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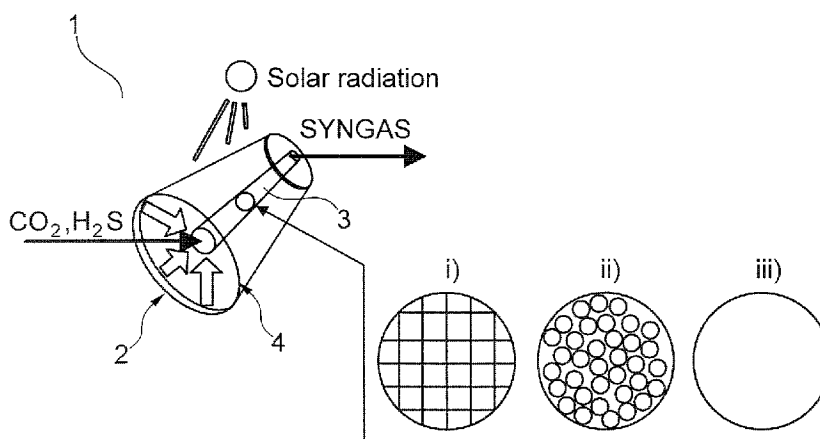


Fig. 1

(57) Abstract: Solar concentration catalytic reactor in which not only the solar radiation receiver or reactor is equipped with transparent or semi-transparent walls but also the catalyst arranged inside said reactor is supported on transparent or semi-transparent material and is itself transparent or semi-transparent.



SOLAR CONCENTRATION CATALYTIC REACTOR

Field of the invention

The present invention concerns a solar concentration reactor of the catalytic or even photocatalytic type allowing to provide the necessary energy contribution to carry out
5 endothermal reactions.

State of the art

As known, any use of fossil fuel (crude oil, natural gas, shale gas and oil, coal) and non-fossil fuel (biomass, biogas, geothermal) lead to the joint production of CO₂ and H₂S.

The gases containing such substances in discreet amounts are defined as acidic gases or tail gas
10 and are the object of a substantial scientific discussion for their dramatic impact in terms of global warming and climate change, for which they are the main culprits.

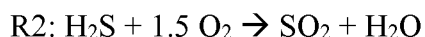
Currently, acidic gases are not reused, except in small quantities, and the only alternative to their emission in the atmosphere is the sequestering and storage in deep water or in remote underground sites. Such extreme measures are in any case the object of debate on their possible
15 actuation.

WO2015015457A1 in the name of the Applicant describes a use of the aforementioned acidic gases for the production of synthesis gas (CO and H₂, or syngas).

The production of syngas takes place according to the following endothermal reaction:



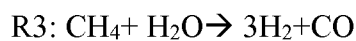
20 The necessary energy contribution is provided by the exothermal reaction:



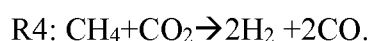
This process, which in any case represents an undoubted versatility since it can be associated with other productions with a few modifications to pre-existing plants, in any case requires considerable activation energy. Indeed, the operating temperatures are very high, greater than
25 800°C and in some cases they exceed 1300°C. Moreover, it is necessary to carefully dose the oxygen to be used in the second exothermal reaction to avoid the excessive oxidation to SO₂, which represents a harmful emission, which must be eliminated for example through use in Claus plants or in production plants of sulphuric acid.

As widely described by Agrafiotis et al (“Solar thermal reforming of methane feed stocks of

hydrogen and Syngas production –A Review” Renewable and sustainable energy reviews” 29 (2014) 656-682), solar concentration reactors are also known, that are used mostly in the production of syngas from natural gas reforming and, respectively, of steam reforming (steam methane reforming, better indicated with the acronym SMR) according to the following equation:



and the dry reforming reaction (dry methane reforming, DMR) according to the following equation



10 These reactions are highly endothermic and would require particularly severe temperatures to take place in homogeneous environments; on the other hand, the catalytic reactors offer an opportunity, industrially applied and economically advantageous, to obtain good conversions to temperatures comprised between 800 and 1000°C. In this way, a substantial reduction in fossil fuel is obtained, which would otherwise be necessary to activate the reaction thermally.

