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(71) Applicants: **KARIMI, Mojtaba** [—/IR]; Nazar Sharghi ave., Neda blind alley, no. 81, Isfahan (IR).
ZENDEHDEL, Mahmoud [—/IR]; Nazar Sharghi Ave., Neda blind alley, No.81, Isfahan (IR).

(74) Agent: **KARIMI, Mojtaba**; Nazar Sharghi Ave., Neda blind alley, No. 81, Isfahan (IR).

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(54) Title: ONE-STEP CONVERSION OF METHANE TO METHANOL AT AMBIENT TEMPERATURE AND ATMOSPHERIC PRESSURE

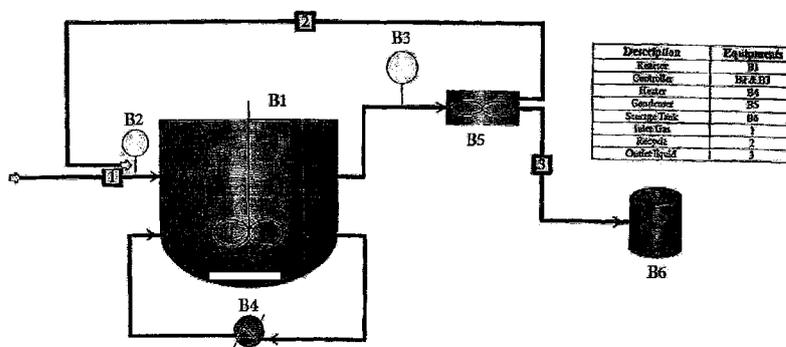


Fig.2. shows a schematic of methan to methanol plant

(57) Abstract: This present invention includes a one-step method for converting methane to methanol at ambient temperature and pressure. In this reactor, methane gas was bubbled in a basic solution containing homogenous and heterogeneous catalysis and partial selective oxidation of methane gas to methanol was done in ambient pressure and temperature. Complex catalytic reaction is one-step with high conversion efficiency (up to 98%).

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ONE-STEP CONVERSION OF METHANE TO METHANOL AT AMBIENT TEMPERATURE AND ATMOSPHERIC PRESSURE

Background of the invention

This present invention related to one-step converting gaseous methane to methanol. The invention is a novel method and apparatus (reactor) for chemically (catalytically) converting methane to methanol at ambient pressure and temperature.

The word need for alternative energy is well known. Methane containing natural gas is a clean and effective alternative energy source. But it is difficult and costly to transfer. Methanol is an important feed compound in petrochemical application.

In previous technologies (EP0448019, US20060235090, JPH04217635, EP2404888, US4277416, EP2021309) oxidation process involves indirect and complex method by reacting methane with steam at high temperature (1500 to 2000 °C) and high pressure (105 bar) to produce synthesis gas (CO + H₂). Methanol is subsequently formed heating synthesis gas in a high pressure.

Huge deposits of methane worldwide are economically "stranded" because of the high capital costs of using existing technology to make it transportable. A system, based on new technology, that would economically convert methane into fuel that could be transported and stored economically, would provide for the first time the capability to monetize the huge stranded gas reserves worldwide, and ultimately tap huge ocean floor deposits of methane hydrate reserves to supply world energy needs for 200 years after petroleum reserves have been exhausted.

Methane is a simplest organic molecule in nature consisting of one carbon atom bonded with four hydrogen atoms. Methanol is only one atom change away, with one of the hydrogen atoms replaced by an OH hydroxyl. Methanol, the initial product of methane oxidation, is a desirable product of conversion because it retains much of the original energy of methane in a room temperature transportable, storable liquid that can be used directly as a fuel or converted to other valuable products. In addition to its commercial importance as a chemical feedstock, there are many advantages of using methanol for broad use as an environmentally compatible and efficient vehicle fuel. It has lower combustion emissions of greenhouse gasses, evaporative hydrocarbons, and particulate pollutants, yet has high energy content. Methanol can even be converted into boiling grade gasoline if necessary.

