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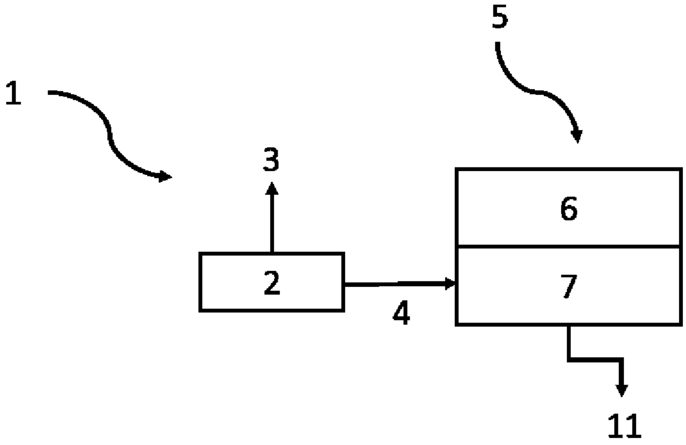

Fig. 1

(57) **Abstract:** Subject of the invention is a carbon capture system which comprises a pressure swing adsorption unit for producing a product gas and a tail gas comprising at least one carbonaceous gas, and a molten carbonate fuel cell having a cathode and an anode for transferring CO_2 from the cathode to the anode, wherein the molten carbonate fuel cell is a multi-stage fuel cell, wherein the anode is in fluid communication with the pressure swing adsorption unit for receiving at least a portion of the tail gas as an inlet stream.

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Carbon Capture System

Field of the invention

The invention relates to carbon capture systems, and further relates to corresponding methods and uses, wherein carbon capture is in particular carbon dioxide (CO_2) capture. The carbon capture system and the corresponding methods and uses are in particular useful in the context of hydrogen production.

Background of the invention

According to the International Energy Agency (IEA), the global demand for hydrogen (H_2) and H_2-derived fuels will significantly increase in the coming years. This is inter alia because H_2 is expected to play a key role in mitigating global warming. However, the production of H_2 often results in the undesired generation and potential emission of the greenhouse gas CO_2. For example, in the so-called partial oxidation (POX), natural gas which predominantly comprises methane (CH_4) as well as other hydrocarbons is reacted with a limited amount of oxygen (O_2). The limited amount of O_2 is a less than stoichiometric amount. Accordingly, this limited amount of O_2 is not sufficient to completely oxidize the methane and other hydrocarbons to CO_2 and water (H_2O). The reaction products are thus primarily H_2 and carbon monoxide (CO). Regularly, in order to increase the H_2 yield, the CO is reacted in a subsequent water-gas shift (WGS) reaction with H_2O to form CO_2 and more H_2, basically following the reaction $CO + H_2O \rightarrow CO_2 + H_2$. Thereby, mixtures comprising H_2 and CO_2 are generated.

Similarly, CO_2 is also generated in so-called steam methane reforming (SMR) which involves the reaction of CH_4 with steam ($H_2O_{(g)}$) at high pressures and temperatures. The reaction yields a mixture containing predominately H_2 and CO, which mixture is also sometimes referred to as syngas. WGS reactors are typically used downstream the SMR to convert the produced CO and additional H_2O into more H_2 and CO_2, thereby increasing the overall H_2 yield. However, again gas mixtures comprising H_2 and CO_2 are generated. Additionally, heat for the endothermic SMR is regularly generated by combusting fuel gas with air in the SMR furnace, thereby contributing to the production of more CO_2. The CO_2 contained in the flue gas is regularly diluted in nitrogen (N_2) and oxygen (O_2) from the combustion air.

Another process for producing H_2 is the so-called auto-thermal reforming (ATR). ATR basically combines POX and SMR, using the heat from the generally exothermic POX to provide heat for the generally endothermic SMR. Usually, a mixture of H_2 and CO is produced, for example according to the reaction $4\ CH_4 + O_2 + 2\ H_2O \rightarrow 10\ H_2 + 4\ CO$. Regularly, for increasing the H_2 yield, also in ATR the produced CO is subsequently converted in a WGS reaction with additional H_2O to CO_2 and H_2, leading once again to a gas mixture comprising CO_2 and H_2.

The above methods for producing H_2 have thus in common that in addition to the desired H_2, also typically large amounts of CO_2 are produced which are regularly admixed with H_2. In other words, the produced H_2 is contaminated with CO_2. In order to purify the H_2 for subsequent use thereof, it is desirable to separate the CO_2 from the H_2. Such a separation also allows to subsequently store the CO_2, thus avoiding an emission of that CO_2 to the environment.

Current methods for capturing CO_2 from gas mixtures like H_2/CO_2 and N_2/CO_2 use for example amine absorption stripper systems. Such systems have however a high heat demand for regeneration of the amine solvent. Additionally, amines easily undergo thermal- and oxidative-degradation, thereby forming hazardous compounds like nitrosamines, nitramines, and amides, which compounds already at very low concentrations are toxic and carcinogenic for humans.

Another way of separating CO_2 from a mixture of gases is to use a pressure swing adsorption (PSA) unit. As further detailed below, PSA is generally a process that separates single gases from a gas mixture. The use of a PSA in an SMR process is for example described in WO 2020/131981 A1. The PSA unit generates a purified H_2 stream and a tail gas, wherein the tail gas is used as fuel in the SMR reactor.

In general, a further way of separating CO_2 from a mixture of gases is to use a molten carbonate fuel cell (MCFC) for increasing the CO_2 concentration in a flue gas. For example, US 2005/0271914 A1 describes a power plant system for processing fossil fuel which is arranged in tandem with an MCFC. The flue gas of the power plant serves exclusively as the inlet gas for the cathode section of the MCFC. No reference to a PSA unit is made, and consequently no relationship of such a PSA unit with other components of the described power plant systems is described. US 2014/260310 A1 describes systems and methods for integrated operation of a molten carbonate fuel cell with turbines for power generation. However, a connection between an outlet of a PSA and a molten carbonate fuel cell is not addressed therein.

A combined use of a PSA unit and a molten carbonate fuel cell is generally described in WO 2017/190066 A1. However, there is no mention of any connection between the PSA unit and the fuel cell. Moreover, the fuel cell is operated in reverse, i.e., in electrolysis mode, in which electric energy is consumed by the fuel cell. For this operation in reverse, the anode of the fuel cell is actually configured to receive a reformed gas from a steam methane reformer. A similar arrangement is described by A. Monforti Ferrario et al. (Front. Energy Res. 9:655915) in which a PSA unit is connected with a molten carbonate fuel cell which also runs in reverse. That is, the respective fuel cell is actually a molten carbonate electrolysis cell (MCEC) which consumes electric energy. In the described arrangement, PSA tail gas is sent to the anode of the MCEC. A combined use of a PSA unit and a molten carbonate fuel cell running in electricity production mode is described by S. Consonni et al. (Advances in Applied Energy 2 (2021) 100010). The described process intends to capture CO_2 from SMR flue gas. However, it is mandatory for the described process that PSA tail gas is sent to the cathode of the MCFC employed, and the overall energy efficiency of the SMR still drops compared to the process without CO_2 capture. WO 2021/181249 A1 also generally describes a combined use of a PSA unit and a molten carbonate fuel cell. However, the molten carbonate fuel cell is a single-stage fuel cell, and gas fed to its anode is regularly pre-treated by compressing, chilling and separating CO_2 which adds to the complexity and the costs of the described systems.

Overall, there remains a general desire for an improved carbon capture system, in particular in the context of hydrogen production.

Problem underlying the invention

It is an object of the present invention to provide a carbon capture system which at least partially overcomes the drawbacks encountered in the art.

It is in particular an object of the present invention to provide a carbon capture system which allows to efficiently capture CO_2, in particular CO_2 generated in a hydrogen production.

It is furthermore an object of the present invention to provide a carbon capture system which, when used in the context of hydrogen production, allows to provide H_2 of improved purity.

It is moreover an object of the present invention to provide a carbon capture system which simultaneously allows both, CO_2 capture and production of electric energy (electricity), preferably followed by an advantageous use of the produced electric energy. In this regard, it is also an object of the present invention to provide a carbon capture system which is at least partially self-supporting.

It is also an object of the present invention to provide a method of capturing carbon which at least partially overcomes the drawbacks encountered in the art.

It is also an object of the present invention to provide uses which at least partially overcome the drawbacks encountered in the art.

It is also an object of the present invention to provide CO_2 which at least partially overcomes the drawbacks encountered in the art.

Disclosure of the invention

Surprisingly, it has been found that the problem underlying the invention is overcome by carbon capture systems, methods, uses, and CO_2 according to the claims. Further embodiments of the invention are outlined throughout the description.

Subject of the invention is a carbon capture system, comprising:

a pressure swing adsorption unit for producing a product gas and a tail gas comprising at least one carbonaceous gas, and

a molten carbonate fuel cell having a cathode and an anode for transferring CO_2 from the cathode to the anode, wherein the molten carbonate fuel cell is a multi-stage fuel cell,

wherein the anode is in fluid communication with the pressure swing adsorption unit for receiving at least a portion of the tail gas as an inlet stream.

A carbon capture system according to the present invention captures carbon in particular in the form of CO_2 and may thus also be termed a CO_2 capture system. More specifically, the molten carbonate fuel cell transfers (or pumps) CO_2 from the cathode to the anode. For this, the cathode is regularly to be fed with a CO_2-containing gas. For example, while the anode receives a first portion of the tail gas as an inlet stream, the cathode may receive a second portion of the tail gas as an inlet stream (cathode inlet stream). For this, the cathode would be in fluid communication with the pressure swing adsorption unit. The second portion of the tail gas sent to the cathode may optionally be mixed with additional air. For this, the fluid communication between the cathode and the pressure swing adsorption unit would have an inlet or a switch for feeding the additional air. Alternatively, or additionally, a CO_2-containing gas sent to the cathode may be flue gas stemming from an auxiliary gas boiler, a furnace, a gas turbine, and/or a steam methane reformer. For this, the cathode would be in fluid communication with the auxiliary gas boiler, the furnace, the gas turbine, and/or the steam methane reformer. The flue gas sent to the cathode may optionally be mixed with additional air. For this, the fluid communication between the cathode and the auxiliary gas boiler, the furnace, the gas turbine, and/or the steam methane reformer would have an inlet or a switch for feeding the additional air.

A pressure swing adsorption (PSA) unit according to the present invention is a unit which allows to perform at least one and preferably more than one (i.e., repeated) cycle(s) of PSA. The PSA unit thus regularly comprises at least two columns which typically contain an absorbent, and regularly comprises more than two columns, especially four to twelve columns. Further, the at least two columns can be individually, and normally alternatingly, fed with fluids and in particular gases. Further, such fluids and in particular gases can individually, and normally alternatingly, be withdrawn from the PSA unit. The PSA unit may further comprise a compressor to feed the at least two columns individually, and normally alternatingly, with pressurized gases. A pressure swing adsorption unit according to the present invention also encompasses a vacuum pressure swing adsorption (VPSA) unit, which further comprises a vacuum pump for generating a vacuum inside the PSA unit to withdraw gases contained in the PSA unit, in particular gases adsorbed by an absorbent. It is preferred that in a PSA unit according to the present invention, absorbents comprising carbon, in particular activated carbon or carbon molecular sieves, or oxide absorbents, in particular zeolites, are contained.

The PSA is generally a process that separates single gases from a gas mixture. According to the present invention, the PSA is preferably used to separate H_2 from a gas mixture, in particular a CO_2-containing gas mixture, so as to purify the H_2. The PSA applies the principle of physically binding impurities contained in the hydrogen, especially CO_2, by an individually selected absorbent. Since the binding forces for such impurities, especially CO_2, depend on the pressure, the PSA operates on an alternating cycle of adsorption at elevated pressures and desorption at decreased pressures. Ideally, only the gas to be separated, preferably CO_2, is adsorbed, while all other gases in the mixture, preferably including H_2, pass through the absorbent.

It is preferred that a PSA process occurring in a PSA unit according to the present invention is divided into four stages that preferably occur in repeated cycles:
<u>Adsorption</u>: adsorption takes place at a high pressure, preferably an absolute pressure above 0.1 MPa and up to 4 MPa. A feed gas mixture, preferably a mixture comprising CO_2 and H_2, is fed to an absorbent. The absorbent binds the more easily absorbable gas molecules, preferably CO_2 molecules, while gas molecules that are not readily absorbable or not absorbable at all, preferably H_2 molecules, pass through the absorbent (or

absorbent bed). The absorbent continues to absorb gas molecules until it reaches its full capacity.

