



(51) International Patent Classification:

C01B 3/38 (2006.01) *F02C 1/10* (2006.01)
F02C 1/04 (2006.01)

(21) International Application Number:

PCT/US2014/058180

(22) International Filing Date:

30 September 2014 (30.09.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

14/043,321 1 October 2013 (01.10.2013) US

(71) Applicant: **L'AIR LIQUIDE, SOCIETE ANONYME
POUR L'ETUDE ET L'EXPLOITATION DES PRO-
CEDES GEORGES CLAUDE** [FR/FR]; 75 quai d'Orsay,
F-75007 Paris (FR).

(72) Inventor; and

(71) Applicant (for US only): **ENG, Bruce** [US/US]; 1434
Woodcrest Drive, Houston, Texas 77018 (US).

(74) Agents: **MURRAY, Justin K.** et al.; 2700 Post Oak
Boulevard, Suite 325, Houston, Texas 77056 (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, BN, 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, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: A CLOSED LOOP SUPERCRITICAL CARBON DIOXIDE POWER CYCLE

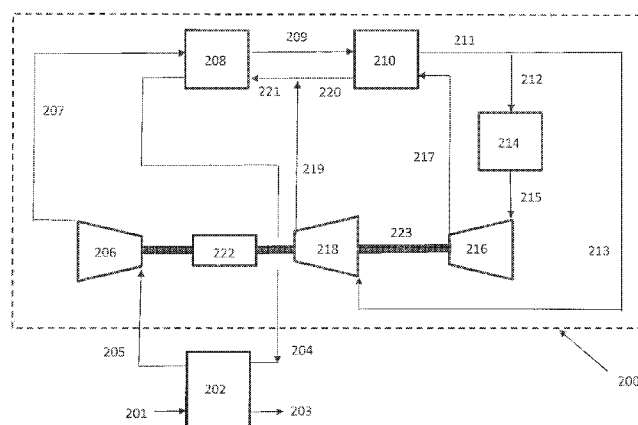


Figure 2

(57) Abstract: One embodiment of a closed loop supercritical carbon dioxide power generation process is provided. This process includes indirectly exchanging heat between a hot gas stream (201) and a warm supercritical carbon dioxide stream (204), expanding the heated supercritical carbon dioxide stream in a turbine (206), indirectly exchanging heat from the expanded supercritical carbon dioxide stream in a high temperature recuperator (208), thereby producing a cooled, expanded supercritical carbon dioxide stream (211), splitting the cooled, expanded supercritical carbon dioxide stream into a first stream (212) and a second stream (213), compressing the first stream in a main compressor (216), and introducing the compressed first stream into the low temperature recuperator (210), and compressing the second stream in a recompressor (218), combining the compressed second stream (219) with the heated first stream (220), and introducing the combined stream (221) into the high temperature recuperator (208), wherein it indirectly exchanges heat with expanded supercritical carbon dioxide stream (207), thereby producing the warm supercritical carbon dioxide stream (204).

A CLOSED LOOP SUPERCRITICAL CARBON DIOXIDE POWER CYCLE

Background

5 In the interest of maximizing thermal efficiency in a standard Steam Methane Reformer (SMR) plant, steam is typically generated from two sources: flue gas waste heat and process heat. This inevitably leads to excess steam generation, more than required internally for the reforming process. In the absence of a steam customer, this results in the last resort measure of installing a steam turbine for realizing economic value.

10

The concept of supercritical carbon dioxide (S-CO₂), as a promising heat extraction working fluid for cool down of nuclear reactors, has been in existence for more than a decade. Most of the technological developments in this area have occurred from a nuclear power perspective. The proof of concept has been well established
15 experimentally. Under the DOE GEN-IV nuclear program, Sandia National lab has developed two small S-CO₂ loops (~1MW): Compression loop (at Sandia) and Brayton loop (at Barber Nichols). In the past few years, the idea of using S-CO₂ cycle for non-nuclear applications has gained traction. Because of a lesser footprint, lower operating and capital costs, it has been proposed to be integrated in solar plants, molten carbonate
20 fuel cells and as first bottoming cycle in combined cycle plants followed by steam as second bottoming cycle. Under the DOE Sunshot initiative (for solar applications), a 10MWe scale up is currently under development along with industry partners. It is to be noted that for a standard SMR (120 MMSCFD), power generation is ~19 MW.