On the other hand, good methods necessitate high costs and high energy. VS. Pat. No. 4,374,288 to Scragg discloses combining methane and oxygen in a high energy electromagnetic field strong enough to atomize the oxygen for combining with methane. United Kingdom Pat. No. 1.244.001 discloses oxidation of methane over a $(\text{Mo}_2\text{O}_3) \text{Fe}_2\text{O}_3$ catalyst on silica/aluminum at high temperature and pressure. US. Pat. No. 5,220,080 to Layons et al catalytic oxidation of methane employing surface oxide chromate catalyst on a metal oxide support of silica, alumina, magnesia, titania or zirconia.

Summary of invention

Methanol is raw material for petrochemical industry. The methanol have $-\text{CH}_2\text{OH}$ bond and hydroxide agent, so, this can use in many reactions. The importance application for this material is production of formaldehyde and resins.

In previous methods, methanol prepared from methane with multi-steps catalytic oxidation reaction, then, the methanol was purified. In this invention, methane is directly converted to methanol by one-step catalytic process. In previous technology, oxidation reaction was done from homogenate and expensive catalysts. Thus, the catalysts were sensitive to reaction conditions. The properties of used catalysts in this invention are reusability and stability. Also, in previous converting process, catalytic reactions were done in high pressure and temperature, while in this invention, all the process was done in ambient pressure and temperature.

In this invention, a novel and cheap technology with high efficiency has been shown. In this method, one step converting methane to methanol in a reactor was done with complex heterogeneous and homogenous catalysts. In this reactor, methane gas was bobbling in aqueous basic solution. In this solution, there are both heterogeneous and homogenous catalysts which prepared by titanium, chromium, carbon, magnesium, manganese, Iron, cobalt, nickel, copper, zinc, potassium, sodium elements and their nanoparticles and nanocomposites. Nanocomposite thin film of heterogeneous catalysts is prepared by dip-coating and spray coating methods on stainless steel plates. Partial oxidation of methane to methanol was done in one-step single reactor at ambient pressure and temperature. After oxidation, synthesized methanol converting to vapor phases in 70°C and inter to condenser. Pure methanol produce was separated from vapor phases and was saved in tank.

Brief description of the drawing

Fig.1. shows a sample of GC-MS analysis from vaporizable materials that existing peak in vaporizable compounds are related to methanol.

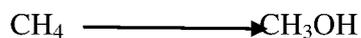
Fig.2. shows a schematic of methane to methanol plants

Table.1. shows the results of catalytic reaction.

Detailed description

The present inventor realized that there is a need for a process that produces methanol in a process that is cost effective, easy to operate, relatively fast and capable for achieving high conversion. One common source of methane can be natural gas. Although inexpensive and abundant, natural gas presents difficulties in its use caused by the fact that it contains a number of constituents besides methane including nitrogen, ethane, propane, butane and carbon dioxide.

The present inventor realized that efficient synthesis of methanol from methane has been an elusive target for many years. It is difficult, if not impossible, because of a basic problem based on a chemistry of methane.



The invention provides a process for the reaction uses catalyst agent to create reactive hydroxyl radicals in short time. Hydroxyl radicals diluted in methane gas, which oxidize the methane molecule to a methanol molecule in a one-step chemical conversion.

The performance of a reactor has been proved with different analysis. That, for this thing, 3 kinds of gas feed used for consideration of process of reactor performance.

We used methane gas as a capsule with 99% purity (M1 sample), the gas of Esfahan city with 80% methane (M2 sample) and biogas with 60% methane (M3 sample), in these tests.

The quality and quantity for M1 and M2 samples and materials in vaporizable phase and non-vaporizable phase have examined with sampling of reactor's liquid and GC-Mass analysis, respectively. For controlling of PPM of import and output methane gas in variety times and

Debbie's, used Geotech gas tester (analyzer). The results of catalytic reaction were shown in table 1.

According to table 1, used reactor in this invention can converting methane with high selectivity, conversion efficiency over 97% and the period time less than 90 min. The used catalytic process in this invention is capable as one-step and in 25 °C and 1 atm pressure. Due to increasing temperature up to 70 °C in M1 and M2 samples, the conversion percent was increasing. But in biogas sample (M3) saw opposing state, that can related to kinds of existing gases in biogas. The biogas is containing methane, oxygen, O₂ and H₂S. In this project, the methane was removed after passing of reactor system. In addition, the percent compound quantity of other gases has changed with removing H₂O, decreasing of CO₂ and increasing oxygen.

