

Pretreatment of C2-C6 alkanes-rich raw natural gas or industry off gas

Description

- 5 The present invention relates to a process for treatment of C2-C6 alkanes rich natural gas having an C2-C6 alkane content of 2.5 to 30 Vol.-% of the total raw natural gas or C2-C6 alkanes rich industry off-gas having an C2-C6 alkane content of 10 to 80 Vol.-% of the total industry off-gas to get pipeline quality natural gas, wherein the pipeline quality natural gas contains at least 95 vol.-% of methane and at most 5 Vol.-% of C2-C6 alkane, or to get pipeline quality hydrogen, wherein the pipeline quality hydrogen contains at least 98 vol.-% of hydrogen, wherein (i) the C2-
10 C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas are introduced via the bottom of said moving bed reactor, having a temperature of 10 to 200°C, and substrates having a particle size of 0.3 to 8 mm are introduced via the top of said moving bed reactor, having a temperature of 10 to 200°C, (ii) the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich off-gas is pyrolyzed in said moving bed reactor into a gaseous product stream containing at least methane and/or hydrogen and into solid carbon, (iii) the solid carbon is separated from that gaseous product stream and (iv) the gaseous product stream is fed into a natural gas grid and/or into a hydrogen grid or
15 the gaseous product stream is used materially or energetically directly.

State of the art

- Due to the rapid increase of the world's primary energy demand of the last decades, exploitation of low-quality natural gas reserves has gained many interests, preferably easily accessible and local natural gas reservoirs. However,
20 the exploitation of said low-quality natural gas reserves should not lead to higher CO₂ emissions.

- Natural-gas processing is needed to get pipeline quality natural gas for pipeline distribution and final use. Such purification processing typically includes removing contaminants such as solids, water, carbon dioxide (CO₂), hydrogen sulfide (H₂S), mercury and higher molecular mass, liquid hydrocarbons (condensate).
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US 2016/340596 discloses a method for providing pipeline quality natural gas from raw natural gas feed stream by separating and recovering natural gas liquids with an adsorption process.

- 30 In view of the hydrocarbons content, the pipeline quality natural gas shall contain at least 75 vol.-% of methane and at most 10 Vol.-% of ethane. For example, natural gas from GUS states contains 98 Vol.-% methane, 1 Vol.-% C2-C5 alkanes and 1 Vol.-% inert gases and natural gas from the Netherlands contains 89 Vol.-% methane, 4 Vol.-% C2-C5 alkanes and 11 Vol.-% inert gases. For separating higher hydrocarbons from methane to reach the allowed limit, cryogenic processes are the most economical method to separate higher hydrocarbons. Cryogenic processes
35 generally involve cooling the raw natural gas stream to temperatures near 188 K. These low temperature requirements have high associated energy consumption costs. The separated C2-C4 alkanes rich off gas reduce the final natural gas yield in the pipeline. In addition, the C2-C4 alkanes rich off gas is typically sold for a lower price than the

pipeline quality natural gas or the C2-C4 alkanes rich off gas is even burned resulting in a higher CO₂-footprint of the pre-processing.

Further, the emissions related to delivered natural gas are increased because of energy demand, leakage and other issues during the processing to remove C2-C4 alkanes. This is typically done with cryogenic processing adding to energy demand. Estimates suggest ~3.8g CO₂e/MJ NG emissions are attributable to the processing steps to remove C2-C4 alkanes. The Inflation Reduction Act Methane Emissions Charge Report indicates up to 14g CO₂e/MJ NG from processing steps, and 444 facilities with emissions totaling 56.7 MMT CO₂e. Using the natural gas without needing extensive processing could reduce those emissions.

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Typically, low-quality gas reserves contain raw natural gas with a higher C2-C4 alkanes content of about 5 to 25 Vol.-% of the total raw natural gas. Thus, exploitation of these reserves might be uneconomic due to the high natural-gas processing costs. In addition, the loss of natural gas share would increase.

15 In addition, C2-C4 alkanes content also adds to the higher heating values (HHV) of natural gas. Gas suppliers are limited to a maximum HHV and therefore might remove some C2-C4 alkanes to meet target values. Hydrogen on the other hand lowers the HHV of natural gas. Blending H₂ in natural gas is already being pursued, and the addition of H₂ also enables higher levels of ethane rejection.

20 Ethane and ethane rich gas is typically used in the plastics manufacturing for production of ethylene by steam cracking. Depending on the value of ethane compared to natural gas, it can be more or less economical to separate and sell the ethane. If the ethane removed has lower value than the natural gas, suppliers will blend ethane back in until it reaches the heating value limit of the grid quality of the natural gas.

25 In addition, ethane is the largest component of natural gas liquids production (NGL) (~45%), and NGLs have higher value than dry gas, so producers especially around the shale gas in the US shift their drilling programs to the more liquids-rich portions of natural gas fields to take advantage of considerable price premiums of the NGL's over dry natural gas. This shift results in an excess supply of ethane; meanwhile demand for ethane, used primarily in plastics manufacturing, has stayed pretty flat.

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Thus, an economically exploitation technology for these low-quality gas reserves with a high C2-C4 alkanes content is needed, as an alternative to the cost-effective cryogenic process. In addition, processes that can directly use low-quality natural gas as methane-containing feed, without any gas pre-treatment of the raw gas, are of great interest.

35 One of the main consumers of natural gas is the steam reforming process on Ni catalysts for production of synthesis gas and hydrogen. As the risk of coking and deactivation of the catalyst gets higher with increasing ethane content, no direct use of such low-quality natural gas is possible for the steam reforming process. In addition, newly developed methane pyrolysis processes might also become a main consumer of natural gas.

- US 2002/7594 discloses a thermocatalytic process for CO₂ free production of hydrogen and carbon from hydrocarbon in a bed of carbon particulates that are continuously reactivated. It is disclosed that carbon particles are heated externally in a burner to 900 to 1500°C and recycled to the reactor. The hydrocarbon feed is preheated before entering the fluidized bed reactor. Said preheating could be done by heat exchange between the feed and the produced hot hydrogen leaving the methane pyrolysis reactor or between the feed and flue gases from a burner, burning some of the hydrocarbon feed. In Example 9, it is disclosed that both methane and propane can be converted into hydrogen in a fluidized bed of carbon black Black Pearls 2000 having a particle size of 0.012 µm, wherein the temperature of the reactor was maintained at 950°C.
- US 2022/212923 discloses a device and process for the production of hydrogen and solid carbon from C₁ to C₄-alkane containing gas by means of thermal plasma resulting in hydrogen and carbon black with a particle diameter in the range of a few to 500 nm. Typically, the feed gas is preheated before entering the reactor to reduce energy expense and improve production capacity.
- In reactor concepts, in which the solid carbon is deposited on a solid carrier material, like in fixed, fluidized or moving bed technologies, the deposition of carbon can result in coke deposition on reactor equipment like feed inlet and on the reactor wall or can result in agglomeration of carrier bed particles. Several negative aspects are associated with this agglomeration process. In fixed bed reactors, stronger agglomerated beds require a more complex, slower procedure to remove the carrier bed. In moving bed reactors, a higher level of agglomeration between carrier particles can lead to a blockage of the solid flow. In fluidized bed reactors, large agglomerates may no longer be fluidized, thus disrupting the fluidization behavior of the bed ending with a collapse of the fluidized bed. In addition, in fluidized beds wherein the system relies on homogenous temperature, the decomposition might already start in or near the inlet feed resulting in a rapid block of the inlet feed equipment.
- Task
- It is an object of the present invention to make the exploitation of low-quality natural gas reservoir economically. It is a further object of the present invention to demonstrate a (pre-)treatment of low-quality natural gas to get pipeline quality gas by selectively converting the impurities C₂ to C₆ alkanes to valuable methane, hydrogen and solid carbon. It is a further object of the present invention to utilize low-quality natural gas by pyrolyzing said C₂ to C₆ alkanes in an optimized reactor and via optimized process conditions to minimize the risk of increased soot formation, agglomeration and clogging given by the active components of C₂ to C₆ alkanes. It is a further object of the present invention to demonstrate a (pre-)treatment of low-quality natural gas to get pipeline quality gas of the allowed heating value ranges, for pipeline distribution and/or final use. It is an object of the present invention to reduce CO₂ emissions in low-quality natural gas exploitation. It is an object of the present invention to reduce CO₂ emissions in the gas distribution network by reducing the fossil carbon reduction in gas distribution network. Preferably, the obtained carbon from the C₂-C₄ alkanes is trapped in a solid state without emitting it to the atmosphere. Such carbon preferably results in a carbon-containing product that can be sold. It is a further object of the present invention to remove effectively solely carbon out of the raw gas as carbon is the driver for the heating value and CO₂ emissions. It is a further

