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(54) **Title:** METHODS FOR THE REMOVAL OF CO₂ FROM ATMOSPHERIC AIR OR OTHER CO₂-CONTAINING GAS IN ORDER TO ACHIEVE CO₂ EMISSIONS REDUCTIONS OR NEGATIVE CO₂ EMISSIONS

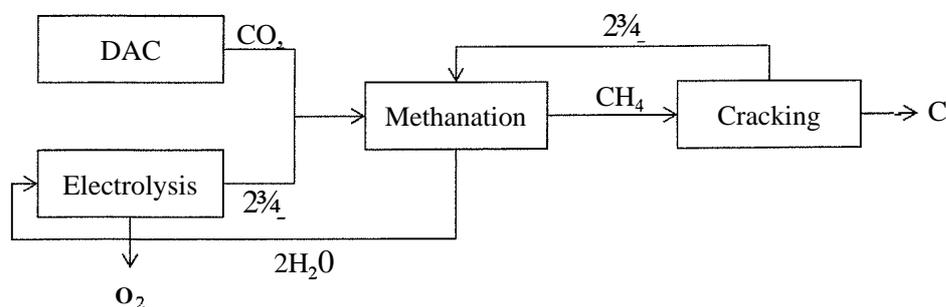


FIG. 2

(57) **Abstract:** A process for the production of at least one of amorphous carbon or graphite, preferably of carbon black, from atmospheric air, biogas or flue gas CO₂ is given, including at least the following steps: a) isolation of concentrated CO₂ of a concentration of at least 50% v/v from atmospheric air, green house air or flue gas preferably by means of a cyclic adsorption/desorption process on amine-functionalized adsorbents; b) conversion of said captured CO₂ into a gaseous or liquid saturated or unsaturated hydrocarbon by hydrogenation; c) cracking of said saturated or unsaturated hydrocarbon to at least one of amorphous carbon or graphite, preferably carbon black, wherein the H₂ resulting from step c) is at least partially used in the hydrogenation of step b).

WO 2018/099709 A1

TITLE

METHODS FOR THE REMOVAL OF CO₂ FROM ATMOSPHERIC AIR OR OTHER CO₂-CONTAINING GAS IN ORDER TO ACHIEVE CO₂ EMISSIONS REDUCTIONS OR NEGATIVE CO₂ EMISSIONS

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TECHNICAL FIELD

The present invention relates to methods for the removal of CO₂ from atmospheric air or other CO₂-containing gases such as biogas or flue gases in order to achieve CO₂ emissions reductions or negative CO₂ emissions.

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PRIOR ART

In order to limit climate change to acceptable levels it is not only necessary to reduce CO₂ emissions in the near future to zero but also to achieve negative CO₂ emissions. More than 87% of modeling scenarios of the Intergovernmental Panel on Climate Change ("IPCC") consistent with 2°C of warming involve large scale deployments of negative emissions technologies ("NET") on a scale of several gigatons of CO₂ annually. Several possibilities exist in order to achieve negative emissions, e.g. combustion of biomaterials for the generation of electricity combined with CO₂ capture from the combustion flue gas and subsequent CO₂ sequestration ("BECCS"), or the direct air capture of CO₂ ("DAC") with machines and subsequent CO₂ sequestration. Although underground CO₂ sequestration is a technically mature technology per se, concerns exist with regard to safe permanent storage of CO₂ underground and most importantly the societal acceptance of underground CO₂ sequestration is considered low. Consequently it will be necessary to identify alternatives to underground CO₂ sequestration with increased societal acceptance and no concerns with respect to safe permanent storage.

25

WO2016/161998 discloses a process for the production of synthetically produced methane. Hydrogen from an electrolytic arrangement which is operated by means of regeneratively generated electric energy and carbon dioxide are reacted in a methane synthesis, the carbon dioxide being produced from an air/gas flow by means of a carbon dioxide recovery system by way of a reversible adsorption process. The heat for reversing the adsorption process is taken at least to some extent from the exothermic methane synthesis.

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WO2015/055349 discloses a method, comprising : a) an industrial operation plant generating CO₂ comprised in a flue gas; said industrial operation plant performing an

industrial combustion or calcination process or metallurgical process; b) a CO₂ separating unit for separating a CO₂ containing gas mixture from the flue gas; c) an electrolysis unit for splitting water by electrolysis to produce H₂ and O₂; d) a methanation unit for converting the CO₂ containing gas mixture and the H₂ by a methanation reaction to a methane rich gas which can be used as or upgraded to synthetic natural gas.

The final product in WO2016/161998 and WO2015/055349 is always methane.

N.Z. Muradov, Int. J. Hydr. Ener, 18(3), p21 1-215 as well as L. Fulcheri et al, Int. J. Hydr. Ener, 20(3), p197-202 disclose the thermocatalytic decomposition of methane to elemental carbon and mention that the elemental carbon can be stored for future use, there is however not in the context of carbon dioxide capture from air.

SUMMARY OF THE INVENTION

The present invention therefore relates to new methods for the removal of CO₂ from atmospheric air or other CO₂-containing gases such as biogas or flue gases in order to achieve CO₂ emissions reductions or negative CO₂ emissions.

The solution to the problem is the method to produce at least one of amorphous carbon or graphite, preferably carbon black, in a multi-step method from CO₂ captured from atmospheric air or other CO₂-containing gases as defined in the claims.