As it was said, the reactor catalytic reaction's base is hydroxide radical formations which according to kind of used catalysts in this reactor, operator can control the quantity of hydroxide radicals. Thus, the starters of preparation of radical are electro-catalyst compounds and quantity of preparation of radicals is related to amount injected electric charge. Electron injection process is controlled by electrical panel on reactor. Used electricity for this work is a kind of Direct Electricity (DC) with 1-20 V amount voltage. The controlling of catalytic process is done by Chronopotential- Coulometry process.

Claims

1. A method for synthesis of catalyst comprising the steps of:
 - a) Synthesis catalysts via sol-gel and hydrothermal routs
 - b) coating paste of catalysts on stainless steel
2. A method for converting methane to methanol comprising the steps of:
 - a) Oxidation reaction of methane with catalysts in ambient temperature and pressure
 - b) Synthesis of methanol with vapor phase at 70 °C
 - c) Separation of methanol and vapor phase
3. An alternate methane to methanol conversion apparatus comprising:
 - a) A closed loop pipe where incoming feed gas is mixed.
 - b) A controller for incoming gas flow rate
 - c) An inlet port for methane.
 - d) Both homogenous and heterogeneous catalyst are working in an apparatus.
4. titanium, chromium, carbon, magnesium, manganese, Iron, cobalt, nickel, copper, zinc, potassium, sodium elements and their nanoparticles and nanocomposites in claim 1.
5. In claim 1, the properties of used catalysts in this invention are reusability and stability.
6. In claim 2, the method for converting methane to methanol is one-step.
7. The invention provides a process for the reaction uses catalyst agent to create reactive hydroxyl radicals in short time.
8. Hydroxyl radicals are reacted with methane gas, which oxidize the methane molecule to a methanol molecule in a one-step chemical conversion.
9. The apparatus in claim 3, where in the heterogeneous catalyst may be coated on stainless steel.

AMENDED CLAIMS

received by the International Bureau on 05 September 2016 (05.09.2016)

Claims

1. An electrochemical method for converting methane to methanol, said method comprising the steps of,
 - a. Physically dissolving of methane molecules to an aqueous electrolyte.
 - b. Formation of active oxygen species from water molecules by electrocatalytic reaction.
 - c. Fast oxidation of physically dissolved methane molecules to methanol by electrochemically formed active oxygen species.
 - d. Separation of methanol from aqueous medium by evaporation of the medium to 70 °C and then condensation of the vapor phase.
 - e. Separation of methanol from aqueous solution by crossing the solution into a methanol selective membrane system.

2. A methane to methanol conversion apparatus comprising:
 - a. A polyethylene cylindrical reactor
 - b. Multi-circular arrangement of electrodes
 - c. Rod-like working electrodes containing of stainless steel 316 which is covered by two layers of electroactive nanocomposites
 - d. Rod-like counter electrodes which prepared by hot-pressing of electroactive nanocomposite and electron conducting polymer
 - e. A condenser system for separation of methanol from gas phase and bypass line of unreacted methane gas to the reactor cycle
 - f. A methanol selective membrane system for separation of methanol from aqueous solution
 - g. A DC electrical power supply system for generation of electrochemical bias potential
 - h. A potentiostat/galvanostat system for controlling of the bias potential and formation of active oxygen species in the surface of electrocatalyst
3. The method of claim 1, can prepare a condition for electrochemically reaction of water with surface of nanocomposite electrocatalyst to generate active oxygen species, such as hydroxyl radicals, that react with physically dissolved methane molecules close to the electrode.
4. The method of claim 1 and related reactor in claim 2, can electrochemically convert methane gas to methanol with high efficiency and one-step, continuously.
5. The method of claim 1 can electrochemically convert methane to methanol in ambient temperature and atmospheric pressure.
6. The apparatus of claim 2 can fabricate in any capacity based on the methane to methanol scale of the plant.
7. Fabricated apparatus of claim 2 can parallel connect together for increase of the plant capacity.
8. According to method of claim 1 and apparatus of claim 2, formation of active oxygen species and advancing of the methane to methanol reaction can accurately determine and control by voltammetry and Controlled Potential Coulometry (CPC) techniques.
9. The method of claim 1 and related apparatus of claim 2 are totally green and can electrochemically convert methane to methanol with a closed loop line and do not spread any bypass products and/or pollution in the nature.
10. According to aqueous-based of method claim 1, the safety of the process toward explosion and ignites is high.

