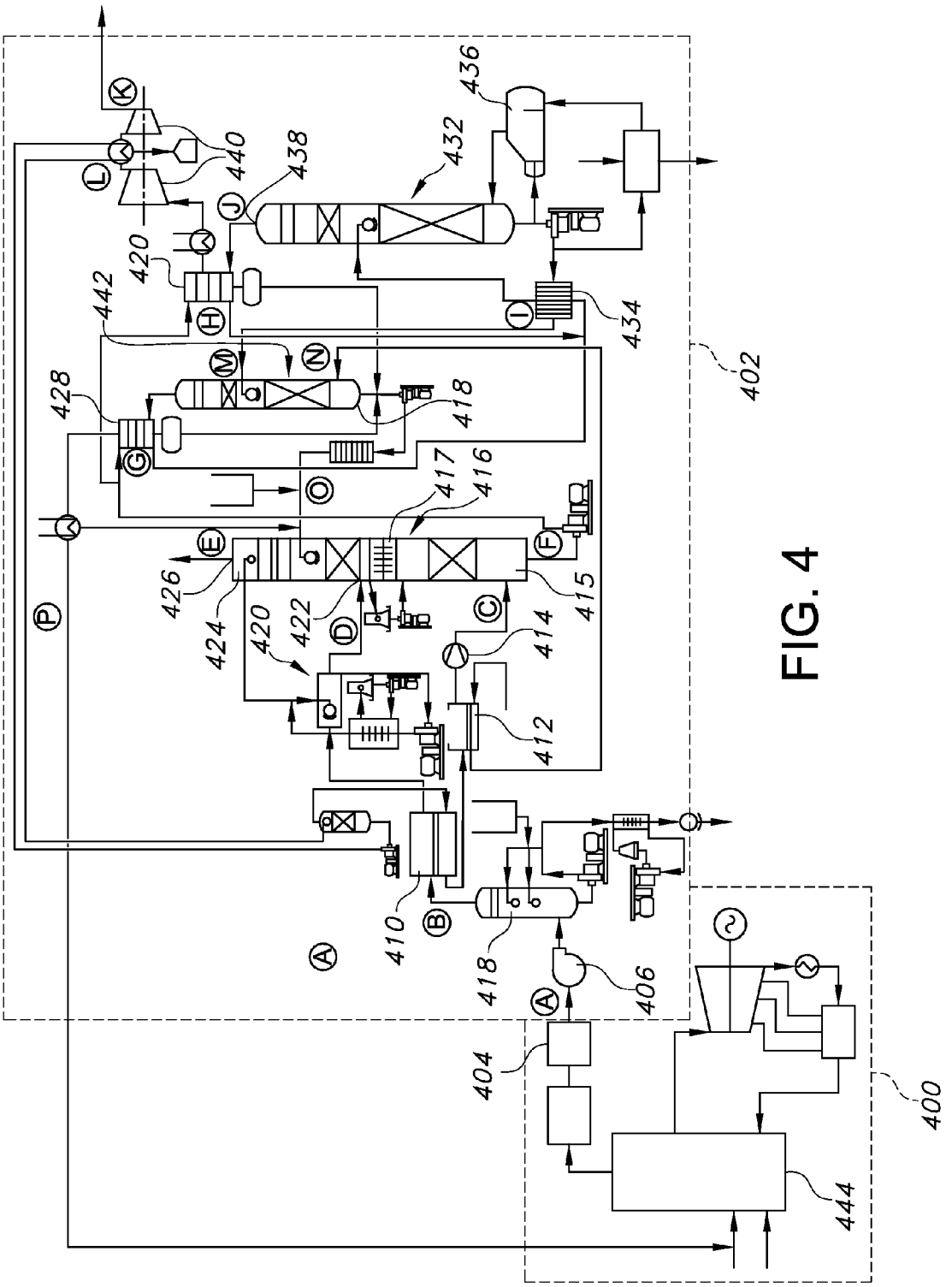

436
432
438
440
420
442
434
402
428
418
417
416
426
424
420
422
415
414
412
410
418
406
404
400
444