Generally several possibilities exist in order to lastingly eliminate CO₂ from atmospheric air or other CO₂-containing gases without the need to sequester it the known way, i.e. without the need to store the CO₂ underground to remove it from the carbon circle:

One possibility is to consider new and safer ways of removal of the CO₂ as such from the system, as alternatives to the underground sequestration of CO₂, including deep sea storage or the like.

A further possibility is to react CO₂ with secondary substances to yield stable compounds which can be either stored or even commercially used. In this sense e.g. carbonation of alkali compounds as described in US 8,709,151.

A further possibility is to convert the captured CO₂ chemically to another molecule which can be safely removed from the carbon circle and stored.

Yet another possibility is to reduce the CO₂ molecule to eventually yield elementary carbon in the form of at least one of amorphous carbon or graphite, which is considered as stable, and can either be stored safely and permanently or used in commercial processes.

The straightforward way of achieving this would be the direct one step conversion (reduction) of CO₂ into at least one of amorphous carbon or graphite, which however is burdened with some practical obstacles.

The present invention proposes to convert CO₂, captured in a DAC process or from other
5 CO₂-containing gases such as biogas or flue gases, in a first hydrogenation step to a hydrocarbon moiety, preferably methane, and to, in a subsequent reduction step, convert the hydrocarbon moiety into at least one of amorphous carbon or graphite, in particular into carbon black. Preferably the process involves a parallel H₂O cracking to elementary oxygen and to elementary hydrogen.

10 So far no prior art exists describing the direct air capture of CO₂, subsequent conversion of CO₂ to hydrocarbons by reacting with hydrogen and final cracking of hydrocarbons to yield at least one of amorphous carbon or graphite and hydrogen in order to achieve CO₂ emissions reductions or negative CO₂ emissions.

WO2014/170184, WO2015/185434 and WO2016/005226 describe devices and processes
15 for the direct capture of CO₂ from ambient air.

EP-A-2682450 describes methods for the production of methane from CO₂ and hydrogen via an electrochemical route. WO2011/003081 describes methods for the production of methane from CO₂ and hydrogen via a biological route and WO2016/161998 describes
20 methods for the production of methane, other gaseous or liquid hydrocarbon products from atmospheric CO₂ and hydrogen via electrochemical routes.

The terminology used of at least one of amorphous carbon or graphite as used in the instant specification shall include allotropic forms of atomic carbon which are different from diamond. Therefore this shall also include fullerenes including buckyballs, carbon
25 nanotubes, carbon nanobuds and nanofibers, glassy carbon, carbon nanofoam and linear acetylenic carbon. It shall also include preferably forms commonly designated as carbon black, activated carbon and the like.

Production of solid carbon from fossil hydrocarbon sources as such is known, e.g. production of carbon black from liquid hydrocarbons in an oven furnace as described in
WO2008/148641 or production of carbon black from methane in a brick reactor ("thermal
30 black") as described in US 5,817,287.

As mentioned above, there is no prior art describing the complete process starting from direct air capture of CO₂, subsequent conversion of CO₂ to hydrocarbons by combination with hydrogen and final cracking of hydrocarbons to yield carbon and hydrogen, in order

to achieve CO₂ emissions reductions or negative CO₂ emissions.

Generally speaking the present invention proposes the following process:

A process for the production of at least one of amorphous carbon or graphite, preferably of carbon black, from atmospheric air, biogas or flue gas CO₂ including at least the following
5 steps, preferably in given order:

a) isolation of concentrated CO₂ of a concentration of at least 50% v/v from atmospheric air, biogas or flue gas, preferably by means of a cyclic adsorption/desorption process on amine-functionalized adsorbents;

b) conversion of said captured CO₂ into a gaseous or liquid saturated or unsaturated
10 hydrocarbon by hydrogenation;

c) cracking of said saturated or unsaturated hydrocarbon to at least one of amorphous carbon or graphite, preferably to carbon black,

wherein the H₂ resulting from step c) is at least partially used in the hydrogenation of step b).

15 At least by way of the provision that the H₂ resulting from step c) is at least partially used in the hydrogenation of step b) provides for the fact that steps b) and c) are not a simple juxtaposition. As a matter of fact, it was found unexpectedly that these two steps can most efficiently be connected with each other in terms of efficiency and reliability by crossover
20 feedback use of the generated H₂. At least this aspect is not mentioned in any prior art document, the documents only disclose steps a), in some cases in combination with b) but never the combination of a)/b) with c) together with the provision that the hydrogen generated in step c) is used for step b). Further the prior art aims to maximize the yield of both, the hydrogenation of step b) as well as the cracking of step c). Herein it was found
25 that the hydrocarbon is just an intermediate and neither complete conversion in steps b) and c) are required, which further allows efficient combination.

As for the step a), reference is e.g. made to processes as described in WO-A-2016/005226 the disclosure of which is incorporated by way of reference for this step.

As for the step b), reference is e.g. made to processes as described in EP-A-2682450 or WO2016/161998 the disclosure of which is incorporated by way of reference for this step.

30 As for the step c), reference is e.g. made to processes as described in US 5,817,287 or Geissler et al Chemical Engineering Journal 299 (2016) 192-200 the disclosure of which is incorporated by way of reference for this step.

