



(11) **EP 4 001 381 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
25.05.2022 Bulletin 2022/21

(51) International Patent Classification (IPC):
C10L 3/08 ^(2006.01) **C10L 3/10** ^(2006.01)
B01D 5/00 ^(2006.01)

(21) Application number: **21206402.6**

(52) Cooperative Patent Classification (CPC):
C10L 3/08; B01D 5/00; C10L 3/106; C10L 2290/06;
C10L 2290/26

(22) Date of filing: **04.11.2021**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(72) Inventors:
• **CANU, Paolo**
35131 PADOVA (IT)
• **PAGIN, Mattia**
35129 PADOVA (IT)

(74) Representative: **Modiano, Micaela Nadia et al**
Modiano & Partners
Via Meravigli, 16
20123 Milano (IT)

(30) Priority: **17.11.2020 IT 202000027474**

(71) Applicant: **K-Inn Tech S.r.l.**
35121 Padova (IT)

(54) **METHOD FOR THE PRODUCTION OF HIGH-PURITY BIOMETHANE**

(57) A method for the production of biomethane (10) from biogas (100), wherein the biogas (100) is subjected to at least two steps of biogas upgrading, with intermediate removal of H₂O, the biogas upgrading step consisting in the direct methanation reaction of the CO₂ that is present in the biogas:

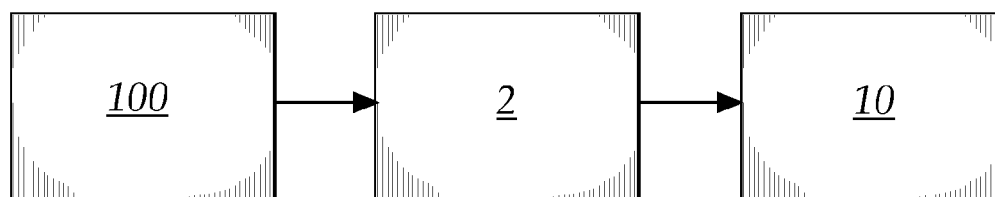
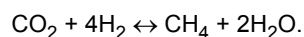


Fig.1

Description

[0001] The present invention relates to a method for the production of high-purity biomethane from biogas.

[0002] The expression "high-purity biomethane" is understood to mean biomethane with less than 1% hydrogen (H_2) by volume with less than 2.5% molar carbon dioxide (CO_2) and less than 0.1% molar carbon monoxide (CO).

[0003] The invention can be used in the industrial/chemical field in the renewable energy industry sector.

[0004] UNI EN 16723 standard entitled "Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network" was issued in December 2016.

[0005] Ministerial Decree dated 2 March 2018, which defines the methods and incentives for the injection of biomethane into the national natural gas network and for use in transport, was issued in 2018.

[0006] As a result, the production of biomethane and its injection into the natural gas network has increased significantly in Italy.

[0007] Biogas is a renewable energy source obtained from:

- agricultural biomass, such as dedicated crops and/or agricultural byproducts and waste and/or animal manure,
- and/or agro-industrial biomass, such as processing waste of the food supply chain,
- and/or the organic fraction of municipal solid waste (OFMSW).

[0008] Biomethane is obtained from biogas by means of two successive steps:

- production of raw biogas, a mixture composed mainly of methane (CH_4) and carbon dioxide (CO_2), by means of the anaerobic digestion of biomass and subsequent purification from unwanted compounds such as hydrogen sulfide (H_2S), ammonia (NH_3), water (H_2O), siloxanes and chlorine (Cl) compounds;
- selective separation of CO_2 from CH_4 through a process known as biogas upgrading.

[0009] The expression "anaerobic digestion" is understood to mean the degradation of biomass by bacteria in the absence of molecular oxygen.

[0010] Biogas upgrading is a process suitable to increase the methane content in the initial biogas, obtaining biomethane which can be likened to natural gas.

[0011] The techniques used industrially to perform biogas upgrading are essentially three:

- "scrubbing" with water, organic solvents or amines;
- "pressure swing adsorption" with activated carbons or molecular sieves (zeolites);
- separation with membranes.

[0012] With each of these three techniques it is possible to obtain biomethane with a CH_4 concentration higher than 95% by volume.

[0013] These known techniques, however, have drawbacks.

[0014] In fact, in addition to obtaining high-purity methane, a significant amount of residual CO_2 is obtained as a consequence of the separation and must be somehow used or disposed of with additional costs.