FIG. 4

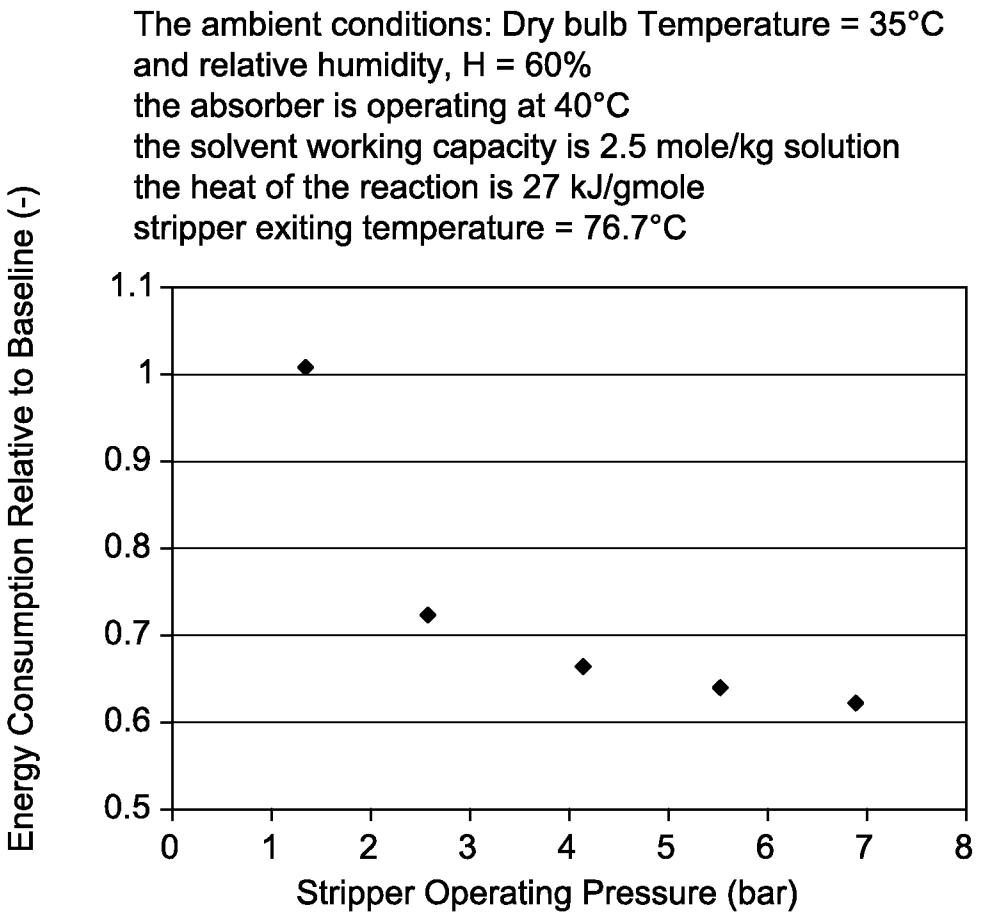

The ambient conditions: Dry bulb Temperature = 35°C
and relative humidity, H = 60%
the absorber is operating at 40°C
the solvent working capacity is 2.5 mole/kg solution
the heat of the reaction is 27 kJ/gmole
stripper exiting temperature = 76.7°C
Energy Consumption Relative to Baseline (-)
1.1
1
0.9
0.8
0.7
0.6
0.5
0
1
2
3
4
5
6
7
8
Stripper Operating Pressure (bar)

FIG. 5

HYBRID PROCESS USING A MEMBRANE TO ENRICH FLUE GAS CO_2 WITH A SOLVENT-BASED POST-COMBUSTION CO_2 CAPTURE SYSTEM

This utility patent application claims the benefit of priority in U.S. Provisional Patent Application Ser. No. 61/924,373 filed on Jan. 7, 2014, the entirety of the disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

The present disclosure relates to removal of CO_2 from post-combustion gases. In particular, the disclosure relates to a hybrid process for CO_2 removal including membrane-based pre-concentration of CO_2 in flue gas, followed by passage through a two-stage stripping unit for solvent regeneration. The described process finds utility in post-combustion carbon dioxide (CO_2) capture, such as from utility flue gases in coal-fired power plants and natural gas-fired power plant.

BACKGROUND OF THE INVENTION

In a typical coal-fired power plant, coal is burned in a boiler to make high temperature and pressure steam to drive a steam turbine and electricity generator. For the steam-side process, the initial superheated steam drives the high-pressure turbine first for power generation, before returning to the boiler for reheating to bring steam temperature back to over 540° C. (according to the steam cycle specifications and boiler design). The reheated steam then enters intermediate-pressure and low-pressure turbines to generate additional electricity. The steam pipe connecting the intermediate-pressure turbine exhaust and the low-pressure turbine inlet is called the cross-over section, where the steam for solvent regeneration in the CO_2 capture process is extracted. The exiting saturated steam from the low-pressure turbine is condensed in a water-to-steam heat exchanger (or condenser). The condensate is pressurized via feedwater pumps, heated via feedwater heaters and economizers, and fed back to the boiler to complete the steam cycle.

For the gas-side process, typically after combustion of the coal in low NOx burners the combustion gases leave the boiler and are treated by a NOx removal technology called Selective Catalytic Reduction (SCR). After the SCR treatment, the gas is further treated in a fly ash removal device, such as an electrostatic precipitator, to remove particulates. After this treatment, the gas is routed through an SO_2 removal device (SO_2 scrubber or polisher). At this point, the carbon capture process begins.