Depressurization: depressurization is a first regeneration (or desorption) step of the absorbent carrying the absorbed gas molecules, preferably CO_2 molecules. As the pressure drops, the gas molecules in the absorbent, preferably CO_2 molecules, are released and are discharged from a section of the PSA unit in which the absorbent is located, typically one or more columns (or vessels, or containers) loaded with the absorbent.

Purging: the absorbent is purged with gas, preferably with H_2, to regenerate it.

Re-pressurization: the PSA unit is pressurized again, preferably using the feed gas mixture, until the process conditions for adsorption have been restored.

A molten carbonate fuel cell (MCFC) according to the present invention comprises a cathode and an anode as fuel cell electrodes. It is noteworthy here that because the MCFC is a multi-stage MCFC, the overall cathode of the MCFC is composed of two or more separate cathode portions in series, and the overall anode of the MCFC is composed of two or more separate anode portions in series. These electrodes (or electrode portions) are typically made of metal, in particular nickel. Between the electrodes, the MCFC regularly further comprises an electrolyte which comprises at least one carbonate. It is noteworthy here that because the MCFC is a multi-stage MCFC, the overall electrolyte of the MCFC is composed of two or more separate electrolyte portions sandwiched between the two or more cathode portions in series and the two or more separate anode portions in series. The electrolyte preferably comprises a blend of alkali metal carbonates, more preferably a blend of lithium carbonate (Li_2CO_3) and potassium carbonate (K_2CO_3). An MCFC is suitable for distributed power generation with high efficiency conversion of energy, flexible operation and combined heat and power (CHP) production. MCFCs are already commercially available in medium- to large scale power generation (see for example I. Rexed, “Applications for Molten Carbonate Fuel Cells”, PhD thesis, 2014, KTH Royal Institute of Technology, Stockholm, Sweden).

At ambient temperature (e.g., around 25°C), the carbonate(s) in the MCFC is/are solid. The MCFC is regularly operated at temperatures above ambient, typically within a preferred temperature range of 540 to 750°C, more preferably in the range of 550 to 700°C, and still more preferably in the range of 575°C to 675°C. At such temperatures, the contained carbonate(s) is/are molten, leading to the term “molten carbonate fuel cell”. The MCFC produces electric energy (generates electricity).

The electric energy produced by the MCFC can be advantageously used within the carbon capture system itself for at least partially operating one or more devices (PSA, means, units, etc.) of the carbon capture system, as further exemplified herein. The electric energy is generally produced by the MCFC according to the following scheme:
O_2 and CO_2, which are regularly contained in combustion gases or that may be added separately, are reduced at the cathode into carbonate ions (CO_3^{2-}) following the reaction:
$\frac{1}{2} O_2 + CO_2 + 2e- = CO_3^{2-}$
The carbonate ions CO_3^{2-} are transferred through the electrolyte to the anode.
Carbonaceous gas stemming from the PSA (contained in the tail gas; “tail gas” is herein sometimes also referred to as “off-gas”) typically comprising CO_2 and additional CO, H_2 and reformable fuels, especially methane CH_4, which may also stem from the PSA or may be added separately, are sent to the anode with steam so that the following reactions take place:
$CH_4 + H_2O \rightarrow 3H_2 + CO$
$H_2 + CO_3^{2-} \rightarrow CO_2 + H_2O + 2e-$
$CO + CO_3^{2-} \rightarrow 2\ CO_2 + 2e-$
It is seen that CO_2 is effectively transferred (or separated, or pumped) from the cathode to the anode of the MCFC. As a result, the outlet stream leaving the anode (the anode outlet stream) has an increased CO_2 concentration. The MCFC therefore acts as an effective CO_2 capture unit (and hence as a carbon capture unit). Apart from CO_2, the anode outlet stream can contain further gases, in particular hydrogen (H_2) and/or carbon monoxide (CO). Additionally, the anode outlet stream may further contain water (H_2O) and/or unreacted components of the reformable fuel, especially methane (CH_4). As used herein, the term “stream” refers to a fluid, wherein a fluid is composed of either gaseous components, or of liquid components, or of a mixture of gaseous and liquid components. The anode outlet stream regularly comprises gaseous components and may in some cases consist of gaseous components. As such, the anode outlet stream is preferably an at least partially gaseous stream and is more preferably a completely gaseous stream.

A fluid communication according to the present invention allows an active or passive transfer of a fluid from a first physical device (e.g., PSA, fuel cell, means, units, etc.) of the carbon capture system to a second physical device (e.g., PSA, fuel cells, means, units, etc.) of the carbon capture system. An active transfer can for example be achieved using one or more compressors, blowers and/or fans. A passive transfer can for example be achieved using gravity. As used herein, a fluid is composed of either gaseous components, or of liquid components, or of a mixture of gaseous and liquid components. The communication between the first and the second physical device of the carbon capture system can for example be achieved using one or more pipes, tubes, hoses, etc., which connect the first and the second physical device of the carbon capture system. The communication itself does not qualify as a physical device within the meaning of the present invention, and the communication does especially not have an active influence on a fluid transferred therewith. A third and further physical devices may be arranged between the first physical device and the second physical device, provided fluid can still be transferred from the first physical device to the second physical device.

According to the present invention, the anode of the MCFC is in fluid communication with the PSA unit for receiving at least a portion of the tail gas produced by the PSA unit (PSA tail gas) as an inlet stream. The PSA tail gas comprises at least one carbonaceous gas, i.e., at least one carbon-containing gas. The at least one carbonaceous gas is preferably CO_2, CH_4 and/or CO, in particular at least CO_2. The PSA tail gas may thus comprise one of the following gas mixtures: CO/CO_2, CO/CH_4, CO_2/CH_4 and $CO/CO_2/CH_4$. The PSA tail gas may also comprise alkanes higher than CH_4 of general formula C_nH_{2n+2} (with n>1) alkenes (general formula C_nH_{2n}; n>1) and alkynes (general formula C_nH_{2n-2}; n>1), but is preferably free of such higher alkanes, alkenes and/or alkynes.

It has been surprisingly found that by feeding at least a portion of the tail gas of the PSA unit, which comprises at least one carbonaceous gas, in particular at least CO_2, CH_4 and/or CO, more specifically at least CO_2, to the anode of the MCFC, additional CO_2 sent to the cathode of the MCFC can be efficiently transferred and separated as described above so that overall CO_2 can be captured by the inventive carbon capture system in an efficient manner. That is, a particularly CO_2-rich anode outlet stream can be produced with the combination of PSA and MCFC according to the present invention. Further, the use of CO_2 in the operation of the MCFC can simultaneously allow to produce electric energy by the MCFC. The produced electric energy can be used within the carbon capture system itself, for example for at least partially operating a CO_2 separation means. The carbon capture system can thereby advantageously become an at least partially self-supporting carbon capture system. The carbon capture system may thereby advantageously also become an exporter of electricity.

In principle, feeding CO_2 to the anode of an MCFC is counter-intuitive as an MCFC regularly requires CO_2 being present at its cathode side as described above. However, without wishing to be bound by theory, it is assumed that the effects of the tail gas, which comprises at least one carbonaceous gas, being fed to the anode of the MCFC as observed in the present invention are at least partially due to a low to very low concentration (including complete absence) of higher hydrocarbons in the PSA tail gas. There is thus no need for any pre-reforming of the feed sent to the anode, and part of the PSA tail gas including at least one carbonaceous gas can be sent in admixture with further fuel and water directly to the anode for the reforming reaction. This also lowers the requirement for CO_2 to be additionally separated by migrating from the cathode to the anode of the MCFC and hence also reduces the size of the MCFC unit for a given overall carbon capture rate of the process. As a result, the overall concentration of captured CO_2 leaving the MCFC as an anode outlet stream can be increased, which adds to the observed advantageous effects.

Additionally, according to the present invention, the molten carbonate fuel cell (MCFC) is a multi-stage fuel cell (or multi-stage MCFC), preferably a two-stage fuel cell (or two-stage MCFC). As used herein, a multi-stage MCFC is an MCFC in which two or more MCFCs (or MCFC stages) are in fluid communication, constituting a sequence of stages, where fuel and/or oxidant streams are entering in sequence the first and the following stages. Because a multi-stage MCFC is employed, the efficiency of the CO_2 capture can be further improved.

In a multi-stage MCFC, the cathode outlet stream of an upstream cell is used as the cathode inlet stream of the subsequent cell, i.e., the next more downstream cell. As an example, in a two-stage MCFC, the cathode outlet stream of a first (upstream) cell is used as the cathode inlet stream of the second (downstream) cell. When reference is made herein to “a cathode” or “the cathode” without indicating a particular stage, regularly the overall cathode of the MCFC is meant, which is composed of two or more separate cathode portions in series. However, when reference is made herein to a cathode inlet, a cathode inlet stream, a cathode feed, a feed or stream directed to the cathode or the like, this is meant to refer to the first cathode portion of the two or more separate cathode portions in series. Similarly, when reference is made herein to a cathode outlet, a cathode outlet stream, a feed or stream stemming from the cathode or the like, this is meant to refer to the last cathode portion of the two or more separate cathode portions in series.

In the multi-stage fuel cell, the anode outlet stream of an upstream cell is used as the anode inlet stream of the subsequent cell, i.e., the next more downstream cell. As an example, in a two-stage fuel cell, the anode outlet stream of a first (upstream) cell is used as the anode inlet stream of the second (downstream) cell. When reference is made herein to “an anode” or “the anode” without indicating a particular stage, regularly the overall anode of the MCFC is meant, which is composed of two or more separate anode portions in series. However, when reference is made herein to an anode inlet, an anode inlet stream, an anode feed, a feed or stream directed to the anode or the like, this is meant to refer to the first anode portion of the two or more separate anode portions in series. Similarly, when reference is made herein to an anode outlet, an anode outlet stream, a feed or stream stemming from the anode or the like, this is meant to refer to the last anode portion of the two or more separate anodes in series.

Typically, at the first cell, the second cell and potentially further cells, there will be a lower air dilution at the inlet of the cathode and hence a higher CO_2 concentration, which can lead to a higher CO_2 utilisation factor and a higher CO_2 capture rate. A multi-stage MCFC and in particular a two-stage MCFC represents a highly beneficial design to maximise the capabilities of the cells of separating CO_2 and, at the same time, this configuration can also lead to a higher electric power output due to the combined effects of higher electricity output from the cells and lower utilities consumptions for air inlet to the cathode (smaller heat exchanger for air preheating). A multi-stage MCFC and in particular a two-stage MCFC can further result in an overall lower cell area, compared to a single-stage MCFC. Additionally, a multi-stage MCFC and in particular a two-stage MCFC gives the possibility of tuning the voltage of the two stages independently.

Moreover, for the multi-stage MCFC of the carbon capture system according to the present invention a two-stage MCFC is preferred over an MCFC having more than two stages because it achieves a balance between realizing the advantages of a multi-stage

MCFC described herein on the one hand, and excessive expenditures for additional stages of the multi-stage MCFC on the other hand.

It is in particular preferred that the molten carbonate fuel cell is a two-stage cell having a first cell and a second cell which are in fluid connection, wherein the fluid connection comprises one or more cooling means and/or one or more mixing means. With such a two-stage fuel cell having one or more cooling and/or mixing means arranged between the two cells, the efficiency of the CO_2 capture may be even further enhanced. In particular, when the fluid connection comprises one or more cooling means, it becomes possible to actively control the cell temperature of the second cell which can improve the overall CO_2 capture efficiency.

In order to achieve the advantages associated with the use of tail gas of the PSA unit as an anode feed, to keep the overall carbon capture system simple and to avoid unnecessary costs, it is preferred that there is no compressor arranged between the pressure swing adsorption unit and the molten carbonate fuel cell, especially not between the pressure swing adsorption unit and an inlet of the anode of the molten carbonate fuel cell. In other words, it is preferred that the pressure swing adsorption unit is downstream thereof not in fluid communication with a compressor which compressor would be downstream thereof furthermore in fluid communication with the molten carbonate fuel cell and especially with an inlet of the anode of the molten carbonate fuel cell. This is different to the system of WO 2021/181249 A1 in which such a compressor is arranged between a pressure swing adsorption unit and an anode of a molten carbonate fuel cell.

