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(54) HIGH CALORIFIC SYNTHETIC NATURAL GAS (SNG) THROUGH LOW-TEMPERATURE INDIRECT GASIFICATION

(57) The invention concerns a process for the production of a synthetic natural gas (SNG) from biomass. Biomass is indirectly gasified and the product gas comprising higher alkanes, alkenes and/or alkynes is subjected to hydrogenation, a water gas shift reaction and isothermal methanation. The invention furthermore concerns a system for the production of a synthetic natural gas.

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Description

Introduction

[0001] Synthetic natural gas (SNG) has emerged as a promising alternative to conventional natural gas, offering potential benefits in terms of energy security and environmental sustainability. SNG can be produced from various feedstocks, including biomass, through gasification and subsequent methanation processes. This approach allows for the utilization of renewable resources to create a fuel that is compatible with existing natural gas infrastructure.

[0002] To be exchangeable with natural gas, the energy content of the SNG needs to be the same. There are different grades of natural gas, for example in some case a difference is made between low caloric gas having a higher heating value (HHV) of 35.1 MJ/Nm^3 and high caloric gas with a HHV of about 40.0 MJ/Nm^3. The difference in heating value depends on the amount of non-combustible gas such as N_2 and CO_2 in the natural gas and the energy density of the gasses that are comprises in the natural gas. For example, methane has a HHV of about 39.7 MJ/Nm^3 whilst ethane as a HHV of about 69.7 MJ/Nm^3.

[0003] By making use of indirect gasification instead of direct gasification introduction of non-combustible N_2 or (excess) CO_2 can be prevented. In direct gasification, oxygen is introduced into the gasification with the feedstock diluting the gas with CO_2 formed in the combustion of part of the feedstock. If oxygen is introduced as air, additionally N_2 dilution occurs. During low temperature indirect gasification of biomass some C2, C3 and C4 alkynes, alkenes and alkanes are formed.

[0004] In US 8821153 B2 a process is described in which a fuel which is optionally biomass is gasified in the presence of oxygen, the higher hydrocarbons are broken down, an amount of H_2O and CO_2 are removed and finally the resulting gas is subjected to a methanation step. By the breakdown of the higher hydrocarbons the energy density of the gas per cubic meter is reduced and relatively low caloric natural gas substitute is produced. The feed for the methanation step comprises both CO and CO_2.

[0005] WO 2015/011503 A1 discloses a process for producing a substitute natural gas. In this process a synthesis gas (syngas) comprising primarily H_2 and CO is subjected to a water gas shift reaction to increase the H_2 to CO ratio and the resulting product is subsequently subjected to a methanation reaction to form a methane enriched gas; a methane-containing gas is recovered from the methane enriched gas. The energy density may be increased by adding an additional step in which part of the WGS treated syngas is converted into C2, C3 and/or C4 alkanes/alkenes. Syngas does not comprise higher hydrocarbons. The feed for the methanation step comprises both CO and CO_2.

[0006] There is need for an efficient process to produce an SNG of which the energy density is relatively high.

Summary of the invention

[0007] The present invention provides a novel process for producing synthetic natural gas (SNG) with a high calorific value from biomass which starts with indirect gasification of the biomass. This process significantly improves upon prior art methods by maintaining higher hydrocarbons that are formed during the indirect gasification in the final SNG product, resulting in increased energy content.

[0008] Unlike conventional approaches that degrade valuable higher carbons during downstream processing, the current method carefully controls reaction conditions to preserve these higher hydrocarbons. This advancement addresses the challenge of maximizing the calorific value of SNG produced from biomass feedstocks.

[0009] The invention utilizes a unique combination of process steps, including indirect gasification, hydrogenation of alkynes and alkenes, water-gas shift reaction, and isothermal methanation. By operating these steps under specific reaction conditions, the process maintains the higher hydrocarbon content in the product gas while effectively converting CO and CO_2 with H_2 to methane. For example, example 2 demonstrates that isothermal methanation prevents breakdown of higher alkanes. In contrary, Gomez et al. (Chemical Engineering Science 267 (2023) 118291, https://doi.org/10.1016/j.ces.2022.118291) demonstrate in Table 4, experiment 5 that ethene fully disappears during adiabatic methanation. Example 1 demonstrates that indirect gasification at a lower temperature results in that an amount of C2 - C4 hydrocarbon is formed and that these C2 - C4 hydrocarbons are preserved when the product gas undergoes a hydrogenation reaction that hydrogenates the C2 - C4 alkynes and alkenes

[0010] In addition, the inventor found that the catalyst surprisingly rapidly deactivates for isothermal methanation of a product gas that comprises an amount of CO. Example 2 demonstrates that in the presence of CO in the product gas catalyst deactivation is observable within 5 hours. The invention provides a solution to the problem of this catalyst coking during methanation. By incorporating a separate water-gas shift step prior to methanation, or combining it with the hydrogenation step, the CO content of the gas stream entering the methanation reactor is reduced. This approach minimizes coke formation on the methanation catalyst, leading to improved catalyst longevity and process stability.

[0011] The process is further enhanced by the flexibility to adjust CO2 levels either before or after the methanation step. This allows for precise control over the final SNG composition, enabling customization to meet specific energy content requirements or pipeline specifications.

[0012] Overall, the present invention offers a more efficient and effective method for producing high-quality SNG from biomass, with potential applications in renewable energy production and utilization of waste biomass resources.

Detailed Description

[0013] In a first embodiment, the invention concerns a process for the production of a synthetic natural gas (SNG) comprising the following steps:

a) indirect gasification of biomass to produce a product gas,
b) subjecting the product gas to a hydrogenation reaction to convert alkenes and alkynes to alkanes producing a hydrogenated product gas,
c) subjecting the hydrogenated product gas to a water gas shift reaction (WGS) producing a WGS-treated product gas, and
d) subjecting the WGS-treated product gas to an isothermal methanation step to form the synthetic natural gas,

wherein

- the product gas comprises alkenes wherein the amount of the alkenes is 1 - 15 vol.% based on total water-free volume of the product gas,
- step a) is carried out at a temperature in the range of 500 - 1000°C; and
- step c) is carried out at a temperature in the range of 200 - 550°C,

and wherein step c) is carried out as a separate step after step b) or is carried out in combination with step b) wherein in the combined step a WGS-treated product gas is produced. Step a) of this process may also be phrased as providing a product gas obtained from indirect gasification of biomass.

[0014] In a further embodiment, the invention concerns a system for the production of a synthetic natural gas (SNG) comprising

I an indirect biomass gasification reactor having an inlet for solid and/or liquid biomass and an outlet for a product gas,
II a hydrogenation reactor of which the inlet is in fluid connection to the product gas outlet of the indirect biomass gasification reactor and having an outlet for a hydrogenated product gas,
III a WGS reactor of which the inlet is in fluid connection to the hydrogenated product gas outlet of the hydrogenation reactor and having an outlet for a WGS-treated product gas, and
IV a methanation reactor of which the inlet is in fluid connection to the WGS-treated product gas outlet of the WGS reactor and having an outlet for the synthetic natural gas,

or comprising

I an indirect biomass gasification reactor having an inlet for solid and/or liquid biomass and an outlet for a product gas,
IIa a combined water gas shift and hydrogenation reactor of which the inlet is in fluid connection to the product gas outlet of the indirect biomass gasification reactor and having an outlet for a hydrogenated WGS-treated product gas,
IV a methanation reactor of which the inlet is in fluid connection to the hydrogenated WGS-treated product gas outlet of the combined water gas shift and hydrogenation reactor and having an outlet for the synthetic natural gas.

