(19) DANMARK

(10) DK/EP 3280807 T3

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: *C 12 P 5/02 (2006.01)* *B 01 D 53/62 (2006.01)* *B 01 D 53/84 (2006.01)* *B 01 D 53/85 (2006.01)* *E 21 B 41/00 (2006.01)* *F 17 C 1/00 (2006.01)*

(45) Oversættelsen bekendtgjort den: **2019-11-25**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2019-10-09**

(86) Europæisk ansøgning nr.: **16713366.9**

(86) Europæisk indleveringsdag: **2016-03-24**

(87) Den europæiske ansøgnings publiceringsdag: **2018-02-14**

(86) International ansøgning nr.: **EP2016056521**

(87) Internationalt publikationsnr.: **WO2016151078**

(30) Prioritet: **2015-03-26 EP 15161055**

(84) Designerede stater: **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**

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(54) Benævnelse: **Fremgangsmåde til hydrogenotrof methanogenese af H2 og CO2 til CH4**

(56) Fremdragne publikationer:
EP-A1- 0 963 780
WO-A1-2008/128331
WO-A1-2012/110256

The present invention relates to a method for the hydrogenotrophic methanogenesis of H_2 and CO_2 to CH_4 by feeding a gas mixture comprising hydrogen, carbon dioxide and at least 10 vol% natural gas, into a gas zone of an underground storage facility and storing there in the presence of methanogenic microorganisms.

In order to balance the availability of renewable energy sources that depend on the time of day and/or the weather situation, such as wind and sunlight, and to provide a corresponding adjustment to the respective power demands, storage facilities for said renewable energies are required. In this manner it is possible to store energy produced in excess, e. g. in times of strong wind, and to utilize it at a later point in time, e. g. in times of high power demand, or to supply it to other energetic gas applications.

Energy storage facilities serve to store energy which is to be utilized at a later point in time. If the storage of one form of energy is not favorable, e. g. due to technical difficulties, insufficient capacity or downtime losses, said energy is converted to another form of energy that is more suitable for storage, is then stored and may later be reconverted as required. One example in this context is the conversion of chemical energy (fuel) to thermal energy (heat) or the conversion of electrical energy (electricity) to chemical energy (fuel) or thermal energy (heat). In both storage and conversion of energy, losses are bound to occur.

The direct storage of electrical energy is very difficult to achieve and it is thus usually required to convert electrical energy to another form of energy and later reconvert it as required.

In this context, the power-to-gas approach has been developed in recent years and already been demonstrated in initial demonstration plants. In this approach, electrical energy is converted to gases and can thus be more easily stored. In Falkenhagen (Germany), for example, a plant has been established in which water is electrolytically split into hydrogen and oxygen using wind energy and is subsequently fed into the local natural gas network. Another plant in Werlte (Germany) also uses electrical energy to split water into hydrogen and oxygen,

followed by a further catalytic process step in which methane is formed from hydrogen and carbon dioxide and is in turn fed into the natural gas infrastructure.

Hydrogen at a concentration of 4 to 75 % forms a flammable mixture with air; an explosive mixture (oxyhydrogen) is only obtained with a hydrogen concentration of 18 % and more. Having the lowest atomic weight of all elements, hydrogen evaporates in an open environment before it can form an explosive mixture, or it already combusts at a concentration of 4 % in a hot environment (unless indicated otherwise, any percentage values given in the present description or the patent claims denote percent by volume when relating to mixtures of gases and percent by mass when relating to solids and liquids).

The most commonly known and frequently utilized storage form of hydrogen is the so-called pressure gas storage which is based on pressure vessels, such as gas cylinders. In this case, hydrogen is stored in suitable vessels at pressures of about 200 to 800 bar; pressure vessels with a storage pressure of up to 1,200 bar are also known. Owing to the required stability of the pressure vessels, the storage density is about 1 kg hydrogen in 70 to 80 kg vessel mass, which renders pressure gas storage highly uneconomical in terms of transport. For this reason, only about 1 % of the hydrogen produced worldwide is stored and transported in this manner.

In the natural gas industry, the storage of natural gas in underground storage facilities is state of the art. A distinction is made between natural storage formations, such as depleted oil and gas deposits and aquifers, and artificially created cavities, such as salt cavities and mining tunnels. The natural storage formations are also referred to as pore storage facilities as the gas is stored directly in the rock pores.

One indicator for the storage of gases from extraneous deposits is the storage of city gas. For example, the municipal utilities of Kiel, Germany, have operated since 1971 a gas cavity the size of 32,000 m^3 for the storage of city gas having a hydrogen concentration of up to 50 %. The cavity is located at a depth of 1,330 m and the gas is stored at a pressure of 80 to 160 bar, with a total annual gas loss of only 1 to 3 % of the total storage volume. Contrary to common belief, city gas storage cannot be

directly compared to the storage of hydrogen or the generation of biogas because, in particular, the carbon monoxide contained in city gas is another highly reactive component which triggers further chemical processes. However, empirical values with respect to the industrial storage of hydrogen have already been obtained in Teeside (Great Britain) and Bakniev (Russia) and can be used as a comparative reference. Finally, the experience in the field of CO_2-supported EOR (Enhanced Oil Recovery) may also be utilized.

Accordingly, the behavior of hydrogen present underground or stored in the geological subsoil according to the state of the art can be predicted based on many years of practical experience.

The admixture of hydrogen to natural gas is subject to the Natural Gas Standards which at present provide a decentralized regulation to allow different hydrogen concentrations in different countries. In Austria, for example, the ÖVGW guideline G31 defines a maximum hydrogen concentration of 4 % in each part of a natural gas network. If the feed point is located in the vicinity of a natural gas fuel station, the hydrogen concentration is further limited to a maximum of only 2 %. In Germany, the DVGW Worksheet G 260 'Gasbeschaffenheit' (gas quality) allows hydrogen admixtures in a one-digit percentage range, wherein the corresponding actual limit has to be determined for each case individually.

