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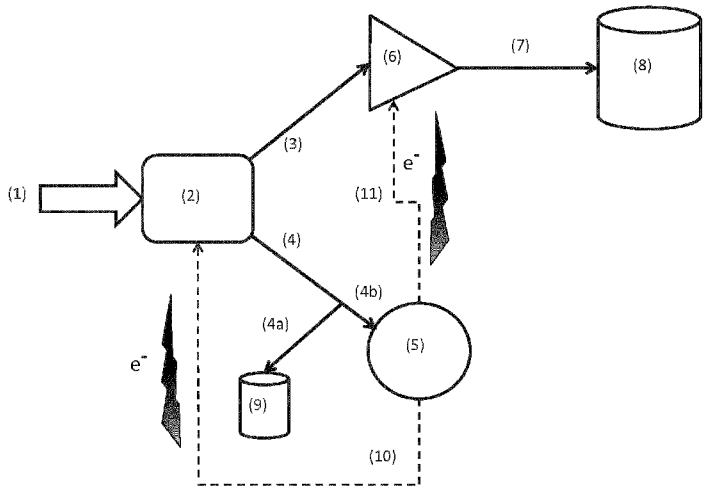
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(54) Title: HYDROGEN SEPARATION FROM NATURAL GAS

Figure 1



(57) Abstract: A process and apparatus for the separation of hydrogen gas from an input stream comprising gaseous methane and gaseous hydrogen is disclosed. The apparatus comprises an electrochemical pump, a gas compression apparatus and a fuel cell. The electrochemical pump is capable of separating the input stream into a first output stream comprising gaseous methane, and a second output stream comprising at least 95 % vol. hydrogen gas. The electrochemical pump and the gas compression apparatus are each capable of using at least a portion of the electricity generated by the fuel cell. At least a portion of the first output stream comprising gaseous methane is supplied to a gas compression apparatus to compress the first output stream to a pressure of at least 0.1MPa. The pressure of the second output stream comprising at least 95% hydrogen gas separated by the electrochemical pump is at least 30MPa.

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HYDROGEN SEPARATION FROM NATURAL GAS

Field of the Invention

This invention relates to a process and an apparatus for the separation of hydrogen gas from an input stream comprising gaseous methane and gaseous hydrogen.

Background of the Invention

In recent years, there has been an increasing interest and activity in the development of non-fossil fuel derived energy sources, such as electricity generated from solar energy or from wind energy, as well as electricity generated from hydrogen gas.

In the case of hydrogen, fuel cells have been developed which generate electricity from hydrogen gas, and such electricity can then be used to drive machinery and propel vehicles. An advantage of using hydrogen for vehicle propulsion is that, at its point of use, it does not produce compounds that are deemed harmful to the environment such as CO_2, CO, particulates and unburned hydrocarbons. However hydrogen's environmental impact is dependent on the way in which it is produced. For example, hydrogen produced from fossil fuel derived compounds may result in the unwanted production of the abovementioned compounds. To overcome both the fossil fuel use and the generation of the abovementioned compounds associated with hydrogen production, processes are being developed, such as the coupling of wind-generated electricity to hydrogen production from water by electrolysis. Such processes are particularly advantageous because during periods of low electricity demand, or when the electricity grid is already at full capacity, instead of switching off the wind-driven

turbines, electricity production can be continued and used in the vicinity of the wind-driven turbines for hydrogen production by electrolysis.

In many instances, wind farms that generate electricity are located some distance from population centres, in remote locations and even in marine environments. Unlike the situation with electricity and natural gas, no network exists for the high-volume long-distance transmission and distribution of hydrogen, which would be required if hydrogen gas is to become a common fuel. This means that if hydrogen gas is produced at a remote location, currently it is impractical for it to be transported in bulk to end-users. Across Europe, the European Union Directive 2003/55/EC has opened up non-discriminatory access to the existing natural gas transmission and distribution networks, and storage facilities, for the transmission, distribution and storage of (1) biogas, (2) gas from biomass and (3) other types of gas, provided that it is 'permanently compatible and safe'. This legislation has opened up the possibility of co-transporting hydrogen gas, as a mixture with natural gas, by using the existing natural gas transmission and distribution networks and storage facilities.

The issue of whether it is 'permanently compatible and safe' to co-transport hydrogen gas as a mixture with natural gas was assessed by the European Union funded 'NaturalHy' project, between 2002 and 2006. Melaina et al. (2013, "Blending of Hydrogen into Natural Gas Pipeline Networks: A Review of Key Issues", Technical Report NREL/TP-5600-51995, available from U.S. Department of Energy, Office of Scientific and Technical Information, Oak Ridge, TN 37831-0062) reviews the

findings of the NaturalHy project, as well as other related projects listed therein. This and other reviews (for example, Altfeld & Pinchbeck (2013), "Admissible Hydrogen Concentrations in Natural Gas Systems", Gas for Energy, 3, 2013, ISSN 2192-158X) discuss the significant constraints on the compatibility and safety of co-transporting mixtures of natural gas and hydrogen.

Amongst these constraints is 'hydrogen embrittlement', a property of hydrogen that diminishes the tensile strength of certain materials such as metals and elastomers. This is of particular importance to the natural gas transmission and distribution network operators because the co-transported hydrogen can diminish the physical integrity of components such as pipes, storage tanks and their seals. This problem is exacerbated at high gas pressures, such as in storage tanks and cylinders. Since a significant sector of natural gas end-users require natural gas at high pressure (i.e. as 'compressed natural gas' or 'CNG'), hydrogen embrittlement is a significant drawback to co-transporting hydrogen with natural gas.