[0015] The invention furthermore concerns synthetic natural gas (SNG) composition comprising

- 80 - 98 vol.% CH_4,
- 0.1 - 3.0 vol.% CO_2,
- 0.1 - 10 vol.% N_2
- 0.1 - 3.0 vol.% H_2, and
- 2.0 - 15 vol.% of the sum of ethane, propane and butane, preferably 4.0 - 8 vol.%;

wherein the vol.% are based on total water-free volume of the product gas. The synthetic natural gas may be obtained by the process described in the first embodiment.

[0016] The current invention concerns a process for the production of a synthetic natural gas comprising different steps and which is carried out in multiple reactors, a synthetic natural gas obtained by the process and a system for the production of a synthetic natural gas. Any embodiment or feature that is discloses for the process also applies for the SNG produced by the process and for the system, any embodiment or feature that is discloses for the SNG produced by the

process also applies for the process and for the system, and any embodiment that is discloses for the system also applies for the process and for the SNG produced by the process.

a) Indirect gasification of biomass

[0017] The process for producing synthetic natural gas (SNG) begins with indirect gasification of biomass to produce a product gas. This indirect gasification method operates at lower temperatures compared to traditional direct gasification processes, typically in the range of 500-1000°C. Preferably, the temperature range is in the range of 550-900°C, or more preferably 600-850°C. At lower temperatures more alkanes, alkenes and alkynes are formed that have two or more carbon atoms.

[0018] In the indirect gasification process, biomass is fed into a pyrolysis chamber where it undergoes thermal decomposition in the absence of O_2. This O_2 free gasification allows to produce a product gas with a higher concentration of valuable components such as hydrogen, carbon monoxide, and light hydrocarbons. Typically, the remaining solids of the indirect gasification process are combusted, and the combustion energy is used to heat the indirect gasification process. In this scenario, heat production takes place outside the reactor where heat is needed. That means that gasification and combustion take place in different reactors, mass and energy being transferred between them. Such a process has been implemented and used in a reactor for producing a product gas from a fuel, developed by the applicant. The reactor and the process are described in WO2014/070001A1. WO2016/091828A1 describes gasification of a biomass in the aforementioned reactor.

[0019] The product gas produced by indirect gasification contains a mixture of components including hydrogen, carbon monoxide, carbon dioxide, methane, and higher hydrocarbons. The higher hydrocarbons typically are C2, C3 and C4 hydrocarbons, so C2 - C4 hydrocarbons. Higher hydrocarbons are hydrocarbons comprising more than 1 carbon atom. C2 refers to that a hydrocarbon comprising two carbon atoms, C3 refers to that a hydrocarbon comprising three carbon atoms, C4 refers to that a hydrocarbon comprising four carbon atoms. Preferably the higher hydrocarbons are C2 - C4 alkanes, alkenes and alkynes. For the current invention, the product gas comprises 1 - 15 vol.% of the sum of C2 - C4 alkanes, alkenes and alkynes based on total water-free volume of the product gas, preferably the product gas comprises 2 - 10 vol.% of the sum of C2 - C4 alkanes, alkenes and alkynes based on total water-free volume of the product gas, even more preferably 3 - 8 vol.%. Typically, ethene is the dominant higher hydrocarbon in the product gas. In a preferred embodiment the product gas comprises ethene in an amount of 1 - 15 vol.% based on total water-free volume of the product gas, preferably the product gas comprises 2 - 10 vol.% ethene based on total water-free volume of the product gas, even more preferably 3 - 8 vol.%. The concentration of C2 - C4 alkanes, alkenes and alkynes may be adjusted by adapting the process conditions of the indirect gasification process, especially by adapting the temperature. The skilled person may adjust the indirect gasification step to yield an higher hydrocarbon concentration that is useful to reach a specific energy density of the resulting SNG.

[0020] Preferably the product gas comprises based on total dry volume of the product gas:

- 10-50 vol.% CO,
- 10-40 vol.% CO_2,
- 10-40 vol.% H_2,
- 5-25 vol.% CH_4, and
- 1-15 vol.% of the sum of C2 - C4 alkanes, alkenes and alkynes.

[0021] In a preferred embodiment the pressure during the indirect gasification process is in the range of 1-10 bar, preferably 1-5 bar.

[0022] After the indirect gasification step, the product gas may undergo further processing to remove impurities and adjust its composition making use of known state of the art technologies. One such processing step involves tar removal from the product gas. Tar may be defined as all hydrocarbons with a molecular weight higher than benzene. In a preferred embodiment in step a1) after step a) but before step b) tar is removed from the product gas.

[0023] Tar removal may be accomplished using various methods, such as the OLGA (oil-based gas washing) process. Other processes are also known in the art (as described by Chen et al., J. of Cleaner Production, Volume 384, 15 January 2023, 135575, https://doi.org/10.1016/j.jclepro.2022.135575). In the OLGA process, the product gas is passed through a series of oil scrubbing reactors operating at different temperatures. The tar components are selectively absorbed by the scrubbing oil, which can then be regenerated and reused. This OLGA technology is further described in TNO report 866312 ("OLGA" TAR REMOVAL TECHNOLOGY Proof-of-Concept (PoC) for application in integrated biomass gasification combined heat and power (CHP) systems, Boerrigter et al. 2009). The pressure during the tar removal step preferably is in the range of 1-10 bar, more preferably 1-5 bar.

[0024] Following tar removal, water may be removed from the product gas. In a preferred embodiment in step a2) after step a) or after step a1) when step a1) is present but before step b) water is removed from the product gas, preferably by

condensation. Preferably for the condensation the temperature of the product gas is lowered to below 50°C. Water removal serves multiple purposes: reducing the water content in the product gas, removing water-soluble impurities, and potentially condensing out other condensable components. Reducing the water content in the product gas helps when the product gas is further pressurized in preventing the condensation of water upon this pressurization. Preferably the water content after step a2) is in the range of 0 - 10 vol.% based on total volume of the product gas, more preferably in the range of 0 - 5 vol.%. Alternatively, the water content after step a2) is in the range of 0 - 10 mol.% based on total of the product gas, more preferably in the range of 0 - 5 mol.%. The pressure during the water removal step preferably is in the range of 1 - 10 bar, more preferably 1 - 5 bar.

[0025] In a preferred embodiments also benzene, toluene and xylene (BTX) is removed from the product gas in step a3). Although BTX components may Technologies to remove BTX are known to the skilled person. For example, in EP 3622041 A1 such method is described. Step a3) when applied is before step b) and after step a).