The saturated or unsaturated hydrocarbon is preferably selected from the group consisting

of: linear, branched or cyclic alkanes, linear, branched or cyclic alkenes, alkynes, or a mixture thereof. Further preferably the saturated or unsaturated hydrocarbon is selected from the group consisting of: methane, ethane, propane, butane, ethylene, propene, butylene, or a mixture thereof.

5 Further H₂ required for step b) can preferably be provided via splitting of H₂O, wherein the splitting of H₂O is preferably a photocatalytic splitting, a photoelectrochemical splitting, a radiolysis, a photobiological splitting, (thermal) plasma splitting or an electrolysis, or a combination thereof. Alternatively the H₂ required for step b) can be obtained by (thermal)
10 cracking of saturated or unsaturated hydrocarbon, in particular of methane, stemming from fossil or biogenic sources, to yield hydrogen and at least one of amorphous carbon or graphite, where the at least one of amorphous carbon or graphite is further utilized or sequestered.

The saturated or unsaturated hydrocarbon can be selected to be methane, and the further two moles H₂ per mole CO₂ required for step b) in this case can be provided via (thermal)
15 cracking of the methane to yield hydrogen and carbon, according to step c).

The concentration of the concentrated CO₂ provided in step a) is preferably in the range of 50-100% v/v, more preferably in the range of 90-100% v/v.

According to a preferred embodiment, the saturated or unsaturated hydrocarbon is selected to be methane, and cracking of methane in step c) is performed thermally above a
20 temperature of 800°C, preferably above 900°C, most preferably in a range of 1100°C-1600°C.

The methane cracking in step c) can be performed in an electrically heated reactor, preferably using renewable electricity.

At least one of steps a) - c) is preferably performed continuously and/or cyclically.

25 Preferably the step c), in the form of methane cracking, is carried out continuously.

The saturated or unsaturated hydrocarbon is preferably selected to be methane, and the methane cracking in step c) is performed in a liquid metal reactor, preferably using liquid tin.

Atmospheric source concentrated CO₂ is preferably provided in step a) by a cyclic
30 adsorption/desorption process, preferably using an amine-functionalized adsorbent where desorption of CO₂ is performed by heating of the adsorbent to above 50°C, preferably above 80°C, more preferably above 90°C, preferably in combination with reducing the pressure to below 500mbar(abs).

The amine-functionalized adsorbent for the DAC process or to capture from other CO₂-containing gases such as biogas or flue gases according to step a) can be a weak ion exchange resin, amine-functionalized cellulose, as described in WO2012/168346, amine-functionalized silica, amine-functionalized carbon or other solid supports featuring amine
5 functions. The amine functions on the solid support can be incorporated either through impregnation or covalent bonds.

The heat stored in the produced carbon and hydrogen in step c) can be used to preheat the hydrocarbon, preferably the methane, entering the reactor of step c) and/or is used to provide heat for the CO₂ desorption step of the CO₂ capture device in step a).

10 The heat recovery of products from step c) to serve step a) is not obvious from prior art and further provides for the fact that the process described herein is not a simple juxtaposition.

Parts of the hydrogen needed for step b), in particular in the form of methanation, can be provided by recycling product hydrogen from the methane cracking reaction and the remainder can be supplied by electrolysis of water using electricity, preferably renewable
15 electricity, where electrolysis is performed by either alkali, polymer electrolyte membrane or solid oxide electrolyzers. Alternatively the remainder H₂ required for step b) can be obtained by thermal cracking of methane, stemming from fossil or biogenic sources, to yield hydrogen and at least one of amorphous carbon or graphite, preferably carbon black, where at least one of amorphous carbon or graphite, preferably carbon black, is further
20 utilized or sequestered.

The heat release from step b), in particular in the form of methanation reaction, can be used to supply heat for the CO₂ desorption step of the CO₂ capture device.

The produced at least one of amorphous carbon or graphite, preferably carbon black, can be used e.g. in metallurgy as carburizer for tungsten carbide or silicon carbide, as reducing
25 agent for solar grade silicon, as rubber filler, as addition for refractory bricks, as black pigment in plastics or concrete, as high temperature insulation, as asphalt or concrete binder or as construction aggregate or sequestered above or underground.

The present invention thus in particular relates to methods for the production of at least one of amorphous carbon or graphite, preferably carbon black, from atmospheric CO₂ in order
30 to achieve CO₂ emissions reductions or negative CO₂ emissions. In a preferred embodiment the at least one of amorphous carbon or graphite, preferably carbon black, is produced from atmospheric CO₂ provided via an adsorption/desorption process on amine-functionalized adsorbents, further providing H₂ via electrolysis of H₂O, subsequent

method might be considered energetically inefficient and consequently not economical. Surprisingly it was however found that above process steps can be combined in an energetically favorable manner yielding an overall economical method for splitting of CO₂. The overall energy consumption per mole of atmospheric CO₂ split to C of an energetically favorable technical process implementation is:

1. CO₂ capture from air via an adsorption/desorption process on amine-functionalized adsorbents, where CO₂ desorption is performed by heating the adsorbent: > 150-300kJ/mol C, where > 25kJ/mol C are required in the form of electricity and the remainder in the form of heat at 50-120°C

2. Electrolysis of H₂O using renewable electricity:

Industrially available alkali or polymer electrolyte membrane electrolysis works with an efficiency of 65-75%, emerging solid oxide electrolysis with an efficiency of up to 85%, so that for the electrolysis 570-740 kJ/mol C are required, depending on the type of electrolysis used. For solid oxide electrolysis another 41 kJ/mol H₂O of heat input have to be added for evaporation of H₂O prior to electrolysis.