In order to achieve the advantages associated with the use of tail gas of the PSA unit as an anode feed, to keep the overall carbon capture system simple and to avoid unnecessary costs, it is preferred that there is no chiller (a cooling means) arranged between the pressure swing adsorption unit and the molten carbonate fuel cell, especially not between the pressure swing adsorption unit and an inlet of the anode of the molten carbonate fuel cell. In other words, it is preferred that the pressure swing adsorption unit is not in fluid communication downstream thereof with a chiller which chiller would be downstream thereof furthermore in fluid communication with the molten carbonate fuel cell and especially with an inlet of the anode of the molten carbonate fuel cell. This is different to the system of WO 2021/181249 A1 in which such a chiller is arranged between a pressure swing adsorption unit and an anode of a molten carbonate fuel cell.

In order to achieve the advantages associated with the use of tail gas of the PSA unit as an anode feed, to keep the overall carbon capture system simple and to avoid unnecessary costs, it is preferred that there is no CO_2 separator arranged between the pressure swing adsorption unit and the molten carbonate fuel cell, especially not between the pressure swing adsorption unit and an inlet of the anode of the molten carbonate fuel cell. In other words, it is preferred that the pressure swing adsorption unit is not downstream thereof in fluid communication with a CO_2 separator which CO_2 separator would be downstream thereof furthermore in fluid communication with the molten carbonate fuel cell and especially with an inlet of with the anode of the molten carbonate fuel cell. This is different to the system of WO 2021/181249 A1 in which such a CO_2 separator is arranged between a pressure swing adsorption unit and an anode of a molten carbonate fuel cell.

In order to achieve the advantages associated with the use of tail gas of the PSA unit as an anode feed, to keep the overall carbon capture system simple and to avoid unnecessary costs, it is more preferred that there is no compressor, no chiller and no CO_2 separator arranged between the pressure swing adsorption unit and the molten carbonate fuel cell, especially not between the pressure swing adsorption unit and an inlet of the anode of the molten carbonate fuel cell. This is different to the system of WO 2021/181249 A1 in which a compressor, a chiller and a CO_2 separator are arranged between a pressure swing adsorption unit and an anode of a molten carbonate fuel cell.

It is preferred that the carbon capture system according to the present invention further comprises a CO_2 removing means upstream the PSA. In other words, such a preferred CO_2 removing means is in fluid communication with the PSA for sending a CO_2-lean stream to the PSA as a feed. With the CO_2 removing means it is possible to effectively remove a substantial portion and potentially even all CO_2 upstream the PSA, typically leaving only CH_4, CO and H_2 in the PSA tail gas which can be fed to the MCFC anode for power production.

It is preferred that the MCFC according to the present invention is configured to run in electricity production mode and/or is configured to not run in electrolysis mode (it does not run in electrolysis mode). In contrast, where an MCFC is configured to run in electrolysis mode, it becomes a molten carbonate electrolysis cell (MCEC) which disadvantageously consumes electric energy instead of producing electric energy as in the present invention. This because in an MCEC, in addition to H_2O and CO_2 electricity is required to perform the reduction reaction at the anode and to produce H_2, CO and carbonate ions CO_3^{2-} according to the following reactions:

$CO_2 + H_2O + 2e^- \rightarrow H_2 + CO_3^{2-}$ (not according to the present invention)

$2CO_2 + 2e^- \rightarrow CO + CO_3^{2-}$ (not according to the present invention)

On the cathode side of an MCEC, the outlet stream contains CO_2 and O_2 resulting from the transportation of CO_3^{2-} ions through the electrolyte according to the following reaction:

$CO_3^{2-} \rightarrow \frac{1}{2} O_2 + CO_2 + 2e^-$ (not according to the present invention)

It is seen that the MCEC is for transferring CO_2 from the anode to the cathode, i.e., opposite to the MCFC of the present invention. Further, an MCEC usually increases the electrical and thermal energy demand of a process in which the MCEC is used. Furthermore, it may be required to utilize a sweeping gas (for example air) to avoid the degradation of the cathode of the MCEC. These disadvantages are avoided when the MCFC according to the present invention is configured to run in electricity production mode and/or is configured to not run in electrolysis mode.

It is preferred that the molten carbonate fuel cell is electrically connected to an electricity consumption means and/or an electricity storage means. More preferably, the electricity consumption means is part of the carbon capture system according to the present invention, more preferably a CO_2 separation means (CO_2 purification means; CO_2 compression means). In particular by making use of the electric energy produced by the carbon capture system within the system itself, the carbon capture system becomes an at least partially self-supporting system. The electric energy produced by the carbon capture system may also be exported to the outside of the system for other use or storage. For example, the produced electric energy may be stored in electricity storage means, more preferably in a primary or secondary battery. By storing the electric energy produced by the carbon capture system, the electric energy can be utilized in a highly variable manner, thereby enhancing the versatility of the carbon capture system.

It is preferred that the carbon capture system according to the present invention comprises a CO_2 separation means which is in fluid communication with the anode of the molten carbonate fuel cell for receiving an outlet stream from the anode (the anode outlet stream), wherein the CO_2 separation means is configured to, i.e., is technically able to, separate CO_2 from the anode outlet stream. The CO_2 separation means is preferably an amine-free CO_2 separation means and is more preferably a solvent-free separation means. By separating CO_2 from the anode outlet stream, the CO_2 separation means produces at least two outlet streams, namely a first stream having a higher CO_2 concentration (a CO_2 rich stream), and a second stream having a lower CO_2 concentration (a CO_2 depleted stream). The CO_2 concentration of the CO_2 rich stream is higher that the CO_2 concentration of the CO_2 depleted stream. Herein, concentration refers to concentration in mol%. By producing the CO_2 rich stream, the CO_2 separation means acts as an effective CO_2 capture unit and further purifies (concentrates) the CO_2 captured with the carbon capture system according to the invention. The CO_2 rich stream is preferably at least partially in a supercritical state and is more preferably completely in a supercritical state. Alternatively, the CO_2 rich stream is preferably an at least partially liquid stream and is more preferably a completely liquid stream. The CO_2 rich stream can be sent to storage means, like one or more containers, so that highly concentrated CO_2 is captured and potentially stored. Such one or more containers are preferably configured for transportation thereof on a ship, a train or a truck. For this, the CO_2 separation means is in fluid combination with the one or more containers. With the CO_2 separation means, the carbon capture system according to the invention can capture CO_2 more efficiently.

It is preferred that the PSA unit is in fluid connection with the CO_2 separation means for receiving an outlet stream from the CO_2 separation means as an inlet stream, more preferably the CO_2 depleted stream. The CO_2 depleted stream may still contain residual H_2, and may further still contain residual CO_2 and potentially CO. The fluid connection between the PSA unit and the CO_2 separation means allows to recirculate the residual H_2, CO and/or CO_2 to the PSA unit. The recirculation can then lead to additional recovery of valuable H_2, and/or additional capture and potential storage of CO_2 which could otherwise disadvantageously be emitted to the environment.

It is preferred that the CO_2 separation means is selected from a membrane unit, a second pressure swing adsorption unit (which is different from the PSA unit the tail gas of which is fed to the anode of the MCFC) and a low temperature phase change separation unit. It is more preferred that the CO_2 separation means is a low temperature phase change separation unit (see for example, Berstad et al., J. Int. Acad. Refrig. Vol. 36, No. 5 (2013), 1403-1416; IEAGHG, 2011. Rotating Equipment for Carbon Dioxide Capture and Storage. IEAGHG report 2010/07). A commercial example of a CO_2 separation means is the Air Liquide Cryocap®. In a low temperature phase change separation unit CO_2 is condensed from the anode outlet stream, i.e., gaseous CO_2 is converted into liquid CO_2, to give a condensed fraction. At the same time, additional components remain mostly gaseous, to give an uncondensed fraction. With a low temperature phase change separation unit, CO_2 can be separated from the anode outlet stream in a particularly effective manner and can be captured in advantageously high purity (high concentration).

It is preferred that the carbon capture system according to the present invention further comprises a (first) water-gas-shift reactor (WGS reactor) between the anode of the MCFC and the CO_2 separation means. Such a WGS reactor can receive at least a portion of the anode outlet stream, for which the WGS reactor is in fluid communication with the anode of the MCFC. The anode outlet stream may still contain residual CO, in particular CO which is not oxidized at the MCFC anode or is produced according to the reaction $CH_4 + H_2O \rightarrow 3H_2 + CO$. The WGS reactor may convert such CO at least partially into CO_2. The WGS reactor can then send this CO_2 to the CO_2 separation means for capturing and potentially storing the CO_2, thereby further enhancing the efficiency of the overall CO_2 capture. For this, the WGS reactor is in fluid communication with the CO_2 separation means.

It is preferred that the CO_2 separation means allows for a separation of CO_2 having a purity of 95 mol% or more, more preferably of 96 mol% or more, still more preferably of 97 mol% or more, even more preferably of 98 mol% or more and most preferably of 99 mol% or more. With such a CO_2 separation means, an advantageous CO_2 capture can be achieved.

It is preferred that the PSA unit is in fluid connection with a steam methane reformer (SMR) for receiving an outlet stream from the steam methane reformer as an inlet stream.

In a steam methane reformer, steam, i.e., gaseous water or $H_2O_{(g)}$, is reacted with one or more hydrocarbons to basically yield H_2 and CO. The one or more hydrocarbons typically comprise methane (CH_4), and more preferably a majority of methane, for example more than 50 mol% CH_4, more preferably more than 60 mol% CH_4, even more preferably more than 70 mol% methane, still more preferably more than 80 mol% CH_4 and most preferably more than 90 mol% CH_4. Taking CH_4 as a representative fuel, the steam methane reforming reaction is: $CH_4 + H_2O \rightarrow 3H_2 + CO$. The resulting gas mixture is preferably sent to a (second) WGS reactor to produce additional H_2 and CO_2. For this, the SMR is in fluid connection with a WGS reactor, and the WGS reactor is in fluid connection with the PSA unit. In other words, the WGS reactor is arranged downstream of the SMR, and the WGS reactor is arranged upstream of the PSA unit. The second WGS reactor may be used together with one or more further WGS reactors downstream of the second WGS reactor. The one or more further WGS reactors downstream of the second WGS reactor are preferably operated at decreasing temperatures. Typically, fuel gas is combusted with air in a furnace of the SMR to provide heat for the SMR reactions, producing a flue gas containing CO_2 diluted in N_2 and O_2 from the combustion air.

Further, when hydrocarbons (like natural gas) are sent to the preferable SMR, this typically results downstream in excess PSA tail gas (or PSA off gas) that can be advantageously used in the MCFC in the configuration of the present invention. More specifically, it is sufficient that the MCFC is fed with PSA tail gas only, so that there is no need of feeding additional natural gas. Conversely, in WO 2021/181249 A1, natural gas is also fed to the MCFC which typically involves the need of a pre-treatment (e.g., desulfurization, pre-reforming) before the MCFC.

A production of hydrogen by SMR can ultimately result in high amounts of CO_2 of as high as about 10 $kgCO_2/kgH_2$. The stream leaving the SMR (the SMR outlet stream) and more preferably the stream leaving the WGS reactor (the WGS outlet stream), which contains such high amounts of CO_2, serves as an input stream for the PSA unit of the carbon capture system. The PSA unit further purifies the received H_2 to give the product gas, and the PSA unit concentrates the received carbonaceous gas(es) (in particular CO_2, CH_4, and/or CO) to give the tail gas. The flue gas from SMR is sent to the cathode of the MCFC wherein CO_2 is separated by transfer from the cathode to the anode. The tail gas is then sent to the anode of the MCFC as carbon-rich fuel. According to the present invention, the

CO_2 produced by the SMR can thus advantageously be captured efficiently and an emission thereof to the environment can be prevented, while simultaneously generating electric energy.

As described above, the PSA tail gas, which comprises at least one carbonaceous gas, in particular CO_2, CH_4, and/or CO, and preferably comprises CO_2, is at least partially sent to the anode of the MCFC. A further part of the PSA tail gas (containing for example 50/25/15/10 mol% $CO_2/H_2/CO/C_1$) may preferably be mixed with additional natural gas, and the resulting mixture may preferably be used as additional fuel in the SMR to provide heat for the highly endothermic SMR reactions. On the other hand, using an MCEC outlet stream as a combustion agent in an SMR furnace, as discussed in WO 2017/190066 A1 and by A. Monforti Ferrario et al., would result in dilution of the produced CO_2 with nitrogen, which would then require undesirable and inefficient downstream polishing steps, i.e., additional purification steps.