15 In the same review an ample description is given of such types of catalytic reactor, which are generally formed by a concentrator or collector of solar energy and by a solar energy receiver, which is the actual reactor. The solar receiver can be classified in two very wide classes according to how the transfer of heat takes place directly or indirectly.

Indirect heat receivers are tubular receivers, which consist of absorbent surfaces exposed to concentrated solar radiation. The heat transfer fluid (a gas) moves perpendicular with respect to the direction of the incident solar radiation.

The heat transfer to the thermal fluid takes place through the opaque walls of the receiver by conduction, first from the outer surface to the inner one of the absorbent wall and subsequently from the innermost surface to the fluid by forced convection.

25 However, the most efficient receivers are those that involve the direct heating of the fluid that transfers heat, thus eliminating the absorbent walls.

A key role of this type of plant is carried out by the so-called absorbent, i.e. the component that absorbs the concentrated solar light and transports its energy to the fluid that transfers the heat that passes inside or above it. Such a type of absorber is of the type structured for example in the form of honeycombs in the form of foams or in the form of a porcupine (with needles) these types of absorbent surfaces can be made of ceramic material. This type of structure, having very large surfaces, transfers the heat in an optimal manner, at the same time offering a large contact

surface between catalyst and reactive fluids. They can be coated with material suitable for catalysing the reaction that takes place inside the receiver.

The same review also says that the Korean university of Inha is investigating the possibility of using metallic foam-based reactors as absorber, in which the front part is not catalytically active and carries out the absorption of solar radiation and the transfer of heat to the reactant gas. The rear part is a metallic foam of Nickel with catalyst based on Ni/alumina.

Even if this type of solar reactor represents an indisputable advantage with respect to conventional techniques that exploit the energy developed by combustible hydrocarbons, with a substantial saving of energy, they cannot be used in endothermic processes that consider the use of photocatalysts.

This type of catalyst can for example be validly used in the production process of H₂ from organic substrates through the so-called photo reforming process as stated in the review of Ilenia Rossetti (ISRN Chemical Engineering “Hydrogen production by photoreforming of renewable substrates”), Article ID 964936, 21 pag. Vol. 2012 (2012).

The purpose of the present invention is a versatile catalytic solar concentration reactor for the endothermic industrial processes. A further purpose of the present invention is a process that makes it possible to obtain syngas through the reaction between CO₂ and H₂S



which does not have the drawbacks of the process described in WO2015015457A1.

These and other purposes have been accomplished with the invention as described in the following summary.

SUMMARY OF THE INVENTION

The Applicant has indeed found that solar concentration catalytic reactors allow the aforementioned technical problems of the prior art to be overcome in which not only the receiver of solar radiation or reactor is transparent or semi-transparent but also the catalyst arranged inside said reactor is transparent or semi-transparent and is in turn deposited stably on transparent or semi-transparent material.

The object of the present invention is therefore a catalytic solar concentration apparatus or reactor comprising:

- a solar radiation concentrator;
- a solar radiation receiver or transparent or semi-transparent reactor, comprising at least

one module,

- a supported catalyst, placed inside said reactor
- a support for said apparatus,

wherein said catalyst is transparent or semi-transparent and is deposited on a support selected
5 from:

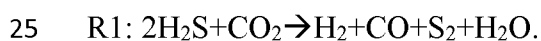
- i) a structured transparent or semi-transparent support.
- ii) a non-structured transparent or semi-transparent support, said support being held inside the reactor by at least one mesh or grid;
- iii) the support is the inner surface of said reactor.

10 A further object of the present invention is the use of said apparatus or photocatalytic reactor according to the present invention to carry out endothermal processes and in general all thermochemical processes.

A further object of the present invention is in particular a process for treating acidic gases that are the waste gases of processing like for example: extraction and refinement of petroleum,
15 extraction of natural gas, extraction of shale oil/shale gas, gasification of coal containing sulphur, extraction of heavy crude oil, treatment of biomass, treatment in biogas plants, in geothermal plants, treatment that foresees the use of the apparatus according to the present invention.