Consequently, there appears to be an upper limit to the amount of hydrogen that can be introduced into the natural gas transmission, distribution and storage network, however, due to many variables inherent to natural gas and its networks across the world, currently there is no global consensus on this limit. Regarding such upper limit, for example, Altfeld & Pinchbeck (2013) report that this can be up to 10% of the natural gas content. However, Melaina et al (2013) report the findings of a US National Renewable Energy Laboratory (NREL) sponsored study conducted by the Gas Technology Institute, which concludes that hydrogen content in

natural gas of up to 20% results in a minor increase in explosion risk.

In the case of CNG however, as hydrogen embrittlement is exacerbated at high gas pressures, the upper limit of hydrogen that can be added to CNG appears to be lower. Further, vessels which use/transmit/store CNG (such as cylinders and other storage tanks, including the CNG tanks of CNG-utilising vehicles) need to be of certain minimum tensile strength to be tolerant to hydrogen. United Nations Economic Commission for Europe Regulation 110 for CNG-utilising vehicles, sets an upper hydrogen limit of 2% vol. if the CNG fuel tank is made from steel of ultimate tensile strength of more than 950 MPa. The same upper hydrogen limit is proscribed in ISO 11439 and in DIN 51624 standards. However, further research is needed to establish and verify theses limits.

A further problem concerns the combustion properties of natural gas-hydrogen mixtures. The presence of hydrogen in natural gas affects the 'Wobbe index', 'methane number' and 'laminar flame speed' of natural gas. This means that for the safe and predictable operation of gas turbines, gas engines and gas burners, at the user-end of the network, natural gas must be free of hydrogen.

Whilst injection of hydrogen gas into natural gas is a relatively simple process and is readily known to the skilled person, the efficient removal of hydrogen from the natural gas supply network requires more research.

Currently, there are three relatively well known ways of extracting hydrogen from gas mixtures. The first of these is the use of pressure swing adsorption units, which work by extracting impurities from hydrogen. The second is the use of porous steel supported hydrogen

permeable palladium membranes, which utilise the selective permeability of hydrogen through a thin palladium layer when a pressure differential is applied across it. The third is the use of electrochemical membrane pumps (or electrochemical hydrogen compressors). These utilise an electric field across a membrane-electrode-assembly to dissociate hydrogen into protons (H^+ ions), then carry these protons across their membrane-electrode-assembly, and finally convert them to hydrogen gas at the cathode. Such a process has been described to selectively accumulate hydrogen gas across the device in granted patent US6168705.

Each of the above-mentioned hydrogen separation methods has its disadvantage(s). In the case of pressure swing adsorption units, once these units are saturated with impurities, they need to be regenerated. For such reason, pressure swing adsorption units work best at high hydrogen concentrations, and not at, for example, the 10% or lower hydrogen levels contemplated for hydrogen-natural gas co-transportation. Further, pressure swing adsorption units work better across a pressure drop, so if deployed as part of the natural gas network, their operation would be more suitably at locations such as at pressure reduction stations, and such locations may not be suitable for the hydrogen distributors. In the case of palladium membranes, up to 99.9999999 %vol. hydrogen purity can be achieved by such membranes, however to achieve such hydrogen purity, these membranes require an operational temperature of about 400°C, and more importantly, a high pressure differential across the membrane. In the case of electrochemical membrane pumps, additional energy has to be spent, not only to purify and accumulate the hydrogen, but also to operate it at its

optimal operational temperature of at least 120 °C.

It would therefore be advantageous to both the operators of natural gas networks, and to the distributors of hydrogen, to have a system that separates hydrogen gas from natural gas in an energy efficient manner, and is capable of being deployed on an industrial scale.

Summary of the Invention

Accordingly, the present invention provides a process for the separation of hydrogen gas from an input stream comprising gaseous methane and gaseous hydrogen, comprising the steps of: (a) supplying the input stream to an electrochemical pump; (b) obtaining from the electrochemical pump a first output stream comprising gaseous methane and a second output stream comprising at least 95 % vol. hydrogen gas; (c) supplying at least a portion of the first output stream to a gas compression apparatus to compress the first output stream to a pressure of at least 0.1 MPa to provide a compressed gas stream; (d) supplying at least a portion of the second output stream to a fuel cell to produce electricity; and (e) using at least a portion of the electricity produced by the fuel cell to power, or partially power, the electrochemical pump and/or the gas compression apparatus.

The present invention also provides an apparatus for the separation of hydrogen gas from an input stream comprising gaseous methane and gaseous hydrogen, comprising: (a) an electrochemical pump; (b) a gas compression apparatus; and (c) a fuel cell; wherein the electrochemical pump comprises an inlet for accepting the input stream; wherein the electrochemical pump is capable of separating the input stream into a first output stream

comprising gaseous methane and a second output stream comprising at least 95 % vol. hydrogen gas; wherein the electrochemical pump comprises a first outlet in fluid connection with the gas compression apparatus for supplying the gas compression apparatus with the first output stream; wherein the electrochemical pump comprises a second outlet in fluid connection with the fuel cell for supplying the fuel cell with at least a portion of the second output stream; wherein the fuel cell is capable of using at least a portion of the second output stream to generate electricity; wherein the fuel cell is connected to the electrochemical pump and the gas compression apparatus by a first electrical connection means and a second electrical connection means respectively; and wherein the electrochemical pump and the gas compression apparatus are each capable of using at least a portion of the electricity generated by the fuel cell.

Thus the apparatus of the present invention is used to carry out the process of the present invention, thereby separating hydrogen gas from an input stream comprising gaseous methane and gaseous hydrogen to produce a compressed natural gas stream, as well as a hydrogen stream at pressure.

Such process can be viewed from the point of view of natural gas distributors, as well as from the point of view of hydrogen gas distributors. Following the co-transportation of natural gas and hydrogen, the natural gas distributors aim to obtain natural gas with less than 2 % vol. hydrogen gas (to be compliant with the United Nations Economic Commission for Europe Regulation 110 for CNG-utilising vehicles), as well as with even less % vol. hydrogen to be compliant with the relevant local natural

gas end-use specifications, so that it can be supplied to the end-users either directly, or as CNG. The hydrogen gas distributors on the other hand, aim to obtain essentially pure hydrogen gas that does not poison or adversely affect fuel cells.