In the atmosphere, CO_2 acts as a greenhouse gas and is considered to be the principal cause of global warming. The separation of CO_2, for example from power plant exhaust gases, can be achieved using various methods, e. g. by CO_2 washing of the exhaust gas after combustion or by separation of CO_2 after coal gasification or combustion in an oxygen atmosphere. One of the suggested options for storing CO_2 that is obtained, e. g., by washing out or separation consists in geological storage, for example in geological formations such as depleted deposits of fossil oil and natural gas and in deep saltwater-bearing aquifers. The most favored option among researchers is the storage of CO_2 in deep sediment layers whose pores are filled with saltwater. At a depth of about 800 m and more, pressures prevail at which the injected CO_2 is compressed to such an extent that it remains in an over-critical state. In order to virtually exclude any resurfacing of the carbon dioxide, these layers must be covered by an impermeable top layer. The pressure prevailing in these depths

compresses the CO_2 to a density approximately equal to that of saltwater and thus enables the compressed CO_2 to displace the saltwater from and occupy the pores. In this process, the saltwater is displaced in the deposit laterally with respect to the injection site. The lateral expansion of the pressure anomaly can be a multiple of the distribution of the CO_2 in an aquifer. Deep injection of CO_2 and displacement of saltwater performed at pressures significantly higher than the formation pressure and tensile stress of the rock may lead to the occurrence of induced earthquakes, which in some cases may even yield tremors exceeding the tactility threshold. The underground storage of CO_2 is thus problematic and, in addition, the utilization of deep aquifers competes with other utilizations, for example with the utilization of these aquifers for sustainable geothermic power generation. Moreover, the storage capacity of aquifers is limited.

Document EP 0 963 780 A1 discloses a method in which hydrogen and CO_2 are stored in a pore storage facility in the presence of methanogenic bacteria (correctly: microorganisms). It is thus already known from this document to separate CO_2 from combustion exhaust gases using known technical means and to subsequently store said CO_2 underground. Hydrogen in pure form or, e. g., in the form of ammonia, methanogenic bacteria, bacterial substrates, catalysts and/or inhibitors can be added to the CO_2 in order to reduce CO_2 to CH_4 during the underground storage period. In this process, the CO_2 that has been separated from an exhaust gas using conventional means, purified, liquified and dried is rendered pumpable through a long-distance pipeline and injected into a neighboring aquifer, an artificially created underground cavity or a deposit of natural gas and fossil oil, respectively. The first two instances are preceded by an inoculation of the geological structure with corresponding bacterial cultures and the pertaining organic substrate, whereas methanogenic bacteria and organic substrates are, of course, already present in the third instance. If this teaching is adhered to, carbonic acid will form in the deposit due to the dissolution of pressure-injected CO_2 in water, which decreases the pH to about 4 at least in the vicinity of the pressure injection probe, which in turn renders the methanogenic microorganisms inactive. Besides, the low pH also has the effect of irreparably damaging carbonate rock present in the deposit. The

carbonic acid formed simply dissolves carbonate rock, which could pose a risk with respect to the stability of the pore storage facility. Moreover, natural gas, hydrogen and CO_2 are not blended, which represents another stress factor for the methanogenic microorganisms.

Document WO 2008/128331 A1 discloses a method in which hydrogen and CO_2 are converted to methane by methanogenic microorganisms in an underground deposit. CO_2 and hydrogen are fed to the deposit.

WO 2012/110256 discloses a method for hydrogenotrophic methanogenesis of hydrogen and carbon dioxide into methane with methanogenic microorganisms. Storing and reacting in underground storage facilities is not disclosed.

Most commonly, the microbial formation of methane is performed with acetate (acetoclastic methanogenesis) or H_2 and CO_2 (hydrogenotrophic methanogenesis) as starting materials. Low-molecular organic compounds, such as methanol, methylamine and formate, are also known as further substrates. In the process of hydrogenotrophic methanogenesis, inorganic carbon is reduced with hydrogen, which is either formed by substrate oxidation or taken up from the environment.

Methanogenic microorganisms (formerly referred to as methane bacteria) are members of the *Archaea* domain. They have a capacity of forming methane and are capable of obtaining energy from this metabolic process. These microorganisms are divided into the classes Methanobacteria, Methanococci, Methanomicrobia and Methanopyri, which altogether comprise six orders. H_2-oxidizing methanogens utilize exergonic methanogenesis, i. e. the reduction of CO_2 with molecular hydrogen to form methane and water, as an energy source. Among the obligately H_2-oxidizing methanogens are, e. g., the classes of Methanococcus, Methanobacterium and Methanopyrus. These are strictly anaerobic microorganisms which are active at temperatures between 0 and 70°C. In general, the metabolic activity of methanogens increases with the temperature. Some of these microorganisms can survive temperatures of more than 70 to 90°C, but the survival rate decreases with further increasing temperatures.

The present invention thus relates to a method of hydrogenotrophic methanogenesis, i. e. the microbial formation of

CH_4 from CO_2 and H_2, characterized in that a gas mixture comprising natural gas, hydrogen and CO_2 having a minimum natural gas concentration of 10 % and preferably having a ratio of hydrogen and CO_2 that is stoichiometric for the formation of CH_4 is fed into an underground storage facility which comprises a gas zone and is stored there in the presence of methanogenic microorganisms. The production of hydrogen is preferably conducted using renewable energy, particularly preferably directly at the storage location by the electrolysis of, e. g., water, followed by mixing the hydrogen thus produced with the natural gas or already present mixtures of natural gas and hydrogen and feeding the resulting mixture into the storage facility through an injection bore. The CO2 is preferably obtained by one of the above-mentioned separation methods. The CO_2 to be converted can also be admixed with the natural gas before the addition of hydrogen. If the hydrogen is obtained by the electrolysis of water, the oxygen recovered as a waste product can also be utilized for the production of particularly pure CO_2. The presence of methanogens can be ensured by injecting such microorganisms into the storage facility, either before or after filling said storage facility, or during the filling process by adding the methanogenic microorganisms to the gas mixture to be stored. Alternatively, the addition of methanogenic microorganisms may also be omitted if such organisms are already present in the storage facility in a sufficient amount. In the method according to the present invention it was surprisingly found that in the operation of an underground storage facility, in particular of an underground natural gas storage facility, it is possible to convert CO_2 and H_2 to CH_4 simultaneously with the normal gas storage operation. The method according to the present invention has significant advantages over the prior art, which are obvious from the increased productivity of the methanogenic microorganisms with the given specific ratio of natural gas, hydrogen and CO_2. Surprisingly, the relatively high concentration of natural gas in the feed gas does not cause end product inhibition with respect to methanogenesis; on the contrary, the presence of the specified minimum proportion of natural gas rather increases productivity. Preferably, the minimum natural gas proportion is at least 20 %, 30 %, 40 %, 50 %, 60 %, 70 %, 80 % or 87.5 %. In case of a