In particular a further object of the present invention is the reduction process of CO₂ to carbon
20 monoxide in the presence of a reducer selected from H₂S, methane, methanol, coal, hydrocarbons, ammonia, hydrogen or other reducing agents with regard to CO₂, carried out in the apparatus according to the present invention.

A further object of the present invention is a preferred form of the reduction process of CO₂ in which the reducing agent is H₂S and is carried out according to the reaction



Preferably, for this type of reaction a catalyst based on alumina, MgO, MgAl₂O₄ or mixtures thereof is particularly preferred, preferably it is gamma alumina ($\gamma\text{-Al}_2\text{O}_3$).

A further object of the present invention is a photoreforming process for which photocatalysts are used, a process that contemplates the use of the catalytic solar concentration reactor object
30 of the present invention.

DESCRIPTION OF THE FIGURES

Figure 1 shows a particularly preferred embodiment of the apparatus or collector, in particular of cylindrical shape, object of the present invention seen in perspective, and in particular adapted for the process for producing syngas from CO₂ and H₂S according to the reaction R1.

Figure 2 represents preferred embodiments of the receiver/reactor object of the present invention.

5 DETAILED DESCRIPTION OF THE INVENTION

The definitions of respectively transparent or semi transparent material is generally based on the concept of transmittance of the incident light inside the same material.

The parameter, allowing to quantify in some way the above mentioned definitions of transparent or semi transparent material, is the amount of light power per surface unit,,

10 expressed for example in $\frac{W}{m^2}$.

The incident light power refers to light entering a material, whereas the transmitted light power relates to the light passing through and therefore not absorbed by the material.

As a consequence the parameter "Light Power Decrease (LPD)", is given by the following equation:

$$15 \quad \text{light power decrease (LPD)} = \frac{\text{transmitted light power} \left(\frac{W}{m^2} \right)}{\text{incident light power} \left(\frac{W}{m^2} \right)} \times 100$$

For the purposes of the present invention we define:

- a semi transparent material: a material having an LPD ranging from 20 to 90%, preferably from 50 to 85%;
- 20 - a transparent material a material having an LPD ranging from 90 to 100%.

LPD may depend on several parameters in the catalytic reactor according to the invention such as the material of the reactor itself and catalyst support, the type of incident light (wavelength and power), particles size (being always nanometric), the amount of catalyst/per surface unit, the catalyst thickness, the physical chemical properties of the catalyst itself.

25 For the purposes of the present invention the term:

- structured support of a catalyst means a single solid three-dimensional rigid support with fixed size and shape and that is fixed to the receiver or reactor or it is integral or made in one piece with the reactor itself;
- Non-structured support means a solid support formed by many components for
30 example: pellets, raschig rings, balls or saddles not fixed to the reactor, which thus tend

to take the form of the receiver or reactor that contains them. They are held inside the reactor by at least one grid, preferably there are two grids when the reactor is of the tubular type or one when the reactor is of the batch type.

5 The supported catalyst of type i) or ii) and the catalyst of type iii) preferably are not distributed for, respectively, the entire volume or inner area of the reactor. The entry part of the reactants can be left free so as to allow the temperature to reach the desired values to activate the reactor and promote endothermal synthesis.

Preferably, the catalyst of type i) or ii) occupies at least 80%, preferably at least 85%, more preferably 90% and even more preferably 95% of the volume of said reactor.

10 Similarly, when the support is of type i) it preferably occupies at least 80%, more preferably at least 85%, even more preferably at least 90% and according to a particularly preferred solution at least 95% of the inner area of said receiver or reactor.

The concentrator in the apparatus object of the present invention is of the linear-parabolic, Fresnel, parabolic or oriented planes type, preferably linear parabolic or Fresnel, even more
15 preferably linear parabolic.

In the apparatus object of the present invention the receiver or reactor is preferably arranged in the axial or radial direction with respect to the concentrator, more preferably it is arranged in the axial direction.