Table.1. shows the results of catalytic reaction

Sample NO.	Kind of feed gas	Conversion (%)	Methanol (%)	Other oxidation produces	Reactor temperature (°C)	Pressure (atm)	Time (min)
1	M1	65	64	1	25	1	15
2	M1	84	82	2	25	1	30
3	M1	89	87	2	25	1	45
4	M1	92	90	2	25	1	60
5	M1	97	94	3	25	1	90
6	M1	86	84	1	70	1	30
7	M1	95	90	5	70	1	60
8	M1	98	91	7	70	1	90
9	M2	42	38	4	25	1	15
10	M2	49	45	4	25	1	30
11	M2	58	53	5	25	1	45
12	M2	60	55	5	25	1	60
13	M2	58	61	7	25	1	90
14	M2	54	50	4	70	1	30
15	M2	62	58	5	70	1	60
16	M2	69	63	6	70	1	90
17	M3	39	36	3	25	1	15
18	M3	44	41	3	25	1	30
19	M3	50	46	4	25	1	45
20	M3	53	48	5	25	1	60
21	M3	59	55	4	25	1	90
22	M3	42	37	5	70	1	30
23	M3	46	40	6	70	1	60
24	M3	50	43	7	70	1	90

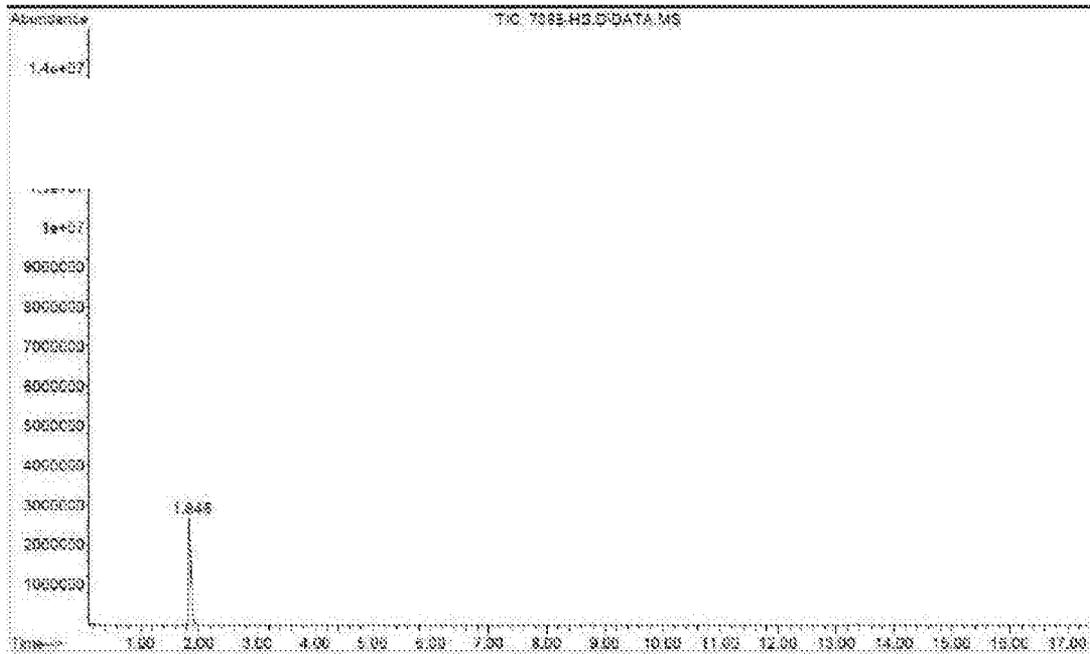
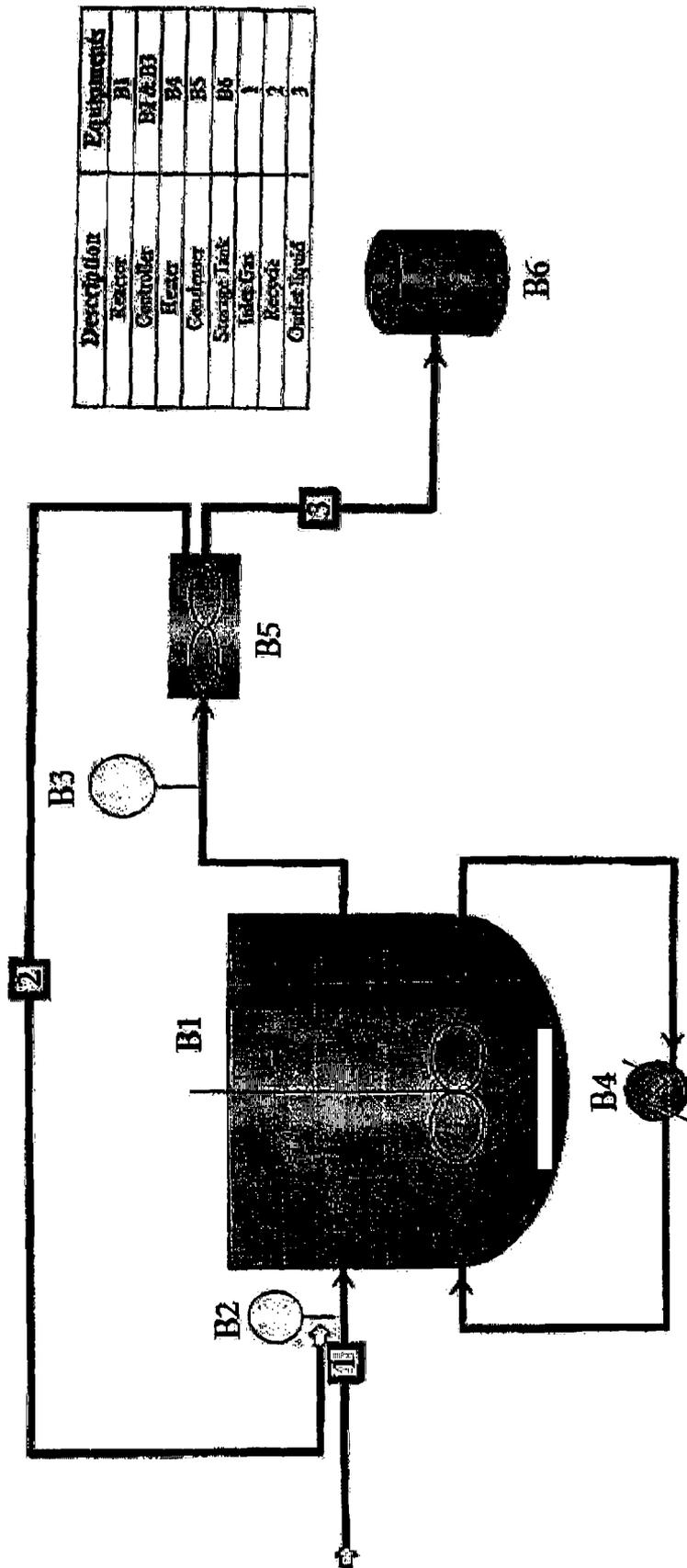


Fig.1. shows a sample of GC-MS analysis from vaporizable materials that existing peak in vaporizable compounds are related to methanol.



Description	Equipments
Reactor	B1
Controller	B1/B3
Heater	B4
Condenser	B5
Storage Tank	B6
Inlet Gas	1
Recycle	2
Outlet Liquid	3