[0026] The preferred removal of tar, BTX and water from the product gas prepares the product gas for subsequent processing steps, such as hydrogenation and methanation. These removal steps may help to prevent fouling of downstream catalysts and equipment and ensure a more consistent gas composition for further reactions.

b) Hydrogenation

[0027] In step b) the product gas from the indirect gasification process undergoes a hydrogenation step to convert alkenes and alkynes to alkanes. This step primarily focuses on the conversion of ethene, ethyne, propene and propyne and butene and butyne into ethane, propane, and butane respectively. The hydrogenation reaction may also convert other alkenes and alkynes present in the product gas. Typically, the temperature range for the hydrogenation step b) is in the range of 200-500°C. Preferably the temperature of the hydrogenation step b) is in the range of 300 - 450°C. As example 1 demonstrates, hydrogenation at typical hydrogenation temperatures in the absence of or at low concentrations of H_2O in the product gas (so that no significant WGS reaction takes place) is effective for alkene and alkyne hydrogenation and does not break down the alkanes and alkynes with 2 or more carbon atoms. In case the WGS step c), for which typically additional steam is provided to the product gas, is combined with hydrogenation step b) a lower hydrogenation temperature may be preferred, such as 150 - 400°C, even more preferably in the range of 150 - 300°C, even more preferably in the range of 150 - 295°C, to not break down hydrocarbons with 2 or more carbon atoms. So, when step c) is carried out as a separate step after step b) the temperature of the hydrogenation step b) is typically in the range of 200 - 500°C, preferably in the range of 300 - 450°C, and when step c) is carried out in combination with step b) the temperature of the hydrogenation step b) is preferably in the range of 150 - 400°C, more preferably in the range of 150 - 300°C, even more preferably in the range of 150-295°C. The pressure during the hydrogenation step b) preferably is in the range of 1-50 bar, more preferably in the range of 5-20 bar.

[0028] The hydrogenation step is preferably carried out as part of a hydrodesulfurization (HDS) process. In a HDS process, organosulfur compounds present in the product gas are in a HDS reactor converted into sulfur compounds, typically into hydrogen sulfide (H_2S) and carbonyl sulfide (COS). It is known in the art that in a HDS reactor alkenes and alkynes that may be present in the feed are hydrogenated to alkanes. So, the hydrogenation reaction of step b) preferably is in a HDS reactor. This HDs reactor may be one reactor or a combination of reactors.

[0029] Various catalysts may be used for the hydrogenation reaction of step b). Preferably the hydrogenation catalyst is selected from the list consisting of nickel-based catalysts, cobalt-molybdenum catalysts, molybdenum disulfide-based catalysts, ruthenium disulfide-based catalysts and combinations thereof. Preferably, the nickel-based catalyst is a nickel-molybdenum catalyst or a nickel-tungsten catalyst. These catalysts are suitable for hydrogenation of alkynes and alkenes and for hydrodesulfurization.

[0030] Following the hydrogenation and HDS reactions, the hydrogenated product gas preferably is subjected to a step b1) to remove the sulfur compounds such as H_2S and COS. Preferably the sulfur compounds are H_2S and COS. This step typically is a part of a HDS process. The combination of the combined hydrogenation and hydrodesulfurization reaction in step b) and the removal step b1) is important for downstream processing and the overall efficiency of the SNG production process, as sulfur compounds can poison catalysts used in subsequent steps. Moreover, sulfur compounds are undesired in SNG as they form sulfur oxides when the SNG is combusted, these sulfur oxides are harmful for the environment. The sulfur removal step b1) removal step preferably is carried out in

[0031] The sulfur compound removal process preferably involves adsorption of the sulfur compounds such as H_2S and COS on a sorbent, preferably a zinc oxide (ZnO) sorbent. The sorbent selectively adsorbs the sulfur compounds from the hydrogenated product gas. The temperature for this adsorption process preferably is in the range of 200-400°C. The pressure may be similar to that of the hydrogenation step, preferably in the range of 1-50 bar, more preferably in the range of 5-20 bar.

[0032] The sulfur compound removal step preferably is carried out in a fixed-bed reactor filled with a sorbent, preferably a ZnO sorbent. As the hydrogenated product gas passes through the reactor, the sulfur compounds react with the ZnO to form zinc sulfide (ZnS), effectively removing them from the gas stream. The reactor preferably is designed to allow for

periodic replacement or regeneration of the ZnO sorbent to maintain its effectiveness.

[0033] In some examples, multiple adsorption reactors may be used in parallel, allowing for continuous operation while individual reactors undergo sorbent replacement or regeneration. This configuration ensures uninterrupted gas processing and maintains the overall efficiency of the SNG production process.

[0034] The removal of sulfur compounds such as H_2S and COS from the hydrogenated product gas prepares the gas stream for subsequent processing steps, such as the water gas shift reaction and methanation. By removing these sulfur compounds, the risk of catalyst poisoning in downstream reactors is significantly reduced, leading to improved catalyst longevity and process efficiency.

c) Water gas shift reaction (WGS reaction)

[0035] In the process of the invention, the hydrogenated product gas or the product gas undergoes a water gas shift (WGS) reaction to convert carbon monoxide of the hydrogenated product gas or the product gas to carbon dioxide. In this way rapid inactivation of the methanation catalyst that is used in step d) may be prevented. The WGS reaction converts carbon monoxide and water vapor into carbon dioxide and hydrogen according to the following reaction equation:

$$CO + H_2O \rightarrow CO_2 + H_2$$

[0036] The WGS reaction may be carried out as a separate step after the hydrogenation step b) or in combination with the hydrogenation reaction in step b). In case the WGS step c) is carried out in combination with step b) the combined step produces a WGS-treated product gas. When performed as a separate step, the WGS reaction occurs in a dedicated reactor or combination of reactors. When combined with the hydrogenation step, both reactions take place simultaneously in a single reactor or a in combination of reactors.

[0037] The WGS reaction is preferably conducted at low temperatures to maintain the C2 - C4 hydrocarbons present in the gas stream. The temperature range for the WGS reaction is 200-550°C. Preferably, the WGS reaction is carried out at a temperature in the range of 150 - 400°C, preferably in the range of 150 - 300°C, more preferably in the range of 150 - 295°C. The pressure during the WGS reaction preferably is in the range of 1 - 50 bar, more preferably in the range of 5 - 20 bar.

[0038] Various catalysts may be used for the WGS reaction. The WGS catalyst preferably is a transition metal-based catalyst, an oxide of a transition metal-based catalyst or a combination thereof. The transition metal preferably is selected from nickel, iron, copper, zinc, chromium, or combinations thereof. These catalysts facilitate the conversion of carbon monoxide and water vapor into carbon dioxide and hydrogen. In case the WGS step is combined with the hydrogenation step, both a WGS catalyst as a hydrogenation catalyst may be present in the reactor or one catalyst is present that catalyzes both reactions.

[0039] The WGS reaction preferably is carried out in a fixed-bed reactor filled with the selected catalyst. As the hydrogenated product gas passes through the reactor, the carbon monoxide reacts with water vapor in the presence of the catalyst to produce carbon dioxide and hydrogen.