The reactor is preferably of the star, spiral, internally and/or externally finned or cylindrical
20 type.

More preferably it is cylindrical, even more preferably it is tubular (in which the bases of the cylinder or parts thereof are absent) or of the batch type in which only a base of the cylinder or part thereof is absent.

25 According to a particularly preferred solution the reactor is of the tubular type and is arranged along the axis of the concentrator exactly at the location of the reflection focuses of solar radiation.

Preferably, the receiver comprises at least 1 module; in the case of many modules, they can be arranged in series or in parallel.

30 For the purposes of the present invention the term reactors arranged in series means that the second reactor receives the effluents in outlet from the first reactor.

The term reactors arranged in parallel means that the supply of each reactor is a portion of the entire supply in inlet to said reactors.

As above underlined the transparent or semi-transparent catalyst is in nanoparticle form. The transparency or semi-transparency depends, as above highlighted, not only on the size of the particle that as stated above is nanometric, but also by the amount of catalyst deposited per unit surface, and thickness thereof. All these parameters can vary according to the type of catalyst used.

In any case the skilled person is able to select the type of catalyst and the relative amount, in order to meet the desired transparency or semitransparency requirements.

The support i) preferably has a honeycomb, lamellar, foamed or pinned structure.

The support ii) preferably consists of pellets, balls, raschig rings, saddles.

10 The transparent or semi-transparent material of which the reactor/receiver consists and also that used to prepare the supports of type i) and ii) is a material that does not decompose at the operating temperatures and is preferably quartz, but also glass in the case of operation at much lower temperatures like for example that of the aforementioned photoreforming reactions. In extremely bland conditions, it is possible to use a polymer.

15 The support material of the apparatus according to the present invention must be adapted to support it also in the case in which it is large in size and preferably is a ceramic and/or metallic material.

The category of thermochemical processes includes for example gasification, cracking, pyrolysis, reforming.

20 As stated above, the catalytic solar concentration reactor is in particular suitable for the treatment of acidic gases and in particular of CO₂ and H₂S that come from processing such as extraction and refinement of petroleum, extraction of natural gas, extraction of shale oil/shale gas, gasification of coal containing sulphur, extraction of heavy crude oil, treatment of biomass, treatment in biogas plants, in geothermal plants.

25 Therefore, this reactor is preferably used in the reduction treatments of CO₂ to carbon monoxide, wherein the reducer is preferably selected among H₂S, methane, methanol, coal, hydrocarbons, ammonia, hydrogen and more preferably H₂S.

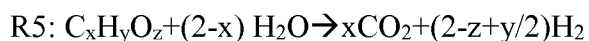
In this case, as stated above, this process is carried out according to the aforementioned reaction R1: $2\text{H}_2\text{S} + \text{CO}_2 \rightarrow \text{H}_2 + \text{CO} + \text{S}_2 + \text{H}_2\text{O}$.

30 Indeed, the Applicant has found that such a process can be carried out using the apparatus object of the present invention from 250°C, preferably from 400 °C, more preferably from 600°C and even more preferably from 650°C.

A further field of application of such a reactor is also the so-called photoreforming.

In this case, the catalysts are photocatalysts.

A typical photoreforming reaction is for example the production of hydrogen from alcohols, organic acids and different carbohydrates like glucose, arabinose, ribose, fructose, mannose
5 according to the following reaction.



The photocatalyst for this preferred type of reaction is titanium dioxide since it is the least expensive.

In this case, the reaction temperatures, in the reactor or receiver preferably start from 60°C,
10 preferably from 100°C, temperatures at which the reactants can be in liquid phase.

Figure 1 shows a particularly preferred solution of the catalytic solar concentration reactor or apparatus 1 object of the present invention in particular dedicated to the production process of syngas according to the reaction R1.