stoichiometric ratio of hydrogen and CO_2 for the formation of CH_4, the minimum proportion of natural gas can also be calculated based on values lying between the above-mentioned minimum proportions; correspondingly, the same applies to the amounts of hydrogen and CO_2 specified in the following. The method according to the present invention allows the conversion of CO_2 separated from waste gas to form natural gas with the aid of H_2. In a particular embodiment, the present invention also allows the purification and CO_2-depletion of a CO_2-contaminated natural gas directly at a deposit or storage site thereof. In such a case the ratio of hydrogen and CO_2 in the gas mixture to be fed needs to be adapted such that the stoichiometric ratio of hydrogen and CO_2 that is required for the formation of CH_4 is only achieved with the addition of the CO_2 which is already present in the deposit and contaminates the stored natural gas. The purified natural gas, i. e. CH_4, can then be withdrawn from the storage facility on demand through a withdrawal bore.

According to a preferred embodiment, the present invention is characterized in that the residence time of the gas mixture in the underground storage facility is determined by the distance between injection and withdrawal bore such that natural gas having a content of less than 18 %, preferably less than 10 %, particularly preferably less than 5 %, of the injected CO_2 is withdrawn at the withdrawal bore. It has surprisingly turned out - provided that the distance between injection and withdrawal bore is suitably selected depending on the geology of the underground storage facility - that already after a few duty cycles, i. e. cycles of conversion of CO_2 and H_2 to CH_4 by hydrogenotrophic methanogenesis, the reaction rate of the conversion, even without the addition of a substrate, is already high enough to allow a continuous conversion of CO_2 and H_2 to CH_4 by hydrogenotrophic methanogenesis, i. e. that the CO_2 and H_2 fed into the storage facility through the injection bore is already fully converted to CH_4 upon reaching the withdrawal bore. As will be shown in the following Examples, the duty cycle period is shortened by a factor of three and more as soon as a sufficiently large population of methanogenic microorganisms has formed in the underground storage facility. In this context, it has also turned out that the hydrogen required for the formation of CH_4 does not originate from the water

contained in the pores but rather from the added gaseous H_2, which contradicts the teaching of prior art document EP 0 963 780 A1.

In the fields of geology, hydrogeology and pedology, the porosity denotes the ratio of the total volume of all cavities of a porous soil or rock to the outer volume thereof. It is a measure of the space within a given volume that is filled by the rock based on its grain size or jointing, respectively of the cavities it leaved within said volume. The pores or capillaries are usually filled with air and/or water. The porosity (also referred to as pore space or pore volume) refers to the volume and is usually expressed as a percentage or fraction (fractions of 1 = 100 %) and designated with the Greek letter Φ in formulas.

With a proportion of pore water in the underground storage facility of preferably at least 15 % of the pore space, it has surprisingly turned out that the conversion of CO_2 and H_2 to CH_4 by hydrogenotrophic methanogenesis can be performed in a continuous operation of the storage facility. A continuous operation is defined such that the gas volume withdrawn from the storage facility corresponds to the gas volume fed to the storage facility. A specific spatial distance between injection and withdrawal bore is not required in this case.

According to a preferred embodiment of the present invention, the pH value in the gas zone of the storage facility is regulated by means of a controlled addition of hydrogen and/or CO_2 and is kept within a range that is optimal with respect to the productivity of the methanogenic microorganisms. This range varies depending on the microorganism population present and is in general between pH 5 and pH 10, preferably between pH 6 and pH 9 and particularly preferably between pH 7 and pH 8. The pH value is adjusted as follows: if the pH value is too high, the supply of CO_2 to the gas zone is increased, which causes a pH reduction, and if the pH value is too low, the supply of molecular hydrogen is increased, which causes a pH increase. Optionally, the supply of CO_2 and/or hydrogen may be automated to maintain the pH value within a predetermined range based on the evaluation of data obtained by a pH probe that is located in the gas zone of the storage facility.

According to another preferred embodiment of the present invention, the methanogenic microorganisms are provided by means

of inoculating the storage facility with deposit water from other storage facilities that are already in operation. The deposit water from a second storage facility already in operation has proved to be advantageous due to the population of microorganisms suitable for methanation that has already formed in said deposit water. After the inoculation, this population also propagates more rapidly in the new storage facility than a new population would have been able to. During the growth period in the new storage facility the composition of the population will, if necessary, undergo changes and adapt to the prevailing conditions. In general, the bacteria populations of the storage facilities have basically identical compositions; however, the compositions may differ, in particular with respect to the Archaea that are capable of performing hydrogenotrophic methanogenesis, but in most cases this difference will only relate to the percentages.

The microbial community in the reactors used in the evaluation of the method according to the present invention may be considered as an example of a population present in a storage facility. In a total of eight reactors used, the microbial consortium contained identical genera in all reactors.

In H_2-exposed reservoirs there are bacteria and archaea that are responsible for microbial processes such as methanogenesis, homoacetogenesis as well as sulfate and iron reduction. Methanobacteriaceae are the only family hitherto known to be capable of generating methane from carbon dioxide or monoxide and hydrogen. Moreover, the individual species are capable of adapting to a wide range of environmental conditions, such as pH value, temperature and nutrient availability. In the microbial community present in the reactors, a low proportion (0.3 to 1.2 %) of the genus Methanobacterium was found, which is known to have an obligately anaerobic and chemolithotrophic metabolism.

