A method for converting a raw gas into a methane-rich and/or hydrogen-rich gas includes the following steps: a) providing the raw gas stemming from a coal and/or biomass gasification process, thereby the raw gas comprising beside a methane and hydrogen content carbon monoxide, carbon dioxide, alkanes, alkenes, alkynes, tar, especially benzene and naphthalene, COS, hydrogen sulfide and organic sulfur compounds, especially thiophenes; thereby the ratio of hydrogen to carbon monoxide ranges from 0.3 to 4; b) bringing this raw gas into contact with a catalyst in a fluidized bed reactor at temperatures above 200° C. and at pressures equal or greater than 1 bar in order to convert the raw gas into a first product gas, thereby simultaneously converting organic sulfur components into hydrogen sulfide, reform tars, generate water/gas shift reaction and generate methane from the hydrogen/carbon monoxide content; c) bringing the first product gas into a sulfur absorption process to generate a second product gas, thereby reducing the content of hydrogen sulfide and COS from 100 to 1000 ppm down to 1000 ppb or less; d) optionally bringing the second product gas into a carbon dioxide removal process to generate a third product gas at least almost free of carbon dioxide; e) bringing the third product gas into a second methanation process to generate a fourth product gas having a methane content above 5 vol %; f) optionally bringing the fourth product gas into a carbon dioxide removal process to generate a fifth product gas at least almost free of carbon dioxide; g) bringing the fifth product gas into an hydrogen separation process in order to separate a hydrogen rich gas from a remaining methane-rich gas, called substitute natural gas.
1. Low Temp. gasification
   2. Scrubber
   3. Absorption (H₂S; COS)
      4. WG-Shift
      5. CO₂-Separation
      6. 1ˢᵗ Methanation
      7. CO₂-Separation
      8. 2ⁿᵈ Methanation
      9. H₂-Separation
   SNG

FIG. 1A

1. High Temp. gasification
   2. S-resistant WGS
   3. S-resistant Methanation
      4. Absorption (H₂S; COS)
      5. CO₂-Separation
      6. 2ⁿᵈ Methanation
      7. H₂-Separation
   SNG

FIG. 1B
1. Low Temp. gasification

2. -HDS/HDN
   -S-resistant Methanation
   -S-resistant WGS
   -Tar-reforming, cracking
   -Hydrogenation, reforming of alkanes, alkenes, alkynes

3. H₂S; COS-Absorption

4. CO₂-Separation

5. 2nd Methanation

6. H₂-Separation

SNG

FIG. 2
PROCESS TO PRODUCE A METHANE RICH GAS MIXTURE FROM GASIFICATION DERIVED SULPHUR CONTAINING SYNTHESIS GASES

[0001] The present invention relates to a method for converting coal or biomass to at least almost sulfur-free substitute natural gas. Further, the invention relates to a process to produce a methane rich gas mixture from gasification derived sulphur containing synthesis gases.

[0002] In particular, the present invention relates to a continuous production process of synthetic natural gas (SNG) from biomass, coal or naphtha. More specifically, the present invention relates to the production of clean gaseous heating fuels from these less valuable sulphur containing hydrocarbonaceous materials.

DESCRIPTION OF THE PRIOR ART

[0003] The production of SNG from biomass is the conversion of a “dirty/difficult” fuel into a clean burning well known commodity. The customer has the freedom to use the SNG for power generation, heating or mobility. A big plus is the already existing infrastructure such as pipelines and compressed natural gas (NG) cars. To insert the product gas of the methanation into the grid it has to be cleaned of CO₂ and compressed to 5 to 70 bars to meet the standards of average natural gas.

[0004] The conversion of biomass to SNG is a complex process, which can be structured roughly into four main units: gasification, raw gas cleaning, fuel synthesis and gas sweetening. A solid feed is thermally converted into a raw gas and subsequently cleaned of particles, tars and sulphur. In the fuel synthesis, the raw gas is converted into raw SNG (a CH₄/CO₂ mixture) that is cleaned from CO₂ and optionally H₂ (gas sweetening) before injection into the natural gas grid.