The present inventors have not only found that carrying out the present process using the apparatus described herein results in the efficient separation of hydrogen gas from natural gas, but also surprisingly that the apparatus operates with energy efficiency. In particular, the electrical energy consumption of the electrochemical pump and the gas compression apparatus is offset by feeding to the fuel cell a portion of hydrogen gas extracted from the input stream to generate electricity, which in turn is fed to the power in full, or in part, the electrochemical pump and the gas compression apparatus.

The process and the apparatus of the present application is therefore a benefit to both natural gas distributors and to hydrogen distributors, by providing each with a means to produce an end product suitable for their respective markets.

Brief Description of the Drawings

Figure 1 shows a simplified schematic diagram of the process and the apparatus according to the invention.

Figure 2 provides a schematic representation of the process and the apparatus according to the invention illustrating an embodiment of the invention, where the input stream (1) is split into more than one input stream (1a, 1b and 1c), each of which is supplied to a different electrochemical pump (2a, 2b and 2c).

Figure 3 provides a schematic representation of the process and the apparatus according to the invention

illustrating an embodiment of the invention, where the input stream (1) is supplied to a first electrochemical pump (2a), arranged in series with a second electrochemical pump (2b) and a third electrochemical pump (2c).

Figure 4 provides a schematic representation of the process and the apparatus according to the invention illustrating an embodiment of the invention, where a portion of the first output stream (3d) is recycled back into the input stream (1).

Detailed Description of the Invention

In the present invention, suitably, the input stream (1) is the feed from the natural gas network that goes into the apparatus of the present invention to carry out the process of the present invention. The input stream comprises gaseous methane and gaseous hydrogen.

In one embodiment, the input stream (1) comprises natural gas. Depending on the location where natural gas is extracted, the wellhead composition of natural gas comprises varying proportions of methane as its principal component, as well as varying proportions of higher hydrocarbons such as ethane, propane, butane, pentane, hexane, pentane, octane and decane, including their respective isomers. Wellhead composition of natural gas also comprises varying amount of lesser constituents such as carbon dioxide, nitrogen, hydrogen sulphide and water vapour. During a number of process steps known to the skilled person, these lesser constituents are extracted so that its composition and characteristics comply with the relevant local natural gas end-use specifications. Examples of such process steps include the removal of sulphur, acid gases, water and mercury.

An example of the acceptable end-use specification

of marketed natural gas, for example in the USA, can be found in the Kirk-Othmer Encylopedia of Chemical Technology (fourth edition, volume 12, page 330, Table 6, ISBN 0-471-52681-9).

It must be noted that the end-user specification of natural gas does not just concern its chemical composition, but also its physical characteristics (e.g. dew point) as well as its combustion properties (Wobbe index, heating value etc.). Also it must be noted that the chemical composition of natural gas varies as it travels across the distribution network as it gets processed along the way, making the composition of the natural gas at the wellhead-end of the network more varied than at the end-user-end. Therefore, all references in this application to 'natural gas' must be construed in accordance with such inherent variability in the composition of natural gas.

Further, from the point of view of hydrogen distributors, for the purposes of practising the process of the present invention, neither the actual methane content, nor the actual hydrocarbon composition of the input stream matter, although from the point of view of natural gas distributors, input stream is likely to comply with the requirements of relevant specifications for natural gas.

In the process of the present application, the input stream (1) comprises gaseous hydrogen, the origin of which is suitably hydrogen gas that is added to the natural gas network so that it can be carried from the hydrogen production sites towards the hydrogen end-user through the natural gas network. The hydrogen gas can be added to the natural gas network by any method known to the skilled person.

The hydrogen may be produced by any number of ways, including by electrolysis of water, steam reforming of methane, or by any other method known to the skilled person. Depending on which one of these methods is used, the resultant hydrogen gas may comprise different amounts of impurities. For example, if electrolysis of water is used, essentially pure hydrogen can be produced.

However, hydrogen produced by the steam reforming of methane or natural gas produces carbon monoxide in addition to hydrogen. In most cases, such a mixture is then subjected to water-gas shift reaction to produce further hydrogen, but this time with carbon dioxide as a co-product. To obtain purer hydrogen from steam reforming, usually either pressure swing adsorption units and/or porous steel supported hydrogen permeable palladium membranes are deployed.

The point along the natural gas network at which the hydrogen gas may be added to the natural gas network for co-transportation depends on the purity of the hydrogen. Purer hydrogen can be added more or less at any point along the natural gas network, whereas less pure hydrogen is more likely to be added upstream of the number of process steps known to the skilled person that extract the lesser constituents of natural gas, as discussed above.

In the current climate of aiming to reduce greenhouse gas production, electrolysis provides an attractive hydrogen production process, although its use can be restricted by the availability and price of electricity, as well as its production capacity.

In one embodiment of the process of the invention, electrolysis is used to produce the hydrogen gas. The electrolysis apparatus may obtain its electricity from

any electricity generation methods, including from wind turbines or solar panel arrays. In such embodiment, the produced hydrogen is preferably at least 90 %vol. pure, more preferable at least 95 %vol. pure, even more preferably at least 98 %vol. pure, and most preferably at least 99 %vol. pure.

Suitably, the input stream (1) is the feed from the natural gas network that goes into the apparatus of the present invention. Due to the inherent variation of the natural gas composition discussed above, the composition of the input stream (1) is better defined by its hydrogen content. The hydrogen content of the input stream (1) may be preferably at least 0.001 %vol., more preferably at least 0.01 %vol., even more preferably at least 0.1 %vol., and most preferably at least 1 %vol.

With respect to the process of the present invention, there is no upper limit to the proportion of hydrogen of the input stream (1), however in practice such limit will be determined by the relevant safety legislation, rules and/or specifications.