[0040] In some examples, multiple WGS reactors may be used in series or parallel, allowing for better control of the reaction conditions and improved overall conversion efficiency. This configuration may also allow for the use of different catalysts or operating conditions in each reactor to optimize the WGS reaction for different gas compositions or process requirements.

[0041] The WGS reaction serves to increase the hydrogen content of the gas stream and reducing the carbon monoxide content. This adjustment of the gas composition prepares the gas stream for the subsequent methanation step, where the hydrogen and carbon oxides are converted into methane to produce the final synthetic natural gas product. In a preferred embodiment after the WGS reaction the

[0042] As typically the hydrogenated product gas comprises no or low amounts of water, and water is a prerequisite for the WGS, preferably steam is provided in step c), or in case step b) and c) are combined steam is provided in the combined step. Also for the combined step the providing of steam is preferred as typically the product gas is dried before being fed to step b). The skilled person known how to optimize the amount of steam that is provided based on the composition of the product gas or hydrogenated product gas. Particularly, the amount of CO present in the product gas or hydrogenated product gas is leading as this CO is converted together with the steam to CO_2 and steam.

[0043] The WGS-treated product gas preferably comprises 0 - 10 vol.% CO based on total volume of the dry product gas, more preferably 0 -5 vol.% even more preferably 0 - 1 vol.%. Alternatively, WGS-treated product gas preferably comprises 0 - 10 mol% CO based on total volume of the dry product gas, more preferably 0-5 mol% even more preferably 0 - 1 mol%.

d) Isothermal methanation

[0044] In step d) the WGS-treated product gas undergoes an isothermal methanation step to form the synthetic natural gas. The methanation reaction converts carbon monoxide and carbon dioxide to methane according to the following

equations:

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$

[0045] Although the feed of the methanation step is low in CO, any CO that is present will be converted during methanation. The methanation step is conducted at relatively low temperatures under isothermal conditions to produce methane from carbon monoxide and carbon dioxide while avoiding degradation of higher alkanes such as ethane and propane. The temperature for the isothermal methanation preferably is in the range of 200-550°C, more preferably in the range of 200-400°C, even more preferably in the range of 200-350°C.

[0046] The isothermal nature of the methanation process is a key feature that distinguishes this method from conventional adiabatic methanation processes. In an isothermal process, the temperature is maintained within a narrow range throughout the reaction. Methanation is a highly exothermic process which when carried out adiabatically results in a temperature increase of typically 200°C or more. The difference between the highest and lowest temperature in the isothermal methanation step preferably is in the range of 0-100°C, more preferably in the range of 0-50°C, even more preferably in the range of 0-20°C. or alternatively, the difference between the highest and lowest temperature in the isothermal methanation reactor or combination of reactors preferably is in the range of 0-100°C, more preferably in the range of 0-50°C, even more preferably in the range of 0-20°C.

[0047] The importance of an isothermal process can be understood by comparing it to adiabatic methanation. For example, Gomez et al. (Chemical Engineering Science 267 (2023) 118291, https://doi.org/10.1016/j.ces.2022.118291) demonstrate in Table 4, experiment 5 that ethene fully disappears during adiabatic methanation. In this experiment the adiabatic temperature rise (Delta T) is 218°C and the maximum temperature (Tmax) is 485°C. In contrast, Example 2 of the present application shows that in the isothermal process, ethane is not broken down. This comparison underscores the advantages of the isothermal process over adiabatic methanation in preserving higher alkanes and maintaining a high calorific value in the synthetic natural gas product.

[0048] The pressure during the methanation step preferably is in the range of 1-100 bar, more preferably is in the range of 10-50 bar.

[0049] Various catalysts may be used for the methanation reaction. The methanation catalyst preferably is a transition metal-based catalyst, an oxide of a transition metal-based catalyst or a combination thereof. The transition metal preferably is selected from the list consisting of nickel, iron, copper, zinc, and combinations thereof. In a preferred embodiment, the catalyst is a nickel-based catalyst, an iron-based catalyst or combinations thereof. These catalysts facilitate the conversion of carbon oxides and hydrogen into methane.

[0050] The methanation reactor is carried out in one or more methanation reactors. The methanation reactor preferably is selected from a fluidized bed reactor, a slurry reactor and a fixed bed reactor, preferably the methanation reactor is a fixed bed reactor. As the WGS-treated product gas passes through the reactor, the carbon oxides react with hydrogen in the presence of the catalyst to produce methane and water.

[0051] In a preferred embodiment, multiple methanation reactors are used in series, allowing for better control of the reaction conditions such as for example temperature and improved overall conversion efficiency. This configuration may also allow for the use of different catalysts or operating conditions in each reactor to optimize the methanation reaction for different gas compositions or process requirements while maintaining isothermal conditions throughout the process.

[0052] The isothermal methanation step serves to convert the remaining carbon oxides into methane, increasing the methane content of the gas stream while preserving the higher alkanes present. This process results in a synthetic natural gas with a high calorific value due to the retention of ethane, propane, and other higher alkanes.

[0053] The removal of carbon dioxide (CO_2) from the synthetic natural gas (SNG) production process may be necessary to achieve a high calorific content in the final SNG product. CO_2 is a non-combustible component that dilutes the energy content of the gas, lowering its heating value. By removing CO_2, the relative concentration of combustible components, such as methane and higher hydrocarbons, increases, resulting in a higher calorific value for the SNG. Although most or all the CO_2 is converted during the methanation step, in some occasions it may be preferred for overall process efficiency to not fully convert CO_2 in the methanization step but to remove CO_2 after step c) and/or after step d).

[0054] CO_2 removal may be performed at different stages of the SNG production process. In one preferred embodiment, CO_2 is removed from the WGS-treated product gas after the water gas shift reaction. This approach allows for adjustment of the gas composition before the methanation step, potentially optimizing the stoichiometry for the methanation reaction. In another preferred embodiment, CO_2 removal is carried out after the methanation step, treating the synthetic natural gas directly. This method may be advantageous when the methanation step does not achieve complete conversion of CO_2, allowing for final adjustment of the synthetic natural gas to meet desired specifications.

[0055] Various methods may be employed for CO_2 removal, preferred methods are absorption processes using chemical or physical solvents, adsorption processes using solid sorbents, or membrane separation technologies. The

choice of CO_2 removal method may depend on factors such as the gas composition, process conditions, and desired level of CO_2 removal.

[0056] An alternative preferred approach to lowering CO_2 levels in the final SNG product involves providing additional hydrogen (H_2) to the feed in the methanation step. This method leverages the stoichiometry of the methanation reaction to shift the equilibrium towards increased methane production and reduced CO_2 content.

[0057] By increasing the H_2 concentration in the feed, the reaction equilibrium shifts towards the products, promoting the conversion of CO_2 to methane. This approach may reduce the need for separate CO_2 removal steps, potentially simplifying the overall process and reducing operational costs.

[0058] The additional H_2 may be sourced from various methods, such as electrolysis of water, steam methane reforming, or by adjusting the water gas shift reaction conditions to produce more H_2. The optimal amount of additional H_2 may be determined based on the initial gas composition and the desired final CO_2 content in the SNG product.