object of the present invention to find processes that can use low-quality natural gas as methane/hydrocarbon-containing feed directly/unrefined, without any gas pre-treatment of the raw gas.

Invention

- 5 This task is solved by the present invention relating to a process for treatment of C2-C6 alkanes rich natural gas having an C2-C6 alkane content of 2.5 to 30 Vol.-% of the total raw natural gas or C2-C6 alkanes rich industry off-gas having an C2-C6 alkane content of 10 to 80 Vol.-% of the total industry off-gas to get pipeline quality natural gas, wherein the pipeline quality natural gas contains at least 95 vol.-% of methane and at most 5 Vol.-% of C2-C6 al-
- 10 kane, or pipeline quality hydrogen, wherein the pipeline quality hydrogen contains at least 98 vol.-% of hydrogen, wherein (i) the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas are introduced via the bottom of a moving bed reactor, having a temperature of 10 to 200°C, and substrates having a particle size of 0.3 to 8 mm are introduced via the top of said moving bed reactor, having a temperature of 10 to 200°C, (ii) the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich off-gas are/is pyrolyzed in said moving bed reactor into a gase-
- 15 ous product stream containing at least methane and/or hydrogen and into solid carbon, (iii) the solid carbon is separated from that gaseous product stream and (iv) the gaseous product stream is fed into a natural gas grid and/or into a hydrogen grid or the gaseous product stream is used materially or energetically directly.

- Pipeline quality natural gas is depending on national regulations. Typically, a high methane content and a low C2-C4 alkanes content is favorable: at least 75 vol.-% of methane, preferably at least 80 Vol.-%, at least 85 Vol.-%, preferably
- 20 bly at least 90 Vol.-%, even more preferably at least 95 Vol.-% of methane and at most 10 Vol.-% of C2-C4 alkanes, preferably at most 5 Vol.-%, preferably at most 2 Vol.-% of C2-C4 alkanes.

Details to the invention

- Beside the ability of exploitation of low-quality gas reserves commercially, by implementing the present invention the previously emitted carbon as CO₂ by the gas welling and pre-treatment process is now obtained as solid carbon and
- 25 can be used in products to be sold.

Hydrocarbon pyrolysis is a technology that splits hydrocarbons, especially aliphatic hydrocarbons such as methane, ethane, propane and/or butane, directly into hydrogen and solid carbon.

- For example, the obtained solid carbon can be sold as a commercial product for selected applications, depending on
- 30 the carbon morphology and physical/chemical properties. For example, the solid carbon from methane pyrolysis may be used for aluminum and steel production, tire manufacturing, electrode manufacturing, polymer blending, additive for construction materials, carbon devices like heat exchangers, soil conditioning, etc.

Natural gas extraction / gas well

- 35 Natural gas is extracted as known in the state of the art. Preferably, natural gas is extracted from low-quality gas reserves containing raw natural gas with a content of C2-C6 alkanes, preferably ethane and propane, of about 5 to 25 Vol.-% of the total raw natural gas, preferably of about 7.5 to 20 Vol.-% of the total raw natural gas, more preferably 10 to 15 Vol.-% of the total raw natural gas.

Such a raw natural gas typically has the following composition: methane from 50 to 95 Vol.-%, preferably 60 to 90 Vol.-%, ethane from 2.5 to 25 Vol.-%, preferably from 5 to 20 Vol.-%, preferably from 10 to 15 Vol.-%, propane from 0 to 15 Vol.-%, preferably from 0.5 to 10 Vol.-%, preferably from 0.5 to 5 Vol.-%, butane from 0 to 10 Vol.-%, preferably from 0.5 to 5 Vol.-%, preferably from 0.5 to 2.5 Vol.-%, pentane from 0 to 5 Vol.-%, preferably from 0 to 2.5 Vol.-%, CO₂ from 0 to 5 Vol.-% and N₂ from 0 to 10 Vol.-%, preferably from 1 to 5 Vol.-%, sulfur components from 0 to 30 Vol.-%, preferably from 0 to 20 Vol.-%, preferably from 0 to 10 Vol.-%, of the total raw natural gas.

C₂-C₆ alkanes rich off-gas

Alternatively, or in addition to C₂-C₆ alkanes rich natural gas, C₂-C₆ alkanes rich industry off gas from other industry processes like petroleum refineries could be used as a feedstock for the pyrolysis unit.

Preferably, industry off gas has the following content of C₂-C₄ alkanes: 2.5 to 70 Vol.-% ethane, 2.5 to 70 Vol.-% butane, 2.5 to 70 Vol.-% propane and trace N₂, CO, and H₂S.

Preferably, such refinery off gas, liquified petroleum gas, as the following content of C₂-C₄ alkanes: 0 to 5 Vol.-% ethane, 25 to 45 Vol.-% propane, 50 to 70 Vol.-% butane and trace N₂, CO, and H₂S.

Processing/purification

The (pre-)processing of the extracted raw natural gas is known in the state of the art. Typically, solid particles (e.g. sands) and liquids (e.g. water, oil) are separated upfront.

Preferably, the extracted and pre-processed raw natural gas is directly fed into the pyrolysis reactor. Preferably, the extraction unit is upstream of and fluidically connected to the pre-processing/purification unit and the pre-processing/purification unit is upstream of and fluidically connected to the hydrocarbon pyrolysis unit.

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Pyrolysis Process

In the hydrocarbon pyrolysis step ethane, propane etc. are pyrolyzed into methane, hydrogen and solid carbon. The process is referred to as pyrolysis since no oxygen is involved. The pyrolysis, also called decomposition, can be conducted in different ways known to the persons skilled in the art: catalytically or thermally, and with heat input via plasma, resistance heating, liquid metal processes or autothermal (see for example N. Muradov and T. Veziroglu: "Green" path from fossil-based to hydrogen economy: An overview of carbon-neutral technologies", International Journal Hydrogen Energy 33 (2008) 6804-6839, H.F. Abbas and W.M.A. Wan Daud: Hydrogen production by methane decomposition: A review, International Journal Hydrogen Energy 35 (2010) 1160-1190), R. Dagle et al.: An Overview of Natural Gas Conversion Technologies for Co-Production of Hydrogen and Value-Added Solid Carbon Products, Report by Argonne National Laboratory and Pacific Northwest National Laboratory (ANL-17/11, PNNL-26726) November 2017).