It is well-known in the art to use CO_2 absorbers/scrubbers including scrubbing solvents for capturing CO_2 from post-combustion gases, such as from utility flue gases. As an example, a conventional solvent often used is 30 weight percent monoethanolamine (MEA). Likewise, it is known to use solvents comprising piperazine, $K_2CO_3/KHCO_3$, NH_3, and others. In commercial use, the solvents must be regenerated, i.e. have absorbed CO_2 removed, for continued use in the systems. All of these processes incur costs in the form of at least energy costs and capital costs for equipment to accomplish them. An industry goal is to provide processes and systems for carbon capture and recovery, such as in commercial scale power plants, with as minimal an energy and capital cost as possible, to provide power at as low a cost as possible.

To address the aforementioned and other issues, and to meet the U.S. Department of Energy's goals of 90% CO_2 capture with 95% CO_2 purity at a cost of no more than $40/tonne of CO_2 captured, a hybrid process is described to achieve high percent CO_2 capture from low driving force coal post-combustion flue gas, CO_2 purity for compression, and low process energy requirement. The described process incorporates membrane-based CO_2 enrichment of post-combustion gases, coupled with a heat-integrated aqueous CO_2 capture system and a two-stage solvent regeneration process to provide a desired CO_2 purity from utility flue gases.

SUMMARY OF THE INVENTION

In accordance with the purposes and advantages of the present invention as described herein, in one aspect of the present disclosure a process for removal and recovery of CO_2 from a post-combustion gas such as a boiler or a gas turbine exhaust flue gas is described. The process includes steps of pre-concentrating a CO_2 component of the boiler exhaust gas by passing the flue gas through a CO_2-selective membrane module to provide a CO_2-enriched post-combustion gas and a CO_2-lean stream gas. Next, in a CO_2 absorber, the CO_2-enriched post-combustion gas is fed to a CO_2 absorber bottom and contacted with a scrubbing solvent to absorb CO_2 and provide a carbon-rich scrubbing solvent. The CO_2-lean stream is fed to the CO_2 absorber at an intermediate height to achieve 90% overall CO_2 removal. Then, absorbed CO_2 is stripped from the carbon-rich scrubbing solvent by a two-stage CO_2 stripping system. The process may further include evaporating at least a portion of a water as carrier vapor for permeate stream before the step of pre-concentrating the post-combustion gas CO_2 component. In embodiments, a CO_2-rich permeate stream is passed from the CO_2-selective membrane module to a bottom portion of the CO_2 absorber, and a CO_2-lean reject stream is crossed from the CO_2-selective membrane module to the CO_2 absorber at an appropriate point above the CO_2-rich permeate stream feed point of the CO_2 absorber. The CO_2-membrane module may be a high flux, low pressure drop, low CO_2 selectivity membrane.

The two stage stripping system includes a primary CO_2 stripping column for stripping CO_2 from the carbon-rich scrubbing solvent exiting the CO_2 absorber and a secondary CO_2 stripping column for stripping CO_2 from a carbon-lean scrubbing solvent exiting the primary CO_2 stripping column. In an embodiment, the secondary CO_2 stripping column is an ambient pressure air-swept, packed column secondary CO_2 stripping column. The process may include a step of passing a CO_2-enriched air source exiting the secondary CO_2 stripping column to a preheater and therefrom for use as a boiler combustion air for a pulverized coal boiler of a pulverized coal plant.

In an embodiment, the CO_2 absorber includes a bottom packing portion with a first cross-sectional dimension, and a top packing portion with a second cross-sectional dimension that is different from the first cross-sectional dimension. One or more intercoolers may be disposed on the absorber. The location of the intercooler(s) may be between the bottom packing portion and the top packing portion and/or at an individual section. In another embodiment, the first cross-sectional dimension is approximately ⅓ that of the second cross-sectional dimension.

In another aspect, a CO_2 capture and recovery system for recovery of CO_2 from a post-combustion gas is described, including systems and devices for accomplishing the process as described above. Incorporation of the described CO_2 capture and recovery system into a pulverized coal-fired power plant is described.