As can be seen, the reactants heated in the concentrator 2 enter the tubular reactor 3 arranged
15 axially with respect to the concentrator 2. The apparatus 1 may be also provided with a conventional robotized device 4 (for this purposes represented in this figure in a very stylized form) cleaning periodically the entire solar collector and, therefore, also the reactor/receiver, from atmospheric agents and dust, but also from sand. The figure also shows an enlarged view of the perpendicular section of the reactor, on which the catalyst is supported, the support of
20 which can be of three types as indicated in the figure with i) –iii).

As can be seen, the first depiction shows the catalyst in which the relative support is structured and specifically has a monolithic shape, the second section on the other hand represents the catalyst in which the support is not structured and specifically consists of transparent spherical pellets. The third case, on the other hand, is that in which the catalyst is applied directly on the
25 walls of the reactor (support of type iii)).

Figure 2 for illustrative, but not limiting purposes shows some preferred examples of the catalytic solar concentration apparatus or reactor or apparatus according to the present invention.

In the case of plants for large-scale productions, it could be preferable to divide the reactants
30 heated with solar radiation through collectors of tubes or multi-way valves in many modules or lines arranged in parallel.

Each of the reactants thus divided pass in each module or solar reactor/receiver where the

catalytic conversion takes place. Downstream of each reactor the gases are combined and mixed again for successive treatments, if necessary. This type of receiver is represented in Figure 2 A).

5 In the case of plants for small-scale production, or ones that use blander operating conditions, it is possible to hypothesise a set of modules arranged in series, the pre-heated reactants enter the first receiver/reactor, where they are partially converted, the effluent in output from the first reactor then enters in the second reactor where there is a further conversion of the reactants and so on up to the last reactor. This type of reactor is represented in figure 2B.

10 In the case of plants for large-scale productions and again in blander conditions it is possible to hypothesise many hybrid solutions with modules in series and in parallel such a situation represented in Figure 2C.

Figure 2D, on the other hand, represents the situation in which the receiver/reactor consists of a single module and shows a partial detail thereof.

Claims

1. Solar concentration apparatus or catalytic reactor (1), comprising:

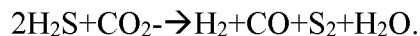
- a solar radiation concentrator (2) ;
- 5 • a solar radiation receiver (3) or transparent or semi-transparent reactor comprising at least one module;
- a supported catalyst, placed inside said reactor,
- a support for said apparatus

said apparatus being characterised in that said catalyst is transparent or semi-transparent and is
10 deposited on a support selected among:

- i) a structured transparent or semi-transparent support;
 - ii) a non-structured transparent or semi-transparent support, said support being held
inside the reactor by at least one mesh or grid;
 - iii) the support is the inner surface of said transparent reactor.
- 15 2. Apparatus according to claim 1, wherein the concentrator is of the linear-parabolic, Fresnel, parabola or oriented planes type, preferably linear parabolic or Fresnel, even more preferably linear parabolic.
3. Apparatus according to any one of claims 1 or 2, wherein the reactor or receiver (3) is arranged in the axial or radial direction with respect to the concentrator (2), preferably it is
20 arranged in the axial direction.
4. Apparatus according to claim 3, wherein the reactor is of a star type, internally and/or externally finned, of a a spiral or cylindrical type.
5. Apparatus according to claim 3, wherein the reactor (3) is cylindrical and arranged along the axis of the concentrator (2) and is tubular or of the batch type, preferably it is tubular.
- 25 6. Apparatus according to any one of claims 1-5, wherein the catalyst support (i) has a honeycomb, foamed lamellar or pinned structure.