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Thus, the generic term hydrocarbon pyrolysis covers a wide range of processes. The best known and most advanced of these are: Plasma pyrolysis, Metal melting/ Metal salt melting, Moving bed process, Fluidized and fixed bed catalytic process and Partial combustion. These processes differ in the form of the energy used (thermal, electrical, etc.), the process conditions (temperature, pressure, etc.), the catalysts and/or auxiliary materials used, the process flow etc.

The solid carbon type generated in the decomposition depends on the reaction conditions, reactor and heating technology. Examples are: carbon black from plasma processes, carbon powder from liquid metal processes and granular carbon from thermal decomposition in fixed, moving or fluidized bed reactors. Preferably, a transportable solid carbon is obtained, for example a granular carbon preferably having a bulk density in the range of 0.5 to 2.5 g/cc and a particle size of 0.1 mm (d₁₀) to 10 mm (d₉₀).

Separation of carbon

The separation of solid carbon depends on the chosen pyrolysis technology and is known by the skilled person in the art.

As mentioned above, for example, in a plasma pyrolysis the solid carbon in the form of carbon black is discharged from the reactor with the gas and then separated, e.g. by a cyclone. The solid carbon might be post-treated, e.g. agglomerated. Depending on the process and the metals used in molten metal pyrolysis, the carbon floats on the melt and is skimmed off or leaves the reactor together with the gas stream and is then separated, e.g. filter/cyclone. In addition, a purification step to remove residual metal from the carbon could be required e.g. washing, evaporation. In the catalytic pyrolysis technology and in the fixed and moving bed technology, the solid carbon is deposited on the surface of the catalyst and/or support and taken off the reactor via the catalyst and/or support.

Hydrogen / H₂-enriched & ethane-reduced natural gas

The "gaseous product stream" resulting from the hydrocarbon pyrolysis process comprises hydrogen and/or methane as its main constituent depending on the pyrolysis conditions and the feed.

Depending on the infrastructure, the kind of available gas network and the needs of the gas consumer, natural gas or hydrogen, material use or thermal use, the composition of the gaseous product stream can be adjusted in broad ranges by the process conditions, temperature, pressure, deposition rate, conversion rate, dilution rate etc.

Typically, the "gaseous product stream" has the following composition: 1 to 99.9 Vol.-% of hydrogen, 5 to 99 Vol.-% of hydrogen, 10 to 98 Vol.-%, 20 to 98 Vol.-% of hydrogen, preferably 50 to 95 vol.-% of hydrogen and the remainder methane and residual C₂-C₄ alkanes, preferably 0 to 90 Vol.-% methane, preferably 0 to 50 Vol.-% methane, dependent on the gas well up to 30 Vol.-% hydrogen sulfide and up to 30 Vol.-% inert gases, especially nitrogen. Preferably, the gaseous product stream comprises less than 5 vol.-% of C₂+ alkanes, more preferably less than 2 vol.-%, even more preferably less than 1 vol.-%, even more preferably less than 0.5 vol.-%.

- If option #2a (see Figure 2) is preferred that means C2-C6 alkanes-rich natural gas is processed in a methane pyrolysis process to result in solid carbon and H₂-enriched & C2-C4 alkanes -reduced natural gas: the "gaseous product stream" preferably contains 0.1 to 30 Vol.-% hydrogen, preferably 5 to 15 Vol.-% hydrogen, even more preferably 5 to 10 Vol.-% hydrogen and the remainder methane and residual, reduced C2-C4 alkanes. The reactor is operated preferably at 800 °C – 1400 °C and more preferably from 900 °C – 1100 °C. Beside the temperature, the process is preferably be controlled by diluting the C2-C6 alkanes-rich natural gas feed with hydrogen to a volume ratio of preferably H₂/C₁+ of 0.01 to 1, even more preferably 0.05 to 0.2, in particular 0.05 to 0.1. C₁+ stands for all hydrocarbons. Preferably, the H₂/C₁+ ratio is a H₂/(C₁-C₆) ratio.
- 10 If option #2b (see Figure 2) is preferred that means C2-C4 alkanes -rich natural gas is processed in a methane pyrolysis process to result in solid carbon and H₂-enriched & C2-C4 alkanes -reduced natural gas and said H₂-enriched & C2-C4 alkanes -reduced natural gas is mixed with C2-C4 alkanes rich raw natural gas in such an amount which is permissible in view of the allowed heating values: the "gaseous product stream" preferably contains 50 to 99.9 Vol.-% hydrogen, preferably 70 to 99 Vol.-% hydrogen, and the remainder methane and residual, reduced C2-C4 alkanes.
- 15 The reactor is operated preferably at 800 °C – 1800 °C and more preferably from 1200 °C – 1600 °C. Beside the temperature, the process is preferably be controlled by diluting the C2-C6 alkanes-rich natural gas feed with hydrogen to a volume ratio of preferably H₂/C₁+ of 0.1 to 25, even more preferably 0.5 to 25, in particular 1 to 25, even more preferably 2 to 25. C₁+ stands for all hydrocarbons. Preferably, the H₂/C₁+ ratio is a H₂/(C₁-C₆) ratio.
- 20 If option #3 (see Figure 1) is preferred that means the processing of the C2-C4 alkanes -rich industry off gas to solid carbon and hydrogen: the "gaseous product stream" preferably contains 50 to 99.9 Vol.-% hydrogen, preferably 70 to 99.9 Vol.-% hydrogen, more preferably 95 to 99.9 Vol.-% hydrogen and the remainder methane and residual, reduced C2-C4 alkanes. The reactor is operated preferably at 800 °C – 1800 °C and more preferably from 1200 °C – 1600 °C. Beside the temperature, the process is preferably be controlled by diluting the C2-C4 alkanes -rich industry
- 25 off gas feed with hydrogen to a volume ratio of preferably H₂/C₁+ of 0.1 to 25, even more preferably 0.5 to 25, in particular 1 to 25, even more preferably 3 to 25. C₁+ stands for all hydrocarbons. Preferably, the H₂/C₁+ ratio is a H₂/(C₁-C₆) ratio.
- If option #4 (see Figure 1) is preferred that means the processing of the C2-C4 alkanes -rich natural gas to solid
- 30 carbon and hydrogen: the "gaseous product stream" preferably contains 50 to 99.9 Vol.-% hydrogen, preferably 70 to 99.9 Vol.-% hydrogen, more preferably 95 to 99.9 Vol.-% hydrogen and the remainder methane and residual, reduced C2-C4 alkanes. The reactor is operated preferably at 800 °C – 1800 °C and more preferably from 1200 °C – 1600 °C. Beside the temperature, the process is preferably be controlled by diluting the C2-C4 alkanes -rich natural gas feed with hydrogen to a volume ratio of preferably H₂/C₁+ of 0.1 to 25, even more preferably 0.5 to 25, in particular 1 to 25, even more preferably 2 to 25. C₁+ stands for all hydrocarbons. Preferably, the H₂/C₁+ ratio is a
- 35 H₂/(C₁-C₆) ratio.