[0015] Such CO_2 is generally sold to other plants/companies and/or stored, for example underground, with the technique known as Carbon Capture and Storage (CCS).

[0016] The recent increase in biomethane production plants entails the risk of leading, in the short term, to the saturation of the CO_2 market, making it necessary to find alternative solutions to its reuse and/or disposal.

[0017] Moreover, CO_2 contains carbon (C) which could be usefully converted into methane.

[0018] Therefore, the need is felt to devise a method for the production of biomethane that makes it possible to obtain biomethane while eliminating the production of CO_2 to be disposed of.

[0019] Therefore, the aim of the present invention is to provide a method for producing biomethane that is capable of improving the background art in one or more of the aspects mentioned above.

[0020] Within this aim, an object of the invention is to provide a method for the production of biomethane that allows full utilization of the carbon contained in the initial biogas as it is.

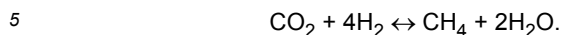
[0021] Another object of the invention is to devise a method for the production of biomethane in which CO_2 , which might not find a commercial use and would then have to be disposed of, is not produced.

[0022] A further object of the present invention is to overcome the drawbacks of the background art in a manner that is alternative to any existing solutions.

[0023] Not the least object of the invention is to provide a method for the production of biomethane that is highly reliable, relatively easy to provide and has competitive costs.

[0024] This aim and these and other objects which will become more apparent hereinafter are achieved by a method

for the production of biomethane from biogas, characterized in that said biogas is subjected to at least two steps of biogas upgrading, with intermediate removal of H₂O, said biogas upgrading step consisting in the direct methanation reaction of the CO₂ that is present in the biogas:



[0025] Further characteristics and advantages of the invention will become more apparent from the description of a preferred but not exclusive embodiment of the method for the production of biomethane, according to the invention, illustrated by way of non-limiting example in the accompanying drawings, wherein:

Figure 1 is a schematic view of a method for the production of biomethane from biogas, according to the invention;
Figure 2 is a detailed diagram of a first embodiment of the method for the production of biomethane from biogas, according to the invention;

Figures 3a and 3b are two different operational diagrams of a second embodiment of the method for the production of biomethane from biogas, according to the invention, in order to obtain a greater energy integration among the steps of the method;

Figure 4 is a schematic view of a portion of the apparatus adapted to provide the method according to the invention.

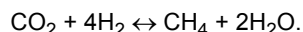
[0026] With reference to the figures, an indicated method for the production of biomethane from biogas, according to the invention, is the one shown schematically in Figure 1.

[0027] The biogas 100 is subjected to at least one biogas upgrading step, a step designated by the reference numeral 2, in Figure 1.

[0028] In the present description, the term biogas 100 is understood to reference biogas purified of contaminants, such as H₂S (hydrogen sulfide), NH₃ (ammonia), siloxanes and/or other acid/base agents and materials that may solidify and/or affect the catalytic converters mentioned hereinafter.

[0029] The step for the production of biogas 100 occurs by producing raw biogas according to a technique known per se, such as the one shown previously, and subsequently purifying it of unwanted compounds such as hydrogen sulfide (H₂S), ammonia (NH₃), water H₂O, siloxanes and chlorine (Cl) compounds.

[0030] One of the particularities of the method according to the invention resides in the fact that the biogas upgrading step consists in the methanation reaction (MET):



[0031] It should be noted that said methanation reaction occurs without prior separation of CO₂ from the purified biogas.

[0032] In practice, the CO₂ of which the biogas 100 is composed is converted through a methanation reaction, which consists in the catalytic hydrogenation of CO₂, obtaining CH₄ and water (H₂O).

[0033] Figure 2 is a detailed diagram of a first embodiment of the method according to the invention.

[0034] Specifically, the method consists of two steps, which occur in two successive apparatus lines L1, L2 fluidically connected to each other.

[0035] Each one of the apparatus lines L1, L2 comprises respectively a reactor R1, R2 and a condenser C1, C2, as explained hereinafter, which is fluidically connected to the preceding one.

[0036] In the first embodiment of the method according to the invention, the two apparatus lines L1, L2 are arranged in series, as shown in Figure 2.

[0037] The biogas 100, together with hydrogen (H) 101, is introduced in the first apparatus line L1, in a first reactor R1, and the mixture crosses a catalytic converter 12 contained inside the first reactor R1.