[0059] In a preferred embodiment, CO_2 is removed after step c), after step d) and/or additional H_2 is provided to step d). One or a combination of CO_2 removal methods and H_2 addition may be employed to achieve the desired SNG composition and calorific value. The specific approach may be selected based on factors such as process efficiency, economic considerations, and the target specifications for the final SNG product.

[0060] Since water is formed in step d) which is not preferred to be present in SNG, in a preferred embodiment water is removed from the synthetic natural gas, preferably by condensation. Preferably for the condensation the temperature of the synthetic natural gas is lowered below 50°C, preferably below 25°C even more preferably below 10°C and the condense water is removed.

Reactors for the process for producing synthetic natural gas (SNG)

[0061] The process for producing synthetic natural gas (SNG) preferably is carried out in a series of reactors, each optimized for a specific step of the process. This configuration allows for independent control of process parameters and conditions in each reactor, enhancing overall efficiency and product quality.

[0062] Preferably, the indirect gasification of biomass (step a) is carried out in an indirect biomass gasification reactor. The indirect biomass gasification reactor includes an inlet for solid and/or liquid biomass and an outlet for a product gas and an outlet for a liquid and/or solid product. The inlet allows for the introduction of biomass feedstock, while the outlet for a product gas provides a means for collecting the product gas generated during the gasification process.

[0063] The hydrogenation reaction (step b) preferably is performed in a hydrogenation reactor. The hydrogenation reactor includes an inlet in open connection with the product gas outlet of the indirect biomass gasification reactor and an outlet for the hydrogenated product gas. This configuration allows for precise control of hydrogenation conditions, such as temperature and pressure, to optimize the conversion of alkynes and alkenes to alkanes.

[0064] The water gas shift reaction (step c) preferably is carried out in a dedicated WGS reactor. The WGS reactor includes an inlet connected to the hydrogenated product gas outlet of the hydrogenation reactor and an outlet for WGS-treated product gas. By separating the WGS reaction into its own reactor, the process conditions can be tailored to maximize the conversion of carbon monoxide and water to hydrogen and carbon dioxide.

[0065] The isothermal methanation step (step d) preferably is carried out in a methanation reactor. The methanation reactor includes an inlet connected to the WGS-treated product gas outlet of the WGS reactor and an outlet for synthetic natural gas. This configuration allows for precise temperature control to maintain isothermal conditions during the methanation process.

[0066] In a preferred embodiment, steps b) and c) are combined in a single reactor. In this alternative configuration, a combined water gas shift and hydrogenation reactor is used instead of separate hydrogenation and WGS reactors. The combined reactor includes an inlet in open connection to the product gas outlet of the indirect biomass gasification reactor and an outlet for WGS-treated product gas. This configuration may offer advantages in terms of process simplification and reduced equipment costs. The flexibility to perform steps b) and c) in either separate reactors or a combined reactor allows for optimization based on specific process requirements, feedstock characteristics, or desired product specifications. The choice between separate or combined reactors for these steps may be made based on factors such as reaction kinetics, heat management, and overall process efficiency.

[0067] In a preferred embodiment, steps a), b), c) and d) are carried out in separate reactors, or when steps b) and c) are combined, step a), combined steps b) and c) and step d) are carried out in separate reactors, wherein a separate reactor may be a single reactor or a combination of reactors. Preferably step a) is carried out in an indirect biomass gasification reactor, step b) is carried out in a hydrogenation reactor, step c) is carried out in a WGS reactor, step d) is carried out in methanation reactor or step a) is carried out in an indirect biomass gasification reactor, steps b) and c) are carried out in a combined water gas shift and hydrogenation reactor, step d) is carried out in methanation reactor, wherein a reactor may be a single reactor or a combination of reactors. In a preferred embodiment the hydrogenation reactor is a HDS reactor. In some cases, one step is carried out in two or more reactors. For example, to have an isothermal methanation a combination of reactors may be helpful to control the temperature.

System for the production of synthetic natural gas (SNG)

[0068] The system for the production of synthetic natural gas (SNG) comprises a series of interconnected reactors designed to efficiently convert biomass into high-quality SNG. The system may include an indirect biomass gasification reactor, a hydrogenation reactor, a water gas shift (WGS) reactor, and a methanation reactor. Alternatively, the system may comprise an indirect biomass gasification reactor, a combined water gas shift and hydrogenation reactor, and a methanation reactor.

[0069] The hydrogenation reactor may be designed to operate at temperatures between 150°C and 500°C and pressures between 1 and 50 bar. The reactor may utilize a fixed-bed configuration with a specialized catalyst formulation optimized for the simultaneous hydrogenation of alkenes and hydrodesulfurization of sulfur compounds. The catalyst may be a nickel-molybdenum or cobalt-molybdenum catalyst supported on a high-surface-area alumina carrier.

[0070] In some examples, the system may include additional units for gas cleaning and conditioning. These may include a tar removal unit utilizing the OLGA (oil-based gas washing) process, a water removal unit based on condensation principles, and a CO_2 removal unit using amine scrubbing or pressure swing adsorption technology.

Synthetic natural gas (SNG)

[0071] The synthetic natural gas (SNG) produced by the process described herein may have a specific composition that contributes to its high calorific value. The invention therefore concerns a synthetic natural gas, preferably produced by the process according to the current invention, comprising:

- 80 - 98 vol.% CH_4,
- 0.1 - 3.0 vol.% CO_2,
- 0.1 - 10 vol.% N_2,
- 0.1- 3.0 vol.% H_2, and
- 2.0 - 15 vol.% of the sum of ethane, propane and butane;

wherein the vol.% are based on total water-free volume of the synthetic natural gas.
Preferably the synthetic natural gas, preferably produced by the process according to the current invention, comprises:

- 80 - 98 vol.% CH_4,
- 0.1 - 3.0 vol.% CO_2,
- 0.1 - 10 vol.% N_2,
- 0.5 - 3.0 vol.% H_2, and
- 2.0 - 15 vol.% of the sum of ethane, propane and butane;

wherein the vol.% are based on total water-free volume of the synthetic natural gas.
Even more preferably the synthetic natural gas, preferably produced by the process according to the current invention, comprises:

- 90 - 98 vol.% CH_4,
- 0.5 - 3.0 vol.% CO_2,
- 0.1 - 10 vol.% N_2,
- 0.5 - 3.0 vol.% H_2, and
- 3.0 - 10 vol.% of the sum of ethane, propane and butane;

wherein the vol.% are based on total water-free volume of the synthetic natural gas.
Even more preferably the synthetic natural gas, preferably produced by the process according to the current invention, comprises:

- 90 - 98 vol.% CH_4,
- 0.5 - 2.0 vol.% CO_2,
- 0.1 - 10 vol.% N_2,
- 0.5 - 2.0 vol.% H_2, and
- 4.0 - 10 vol.% of the sum of ethane, propane and butane;

wherein the vol.% are based on total water-free volume of the synthetic natural gas.