Also of significance is the Thermotogaceae family, which is known for its ability to degrade oil. In the microbial community present in the reactors used, this family is represented by the genera Kosmotoga (detected in percentages of 1.7 to 6.4 %) and Petrotoga (detected in percentages of 2.4 to 6.9 %). Both genera are typical for anaerobic oil reservoirs and occur within a wide range of temperatures from mesophilic (20 to 45°C) to thermophilic (45 to 80°C). They have been described as fermentative bacteria

which are also capable of reducing elemental sulfur to H_2S. Furthermore, a synergistic interaction between methanogenic bacteria and hydrogenic bacteria is known.

Another important family, the Peptococcaceae family (detected in percentages of 12.7 to 17.1 %) is present in the microbial community in the reactors and is represented, e. g., by the following genera: Desulfotomaculum (about 1.2 %), Desulfurispora (about 0.6 %), Dehalobacter (about 0.3 %), Desulfitibacter (about 1.7 %) and further Peptococcaceae which are still uncultivated (14.03 to 7.92 %) at present. The genus Desulfotomaculum represents mesophilic, obligately anaerobic bacteria that have a capacity for the sulfate reaction and the formation of H_2S. They are predominantly found in microbial biofilms, in which they often form synergistic consortia with fermentative bacteria.

The Clostridiaceae family, which has also been detected (in percentages of 1.10 to 1.96 %) in the microbial community present in the reactors used, is capable of reducing amorphous iron(III) oxide by means of peptide fermentation. This family is represented by the genera Natronincola and Proteiniclasticum. Further bacteria that have a capacity to reduce iron and may thus be present in the microbial community of a storage facility when performing the method according to the present invention are Shewanella, Desulfovibrio and Desulfuromonas. These bacteria, however, have an additional capacity for the reduction of manganese.

The family of Thermoanaerobacteraceae (detected in percentages of up to 5 %), represented by Gelria (about 1.40 %), Moorella (about 2.35 %) and Syntrophaceticus (about 1.15 %), is typically found in CO_2-reducing anaerobic conditions. Several species of the genus Moorella are known that are capable of producing hydrogen and directly transferring it to methanogens.

Pseudomonas (detected in percentages of 14.26 to 30.71 %) are members of a group of bacteria which are most versatile with respect to metabolism and habitat. *Pseudomonas stutzeri*, for example, is capable of reducing nitrate to nitrite and further forming molecular nitrogen from said nitrite under anaerobic conditions.

As already mentioned, the legal regulations in Austria limit the maximum hydrogen concentration in natural gas to 4 %, while Germany, for example, allows 5 %. Thus, the hydrogen concentration

provided according to the present invention in the gas mixture to be injected into the storage facility depends on the legal regulations in the respective countries and may be lower than 70 %, 40 %, 30 %, preferably lower than 25 %, 24 %, 23 %, 22 %, 21 %, 20 %, 19 %, 18 %, 17 %, 16 %, 15 %, 14 %, 13 %, 12 %, 11 %, 10 %, 9 %, 8 %, 7 %, 6 %, 5 %, 4 %, 3 % or lower than 2 %. Such a gas mixture (containing, e. g., in Austria less than 4 % hydrogen in the natural gas) may be transported via the existing infrastructure of the gas network and then be depleted of hydrogen during a comparatively short storage period, wherein simultaneously CO_2, which is present, e. g., in the form of a separated fraction of a waste gas, is advantageously converted to methane. In connection with the storage facilities used, the method according to the present invention can also provide a homogenization of fluctuating renewable energy by infiltrating the hydrogen produced using renewable energy into the natural gas network and then methanating said hydrogen on demand while simultaneously utilizing excess CO_2 in the storage facility.

According to a preferred embodiment of the present invention, it is envisaged that the concentration of CO_2 in the gas mixture to be stored is less than 20 %, preferably less than 19 %, 18 %, 17 %, 16 %, 15 %, 14 %, 13 %, 12 %, 11 %, 10 %, 9 %, 8 %, 7 %, 6 %, 5 %, 4 %, 3 %, 2 %, 1 % or less than 0.5 %. The CO_2 concentration can be provided by feeding CO_2 into a mixture of natural gas and hydrogen which is already present in a storage facility. Alternatively, a desired CO_2 content can be adjusted during the storage process using the method according to the present invention, wherein defined amounts of hydrogen produced using renewable energy are added to a stored natural gas having a known concentration of CO_2 according to the chemical equation:

$$CO_2 + 4\ H_2 \longrightarrow CH_4 + 2\ H_2O$$

In the method according to the present invention, hydrogen can preferably be transported in an already existing natural gas network in the form of an admixture with natural gas according to the legal regulations, and the resulting mixture of natural gas, hydrogen and CO_2 is preferably stored in underground pore storage

facilities. Subsequently to withdrawing the stored gas mixture from the deposit and prior to feeding it into the natural gas network, the gas mixture may optionally be subjected to a membrane separation process, whereby the gas mixture is separated into natural gas having a hydrogen content according to the legal regulations for feeding into the natural gas network or, if desired, into one portion of pure natural gas and another portion of a gas mixture to be fed back into the storage facility.

In the method according to the present invention, the methanogenic microorganisms may preferably be selected from the classes of Methanobacteria, Methanococci, Methanomicrobia and Methanopyri as well as mixtures thereof. The selection of suitable methanogenic microorganisms is well within the knowledge of a person skilled in the art and not least also depends on the microorganisms already present in the storage facility, the environmental conditions prevailing in the storage facility, the water content of the storage facility and the gas mixture to be stored. As already mentioned, methanogenic microorganisms may optionally also be provided from other storage facilities that are already in operation by transferring the bacteria to the new storage facility, either before or after filling the new storage facility, or by introducing the microorganisms during the filling process of the new storage facility by adding the methanogenic microorganisms to the gas mixture to be stored.

Particularly preferably, the storage facility used in the method according to the present invention is an underground pore storage facility. Storage in aquifers is also conceivable, but is associated with increased technical and microbiological effort. On the one hand, an aquifer storage facility must be operated at high pressures and on the other hand an aquifer does not contain the same microbes as a formation that is saturated with hydrocarbons. The use of artificially created cavities (caverns and mining tunnels) is also possible, at least in theory, although such cavities only provide a surface area for biofilm formation that is much smaller than that of a pore storage facility.