[0038] Figure 4 shows the first reactor R1, but this illustration also exemplifies the second reactor R2, described hereinafter, which is similar to the first one.

[0039] In said first reactor R1, which is thermally insulated from the surrounding environment, the methanation reaction (MET) of the biogas occurs.

[0040] The supply of hydrogen (H₂) 101 to the first reactor R1 can occur, for example, by using electrolyzers, of a type known per se, and/or lines which carry H₂ from industrial production hubs.

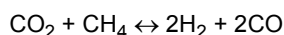
[0041] In this case, the hydrogen 101 is produced by electrolyzers connected to the first reactor R1.

[0042] Besides the methanation reaction (MET), two unwanted secondary reactions may occur in the first reactor R1:

- the "reverse-water gas shift" (RWGS) reaction:



- the "dry reforming" (DR) reaction:



5

[0043] These two reactions, RWGS; DR, entail a production of carbon monoxide (CO), which constitutes an impurity for the injection of the biomethane into the natural gas network.

[0044] Legal requirements prescribe that for the injection of biomethane in the natural gas network said biomethane must have a molar percentage of CO less than or equal to 0.1% mol.

10 **[0045]** For this reason, it is necessary to limit the development of RWGS and DR reactions by virtue of an appropriate choice of the catalytic converter and of the operating pressure and temperature conditions.

[0046] In particular, the first reactor R1, as well as the second reactor R2, is a fixed bed reactor, made of metallic material, preferably of a metallic alloy such as one of those of the family of nickel- and chromium-based alloys known by the trade name "Inconel" and/or stainless steel.

15 **[0047]** In other constructive variations, not shown in the figures, the reactors R1, R2 are of the fluidized bed type.

[0048] The reactors R1, R2 operate at a temperature substantially comprised between 200°C and 350°C and at a pressure substantially comprised between 1 bar and 30 bars.

20 **[0049]** The corresponding catalytic converters 12 of the reactors R1, R2 are provided with a fine dispersion, on ceramic supports, of active metallic material, advantageously based on one or more metals of groups 8-10 of the periodic table of elements.

[0050] In particular, the catalytic converter 12 is, for example, based on ruthenium (Ru) and/or iron (Fe) and/or nickel (Ni) and/or cobalt (Co).

[0051] Said catalytic converter 12 is preferably based on nickel (Ni).

25 **[0052]** The catalytic converter 12 has a porous ceramic support, which is mechanically and thermally stable, such as alumina (Al₂O₃) and/or silica (SiO₂) and/or titanium dioxide (TiO₂) and/or silicon carbide and/or other ceramic materials with a high specific surface.

[0053] The expression "high specific surface" is understood to mean the total surface per unit of mass of the catalytic converter, with which the gas can come in contact, by both internal and external porosity.

[0054] Preferably, the catalytic converter 12 has a catalytic support made of alumina-γ.

30 **[0055]** Such a catalytic converter 12 facilitates the MET reaction and limits the development of RWGS and DR reactions and therefore the production of CO.

[0056] Moreover, the catalytic converter 12 is pretreated in a reducing environment at 600°C with H₂, on the order of 1.9 m³ per kilogram of catalyst.

[0057] Such treatment is necessary only once before starting the reactor.

35 **[0058]** After the methanation reaction in the first reactor R1, the gaseous mixture obtained is made to condense in a first condenser C1, in order to remove the H₂O that prevents the further development of the reaction toward higher purities of biomethane.

40 **[0059]** After condensation on the first reactor C1, the purity of the gaseous mixture is insufficient for injection into the network: in fact, there is still a quantity of H₂ greater than 1% by volume and of CO₂ of approximately 2.5% molar, which is the limit dictated by the standards, and this entails the presence of impure biomethane and the need for a second reaction step, similar to the one just described.

[0060] The values of residual molar percentage of CO meet the requirements dictated by the standards for injection into the network, since they are well below the set threshold.

45 **[0061]** In the present description, the expression "impure biomethane" is understood to mean biomethane which has a volumetric percentage of H₂ greater than 1% and/or which does not meet the legal requirements for direct injection into the natural gas network.

50 **[0062]** Therefore, the gaseous mixture that exits from the first condenser C1, and from the first apparatus line L1, is injected into the second apparatus line L2, into a second reactor R2, without further additions of reagents, which is similar to the first reactor R1 and in which a second methanation reaction occurs, obtaining high-purity biomethane, i.e., with H₂ lower than 1% by volume, with CO₂ lower than 2.5% molar and with CO lower than 0.1% molar.