Using the gaseous product stream materially or energetically

The gaseous product stream containing mainly hydrogen could be used in the gas streams of the gas welling site and/or to generate CO₂-free electricity/power for the gas welling site or other processes close by.

In addition, this potentially cheap source of hydrogen could open up new possibilities for other hydrogen vectors in parallel to natural gas:

- 5 - direct air capture of carbon dioxide + hydrogen to get additional CH₄ or methanol
 - air separation to get nitrogen + hydrogen to get ammonia
- as additional energy carrier to be transported separately.

Feeding into the grid / grid quality

- 10 Typically, the raw gaseous product stream is purified in a removal apparatus, e.g. using adsorption or membrane technologies.

- For example, the gaseous product stream can still contain hydrogen sulfide. Hydrogen sulfide can preferably be removed from the gaseous product stream via gas scrubbing, e.g. via ZnO, CuZnO, Fe(OH)₃, Zeolites, MOFs, as
- 15 known in the state of the art. Typical process conditions of the gas scrubbing are 60 to 180°C and 1 to 100 bar.

- If a gas compressor is needed before the gaseous product stream is fed into a grid, the gas scrubbing is preferably embedded in such a compressor unit. Preferably, the inlet temperature of the absorber bed can be provided by the heat of compression between the compressor stages.

- 20 For example, the gaseous product stream can still contain carbon oxide and inert gases, e.g. nitrogen. Corresponding hydrogen recovery apparatuses are common knowledge to the person skilled in the art, for example pressure swing adsorption or permeation.

- 25 The purified gaseous product stream is preferably dried and compressed dependent on the grid specifications.

- The optionally purified, dried and/or compressed gaseous product stream is preferably fed into a gas grid, depending on the composition into a natural gas grid or into a hydrogen grid.

- 30 Preferably, no extraction of unreacted hydrocarbons is needed e.g. via hydrogen recovery apparatuses, if the gaseous product stream is fed into a natural gas grid.

- If the gaseous product stream is fed into a natural gas grid, the hydrogen content is preferably adjusted so that the proportion of hydrogen which is permissible for introduction into the gas grid is adhered to. An exemplary range is 5-15 vol.-% hydrogen. Ideally, the existing infrastructure is used. If the gaseous product stream exceeds the proportion of hydrogen which is permissible for introduction into a natural gas grid, the stream is to be fed into a gas grid designed for the distribution of hydrogen-rich gases.
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Blending

In addition, the gaseous product stream could be mixed/blended with C2-C6 alkanes rich raw natural gas and/or other natural gas before feeding this blended natural gas mixture into a natural gas grid in such an amount which is permissible in view of the allowed heating values and hydrogen content (see #2b of Figure 2).

5 Hydrocarbon pyrolysis technologies

Plasma Pyrolysis

For plasma pyrolysis (see for example WO2015116797, WO2015116800), a plasma with >3000 °C is generated and mixed with C2-C4 alkanes rich, especially ethane rich, natural gas or off-gas, which is pyrolyzed. The gas mixture
10 leaves the reactor at temperatures between 1500 – 2000 °C. The reaction produces solid carbon in the form of carbon black which is discharged from the reactor with the gas and then separated, e.g. by a cyclone. The solid carbon might be post-treated, e.g. agglomerated. Various technologies such as arc, microwave and gas plasma technologies can be used for this purpose.

15 Partial Combustion process or pulsed reaction process

For a partial or pulsed combustion process, the heat for the thermal pyrolysis reaction is supplied by pulsed combustion (see for example WO2020118417 and US20220185664). Before a feedstock (containing hydrocarbon), is split into hydrogen and solid carbon in a combustion chamber, a combustible gas (containing hydrocarbons and oxidants) is pre-mixed in a mixing chamber. The reaction in the combustion chamber takes place when the gas mixture is
20 heated up to 1350K and a pressure of over 20 bar is reached. Products leaving the reactor will be separated into gas and solid carbon for further processing.

Molten metal / molten metal salt

The pyrolysis processes using molten metals or molten metal salts (see for example WO2020161192,
25 WO2021183959) use the heat from the melt for pyrolysis. In addition, metals can be selected that have a catalytic effect, so that pyrolysis can take place at relatively low temperatures of about 800 – 1200 °C. The C2-C4 alkanes rich, especially ethane rich, natural gas or off-gas is fed into the molten metal; the bubbles formed in the process rise upwards in the reactor, whereby the hydrocarbons decompose and form mainly methane, hydrogen and solid carbon. Depending on the process and the metals used, the carbon floats on the melt and is skimmed off or leaves the
30 reactor together with the gas stream and is then separated, e.g. evaporation, washing. In both cases, the carbon is characterized by a small particle size and bulk density. Due to adhesion of the melt to the carbon particles, purification of the carbon might be necessary for some processes and applications.

Catalytic processes

35 Catalysts can also be used to reduce the high reaction temperatures (see for example WO2011029144, WO2016154666). For hydrocarbon pyrolysis a very cost-effective alternative is the use of iron oxide catalysts. Reaction temperatures of about 700 to 1000°C can be realized. In order to achieve the best possible heat and mass trans-

fer, the reactions take place, for example, in the fluidized bed, with the catalyst as the fluidized material. The hydrocarbon is decomposed at the catalytic surface.

Fixed or Moving bed process

- 5 The hydrocarbon decomposition is preferably conducted in a moving or fixed bed reactor, wherein the bed contains as substrates preferably carbon materials, metals, ceramics, and a mixture thereof, preferably at temperatures ranging from 500 to 2000°C, preferably ranging from 1000 to 1600°C, even more preferably ranging from 1200 to 1500°C, and at pressures ranging from 1 to 100 bar, preferably from 5 to 50 bar.
- 10 The decomposition can either be realized as fixed bed, preferably in a cyclical operation mode, preferably including a production and a regeneration mode as described for example in WO 2018/083002, or in a moving bed as described for example in US 2982622, WO 2019/145279 and WO 2020/200522.

- 15 The process of methane decomposition is also referred to as methane pyrolysis, since in most of the common technologies no oxygen is involved. The decomposition can be conducted in different ways known to the persons skilled in the art: catalytically or thermally, and with heat input via plasma, microwave, heated carrier gas, resistance heating, induction, liquid metal processes or autothermal.

- 20 The decomposition process is preferably heated electrically, even more preferably by resistive heating (Joule heating) of the substrate material as described for example in US 2982622, WO 2019/145279 and WO 2020/200522.

Preferably the pyrolysis process is located at or close by a gas wells.

Preferred Process Conditions: Moving Bed

- 25 Preferably the substrate is guided in form of a moving bed through the reaction chamber, with C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas being passed advantageously in countercurrent to the substrate.

- 30 For this purpose, the reaction chamber is preferably rationally designed as a vertical reactor, which means that the movement of the moving bed is gravity driven. Flow through the moving bed is taking place, advantageously, homogeneously, and uniformly (see for example WO 2013/004398, WO 2019/145279 and WO 2020/200522). C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas are preferably introduced via the bottom of the reactor, preferably having a temperature of 10 to 200°C. The substrate is preferably introduced via the top of the reactor, preferably having a temperature of 10 to 200°C. The gaseous product stream is preferably taken off via the top of the reactor, preferably having a temperature of 10 to 200°C. The granular pyrolytic carbon is preferably taken off via the bottom of the reactor, preferably having a temperature of 10 to 200°C.
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The discharged substrate, preferably carbon, is preferably at least partly recycled and introduced into the reactor again using it as substrate for the moving bed. As a result, a continuous process of the moving bed is achieved. Preferably, the discharged substrate is not activated before introducing into the reactor again, even more preferably, there is no surface activation during the recycling of the substrate.