In the following description there are shown and described several different embodiments, simply by way of illustration

of some of the modes best suited to carry out the invention. As it will be realized, the described subject matter is capable of other different embodiments and its several details are capable of modification in various, obvious aspects all without departing from the invention. Accordingly, the drawings and descriptions will be regarded as illustrative in nature and not as restrictive.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings incorporated herein and forming a part of the specification, illustrate several aspects of the present invention and together with the description serve to explain certain principles of the invention. In the drawings:

FIG. **1** schematically shows a CO_2-selective membrane module according to the present disclosure;

FIG. **2** shows an exemplary membrane for use in the module of FIG. **1**;

FIG. **3** graphically depicts CO_2/N_2 selectivity of the membrane of FIG. **2**;

FIG. **4** schematically depicts integration of a CO_2 stripping and recovery system according to the present disclosure into a pulverized coal-fired power plant; and

FIG. **5** graphically depicts impact of CO_2 stripper operating parameters on energy consumption for solvent regeneration.

Reference will now be made in detail to the present preferred embodiment of the invention, examples of which are illustrated in the accompanying drawings.

DETAILED DESCRIPTION OF THE INVENTION

To solve the foregoing problems, at a high level the present disclosure is directed to a process for capturing CO_2 from low driving force post-combustion flue gases including an initial step of CO_2 enrichment and a subsequent heat integrated aqueous CO_2 capture system utilizing a solvent to upgrade the CO_2 purity. With reference to FIG. **1**, a high flux, low pressure drop and low selectivity membrane **100** is used to split the flue gas **102** exiting an SO_2 polisher (not shown) into two streams. Such membranes are known in the art. The first stream is a CO_2-enriched permeate stream **104** comprising approximately 14% of the total flue gas, and containing approximately 60% CO_2 after removal of water vapor at 40° C. The second stream is a CO_2-lean reject stream **106** (approximately 76% of the total flue gas flow rate) containing approximately 10% CO_2 after water vapor removal at 40° C. CO_2 permeability through the membrane **100** is enhanced by providing low-quality energy available from a CO_2 stripper overhead condenser and/or from CO_2 compression intercoolers, to produce water vapor diluting the membrane permeate stream to reduce the CO_2 partial pressure and maintain a reasonable driving force at relatively low pressure vacuum conditions.

In one embodiment (see FIG. **2**), a modified membrane **200** developed by MTR was used. This membrane comprised a CO_2-selective layer **202**, a gutter layer **204**, a porous support membrane **206**, and a non-woven paper support **208**. As shown in FIG. **3**, such membranes exhibit decreasing selectivity as permeance increases. In laboratory trials evaluating pure CO_2 and N_2 at ambient temperature, the highest permeance sample had a CO_2 permeance of 4100 gpu and a CO_2/N_2 selectivity of 29.

As briefly described above, an effective method for removing CO_2 from post-combustion gases is use of a scrubbing solvent to absorb acidic CO_2. Exemplary solvents for use in this process include primary, secondary, and tertiary amines, although many others are known including piperazine and the stripper disclosed in the present assignee's own U.S. Published Patent Appl. No. 2012/0082604 to Liu et al. for Contaminant-tolerant Solvent and Stripping Chemical and Process for Using Same for Carbon Capture from Combustion Gases, the entirety of the disclosure of which is incorporated herein by reference. Commonly, following removal of CO_2 from post-combustion gases, the solvent is regenerated for re-use by removing CO_2 therefrom by means of a single stage stripper.

In a next aspect of the present disclosure, a two-stage stripping unit for solvent regeneration was provided. As will be described in greater detail, the unit includes an added air-based second stage stripper, inserted between a conventional rich-lean crossover heat exchanger and a lean solution temperature polishing heat exchanger. Advantageously, the outlet stream from the air-based second stage stripper, containing a low concentration of CO_2, is used as combustion air for a pulverized coal-fired boiler (see description of FIG. **4** below), enriching the flue gas with CO_2 (with approximately 0.7% de-rating of boiler efficiency).

In an embodiment (see FIG. **4**), the described CO_2-enriching membrane and two-stage stripping unit are integrated into an existing power plant **400**. The CO_2 capture and compression system of the present disclosure are generally referenced as block **402**. Summarizing, the CO_2 capture and compression system **402** includes at least a pre-treatment tower, a membrane module (see FIG. **1**) coupled with a water evaporator, a moisture separator, a vacuum pump, a packed column CO_2 absorber, two packed bed CO_2 strippers with one reboiler and reclaimer, and various heat exchangers, pumps, filtration devices, and a multistage compressor with intercoolers.

In more detail, after passage of post-combustion gas through an SO_2 polisher **404**, flue gas enters a booster fan **406** to overcome downstream pressure drop. At this point (A) the flue gas is saturated with water at a temperature of around 55° C., water content of 17 vol. %, and CO_2 concentration of approximately 15.8 vol. % of the total wet gas stream. The flue gas then enters a counter-flow pretreatment tower **408** which uses a dilute caustic solution for further SO_2 and other contaminant removal. Tower **408** polishes the flue gas to <5 ppm SO_2, which minimizes solvent degradation and potential membrane fouling. The spent solution is cooled, crystallizing a portion of the sulfur product that is then removed via filtration.