Subject of the invention is also a method of capturing carbon, comprising:

producing a product gas and a tail gas by pressure swing adsorption, wherein the tail gas comprises at least one carbonaceous gas, and

feeding at least a portion of the tail gas as an inlet stream to an anode of a molten carbonate fuel cell (MCFC), wherein the molten carbonate fuel cell is a multi-stage fuel cell,

wherein the molten carbonate fuel cell produces electric energy and transfers CO_2 from a cathode to the anode.

The preferred embodiments of the inventive carbon capture system described herein including the claims are likewise preferred for this inventive method in an analogous manner. With such a method, CO_2 can be captured efficiently. In particular, when the CO_2 is part of a gas mixture resulting from a hydrogen production (which mixture is subjected to the pressure swing adsorption), the CO_2 can be separated from the hydrogen and can be captured efficiently. Further, using the PSA tail gas at least partially as an anode feed for the MCFC can allow to simultaneously produce electric energy by the MCFC. The produced electric energy can be used within the method of capturing carbon itself, for example for CO_2 separation, in particular by compression. The inventive method of capturing carbon can thereby advantageously become an at least partially self-supporting method of capturing carbon.

Subject of the invention is also a use of the inventive carbon capture system for capturing CO_2. The preferred embodiments of the inventive carbon capture system described herein including the claims are likewise preferred for this inventive use in an analogous manner. With such a use, CO_2 can be captured efficiently. Moreover, when the CO_2 is part of a gas mixture resulting from a hydrogen production, the CO_2 can be separated from the hydrogen and can be captured efficiently. Further, using the PSA tail gas at least partially as an anode feed for the MCFC of the system can allow to simultaneously produce electric energy by the MCFC. The produced electric energy can be used within the use for capturing carbon itself, for example for CO_2 separation, in particular by compression. The inventive use for capturing carbon can thereby advantageously become an at least partially self-supporting use.

Subject of the invention is also a use of a pressure swing adsorption unit and/or a molten carbonate fuel cell in a carbon capture system according to the invention, or in a method of capturing carbon according to the invention. The preferred embodiments of the inventive carbon capture system described herein including the claims are likewise preferred for this inventive use in an analogous manner. With such a use, CO_2 can be captured efficiently. Moreover, when the CO_2 is part of a gas mixture resulting from a hydrogen production, the CO_2 can be separated from the hydrogen and can be captured efficiently with this inventive use. Further, using the PSA tail gas at least partially as an anode feed for the MCFC of the system can allow to simultaneously produce electric energy by the MCFC. The produced electric energy can be used within the carbon capture system itself, for example for CO_2 separation, in particular by compression. This inventive use can thereby advantageously become an at least partially self-supporting use.

Subject of the invention is also CO_2 captured with a carbon capture system according to the invention, or captured with a method of capturing carbon according to the invention, or captured by the use of the inventive carbon capture system for capturing CO_2 according to the invention. The preferred embodiments of the inventive carbon capture system described herein including the claims are likewise preferred for this inventive CO_2. Such CO_2 may be captured in a particularly effective manner and may further help to produce electric energy. Additionally, emission of such captured CO_2 into the atmosphere can be prevented.

Brief description of the drawings

Fig. 1 shows a basic embodiment of a carbon capture system according to the invention.

Fig. 2 shows a preferred embodiment of a carbon capture system according to the invention.

Fig. 3 shows another preferred embodiment of a carbon capture system according to the invention.

Fig. 4 shows another preferred embodiment of a carbon capture system according to the invention.

Fig. 5 shows an embodiment of a carbon capture system as used in the experimental section.

Fig. 6 shows a further embodiment of a carbon capture system as used in the experimental section.

Exemplary embodiments

Exemplary embodiments of the present invention are described with reference to the accompanying figures. Where arrows are used, the rectangular end represents the “upstream” side or position, while the arrow end represents the “downstream” side or position.

Fig. 1 shows a basic embodiment of a carbon capture system 1. The carbon capture system 1 comprises a pressure swing adsorption unit 2 (PSA unit 2) which produces a product gas 3 and a tail gas 4 comprising at least one carbonaceous gas. The tail gas 4 regularly comprises CO_2 and typically further comprises CH_4 and CO as carbonaceous gas(es). The carbon capture system 1 further comprises a molten carbonate fuel cell 5 (MCFC), which although not explicitly shown is a multi-stage MCFC. The MCFC 5 comprises two electrodes, namely a cathode 6 and an anode 7. The MCFC 5 further comprises an electrolyte between the two electrodes (not shown). The MCFC 5 is further operated such that it generates electricity, i.e., the MCFC 5 produces electric energy 11 (that is, MCFC 5 is configured to run in electricity production mode; alternatively, it can be said that MCFC 5 is configured to run not in electrolysis mode). The anode 7 is in fluid communication with the pressure swing adsorption unit 2 and receives at least a portion of the tail gas 4 as an inlet stream.

Fig. 2 shows a preferred embodiment of a carbon capture system 1. The carbon capture system 1 comprises the same components as the carbon capture system 1 shown in Fig. 1. The carbon capture system 1 of Fig. 2 is used in the context of hydrogen production, more specifically the production of hydrogen via steam methane reforming. Accordingly, the carbon capture system 1 of Fig. 2 comprises a steam methane reformer 10 (SMR 10). The product of this SMR 10, i.e., its outlet stream, is sent via a fluid connection to PSA unit 2 for a separation of CO_2 from H_2, which CO_2 and H_2 are regularly contained in admixture in an outlet stream of a hydrogen production unit like SMR 10. The PSA unit 2 produces a H_2-rich product stream and a tail gas 4. The tail gas 4 regularly comprises CO_2, CH_4, CO and residual H_2 from the steam methane reforming. The cathode inlet stream 16 comprises CO_2 and O_2. The cathode inlet stream may in particular comprise exhaust combustion gases which may optionally be admixed with additional air or may be added separately by recirculating a portion of the PSA tail gas 4 with or without additional air. It is particularly preferred that the cathode inlet stream 16 comprises flue gases deriving from a combustion in the SMR 10 as indicted in Fig. 2 by a dotted line. The CO_2 fed to cathode 6 is transferred from the cathode 6 to the anode 7 to yield a CO_2 depleted cathode outlet stream (thus, CO_2 is captured by system 1 from the cathode inlet stream 16). The carbon capture system 1 of Fig. 2 further comprises a CO_2 separation means 8. This CO_2 separation means 8 is in fluid communication with the anode 7 of MCFC 5 and receives an outlet stream from the anode 7. Further, the CO_2 separation means 8 has such a structure (or configuration) that it separates CO_2 from the outlet stream which comes from anode 7. In Fig. 2, CO_2 separation means 8 is fluidly connected to (in fluid connection with) PSA unit 2. This configuration allows for a recirculation of a CO_2 depleted stream leaving CO_2 separation means 8 to the PSA unit 2 for further hydrogen recovery. Further, in Fig. 2, the CO_2 separation means 8 is a low temperature phase change separation unit which separates CO_2 by liquifying the same under reduced temperature and/or increased pressure. The carbon capture system 1 of Fig. 2 further comprises a water-gas-shift reactor 9 which is located between anode 7 of the MCFC 5 and the CO_2 separation means 8. In the carbon capture system 1 of Fig. 2, CO_2 separation means 8 regularly separates CO_2 which has a purity of at least 95 mol%

and typically above 95 mol%. While not shown in Fig. 2, MCFC 5 may be electrically connected to an electricity consumption means and/or an electricity storage means, in particular to a further component of the carbon capture system 1, like the CO_2 separation means 8, the water-gas-shift reactor 9 and/or the steam methane reformer 10, most preferably to the CO_2 separation means 8.

Fig. 3 shows another preferred embodiment of a carbon capture system 1. The carbon capture system 1 comprises the same components as the carbon capture system 1 shown in Fig. 2. In Fig. 3, the MFCF 5 is a two-stage fuel cell as an example for the multi-stage fuel cell. MFCF 5 thus has a first cell and a second cell which are in fluid connection. Specifically, the cathode outlet stream from the first cell is used as a cathode inlet stream for the second cell. Accordingly, the anode outlet stream from the first cell is used as an anode inlet stream for the second cell.

Fig. 4 shows another preferred embodiment of a carbon capture system 1. The carbon capture system 1 comprises the same components as the carbon capture system 1 shown in Fig. 3. In Fig. 4, the fluid connection between the first cell and the second cell comprises a cooling means 17 for cooling fluid transferred from the first cell to the second cell. Specifically, the cathode outlet stream from the first cell is cooled in a cooling means 17 and is thereafter used as a cathode inlet stream for the second cell. Whilst not shown in either Fig.3 or Fig. 4, it can also be advantageous that the fluid connection between the first cell and the second cell comprises one or more mixing means for mixing fluid transferred from the first cell to the second cell with one or more additional fluids for an improved operation of the second cell.

Experimental section

A case study for a carbon capture system (PSA-MCFC integrated plant) used for capturing CO_2 stemming from H_2 production by means of steam methane reforming was performed. The applied method for calculation of the mass and energy balances of respective hydrogen production plants is described hereinafter.

The following cases were analysed:

1. Reference SMR hydrogen plant without CO_2 capture
2. SMR hydrogen plant with CO_2 capture with MCFC fed with natural gas (NGF case). This case represents a configuration for CO_2 capture with MCFC separator and its configuration is shown in Fig. 5.
3. SMR hydrogen plant with CO_2 capture with MCFC fed with PSA off-gas (OGF case; off-gas, or tail gas, from the PSA sent to anode of MCFC). The configuration of this case is shown in Fig. 6.
4. SMR hydrogen plant with CO_2 capture with two-stage MCFC fed with PSA off-gas (OGF-2 case; off-gas, or tail gas, from the PSA sent to anode of first MCFC). This case is in accordance with the present invention.

The main calculation assumptions are included in the next sections, along with the description of the assessed cases.

Technical description of the PSA-MCFC integrated plant

Reference SMR without CO_2 capture

The base case SMR configuration without CO_2 capture consists of a fired tubular reforming system for combined H_2 production, electricity generation and steam export. This system is aimed at producing 100’000 Nm^3/h of H_2 from natural gas (NG), the composition of which is reported in Table 1. In particular, the system includes the following unit operations: a desulfurization unit, an adiabatic pre-reformer, a fired tubular steam reformer, a water gas shift (WGS) section and a pressure swing adsorption (PSA) unit. Input data for the SMR are summarised in Table 2.

Table 1. Specifications of the NG considered for performance evaluation

Molar composition		$\%_{mol}$
CH_4	Methane	89.00
C_2H_6	Ethane	7.00
C_3H_8	Propane	1.00
C_4H_{10}	Butane	0.10
C_5H_{12}	Pentane	0.01
CO_2	Carbon dioxide	2.00
N_2	Nitrogen	0.89
Molar mass	kg/kmol	18.018
Lower heating value	MJ/kg	46.482
Higher heating value	MJ/kg	51.454
CO_2 specific emission	gCO_2/MJ_{LHV}	56.99

Table 2. Summary of the main input data for SMR

Unit	Component	Parameter	Unit	Value
SMR	Pre-reformer	Inlet temperature	°C	490
SMR	Pre-reformer	Pressure	bar	38
SMR	Pre-reformer	Steam to carbon ratio	-	3.4
SMR	Reformer	Inlet temperature	°C	620
SMR	Reformer	Outlet temperature	°C	890
SMR	WGS	Inlet temperature	°C	330
SMR	WGS	Inlet pressure	bar	32
SMR	PSA	Inlet temperature	°C	31
SMR	PSA	Inlet pressure	bar	30
SMR	PSA	Hydrogen recovery	%	90%
SMR	H_2 compressor	Isentropic efficiency	%	84%
SMR	H_2 compressor	Mechanical and electrical efficiency	%	94%
SMR	Comb. air fan	Isentropic efficiency	%	80%
SMR	Comb. air fan	Mechanical and electrical efficiency	%	94%
SMR	Water pump	Isentropic efficiency	%	70%
SMR	Water pump	Mechanical and electrical efficiency	%	84%
SMR	LP steam	Pressure/temperature	bar/°C	6/160
SMR	MP steam	Pressure/temperature	bar/°C	40/348
SMR	HP steam	Pressure/temperature	bar/°C	100/485
SMR	LP/HT turbine	Isentropic efficiency	%	87%
SMR	LP/HP turbine	Mechanical and electrical efficiency	%	99.6%

Firstly, the NG is treated to remove sulfur that may poison the reformer catalyst. Desulfurization is usually carried out in a two-stage process operating in the 300-400°C temperature range. A portion of the produced H_2 is mixed to NG in order to drive at a satisfactory rate ($2\%_{mol}$ of H_2 in the mixture NG-H_2) the hydrogenation reactions of organic sulfur compounds to H_2S. H_2S is then removed in a zinc oxide adsorption bed, capable to reduce sulfur concentration to below 100 ppb.