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The flow velocity of the substrate is advantageously in the range of 0.005 to 0.5 cm/s. The flow velocity of the gas flow is advantageously in the range of 0.025 to 2 m/s.

10 The gas residence time in the reactor is advantageously between 0.5 and 50 s, preferably between 1 and 20 s. The residence time of the substrate is preferably between 0.5 and 15 hours, preferably between 1 and 10 hours and more preferably between 2 and 8 hours.

Substrate

15 The substrate can either be a support substrate in the reactor (a pre-installed part) or a granular material. The preferred substrate is a carbon-containing substrate, for example pyrolytic carbon itself. The particle size of a preferred substrate is in the range of 0.1 to 10 mm, preferably 0.3 to 8 mm.

20 Preferably the substrates are carbonaceous materials that are macro-structured carbonaceous materials, wherein the porosity of the carbonaceous material is in the range of 30 to 70 vol.-% and the carbonaceous material contains of a carbon content of 98 Vol.-% to 100 Vol.-%, preferably 99 Vol.-% to 100 Vol.-%, even more preferably 99.5 Vol.-% to 100 Vol.-% and a content of alkaline-earth metals, transition metals and metalloids of 0 and 2 Vol.-%, preferably 0 to 1 Vol.-%, even more preferably 0 to 0.5 Vol.-%, in relation to the total mass of solid carbonaceous material (see WO 2023/057242).

25 The BET surface area of the substrate is preferably between 0.1 and 100 m²/g, preferably 0.1 and 50 m²/g, in particular 0.1 to 30 m²/g.

Preferably, the real density of the substrate is in the range of 1.5 to 2.5 g/cc (real density in xylene, ISO 8004). Preferably, the bulk density of the substrate is in the range of 0.5 to 1.5 g/cc.

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Pyrolytic granular carbon

Typically, the real density of the granular pyrolytic carbon produced via the described methane decomposition process is in the range of 1.5 to 2.5 g/cc, preferably 2.0 to 2.3 g/cc (real density in xylene, ISO 8004). Typically, the bulk density of the granular pyrolytic carbon is in the range of 0.5 to 1.5 g/cc, more preferably 0.7 to 1.3 g/cc.

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Typically, the ash content of the granular pyrolytic carbon composition is in the range of 0.001 to 1 weight-% of the composition, preferably 0.01 to 0.2 weight-%.

Typically, the carbon content of the granular pyrolytic carbon composition is in the range of 98 to 100 weight-%, more preferably 99.5 to 100 weight-%, even more 99.75 to 100 weight-%, even more 99.9 to 100 weight-%.

Typically, the impurities of the granular pyrolytic carbon are: S in the range of 0 to 0.5 weight-%, more preferably 0 to 0.1 weight-%, Fe in the range of 0 to 1000 ppm, preferably 0 to 500 ppm, Ni in the range of 0 to 250 ppm, preferably 0 to 100 ppm, V in the range of 0 to 250 ppm, more preferably 0 to 100 ppm. Na in the range of 0 to 200 ppm, preferably 0 to 100 ppm. Oxygen is in the range of 0 to 100 ppm, preferably below the detection limit.

Typically, 90 weight-% of the carbon of the granular pyrolytic carbon composition is not-functionalized, preferably 95 weight-%, even more preferably 98 weight-%, especially 99 weight-%, wherein carbon functionalization refers to a reaction in which a carbon-carbon bond is broken and replaced by a carbon-X bond (where X is usually hydrogen, oxygen, sulfur, phosphorus, nitrogen, halogens, and/or metals).

Typically, the cation exchange capacity (CEC) of granular pyrolytic carbon is about 0.01 to 1.5 cmol/kg, preferably 0.025 to 0.75 cmol/kg.

Typically, the particle size of the granular pyrolytic carbon directly resulting of the decomposition of gaseous hydrocarbons – without any agglomeration step – is in the range of 0.3 mm (d10) to 8 mm (d90), preferably 0.5 mm (d10) to 5 mm (d90), more preferably 1 mm (d10) to 4 mm (d90).

Typically, the porosity of the granular pyrolytic carbon is between 0% to 15%, preferably 0.2% to 10%, most preferably 0.2% to 5% (Hg porosimetry, DIN66133).

Typically, the specific surface area of the granular pyrolytic carbon measured by Hg porosimetry (DIN66133) is in the range of 0.001 to 10 m²/g, preferably 0.001 to 5 m²/g, even more preferably 0.05 to 2 m²/g.

Preferred Reactor

Preferably, the reactor for carrying out the methane decomposition, in which methane, hydrogen and granular pyrolytic carbon are produced from C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas, comprises:

- a reactor surrounding a reactor interior
- the reactor is configured to provide a gravity-driven moving bed in a reaction zone of the reactor interior, which gravity-driven moving bed comprises a large number plurality of solid substrates, wherein the reactor is also configured to guide C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas into the reaction zone, wherein, in order to heat C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas, the reactor is configured to heat the solid substrates in the reaction zone by generating an electric current in the solid substrates between a pair of first and second electrodes such that, by transfer-

- ring heat from the solid substrates to C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas,
- C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in the reaction zone can be heated to a reaction temperature to produce methane, hydrogen and granular pyrolytic carbon,
 - 5 - and wherein the reactor interior also comprises a first heat integration zone in which heat from methane and hydrogen produced in the reaction zone can be transferred to solid substrates of the reactor gravity driven moving bed which are to be guided into the reaction zone, and wherein the reactor interior also comprises a second heat integration zone in which heat from solid substrates of the reactor gravity driven moving bed coming from the reaction zone can be transferred to C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in order to preheat C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas, wherein said reaction zone is arranged between said pair of first and second electrodes and said first heat integration zone is arranged above said first electrode and said second heat integration zone is arranged below said second electrode.
 - 10
 - 15 Preferably, the electrodes comprise a grid or are formed by a grid.

Preferred Moving Bed Method

Preferably a moving bed technology is used for the decomposition of C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas comprising:

- 20 - a plurality of solid substrates is guided into the first heat integration zone and from there into the reaction zone,
- the solid substrates are heated in the reaction zone,
- the solid substrates are guided from the reaction zone into the second heat integration zone and are withdrawn from the second heat integration zone,
- 25 - C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is introduced into the second heat integration zone and from there into the reaction zone, wherein C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in the second heat integration zone is heated against solid substrates coming from the reaction zone, wherein the solid substrates are cooled, and wherein the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is contacted with the heated solid substrates in the reaction zone, wherein heat from the heated solid substrates is transferred to C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in order to heat C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in the reaction zone, wherein C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is decomposed to methane, hydrogen and granular pyrolytic carbon in the reaction zone,
- 30 - methane and hydrogen produced is guided from the reaction zone into the first heat integration zone, wherein the solid substrates in the first heat integration zone are preheated against methane and hydrogen coming from the reaction zone, wherein methane and hydrogen is cooled, and wherein
- 35 - methane and hydrogen, the gaseous product stream, is withdrawn from the first heat integration zone
- granular pyrolytic carbon produced is deposited on solid substrates and withdrawn with the substrates

- withdrawn substrate is preferably at least partly recycled and introduced into the reactor
- withdrawn hydrogen is preferably at least partly recycled and introduced into the reactor.