Fig.2. shows a schematic of methanol to methanol plants

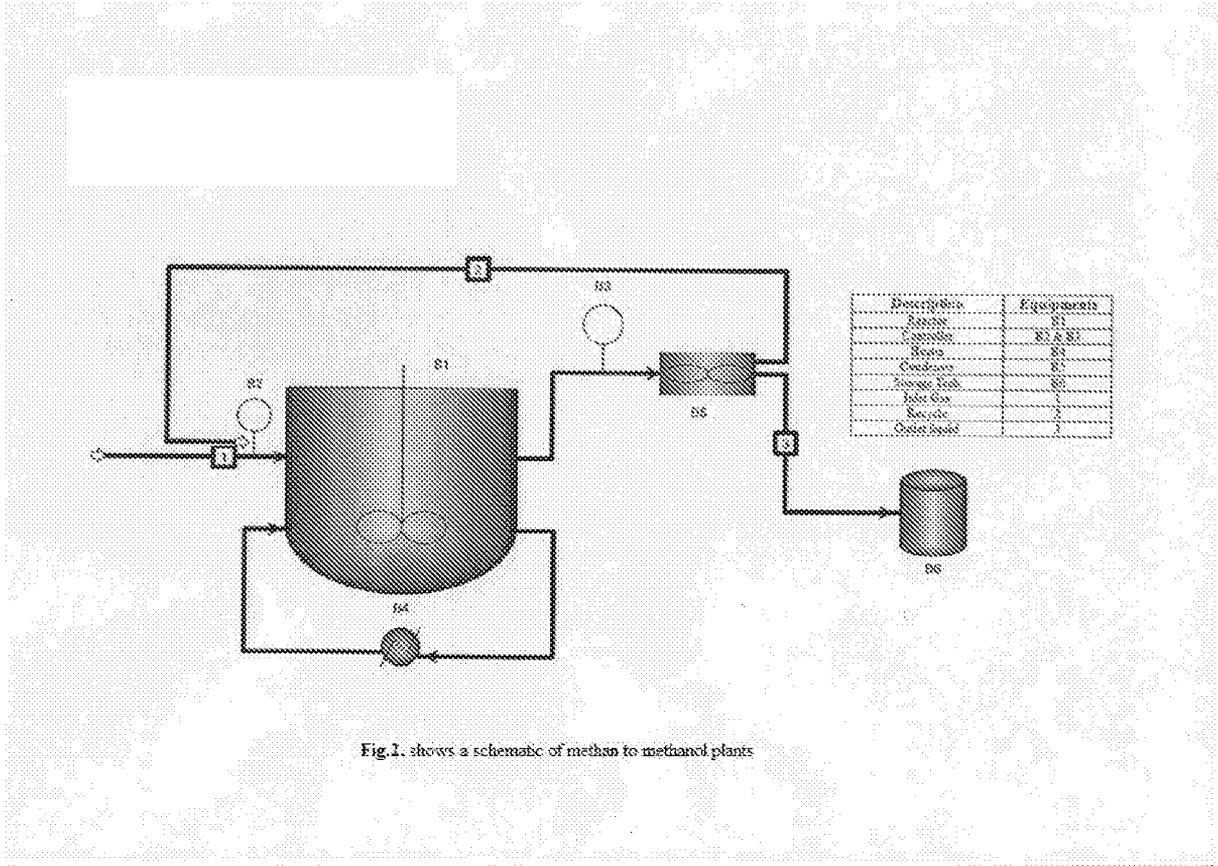


Fig.1. shows a schematic of methan to methanol plants

Fig.2. shows a schematic of methane to methanol plants

INTERNATIONAL SEARCH REPORT

International application No PCT/IB2015/054899

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01J37/03 B01J37/10 C07C29/48 C07C31/04 B01J23/72
 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)
 B01J C07C C10J

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/270512 A1 (EDWARDS JOHN LEE [US]) 22 November 2007 (2007-11-22) the whole document paragraphs [0029], [0054], [0057] figures 3,5 claims	1-9
X	----- US 6 328 854 B1 (SHERMAN JEFFREY H [US] ET AL) 11 December 2001 (2001-12-11) the whole document	1-9
X	----- US 6 156 211 A (GONZALEZ-MARTIN ANUNCIA [US] ET AL) 5 December 2000 (2000-12-05) the whole document figures claims	1-9
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Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search 17 June 2016	Date of mailing of the international search report 28/06/2016
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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 100 06 696 A1 (SCHINDLER ERHARD [DE]) 16 August 2001 (2001-08-16) the whole document -----	8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/054899

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2007270512	A1	22-11-2007	NONE

US 6328854	B1	11-12-2001	NONE

US 6156211	A	05-12-2000	NONE

DE 10006696	A1	16-08-2001	NONE