25 In SMR's, for good thermal efficiency purposes, the following ideas have been proposed/implemented. As discussed earlier, installation of a steam turbine to realize economic value out of excess steam. Multiple pre-reformers may be implemented to minimize excess steam. Helical Tube Reactor (HTR) technology has been developed to lower the temperature out of the reformer on the process side.

30

To date, no prior art exists which advocates the integration of S-CO₂ in an SMR in the configuration as proposed herein for significant reduction or, possibly, an elimination of export steam.

Summary

One embodiment of a closed loop supercritical carbon dioxide power generation process is disclosed. This process includes Indirectly exchanging heat between a hot gas stream and a warm supercritical carbon dioxide stream, expanding the heated supercritical carbon dioxide stream in a turbine, indirectly exchanging heat from the expanded supercritical carbon dioxide stream in a high temperature recuperator and the a temperature recuperator, thereby a cooled, expanded supercritical carbon dioxide steam, splitting the cooled, expanded supercritical carbon dioxide stream into a first stream and a second stream, compressing the first stream in a main compressor, and introducing the compressed first stream into the low temperature recuperator, and compressing the second stream in a recompressor, combining the compressed second stream with the heated first stream, and introducing the combined stream into the high temperature recuperator, wherein it indirectly exchanges heat with expanded supercritical carbon dioxide stream, thereby producing the warm supercritical carbon dioxide stream.

Brief Description of the Figures

Figure 1 is a schematic representation of one embodiment of the present invention.

Figure 2 is a schematic representation of one embodiment of the present invention.

Figure 3 is an illustration of the cycle efficiency of the various cycles as a function of source temperature.

Description of Preferred Embodiments

Illustrative embodiments of the invention are described below. While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof have been shown by way of example in the drawings and are herein described in detail. It should be understood, however, that the description herein of specific embodiments is not intended to limit the invention to the particular forms disclosed, but on the contrary, the intention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

It will of course be appreciated that in the development of any such actual embodiment, numerous implementation-specific decisions must be made to achieve the developer's specific goals, such as compliance with system-related and business-related constraints, which will vary from one implementation to another. Moreover, it will be appreciated

that such a development effort might be complex and time-consuming, but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure.

5 In the present innovation, it is proposed to use the S-CO₂ closed power loop for better exploiting the waste heat in the SMR flue gas section by splitting the flue gas outlet (T~750 deg C) of the pre-reformer super-heater in the following fashion:

10 Since the integration is deliberately done in the 450-700°C range, all the key SMR process parameters (i.e. pre-reformer S/C, pre-reformer inlet T, reformer S/C, reformer inlet T and WGS inlet T), input natural gas feed and hydrogen production have not been effected. It is anticipated that excess steam may still be generated, but this excess steam will be 12% of the original stream production, or less. The 12% excess steam can either be directly sold or used for electricity generation by installing a small steam turbine
15 (which will be 1/8th size of the steam turbine in a typical standard SMR).

In a supercritical cycle the working fluid is maintained above the critical point during the compression phase of the cycle.

20 As shown in Figure 3, a simple SC CO₂ Brayton cycle (comprising one turbine and one compressor) has higher thermodynamic efficiency than a steam (Rankine) cycle for temperatures greater than 450 deg C. The more complex 3t/6c (comprising three turbines and six compressors) He Brayton cycle has higher efficiencies than the simple SC CO₂ Brayton cycle for temperatures greater than 700 deg C. Hence, in the
25 temperature range 450-700 deg C, CO₂ is the optimum working fluid for heat extraction.

By adding an extra compressor and, the SC CO₂ cycle achieves a thermodynamic efficiency of 50% in the same temperature range. The gain in efficiency, as compared to
30 steam, is primarily because of

- a) a significant reduction in compression work due to the liquid like density near the critical point,
- b) there are no pinch limitations as encountered in steam generation, since SC CO₂ behaves like a single phase fluid in supercritical region, and

c) the critical point (31 deg C) is near the desired heat rejection temperature of 20 deg C.