[0063] The gaseous mixture that exits from the second reactor R2 is made to condense in a second condenser C2 in order to remove the H₂O that is present.

[0064] Biomethane 10 that meets the purity requirements necessary for injection into the natural gas network exits from the second condenser C2.

55 **[0065]** It should be noted that due to the high exothermicity of the methanation reaction in the first reactor R1, the heat Q produced by the first reactor R1 can be used to:

- compensate for the dissipations in the first reactor R1 and allow auto-thermal operation, and in this case only an

external heating contribution is needed during starting,

- and/or preheat the second reactor R2 and facilitate the starting of the reaction and the compensation of its thermal dissipations, since the reaction in the second reactor R2 produces less heat.

[0066] The expression "auto-thermal operation", in the present description, is understood to mean that the thermal energy necessary for the operation of the reactor is obtained directly from the reaction that occurs inside it, including its outward dispersions.

[0067] Laboratory tests have shown that a method according to the invention produces biomethane with a concentration of CH₄ greater than 99% by volume.

[0068] It should be noted that the H₂O obtained from the condensation in the first condenser C1 and in the second condenser C2 can be reused by the optional electrolyzer for the supply of hydrogen (H) 101.

[0069] In a second embodiment of the method according to the invention, shown in Figures 3a and 3b, the two apparatus lines L1 and L2 are arranged in parallel and are fluidically connected, upstream of the respective reactors R1 and R2 and downstream of the respective condensers C1 and C2, by means of two four-way valves V1, V2, respectively:

- a first valve V1, upstream of the two reactors R1, R2 and fluidically connected thereto,
- a second valve V2, downstream of the condensers C1 and C2 and fluidically connected thereto.

[0070] In the second embodiment of the method according to the invention, the two valves V1, V2, change position simultaneously, passing from the configuration shown in Figure 3a to the one shown in Figure 3b, and vice versa, depending on the production step, and in a sequential manner.

[0071] Such apparatus structure makes it possible to swap periodically the reactor R1 with the reactor R2, in which the first reaction, which is the most exothermic one, occurs, in order to utilize the sensible heat accumulated inside the reactor by changing the position of the first valve V1 and of the second valve V2.

[0072] This makes it possible to heat both reactors R1, R2, by virtue of the heat released by the methanation reaction, accumulated as sensible heat in the material of the catalytic bed, without having additional heating units.

[0073] This second embodiment of the method allows therefore a reduction of the initial apparatus costs and the operating costs due to the use of service fluids.

[0074] Starting from the configuration shown in Figure 3a, the method corresponds to the one of the first embodiment described above and one obtains in output from the second condenser C2 biomethane 10 which meets the requirements for injection into the natural gas network.

[0075] Subsequently, with the simultaneous change in the position of both valves V1 and V2, the order of the reactors R1, R2 and of the corresponding condensers C1, C2 is inverted.

[0076] The biogas 100 and the hydrogen 101 are then injected into the second apparatus line L2, in which the first reaction step occurs, and into the second reactor R2, in which the first methanation reaction occurs.

[0077] In this case, the second reactor R2 is heated more, while the second reaction step, with the second methanation reaction, downstream of the second condenser C2, which is less exothermic due to the lower concentration of reactants, occurs in the first apparatus line L1, inside the first reactor R1, which is already hot as a result of the previous configuration.

[0078] Downstream of the first reactor R1, the gaseous mixture is made to condense on the first condenser C1, obtaining high-purity biomethane 10 (Figure 3b) to be injected into the natural gas network.

[0079] Starting from the subsequent swapping of the valves V1, V2, both reactors R1 and R2 are hot, at a sufficient temperature, and it is no longer necessary to supply energy to the apparatus from the outside.

[0080] This apparatus structure eliminates the heat exchanges between the reactors R1, R2 of the first apparatus structure and utilizes the thermal inertia of the catalytic beds, possibly modified by using also inert fillers with high thermal capacity, such as for example silicon carbide.

[0081] In both of the embodiments of the method described above, the reactor R1, R2 is thermally insulated in order to work in adiabatic conditions with contact times comprised between 40 m³/(Kgcat·h) and 80 m³/(Kgcat·h) and a pressure comprised between 1 bar and 30 bars.