3. Methanation of CO₂ and H₂:

Methanation proceeds without significant conversion losses. For technical systems heat losses and heat exchange efficiencies are considered so that in total 90% of the exothermic heat release (amounting to -149 kJ/mol C) can be recovered and used to supply a large share of the energy demand of the DAC system.

4. Cracking of methane:

Cracking of methane proceeds without significant conversion losses. For technical systems heat losses and heat exchange efficiencies are considered so that in total the heat requirement is 85 kJ/mol C. Further a technical system requires heating of the educts to the specified reaction temperature. The resulting products leave the reactor at the specified reaction temperature and heat stored in the products can be recovered for heat regeneration processes as further laid out below.

Consequently an energetically favorable technical process implementation is considered to consume a minimum energy input of roughly 750kJ/mol C. Preferably such energy input is in the form of renewable electricity.

When using above described process to produce at least one of amorphous carbon or graphite, preferably carbon black, for further utilization and consequently comparing above process to existing cracking of fossil methane (thermal black) reveals that above process is

energetically more favorable per mol of C obtained. In order to obtain 1 mol of C by thermal cracking of fossil methane 1 mol of CH₄ needs to be supplied, which has a standard (25 °C, 101kPa) net enthalpy of combustion (assuming the combustion products are gaseous) of 803 kJ/mol CH₄, which can be considered as the energy input into the process. The released hydrogen is combusted and used to heat the methane cracking reactor and the remainder of the heat is dissipated or in rare cases used for district heating networks. If renewable electricity has the same cost or even lower than fossil CH₄ per energy value than above process implementation can be economically more favorable, which is surprising.

10 Further comparing above process for the production of at least one of amorphous carbon or graphite, preferably carbon black, for further utilization to the conventional process of e.g. thermal black production reveals that due to the high purity of CO₂ captured from the atmosphere and the consequently high purity of the CH₄ produced through hydrogenation of atmospheric CO₂, the resulting at least one of amorphous carbon or graphite, in particular in form of carbon black, has high purity offering economic advantages.

15 The major motivation for above process is the goal of CO₂ emissions reductions or the creation of negative CO₂ emissions. Comparing above process to other processes to achieve emissions reductions, e.g. the production of renewable methane from atmospheric CO₂, the comparison reveals that per mole of CH₄ produced from atmospheric CO₂ and renewable H₂ energy input of well above 1300kJ/mol CH₄ is required, which is significantly higher than the energy consumption of above described process. Therefore the above process offers significant, inter alia economic advantages for CO₂ emissions reductions or negative CO₂ emissions.

20 It is surprising that subsequent splitting of CH₄ reduces total process energy consumption, majorly due to the possibility to recycle H₂, which in the process described above does not need to be combusted in order to supply process heat. Process heat is rather more efficiently provided by renewable electricity reducing conversion losses.

25 So far no industrial technologies for direct splitting of CO₂ are available. In contrary all process steps of the herein described method can be implemented on an industrial scale, allowing splitting of atmospheric CO₂ via the proposed route of methanation and subsequent methane cracking. This patent application describes important embodiments for energy and cost efficient combination of all process steps.

Cracking of methane to yield carbon and hydrogen as such is well known and industrial-

scale technology and is available supplying roughly 100'000 tons of thermal black for market applications annually. Industrial processes for the production of thermal black rely on a batch process, where in a first step a brick reactor is heated by the combustion of hydrogen and once it reaches the desired reaction temperature, methane is introduced, which decomposes on the hot brick walls to yield C and H₂. Once the brick temperature drops below a threshold value the methane feed is stopped and switched to a second brick reactor, which was heated by combustion of hydrogen supplied as product from the first brick reactor. Although the existing industrial technology for methane cracking would work for the method proposed in this patent application, it is preferred to use electricity, preferably renewable electricity, in order to supply the heat for the methane cracking reaction, rather than burning the produced hydrogen, in order to achieve high system efficiencies. Further it is favorable to use a continuous methane cracking process rather than a batch process in order to avoid cyclic heating and cooling of the reactor and rather achieve constant product output. Concepts of continuous methane cracking reactors which can be heated by electricity are known in the scientific literature, as e.g. reported in Chemical Engineering Journal 299 (2016) 192-200.

Further embodiments of the invention are laid down in the dependent claims.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described in the following with reference to the drawings, which are for the purpose of illustrating the present preferred embodiments of the invention and not for the purpose of limiting the same. In the drawings,

Fig. 1 shows in a) the most general conversion scheme involving DAC and subsequent conversion via a hydrocarbon to elementary carbon and in b) the situation where the hydrocarbon is alkene so as to have a closed stoichiometry;

Fig. 2 a material flow diagram of the method for the production of carbon from atmospheric CO₂ via methanation;

Fig. 3 shows the energy consumption of the process steps of the method for the production of carbon from atmospheric CO₂, wherein all enthalpy of formation values are considered at standard states of 25 °C and 101 kPa..