[0072] Preferably the synthetic natural gas comprises 85 - 98 vol.% CH_4, more preferably 90 - 98 vol.%, even more

preferably 90 - 95 vol.%, wherein the vol.% are based on total water-free volume of the synthetic natural gas. Preferably the synthetic natural gas comprises 3.0 - 15 vol.% of the sum of ethane, propane and butane, more preferably 3.0 - 10 vol.%, wherein the vol.% are based on total water-free volume of the synthetic natural gas. Preferably the synthetic natural gas comprises 0.2 - 10 vol.% N_2, more preferably 0.5 - 5.0 vol.%, even more preferably 1.0 - 5.0 vol.%, wherein the vol.% are based on total water-free volume of the synthetic natural gas. Preferably the synthetic natural gas comprises 0.2 - 3.0 vol.% CO_2, more preferably 0.5 - 3.0 vol.%, even more preferably 1.0 - 2.0 vol.%, wherein the vol.% are based on total water-free volume of the synthetic natural gas. Preferably the synthetic natural gas comprises 0.2 - 3.0 vol.% H_2, more preferably 0.5 - 3.0 vol.%, even more preferably 1.0 - 3.0 vol.%, wherein the vol.% are based on total water-free volume of the synthetic natural gas. Preferably the synthetic natural gas comprises 3.0 - 10 vol.% of the sum of ethane, propane and butane, more preferably 3.0 - 8.0 vol.%, even more preferably 4.0 - 8.0 vol.%, wherein the vol.% are based on total water-free volume of the synthetic natural gas.

[0073] The synthetic natural gas preferably has a higher heating value (HHV) of at least 36 MJ/Nm^3, more preferably, at least 39 MJ/Nm^3, even more preferably at least 40 MJ/Nm^3. The higher heating value is known in the art and is defined as the amount of heat released by combusting a specified quantity of gas and returning the temperature of the combustion products to the initial temperature of 25°C, wherein the latent heat of vaporization of water in the reaction products is recovered. Preferably, the sum of ethane, propane, and butane in the synthetic natural gas is 4.0-10 vol.%, even more preferably 5.0 - 9.0 vol.%, wherein the vol.% are based on total water-free volume of the product gas. The presence of these higher alkanes contributes to the increased calorific value of the SNG compared to conventional natural gas or synthetic natural gases with lower alkane content.

[0074] The amount of water in the synthetic natural gas may be defined based on the total volume of the product gas. Preferably, the water content in the synthetic natural gas is 0-5.0 vol.%, more preferably 0-2.0 vol.%. even more preferably 0-1.0 vol.% based on the total volume of the product gas. Since the process for the production of a synthetic natural gas (SNG) does not introduce air into the product gas, the N_2 content is low. Preferably, the N_2 content in the synthetic natural gas is 0-2.0 vol.%, more preferably 0-0.50 vol.%. even more preferably 0-0.25 vol.% based on the total volume of the product gas.

General Definitions

[0075] In this document and in its claims, the verb "to comprise" and its conjugations is used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. In addition, reference to an element by the indefinite article "a" or "an" does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there be one and only one of the elements. The indefinite article "a" or "an" thus usually means "at least one".

[0076] The present invention has been described above with reference to a number of exemplary embodiments. Modifications and alternative implementations of some parts or elements are possible, and are included in the scope of protection as defined in the appended claims. All citations of literature and patent documents are hereby incorporated by reference.

[0077] Bara stands for bar absolute and concerns the pressure that is zero-referenced against a perfect vacuum. 1 bar is 100,000 N/m^2. 1 bar is 100,000 Pascal.

[0078] The term **"SNG"** as used herein refers to synthetic natural gas, which is a fuel gas consisting primarily of methane that is produced from feedstocks other than natural gas. In the context of this invention, SNG is produced through the indirect gasification of biomass as described in this document.

[0079] The term **"biomass"** as used herein refers to organic matter derived from living or recently living organisms, typically plant-based materials. The biomass can be used as a feedstock for energy production. Biomass consists of wood, wood residues, energy crops, agricultural residues including straw, and organic waste from industry and households. **Organic waste** is any material that is biodegradable and comes from either a plant or an animal. In the context of this invention, biomass serves as the primary input for the gasification process to produce SNG.

[0080] The term **"indirect gasification"** as used herein refers to a process where biomass is converted into a combustible gas in the absence of O_2. In this process, the biomass is first pyrolyzed in one chamber, and the resulting char is then preferably combusted in a separate chamber to provide heat for the pyrolysis reaction.

[0081] The term **"alkanes"** as used herein refers to saturated hydrocarbons with the general formula CnH_2n+2, where all carbon-carbon bonds are single bonds. In the context of this invention, alkanes such as ethane, propane, and butane are desirable components in the final SNG product due to their contribution to the gas's calorific value.

[0082] The term **"alkenes"** as used herein refers to unsaturated hydrocarbons containing at least one carbon-carbon double bond, with the general formula CnH_2n. In the context of this invention, alkenes such as ethene, propene, and butene are present in the initial product gas and are subsequently converted to alkanes during the hydrogenation step.

[0083] The term **"higher heating value"** as used herein refers to the total amount of heat released by a specified quantity of fuel when it is combusted, and the products have returned to an initial temperature of 25°C. This assumes the

latent heat of vaporization of water in the reaction products is recovered. It is typically expressed in units of MJ/Nm3 for gases.

[0084] The term **"based on total water-free volume"** as used herein refers to the measurement or calculation of gas composition where water vapor has been excluded from the total volume. This allows for consistent comparison of gas compositions regardless of their moisture content.

[0085] The phrase that **'step c) is carried out in combination with step b)'** points to that these steps are carried out in the same reactor.

Example 1

[0086] This example demonstrates that indirect gasification at a lower temperature results in that an amount of C2 - C4 hydrocarbon is formed and that these C2 - C4 hydrocarbons are preserved when the product gas undergoes a hydrogenation reaction that hydrogenates the C2 - C4 alkynes and alkenes.

Materials and method

[0087] Product gas was produced in a 30 kW Milenan indirect gasifier using beech wood as feedstock. A slipstream of the product gas was further used for the test. The Milenan indirect gasifier consists of a riser, where the fast devolatilization/gasification of biomass takes place, and a combustor, where the remaining char is burned. In the settling chamber, solids (char and bed material) are separated from the producer gas and recirculated to the combustor via the downcomer. Heat is transferred between the combustor and the riser through the circulation of bed material. Steam (0.85 - 1 kg/h) was used as fluidizing gas in the riser. In the combustor zone, approximately 110 NL/min primary air was used to oxidise the char circulated from the riser zone. The temperature in the riser was about 830°C. The Milena reactor is amongst others described in US 10844300 B2 and in C.M. van der Meijden, Development of the MILENA gasification technology for the production of Bio-SNG. Doctoral Thesis. Eindhoven University of Technology, 2010. ISBN: 978-90-386-2363-4.

[0088] Tar was removed from the product gas based on oil scrubbing in a series of reactors (OLGA technology). The collector operated with an axial temperature profile ranging from 85°C to 250°C. The gas is cooled to 5°C to remove the water.