[0082] It should be noted that it is possible to optimize the operating parameters of the reactors R1, R2 and to also provide an energy recovery in order maximize the heat generation of the MET reaction and reuse it in other operations/processes.

[0083] In both of the embodiments described above, the method occurs substantially by means of two successive steps, each consisting of a methanation reaction and a condensation.

[0084] In practice, the method according to the invention consists in:

- introducing biogas 100 and hydrogen 101 in the first reactor R1, performing a first methanation reaction, obtaining a first gaseous mixture,
- making the H₂O in the first gaseous mixture condense in the first condenser C1, separating the H₂O from the rest

- of the first gaseous mixture, obtaining impure biomethane,
- introducing the impure biomethane in the second reactor R2, performing a second methanation reaction, obtaining a second gaseous mixture,
 - making the H₂O in the second gaseous mixture condense in the second condenser C2, separating the H₂O from the rest of the second gaseous mixture, obtaining a high-purity biomethane 10.

[0085] In practice it has been found that the invention achieves the intended aim and objects, utilizing the principles of the chemical equilibrium which limits the reaction in a single step, and providing a method for the production of biomethane that allows full utilization of the initial biogas.

[0086] The invention provides a method for the production of biomethane from biogas in which CO₂ which might not find a commercial use is not produced.

[0087] It should be noted that with the method with the two reactors in series both the residual CO₂ and the residual H₂ after the MET reaction are within the injection limits prescribed by the currently applicable standards.

[0088] Furthermore, the invention provides a method for the production of biomethane from biogas in which all the carbon C contained in the CO₂ is converted into CH₄.

[0089] This further enhances the value of the biomethane produced and increases the economic return provided by the sale of CICs (Certificates of Release for Consumption) as required by Ministerial Decree of 2 March 2018. Moreover, the costs due to CO₂ disposal, which typically burden traditional apparatuses for production of biomethane from biogas, are eliminated.

[0090] Moreover, with the method according to the invention there are no byproducts and therefore there is no need for separation steps subsequent to the methanation steps.

[0091] It should also be noted that with a method according to the invention there are energy costs only for starting the process, since the reaction is self-sustaining and the reactor is adiabatic.

[0092] The expression "the reaction is self-sustaining" in the present description is understood to mean that the reaction, once triggered, releases a quantity of heat capable of sustaining the activation energy demand of the reaction itself and the residual heat dispersions.

[0093] Therefore, it does not need heat supplied from outside.

[0094] The invention thus conceived is susceptible of numerous modifications and variations, all of which are within the scope of the inventive concept; all the details may furthermore be replaced with other technically equivalent elements.

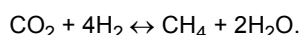
[0095] In practice, the materials used, as long as they are compatible with the specific use, as well as the contingent shapes and dimensions, may be any according to the requirements and the state of the art.

[0096] The disclosures in Italian Patent Application No. 102020000027474 from which this application claims priority are incorporated herein by reference.

[0097] Where technical features mentioned in any claim are followed by reference signs, those reference signs have been included for the sole purpose of increasing the intelligibility of the claims and accordingly such reference signs do not have any limiting effect on the interpretation of each element identified by way of example by such reference signs.

Claims

1. A method for the production of biomethane (10) from biogas (100), **characterized in that** said biogas (100) is subjected to at least two steps of biogas upgrading, with intermediate removal of H₂O, said biogas upgrading step consisting in the direct methanation reaction of the CO₂ that is present in the biogas:



2. The method according to claim 1, **characterized in that** it further comprises the steps of:

- introducing said biogas (100) and hydrogen (101) into a first reactor (R1, R2), performing a first methanation reaction, obtaining a first gaseous mixture,
- making the H₂O in said first gaseous mixture condense in a first condenser (C1, C2), separating the H₂O from the rest of the first gaseous mixture, obtaining an impure biomethane,
- introducing said impure biomethane into a second reactor (R2, R1), performing a second methanation reaction, obtaining a second gaseous mixture,
- making the H₂O in said second gaseous mixture condense in a second condenser (C1, C2), separating the H₂O from the rest of the second gaseous mixture, obtaining said biomethane (10).

3. The method according to one or more of the preceding claims, **characterized in that** said first reactor (R1) and

said second reactor (R2) comprise a catalytic converter (12).