The SO_2-polished flue gas then enters (see point B) a CO_2 membrane pre-concentration module **410** (in the depicted embodiment having a selectivity of approximately 8 and a permeance of ≥5000 gpu) to produce two streams as described above.

In pilot testing, the effect of pre-concentration of CO_2 by a membrane as described was evaluated. Specifically, a pre-concentration membrane provided by MTR was evaluated (see Table 1), using a stripper operated at 45 psi to eliminate any effect of discrepancy of thermal compression from various carbon loadings obtained at the CO_2 absorber. Various liquid/gas ratios were tested to ensure a capture efficiency of approximately 80% or greater. As indicated with similar carbon/nitrogen ratios in a lean solution returning to the CO_2 absorber by varying heat flux at a bottom of the CO_2 stripper, supplying a high CO_2 inlet concentration to the CO_2 absorber reduced energy consumption required for solvent regeneration. The energy needed for regeneration with a pre-concentration membrane was found to be approximately 30% less than that obtained from 14 vol. % CO_2 inlet concentration without the membrane installed.

TABLE 1

Summary of Carbon Loadings and Energy of Regeneration for Various Experiments.

Expt	Feed CO_2 (%)	Perm. CO_2 (%)	Residue CO_2 (%)	L/G (wt/wt)	Stripper bottom. temp. (° C.)	% Capture	Energy Btu/lb CO_2
M4	14	—	9	2.9	136	80	1007
M5	14	25	—	3.0	136	79	956
M6	14	29	—	3.2	136	81	1074
R1	14	—	—	4.8	133	79	1468
R2	14	—	—	5.0	132	75	1445

Using the total pressure (P_{tot}) in the stripper of 45 psi (310 kPa) and the partial pressure of steam (P_{H2O}) at the stripper exhaust temperature, the partial pressure of CO_2 (P_{CO2}) was estimated as $(P_{tot})=(P_{H2O})+(P_{CO2})$. As shown in Table 2, a reduction of steam requirement was observed by inclusion of the pre-concentration membrane.

TABLE 2

Partial Pressure of H_2O and CO_2 at Stripper Exhaust.

Expt	Stripper Exhaust Temp. (° C.)	Steam Partial Pressure (P_{H2O}) kPa	CO_2 Partial Pressure (P_{CO2}) kPa	P_{CO2}/P_{H2O}
With membrane	105	121	189	1.56
Without	107	130	180	1.38

In the depicted embodiment the membrane module **410** is operated at 55° C., and at slightly above ambient pressure at the reject side, and at a vacuum of 30 kPa at the permeate side. The permeate passes through a moisture separator or condenser **412**, a compressor **414**, and then enters a bottom **415** of a CO_2 absorber **416** (see point C). At this point, the permeate stream consists of approximately 60 vol. % CO_2, 31 vol. % N_2+O_2+Ar, trace SO_2 and halogens, and the balance of water vapor. In the depicted embodiment, moisture separator **412** is a membrane separator of known design. In such embodiments, a portion of the combustion air is used as a carrying gas at the permeate side of moisture separator **412**. The moisture-rich air is then fed to a secondary air-based CO_2 stripper **418** (see point N) for CO_2 stripping as described below.

The reject stream proceeds through a direct water contactor **420** (in the depicted embodiment being a water spray system with liquid collection at a bottom thereof) and enters the CO_2 absorber **416** at an intermediate portion **422** (see point D). This is unlike conventional CO_2 absorber configurations including only one feed point for flue gases. The reject stream includes 10 vol. % CO_2 prior to entering the CO_2 absorber **416**.

In an embodiment, the cross-sectional dimension of the bottom packing of CO_2 absorber **416** is approximately ⅓ of the cross-sectional dimension of the top packing, to balance the gas-side pressure drop and mass transfer requirements. An intermediate heat exchanger (cooler) **417** is interposed between the top and bottom portions of CO_2 absorber **416**. CO_2-depleted flue gas is treated in a water-wash section **424** disposed at a top of the CO_2 absorber, using water from the direct water contactor **420** to remove residual solvent. At an exhaust point **426** of CO_2 absorber **416** (see point E), the flue gas is saturated with water at approximately 42° C.

After gaseous CO_2 is transferred to the liquid phase, the carbon-rich solution exits the CO_2 absorber (see point F), is pressurized, and is sent to a heat recovery unit **428** (see point G) and then to an overhead condenser **430** of a primary CO_2 stripper **432** (see point H). Then, the carbon rich solution proceeds to a lean/rich heat exchanger **434** (see point I). Then, the solution proceeds to the primary CO_2 stripper **432**, which is a conventional stripper of known design. This portion of the process requires external energy to drive a steam reboiler **436**. At an exit point **438** of the primary stripper **432** (see point J), the gas stream consists primarily of CO_2 (60 vol. %) and water vapor (40 vol. %) at a pressure of approximately 3.7 bar and a temperature of approximately 110° C.