Preferred process Conditions

5

Preferably, the deposition rate for the decomposition of the C2 to C6 alkanes being a reactive feedstock is to be kept in a range of preferably 0.1 to 20 wt.-%, more preferably 1 to 15 %, more preferably 2 to 12 %, even more preferably 3 to 10 wt.-%, even more preferably 4 to 8 wt.-%.

10 The definition of the specific carbon deposition rate depends on the reactor type and is defined as follows for a moving bed: The solid carbon mass from hydrocarbon pyrolysis deposited on one solid granule in one pass through the reactor divided by the mass of the said one solid granule before entering the reactor. The mass of the said solid particle is calculated by the Sauter mean diameter of the particle size distribution of the used granule.

15 Beside the temperature and the pressure, the deposition rate is preferably be controlled by diluting the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas feed with hydrogen to a volume ratio of preferably H₂/C₁₊ of 0.1 to 25, even more preferably 0.5 to 10, in particular 1 to 8, even more preferably 2 to 6. C₁₊ stands for all hydrocarbons. Preferably, the H₂/C₁₊ ratio is a H₂/(C₁-C₆) ratio.

20 The carbon deposition rate is preferably also be controlled by the conversion rate that is preferably 5 to 85 %, more preferably 10 to 80 %, more preferably 25 to 80 %, even more preferably 50 to 80 % (based on the hydrocarbons in the feed stream).

For option #2a the conversion rate is preferably 1 to 30 %, more preferably 4 to 25 %, more preferably 5 to 20 %.

For options #2b, #3 and 4 the conversion rate is preferably 25 to 85 %, more preferably 30 to 80 %, more preferably

25 50 to 80 %.

H₂/C₁₊ ratio

Preferably, the H₂/C₁₊ ratio of the total reactor feed containing (i) C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas and (i) additional hydrogen stream ranges from 0.5 to 25, more preferably from 0.75 to

30 10, even more preferably from 1 to 8, even more preferably 2 to 6.

Typically, the total reactor feed stream contains preferred 50 to 95 Vol.-% hydrogen, more preferred 65 to 85 Vol% hydrogen, and 5 to 50 Vol.-% hydrocarbons, more preferred 35 to 15 vol% hydrocarbons, and 0 to 3 Vol.-% inert gases, particularly nitrogen and argon.

35

There are several process layouts how to realize said H₂/C₁₊. Without excluding further options, preferred layouts are:

- Internal, direct gas recycle (see Figure 4, internal gas recycling): a portion of the gaseous product stream is recycled without any purification steps. The gaseous product stream may or may not be cooled or heated.
- Recycle after purification unit (see Figure 5, internal purge recycle): The hydrogen depleted product gas stream after any purification or gas separation unit is recycled to the reactor, while a fraction is purged.
- 5 - Gas streams employed for pneumatic transport of solids are recycled to the reactor.
- Hydrogen containing gas streams from different processes or other sources are mixed to the hydrogen feed stream.

10 Preferably, an internal direct recycle of the hydrogen-containing gaseous product stream is used to dilute the feed stream and control the H₂/C₁+ volume ratio, that means, a portion of the raw gaseous product stream is recycled without any purification steps (see Figure 4). Said recycled gaseous product stream may or may not be cooled, heated and/or compressed.

15 The gaseous product stream leaving the reaction chamber preferably enters a distribution unit. This distribution unit typically includes a valve, a flow meter, and a meter to determine the H₂ concentration.

20 Preferably, 10 vol-% to 90 vol-% of the gaseous product stream is separated in the distribution unit and recycled to the reaction chamber, more preferably 20 vol-% to 85 vol-%, more preferably 30 vol-% to 85 vol-%, even more preferably 40 vol-% to 80 vol-%, even more preferably 50 vol-% to 80 vol-%. The vol-% of the gaseous product stream taken for the internal direct recycle is preferably adjusted to a volume ratio H₂/C₁+ of the total reactor feed stream ranging from 0.1 to 25, more preferably from 0.5 to 10, even more preferably from 1 to 8.

25 The recycled gaseous product stream is mixed with the external feed stream, C₂-C₆ alkanes rich natural gas and/or C₂-C₆ alkanes rich industry off-gas, inside or outside the reaction chamber. Before mixing, the temperature of the internally recycled hydrogen-containing gaseous product stream is preferably between 10°C and 200°C, even more preferably between 15 and 150°C and in particular between 20 and 100°C. Preferably, the external feed stream, C₂-C₆ alkanes rich natural gas and/or C₂-C₆ alkanes rich industry off-gas, and the internally recycled hydrogen-containing gaseous product stream are mixed before entering the reaction chamber, outside of the reactor. Alternatively, the streams are separately introduced into the reaction chamber.

30 Therefore, preferably, the total feed of the pyrolysis process contains at least two feed streams: (i) external feed stream containing C₂-C₆ alkanes rich natural gas and/or C₂-C₆ alkanes rich industry off-gas and (ii) an internally recycled hydrogen-containing gaseous product stream.

35 Preferably the ratio of the volume of the internally recycled hydrogen-containing gaseous product stream to the volume of the external feed stream is between 0.1 to 20, more preferably between 0.3 and 8, even more preferably between 0.8 and 6.

Preferably, the total feed of the pyrolysis process has a fixed $H_2/C+$ feed molar, the operation point. The operating point enables an optimal heat integration and is dependent on the hydrocarbon concentration, the substrate used and the deposition rate of the solid carbon. To adjust the feed concentration/composition, preferably to continuously adjust the feed concentration/composition, a dedicated amount of hydrogen could be recycled or added, preferably recycled as mentioned above and shown in the Figures 4 and 5.

Preferably, the operation point of the pyrolysis unit is preferably set between 50 to 99 vol.%, more preferably between 70 and 99 vol.-% hydrogen and 1 to 50 vol.-%, more preferably 1 and 30 vol.-% hydrocarbons related to the total volume of the total feed. Due to the fact that the total feed concentration of the reactor could be controlled by a hydrogen recycle, there is a broad and fluctuating range for the concentration of hydrocarbons in the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas applicable.

Preferably, the hydrogen and/or hydrocarbon concentration of the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is measured before feeding into the pyrolysis unit. Depending on the difference of said concentration to the operation point, the additional hydrogen feed, preferably said hydrogen recycle, is increased or decreased during the pyrolysis process (see Figures 4 and 5). Optionally, additional hydrogen is added to the pyrolysis unit for adjusting, preferably continuously adjusting, the concentration to the operation point. Optionally, additional hydrocarbons, like natural gas or biomethane, are added to the pyrolysis unit for continuously adjusting the concentration to the operation point.

Advantages and Challenges of the different Pyrolysis Technology

The moving bed technology is the preferred pyrolysis technology. The moving bed is less sensitive to clogging. The moving bed has the advantage of producing a granular solid carbon product directly that can be easily transported. Further advantages are low CO₂ emissions and a low energy demand. In addition, impurities of the raw natural gas can be taken out via the moving bed without ending up in the gaseous product stream. As the moving bed is heat-integrated it can be easily operated in remote locations.