According to another embodiment of the present invention, the gas mixture used in the method is an L-gas. An L-gas (low (calorific) gas) is a natural gas with a methane content of 80 to 87 % by volume which, in addition to methane, contains larger

amounts of nitrogen and carbon dioxide. By means of the method according to the present invention, such an L-gas can rapidly and easily be converted to H-gas (high (calorific) gas) having a methane content of up to 99 % by volume. In case of utilizing an already existing storage facility for L-gas, the method according to the present invention may comprise the introduction of hydrogen produced using renewable energy, optionally in admixture with methanogenic microorganisms, as mentioned above, into the already existing deposit, followed by hydrogenotrophic methanogenesis of present CO_2 using up the hydrogen added, which occurs in the storage facility and results in the formation of a natural gas which has a high methane content and, if desired, is entirely depleted of CO_2 and hydrogen.

Likewise, it is envisaged that the method according to the present invention may be used for regulating the CO_2 and/or hydrogen content of a natural gas. To this end, it is either possible to reduce a given amount of CO_2 added to a desired amount using methanogenic microorganisms with the addition of an optionally stoichiometrically calculated amount of hydrogen during the storage period, or the total amount of CO_2 in the stored gas mixture may be removed by adding an excess of hydrogen, wherein the gas mixture remaining in the deposit may optionally be depleted from the remaining excess hydrogen by means of membrane separation upon withdrawal.

As a so-called accompanying gas, which may also be loaded with CO_2, is also co-extracted from fossil oil deposits, a preferred embodiment of the present invention provides the introduction of hydrogen for reducing CO_2 according to the present invention in fossil oil deposits. To this end, the method according to the present invention is used to reduce the CO_2 content in the gas zone of a naturally occurring fossil oil or natural gas deposit, either before or after the extraction. Hydrofracking of higher hydrocarbons as well as EOR are also conceivable as positive side effects due to pressure maintenance.

It is noted in this context that for the purposes of the present invention both the above-mentioned accompanying gas of fossil oil deposits and any other CO_2-containing gases occurring in connection with the presence or the underground deposition and/or storage of fossil oil or natural gas are considered as being

encompassed by the term 'natural gas' as used in the present description.

In particular in the new implementation of the method according to the present invention in an already existing conventional natural gas storage facility it must be expected, at least during the initialization phase and/or the first duty cycles, that the residence time below ground may not be sufficient for a complete conversion of hydrogen and CO_2 to form CH_4. Accordingly, the method according to the present invention may provide the installation of a separator (membrane or ceramic) at the gas outlet of the withdrawal bore for processing the gas withdrawn from the storage facility according to the standardized specifications. Subsequently, the resulting separated, non-converted CO_2/H_2 gas mixture may be re-injected into the underground storage facility and thus be recycled into the conversion process.

The following Examples will explain the invention.

Into a total of eight bioreactors, each of which contained a microbial community according to the preceding description, a mixture of CO_2 and H_2 was injected in order to recover CH_4 by means of hydrogenotrophic methanogenesis. The injected gas mixture contained 10 % of H_2, 2.5 % of CO_2 and 87.5 % of CH_4; the gas conversion was detected using gas chromatography. The results obtained are depicted in Figure 1.

In the experiments it was unambiguously established that the conversion time of the components CO_2 and H_2 is reduced with an increasing number of duty cycles (filling cycles), i. e. from 29 days in the initialization phase to 12 days in the second duty cycle. It was found that this was based on the fact that the microorganisms present in the reactor require a certain initialization time in order to adapt to the injected gas mixture. During this initialization period, microbial processes are established that occur within a community of microorganisms and are required for processing newly introduced substrates. In addition, there is an increase in microbial growth, i. e. in the number of substrate-processing microorganisms, which then in turn convert the injected gas mixture, which results in a substantial acceleration of the process.

A further reduction of duty cycles is certainly to be

expected in continuous operation. With respect to the initialization phase, a solution in terms of operational management is conceivable. For instance, the residence time of the gas mixture in the underground storage facility may be increased as is required for its complete conversion; alternatively, a circulating operation may be provided, in which excess CO_2/H_2 is separated from the withdrawn gas using membranes. At the present stage, the ideal system is expected to establish itself after 3 to 4 duty cycles.

In the experiments according to Figures 2 and 3, the above-mentioned eight bioreactors were used, each containing a microbial community according to the above description. According to Figure 2, a gas mixture of 20 % of H_2, 5 % of CO_2 and 75 % of CH_4 was used; according to Figure 3, a mixture of 40 % of H_2, 10 % of CO_2 and 50 % of CH_4 was used. Surprisingly, a higher hydrogen content in the stored gas has a negative effect on the conversion rate as calculated from the linear region of the hydrogen partial pressure progression after the onset of the experiment (Figure 4). The conversion rate with an initial content of 10 % of H_2 (2.5 % of CO_2, 87.5 % of CH_4) is 0.54 bar/d, with 20 % of H_2 (5 % of CO_2, 75 % of CH_4) it is 0.44 bar/d and with 40 % of H_2 (10 % of CO_2, 50 % of CH_4) it is 0.34 bar/d. In the absence of methane (80 % of H_2, 20 % of CO_2) no hydrogenotrophic methanogenesis could be observed at all, which led to the surprising conclusion that the presence of methane in the initial gas mixture is mandatory in the method according to the present invention.

P A T E N T K R A V

1. Fremgangsmåde til hydrogenotrof methanogenese af H_2 og CO_2 til CH_4, k e n d e t e g n e t ved, at en gasblanding omfattende naturgas, hydrogen og CO_2 med en mindstekoncentration af naturgas på 10 volumenprocent, og fortrinsvis med et til dannelse af CH_4 støkiometrisk forhold mellem hydrogen og CO_2, indbringes i et underjordisk lager omfattende en gaszone og lagres der under tilstedeværelse af methanogene mikroorganismer.

2. Fremgangsmåde ifølge krav 1, k e n d e t e g n e t ved, at opholdstiden for gasblandingen i det underjordiske lager bestemmes ud fra afstanden mellem injektions- og udtagsboring således, at der ved udtagsboringen udtages naturgas med en andel på under 18 volumenprocent, fortrinsvis under 10 volumenprocent, særligt foretrukket under 5 volumenprocent af det indbragte CO_2.