7. Apparatus according to any one of claims 1-5, wherein the catalyst support (ii) consists of raschig rings, pellets, balls, saddles.
8. Apparatus according to claim 7, wherein, when the reactor is tubular the support ii) is held by at least two grids arranged close to the entrance and exit of said reactor.
- 5 9. Apparatus according to claim 7, wherein when the reactor is of the batch type, the support ii) is held by a grid.
- 10.Apparatus according to any one of claims 1-9, wherein, when the support is of type i) or ii) it occupies at least 80%, preferably at least 85%, more preferably 90% and even more preferably 95% of the volume of said reactor.
- 10 11. Apparatus according to any one of claims 1-5, wherein, when the support is of type iii) it occupies at least 80%, preferably at least 85%, more preferably at least 90% and even more preferably 95% of the inner area of said receiver or reactor (3).
12. Apparatus according to any one of claims 1-11 comprising many modules arranged in series or in parallel.
- 15 13. Apparatus according to any one of claims 1-12, wherein the entire reactor (3) is provided with a robotized device cleaning periodically the external surface of said reactor from atmospheric agents and dust.
14. Use of the apparatus according to any one of claims 1-10, to carry out processes that involve thermochemical processes.
- 20 15. Process for treating acidic gases that occurs in a processing selected from: extraction and refinement of petroleum, extraction of natural gas, extraction of shale oil/shale gas, gasification of coal containing sulphur, extraction of heavy crude oil, treatment of biomasses, treatment in biogas plants, in geothermal plants, characterised in that it is carried out in the apparatus according to any one of claims 1-13.
- 25 16. Reduction process of CO₂ in the presence of a reducer selected among H₂S, methane, methanol, coal, hydrocarbons, ammonia, hydrogen and any potentially reducing agent for CO₂, carried out in the apparatus according to any one of claims 1-13.

17. Process according to claim 16, wherein when the reducing agent is H₂S it is carried out according to the reaction



18. Process according to claim 17, carried out at a temperature greater than 250°C, preferably greater than 400 °C, more preferably greater than 600°C and even more preferably greater than 650°C.

19. Process according to claim 17, wherein the catalyst is selected among alumina MgO, MgAl₂O₄ or mixtures thereof, preferably gamma alumina or it is a catalyst supported on gamma alumina, or it is a catalyst supported on gamma alumina

20. Process for carrying out the photoreforming process, characterised in that an apparatus according to any one of claims 1-13 is used.