Advantages of the present invention

There are reserves which have high C2-C6 alkanes content, especially ethane, that cannot be exploited economically as the pipeline specs cannot tolerate the high C2-C6 alkanes content. Removal of C2-C6 alkanes requires an additional processing plant. Today, the extracted C2-C6 alkanes are sold at a loss compared to its heating value, sometimes even flared. Using the present invention, the methane pyrolysis step can be used as processing plant, avoid loss of a large natural gas share, avoid CO₂ emission by flaring and avoiding costly energy-intensive pre-treatment. Summing up, the present invention will facilitate the exploitation of gas reserves that were previously unsuitable, uneconomically.

Fig 1: Schematic presentation of the present invention

Figure 1 shows in comparison the state of the art and the three possible alternative routes of the present invention.

The state of the art (#1) shows the known natural gas purification process of C2-C4 alkanes -rich natural gas, resulting in grid-grade natural gas and C2-C4 alkanes off gas. In the preferred embodiment of the present invention (#2), C2-C4 alkanes -rich natural gas is processed in a methane pyrolysis process to result in solid carbon and H2-

- 5 enriched & C2-C4 alkanes -reduced natural gas. An alternative embodiment (#3) shows the processing of the C2-C4 alkanes -rich off gas from #1, resulting in solid carbon and H2. An alternative embodiment (#4) shows the processing of the raw natural gas to solid carbon and H2.

- Figure 2 shows another preferred embodiment (#2b), C2-C4 alkanes -rich natural gas is processed in a methane pyrolysis process to result in solid carbon and H2-enriched & C2-C4 alkanes -reduced natural gas. This H2-enriched
10 & C2-C4 alkanes -reduced natural gas is mixed with C2-C4 alkanes rich raw natural gas in such an amount which is permissible in view of the allowed heating values.

Fig 3 shows the block diagram of a general embodiment of the process of the invention.

Fig 4 shows the block diagram of a general embodiment of the process of the invention in which part of the gaseous product stream is recycled to the pyrolysis unit.

- 15 Fig 5 shows the block diagram of a general embodiment of the process of the invention in which also a part of the off gas from the hydrogen recovery is recycled to the pyrolysis unit.

Fig 6 shows the block diagram of a general embodiment of the process of the invention in which part of the solid carbon are recycled to the pyrolysis unit.

- Figures 7 to 10 show a fast decomposition using C2H6 or C3H8 as part of the feed gas (compared to pure CH4) and
20 thus indicate a higher risk for clogging or soot formation.

Comparison:

#1 (state of the art)	+ use of existing infrastructure - energy-intensive pre-treatment - loss of a large natural gas share → 0% fossil carbon reduction in gas distribution network
#2 (inventive example)	+ use of existing infrastructure + grid quality still in spec for industrial processes + high-value byproduct instead of purge stream → H₂-share can be varied through methane pyrolysis and defines percentage between >0-100% of fossil carbon reduction in gas distribution network via transfer of alkanes into solid carbon and separation of said solid carbon from the gas stream compared to #1
#2b (inventive example)	+ use of existing infrastructure + grid quality still in spec for Industrial processes + high-value byproduct instead of purge stream + smaller methane pyrolysis process necessary while achieving the same results as #2a - Compared to #2a, additional process control infrastructure is required for the blending step → H₂-share can be varied through methane pyrolysis and defines percentage between 0-100% of fossil carbon reduction in gas distribution network via transfer of alkanes into solid carbon and separation of said solid carbon from the gas stream compared to #1
#3 (inventive example)	+ Avoidance of purge streams + Additional hydrogen supply - New H₂-infrastructure required → 100% decarbonization of off-gas via transfer of alkanes into solid carbon and separation of said solid carbon from the off gas, 0% fossil carbon reduction in gas distribution network
#4 (inventive example)	+ Large hydrogen supply + Large high-purity carbon supply - New H₂-infrastructure required

	→ 100% fossil carbon reduction in gas distribution network via transfer of alkanes into solid carbon and separation of said solid carbon from the gas stream compared to #1
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Working examples:

Methane pyrolysis was performed in a laboratory-scale fixed-bed reactor setup with inner tube diameter of 50 mm and a length of the fixed-bed of 0.5 m. In the center of the fixed-bed, another tube with outer diameter of 10 mm is positioned, which is equipped for measurement of temperature. For pyrolysis, the reactor tube was heated externally to 1450°C.

Example 1: Pyrolysis was performed at a volume flow of methane of 220 NI/h, diluted in hydrogen and argon.

Example 2: Pyrolysis was performed at a volume flow of methane of 220 NI/h (91.7 %) and ethane of 20 NI/h (8.3 %), diluted in hydrogen and argon.

Table 1: Change in product mass flow normed to the total mass flow of hydrocarbons in the product gas.

Measured hydrocarbons in the product gas	Delta of product mass between example 2 and 1
Delta CH4	1,936%
Delta C2H6	-0,040%
Delta C2H4	0,000%
Delta C2H2	-0,245%
Delta C3H6	0,009%
Delta C6H6	-0,026%

Table 2: Change in conversion rate of hydrocarbons.

Delta conversion normed to total hydrocarbon feed between example 2 and 1	7,3%
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Conclusion: The composition of the hydrocarbons in the product gas in example 1 and 2 was almost identically. The conversion rate of example 2 is significantly higher than of example 1. Therefore, the ethane shares in the feed gas of example 2 was almost completely converted to hydrogen and solid carbon.

Example 3: Long-time experiment in a moving bed reactor

Pyrolysis of natural gas to H2 and solid C was carried out in a moving bed reactor. The reactor had an inner tube diameter of 190 mm and a solid bed height of 3m. The solid bed comprised carbon granules with particle sizes from 2 – 4 mm. The particle comprised a mixture of calcinated petroleum coke (CPC) and the pyrolytic carbon, deposited

on the particle from the methane pyrolysis. The bed was direct electrically heated. In addition to that the wall of the inner tube was electrically heated to compensate heat losses,

The process conditions are summarized in table 3.

The natural gas comprised a significant share of ethane and propane as shown in table 4. Ethane and propane were to > 99 vol% converted to hydrogen and solid carbon while the CH₄ conversion was 20 %. The overall specific carbon deposition rate was 3 w%. The moving bed was operated for 480 hours under these conditions without any sign for reactor clogging.

Table3: Process conditions natural gas pyrolysis in a moving bed reactor

	Example 3
Gas-Feed	18 vol% Natural Gas 82 vol% H ₂
Max Temperature [°C]	1250
Operating pressure [bara]	4
Operation time [h]	480

Table 4: Natural Gas Composition

CH ₄	90 vol %
C ₂ H ₆	5.5 vol %
C ₃ H ₈	1.2 vol %
Others	3.3 vol%

Comparison of pure methane and mixture of methane with ethane or propane: fluidized bed and moving bed:

General information:

- The risk for clogging or soot formation in the inlet of a fluidized bed compared to a moving bed is compared assuming that the feed gas in case of the fluidized bed is be heated to maintain homogenous temperature before entering the reactor. In the moving bed, the heating occurs within the moving bed, i.e., in the reaction zone.
- To compare the risk for clogging or soot formation in both reactors concepts chemical kinetics simulations were performed using the open-source software Cantera and the chemical reaction mechanism CRECK 2003 from Politecnico di Milano.