In the process of the present invention, the input stream (1) is supplied to an electrochemical pump (2). In brief, electrochemical pumps are devices that use electricity to separate hydrogen gas from gaseous mixtures that contain hydrogen, and in the process of doing so, accumulate almost pure hydrogen gas at pressure. An essential feature of electrochemical pumps is their proton exchange membrane, which are permeable only to ionised hydrogen (otherwise known as 'H^+ ions', or 'protons'), and not permeable to any other gaseous components. For the proton exchange membrane to work as such, it must be sandwiched between two electrodes (the anode and the cathode). Such electrodes have embedded in

them transition metal(s), such as platinum and/or ruthenium, to catalyse the dissociation of hydrogen into protons and electrons. An external electricity source provides a potential difference across the electrodes. At the surface of the anode (+ve electrode), catalysed by the embedded transition metal(s) in an aqueous environment, each hydrogen molecule dissociates into two protons and two electrons. The potential difference across the electrodes then attracts the positively charged protons to the cathode (-ve electrode) across the proton exchange membrane. The separated electrons that cannot cross the proton exchange membrane are transmitted via an external circuit to the cathode, where they form hydrogen atoms, which then associate back into gaseous hydrogen molecules.

An example of a group of materials that can function as a proton exchange membrane is fluoropolymers. Examples of such fluoropolymers are the various sulphonated tetrafluoroethylenes, which are marketed by DuPont under the trade mark 'Nafion®'.

An electrochemical pump may have multiple 'stacks' in series, i.e. multiple electrode-proton exchange membrane sandwiches, to enable the electrochemical pump to have sufficient capacity to increase the pressure of the hydrogen it filters. By virtue of such a setup, such pumps are capable of compressing hydrogen gas, for example, up to around 70 MPa. Suitably, the electrochemical pump (2) of the present invention is capable of compressing hydrogen gas to pressure, preferably to a pressure of at least 30 MPa, more preferably at least 50 MPa, more preferably at least 60 MPa, and most preferably at least 70 MPa.

The input stream (1) is supplied to the

electrochemical pump (2) at pressure. Before discussing the details of such pressure, it is worth putting such pressure into the context of the natural gas network. To that end, typically, gas pressures across the natural gas network is such that the long-distance transmission end of the network is typically maintained at around between 10 MPa to 3 MPa, whereas the end-user end of the network is maintained at around between 1 MPa to 0.001 MPa. Suitably, the apparatus of the present invention is located at the user-end of the natural gas network, and preferably the pressure of the input stream (1) is at least 0.001 MPa, more preferably at least 0.01 MPa and most preferably at least 0.1 MPa. Preferably the pressure of the input stream is at most 1 MPa, more preferably at most 0.5 MPa and most preferably at most 0.25 MPa.

In the process of the present invention, the input stream (1) is supplied to the electrochemical pump (2), which then uses the input stream (1) to generate a first output stream (3) and a second output stream (4), which are separated from each other.

The first output stream (3) comprises gaseous methane; however it may also comprise hydrogen gas, which is preferably at most 30% vol. hydrogen gas, more preferably at most 5% vol. hydrogen gas, even more preferably at most 0.1% vol. hydrogen gas, and most preferably at most 0.001% vol. hydrogen gas.

The first output stream (3) may be supplied directly to a gas compression apparatus (6), and compressed to produce compressed natural gas (7) (or 'CNG').

The hydrogen content of the first output stream (3) is directly influenced by the electrochemical pump (2). Ideally, the electrochemical pump's (2) main action is to

remove as much hydrogen as possible from the input stream (1), such that the first output stream (3) may be used by the natural gas end-users without the need for further processing. As electrochemical pumps are developed and improved, their hydrogen removal efficiency is likely increase, so the hydrogen content of the first output stream (3) will tend towards zero % vol. hydrogen.

The processing capacity of the electrochemical pump (2) will also influence the hydrogen content of the first output stream, such that the electrochemical pump (2) may not be able to remove all the hydrogen from the input stream (1), leading to a first output stream (3) of the higher end of the hydrogen content stated above.

Suitably, to capture the hydrogen content of the first output stream (3) containing the higher end of the hydrogen content stated above, in one embodiment, a portion of the first output stream (3d) may be recycled back into the input stream (1).

In the process of the present invention, the input stream (1) is supplied to the electrochemical pump (2), which generates a first output stream (3) and a second output stream (4). As with the first output stream (3), the hydrogen content of the second output stream (4) is also directly influenced by the electrochemical pump (2). Preferably, the second output stream (4) comprises at least 95 % vol. hydrogen gas, more preferably at least 98% vol. hydrogen gas, even more preferably at least 99% vol. hydrogen gas, and most preferably at least 99.99% vol. hydrogen gas. Even most preferably, the second output stream (4) comprises at most 100 % vol. hydrogen gas.

At least a portion of the second output stream (4b) may be supplied directly to one or more fuel cell (5),

for the purposes of generating electricity by the fuel cell(s).

Ideally, the hydrogen composition of the second output stream (4) is sufficient suitable to be used directly by the one or more fuel cells (5), and with no contaminating substances that may poison the fuel cells (5). Optionally, to enable a higher purity of hydrogen, the second output stream (4) may be supplied to a second electrochemical pump, or to a hydrogen permeable palladium membrane, or to a pressure swing adsorption unit before the second output stream (4) reaches the fuel cell(s) (5).

At least a portion of the second output stream (4) may be supplied directly for use by hydrogen end-users (9). For such purpose, at least a portion of the second output stream (4a) may be supplied to a hydrogen storage vessel (9), or supplied continuously to the end-user (9). The second output stream (4a) may be supplied to the hydrogen storage vessel (9) or to the end-user (9) under pressure.