[0005] The presence of sulphur in the feedstocks leads to the formation of H₂S, COS or organic sulphur species, depending on the temperature of the gasification. Low temperature (LT) gasification promotes the formation of organic sulphur species such like thiophenes, mercaptanes and thioethers, whereas high temperature (HT) gasification leads to the formation of exclusively H₂S and COS.

[0006] The typical raw gas composition of HT and LT gasification is shown in table 1.

| TABLE 1 |
|---------------------------------|---------------------------------|
| Low Temperature gasification   | High Temperature gasification   |
| (600-1000°C)                   | (1000-2000°C)                   |
| CH₄                             | a few ppm                       |
| alkanes, alkenes, alkanes      | nil                             |
| (especially ethylene)          | nil                             |
| Tars (Naphthalene, ... )       | H₂S, COS                        |
| H₂S, COS                       | Org. S-species (mercaptanes, thio-
| ether, thiophenes              | ethers, thiophenes              |
| HCN, N₂                         | Org. N-species (e.g. pyridine)  |
|                                |                                  |

[0007] For the synthesis of SNG, LT-gasification is advantageous (higher overall cold-gas efficiency), as the raw gas contains already substantial amounts of CH₄. Drawbacks of this kind of raw gas are the high amount of poisonous components, such as alkenes, alkylnes, H₂S, COS, organic S-species, HCN, NH₃, organic N-species.

[0008] For that reason, an efficient gas cleaning is required to protect the catalysts applied in the fuel synthesis. An example of a state of the art to produce synthesis gas for applications such as Fischer-Tropsch-Synthesis or production of Methanol, DME, and SNG is shown in FIG. 1a.

[0009] A scrubber at low temperatures is used to remove the tars and the organic S-species and N-species. H₂S, COS are absorbed on solid absorbents available for this duty (active carbon, ZnO or other metal oxides ...). In general, the gas cleaning is followed by a Water-Gas-Shift reactor, CO₂-separation and multiple methanation units. To increase the caloric value of the gas to the quality limits of the gas grid, CO₂ and H₂ is removed. The order of units 4-9 can be different.

[0010] Disadvantage of this process scheme is the high number of operation units and the different temperature levels of the units (especially cooling down to the scrubber temperature). To avoid this kind of temperature gradients in the process, the use of raw gas from a HT-gasification is common, an example of such process is shown in FIG. 1b (U.S. Pat. No. 3,928,000, EP 0,120,590). The different gas composition enables S-resistant Water-Gas-Shift (WGS) and S-resistant Methanation and lowers the amount of operation units. However, the raw gas composition is less favorable for the SNG synthesis as the SNG composition results in higher energetic losses.

[0011] First, the energetic effort in the gasification unit is higher for the production of pure H₂, CO, CO₂-mixtures; secondly the pure H₂, CO, CO₂-mixtures result in higher thermal losses in the synthesis due to the exothermic enthalpy of the methanation reaction.

DESCRIPTION OF THE INVENTION

[0012] By means of the subject process, the unfortunate temperature level sequence and the number of operation units of the process shown in FIG. 1a as well as the energetic losses of the process shown in FIG. 1b can be avoided. A methane-rich stream can be produced from sulphur containing feedstocks containing 10 to 95 mol % of methane.

[0013] The first step following the Low-Temperature-gasification is a multifunctional process unit featuring hydrodesulphurization/denitrogenation, methanation, WGS, tar reforming and cracking and the hydrogenation/reforming of alkenes and alkylamines simultaneously. The H₂S produced from the organic sulphur species by hydrolysis and the COS are removed by absorption on common absorbent materials such like ZnO, CuO. CO₂ can be removed before or after the 2nd methanation step. For the adjustment of the caloric value excess H₂ is separated and may be recycled to unit 2.