[0089] Subsequently the product gas underwent a hydrogenation reaction in a hydrogenation reactor. This hydrogenation reactor is a catalytic fixed-bed reactor with three external trace heating zones to compensate for heat loss and provided with thermocouples along the reactor axis (see Figure 6). The hydrogenation catalyst used is a commercial CoMoO catalyst. The hydrogenation catalyst converts the organic sulphur compounds (e.g. thiophene) into mainly H_2S and COS and hydrogenates alkanes and alkynes into alkanes (e.g. C_2H_4 and C_2H_2 into C_2H_6). The water gas shift (WGS) reaction may also proceed in this reactor. The produced H_2S and COS is removed from the gas downstream in a conventional ZnO adsorption bed and a guard bed. The hydrogenation reactor is operated at approximately 6 bars. The trace heating zones were set at 280°C, 420°C, and 460°C.

[0090] Gas compositions were measured before and after the hydrogenation reactor using an online GC equipped with separate channels for the detection of N_2, Ar, CO_2, CH_4, CO (HS-N column with TCD detector), H_2 (Molsieve 5A column 388 with TCD detector) and C1-C4 (PlotQ column with FID detector). Results are in below table 1.

Table 1: *Gas compositions before and after the HDS treatment based on dry gas volume.*

Component	Before hydrogenation (vol.%)	After hydrogenation (vol.%)
CO	24.1	24.7
H_2	29.1	24.8
CO_2	27.9	29.3
N_2	3.1	3.2
CH_4	10.9	12.6
C_2H_2	0.15	0.01
C_2H_4	2.9	0.02
C_2H_6	0.2	3.6

[0091] Table 1 demonstrates that the hydrogenation reactor is suitable for converting alkanes into alkenes. Moreover, it is evident since the amount of ethane formed is about equal to the sum of ethyne ethene and ethane before the hydrogenation, that during the hydrogenation process the alkenes are not converted into methane, CO or CO_2.

Example 2

[0092] This example demonstrates the effect of different product gas compositions on catalyst coking during methanation reactions and the effect on alkane conversion of isothermal methanation of a product gas.

Materials and method

[0093] A series of experiments were conducted using a Ni-based catalyst (Albemarle MethaneCat-540) in a micro-flow reactor unit with 4 parallel reactor tubes. These reactor tubes are placed in a single heated block to run under identical conditions i.e., feed composition, flow, temperature, pressure and gas/liquid separation. Where the flow of the required gas mixture is set using a Coriolis massflow controller. Condensation of the wax and light hydrocarbons from the reactor outlet gas occurs in respectively a hot (170°C) and cold (5°C) separator at the reactor pressure. The stainless-steel reactor tubes have an inner diameter of 8 mm, and a 100 mm long isothermal zone with a 3-point thermocouple in the center line. Physical mixtures of catalyst (1.5 g) and alumina diluent were placed in the isothermal zone of each reactor tube for the catalytic runs. Gas samples from each reactor were withdrawn downstream the hot separators. The gases were measured using an online GC equipped with separate channels for the detection of N_2, Ar, CO_2, CH_4, CO (HS-N column with TCD detector), H_2 (Molsieve 5A column 388 with TCD detector) and C1-C4 (PlotQ column with FID detector).

[0094] Three different product gas compositions were tested:

1. a CO-rich stream
2. a CO2-rich stream
3. a mixed CO/CO2 stream (simulating HDS gas outlet)

The reactor was operated at 300°C (composition 1 and 2) and 350°C (composition 3) and 5 barg pressure. The CO conversion was determined based on the ingoing and outgoing CO concentration. For mixed stream 3 two different conditions were tested. First conversion under dry conditions was established, subsequently 30 vol.% steam was added to measure conversion under wet conditions.

[0095] The inlet gas compositions for each variant are presented in Table 2.

Table 2: *Inlet gas compositions for different experimental variants based on dry gas volume.*

Component	CO-rich stream (vol.%)	CO_2-rich stream (vol.%)	Mixed CO/CO_2 stream (vol.%)
CO	24.0	0.0	32.6
H_2	71.0	76.0	22.1
CO_2	0.0	19.0	20.0
N_2	5.0	5.0	3.1
CH_4	0.0	0.0	15.8
C_2H_6	0.0	0.0	6.3

The catalyst was initially activated at 550°C under a H_2/N_2 mixture. Each gas composition was then tested for several days, monitoring the conversion and catalyst stability.

Results

[0096] For the CO-rich stream, the initial CO conversion was 100%. Due to the highly exothermic nature of the reaction the measured temperatures were higher than the temperature setpoint. The temperature at the top of the bed decreased already from the start of the experiment, from about 370°C at the start of the experiment to about 345°C after 12 hours which is an indication that the exothermic reaction is rapidly halted at the top of the reactor due to catalyst deactivation (coking). The rapid decay in temperature at the top of the bed was taken over by the middle of the bed, which temperature increased. Which, after 3 days, repeats itself further down the catalyst bed.

[0097] The CO_2-rich stream had an initial CO_2 conversion of 98% which is due to less favourable thermodynamic equilibrium. No catalyst deactivation was observed over several days, the temperature at the top of the bed remained stable at 320°C. Little to no coking took place.

The mixed CO/CO_2 stream has a gas composition that is in line with the gas composition from a gasification process of beech wood after tar and water removal and hydrodesulphurization (Liakakou et al., Fuel 290 (2021) 120054, https://doi.

org/10.1016/j.fuel.2020.120054 - a.o table 4). The initial CO conversion under dry conditions was 70%. The ethane conversion was 0%, indicating that the ethane is not affected in the methanation. Rapid deactivation by coking was amongst others observed in that the CO conversion dropped from the start of the reaction to about 50% within 5 hours. After introducing of the steam, the conversion temporarily increased to 100% but again due to coking dropped to 50% within a day. The additional steam resulted in also a WGS reaction taking place in the reactor which was apparent from a direct increase in H_2 in the reaction product. Also in the presence of steam ethane was not converted.

Conclusions

[0098] The example demonstrates that the presence of an amount of CO in the inlet stream leads to rapid catalyst deactivation, likely due to coking. In contrast, when CO_2 is the primary carbon source, the catalyst remains stable over a longer period, suggesting minimal coking. In addition, ethane present in the inlet stream is not convert, even whilst the WGS reaction simultaneously occurs. These results indicate that for prolonged catalyst stability and reduced coking, it is beneficial to convert CO to CO_2 via a water-gas shift reaction prior to the methanation step.

Claims

1. A process for the production of a synthetic natural gas (SNG) comprising the following steps:

a) indirect gasification of biomass to produce a product gas,
b) subjecting the product gas to a hydrogenation reaction to convert alkenes and alkynes to alkanes producing a hydrogenated product gas,
c) subjecting the hydrogenated product gas to a water gas shift reaction (WGS) producing a WGS-treated product gas, and
d) subjecting the WGS-treated product gas to an isothermal methanation step to form the synthetic natural gas,

wherein

- the product gas comprises alkenes wherein the amount of the alkenes is 1-15 vol.% based on total water-free volume of the product gas,
- step a) is carried out at a temperature in the range of 500 - 1000°C; and
- step c) is carried out at a temperature in the range of 200 - 550°C,

and wherein step c) is carried out as a separate step after step b) or is carried out in combination with step b) wherein in the combined step a WGS-treated product gas is produced.