The maximum pressure of the second output stream (4) will depend on the specification of the electrochemical pump used, however, if the hydrogen is to be supplied to hydrogen-utilising vehicles, Society of Automotive Engineers (SAE) Protocol J2601 states that heavy-duty hydrogen-utilising vehicles are to be refuelled with hydrogen gas at 70 MPa, and light-duty hydrogen-utilising vehicles are to be refuelled with hydrogen gas at 30 MPa. Therefore, preferably, the pressure of the second output stream (4), separated by the electrochemical pump (2), is at least 30 MPa, more preferably at least 50 MPa, more preferably at least 60 MPa, and most preferably at least 70 MPa.

To increase the processing capacity of the process of the present invention, as well as to decrease the hydrogen content of the first output stream (3), the following embodiments are discussed below.

In one embodiment of the invention, the input stream (1) is split into more than one stream (e.g. Figure 2, 1a, 1b, 1c), each of which is supplied to a different electrochemical pump (e.g. Figure 2, 2a, 2b, 2c), each operating in parallel with respect to the input stream (1) flow. Such an embodiment increases the capacity of the process to treat the input stream (1).

In a second embodiment, the input stream (1) is supplied to a first electrochemical pump (e.g. Figure 2, 2a), a first output stream of which (3a, comprising gaseous methane) is supplied directly into a second electrochemical pump (e.g. Figure 2, 2b). Such an arrangement may be repeated one or more times, such that a third (e.g. Figure 2, 2c), fourth etc. electrochemical pump is connected in series to a next electrochemical pump. A second output stream generated by each electrochemical pump, comprising at least 95 % vol. hydrogen gas (e.g. Figure 2, 4d, 4d, 4e) is collected and combined, and a portion of it (4a) may be supplied to one or more fuel cell (5), and the other portion of which (4b) may be either supplied directly to, or stored for use by, the hydrogen end-user (9). Such embodiment enables the hydrogen content of the first output stream (1) to be reduced substantially.

In a third embodiment, an array of electrochemical pumps is arranged such that the array combines the features of the abovementioned first embodiment with the features of the abovementioned second embodiment. Such embodiment enables the apparatus of the present invention

to have both an increased capacity to process the input stream, as well as the capability to produce a first output stream, the hydrogen content of which is reduced substantially.

The first output stream (3) may be supplied directly to a gas compression apparatus (6) to produce a compressed gas stream (7). This enables the production of compressed natural gas (or 'CNG').

The gas compression method used to compress the first output stream in the process of the present invention may be any way known to the skilled person that is suitable for natural gas and methane compression purposes.

The gas compression apparatus (6) used to compress the first output stream (3) in the process of the present invention may be any type known to the skilled person that is suitable for natural gas and methane compression purposes.

An example of a suitably type of gas compression apparatus may be a centrifugal compressor. The power of such compressor may range from order of 5 kW to 5 MW.

In the process of the present invention, the compressed gas stream (7) may be stored in bulk CNG tanks (8) or in cylinders (8) prior to its future use, or may be supplied to, for example, to CNG-utilising vehicles (8).

Preferably, the gas compression apparatus (6) is capable of producing a compressed gas stream (7) of at least 0.1 MPa, more preferably a compressed gas stream (7) of at least 0.5 MPa, even more preferably a compressed gas stream (7) of at least 1 MPa and most preferably a compressed gas stream (7) of at least 5 MPa. Preferably, the gas compression apparatus is capable of

producing a compressed gas stream (7) of at most 7 MPa, more preferably a compressed gas stream (7) of at most 10 MPa, even preferably a compressed gas stream (7) of at most 15 MPa, and most preferably a compressed gas stream (7) of at most 25 MPa.

In the process of the present invention, a fuel cell (5) generates electricity from at least a portion of the second output stream (4b). The fuel cell (5) is a hydrogen fuel cell, which functions to convert the energy stored in hydrogen molecules to electricity.

Hydrogen fuel cells currently available may be categorised into the following five types: proton exchange membrane, phosphoric acid, solid oxide, alkali and molten carbonate, each characterised by their different electrolyte as suggested by their names. Typically to increase their output, fuel cells comprise multiple stacks of electrodes sandwiching the electrolyte. The important function of the electrolyte is to be permeable to specific ion(s), and impermeable to other ions of the opposite charge and other molecules. Each of these fuel cells will be reviewed below in turn. However, it must be noted that as research into these fuel cells progress, some of their operational parameters, such as, their efficiency and electrical output will change, so the parameters quoted below are only for the purpose of general guidance.

Proton exchange membrane hydrogen fuel cells have a water-based polymer electrolyte, for example made from sulphonated tetrafluoroethylenes. The polymer is only permeable to protons. To generate electricity, primarily they require pure hydrogen gas, as well as an oxygen source, such as air. For the operation of the fuel cell, both the anode and the cathode electrodes require a

transition metal embedded in them so that the transition metal can act as a catalyst in the process of splitting hydrogen molecules into protons and electrons. These fuel cells generally operate at around 80°C, with about 40 to 50% efficiency. Each unit of the electrolyte sandwiched between the anode and the cathode is a membrane electrode assembly, and by introducing multiple membrane electrode assemblies, the fuel cell's electric output may be tailored according to actual need, for example, from about 50 kW to about 250 kW. The cell generates water as an end-product. These fuel cells are generally more compact and sturdy that the other types of hydrogen fuel cells mentioned here, but have the disadvantage that they require pure hydrogen to avoid poisoning of the catalyst at the electrodes.

Phosphoric acid hydrogen fuel cells have phosphoric acid as their electrolyte, which is permeable to only protons. To generate electricity, they require hydrogen gas, as well as an oxygen source, such as air. For the operation of the fuel cell, both the anode and the cathode electrodes have to be embedded with a transition metal acting as a catalyst. Generally these fuel cells operate at around 150°C to 200°C, with about 40 to 50% efficiency. Some units can be capable of an electrical output of around 100 kW to 400 kW, and generate water as an end-product. Phosphoric acid fuel cells can be resistant up to about 1.5 %vol. carbon monoxide in its hydrogen stream, which means hydrogen of lesser purity (e.g. direct output of steam reforming) can be used as its fuel source. The corrosive property of phosphoric acid requires the internal parts of this type of fuel cell to be sturdy to retain the phosphoric acid, and be made of materials that are resistant to acid corrosion.

