(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 August 2013 (29.08.2013)

WIPO | PCT

(10) International Publication Number
WO 2013/124632 A3

(51) International Patent Classification:
C25B 1/04 (2006.01) *C01B 13/02* (2006.01)
C07C 1/12 (2006.01) *C10G 2/00* (2006.01)
C07C 9/04 (2006.01) *F01K 19/00* (2006.01)
B01D 53/62 (2006.01) *F17D 1/02* (2006.01)
C01B 3/02 (2006.01)

(21) International Application Number:
PCT/GB2013/050375

(22) International Filing Date:
18 February 2013 (18.02.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1202791.8 20 February 2012 (20.02.2012) GB

(71) Applicant: **AVONDALE ASSOCIATES LIMITED** [GB/GB]; 7 Main Street, Largs KA30 8AA (GB).

(72) Inventor: **SIMPSON, Robert**; 7 Main Street, Largs KA30 8AA (GB).

(74) Agent: **HARRISON GODDARD FOOTE**; Delta House, 50 West Nile Street, Glasgow G1 2NP (GB).

(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, 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, PA, 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).

Published:

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

— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

[Continued on next page]

(54) Title: METHODS AND SYSTEMS FOR ENERGY CONVERSION AND GENERATION INVOLVING ELECTROLYSIS OF WATER AND HYDROGENATION OF CARBON DIOXIDE TO METHANE

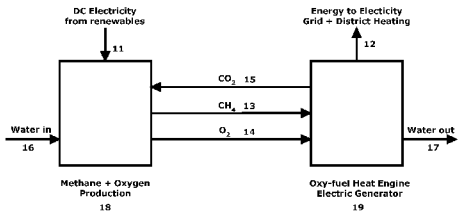

Figure 1a. Energy Transference

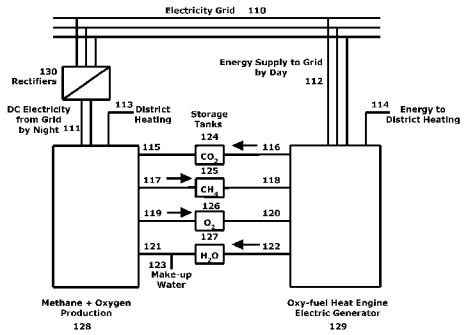

Figure 1b. Time Phased Energy Transference

(57) Abstract: The invention relates to methods and systems of converting electrical energy to chemical energy and optionally reconverting it to produce electricity as required. In preferred embodiments the source of electrical energy is at least partially from renewable source. The present invention allows for convenient energy conversion and generation without the atmospheric release of C02. One method for producing methane comprises electrolysis of water to form hydrogen and oxygen, and using the hydrogen to hydrogenate carbon dioxide to form methane. It preferred to use the heat produced in the hydrogenation reaction to heat the water prior to electrolysis. The preferred electrical energy source for the electrolysis is a renewable energy source such as solar, wind, tidal, wave, hydro or geothermal energy. The method allows to store the energy gained at times of low demand in the form of methane which can be stored and used to generate more energy during times of high energy demand. A system comprising an electrolysis apparatus and a hydrogenation apparatus, and a pipeline for the transportation of two fluids, is also described.

WO 2013/124632 A3

(88) Date of publication of the international search report:
31 October 2013

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/050375

A. CLASSIFICATION OF SUBJECT MATTER
INV. C25B1/04 C07C1/12 C07C9/04 B01D53/62 C01B3/02
C01B13/02 C10G2/00 F01K19/00 F17D1/02
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 C01B C07C C10G C25B F01K F17D

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, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 128 003 A (MURDOCH KAREN E [US] ET AL) 7 July 1992 (1992-07-07)	1,6,7, 12,26, 27,29
Y	abstract; claims 1-3,5,6,8; figure; example	1-40

X	US 2009/289227 A1 (RISING BRUCE W [US]) 26 November 2009 (2009-11-26)	1,2,4-8, 12,23-29
Y	abstract; claims 1-3,11,12,15,16; figure 5 page 3, column 1, paragraph [0023] page 4, column 1, paragraph [0034]	1-40

X	WO 00/25380 A2 (QUADRISE LIMITED) 4 May 2000 (2000-05-04) abstract; claims 11,17	1,7,12, 26,27,29

	-/--	

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

[X] 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	Date of mailing of the international search report
24 May 2013	28/08/2013

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

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2013/050375

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 452 676 A (BIRBARA PHILIP J [US] ET AL) 5 June 1984 (1984-06-05)	1,7,12, 15,23, 26,27
Y	abstract; claim 1; figure 1 column 2, lines 38-50 column 4, lines 20-30	1-40

