A METHOD OF PREPARING ACETYLENE (C_2H_2)

The present invention relates to a method of preparing acetylene (C_2H_2).

Various methods of preparing acetylene are known in the art.

As an example, the article by H. Schobert in Chem. Rev. 2014, 114, pages 1743-1760 provides an overview of the production of acetylene and acetylene-based chemicals from coal. A problem associated with coal-based processes for preparing acetylene is that several contaminants appear in the (intermediate) products, as a result of which the products need further purification and the recycling of intermediate products is not optimal. As a mere example, Schobert mentions that the recycle of $Ca(OH)_2$ for carbide production is limited to a maximum of 60% to avoid accumulation of impurities (see bottom of right-hand column of page 1744). This limited recycling leads to an undesired high CO_2 footprint (weight of CO_2 per unit weight of acetylene), presents environmental challenges and requires addition of fresh CaO, typically obtained by calcination of $CaCO_3$ ($CaCO_3$ -> CaO + CO_2).

Further, EP3029016A1 (Bestrong International Limited) discloses a method of producing acetylene or ethylene starting from methane that originates from fermentable and/or combustible waste, whilst using a catalyst system for conversion of the methane to carbon (as an intermediate product). A problem with catalyst-based methane-to-carbon conversion processes is that catalyst traces will appear in the carbon produced thereby resulting in loss of catalyst and requiring further

purification of the catalyst-contaminated products obtained in the process of preparing acetylene. Dependent on the catalyst used, these catalyst traces in the carbon and other products may also result in undesired by-products (and a lower yield of acetylene) while by-products need to be separated as well.

It is an object of the present invention to overcome or minimize one or more of the above problems.

It is a further object of the present invention to provide an alternative method for producing acetylene, resulting in less impurities in the acetylene and intermediate products (such as carbon, CaC_2, $Ca(OH)_2$ and CaO) obtained and wherein more recycling of intermediate products (such as $Ca(OH)_2$) can be arranged.

One or more of the above or other objects can be achieved by providing a method of preparing acetylene (C_2H_2), the method at least comprising the steps of:

a) providing a methane-containing stream;

b) subjecting the methane-containing stream provided in step a) to non-catalytic pyrolysis, thereby obtaining carbon and hydrogen;

c) reacting the carbon obtained in step b) with CaO, thereby obtaining CaC_2 and CO;

d) reacting the CaC_2 obtained in step c) with H_2O, thereby obtaining acetylene (C_2H_2) and $Ca(OH)_2$;

e) decomposing the $Ca(OH)_2$ obtained in step d), thereby obtaining CaO and H_2O;

f) using the CaO as obtained in step e) in the reaction of step c).

It has surprisingly been found according to the present invention that the acetylene produced (in step d)), as well as the intermediate products as obtained in the other steps, contain a relatively low amount of

impurities (such as ash content). Furthermore, recycling of intermediate products such as CaC_2, $Ca(OH)_2$ and CaO can be done to a relatively high extent as the carbon obtained and used in the method according to the present invention has a very low ash content (see also Table 1 hereafter).

Also, the carbon obtained using non-catalytic pyrolysis has a relatively high surface area (typically in the range of from 60 to 120 m^2/g as determined in accordance with the well-known BET physisorption technique such as described in e.g. "*Adsorption of gases in multimolecular layers*" by S. Brunauer, P.H. Emmett and E. Teller, Journal of American Chemical Society, 60 (1938) 309-319) and small average particle size when compared to carbon (or coke) obtained from coal or using catalytic pyrolysis, resulting in a higher reactivity of the carbon (and consequently in lower operating temperatures).

The effect of particle size of coke, ash content in the coke and its impact on the reactivity with CaO to CaC_2 has been reported in:

- "*Production of Calcium Carbide from fine Biochars*" by G. Li et al., Angew. Chem. Int. Ed. 2010, 49, 8480-8483; and
- "*CaC_2 production from pulverized coke and CaO at low temperatures – Reaction mechanisms*" by Z. Liu et al., Industrial & Engineering Chemistry Research 51 (2012), 10742-10747.

In step a) of the method according to the present invention, a methane-containing stream is provided. The person skilled in the art will readily understand that this methane-containing stream can vary widely and may contain additional components dependent on the origin.

Typically, the methane-containing stream provided in step a) comprises at least 30 mol.% methane, preferably at least 50 mol.%, more preferably at least 70 mol.%, even more preferably at least 90 mol.% methane.