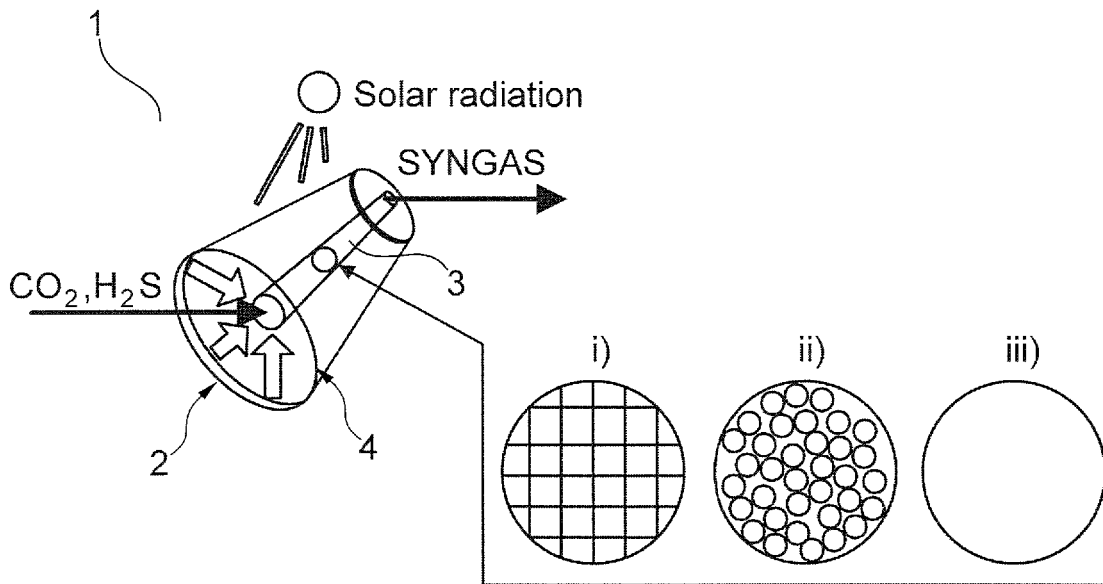


Fig. 1

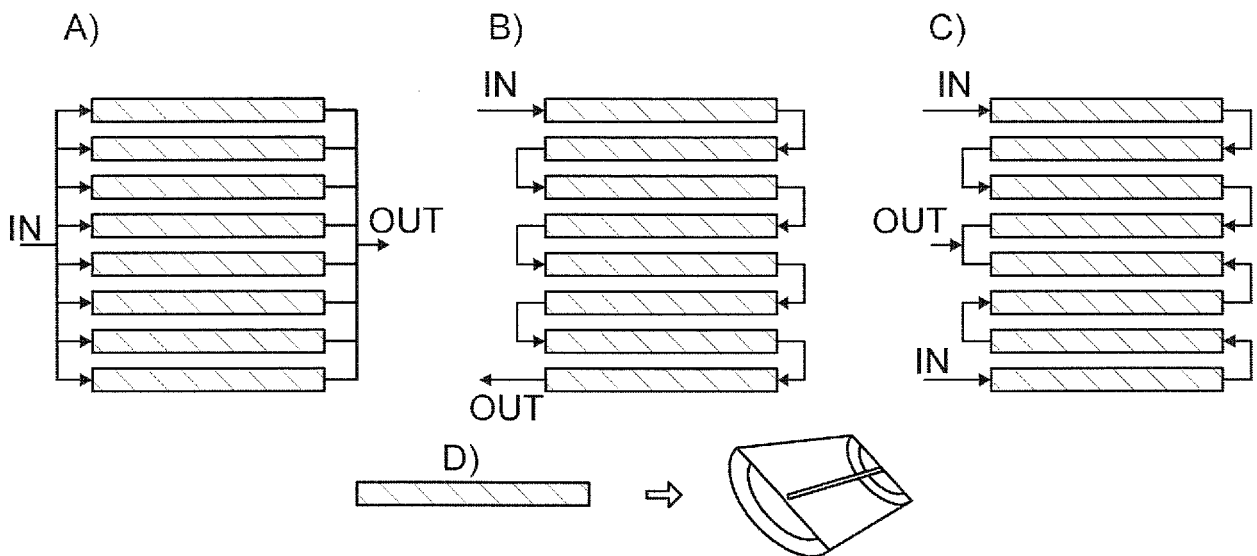


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/050271

A. CLASSIFICATION OF SUBJECT MATTER
 INV. B01J8/06 B01J19/12 B01J21/10 B01J35/00
 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 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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHRISTOS AGRAFIOTIS ET AL: "Solar thermal reforming of methane feedstocks for hydrogen and syngas production-A review", RENEWABLE AND SUSTAINABLE ENERGY REVIEWS., vol. 29, 1 January 2014 (2014-01-01), pages 656-682, XP055256195, US ISSN: 1364-0321, DOI: 10.1016/j.rser.2013.08.050 cited in the application page 662, paragraph start of 3.1 - page 667, paragraph end of 3.2; figures page 673, paragraph 3.3.1.2 - page 679, paragraph first par. left column; figures ----- -/--	1-20

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "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
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Date of the actual completion of the international search 18 April 2018	Date of mailing of the international search report 23/05/2018
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 Cagnoli, Michele

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/050271

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	M. NAFTALY ET AL: "Silicon carbide-a high-transparency nonlinear material for THz applications", OPTICS EXPRESS, vol. 24, no. 3, 1 February 2016 (2016-02-01), page 2590, XP055410183, DOI: 10.1364/OE.24.002590 the whole document -----	1-20
A	Ilenia Rossetti: "Hydrogen Production by Photoreforming of Renewable Substrates", ISRN Chemical Engineering, 11 October 2012 (2012-10-11), pages 1-21, XP055410037, DOI: 10.5402/2012/964936 Retrieved from the Internet: URL: http://downloads.hindawi.com/journals/isrn/2012/964936.xml [retrieved on 2017-09-26] cited in the application the whole document -----	1-20
A	WO 2016/193518 A1 (SENER INGENIERIA Y SISTEMAS S A [ES]) 8 December 2016 (2016-12-08) the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

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