An added benefit, as compared to a steam cycle for same power output, is that the overall footprint is significantly reduced. The high pressure range (typically 70 -200 bara) helps in reducing the size of the compressors, turbines and heat exchangers by orders of magnitude. Further, CO₂ is a non-toxic, inexpensive, stable, inert, relatively non-corrosive, inflammable and well characterized fluid.

Following are the key advantages realized from the proposed integration with an SMR:

- a) the ability to minimize or, possibly, eliminate export steam generation.
- b) due to the higher efficiency of SC CO₂ cycle, there is approximately a 12% gain in power generation when compared with a steam cycle. This is assuming a small steam turbine (~1/8th size of the steam turbine in a pure steam cycle, 80% efficiency and condensing) is installed.
- c) the flue gas steam generator is eliminated and there is approximately a 35% reduction in boiler feed water requirement.
- d) as previously mentioned, the overall footprint, as compared to steam cycle for the same power output, is significantly reduced.

Turning now to Figure 1, one embodiment of the present invention is presented. Hydrocarbon fuel stream 101 and steam stream 102 are combined into pre-reformer mixture stream 133 and introduced into pre-reformer preheating module 125. Within module 125, pre-reformer mixture stream 133 is heated against flue gas stream 124, thereby producing heated pre-reformer stream 134 and flue gas stream 126.

Pre-reformer mixture stream 133 may have a temperature of between 275 and 350 C, preferably 310 C. Heated pre-reformer stream 134 may have a temperature of between 475 and 525 C, preferably 490 C. Flue gas stream 124 may have a temperature of between 825 and 875 C, preferably 850 F. Flue gas stream 126 thus exits module 125 with a reduced temperature of between 725 and 775 C, preferably 750 C.

Heated pre-reformer stream 134 is then introduced into pre-reformer 103, thereby producing reformer mixture 105. Reformer mixture 105 is then combined with steam

stream 104 thereby forming reformer mixture 110. Reformer mixture 110 may have a temperature of between 575 and 625 C, preferably 600 C.

5 Reformer mixture 110 is then introduced into reformer preheating module 109. Within module 109 reformer mixture stream 110 is heated against flue gas stream 114, thereby producing heated reformer stream 136 and flue gas stream 111.

10 Heated reformer stream 136 is then combined with steam stream 137 thereby forming reformer mixture stream 138. Reformer mixture stream 138 is further heated in reformer pre-heating module 107. Within module 107, reformer mixture 138 is heated against flue gas stream 111, thereby producing heated reformer stream 108 and flue gas stream 124. .

15 Flue gas stream 111 may have a temperature of between 875 and 925 C, preferably 900 C. Flue gas stream 114 may have a temperature of between 1025 and 1075 C, preferably 1057 C. Heated reformer stream 108 may have a temperature of between 625 and 675 C, preferably 652 F.

20 Heated reformer stream 108 then enters reformer 113, wherein it is heated and catalytically produces process gas stream 115. Fuel stream 112 and heated air stream 130 are introduced into reformer 113, where they combust, thereby providing heat for the above catalytic reaction, and producing flue gas stream 114. Process gas stream 115 enters heat recovery boiler 116, wherein condensate stream 118 is heated to produce process boiler steam stream 117, and syngas stream 119. Process boiler steam stream 25 may have a temperature of between 250 and 300 C, preferably 270 C.

30 Flue gas stream 126 splits into flue gas stream 128 and flue gas stream 127. Flue gas stream 128 may comprise between 50 and 70%, preferably 60% of flue gas stream 126. At least a portion 121 of process boiler steam stream 117 enters superheater module 122, wherein it exchanges heat with flue gas stream 127, thereby producing flue gas stream 135 and super heated steam stream 123. Steam stream 123 is then split into at least stream 102, 104, and 137. Excess steam stream 120 may comprise less than 20% of the total process boil steam stream 117. Excess steam stream 120 may comprise between 10 and 15%, preferably 12% of the total process boil steam stream 117. Superheated steam

stream 123 may have a temperature of between 300 and 350 C, preferably 335 C. Flue gas stream 135 may have a temperature of between 600 and 650 C, preferably 630 C.