Also, it is preferred that the methane-containing stream provided in step a) comprises at most 500 ppm H_2S, preferably at most 200 ppm, more preferably at most 100 ppm, even more preferably at most 50 ppm, yet even more preferably at most 25 ppm.

Further, it is preferred that the methane-containing stream provided in step a) comprises at most 10 mol.% nitrogen (N_2), more preferably at most 5 mol.%, preferably at most 2 mol.%. Also, it is preferred that the methane-containing stream comprises at most 5 mol.% CO_2, preferably at most 1 mol.%. Further, it is preferred that the methane-containing stream comprises at most 1 mol.% CO.

In a particularly preferred embodiment of the present invention, the methane-containing stream provided in step a) is a refinery off-gas stream (thereby reducing the carbon footprint of the refinery in question). Typically, such a refinery off-gas stream comprises at least 30 mol.% methane, at least 15 mol.% ethane, at least 5 mol.% ethylene and at least 5 mol.% hydrogen (H_2).

In step b), the methane-containing stream provided in step a) is subjected to non-catalytic pyrolysis, thereby obtaining carbon and hydrogen.

As the person skilled in the art is familiar with non-catalytic pyrolysis, this is not discussed here in detail. A general description of non-catalytic pyrolysis is discussed in for example:

- "*Hydrogen production by methane decomposition. A review.*" by H.F. Abbas et al., International Journal of Hydrogen Energy 35 (2010), 1160-1190; and
- "*Plasma pyrolysis of methane to hydrogen and carbon black*" by J.R. Fincke et al., Industrial & Engineering Chemistry Research 41 (2002), 1425-1435.

The person skilled in the art will readily understand that the non-catalytic pyrolysis of step b) can be performed at a wide range of temperatures. Typically, the non-catalytic pyrolysis of step b) is performed at a temperature of at least 800°C. Preferably, the non-catalytic pyrolysis of step b) is performed at a temperature of at least 900°C, preferably at least 1000°C, more preferably at least 1100°C, even more preferably at least 1300°C. Typically, the temperature in step b) is at most 2000°C.

Further, it is preferred that an electric arc furnace is used, wherein renewable electricity (i.e. from a renewable source) is used.

The person skilled in the art will readily understand that the non-catalytic pyrolysis of step b) can be performed at a wide range of pressures. Preferably, the non-catalytic pyrolysis of step b) is performed at a pressure of less than 10 bara, more preferably less than 5 bara, even more preferably at atmospheric pressure.

The carbon obtained in step b) is further reacted in step c) as mentioned below, whilst the hydrogen (H_2) can be sold as product stream or used in a separate process.

In step c), the carbon obtained in step b) is reacted with CaO, thereby obtaining CaC_2 and CO.

As the person skilled in the art is familiar with the reaction of C and CaO into CaC_2 and CO, this is not discussed here in detail. A general description of this

reaction is discussed in for example "*Calcium Carbide: A unique reagent for organic synthesis and nanotechnology*" by K.S. Rodygin et al., Chemistry – An Asian Journal, 2016, 11, 965-976. Typical conditions for the reaction include temperatures in the range of from 1000° to 2200°C, generally between 1400°C and 1850°C, and pressures in the range of from 1 to 2 bara. Preferably, renewable electricity (i.e. from a renewable source) is used in step c). The CO obtained in step c) can be sold as product stream or used in a separate process, whilst the CaC_2 is further used in step d). Typically, carbon and CaO are used in stoichiometric amounts in step c).

Typically, the carbon as used in step c) has an average particle size of at most 2 mm, preferably at most 1 mm, more preferably at most 0.5 mm. This small average particle size is obtained by the use of the non-catalytic pyrolysis process as used in step b). The advantage of this small average particle size for the carbon is that it results in a higher reactivity of the carbon and consequently allows for lower operating temperatures. See in this respect also the article by Z. Liu in Industrial & Engineering Chemistry Research as mentioned above.

Preferably, the ash content of the carbon used in step c) is below 2.0 wt.%, preferably below 1.0 wt.%, more preferably below 0.6 wt.%.