3. Fremgangsmåde ifølge krav 1 eller 2, k e n d e t e g n e t ved, at det underjordiske lager frembyder en vandandel på mindst 15 % på basis af lagerbjergartens porerum, og omsætningen finder sted under den kontinuerlige drift af lageret.

4. Fremgangsmåde ifølge et af kravene 1 til 3, k e n d e t e g n e t ved, at pH-værdien i gaszonen i lageret styres eller reguleres ved doseret tilsætning af hydrogen og/eller CO_2 og holdes i det område, hvor de methanogene mikroorganismer udviser et optimum.

5. Fremgangsmåde ifølge et af kravene 1 til 4, k e n d e t e g n e t ved, at de methanogene mikroorganismer etableres ved podning af lageret ved hjælp af formationsvand fra et andet lager, der allerede er i drift.

6. Fremgangsmåde ifølge et af kravene 1 til 5, k e n d e t e g n e t ved, at hydrogenkoncentrationen i gasblandingen, der skal lagres, efter volumen andrager under 72 %, fortrinsvis under 40 %, særligt foretrukket under 30 %, 20 %, 13 %, 12 %, 11 %, 10 %, 9 %, 8 %, 7 %, 6 %, 5 %, 4 %, 3 % eller under 2 %.

7. Fremgangsmåde ifølge et af kravene 1 til 6, k e n d e t e g n e t ved, at CO_2-koncentrationen i gasblandingen, der skal lagres, efter volumen andrager under 18 %, fortrinsvis under 10 %, 9 %, 8 %, 7 %, 6 %, 5 %, 4 %, 3 %, 2 %, 1 % eller under 0,5 %.

8. Fremgangsmåde ifølge et af kravene 1 til 7, k e n d e t e g n e t ved, at der anvendes bakterier udvalgt blandt klasserne Methanobacteria, Methanococci, Methanomicrobia og Methanopyri samt blandinger deraf.

9. Fremgangsmåde ifølge et af kravene 1 til 8, k e n d e t e g n e t ved, at det underjordiske lager er et porelager.

10. Anvendelse af fremgangsmåden ifølge et af kravene 1 til 9 til reduktion af CO_2-andelen af gaszonen i en naturlig naturgas- eller råolieforekomst før eller under befordringen af råolie fra forekomsten.

11. Anvendelse af en fremgangsmåde ifølge et af kravene 1 til 9 til styring af indholdet af CO_2 og/eller hydrogen i en naturgas.

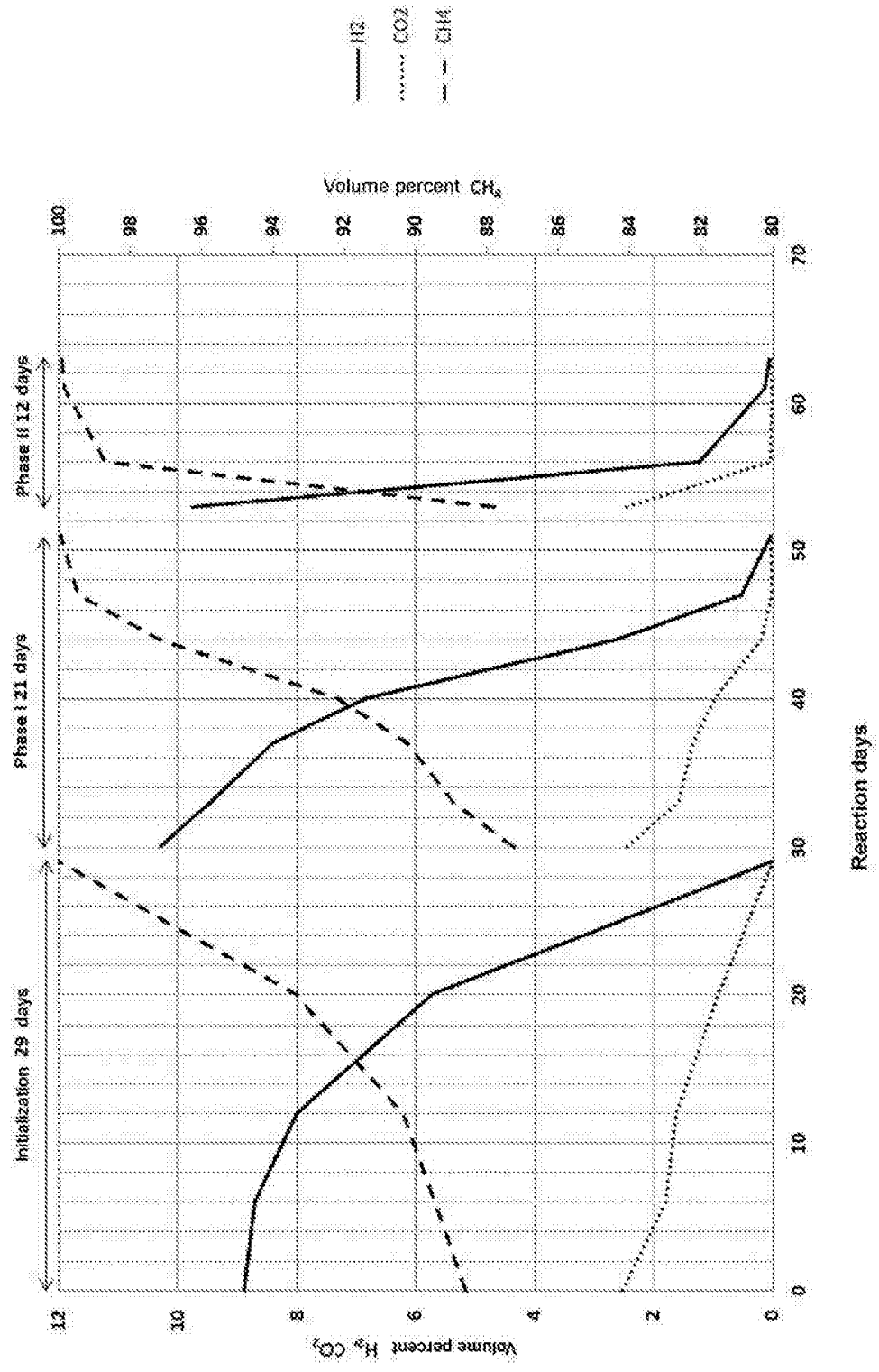

Fig. 1: Measured conversion rates with proportions of 10% H_2, 2.5% CO_2 and 87.5% CH_4