5 Flue gas stream 135 is recombined with flue gas stream 128, thus producing flue gas stream 201. Flue gas stream 201 may have a temperature of between 675 and 725 C, preferably 700C.

10 Flue gas stream 201 enters power cycle reheat module 202, wherein it indirectly exchanges heat with warm supercritical carbon dioxide stream 204, thereby producing heated supercritical carbon dioxide stream 205, and flue gas stream 203. Cooled combined flue gas stream 203 may further indirectly exchange heat with process streams, such as ambient air stream 114, thereby producing hot air stream 116 and exhaust gas stream 117. Cooled combined flue gas stream 203 may have a temperature of between 435 and 485 C, preferably 460 C. Exhaust gas stream 117 may have a temperature of
15 between 100 and 200 C, preferably between 125 and 175 C, more preferably 150 C.

Flue gas stream 203 then enters air heater module 129, wherein it indirectly exchanges heat with inlet air stream 130, thereby producing heated air stream 131 and stack stream 132. Inlet air stream 130 may be ambient temperature. Inlet air stream 130 may have a
20 temperature of between 0 and 40 C. preferably between 10 and 30, more preferably 20 C. Stack stream 132 may have a temperature of between 125 and 175 C, preferably 150 C.

Turning now to Figure 2, one embodiment of the present invention is presented. Hot gas stream 201 indirectly exchanges heat with warm supercritical carbon dioxide stream 204,
25 thereby producing heated supercritical carbon dioxide stream 205, and cooled combined flue gas stream 203.

Heated supercritical carbon dioxide stream 205 then enters turbine 206, wherein it is expanded, thus producing energy. The energy is mechanically introduced into shaft 223,
30 wherein it powers main compressor 216 and re-compressor 218, with excess mechanical energy being converted to electricity in generator 222. As heated supercritical carbon dioxide stream 205 is expanded, it exits turbine 206 as expanded supercritical carbon dioxide stream 207. Expanded supercritical carbon dioxide stream 207 then enters high

temperature recuperator 208, wherein it indirectly exchanges heat with combined stream 221 (described below).

5 This produces cooled expand supercritical carbon dioxide stream 209, and warm supercritical carbon dioxide stream 204. Cooled expand supercritical carbon dioxide stream 209 is then introduced into low temperature recuperator 210, wherein it indirectly exchanges heat with compressed first stream 217 (described below). This produces heated first stream 220 and cooled, expanded supercritical carbon dioxide stream 211. Cooled, expanded supercritical carbon dioxide stream 211 is then divided into first
10 stream 212 and second stream 213. The first stream 212 may comprise between 50% and 70%, preferably between 55% and 65%, more preferably 60% of cooled, expanded supercritical carbon dioxide stream 211.

15 First stream 212 may enter reject heat exchanger 214, wherein it is cooled, thereby producing cooled first stream 215. Cooled first stream 215 then enters main compressor 216, wherein it is compressed into compressed first stream 217.