Solid oxide hydrogen fuel cells, as their electrolyte, have a metal oxide (of calcium or zirconium) stabilised with yttrium oxide to form a hard ceramic-like compound, which is permeable to only oxygen ions. To generate electricity, they require hydrogen gas, as well as an oxygen source, such as air. Generally they operate at around 800°C to 1000°C, with around 60% efficiency, and can generate electrical an output of up to 100 kW. These cells generate water and carbon dioxide as their end-product. As a result of their high operational temperature, they have an advantage of being resistant to impurities in its hydrogen input stream, which means hydrogen of lesser purity (e.g. direct output of steam reforming) can be used as its fuel source. Further, their high operational temperature may negate the need to deploy a metal catalyst. However, the fragility of their electrolyte, together with their high operational temperature can present restrictions to their use.

Alkali hydrogen fuel cells generally have an aqueous solution of potassium hydroxide as their electrolyte, which is permeable only to hydroxyl ions (OH^-). To generate electricity, they require pure hydrogen gas, as well as an oxygen source, such as air. Generally these fuel cells operate at around 150°C to 250°C, although they can operate at around 70 °C. They can operate at about 60% to 70% efficiency. Their typical electrical output ranges from about 300 W to around 5 kW. If platinum catalyst is used, they need to use pure hydrogen to avoid poisoning the catalyst, however other metals (such as nickel) are also successfully deployed in alkali fuel cells. Their liquid electrolyte necessitates them to be physically sturdy.

Molten carbonate hydrogen fuel cells, as their

electrolyte, have molten carbonate salts of group 1 metals such as lithium, sodium and potassium as a mixture suspended in a porous chemically inert ceramic matrix of $LiAlO_2$. This electrolyte is permeable to carbonate ions. These fuel cells require hydrogen, oxygen and carbon dioxide to operate. They operate at around 650 °C, and at around 60%, they are more efficient than, for example, phosphoric acid hydrogen fuel cells, capable of generating around 100 kW to 500 kW electricity. Their anode comprises a porous nickel-based alloy with aluminium or lithium. Their cathode comprises porous nickel oxide crystals intercalated with lithium. Lower cost of nickel compared to, for example, platinum is an advantage for this type of fuel cell.

Any of the one of the fuel cells reviewed above, or indeed any other hydrogen utilising fuel cell, may be used in the present invention as one or more fuel cell (5).

In the process of the present invention, at least a portion, or whole, of the electricity produced by the fuel cell (5) may be used to power the electrochemical pump (2) and/or the gas compression apparatus (6).

In one embodiment, at least a portion of the second output stream (4b) is supplied to more than one fuel cell, for each fuel cell to produce electricity. At least a portion, or whole of, the electricity produced by the more than one fuel cells may be used to power the electrochemical pump (2) and/or the gas compression apparatus (6).

The power output of the fuel cell (5) is dependent on at least two main factors. The first of these is the number of electrode-electrolyte so-called sandwiches, or stacks, making up the fuel cell. The second of these is

the amount of hydrogen supplied to it, which in turn ultimately depends on the hydrogen content of the input stream (1). It is envisaged that the fuel cell(s) may produce enough electricity to power both the electrochemical pump (2) and the gas compression apparatus (6). Alternatively, the fuel cell(s) (5) may produce only enough electricity to power either the electrochemical pump (2) or the gas compression apparatus (6). Alternatively, the fuel cell(s) may only produce enough electricity to partially power the electrochemical pump (2) and the gas compression apparatus (6). Where the fuel cell(s) (5) only produce enough electricity to partially power the electrochemical pump (2) and/or the gas compression apparatus (6), externally produced electricity will be used to make up the power needed for the functioning of the electrochemical pump (2) and/or the gas compression apparatus (6).

In the process of the present invention, the compressed gas stream (7) is intended to be stored for future use, and the compressed gas stream is fed to a storage tank (8). Alternatively, the compressed gas stream may be supplied directly to end-user(s) (8). Such end-users (8) may be any user of compressed natural gas for any application, including industrial users for industrial applications.

Suitably, the compressed gas stream may be captured in a storage tank (8), such as fuel tank of vehicles, compressed gas storage cylinders or immobile units. Such storage tanks will be known to the skilled person.

The present invention also provides an apparatus for the separation of hydrogen gas from an input stream (1) comprising gaseous methane and gaseous hydrogen, comprising an electrochemical pump (2), a gas compression

apparatus (6) and a fuel cell (5). The electrochemical pump, the gas compression apparatus and the fuel cell, each carry out the parts of the process of the present invention as described above.

Further to the abovementioned description, the electrochemical pump (2) is capable of separating the input stream into a first output stream (3) comprising gaseous methane and a second output stream (4) comprising at least 95 % vol. hydrogen gas.

To enable this, the electrochemical pump (2) comprises an inlet for accepting the input stream. The electrochemical pump (2) also comprises a first outlet in fluid connection with the gas compression apparatus (6) for supplying the gas compression apparatus with the first output stream (3), and a second outlet in fluid connection with the fuel cell (5) for supplying the fuel cell with at least a portion of the second output stream (4b).

To off-set the energy demand of the electrochemical pump (2) and the gas compression apparatus (5), the present invention carries out the process of separating the input stream (1) into the first output (3) and the second output stream (4) by using at least a portion of the second output stream (4b) to generate electricity using the fuel cell (5).

The fuel cell (5) may be any one of the fuels cells described above, or any other, as long as it is a hydrogen-utilising fuel cell. In the case of using a molten carbonate fuel cell, unlike the other types of fuel cells mentioned herein, a supply of carbon dioxide is required as an additional feature for it to produce electricity.