In step d), the CaC_2 obtained in step c) is reacted with H_2O, thereby obtaining acetylene (C_2H_2) and $Ca(OH)_2$. As the person skilled in the art is also familiar with the reaction of CaC_2 with H_2O into acetylene and $Ca(OH)_2$, this is not discussed here in detail. A general description of this reaction is discussed in for example US6294148. Typical conditions for the reaction include temperatures in the range of from 20 to 90°C (preferably

above 50°C, more preferably above 70°C) and pressures in the range of from 0.5 to 2 bara, preferably above 1.3 bara and preferably below 1.5 bara. The acetylene obtained can be sold as product stream (or converted in other products) or used in a separate process, whilst the $Ca(OH)_2$ is further used in step e). Examples of other products that can be obtained based on acetylene are described in Section 5 ("*Conversion of acetylene to commodity chemicals and materials*") of the above-mentioned article by Schobert in Chemical Reviews.

An important advantage of the present invention is that the acetylene, CO and $Ca(OH)_2$ contain relatively little impurities when compared to e.g. the coal-based processes. Typically, the $Ca(OH)_2$ contains an ash content of at most 2.0 wt.%.

As a result of the relatively low content of impurities, at least 65 mol.% of the $Ca(OH)_2$ as obtained in step d) is used in the decomposition of step e), preferably at least 70%, more preferably at least 80%, even more preferably at least 90%, yet even more preferably at least 95%. Please note in this respect the teaching in the above-mentioned article by Schobert in Chemical reviews that "*Recycle* [of $Ca(OH)_2$] *is limited to a maximum of ~60%, to avoid accumulation of impurities in the furnace*" at the bottom of the right-hand column of page 1744. Increased recycling of $Ca(OH)_2$ thus helps to avoid fresh use of CaO (typically obtained from $CaCO_3$) and thus lowers CO_2 footprint.

In step e), the $Ca(OH)_2$ obtained in step d) is decomposed, thereby obtaining CaO and H_2O.

As the person skilled in the art is also familiar with the decomposition of $Ca(OH)_2$ into CaO and H_2O, this is not discussed here in detail. A general description of

this decomposition is discussed in for example "*Thermal dehydration of calcium hydroxide. 2. Surface area evolution*" by A. Irabien et al., Ind. Eng. Chem. Res. 1990, 29, 1606-1611. Typical conditions for the decomposition include temperatures in the range of from 500 to 600°C and pressures in the range of from 1 to 2 bara.

Preferably, the H_2O obtained in step e) is used in the reaction of step d).

In step f), the CaO as obtained in step e) is used in the reaction of step c).

Preferably, at least 80 mol.% of the CaO as obtained in step f) is used in the reaction of step c), preferably at least 85 mol.%, more preferably at least 95 mol.%.

Hereinafter the present invention will be further illustrated by the following non-limiting drawings. Herein shows:

Fig. 1 schematically a flow scheme of an embodiment of the method of preparing acetylene according to the present invention.

As shown in Fig. 1, a methane-containing stream is provided and subjected to non-catalytic pyrolysis, thereby obtaining carbon and hydrogen (the latter can e.g. be sold as product).

The obtained carbon is reacted with CaO (preferably using renewable electricity), thereby obtaining CaC_2 and CO. The CO may be sold as a separate product. The CaC_2 is (after possible temporary storing) with H_2O, thereby obtaining acetylene (C_2H_2) and $Ca(OH)_2$.

The acetylene may be sold as a separate product or used to produce derivative compounds. The $Ca(OH)_2$ is decomposed thereby obtaining CaO and H_2O (the latter may

be recycled). The CaO is reused in the reaction with carbon.

Hereinafter the invention will be further illustrated by the following non-limiting examples.

Examples

Production of carbon

Comparative Example 1

A commercially available carbon powder of high level purity (GF44538295-1EA; 99.997% purity) was obtained from Sigma Aldrich. The carbon powder had a particle size of about 0.075 mm. There was no information available on how the carbon was obtained.

Comparative Example 2

A methane-containing stream (1 Nl/hour CH_4 and 1 Nl/h N_2; i.e. containing 50 mol.% methane and 50 mol.% N_2), was subjected to non-catalytic pyrolysis in a bubble column molten salt reactor (made from alumina) of 1 inch diameter containing molten NaCl (99% pure; commercially available from Sigma Aldrich/Merck (Darmstadt, Germany)) and dispersed iron nanoparticles (99.9% pure, with an average particles distribution of 20 nm; commercially available from Sky-Spring Nanomaterials (Houston, USA)). The amount of dispersed iron nanoparticles was 1 wt.% of the total NaCl salt weight.