After exiting the heat recovery unit **420**, the CO_2 enriched gas stream is pressurized to approximately 153 bar with intercooling for downstream utilization or sequestration (see point K). Sensible heat rejected from intercoolers **440** (see point L) is used for water evaporation to increase CO_2 permeance driving force through CO_2 membrane pre-concentration module **410** as described above.

Carbon-lean solution exiting the primary stripper **432** is sent to a lean/rich heat exchanger **434** (see point I) where the heat is recovered with the carbon-rich solution. Next, the carbon-lean stream (temperature approximately 90° C.) is sent to a top (see point M) of an ambient pressure air-swept, packed column secondary CO_2 stripper **442** to further reduce the carbon load. An air-swept secondary CO_2 stripper **442** was selected due to the discovery that this system improved CO_2 stripping from solvent compared to conventional systems at like operating temperatures. As shown in Table 3, under laboratory conditions, at the same column operating temperature the CO_2 concentration in the evolved stream from the air-based stripper increased with increased solvent solution carbon loading compared to conventional systems. Likewise, at a same solvent carbon loading, high operating temperatures provided a high stream CO_2 concentration.

TABLE 3

Impact of Stripping Conditions on Carbon Release (30 wt % MEA solvent).

Temperature (° C.)	Carbon Loading (mol C/kg soln.)	% CO_2 in evolved gas
80	1.90	2.43
	2.00	2.59
90	1.80	3.55
	1.86	4.35
	1.90	5.06
	1.93	5.08
95	1.89	5.92
	1.95	6.40

Finally, the carbon-lean stream was cooled to approximately 40° C. by power plant cooling water, and recycled to the CO_2 absorber **416** (see point O). Water-saturated air used as carrying gas for CO_2 stripping is obtained from the membrane moisture separator **412** described above. The CO_2 enriched air exiting the secondary CO_2 stripper **442** (approximately 2-4% CO_2 content) is fed to an air preheater and sent to the pulverized coal boiler **444** of the pulverized coal plant **400** as boiler combustion air.

Advantageously, the processes and systems of the present disclosure provide significant advantages over conventional CO_2 recovery technology. According to the Gibbs free energy equations (Gibbs-Helmholtz equation and Clausius-Clapeyron relation), the CO_2 partial pressure at a top of a CO_2 stripper can be expressed as:

$$P_{CO_2} = P^*_{CO_2,scrub} \times e^{\left[\frac{\Delta h_{abs,co2}}{R} \times \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right]}$$

where $P^*_{CO_2scrub}$ is the CO_2 equilibrium pressure in the carbon rich solution with a carbon loading at the bottom of a CO_2 absorber with a temperature of T_{ref}. For a given solvent and a temperature, $P^*_{CO_2scrub}$ directly corresponds to the carbon loading (Carbon/Nitrogen, C/N ratio) resulting from the mass transfer M inside the CO_2 absorber and guided by the equation of $M=K_G$ (overall mass transfer coefficient)·A (active surface area)·ΔP_{CO2} (driving force defined by differential CO_2 pressure between gas and liquid phase). With an increased CO_2 driving force, a higher C/N ratio is achieved at a bottom of the CO_2 absorber, resulting in a high CO_2 partial pressure at a top of the CO_2 stripper at a desired temperature. This reduces the energy required to regenerate the same amount of CO_2 from a stripping solvent.

As shown in Table 4, compared to conventional equipment and a benchmark solvent (30 wt % monoethanolamine), the presently disclosed processes and systems provide a significant advantage over conventional configurations including CO_2 absorbers with a single feeding point. At an identical flue gas temperature (40° C.) and lean solution temperature (40° C.) fed into the CO_2 scrubber and a constant flue gas flowrate, the presently described technology from process simulation provided an 8% increase in carbon loading, a 19% reduction in liquid recirculation, and a 15% reduction in energy consumption while maintaining a same carbon loading of the lean solution and a 90% overall CO_2 capture efficiency.

TABLE 4

Comparison of CO_2 absorber with a single flue gas feed point to a CO_2 absorber with two flue gas feed points.