4. The method according to one or more of the preceding claims, **characterized in that** said first reactor (R1) and said second reactor (R2) operate at a temperature substantially comprised between 200°C and 350°C and at a pressure substantially comprised between 1 bar and 30 bar.
5. The method according to one or more of the preceding claims, **characterized in that** said at least two steps occur in two successive apparatus lines (L1, L2), fluidically connected to each other, each one of said apparatus lines (L1, L2) comprising a reactor (R1, R2) and a condenser (C1, C2).
6. The method according to the preceding claim, **characterized in that** said apparatus lines (L1, L2) are arranged in series.
7. The method according to claim 6, **characterized in that** the heat (Q) produced by said first reactor (R1) is used to:
 - compensate for the dissipations in said first reactor (R1) and allow auto-thermal operation,
 - and/or preheat said second reactor (R2).
8. The method according to claim 5, **characterized in that** said apparatus lines (L1, L2) are arranged in parallel and are fluidically connected, upstream of the respective reactors (R1, R2) and downstream of the respective condensers (C1, C2), by means of two four-way valves (V1, V2), respectively:
 - a first valve (V1), upstream of said reactors (R1, R2) and fluidically connected thereto,
 - a second valve (V2), downstream of the condensers (C1, C2) and fluidically connected thereto.
9. The method according to claim 8, **characterized in that** it further comprises the step of swappig periodically the reactor (R1, R2) in which the first methanation reaction occurs, by means of a change in position of said first valve (V1) and of said second valve (V2).