DESCRIPTION OF PREFERRED EMBODIMENTS

Figure 1a shows the most general conversion scheme for the sequence DAC (or capturing from other CO₂-containing gases such as biogas or flue gases) → hydrocarbon → elementary carbon in the form of at least one of amorphous carbon or graphite, in particular of carbon black. The first step is the step of direct air capture, either directly
 5 from the atmosphere with a CO₂ content in the range of above 350 ppm v/v or from flue gas with a CO₂ content in the range of 2-20% v/v, or 5 - 15% v/v, or from biogas with a CO₂ content in the range of 30 - 70% v/v, or 40 - 55% v/v. The isolated CO₂, in liquid or gaseous form, is subjected to a step of hydrogenation to a hydrocarbon. Depending on the type of reaction of the hydrogenation a further supply of H₂ beyond the ½ nH₂
 10 indicated may be required. In the following step the hydrocarbon is cracked to at least one of amorphous carbon or graphite, preferably carbon black.

Figure 1b) shows one possible implementation of such a process where the hydrocarbon into which the captured CO₂ is converted is alkene.

In both cases of figures 1a) and b) the elementary oxygen resulting from the hydrogenation
 15 process is either obtained directly or indirectly. In case where the oxygen is obtained indirectly this usually means that first water results from the hydrogenation which water is subsequently split into hydrogen and oxygen, and the hydrogen of that splitting is used again in the hydrogenation process as illustrated in figure 2. It is also possible that the water resulting from the hydrogenation process is removed from the system and the
 20 additional hydrogen required in the hydrogenation process in this case where water is generated is provided by a different source, e.g. by cracking of additional hydrocarbon from a different source.

Figure 2 schematically shows the situation where the conversion takes place via methane as the hydrocarbon. In this case per mole C two additional moles H₂ are required for the
 25 methanation, which are made available via a step of cracking H₂O, again offering the benefit of having a closed system and, as in case of the scheme according to Fig. 1b, a total overall reaction equation of

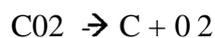


Figure 3 finally shows the scheme according to figure 2 with the thermodynamic
 30 considerations showing the unexpected economic feasibility of the process using the methanation route. Given with solid arrows are the material transport pathways, dashed arrows indicate possible heat transport pathways allowing for an overall optimized thermal structuring of the process for optimum energy use, as will also be detailed further below.

Example 1. Heat recovery from produced carbon and hydrogen

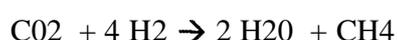
The carbon produced by cracking of methane is leaving the cracking reactor as either hot carbon aerosol or hot carbon particles, which roughly have the same temperature as the methane cracking reactor temperature. The carbon product particles or carbon product aerosol have to be cooled before final collection e.g. through water sprays. The heat transferred from the hot particles or hot aerosol to the water can be collected as steam or hot water, which can then be subsequently used to e.g. supply heat for the operation of the DAC plant. The heat capacity of carbon is 8.5 J/mol/K. Assuming the methane cracking reactor is operated at 1550°C, which is also roughly the temperature of the carbon product, and the carbon product is subsequently cooled to 100°C, the heat which can be recovered from cooling the carbon product is $(8.5 \text{ J/mol carbon/K} * 1450\text{K}) = 12.3 \text{ kJ/mol carbon}$.

Similarly to the carbon product the hydrogen leaving the cracking reactor is cooled together with carbon product. It is possible to cool the hydrogen to a final temperature of 150-300°C, which is a possible operation temperature range of the methanation reactor, so that heating of at least parts of the methane is avoided. Different final cooling temperatures of carbon and hydrogen can be achieved by separation of hydrogen and carbon, e.g. through a cyclone. The isobaric heat capacity of hydrogen is 28.8 J/mol/K. Assuming the methane cracking reactor is operated at 1550°C and the hydrogen product is cooled to 250°C, the heat which can be recovered from cooling the hydrogen product is $(28.8 \text{ J/mol H}_2\text{/K} * 1300 \text{ K} * 2 \text{ mol H}_2\text{/mol carbon}) = 74.9 \text{ kJ/mol carbon}$.

The heat recovered from cooling the carbon and hydrogen product can be used to supply heat for the DAC plant, which requires heat at around 80-120°C for the CO₂ desorption process, as further described in WO2016/005226. The total amount of heat which can be supplied from cooling the carbon and hydrogen product is $12.3 \text{ kJ/mol carbon} + 74.9 \text{ kJ/mol carbon} = 87.2 \text{ kJ/mol carbon}$, which can supply a significant part of the thermal energy requirement of the DAC process. Alternatively a part of the heat from the carbon and hydrogen product can be used to pre-heat the methane input into the methane cracking reactor, however, this process layout is technically more challenging (possibility of carbon black deposits in the heat exchanger, slow indirect gas to gas heat exchange process).

Example 2. Heat recovery from methanation

Methanation proceeds according to the following reaction scheme:



Methanation is an exothermic reaction providing 165 kJ of heat per mole of CH₄

produced. Depending on the type of methanation used, the heat is released at different temperatures, e.g. if chemical methanation system is used the reaction occurs at a temperature of 150-300°C and if biological methanation system is used the reaction occurs at a temperature of 50-100°C. Chemical methanation systems are especially interesting
5 since heat release is at a temperature sufficiently high, so that the supplied heat can be used to provide heat for the DAC plant, as described in Example 1.