The second output stream may be supplied to more

than one fuel cell (5) to increase the electrical output, so that sufficient electricity may be produced to power the electrochemical pump (2) and the gas compression apparatus (6).

To enable the electricity to be supplied from the fuel cell (5) to the electrochemical pump (2) and the gas compression apparatus (6), the fuel cell (5) and the electrochemical pump (2) are connected with a first electrical connection means (10), and the fuel cell (5) and the gas compression apparatus (6) are connected with a second electrical connection means (11).

Detailed Description of the Drawings

Figure 1 shows a simplified schematic diagram of the process and the apparatus according to the invention, illustrating that an input stream (1) is supplied to an electrochemical pump (2), by which a first output stream (3) and a second output stream (4) are generated. The first output stream comprising gaseous methane is then supplied to a gas compression apparatus (6) to produce a compressed gas stream (7), which may be supplied to a storage tank (8), or directly to a natural gas end-user (8). The second output stream (4) comprising at least 95 % vol. hydrogen gas may be split into two streams (4a and 4b), where at least a portion of the second output stream (4a) is supplied to a hydrogen end-user (9), and at least a portion of the second output stream (4b) is supplied to a fuel cell (5) for it to produce electricity (e^-). At least a portion of the electricity (e^-) produced by the fuel cell conveyed along the first electrical connection means (10) is used to power the electrochemical pump (2), and at least a portion of such electricity conveyed along the second electrical connection means (11) is used to power the gas compression apparatus (6).

Figure 2 provides a schematic representation of the process and the apparatus according to the invention illustrating an embodiment of the invention, where the input stream (1) is split into more than one input stream (1a, 1b and 1c), each of which is supplied to a different electrochemical pump (2a, 2b and 2c), each operating in parallel with respect to the input stream flow. Each electrochemical pump (2a, 2b and 2c) produces a first output stream comprising gaseous methane, which may be combined as a single first output stream (3). Each electrochemical pump (2a, 2b and 2c) produces a second output stream (4) comprising at least 95 % vol. hydrogen gas, a portion of which may be separated into stream '4a' and a stream '4b'. Stream '4a' from each electrochemical pump may be combined, and a stream '4b' from each electrochemical pump may be combined.

Figure 3 provides a schematic representation of the process and the apparatus according to the invention illustrating an embodiment of the invention, where the input stream (1) is supplied to a first electrochemical pump (2a), the first output stream of the first electrochemical pump (3a) comprising gaseous methane is supplied directly into a second electrochemical pump (2b), the first output stream of the second electrochemical pump (3b) comprising gaseous methane is supplied directly into a third electrochemical pump (2c). The third electrochemical pump (2c) produces its first output stream (3c) comprising gaseous methane, which may be supplied to a gas compression apparatus (not shown). Each electrochemical pump (2a, 2b and 2c) also produces second output streams (4c, 4d and 4e) comprising at least 95 % vol. hydrogen gas, a portion of which may be supplied to a fuel cell (not shown), or a portion of

which may be supplied to a hydrogen end-user (not shown).

Figure 4 provides a schematic representation of the process and the apparatus according to the invention illustrating an embodiment of the invention, where a portion of the first output stream (3d) comprising gaseous methane is recycled back into the input stream (1).

C L A I M S

1. A process for the separation of hydrogen gas from an input stream (1) comprising gaseous methane and gaseous hydrogen, comprising the steps of:

(a) supplying the input stream (1) to an electrochemical pump(2);

(b) obtaining from the electrochemical pump (2) a first output stream (3) comprising gaseous methane and a second output stream (4) comprising at least 95 % vol. hydrogen gas;

(c) supplying at least a portion of the first output stream (3) to a gas compression apparatus (6) to compress the first output stream (3) to a pressure of at least 0.1 MPa to provide a compressed gas stream (7);

(d) supplying at least a portion of the second output stream (4b) to a fuel cell (5) to produce electricity; and

(e) using at least a portion of the electricity produced by the fuel cell to power, or partially power, the electrochemical pump (2) and/or the gas compression apparatus (6).

2. The process claimed in Claim 1, wherein at least a portion of the first output stream (3) is supplied back into the input stream (1).

3. The process claimed in Claim 1 or Claim 2, wherein the compressed gas stream (7) is fed to a storage tank (8).

4. The process claimed in Claim 3, wherein the storage tank (8) is one or more immobile units, or one or more fuel tanks of vehicles, or one or more compressed gas storage cylinders.

5. The process claimed in Claim 1, wherein the pressure of the second output stream (4) comprising at least 95 % vol. hydrogen gas is at least 30 MPa.

6. An apparatus for the separation of hydrogen gas from an input stream (1) comprising gaseous methane and gaseous hydrogen, comprising:

(a) an electrochemical pump (2);

(b) a gas compression apparatus (6); and

(c) a fuel cell (5);

wherein the electrochemical pump (2) comprises an inlet for accepting the input stream (1);

wherein the electrochemical pump is capable of separating the input stream into a first output stream (3) comprising gaseous methane, and a second output stream (4) comprising at least 95 % vol. hydrogen gas;

wherein the electrochemical pump comprises a first outlet in fluid connection with the gas compression apparatus (6) for supplying the gas compression apparatus (6) with the first output stream (3);

wherein the electrochemical pump comprises a second outlet in fluid connection with the fuel cell (5) for supplying the fuel cell (5) with at least a portion of the second output stream (4b);

wherein the fuel cell (5) is capable of using at least a portion of the second output stream (4b) to generate electricity;

wherein the fuel cell (5) is connected to the electrochemical pump (2) and the gas compression apparatus (6) by a first electrical connection means (10) and a second electrical connection means (11) respectively; and

wherein the electrochemical pump (2) and the gas compression apparatus (6) are each capable of using at

least a portion of the electricity generated by the fuel cell (5).