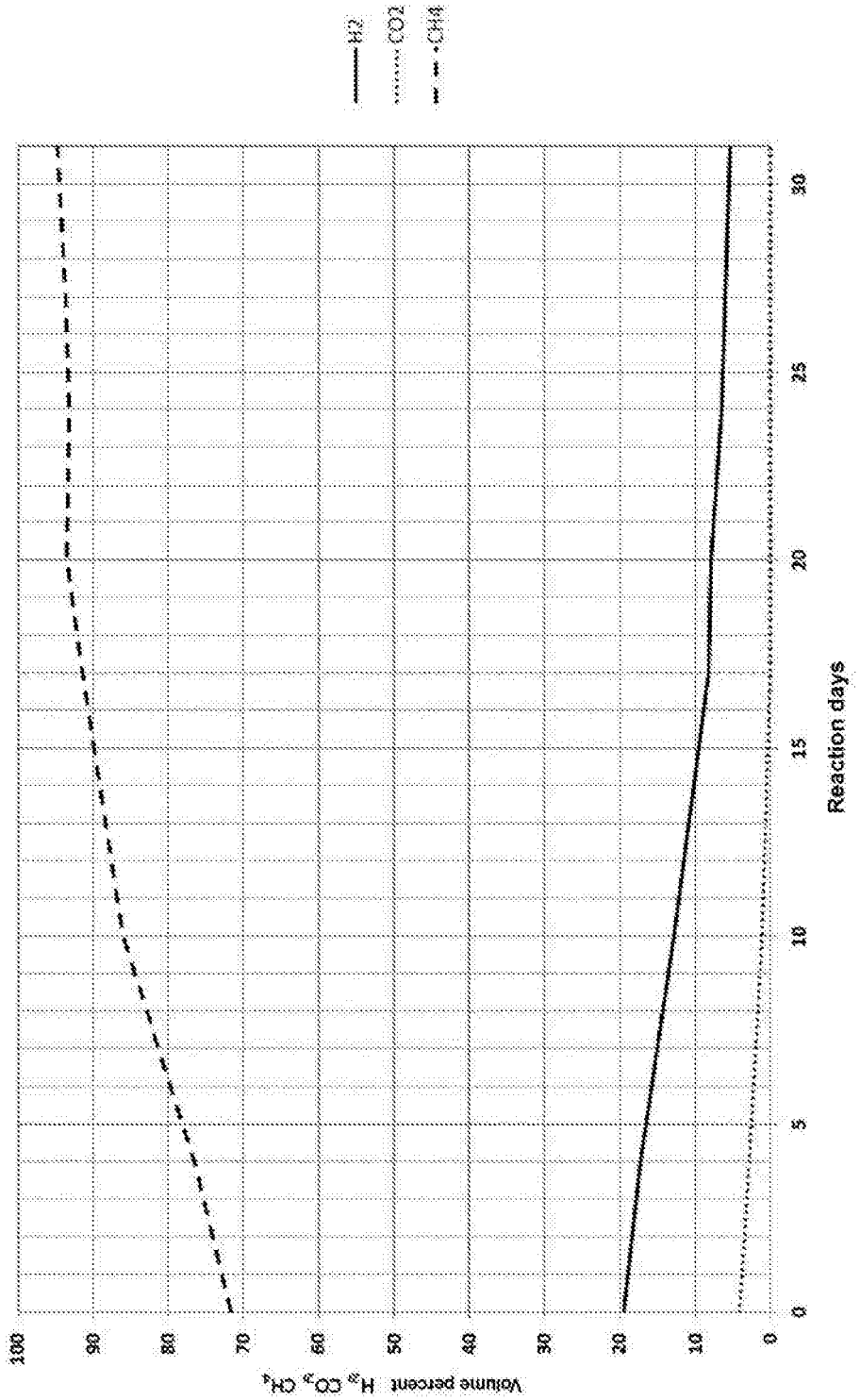

Fig. 2: Measured conversion rates with proportions of **20% H_2, 5% CO_2** and **75% CH_4**