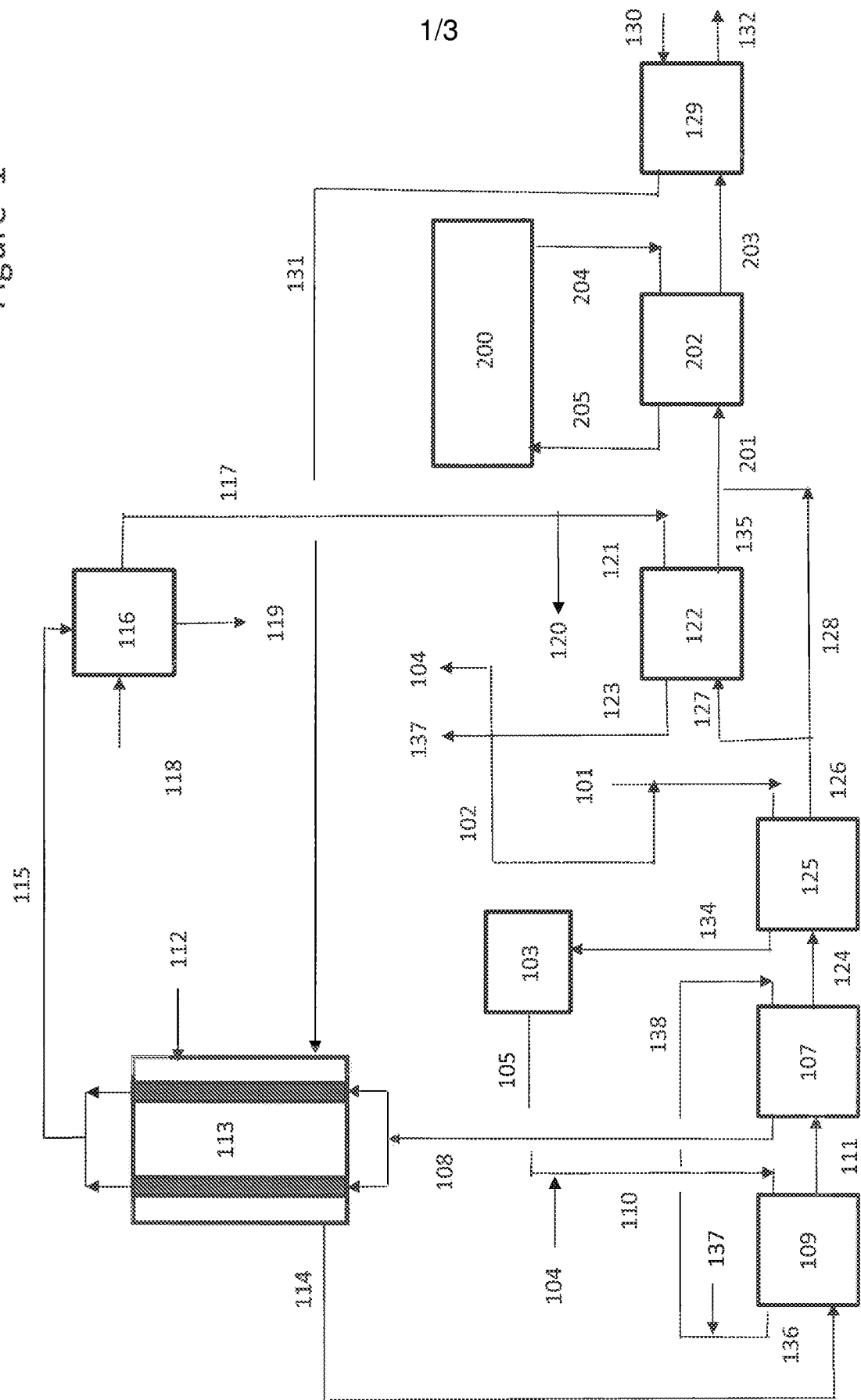
20 Second stream 213 enters re-compressor 218, wherein it is compressed into compressed second stream 219. Compressed second stream 219 is then combined with heated first stream, to produce combined stream 221.

What is claimed is:

1. A closed loop supercritical carbon dioxide power generation process, comprising:
 - indirectly exchanging heat between a hot gas stream (201) and a warm
5 supercritical carbon dioxide stream (204);
 - expanding the heated supercritical carbon dioxide stream (205) in a turbine (206);
 - indirectly exchanging heat from the expanded supercritical carbon dioxide stream
(207) in a high temperature recuperator (208) and a low temperature recuperator
(210), thereby producing a cooled, expanded supercritical carbon dioxide steam
10 (211);
 - splitting the cooled, expanded supercritical carbon dioxide stream (211) into a
first stream (212) and a second stream (213);
 - compressing the first stream (212) in a main compressor (216), and introducing
the compressed first stream into the low temperature recuperator (210); and
15
 - compressing the second stream (213) in a recompressor (218), combining the
compressed second stream (219) with the heated first stream (220), and
introducing the combined stream (221) into the high temperature recuperator
(208), wherein the combined stream (221) indirectly exchanges heat with
expanded supercritical carbon dioxide stream (207), thereby producing the warm
20 supercritical carbon dioxide stream (204).
2. The closed loop supercritical carbon dioxide power generation process of claim
1, wherein the first stream (212) comprises between 50% and 70% of cooled, expanded
supercritical carbon dioxide stream (211).
- 25 3. The closed loop supercritical carbon dioxide power generation process of claim
2, wherein the first stream (212) comprises between 55% and 65% of cooled, expanded
supercritical carbon dioxide stream (211).
4. The closed loop supercritical carbon dioxide power generation process of claim
30 4, wherein the first stream (212) comprises 60% of cooled, expanded supercritical carbon
dioxide stream (211).