Example 3. Recycling of hydrogen from methane cracking to methanation reactor

The methane cracking reaction, e.g. according to the process as proposed by Geissler et al in Chemical Engineering Journal 299 (2016) 192-200, yields two moles of hydrogen per
10 one mole of carbon produced, according to the following reaction scheme:



State of the art carbon black processes combust the produced hydrogen to provide heat for the methane cracking reaction as well as other process heat. In order to reduce electricity consumption for the electrolysis of water, it is favorable to separate the product hydrogen
15 from the product carbon and feed the hydrogen back to the methanation reactor, which works according to the reaction scheme provided in Example 2. If two moles of hydrogen from methane cracking are fed back to the methanation reactor, two moles of hydrogen have to be supplied from electrolysis instead of 4 moles of hydrogen which would be necessary if no hydrogen recycling was implemented. Due to the relatively high energy
20 demand for the electrolysis of water (286 kJ/mol H₂O), recycling of hydrogen from methane cracking to methanation reactor is energetically highly favorable.

If product hydrogen from methane cracking contains remainders of methane, such methane can also be fed back to the methanation reactor, keeping system complexity for the hydrogen recycling step low.

CLAIMS

1. Process for the production of at least one of amorphous carbon or graphite, preferably carbon black, from atmospheric air, biogas or flue gas CO₂ including at least the following steps:
 - a) isolation of concentrated CO₂ of a concentration of at least 50% v/v from atmospheric air, biogas or flue gas;
 - b) conversion of said captured CO₂ into a gaseous or liquid saturated or unsaturated hydrocarbon by hydrogenation;
 - c) cracking of said saturated or unsaturated hydrocarbon to at least one of amorphous carbon or graphite, preferably carbon black,wherein the H₂ resulting from step c) is at least partially used in the hydrogenation of step b).
2. Process according to claim 1, wherein the saturated or unsaturated hydrocarbon is selected from the group consisting of: linear, branched or cyclic alkanes, linear, branched or cyclic alkenes, alkynes, or a mixture thereof, wherein preferably the saturated or unsaturated hydrocarbon is selected from the group consisting of: methane, ethane, propane, butane, ethylene, propene, butylene, or a mixture thereof.
3. Process according to any of the preceding claims, wherein further H₂ required for step b) is provided via splitting of H₂O, wherein preferably the splitting of H₂O is a photocatalytic splitting, a photoelectrochemical splitting, a radiolysis, a photobiological splitting, (thermal) plasma splitting or an electrolysis, or a combination thereof.
4. Process according to any of the preceding claims, wherein further H₂ required for step b) is provided via cracking, preferably thermal cracking, of saturated or unsaturated hydrocarbon, preferably of methane, in a step according to step c), said saturated or unsaturated hydrocarbon stemming from fossil or biogenic sources, wherein the produced carbon is further used or sequestered, preferably

according to claim 15.

5. Process according to any of the preceding claims, wherein the saturated or unsaturated hydrocarbon is selected to be methane, and wherein the further two moles H₂ per mole CO₂ required for step b) is provided via splitting of H₂O, wherein preferably the splitting of H₂O is a photocatalytic splitting, a photoelectrochemical splitting, a radiolysis, a photobiological splitting, (thermal) plasma splitting or an electrolysis, or a combination thereof, preferably electrochemical splitting by using electricity from renewable sources.
6. Process according to any of the preceding claims, where isolation of concentrated CO₂ of a concentration of at least 50% v/v from atmospheric air, biogas or flue gas in step a) is performed by means of a cyclic adsorption/desorption process on amine-functionalized adsorbents, wherein preferably the concentration of the concentrated CO₂ provided in step a) is in the range of 50-100% v/v, preferably in the range of 90-100% v/v and wherein the amine-functionalized adsorbent is further preferably either a weak base ion exchange resin, amine-functionalized cellulose, amine-functionalized silica, amine-functionalized carbon or another solid support featuring amine functions.
7. Method according to any of the preceding claims, wherein the saturated or unsaturated hydrocarbon is selected to be methane, and wherein cracking of methane in step c) is performed thermally above a temperature of 800°C, preferably above 900°C, most preferably in a range of 1100°C-1600°C.
8. Method according to claim 7, wherein methane cracking in step c) is performed in an electrically heated reactor, preferably using renewable electricity.
9. Method according to any of the preceding claims, where at least one of steps a) - c) is performed continuously and/or cyclically, wherein preferably the step c) preferably in the form of methane cracking, is carried out continuously.
10. Method according to any of the preceding claims, wherein the saturated or

unsaturated hydrocarbon is selected to be methane, and wherein methane cracking is step c) is performed in a liquid metal reactor, preferably using liquid tin.

11. Method according to claim 1, wherein atmospheric CO₂ is provided in step a) by an adsorption/desorption process using an amine-functionalized adsorbent where desorption of CO₂ is performed by heating of the adsorbent to above 50°C, preferably above 80°C, more preferably above 90°C, preferably in combination with reducing the pressure to below 500mbar(abs).
12. Method according to any of the preceding claims, wherein the heat stored in the produced carbon and/or hydrogen in step c) is used to preheat the hydrocarbon, preferably the methane, entering the reactor of step c) and/or is used to provide heat for the CO₂ desorption step of the CO₂ capture device in step a).
13. Method according to any of the preceding claims, wherein parts of the hydrogen needed for step b), in particular in the form of methanation, is provided by recycling product hydrogen from the saturated or unsaturated hydrocarbon cracking reaction in step c), preferably from the methane cracking reaction in step c)
and the remainder hydrogen is supplied by electrolysis of water using electricity, preferably renewable electricity, where electrolysis is performed by either alkali, polymer electrolyte membrane or solid oxide electrolyzers
and/or wherein the remainder hydrogen is supplied by cracking according to step c), preferably thermal cracking according to step c), of saturated or unsaturated hydrocarbon, preferably of methane, stemming from fossil or biogenic sources.
14. Method according to any of the preceding claims, wherein heat release from step b), in particular in the form of methanation reaction, is used to supply heat for the CO₂ desorption step of the CO₂ capture device.
15. Method according to any of the previous claims, where the produced at least one of amorphous carbon or graphite, preferably carbon black, is used in metallurgy as carburizer for tungsten carbide or silicon carbide, as reducing agent for solar grad