NG is then mixed with steam (with a steam to carbon ratio equal to 3.4) and sent to a pre-reformer, where a nickel-based catalyst decomposes complex hydrocarbons to avoid cracking in the downstream fired tubular reformer and also to favour a more uniform feeding of the reformer, independently from the composition of the original feedstock. The pre-reformer is modelled as an adiabatic reactor at chemical equilibrium, with an inlet feed at 490°C and 37 bar.

The pre-reformed charge is sent to a fired tubular steam reformer, which is composed of a furnace whose burners radiate on tubes filled with nickel-based catalyst to provide the heat required to sustain the endothermic methane reforming reaction. The reformer is modelled at chemical equilibrium, with exit temperature and pressure of 890°C and 35 bar. The air flowrate to the burners is set to obtain a molar fraction of O_2 in the flue gases equal to $1.5\%_{mol}$. The reformer fuel is constituted by a mixture of NG and PSA off-gas (tail gas).

At the SMR exit, the reformed syngas is cooled down by producing steam and fed to a WGS reactor at 330°C, which is calculated as an adiabatic reactor at chemical equilibrium. Subsequently, the syngas is cooled down to nearly ambient temperature and sent to the PSA section.

PSA section

A 90% hydrogen recovery efficiency is assumed for the PSA according to current industrial practice. The off-gas stream from the PSA is burned with additional NG in the SMR furnace to sustain reforming.

Heat recovery and steam cycle

A heat recovery system is in place to: (i) cool down the SMR flue gas from the assumed furnace exit temperature of 1010°C to 142°C and provide heat to the pre-reformer charge and to the natural gas inlet, to pre-heat combustion air (425°C) and generate high pressure (HP) steam (100 bar, 485°C); and (ii) cool down the hot syngas produced by the SMR at 890°C to 171°C to produce HP steam.

The steam cycle consists of a high-pressure turbine, delivering medium pressure (MP) steam at 40 bar and 348°C to a low pressure (LP) backpressure turbine (exit at 6 bar, 160°C), which provides LP steam to the refinery. Both turbines have an isentropic efficiency of 87% and a mechanical and electrical efficiency of 99.6%. Liquid water is assumed to be fed to the heat recovery section at 151°C, i.e. as condensate returning form thermal users in the refinery.

Case study NGF: Integrated PSA-MCFC with NG feed to cell anode

The integration of an MCFC requires some modifications to the reference SMR reported in the previous section. The main modifications are the addition of an MCFC system, followed by a low temperature CO_2 purification unit (CPU) to generate a high purity CO_2 stream and recover the H_2. A greenfield design approach has been assumed, entailing the preference of feeding the SMR flue gases to the cell cathode at high temperature to comply with the MCFC design inlet temperature of 575°C. As a result, the preheating requirements in the SMR section are now largely fulfilled by the hot cathode off-gas rather than by the hot flue gases from the SMR furnace. The distinctive element of this case study (natural gas feed: NGF case) is represented by the choice of feeding the cell anode with additional NG.

CO_2 separation by MCFC

Input data for the MCFC are summarised in Table 3. The MCFC unit consists of an anode, a cathode and a reforming layer upstream the anode, while a pre-reformer (upstream the MCFC) and a WGS section (downstream the MCFC) complete the separation system. The flue gases deriving from the combustion in the SMR section are sent to the MCFC cathode, while the anode feed is constituted by NG with the same characteristics as that reported in Table 1.

The flue gases deriving from the combustion in the SMR (74 kg/s) are firstly mixed with air (264 kg/s). The temperature of this air is determined to obtain 575°C after mixing with the flue gases. The flowrate of air is determined to keep the cell outlet temperature constant and equal to the design value of 645°C. Then, the mixture of flue gases and air is sent to the MCFC cathode.

The amount of CO_2 permeating from the cathode to the anode is set to obtain a CO_2 molar fraction in the cathode exhaust gas equal to 1%mol. H_2O permeation from the cathode to the anode, alongside O_2 permeation, is taken into account by imposing a value of transference number equal to 0.75. Hence, for each mole of CO_2 permeating, there will be accordingly 1/3 moles of H_2O and (1+1/3)/2=2/3 moles of O_2 co-permeating. At the exit, the cold cathode exhaust is vented to the atmosphere at 1.01 bar and 168°C, after heat recovery.

The NG fed to the anode (3.46 kg/s) is heated up to 600°C and sent to the adiabatic pre-reformer, that operates at 4 bar with a steam to carbon ratio equal to 2.1. The target steam to carbon ratio is obtained by mixing 7.73 kg/s of LP steam. The pre-reformed stream exits at 404°C, is heated up again up to 450°C and fed to the MCFC, where it mixes with the CO_2, H_2O and O_2 permeating from the cathode to the anode to produce the anode off-gas at 645°C. The hot anode exhaust gas is cooled by generating LP steam and pre-heating the NG, the pre-reformer charge and the reformer charge. Finally, the anode exhaust gas is further cooled down to ambient temperature to condense water and sent to the CPU.

Table 3. Summary of the main input data for MCFC

Unit	Component	Parameter	Unit	Value
MCFC	Cathode	Inlet temperature	°C	575
MCFC	Cathode	Outlet temperature	°C	645
MCFC	Cathode	CO_2 concentration in cathode exhaust	%	1%
MCFC	Pre-reformer	Inlet temperature	°C	600
MCFC	Pre-reformer	Steam to carbon ratio	-	2.1
MCFC	Anode	Inlet temperature	°C	600
MCFC	Anode	Outlet temperature	°C	645
MCFC	Cell balance	Fuel utilisation factor	-	0.75
MCFC	Cell balance	Cell voltage	V	0.7
MCFC	Cell balance	Heat loss	%LHV	1%
MCFC	WGS	Inlet temperature	°C	330
MCFC	WGS	Inlet pressure	bar	1
MCFC	Cathode air fan	Isentropic efficiency	%	80%
MCFC	Cathode air fan	Mechanical and electrical efficiency	%	94%
MCFC	Water pump	Isentropic efficiency	%	70%
MCFC	Water pump	Mechanical and electrical efficiency	%	84%
MCFC	Outlet fan	Outlet pressure	bar	1.01
MCFC	Outlet fan	Isentropic efficiency	%	80%
MCFC	Outlet fan	Mechanical and electrical efficiency	%	94%

CO_2 purification unit (CPU)

The CPU has two key objectives: (i) to separate additional CO_2 to be sent to storage (i.e., in addition to the separation already operated by the MCFC unit); and (ii) to separate a H_2-rich stream to be recovered and purified in the PSA unit of the SMR. Note that in order to keep consistency with the reference SMR case without CO_2 capture, it is here imposed an overall H_2 production (i.e., combining both the direct production from the SMR and the indirect one from the MCFC anode residue) still equal to 100’000 Nm^3/h.

Input data for the CPU are summarised in Table 4. In particular, the cold anode residue undergoes a first compression, modelled as a 4-stage compressor with inter-cooling with fixed discharge pressure of 32 bar (isentropic efficiency of 84%, mechanical and electrical efficiency of 94%). The resulting stream is then treated in a two-stage phase separation process constituted by two CO_2 separation drums, two expansion valves and two heat exchangers. The resulting flowrates are a CO_2-depleted residue to be sent to the PSA unit of the SMR, and two high-purity CO_2 streams which are then mixed (at 15 bar) and compressed through a 2-stage intercooled compressor with fixed discharge pressure of 100 bar (isentropic efficiency of 84%, mechanical and electrical efficiency of 94%). Then, the CO_2-rich stream is cooled down to ambient temperature and pumped out at 150 bar (isentropic efficiency of 80%, mechanical and electrical efficiency of 84%). The result is a high purity (99%$_{mol}$ of CO_2), HP (150 bar) CO_2 stream (24.93 kg/s), to be sent to storage.

Table 4. Summary of the main input data for CPU

Unit	Component	Parameter	Unit	Value
CPU	Compressor(s)	Isentropic efficiency	%	84%
CPU	Compressor(s)	Mechanical and electrical efficiency	%	94%
CPU	Compressor(s)	Number of stages	-	4+2=6
CPU	Compressor(s)	Final pressure before CO_2 pump	bar	100
CPU	CO_2 pump	Outlet pressure	bar	150
CPU	CO_2 pump	Isentropic efficiency	%	80%
CPU	CO_2 pump	Mechanical and electrical efficiency	%	84%
CPU	Heat exchange	DT min heat exchangers	°C	3
CPU	Drum vessel 1	Outlet temperature	°C	-33.0
CPU	Drum vessel 1	Outlet pressure	bar	31.7
CPU	Drum vessel 2	Outlet temperature	°C	-47.0
CPU	Drum vessel 2	Outlet pressure	bar	31.4

Case study OGF: Integrated PSA-MCFC with PSA off-gas feed to cell anode (inventive case study I)

The configuration involves the possibility to exploit part of the PSA off-gas as (tail gas) feed to the MCFC anode. This can be achieved in the “off-gas feed” (OGF) case, by introducing a split in the PSA off-gas, which can be directed towards the MCFC anode and to the SMR burners. Thanks to the lack of higher hydrocarbons in the PSA off-gas, this configuration allows to eliminate the MCFC pre-reformer unit hence, the anode charge (with the correct steam to carbon ratio equal to 2.1) can be sent directly to the MCFC.

Case study OGF-2: Two-stage MCFC with inter-cooling (inventive case study II)

Under the same technical assumptions already described for case study OGF (i.e., anode fed with PSA off-gas; or tail gas), an alternative design configuration (i.e., OGF-2) entails the use of a two-stage MCFC (i.e., two cells in series) with inter-cooling placed between the two cathodes (see Fig. 4). In particular, the cathode residue 1 from cell 1 is cooled down from 645°C to 575°C, the latter representing the design inlet temperature to the second cathode of the second cell. The inter-cooler is constituted by a heat exchanger which produces HP steam at 485°C and 100 bar, which is added up to the steam already produced by the heat integration in the SMR. Both cells are described in terms of heat balances and they entail the possibility to impose separately the desired values of cell potential (for a given fuel utilisation factor FU), in order to optimise their overall performance. As it will be shown in the results section, this option determines the possibility to reduce the flow rate of dilution air to control the cell temperature and consequently improve the overall CO_2 capture efficiency to over 95% with the assumed CO_2 concentration at cathode outlet.

Results: Technical performance

Assumptions in the calculation of key performance indicators.

Because of the different electricity balance and steam export among the assessed cases, a consistent comparison must take into account the indirect fuel consumption and indirect CO_2 emissions associated to the electricity and steam flows. Ultimately, this allows the calculation of basically equivalent key performance indicators (KPIs) that rely on the definition of two reference scenarios (Table 5). In both Scenario 1 and Scenario 2, reference thermal power is assumed to be produced through an NG boiler with efficiency of 90%, combustion emission factor of 2.7 kg CO_2/kg NG and resulting carbon intensity of 0.064 kg CO_2/MJth. Differently, the two scenarios differ for what concerns power generation. In Scenario 1, the reference electric power is assumed to be generated by an NG combined cycle (NGCC) without CO_2 capture, with overall efficiency of 60% and resulting carbon intensity of 345.0 kg CO_2/MWhel (i.e., 0.097 kg CO_2/MJel). In Scenario 2, the reference electric power is generated with a NGCC with CO_2 capture hence, overall efficiency lowered to 51% and resulting carbon intensity equal to 35.0 kg CO_2/MWhel (i.e., 0.010 kg CO_2/MJel).