Simulation setup:

- Species concentrations change over time, while temperature and pressure are kept constant.
- Changes in residence time are accounted for by adjusting the available reaction time.
- Results are analyzed based on the temporal evolution of species concentrations.

References:

- Cantera: [Open-source chemical kinetics, thermodynamics, and transport — Cantera](#)
- CRECK 2003: [Detailed kinetic mechanisms - Creckmodeling \(polimi.it\)](#)

Results (see Fig. 7 to Fig. 10)

- C₂H₆ and C₃H₈ promote pyrolysis at lower temperature compared to pure CH₄
- Notable formation of soot precursors in less than 1 sec (10³ ms) for C₂H₆ and C₃H₈ mixtures

Summary:

The results show much faster species decomposition when using C₂H₆ or C₃H₈ as part of the feed gas (compared to pure CH₄) and thus indicate a higher risk for clogging, e.g. inside pre-heating equipment necessary for the operation of a fluidized bed reactor. In addition, the results show notable formation of soot precursors in less than 1 sec (10³ ms) for C₂H₆ and C₃H₈ mixtures and thus indicate a higher risk for soot formation and hereafter blocking.

Claims

1. Process for treatment of C2-C6 alkanes rich natural gas having an C2-C6 alkane content of 2.5 to 30 Vol.-% of the total raw natural gas or C2-C6 alkanes rich industry off-gas having an C2-C6 alkane content of 10 to 80 Vol.-% of the total industry off-gas, wherein (i) the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas are introduced via the bottom of a moving bed reactor, having a temperature of 10 to 200°C, and substrates having a particle size of 0.3 to 8 mm are introduced via the top of said moving bed reactor, having a temperature of 10 to 200°C, (ii) the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is pyrolyzed in said moving bed reactor into a gaseous product stream containing at least methane and/or hydrogen and pyrolyzed into solid carbon, (iii) said solid carbon is separated from said gaseous product stream and (iv) said gaseous product stream is fed into a natural gas grid and/or into a hydrogen grid or said gaseous product stream is used materially or energetically directly.
2. Process according to claim 1, wherein said gaseous product stream is taken off via the top of said moving bed reactor, having a temperature of 10 to 200°C, and said solid carbon is taken off via the bottom of said moving bed reactor, having a temperature of 10 to 200°C.
3. Process according to claim 1 or 2, wherein the C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is pyrolyzed at temperatures ranging from 500 to 2000°C and at pressures ranging from 1 to 100 bar into a gaseous product stream containing at least methane and/or hydrogen and pyrolyzed into solid carbon and wherein the deposition rate of the solid carbon is kept in a range of 2 to 20 wt.-%.
4. Process according to claim 3, wherein the deposition rate of the solid carbon is kept in a range of 2 to 15 wt.-% by diluting the hydrocarbon feed of C2-C6 alkanes rich natural gas and/or of C2-C6 alkanes rich industry off-gas with hydrogen to a volume ratio of H₂/C₁+ of 0.5 to 25 of the diluted total reactor feed streams, wherein the total reactor feed streams contain (i) C2-C6 alkanes rich natural gas and/or of C2-C6 alkanes rich industry off-gas and (ii) additional hydrogen.
5. Process according to claim 3 or 4, wherein 10 to 95 vol.-% of said gaseous product stream is recycled internally to said bottom of said moving bed reactor for diluting the hydrocarbon feed of C2-C6 alkanes rich natural gas and/or of C2-C6 alkanes rich industry off-gas with hydrogen to a volume ratio of H₂/(C₁-C₆ alkanes) of 1 to 10 of the diluted total reactor feed streams.
6. Process according to any one of claims 1 to 5, wherein the total feed of the pyrolysis unit is continuously adjusted to a fixed volume ratio of H₂/C₁+, the operation point, by increasing or decreasing the amount of an internal hydrogen product stream recycle and/or by adding additional hydrogen and/or additional hydrocarbons.

- 5
7. Process according to any one of claims 1 to 6, wherein the C2-C6 alkanes rich natural gas is extracted and pre-processed before feeding to the pyrolysis unit, wherein the extraction unit is upstream of and fluidically connected to the pre-processing unit and the pre-processing unit is upstream of and fluidically connected to the pyrolysis unit.
- 10
8. Process according to any one of claims 1 to 7, wherein the C2-C6 alkanes rich natural gas has following content: methane from 50 to 95 Vol.-%, ethane from 2.5 to 25 Vol.-%, propane from 0 to 15 Vol.-%, butane from 0 to 10 Vol.-%, CO₂ from 0 to 5 Vol.-%, N₂ from 0 to 10 Vol.-% and sulfur components from 0 to 30 Vol.-% of the total raw natural gas.
- 15
9. Process according to any one of claims 1 to 8, wherein C2-C6 alkanes rich natural gas is pyrolyzed at temperatures ranging from 900 to 1100°C and keeping a volume ratio of H₂/C₁₊ of 0.05 to 0.2 and wherein the gaseous product stream contains 0.1 to 30 Vol.-% hydrogen and wherein said gaseous product stream is fed into a natural gas grid.
- 20
10. Process according to any one of claims 1 to 6, wherein the C2-C6 alkanes rich industry off-gas has following content: 2.5 to 70 Vol.-% ethane, 2.5 to 70 Vol.-% propane, 2.5 to 70 Vol.-% butane of the total industry off-gas.
- 25
11. Process according to any one of claims 1 to 10, wherein the bulk density of the substrate is in the range of 0.5 to 1.5 g/cc and the BET surface area of the substrate is 0.1 to 30 m²/g.
- 30
12. Process according to any one of claims 1 to 11, wherein the pyrolysis process is electrically heated by resistive heating of the substrates.
- 35
13. The process according to any one of claims 1 to 12, comprising:
- a plurality of solid substrates is guided into the first heat integration zone and from there into the reaction zone of said moving bed reactor,
 - the solid substrates are heated in the reaction zone,
 - the solid substrates are guided from the reaction zone into the second heat integration zone and are withdrawn from the second heat integration zone,
 - C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is introduced into the second heat integration zone and from there into the reaction zone, wherein C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in the second heat integration zone is heated against solid substrates coming from the reaction zone, wherein the solid substrates are cooled, and wherein the C2-C6

- alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is contacted with the heated solid substrates in the reaction zone, wherein heat from the heated solid substrates is transferred to C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in order to heat C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas in the reaction zone, wherein C2-C6 alkanes rich natural gas and/or C2-C6 alkanes rich industry off-gas is decomposed to methane, hydrogen and granular pyrolytic carbon in the reaction zone,
- 5
- methane and hydrogen produced is guided from the reaction zone into the first heat integration zone, wherein the solid substrates in the first heat integration zone are preheated against methane and hydrogen coming from the reaction zone, wherein methane and hydrogen is cooled, and wherein
- 10
- methane and hydrogen, the gaseous product stream, is withdrawn from the first heat integration zone
 - granular pyrolytic carbon produced is deposited on solid substrates and withdrawn with the substrates
 - withdrawn substrate is preferably at least partly recycled and introduced into the reactor.
14. Process according to any one of claims 1 to 13, wherein said gaseous product stream is mixed with C2-C6 al-
- 15
- kanes rich natural gas before feeding into a natural gas grid.
15. Process according to any one of claims 1 to 14, wherein the gaseous product stream containing hydrogen is converted into methane, ammonia and/or methanol.