The NaCl salt was dried and mixed with the iron particles in an oxygen-free gloves box and then loaded as a powder into the reactor.

After melting of the salt, the methane-containing gas stream was introduced at the bottom of the reactor (at about 1000°C) via a deep tube of 1/8 inch (0.32 cm), positioned at the centre of the reactor. The gas flow rate was controlled at about 2 Nl/h.

The carbon material (particle size of about 0.30 mm) produced during the pyrolysis floated on top of the molten salt region of the reactor and was recovered after cooling down of the reactor to room temperature. The carbon was washed with DI (deionized) water until the pH of recovered water was back to 5.5 to remove excess salt contaminant.

Example 1

A methane-containing stream (containing 93.75 mol.% methane and 6.25 mol.% N_2, no H_2S) was subjected to non-catalytic pyrolysis in an empty (i.e. no catalyst) reactor tube (made from alumina) with an internal diameter of 1 cm and a length of 1 m. The isothermal zone of the reactor was 60 cm long.

The methane-containing gas stream was passed through the reactor at a flow rate of 4.6 Nl/h at a temperature of 1400°C and a pressure slightly above ambient (1.1 barg). At this temperature the methane started to crack, producing solid carboneous material that deposited on the wall of the reactor tube. The cracking was continued until a pressure build-up was observed, indicating that the reactor was getting blocked by solid material. The gas flow and the heating was stopped and after cooling down the carbon material was recovered from the reactor.

The properties of the various carbon samples are given in Table 1 below. As can be seen, the carbon samples as generated according to the present invention result in a significantly lower ash content.

The ash content and moisture content of the carbon samples was determined according to Chinese National Standards GB/T 476-2001 and GB/T 212-2008.

Table 1. Properties of carbon

	C. Ex. 1	C. Ex. 2	Ex. 1
C[1] [wt.%]	99.5	98.4	99.7
Moisture[2] [wt.%]	0.1	1.1	0.3
Ash content[2] [wt.%]	0.4	0.5	0.0
Particle size [mm]	0.075 (200-500 mesh)	0.3-0.5	0.3-0.5
Carbon surface area[3]		90	90

[1]As determined according to Chinese National Standard GB/T 476-2001.

[2]As determined according to Chinese National Standard GB/T 212-2008.

[3]As determined according to BET surface area measurement.

The person skilled in the art will readily understand that many modifications may be made without departing from the scope of the invention.

C L A I M S

1. A method of preparing acetylene (C_2H_2), the method at least comprising the steps of:
a) providing a methane-containing stream;
b) subjecting the methane-containing stream provided in step a) to non-catalytic pyrolysis, thereby obtaining carbon and hydrogen;
c) reacting the carbon obtained in step b) with CaO, thereby obtaining CaC_2 and CO;
d) reacting the CaC_2 obtained in step c) with H_2O, thereby obtaining acetylene (C_2H_2) and $Ca(OH)_2$;
e) decomposing the $Ca(OH)_2$ obtained in step d), thereby obtaining CaO and H_2O;
f) using the CaO as obtained in step e) in the reaction of step c).

2. The method according to claim 1, wherein the methane-containing stream provided in step a) comprises at least 30 mol.% methane, preferably at least 50 mol.%, more preferably at least 70 mol.%, even more preferably at least 90 mol.% methane.

3. The method according to claim 1 or 2, wherein the methane-containing stream provided in step a) comprises at most 500 ppm H_2S, preferably at most 200 ppm, more preferably at most 100 ppm, even more preferably at most 50 ppm, yet even more preferably at most 25 ppm.

4. The method according to any one of the preceding claims, wherein the non-catalytic pyrolysis of step b) is performed at a temperature of at least 900°C, preferably at least 1000°C, more preferably at least 1100°C, even more preferably at least 1300°C.

5. The method according to any one of the preceding claims, wherein the carbon as used in step c) has an average particle size of at most 2 mm, preferably at most 1 mm.

6. The method according to any one of the preceding claims, wherein at least 65 mol.% of the $Ca(OH)_2$ as obtained in step d) is used in the decomposition of step e), preferably at least 70%, more preferably at least 80%, even more preferably at least 90%, yet even more preferably at least 95%.

7. The method according to any one of the preceding claims, wherein the H_2O obtained in step e) is used in the reaction of step d).