Table 5. Assumptions on the reference scenarios for the calculation of equivalent emissions

ASSUMPTIONS
Scenario 1: Reference NGCC without CO_2 capture
Scenario 2: Reference NGCC with CO_2 capture

		Scenario 1	Scenario 2	
NGCC plant efficiency	%	60.0%	51.0%	Reference electricity
NGCC electricity carbon intensity	kg CO_2/MWh	348.0	35.0	
NGCC electricity carbon intensity - ε_{el}	kg CO_2/MJ	0.097	0.010	
NG boiler efficiency	%	90.0%	90.0%	Reference heat
NG combustion emission factor	kg CO_2/kg NG	2.7	2.7	
NG combustion emission factor	kg CO_2/GJ LHV	58.0	58.0	
NG boiler carbon intensity - ε_{th}	kg CO_2/MJ	0.064	0.064	

The key performance indicators that will be employed to compare the different case studies analysed are the H_2 production efficiency (i.e., η_{H_2} [%]), the equivalent H_2 production efficiency (i.e., $\eta_{H_2,eq}$ [%]), the carbon capture rate (i.e., *CCR* [%]), and the specific consumption of primary energy per unit of CO_2 avoided (i.e., *SPECCA* [MJ/kg]). On the one hand, both η_{H_2} and *CCR* evaluate the direct performance of the plant (in terms of H_2 production and CO_2 capture) without considering the effect of indirect fuel consumption and emissions, and are defined as:

$$\eta_{H_2} = \frac{\dot{m}_{H_2} \cdot LHV_{H_2}}{\dot{m}_{NG} \cdot LHV_{NG}} \qquad (1)$$

$$CCR = \frac{\dot{m}_{CO_2,storage}}{\dot{m}_{CO_2,storage} + \dot{m}_{CO_2,emission}} \qquad (2)$$

where $\dot{m}_{H_2}$ [kg/s],$\dot{m}_{NG}$ $\dot{m}_{NG}$ [kg/s] and $\dot{m}_{CO_2}$ [kg/s] are the mass flowrates of H_2, NG and CO_2, respectively, while LHV_{H_2} [= 119.91 MJ/kg] and LHV_{NG} [=46.498 MJ/kg] are the lower heating values of H_2 and NG. In particular, *CCR* of Equation (2) represents the CO_2 capture efficiency hence, it measures the amount of carbon that is effectively captured with respect to the total carbon inlet to the plant. On the other hand, indirect emissions are taken into account in the definition of $\eta_{H_2,eq}$ and *SPECCA*:

$$\eta_{H_2,eq} = \frac{\dot{m}_{H_2} \cdot LHV_{H_2}}{\dot{m}_{NG} \cdot LHV_{NG} - \frac{Q_{th}}{\eta_{th}} - \frac{W_{el}}{\eta_{el}}} \qquad (3)$$

$$SPECCA = \frac{NG_{capt,eq} - NG_{no\ capt,eq}}{\dot{m}_{CO_2,no\ capt,eq} - \dot{m}_{CO_2,capt,eq}} \qquad (4)$$

The equivalent-related parameters in Equations (3,4) take into account the energetic contributions of the co-production of thermal power Q_{th} [MW_{th}] and/or electricity W_{el} [MW_{el}] through the conversion efficiencies defined for Scenario 1 and Scenario 2 (Table 5). *SPECCA* of Equation (4) gives an estimate of the additional amount of energy that is required to avoid the emissions to the atmosphere of a reference unit of CO_2 thus, it compares the analysed scenarios with the SMR case without capture, the latter set as benchmark emission case study. As they are defined in Equation (4), *SPECCA* values are comparable among the analysed case studies since they entail the same overall H_2 output, otherwise both NG consumptions and equivalent CO_2 emissions would need to be scaled over the H_2 production. In particular, the equivalent natural gas input $NG_{capt,eq}$ [MW] and $NG_{no\ capt,eq}$ [MW] of Equation (3) are defined as the NG net thermal output in the case of considering or not carbon capture:

$$NG_{capt,eq} = \dot{m}_{NG,capt} \cdot LHV_{NG} - \frac{Q_{th,capt}}{\eta_{th}} - \frac{W_{el,capt}}{\eta_{el}} \qquad (5)$$

$$NG_{no\ capt,eq} = \dot{m}_{NG,no\ capt} \cdot LHV_{NG} - \frac{Q_{th,no\ capt}}{\eta_{th}} - \frac{W_{el,no\ capt}}{\eta_{el}} \qquad (6)$$

whereas equivalent CO_2 emissions $\dot{m}_{CO_2,capt,eq}$ $\dot{m}_{CO_2,capt,eq}$ [kg/s] and $\dot{m}_{CO_2,no\ capt,eq}$ $\dot{m}_{CO_2,capt,eq}$ [kg/s] of Equation (4) are defined in general as the emitted CO_2 flow $\dot{m}_{CO_2,emission}$ $\dot{m}_{CO_2,capt,eq}$ decreased by the emissions avoided as a result of the co-production of electricity W_{el} and heat Q_{th} (calculated through the carbon intensities ε_{el} and ε_{th} reported in Table 5):

$$\dot{m}_{CO_2,eq} = \dot{m}_{CO_2,emission} - Q_{th} \cdot \varepsilon_{th} - W_{el} \cdot \varepsilon_{el} \qquad (7)$$

<u>Base cases: Reference SMR, NGF, OGF</u>

This section details the main results in terms of mass and energy balances, electricity balance, steam balance, CO_2 balance and CO_2 avoidance performance for the following case studies (Table 6):

Reference SMR without CO_2 capture.

- NGF case: integrated PSA-MCFC. Cell potential set equal to 0.7 V, fuel utilisation factor of 0.75.
- OGF case: integrated PSA-MCFC. Cell potential set equal to 0.7 V, fuel utilisation factor of 0.75.

The CO_2 flux throughout the cell reported in Table 6 is defined as the ratio between the mass flow rate of permeating CO_2 and the area of the cell. The CO_2 production density reported in Table 6 is defined as the ratio between the total CO_2 mass flow rate at the anode outlet and the area of the cell. The electric power output from the SMR reference case is equal to 10.4 MW_{el}. The combined contributions of the SMR steam cycle and of the MCFCs determine larger electric power outputs from the cases NGF (59.1 MW_{el}) and OGF (22.1 MW_{el}), with the quantitative difference between NGF and OGF explained by the flow rate of permeating CO_2 across the respective cells (19.6 kg/s for NGF against 8.5 kg/s for OGF). The design steam thermal output from the SMR reference is equal to 23.2 MW_{th}. The steam thermal output from NGF and OGF case studies are 21.5 MW_{th} and 24.6 MW_{th}, respectively.

As for CO_2 capture performances, the OGF system achieves a CCR of 90.3%, while the NGF option entails a slightly worse separation performance (85.0%). Both NGF and particularly OGF exhibit good results in terms of equivalent emissions, with a resulting relative equivalent CO_2 emission closer to 0 kg CO_2eq/kg H_2 (or even negative, depending on the chosen reference scenario for indirect emissions). The H_2 production efficiency is always lower than in the reference SMR (73.5%), but higher in the OGF case (67.7%) with respect to the NGF case (58.5%). This is due to the additional natural gas input of the MCFC-based plants, needed either in the fuel cell (NGF case) or to compensate the loss of PSA off-gas fuel in the SMR burners (OGF case). The higher natural gas consumption of the MCFC plants involve higher power output and heat export, and overall this leads to slightly lower H_2 equivalent production efficiency (up to 80.4% for NGF and 80.6% for OGF) with respect to the SMR case (up to 83.0%). The good equivalent efficiency and emissions lead to low value of SPECCA (between 0.6 and 1.1 MJ/kg CO_2 for NGF and between 0.5 and 0.6 MJ/kg CO_2 for OGF).

Details of the material balances across the cell for cases NGF and OGF are reported in Table 7. The cathode inlet has larger flowrate in the case NGF (11.63 kmol/s) than OGF (5.95 kmol/s). Both cells are designed to obtain a $1\%_{mol}$ CO_2 concentration at the cathode off-gas, which results in the larger permeation through the cell in NGF (0.89 kmol/s) than OGF (0.38 kmol/s). The permeating flux is composed of CO_2, O_2 and H_2O in fixed ratios. Being designed for NG anodic feed, the NGF case clearly shows a different anode inlet composition with respect to OGF, and in particular the CH_4 contents at the anode and the

CO_2 concentration at the cathode are lower than those in case NGF (2.2% for OGF against 8.8% for NGF, and 4.2% for OGF against 4.7% for NGF, respectively).

As for the resulting cell design, the NGF entails a total cell area of 134532.9 m^2, against 91113.5 m^2 in the OGF case (i.e., -32%), corresponding to a specific CO_2 flux through the cell[1] of 0.145 (g/s)/m^2 and of 0.093 (g/s)/m^2, and CO_2 production densities of 0.196 (g/s)/m^2 and 0.254 (g/s)/m^2 for NGF and OGF, respectively. The much higher CO_2 production density (+30%) of the OGF case shows that a correspondingly smaller MCFC is needed for a given overall CO_2 capture rate in the plant.

Due to the higher capture rate, the higher H_2 production efficiency, the lower SPECCA, and lower total cell area the OGF case is considered superior to the NGF case.

Table 6. Technical performance of the analysed base cases

		SMR	NGF	OGF	OGF-2	
		No capture	**SINGLE CELL**	**SINGLE CELL**	**2-STAGE CELL**	
MCFC cell 1 potential	V	-	**0.70**	**0.70**	**0.65**	MCFC
MCFC cell 2 potential	V	-	**-**	**-**	**0.60**	
Area cell 1	m2	-	134532.9	91113.5	37879.2	
Area cell 2	m2	-	-	-	12914.5	
Total area cell 1 + cell 2	**m2**	**-**	**134532.9**	**91113.5**	**50793.7**	
CO2 utilisation factor	%	-	81.71%	77.5%	87.1%	
Fuel utilisation factor	%	-	**75.0%**	**75.0%**	**70.0%**	
CO2 concentration after FTR combustion	%	-	22.0%	11.8%	11.0%	
CO2 concentration at cathode inlet	%	-	4.7%	4.2%	6.3%	
CO2 concentration at anode outlet (dry basis)	%	-	74.8%	84.8%	81.8%	
CO2 concentration at CPU inlet (dry basis)	%	-	76.2%	85.5%	82.7%	
CO2 production density cell 1	(g/s)/m2	-	0.196	0.254	0.427	
CO2 production density cell 2	(g/s)/m2	-	-	-	0.478	
CO2 flux throughout fuel cell 1	(g/s)/m2	-	0.145	0.093	0.178	
CO2 flux throughout fuel cell 2	(g/s)/m2	-	-	-	0.133	
CO2 permeation through cell 1	kg/s	-	19.6	8.5	6.8	
CO2 permeation through cell 2	kg/s	-	-	-	1.7	
Relative CO2 permeation over storage	%	-	78.6%	37.2%	35.7%	

Table 6 - continued

		SMR	NGF	OGF	OGF-2	
		No capture	**SINGLE CELL**	**SINGLE CELL**	**2-STAGE CELL**	
Natural gas input (SMR+MCFC)	kg/s	8.76	11.02	9.51	9.45	Mass/energy balances
Natural gas thermal input (SMR+MCFC)	**MWLHV**	**407.3**	**512.4**	**442.2**	**439.4**	
Natural gas input to SMR	%	100.0%	68.6%	100.0%	100.0%	
of which to FTR combustion	%	17.4%	17.2%	28.2%	28.8%	
of which to SMR reforming	%	82.6%	82.8%	71.8%	71.2%	
Natural gas input to MCFC anode	%	0.0%	31.4%	0.0%	0.0%	
PSA off-gas	**MWLHV**	**97.1**	**90.8**	**95.0**	**94.6**	
of which to FTR combustion	%	100.0%	100.0%	18.9%	12.2%	
of which to MCFC anode	%	0.0%	0.0%	81.1%	87.8%	
Hydrogen output	Nmc/h	100000	10000	100000	100000	
Hydrogen thermal output	**MWLHV**	**299.5**	**299.5**	**299.5**	**299.5**	
LP+HP steam turbine electric power output	MWel	12.2	10.5	11.1	9.2	Electricity balance
MCFC cell 1 electric power output (net)	MWel	-	74.2	32.1	23.8	
MCFC cell 2 electric power output (net)	MWel	-	-	-	5.6	
Auxiliaries	MWel	-1.2	-9.1	-5.0	-2.4	
CPU compressors, boosters, pump el. p. cons.	MWel	-	-15.2	-11.7	-13.1	
Net electric power output	**MWel**	**10.4**	**59.1**	**22.1**	**19.8**	
Steam export at 160°C / 6 bar	kg/s	10.9	9.9	11.3	12.1	Steam
Steam thermal output	**MWth**	**23.2**	**21.5**	**24.6**	**26.2**	

Table 6 - continued(2)