2. The process according to claim 1, wherein

- step a) is carried out at a temperature in the range of 550 - 900°C, preferably in the range of 600 - 850°C,
- step b) is carried out at a temperature in the range of 200 - 500°C, preferably in the range of 300 - 450°C, more preferably in the range of 150 - 400°C, even more preferably in the range of 150 - 300°C, even more preferably in the range of 150 - 295°C,
- step c) is carried out at a temperature in the range of 150 - 400°C, preferably in the range of 150 - 300°C, even more preferably in the range of 150 - 295°C; and/or
- step d) is carried out at a temperature in the range of 200-550°C, preferably in the range of 200 - 400°C, more preferably in the range of 200 - 350°C.

3. The process according to claim 1 or 2, wherein the difference between the highest and lowest temperature in the isothermal methanation step is in the range of 0-100°C, more preferably in the range of 0-50°C, even more preferably in the range of 0-20°C.

4. The process according to any one of the preceding claims wherein

- in step a1) after step a) but before step b) tar is removed from the product gas, and/or
- in step a2) after step a) or after step a1) when step a1) is present but before step b) water is removed from the product gas, preferably by condensation.

5. The process according to any one of the preceding claims wherein step b) is carried out in a hydrodesulfurization (HDS) reactor.

6. The process according to claim 5 wherein sulfur compounds that are formed in step b) subsequently are removed from the hydrogenated product gas in step b1).

7. The process according to any one of the preceding claims wherein CO_2 is removed from the WGS-treated product gas after step c) in step c1) or wherein CO_2 is removed from the synthetic natural gas after step d) in step d1).

8. The process according to any one of the preceding claims wherein

- the pressure in step a), a1, and/or a2) is in the range of 1 - 10 bar, preferably in the range of 1 - 5 bar,
- the pressure in steps b), and/or c) is in the range of 1 - 50 bar, preferably in the range of 5 - 20 bar, and/or
- the pressure in step d) is in the range of 1 - 100 bar, preferably in the range of 10 - 50 bar.

9. The process according to any one of the preceding claims, wherein

- the catalyst for step b) is selected from the list consisting of nickel-based catalysts, cobalt-molybdenum catalysts, molybdenum disulfide-based catalysts, ruthenium disulfide-based catalysts and combinations thereof,
- the catalyst for step c) is a transition metal-based catalyst, an oxide of a transition metal-based catalyst or a combination thereof, wherein the transition metal preferably is selected from nickel, iron, copper, zinc, chromium, or combinations thereof; and/or
- the catalyst for step d) is a transition metal-based catalyst, an oxide of a transition metal-based catalyst or a combination thereof, wherein the transition metal preferably is selected from the list consisting of nickel, iron, copper, zinc, and combinations thereof, preferably the catalyst is a nickel-based catalyst or an iron-based catalyst.

10. The process according to any one of the preceding claims wherein the alkynes are one or more of ethyne, propyne and butyne, the alkenes are one or more of ethene, propene and butene and the alkanes are one or more of ethane, propane, and butane, preferably the alkyne is ethyne, the alkene is ethene and the alkane is ethane.

11. The process according to any one of the preceding claims wherein the sum of the alkenes in the product gas is 1 - 15 vol.% based on total water-free volume of the product gas, preferably 2 - 10 vol.%, even more preferably 3 - 8 vol.%.

12. A synthetic natural gas obtained by the process of any one of claims 1-7.

13. The synthetic natural gas (SNG) according to claim 12 comprising

- 80 - 98 vol.% CH_4,
- 0.1 - 3.0 vol.% CO_2,
- 0.1 - 10 vol.% N_2,
- 0.1 - 3.0 vol.% H_2, and
- 2.0 - 15 vol.% of the sum of ethane, propane and butane, preferably 4.0 - 8.0 vol.%;

wherein the vol.% are based on total water-free volume of the synthetic natural gas.

14. The SNG according to claim 12 or 13, having a higher heating value (HHV) of at least 36 MJ/Nm^3, preferably of at least 39 MJ/Nm^3.

15. A system for the production of a synthetic natural gas (SNG) comprising

I an indirect biomass gasification reactor having an inlet for solid and/or liquid biomass and an outlet for a product gas,
II a hydrogenation reactor of which the inlet is in fluid connection to the product g.0as outlet of the indirect biomass gasification reactor and having an outlet for a hydrogenated product gas,
III a WGS reactor of which the inlet is in fluid connection to the hydrogenated product gas outlet of the hydrogenation reactor and having an outlet for a WGS-treated product gas, and
IV a methanation reactor of which the inlet is in fluid connection to the WGS-treated product gas outlet of the WGS

reactor and having an outlet for the synthetic natural gas,

or comprising

I an indirect biomass gasification reactor having an inlet for solid and/or liquid biomass and an outlet for a product gas,
IIa a combined water gas shift and hydrogenation reactor of which the inlet is in fluid connection to the product gas outlet of the indirect biomass gasification reactor and having an outlet for a hydrogenated WGS-treated product gas,
IV a methanation reactor of which the inlet is in fluid connection to the hydrogenated WGS-treated product gas outlet of the combined water gas shift and hydrogenation reactor and having an outlet for the synthetic natural gas.

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EUROPEAN SEARCH REPORT

Application Number
EP 25 16 8361

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	NORIOKA SHIMPEI ET AL: "Reduction of the Hydrogen Content of CO2 Methanation Product Gas via Catalytic Ethanol Dehydration-Hydrogenation", CATALYSIS LETTERS, J.C. BALTZER, NEW YORK, vol. 155, no. 2, 18 January 2025 (2025-01-18), XP038063385, ISSN: 1011-372X, DOI: 10.1007/S10562-024-04924-3 [retrieved on 2025-01-18]	12-14	INV. C10L3/08 C07C1/12 C07C9/04 C10K1/00 C10K3/02 C10K3/04
A	* abstract *	1-11,15	
X	C.M Van Der Meijden ET AL: "Production of bio-methane from woody biomass using the MILENA gasification technology", ECN-M--15-044, 1 November 2015 (2015-11-01), pages 1054-1064, XP055441681, DOI: 10.1016/j.jclepro.2016.06.144 Retrieved from the Internet: URL:https://www.ecn.nl/publicaties/PdfFetch.aspx?nr=ECN-M--15-044 [retrieved on 2018-01-17]	15	
A	* abstract * * 2.1 Introduction * * 3.1 Gas composition over the ESME system * * figures 2-6 *	1-14	
A	US 3 904 386 A (GRABOSKI MICHAEL S ET AL) 9 September 1975 (1975-09-09) * column 1, line 8 - line 11 * * column 2, line 16 - column 3, line 3 * * column 4, line 58 - column 5, line 7 * * column 7, line 5 - column 8, line 49 * * claim 1; tables II, III *	1-15	

TECHNICAL FIELDS SEARCHED (IPC)
C10L
C07C
C10K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	28 August 2025	Keipert, Olaf

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 25 16 8361

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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