	Single flue gas feed point (normalized to unity)	Dual flue gas feed point
Carbon loading	1	1.08
Solvent recirculation	1	0.81
Energy for regeneration	1	0.85

In turn, the heat integration processes and systems described above provide significant advantages in reduction of energy requirements for recovery of CO_2 compared to conventional systems. In particular, the use of an air-based secondary stripper **442** as described above is advantageous. The extra lean solvent produced from solvent regeneration by the presently described process (compared to conventional systems using a single CO_2 stripper for solvent regeneration) allow use of smaller CO_2 absorbers and CO_2 strippers, reducing capital costs. Further reduction of carbon loading in the lean solvent provides a higher free amine concentration (higher pH) and lower liquid CO_2 partial pressure at a top of the CO_2 absorber. The recycling of CO_2 from the secondary stripper (as combustion air for a pulverized coal boiler, see description above) yields a higher CO_2 concentration (15-20%) compared to conventional systems. Lower liquid CO_2 partial pressure and higher gas phase CO_2 concentration increases the driving force for CO_2 diffusion through a liquid/gas reaction film, resulting in a higher mass transfer coefficient. Still more, reaction kinetics are enhanced by the higher free amine concentration in the upper part of the CO_2 absorber.

Still more, steam increases water vapor concentration in the permeate-side of CO_2-selective membrane module **410** that is generated by heat rejection from compressor intercoolers. This dilutes the permeance to reduce the vacuum requirement for achieving a reasonable driving force between feed and permeate sides of the CO_2-selective membrane, allowing reducing membrane surface area (and associated cost) for a given permeance flux. Moreover, the steam saturates (wets) the portion of combustion air in module **412** used for the secondary CO_2 stripper **442**, reducing energy demand for water evaporation (temperature increase from bottom to top along the secondary CO_2 stripper). In turn, selection of low selectivity/ambient pressure operation membranes for use in the CO_2-selective membrane module **410** allows selection of cost-effective materials for the membrane.

Still yet more, as described above a CO_2 absorber **416** with staged cross-sectional areas is provided, including an intermediate cooler **417**. Unlike conventional absorbers, the CO_2 absorber of the present disclosure includes a bottom packing having a smaller cross-sectional dimension than that of the top packing. This configuration takes advantage of a low flue gas flow rate (14% of total flue gas) while maintaining a reasonable flue gas velocity to minimize gas-side mass transfer resistance and to reduce a flooding tendency caused by a high liquid/gas ratio. In one embodiment, the present CO_2 absorber bottom portion cross-sectional dimension is approximately ⅓ that of the top portion cross-sectional dimension. By use of the described CO_2 absorber including staged cross-sectional areas of this ratio, the liquid/gas ratio is increased 7.7 times in the bottom section of packing to enhance gas-liquid contact and reshape the vapor-liquid-equilibrium operating curve in an interior of the CO_2 absorber, providing maximum benefit from high inlet CO_2 concentration (CO_2 gas pressure).

In another feature, the primary CO_2 stripper **432** is operated at an elevated pressure (approximately 3.7 bar), reducing energy consumption for CO_2 compression by 30% compared to conventional systems. As shown in FIG. **5**, energy consumption is significantly reduced as stripper operating pressure increases. As the stripper pressure increases, the mole ratio of CO_2/H_2O (vapor) at the stripper outlet is increased at a given temperature, leading to overall reduction in energy consumption. The operating pressure (3.7 bar) was found to maximize the energy benefit while minimizing capital investments and solvent degradation (solvent degradation is known to increase with increasing temperature, but energy savings for solvent regeneration by increasing stripper operating pressure reach a point of diminishing returns).

Numerous other advantages accrue from the presently described processes and systems. Combining membrane preconcentration of flue gas CO_2 and use of a two-stage stripping system as described provided a CO_2 mass-transfer flux of energy on average 2.5 times faster than that of conventional systems, with further benefits deriving from the CO_2 absorber including staged cross-sectional dimensions as described. The high mass-transfer flux resulted in the ability to provide a smaller CO_2 absorber to capture the same amount of CO_2 from a flue gas stream. CO_2 absorber size reductions of up to 50% compared to conventional absorbers are anticipated compared to conventional systems/solvents.

Further, the described heat integration processes are anticipated to reduce plant cooling tower heat rejection duty (the amount of heat processes by the cooling tower) by 12-19%, reducing capital cost for the cooling tower and auxiliary equipment by approximately 15%.

The foregoing description has been presented for purposes of illustration and description. It is not intended to be exhaus-

tive or to limit the invention to the precise form disclosed. Obvious modifications or variations are possible in light of the above teachings. The embodiments were chosen and described to provide the best illustration of the principles of the invention and its practical application to thereby enable one of ordinary skill in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. All such modifications and variations are within the scope of the invention as determined by the appended claims when interpreted in accordance with the breadth to which they are fairly, legally and equitably entitled. In turn, the drawings and preferred embodiments do not and are not intended to limit the ordinary meaning of the claims in their fair and broad interpretation in any way when interpreted in accordance with the breadth to which they are fairly, legally and equitably entitled.