		SMR	**NGF**	**OGF**	**OGF-2**	
		No capture	**SINGLE CELL**	**SINGLE CELL**	**2-STAGE CELL**	
CO2 emitted	kg CO2/s	23.2	4.4	2.5	1.3	CO2 balance
CO2 captured	kg CO2/s	0.0	24.9	22.8	23.8	
Specific CO2 emission	kg CO2em/kg H2	9.29	1.75	0.98	0.50	
Hydrogen production efficiency	**%**	**73.5%**	**58.5%**	**67.7%**	**68.2%**	Performance
Carbon capture rate (CCR)	**%**	**0.0%**	**85.0%**	**90.3%**	**95.0%**	
Relative equivalent CO2 emissions	**kg CO2eq/kg H2**	**8.3**	**-1.1**	**-0.5**	**-1.0**	Scenario 1
		9.2	**1.5**	**0.8**	**0.3**	Scenario 2
Hydrogen equivalent prod. efficiency	**%**	**82.3%**	**76.8%**	**79.2%**	**79.4%**	Scenario 1
		83.0%	**80.4%**	**80.6%**	**80.6%**	Scenario 2
SPECCA	**MJ/kg CO2**	**0.0**	**1.1**	**0.6**	**0.6**	Scenario 1
		0.0	**0.6**	**0.5**	**0.5**	Scenario 2

Table 7. Material balances across the cell for NGF and OGF

NGF		AR	CH4	CO	CO2	H2	H2O	N2	O2	TOT [kmol/s]
Cathode	Inlet	0.9	0.0	0.0	4.7	0.0	4.3	73.5	16.7	**11.63**
Cathode	Outlet	0.9	0.0	0.0	**1.0**	0.0	3.3	79.5	15.3	10.73
Permeation		0.0	0.0	0.0	49.8	0.0	**16.6**	0.0	**33.6**	**0.89**
Anode	Inlet	0.0	8.8	6.4	8.6	49.7	26.3	0.2	0.0	0.88
Anode	Outlet	0.0	0.0	3.3	36.9	9.0	50.7	0.1	0.0	1.62

OGF		AR	CH4	CO	CO2	H2	H2O	N2	O2	TOT [kmol/s]
Cathode	Inlet	0.9	0.0	0.0	4.2	0.0	6.8	74.1	14.0	**5.95**
Cathode	Outlet	0.9	0.0	0.0	**1.0**	0.0	6.1	79.2	12.7	5.56
Permeation		0.0	0.0	0.0	50.0	0.0	**16.7**	0.0	**33.3**	**0.38**
Anode	Inlet	0.0	2.2	12.9	34.1	24.3	25.4	1.2	0.0	0.75
Anode	Outlet	0.0	0.0	3.2	50.8	5.0	40.1	0.8	0.0	1.04

OGF-2: Results of two-stage MCFC with inter-cooling

This section details the main results in terms of mass and energy balances, electricity balance, steam balance, CO_2 balance and CO_2 avoidance performance for the following case studies (see also Table 6):

- OGF: integrated PSA-MCFC SMR. Cell potential set equal to 0.7 V, fuel utilisation factor of 0.75.
- OGF-2: integrated PSA-two-stage MCFC. Cell 1 potential set equal to 0.65 V and cell 2 potential equal to 0.6 V, fuel utilisation factor of 0.70.

The use of two cells in series with inter-cooling has a positive effect on the performance of the system in terms of CO_2 separation (CCR increases over 95%, with stable H_2 production efficiency). Case OGF-2 is characterised by a lower air dilution at the inlet of the cathode hence, higher CO_2 concentration, which produces a higher CO_2 utilisation factor (higher than 87%). OGF-2 represents a highly beneficial design to maximise the capabilities of the cells of separating CO_2 and, at the same time, this configuration is also characterised by a higher electric power output due to the combined effects of higher electricity output from the cells and lower utilities consumptions for air inlet to the cathode. The overall result in terms of SPECCA is comparable between cases OGF and OGF-2.

Case OGF-2 (fuel utilisation factor of 70%) is detailed in terms of material balances across the cells in Table 8. The CO_2 concentration at the first cathode inlet is 6.3%, part of it permeates to the first anode (0.16 kmol/s), while the remaining goes to the second cathode (the latter has with an inlet molar fraction of CO_2 of 2.1%). From the second cathode, part of the CO_2 permeates to the second anode (0.04 kmol/s), while the rest is vented with the off-gas (with molar concentration of CO_2 of 1%). As shown in Table 8, the first cathode outlet (3.19 kmol/s) corresponds to the second cathode inlet (3.19 kmol/s), and the first anode outlet (1.06 kmol/s) corresponds to the second anode inlet (1.06 kmol/s).

As for the areas of the cells, OGF-2 configuration is characterised by a total cell area of 50793.7 m2, which is 44% less than the single cell OGF case.

Table 8. Material balances across cell 1 and cell 2 for OGF-2 with fuel utilisation of 70%.

Cell 1 - DV=0.65 V - FU=0.70								Mole fractions [%]		TOT
OGF-2		AR	CH4	CO	CO2	H2	H2O	N2	O2	[kmol/s]
Cathode	Inlet	0.9	0.0	0.0	6.3	0.0	10.6	72.5	9.7	**3.50**
Cathode	Outlet	0.9	0.0	0.0	**2.1**	0.0	10.0	79.5	7.4	3.19
Permeation		0.0	0.0	0.0	50.0	0.0	**16.7**	0.0	**33.3**	**0.31**
Anode	Inlet	0.0	2.1	12.9	34.3	23.9	25.3	1.5	0.0	0.82
Anode	Outlet	0.0	0.0	6.1	46.6	9.4	36.7	1.2	0.0	1.06

Cell 2 - DV=0.60 V - FU=0.70								Mole fractions [%]		TOT
OGF-2		AR	CH4	CO	CO2	H2	H2O	N2	O2	[kmol/s]
Cathode	Inlet	0.9	0.0	0.0	2.1	0.0	10.0	79.5	7.4	**3.19**
Cathode	Outlet	1.0	0.0	0.0	**1.0**	0.0	9.9	81.4	6.7	3.11
Permeation		0.0	0.0	0.0	49.7	0.0	**16.6**	0.0	**33.8**	**0.08**
Anode	Inlet	0.0	0.0	6.1	46.6	9.4	36.7	1.2	0.0	1.06
Anode	Outlet	0.0	0.0	3.9	49.8	6.1	39.0	1.1	0.0	1.11

List of reference signs

1: carbon capture system
2: pressure swing adsorption unit
3: product gas
4: tail gas
5: molten carbonate fuel cell
6: cathode
7: anode
8: CO_2 separation means
9: water gas shift reactor
10: steam methane reformer
11: electric energy
12: de-sulfurization unit
13: natural gas
14: CO_2 depleted cathode outlet stream
15: captured CO_2
16: cathode inlet stream
17: cooling means

Further disclosure

The present invention further provides the following items:

1. Carbon capture system (1), comprising:

a pressure swing adsorption unit (2) for producing a product gas (3) and a tail gas (4) comprising at least one carbonaceous gas, and

a molten carbonate fuel cell (5) having a cathode (6) and an anode (7) for transferring CO_2 from the cathode (6) to the anode (7),

wherein the anode (7) is in fluid communication with the pressure swing adsorption unit (2) for receiving at least a portion of the tail gas (4) as an inlet stream.

2. The system (1) according to item 1, wherein the molten carbonate fuel cell (5) is configured to run in electricity production mode and/or configured to not run in electrolysis mode.

3. The system (1) according to item 1 or 2, wherein the molten carbonate fuel cell (5) is electrically connected to an electricity consumption means and/or an electricity storage means.

4. The system (1) according to any of the preceding items, wherein the molten carbonate fuel cell (5) is a multi-stage fuel cell, preferably a two-stage fuel cell.

5. The system (1) according to item 4, wherein the molten carbonate fuel cell (5) is a two-stage fuel cell having a first cell and a second cell which are in fluid connection, wherein the fluid connection comprises one or more cooling means and/or one or more mixing means.

6. The system (1) according to any of the preceding items, further comprising a CO_2 separation means (8) which is in fluid communication with the anode (7) of the molten carbonate fuel cell (5) for receiving an outlet stream from the anode (7), wherein the CO_2 separation means (8) is configured to separate CO_2 from the outlet stream from the anode (7).

7. The system (1) according to item 6, wherein the pressure swing adsorption unit (2) is in fluid connection with the CO_2 separation means (8) for receiving an outlet stream from the CO_2 separation means (8) as an inlet stream.

8. The system (1) according to item 6 or 7, wherein the CO_2 separation means (8) is a low temperature phase change separation unit.

9. The system (1) according to any of items 6 to 8, further comprising a water-gas-shift reactor (9) between the anode (7) of the molten carbonate fuel cell (5) and the CO_2 separation means (8).

10. The system (1) according to any of items 6 to 9, wherein the CO_2 separation means (8) allows for a separation of CO_2 having a purity of 95 mol% or more.

11. The system (1) according to any of the preceding items, wherein the pressure swing adsorption unit (2) is in fluid connection with a steam methane reformer (10) for receiving an outlet stream from the steam methane reformer as an inlet stream.

12. A method of capturing carbon, comprising:

    producing a product gas (3) and a tail gas (4) by pressure swing adsorption, wherein the tail gas comprises at least one carbonaceous gas, and

    feeding at least a portion of the tail gas (4) as an inlet stream to an anode (7) of a molten carbonate fuel cell (5),

    wherein the molten carbonate fuel cell (5) produces electric energy (11) and transfers CO_2 from a cathode (6) to the anode (7).

13. Use of a system (1) according to any of items 1 to 11 for capturing CO_2.

14. Use of a pressure swing adsorption unit (2) and/or a molten carbonate fuel cell (5) in a system (1) according to any of items 1 to 11, or in a method according to item 12.

15. CO_2 captured with a system (1) according to any of items 1 to 11, or captured with a method according to item 12, or captured by the use according to item 13.

Claims

1. Carbon capture system (1), comprising:

   a pressure swing adsorption unit (2) for producing a product gas (3) and a tail gas (4) comprising at least one carbonaceous gas, and

   a molten carbonate fuel cell (5) having a cathode (6) and an anode (7) for transferring CO_2 from the cathode (6) to the anode (7), wherein the molten carbonate fuel cell (5) is a multi-stage fuel cell,

   wherein the anode (7) is in fluid communication with the pressure swing adsorption unit (2) for receiving at least a portion of the tail gas (4) as an inlet stream.

2. The system (1) according to claim 1, wherein the molten carbonate fuel cell (5) is configured to run in electricity production mode and/or configured to not run in electrolysis mode.

3. The system (1) according to claim 1 or 2, wherein the molten carbonate fuel cell (5) is electrically connected to an electricity consumption means and/or an electricity storage means.

4. The system (1) according to any of the preceding claims, wherein the molten carbonate fuel cell (5) is a two-stage fuel cell.

5. The system (1) according to claim 4, wherein the molten carbonate fuel cell (5) is a two-stage fuel cell having a first cell and a second cell which are in fluid connection, wherein the fluid connection comprises one or more cooling means and/or one or more mixing means.

6. The system (1) according to any of the preceding claims, further comprising a CO_2 separation means (8) which is in fluid communication with the anode (7) of the molten carbonate fuel cell (5) for receiving an outlet stream from the anode (7), wherein the CO_2 separation means (8) is configured to separate CO_2 from the outlet stream from the anode (7).

7. The system (1) according to claim 6, wherein the pressure swing adsorption unit (2) is in fluid connection with the CO_2 separation means (8) for receiving an outlet stream from the CO_2 separation means (8) as an inlet stream.

8. The system (1) according to claim 6 or 7, wherein the CO_2 separation means (8) is a low temperature phase change separation unit.

9. The system (1) according to any of claims 6 to 8, further comprising a water-gas-shift reactor (9) between the anode (7) of the molten carbonate fuel cell (5) and the CO_2 separation means (8).

10. The system (1) according to any of claims 6 to 9, wherein the CO_2 separation means (8) allows for a separation of CO_2 having a purity of 95 mol% or more.

11. The system (1) according to any of the preceding claims, wherein the pressure swing adsorption unit (2) is in fluid connection with a steam methane reformer (10) for receiving an outlet stream from the steam methane reformer as an inlet stream.

12. A method of capturing carbon, comprising:

producing a product gas (3) and a tail gas (4) by pressure swing adsorption, wherein the tail gas comprises at least one carbonaceous gas, and

feeding at least a portion of the tail gas (4) as an inlet stream to an anode (7) of a molten carbonate fuel cell (5), wherein the molten carbonate fuel cell (5) is a multi-stage fuel cell,

wherein the molten carbonate fuel cell (5) produces electric energy (11) and transfers CO_2 from a cathode (6) to the anode (7).

13. Use of a system (1) according to any of claims 1 to 11 for capturing CO_2.

14. Use of a pressure swing adsorption unit (2) and/or a molten carbonate fuel cell (5) in a system (1) according to any of claims 1 to 11, or in a method according to claim 12.