silicon, as rubber filler, as addition for refractory bricks, as black pigment in plastics or concrete, as high temperature insulation, as asphalt or concrete binder or as construction aggregate or it is safely sequestered above or underground.

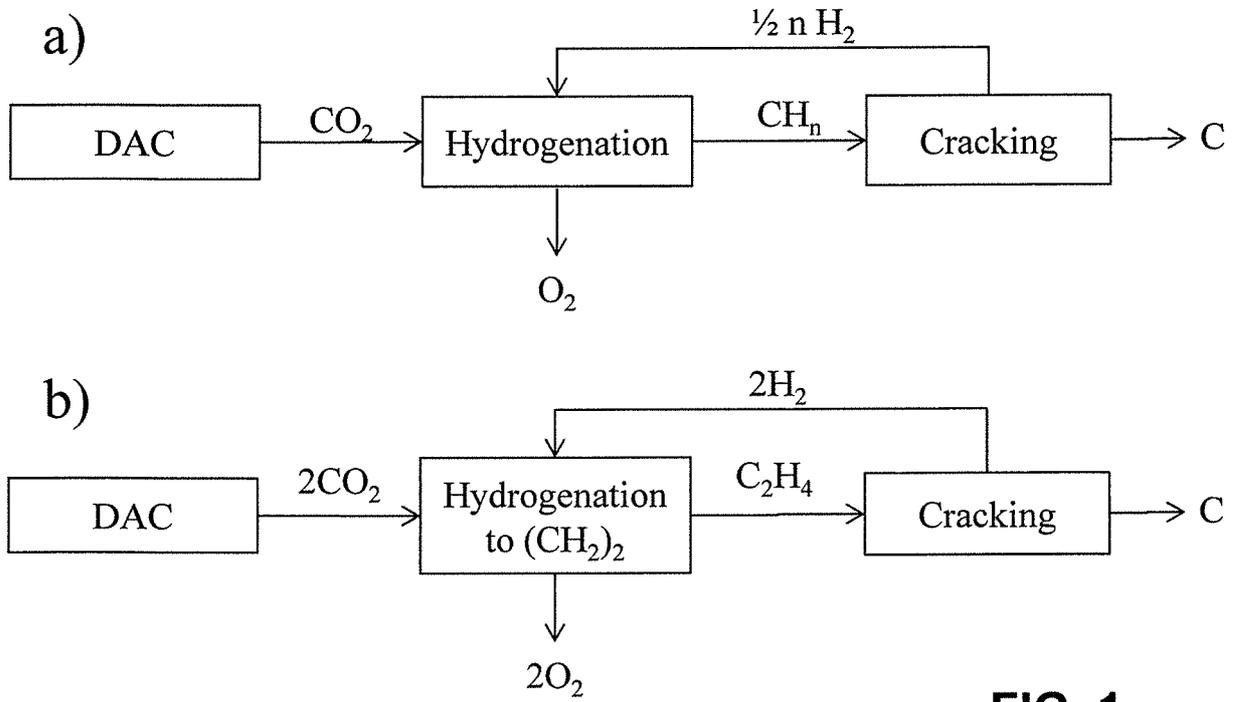


FIG. 1

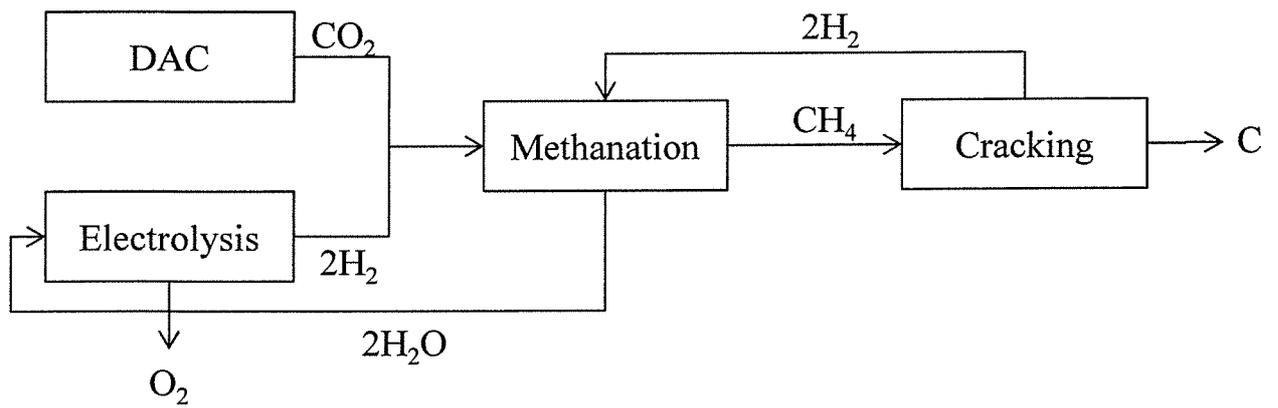


FIG. 2

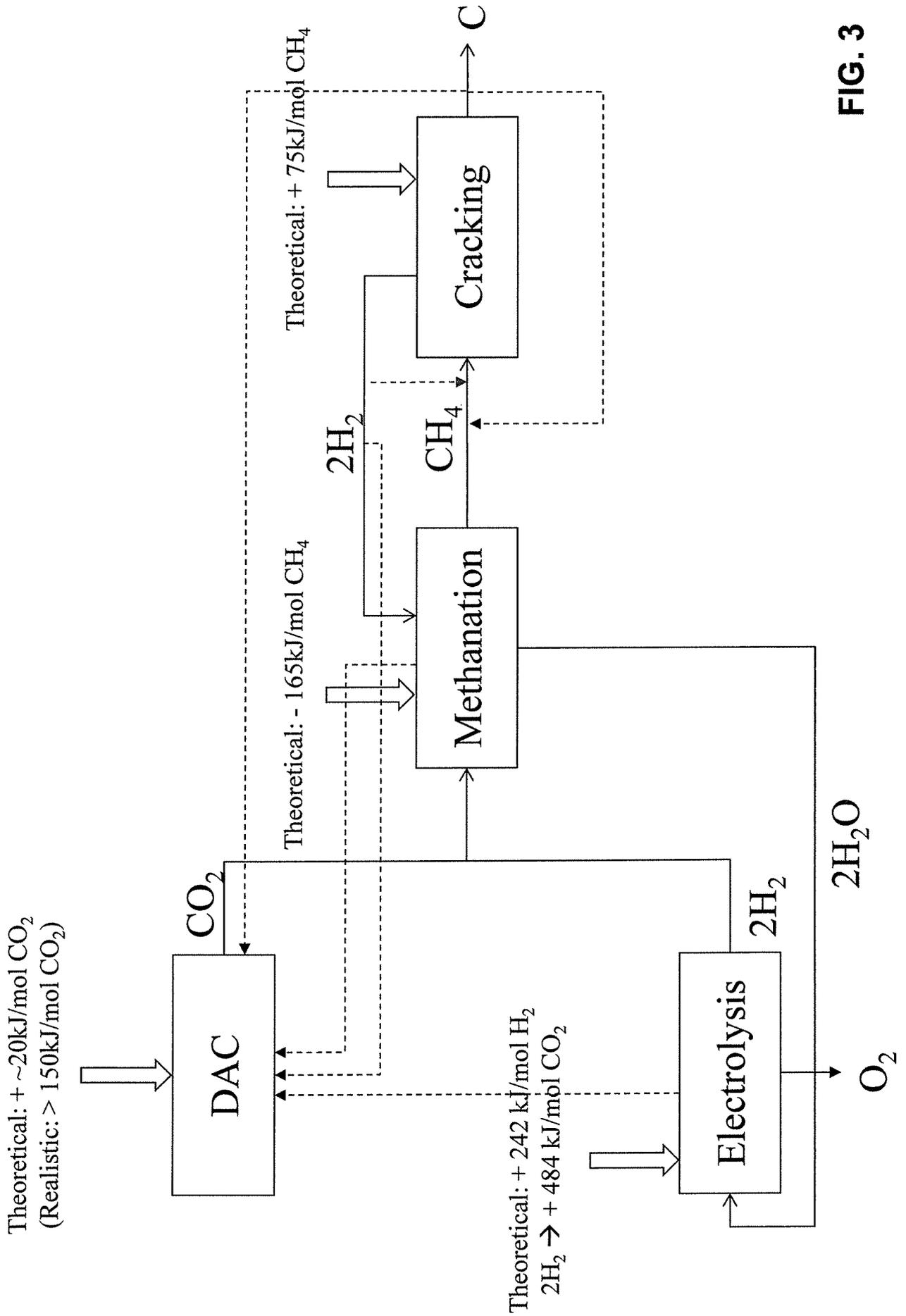


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/078837

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C09C1/48 B01D53/62 C09C1/46
 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)
 C09C B01D 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 , CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	wo 2016/161998 AI (SUNFI RE GMBH [DE] ; CLIMEWORKS AG [CH]) 13 October 2016 (2016-10-13) cited in the applicati on page 2, line 14 - page 3, line 14; claim 1 page 5, line 28 - page 7, line 24 page 9, line 24 - page 10, line 2 the whole document	1-15
Y	wo 2015/055349 AI (SCHERRER INST PAUL [CH]) 23 April 2015 (2015-04-23) claims 1-11 ; figures 1,2	1-15

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 14 December 2017	Date of mailing of the international search report 16/01/2018
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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 Si ebel , Eri c
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/078837

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	N.Z. MURADOV: "How to produce hydrogen from fossil fuels without CO ₂ emission", INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, vol. 18, no. 3, March 1993 (1993-03), pages 211-215, XP002770419, DOI: 10.1016/0360-3199(93)90021-2 the whole document -----	1-15
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/078837

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		WO 2016161998 A1	13-10-2016
		WO 2016162022 A1	13-10-2016

WO 2015055349 A1	23-04-2015	NONE	