What is claimed:

1. A process for removal and recovery of CO_2 from a post-combustion flue gas, comprising:

pre-concentrating a CO_2 component of the post-combustion flue gas by passing the post-combustion flue gas through a CO_2-selective membrane module to provide a CO_2-enriched permeate stream and a CO_2-lean reject stream;

in a CO_2 absorber, contacting the CO_2-enriched permeate stream and the CO_2-lean reject stream with a scrubbing solvent to absorb CO_2 and provide a carbon-rich scrubbing solvent; and

stripping absorbed CO_2 from the carbon-rich scrubbing solvent by a two-stage CO_2 stripping system.

2. The process of claim **1**, further including evaporating at least a portion of a water component of a post-combustion flue gas condensate for use as a carrier vapor for a permeate side of the CO_2-selective membrane module.

3. The process of claim **1**, further including passing a CO_2-rich permeate stream from the CO_2-selective membrane module to a feed point disposed at a bottom portion of the CO_2 absorber and passing the CO_2-lean reject stream from the CO_2-selective membrane module to an intermediate feed point above the CO_2 absorber bottom portion feed point.

4. The process of claim **1**, further including providing a CO_2-membrane module comprising a high flux, low pressure drop, low CO_2 selectivity membrane.

5. The process of claim **1**, further including providing a two stage stripping system comprising:

a primary CO_2 stripping column for stripping CO_2 from the carbon-rich scrubbing solvent exiting the CO_2 absorber; and

a secondary CO_2 stripping column for stripping CO_2 from a carbon-lean scrubbing solvent exiting the primary CO_2 stripping column.

6. The process of claim **5**, including providing an ambient pressure air-swept, packed column secondary CO_2 stripping column.

7. The process of claim **1**, including providing a CO_2 absorber having a bottom packing portion with a first cross-sectional dimension, and a top packing portion with a second cross-sectional dimension that is different from the first cross-sectional dimension.

8. The process of claim **1**, including providing one or more intercoolers at intermediate positions of the CO_2 absorber.

9. The process of claim **7**, wherein the first cross-sectional dimension is approximately ⅓ that of the second cross-sectional dimension.

10. The process of claim **6**, including passing a CO_2-enriched air source exiting the secondary CO_2 stripping column to a preheater and therefrom as a boiler combustion air for a pulverized coal boiler of a pulverized coal plant.

11. A CO_2 capture and recovery system for recovery of CO_2 from a post-combustion gas, comprising:

a CO_2-selective membrane module for pre-concentrating a CO_2 component of an SO_2-depleted post-combustion gas to provide a CO_2-enriched permeate stream and a CO_2-lean reject stream;

a CO_2 absorber for providing a carbon-rich scrubbing solvent by contacting the CO_2-enriched permeate stream and the CO_2-lean reject stream with a scrubbing solvent to absorb CO_2; and

a two-stage CO_2 stripping system for stripping absorbed CO_2 from the carbon-rich scrubbing solvent.

12. The system of claim **11**, further including a moisture separator or condenser for removing at least a portion of a water vapor component of the CO_2-enriched permeate stream.

13. The system of claim **11**, wherein the CO_2-enriched permeate stream from the CO_2-selective membrane module is passed to a feed point disposed at a bottom of the CO_2 absorber and the CO_2-lean reject stream from the CO_2-selective membrane module is passed to an intermediate feed point above the CO_2-absorber bottom feed point.

14. The system of claim **11**, wherein the CO_2-membrane module comprises a high flux, low pressure drop, low CO_2-selectivity membrane.

15. The system of claim **11**, wherein the two stage stripping system comprises:

a primary CO_2 stripping column for stripping CO_2 from the carbon-rich scrubbing solvent exiting the CO_2 absorber; and

a secondary CO_2 stripping column for stripping CO_2 from a carbon-lean scrubbing solvent exiting the primary CO_2 stripping column.

16. The system of claim **15**, wherein the secondary CO_2 stripping column is an ambient pressure air-swept, packed column CO_2 stripping column.

17. The system of claim **15**, wherein the CO_2 absorber includes a bottom packing portion with a first cross-sectional dimension and a top packing portion with a second cross-sectional dimension that is different from the first cross-sectional dimension.

18. The system of claim **11**, wherein the CO_2 absorber further includes one or more intercoolers disposed at intermediate positions of the CO_2 absorber.

19. The system of claim **17**, wherein the first cross-sectional dimension is approximately ⅓ that of the second cross-sectional dimension.

20. The system of claim **16**, wherein a CO_2-enriched air source exiting the secondary CO_2 stripping column is passed to a preheater and therefrom to a pulverized coal boiler of a pulverized coal power plant as a boiler combustion air.

21. A pulverized coal-fired power plant comprising the CO_2 capture and recovery system of claim **11**.

* * * * *