7. The apparatus claimed in Claim 6, wherein the gas compression apparatus (6) is capable of compressing the first output stream (3) to a pressure of a least 0.1 MPa to produce a compressed gas stream (7).

8. The apparatus claimed in Claims 6 and 7, wherein the gas compression apparatus (6) has an outlet, which is capable of being connected to a storage tank (8), or directly to one or more end-user (8).

9. The apparatus claimed in Claim 8, wherein the storage tank (8) is one or more immobile units, or one or more fuel tanks of vehicles, or one or more compressed gas storage cylinders.

10. The apparatus claimed in Claim 6, wherein the pressure of the second output stream (4) separated by the electrochemical pump (2) is at least 30 MPa.

Figure 1

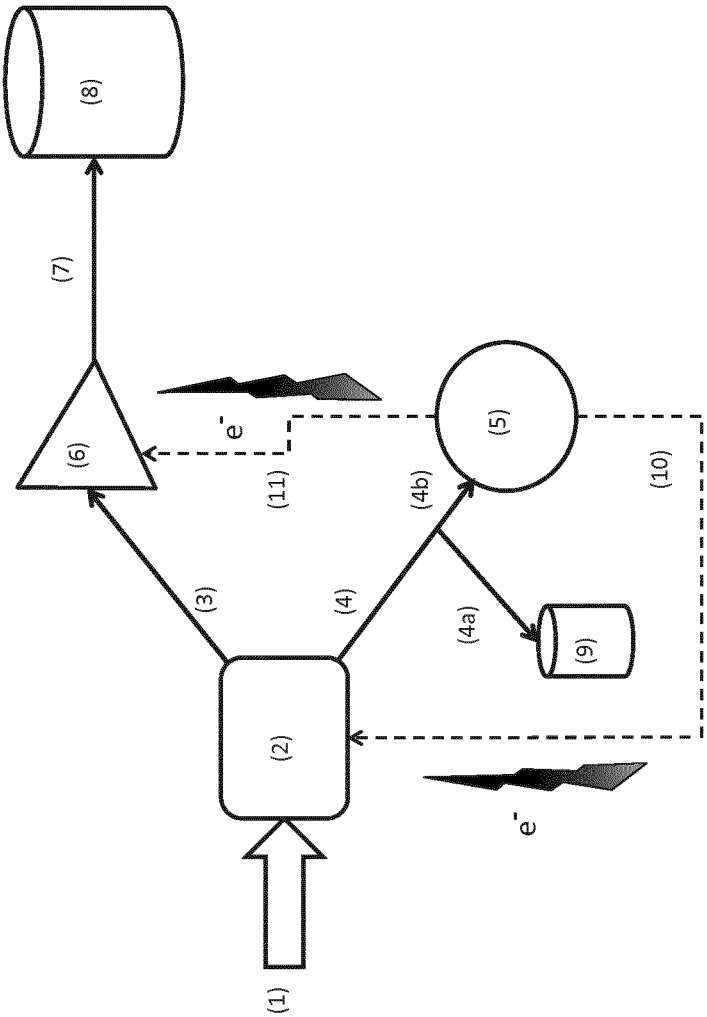


Figure 2

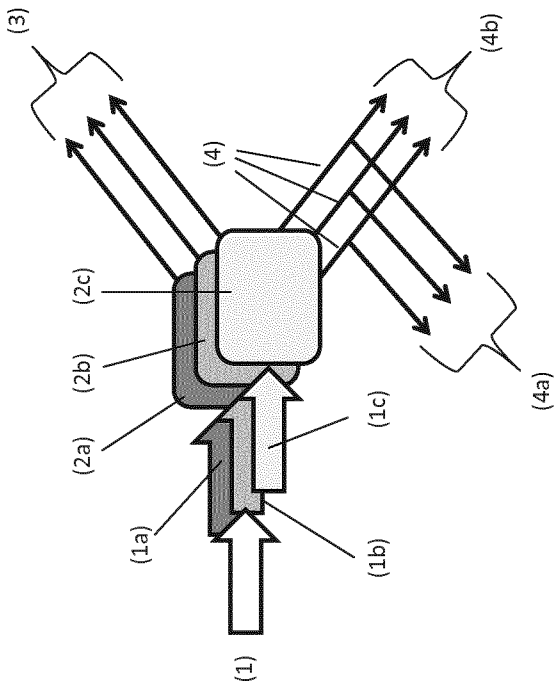


Figure 2 of 4

Figure 3

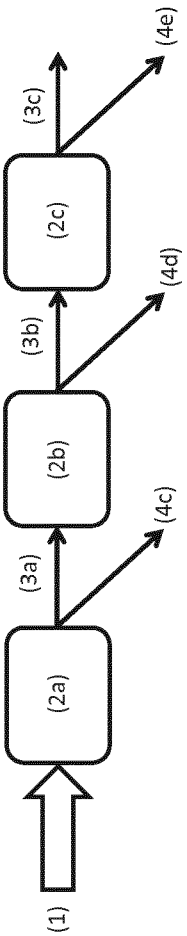
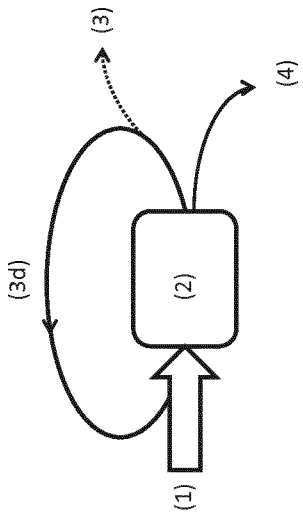


Figure 4



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/080519

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/22 B01D53/32
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

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A	WO 2008/067360 A2 (SHELL OIL CO [US]; SHELL INT RESEARCH [NL]; CLOMBURG JR LLOYD ANTHONY) 5 June 2008 (2008-06-05) tables 1,2	1
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 February 2017	09/03/2017

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

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/080519

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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