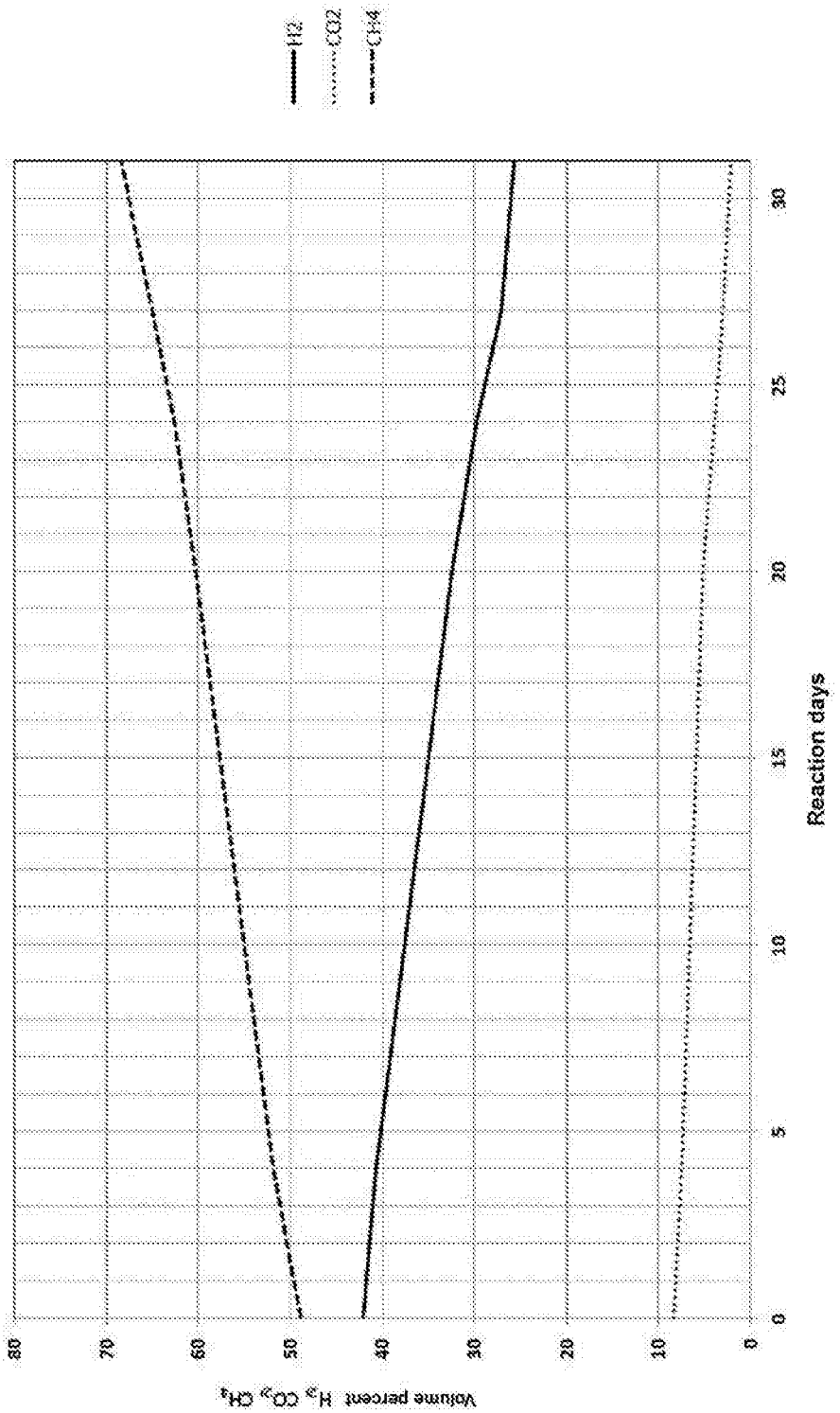

Fig. 3: Measured conversion rates with proportions of **40% H_2, 10% CO_2** and **50% CH_4**

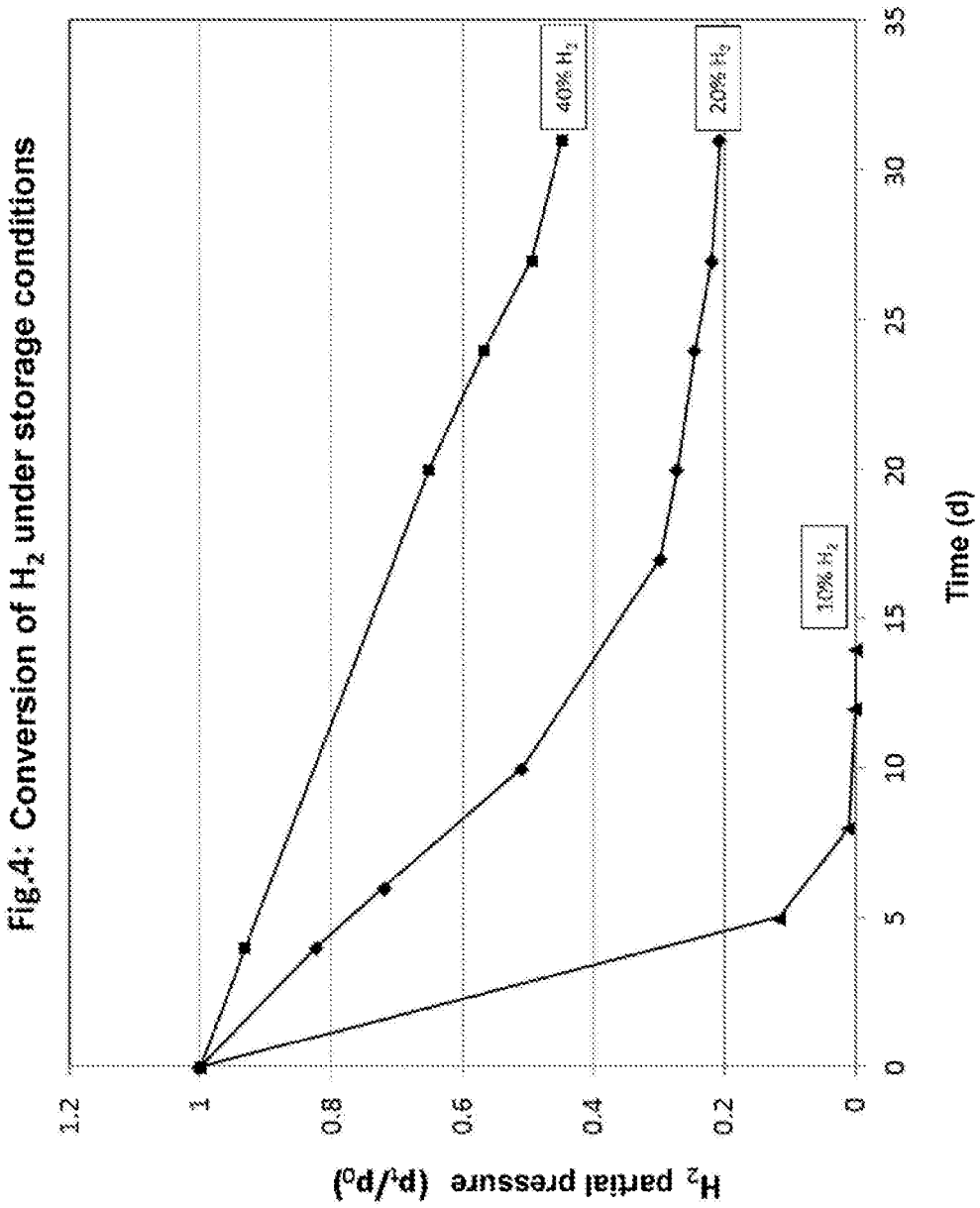

Fig.4: Conversion of H_2 under storage conditions