15. CO_2 captured with a system (1) according to any of claims 1 to 11, or captured with a method according to claim 12, or captured by the use according to claim 13.

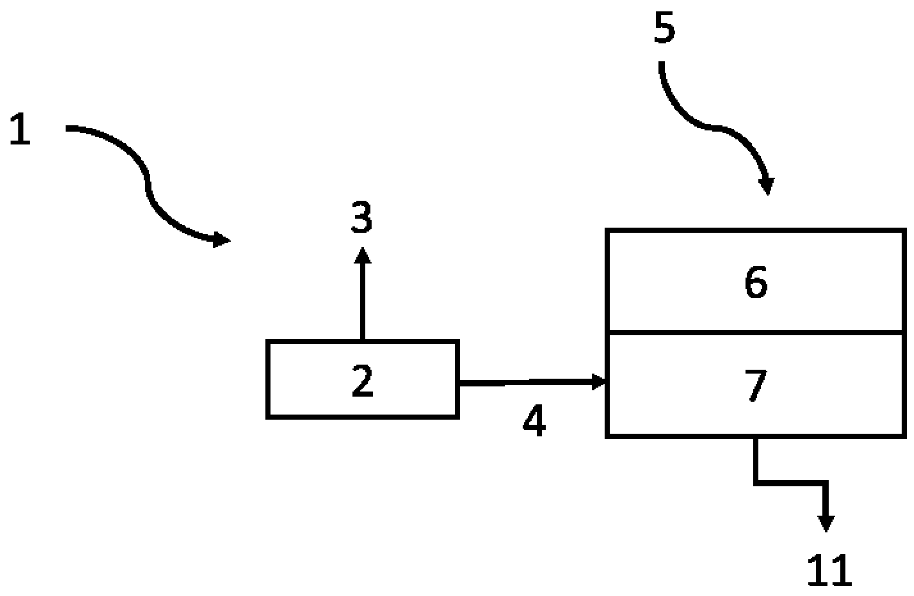

Fig. 1

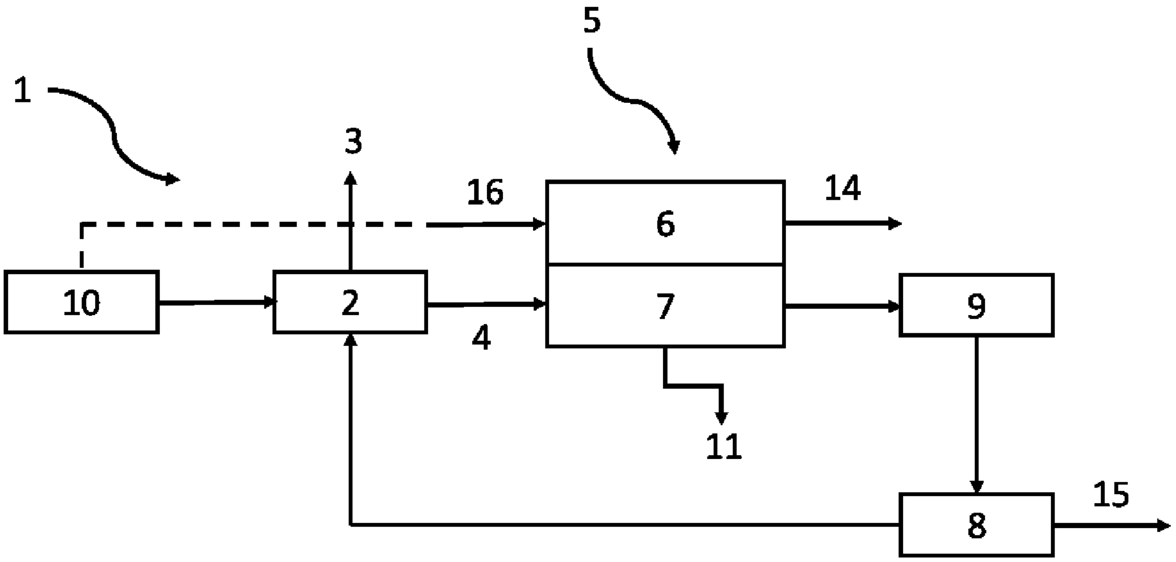

Fig. 2

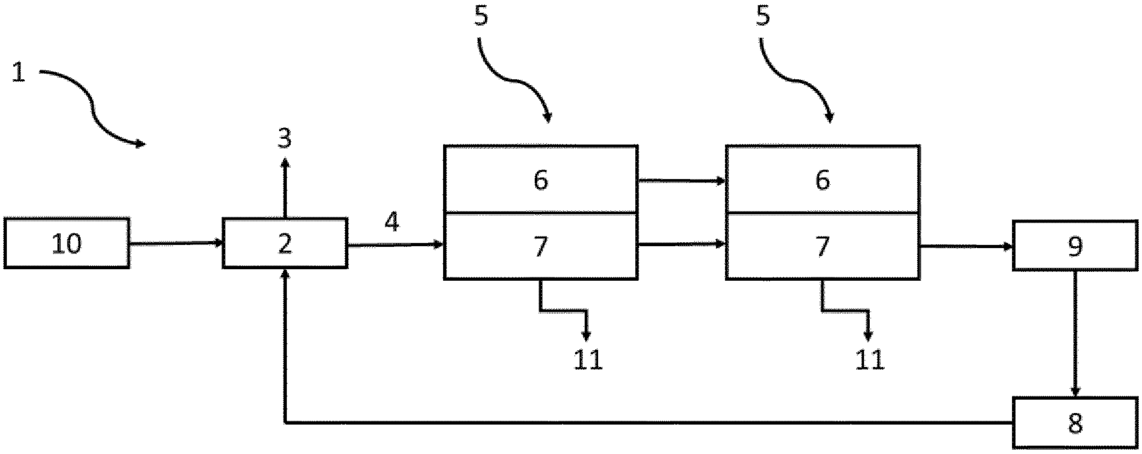

Fig. 3

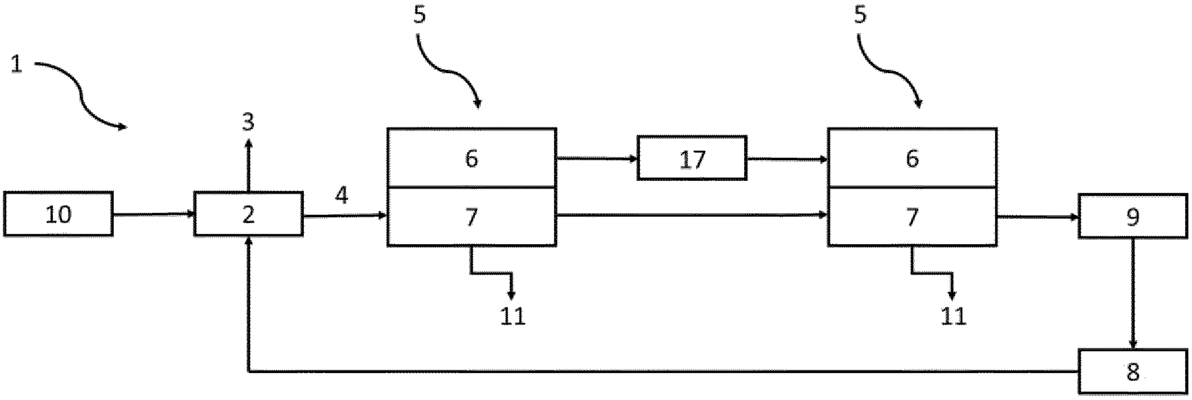

Fig. 4

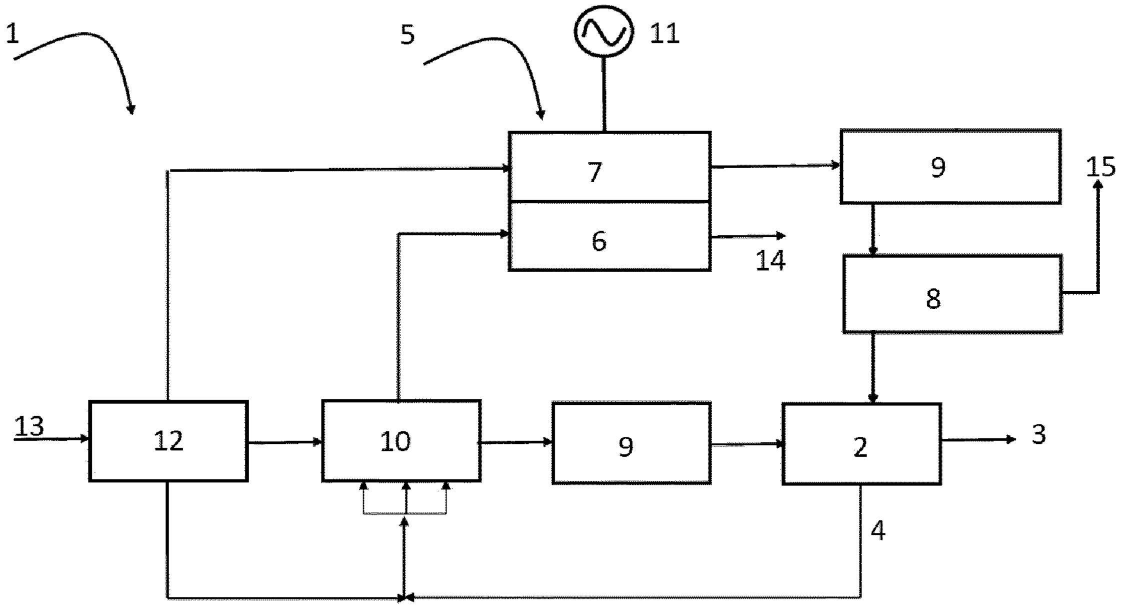

Fig. 5

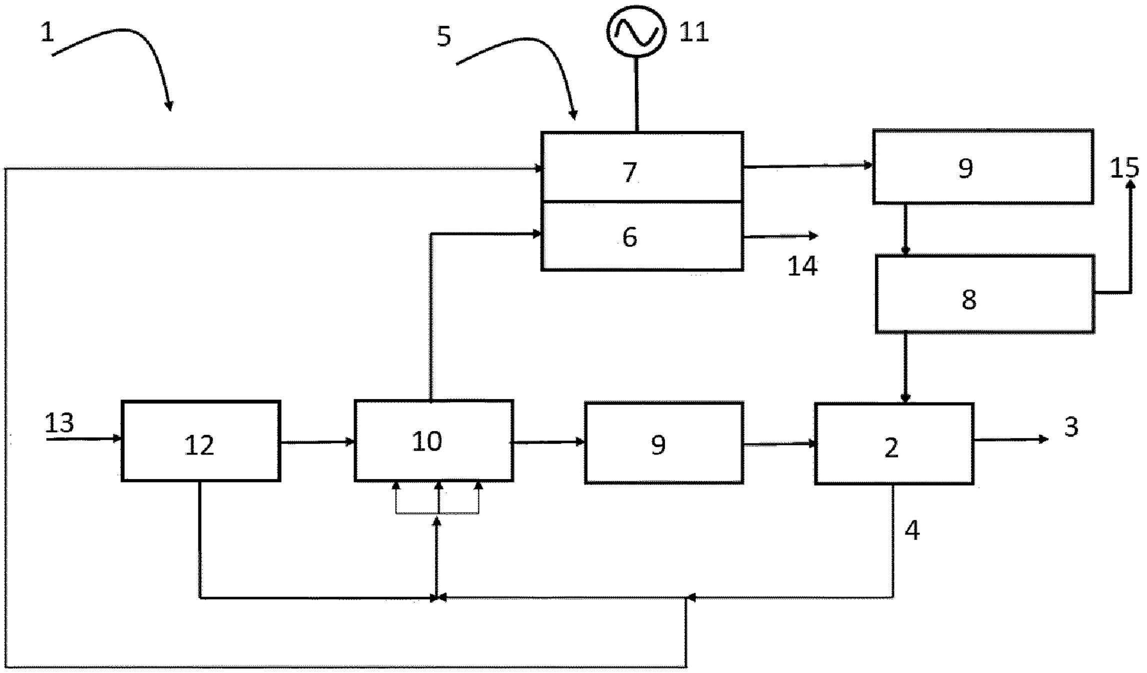

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/051521

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/047 C01B3/00 H01M8/0612 H01M8/24
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 C01C H01M C01B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 12 May 2023	Date of mailing of the international search report 25/05/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Ruiz Martinez, Maria

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