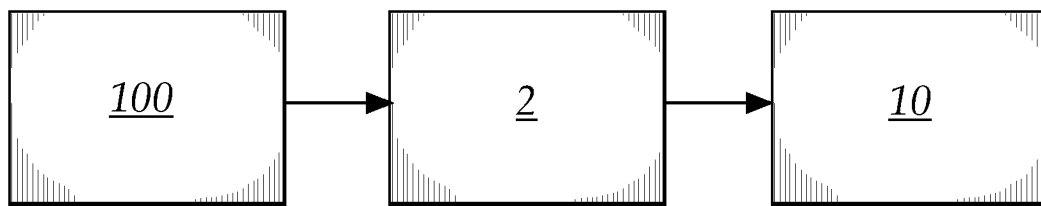


Fig.1

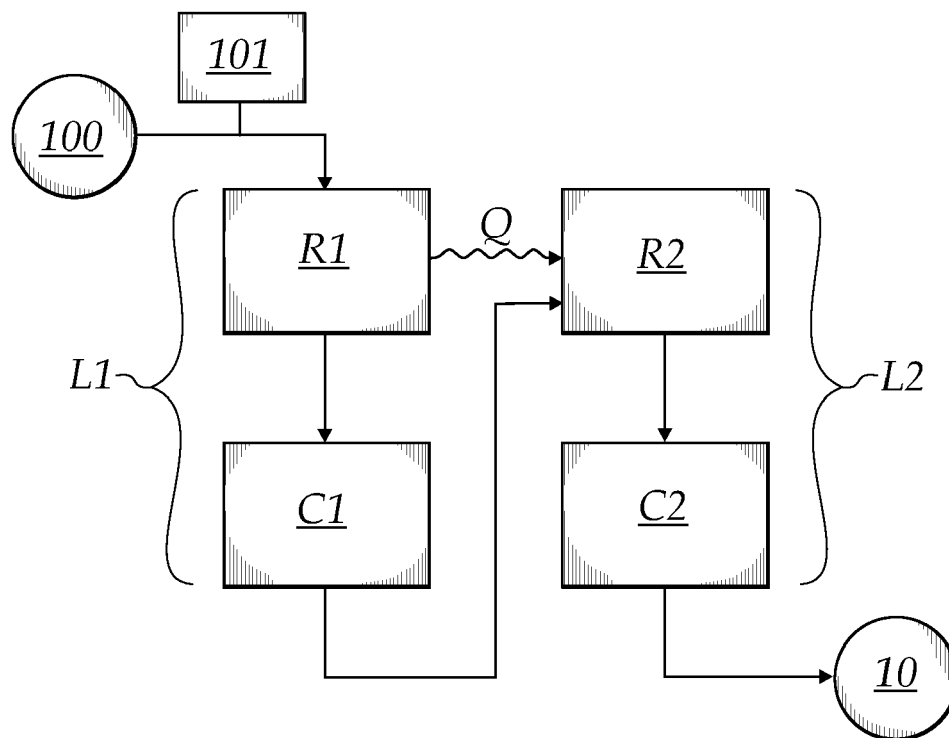
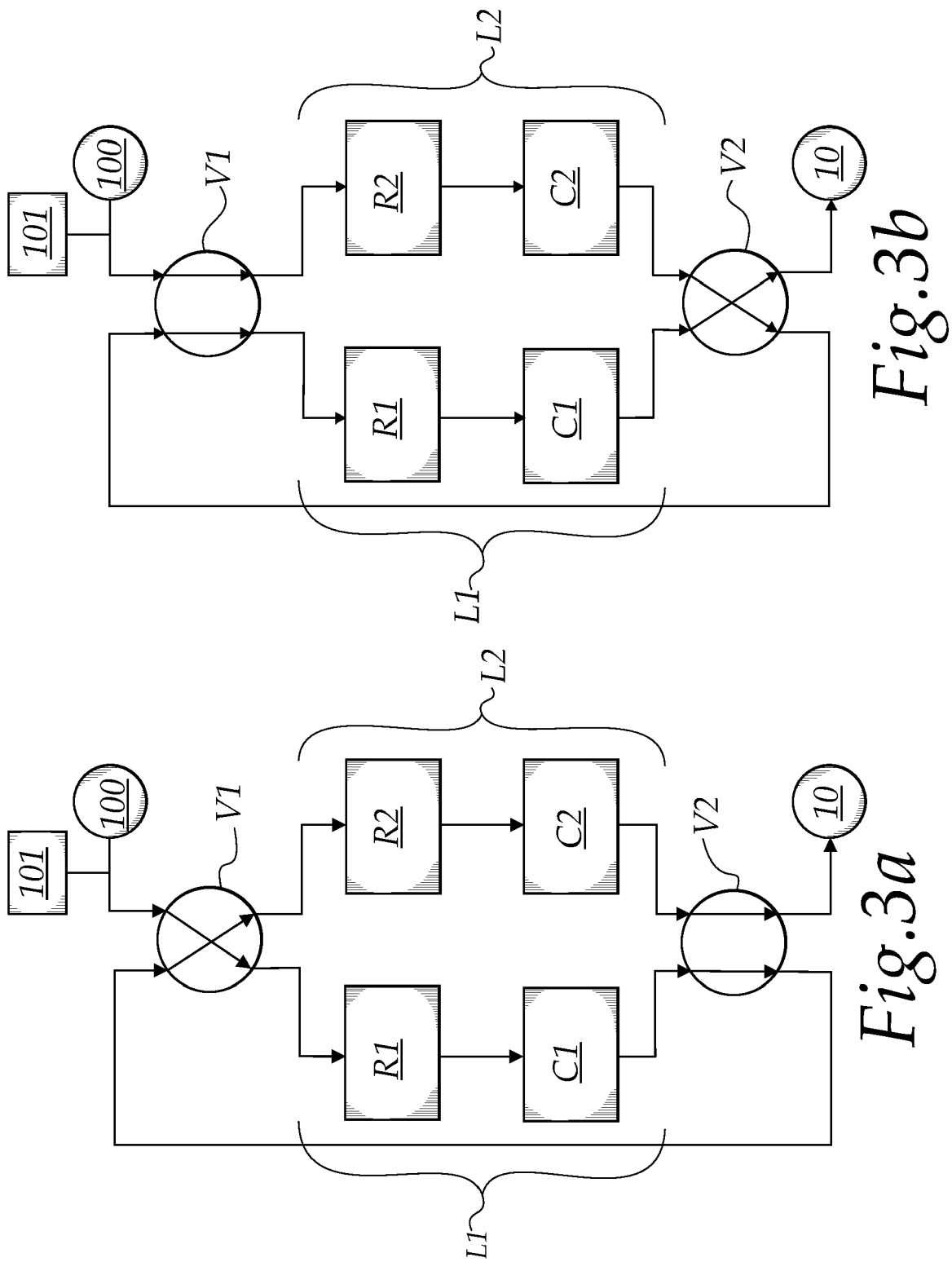