5. The closed loop supercritical carbon dioxide power generation process of any of the preceding claims, wherein the temperature of the hot gas stream (201) is between 650°C and 750°C.
- 5 6. The closed loop supercritical carbon dioxide power generation process of any of the preceding claims, wherein the temperature of the hot gas stream (201) is between 675°C and 725°C.
- 10 7. The closed loop supercritical carbon dioxide power generation process of any of the preceding claims, wherein the temperature of the hot gas stream (201) is 700°C.

1997



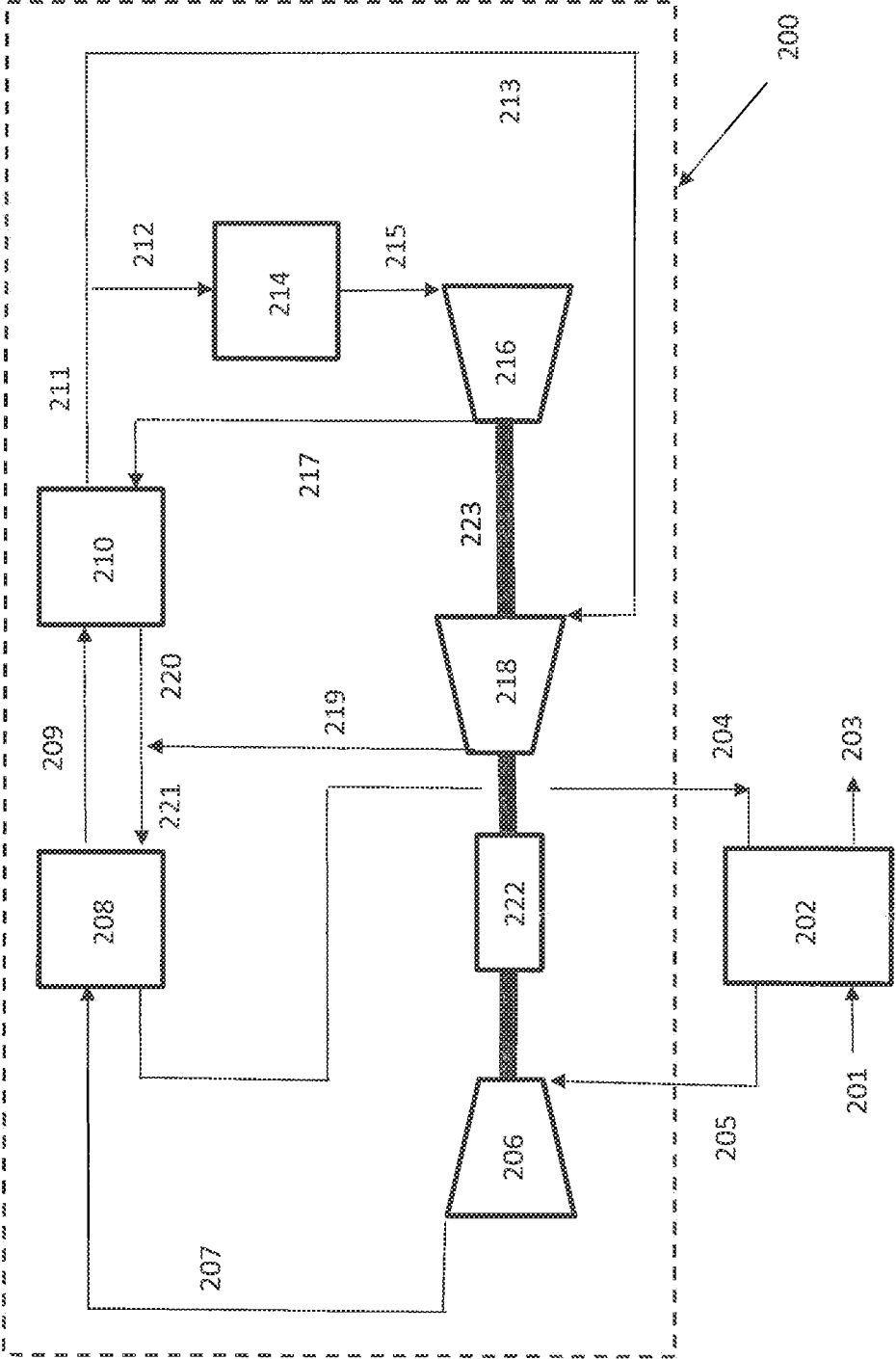


Figure 2

3/3

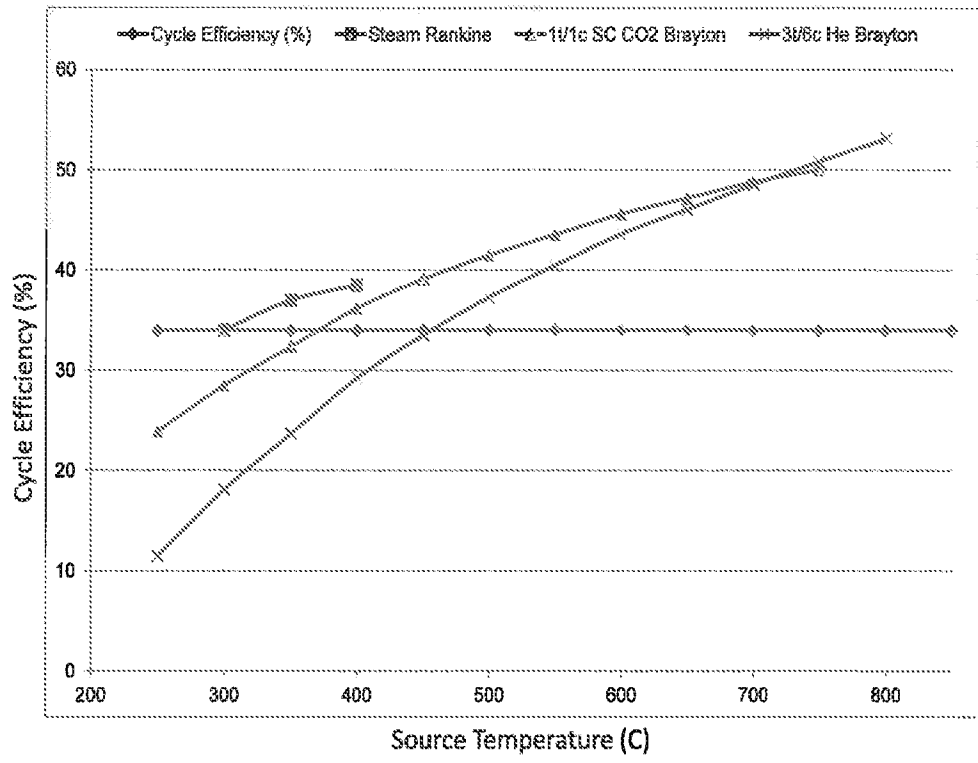


Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/058180

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01B3/38 F02C1/04 F02C1/10
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)

C01B F02C

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)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2012 145092 A (ISHIYAMA SHINTARO) 2 August 2012 (2012-08-02) paragraph [0029]; claims 1,2; figures 1,2 -----	1-7
A	CA 2 860 823 A1 (NIHON NATURE CELL CO LTD [JP]) 27 June 2013 (2013-06-27) paragraphs [0055], [0067] - [0076] -----	1-7
A	US 2012/216536 A1 (MA ZHIWEN [US] ET AL) 30 August 2012 (2012-08-30) paragraphs [0008], [0009]; figures 1,3 -----	1-7



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

15 January 2015

Date of mailing of the international search report

21/01/2015

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

Galleiske, Anke

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2014/058180

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2012145092 A	02-08-2012	NONE	

CA 2860823 A1	27-06-2013	AU 2012355256 A1	24-07-2014
		CA 2860823 A1	27-06-2013
		CN 104126206 A	29-10-2014
		EP 2800099 A1	05-11-2014
		KR 20140103273 A	26-08-2014
		WO 2013094196 A1	27-06-2013

US 2012216536 A1	30-08-2012	NONE	