X	DE 43 32 789 A1 (ABB RESEARCH LTD.) 30 March 1995 (1995-03-30)	1-3,5-7, 12,24, 26,27,29
Y	abstract; claims 1-3; figure 1 column 2, lines 13-17 column 3, lines 49-60	1-40

Y	DE 43 32 790 A1 (ABB RESEARCH LTD [CH]) 30 March 1995 (1995-03-30) abstract columns 1-2	1-40

Y	EP 0 497 226 A2 (MITSUBISHI HEAVY IND LTD [JP]) 5 August 1992 (1992-08-05) abstract; claims page 5, column 5, lines 14-17	1-40

Y	EP 2 100 869 A1 (HARZFELD EDGAR [DE]) 16 September 2009 (2009-09-16) abstract; claims; examples	1-40

Y	EP 0 539 244 A1 (MITSUBISHI HEAVY IND LTD [JP]) 28 April 1993 (1993-04-28) abstract; claims; figures	1-40

Y	WO 2008/012039 A2 (STEAG SAAR ENERGIE AG) 31 January 2008 (2008-01-31) abstract; claims	1-40

X,P	WO 2012/028326 A1 (CARBON-CLEAN TECHNOLOGIES AG) 8 March 2012 (2012-03-08) abstract; claims	1-40

1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB2013/050375

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.:

1-40

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: 1-40

   Process comprising the steps of a) providing a source of electrical energy; b) using said energy to produce hydrogen and oxygen by electrolysis of water; and c) hydrogenating carbon dioxide with said hydrogen to form methane.

   ---

2. claims: 41-64

   System comprising a) a source of electrical energy; b) an electrolysis apparatus coupled to said energy source; c) gas handling means for collecting oxygen and hydrogen produced by electrolysis; d) a source of carbon dioxide; and e) a hydrogenation apparatus.

   ---

3. claims: 65-73

   Pipeline for the transport of two fluids comprising a first pipe and a second pipe surrounding said first pipe.

   ---

4. claims: 74-84

   Combined electrolysis/hydrogenation apparatus comprising a) a high temperature electrolysis apparatus comprising an input water feed conduit; b) gas carrying conduits to collect oxygen and hydrogen produced in said electrolysis apparatus; c) a hydrogenation apparatus which is in thermal communication with the feed conduit of the electrolysis apparatus.

   ---

5. claims: 85-87

   Method for electrolysis of water and generation of methane comprising the steps of a) hydrogenating carbon dioxide to form methane; b) using the heat thus produced to heat water prior to electrolysis; and c) performing high temperature electrolysis on said water to form hydrogen and oxygen.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/GB2013/050375

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5128003 A	07-07-1992	US 5128003 A	07-07-1992
		US 5362373 A	08-11-1994
US 2009289227 A1	26-11-2009	NONE	
WO 0025380 A2	04-05-2000	AU 6358199 A	15-05-2000
		EP 1125337 A2	22-08-2001
		US 2002025457 A1	28-02-2002
		WO 0025380 A2	04-05-2000
US 4452676 A	05-06-1984	DE 3315969 A1	10-11-1983
		FR 2526048 A1	04-11-1983
		GB 2119353 A	16-11-1983
		IT 1161233 B	18-03-1987
		JP H0130761 B2	21-06-1989
		JP S58194712 A	12-11-1983
		US 4452676 A	05-06-1984
DE 4332789 A1	30-03-1995	AU 7156894 A	06-04-1995
		DE 4332789 A1	30-03-1995
		JP H07149670 A	13-06-1995
DE 4332790 A1	30-03-1995	AU 686189 B2	05-02-1998
		AU 7162494 A	06-04-1995
		DE 4332790 A1	30-03-1995
		JP H07173088 A	11-07-1995
EP 0497226 A2	05-08-1992	DE 69229839 D1	30-09-1999
		DE 69229839 T2	10-02-2000
		EP 0497226 A2	05-08-1992
		US 5312843 A	17-05-1994
		US 5479462 A	26-12-1995
EP 2100869 A1	16-09-2009	NONE	
EP 0539244 A1	28-04-1993	AU 656614 B2	09-02-1995
		AU 2213192 A	11-03-1993
		CA 2077880 A1	11-03-1993
		EP 0539244 A1	28-04-1993
		JP H0565237 A	19-03-1993
WO 2008012039 A2	31-01-2008	DE 102006034712 A1	31-01-2008
		EP 2047071 A2	15-04-2009
		WO 2008012039 A2	31-01-2008
WO 2012028326 A1	08-03-2012	DK 2426236 T3	15-04-2013
		EP 2426236 A1	07-03-2012
		ES 2402398 T3	03-05-2013
		US 2013214542 A1	22-08-2013
		WO 2012028326 A1	08-03-2012