Fig.2



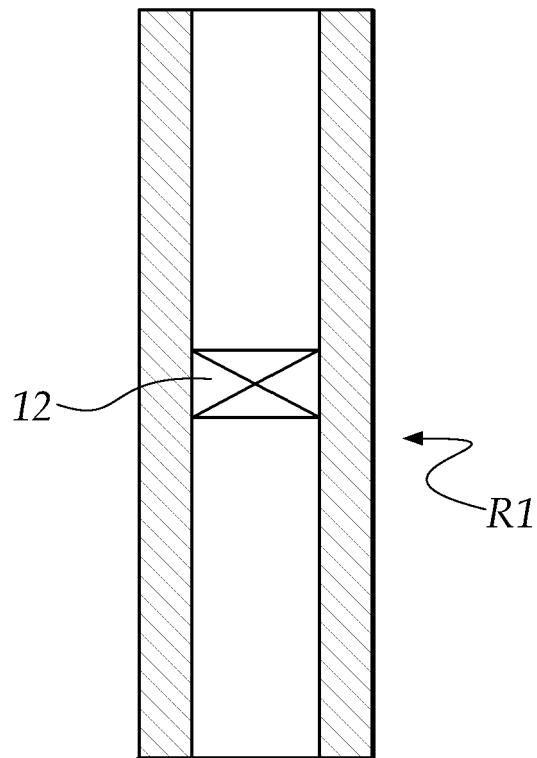


Fig.4



EUROPEAN SEARCH REPORT

Application Number

EP 21 20 6402

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 10 2014 001933 A1 (NIEDERBACHER MICHAEL [IT]) 13 August 2015 (2015-08-13) * paragraphs [0010], [0011]; claims * -----	1-9	INV. C10L3/08 C10L3/10 B01D5/00
X	MUÑOZ RAÚL ET AL: "A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading", REVIEWS IN ENVIRONMENTAL SCIENCE AND BIO-TECHNOLOGY, KLUWER, DORDRECHT, NL, vol. 14, no. 4, 26 September 2015 (2015-09-26), pages 727-759, XP035930331, ISSN: 1569-1705, DOI: 10.1007/S11157-015-9379-1 [retrieved on 2015-09-26] * abstract * * pages 738-740, paragraph 2.2.1; table 3 * * page 752, paragraph 4 * -----	1-9	TECHNICAL FIELDS SEARCHED (IPC) C10L F17C B01D
X	ADNAN ET AL: "Technologies for Biogas Upgrading to Biomethane: A Review", BIOENGINEERING, vol. 6, no. 4, 2 October 2019 (2019-10-02), page 92, XP055644058, DOI: 10.3390/bioengineering6040092 * abstract * * page 9, line 20 - page 11, line 27 * ----- -/--	1-9	
1 The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 14 February 2022	Examiner Péntek, Eric
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)



EUROPEAN SEARCH REPORT

Application Number

EP 21 20 6402

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	NATALIA ALFARO ET AL: "Evaluation of process performance, energy consumption and microbiota characterization in a ceramic membrane bioreactor for ex-situ biomethanation of H ₂ and CO ₂ ", BIORESOURCE TECHNOLOGY, vol. 258, 23 February 2018 (2018-02-23), pages 142-150, XP055701493, AMSTERDAM, NL ISSN: 0960-8524, DOI: 10.1016/j.biortech.2018.02.087 * page 142, column 1, line 1 - page 143, column 2, line 28; figure 1 *	1-9	TECHNICAL FIELDS SEARCHED (IPC)
X	CURTO DIEGO ET AL: "Renewable based biogas upgrading", JOURNAL OF CLEANER PRODUCTION, vol. 224, 20 March 2019 (2019-03-20), pages 50-59, XP085670709, ISSN: 0959-6526, DOI: 10.1016/J.JCLEPRO.2019.03.176 * page 50, line 1 - page 52, line 1; figure 1 *	1-9	
E	WO 2021/234073 A1 (TMA PROCESS [FR] ET AL.) 25 November 2021 (2021-11-25) * claims; figures *	1	
1 The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 14 February 2022	Examiner Péntek, Eric
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 21 20 6402

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-02-2022

10

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102014001933 A1	13-08-2015	DE 102014001933 A1	13-08-2015
		WO 2015120983 A1	20-08-2015
WO 2021234073 A1	25-11-2021	FR 3110601 A1	26-11-2021
		WO 2021234073 A1	25-11-2021

15

20

25

30

35

40

45

50

55

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- IT 102020000027474 [0096]

Non-patent literature cited in the description

- Natural gas and biomethane for use in transport and biomethane for injection in the natural gas network.
UNI EN 16723 standard, December 2016 [0004]