[0014] The hydrodesulphurization unit (HDS) is a common process step for the desulphurisation of feedstocks in the petrochemical industry or of natural gas before steam reforming. The applied catalysts for these units tend to catalyse both methanation and watergas shift reaction which is unwanted as these exothermic reactions may lead to a thermal runaway of the reactor. In the subject process, however, the methanation and WGS-reactions are desired.

[0015] To control the temperature rise due to exothermic reactions, a fluidised bed reactor equipped with means for heat removal can be applied. The catalyst fluidisation offers additionally the potential for internal regeneration of the catalyst from carbon deposits caused by compounds like ethylene or tars in the LT-gasifier producer gas. Such an internal regen-
eration can be found for fluidised bed methanation and can be enhanced by staged addition of recycle \( \text{H}_2 \) and/or steam in the upper part of the fluidised bed.

Moreover, the raw gas stream leaving the unit can be tailored to the requirements of a 2nd methanation unit to minimise the total number of process units by the addition of steam, \( \text{H}_2 \) from the recycle and the proper choice of temperature and pressure. Alkenes and alkynes are simultaneously produced. The \( \text{H}_2 \) made from the organic sulfur species by hydrodesulphurisation and the COS are removed by absorption on common absorbent materials such like \( \text{CuO} \), \( \text{ZnO} \), \( \text{CuO} \), \( \text{CO}_2 \) can be removed before or after the 2nd methanation step. For the adjustment of the calorific value excess \( \text{H}_2 \) is separated and may be recycled to unit 2.

The hydrodesulphurization unit (HDS) is a common process step for the desulphurisation of feedstocks in the petrochemical industry or of natural gas before steam reforming. The applied catalysts for these units tend to catalyse both methanation and watergas shift reaction which is unwanted as these exothermic reactions may lead to a thermal runaway of the reactor. In the subject process, however, the methanation and WGS-reactions are desired.

To control the temperature rise due to exothermic reactions, a fluidised bed reactor equipped with means for heat removal can be applied. The catalyst fluidisation offers additionally the potential for internal regeneration of the catalyst from carbon deposits caused by compounds like ethylene or tar in the LT-gasifier producer gas. Such an internal regeneration can be found for fluidised bed methanation and can be enhanced by staged addition of recycle \( \text{H}_2 \), and/or steam in the upper part of the fluidised bed.

Moreover, the raw gas stream leaving the unit can be tailored to the requirements of a 2nd methanation unit to minimise the total number of process units by the addition of steam, \( \text{H}_2 \) from the recycle and the proper choice of temperature and pressure.

A process for producing a methane-rich gas mixture for further application in high temperature fuel cells or for manufacturing synthetic natural gas (SNG) from gasification-derived synthesis gas mixtures that contain at least some compounds problematic to conventional methanation units, the process which comprises:

at least one unit allowing for methanation, water gas shift reaction, and for converting most or parts of the problematic compounds to less problematic compounds by one or more of the following.

hydrodesulphurization of organic sulfur species;
hydrodenitrogenation of organic nitrogen species;
hydrogenation or reforming of alkanes, alkenes, and alkynes; and
hydrogenation, reforming or cracking of hydrocarbons;
the unit being operated at temperatures between 200°C and 900°C and at pressures between 0.8 bara and 70 bara; and

the unit including a catalyst containing metals forming an active phase selected from the group consisting of molybdenum, cobalt, ruthenium, nickel, tungsten or sulfides thereof, and the active phase metals being supported on materials containing one or more materials selected from the group consisting of aluminium, silicon, titanium, zirconium, cerium, gadolinium, manganese, vanadium, lanthanum, chromium, or oxides thereof.

17. The process according to claim 16, wherein the problematic compounds are compounds selected from the group consisting of organic sulfur or nitrogen compounds, alkanes, alkenes, alkynes, aromatic hydrocarbons or non-aromatic hydrocarbons.

18. The process according to claim 17, wherein the aromatic hydrocarbons are selected from the group consisting of naphthalene, toluene, benzene, and phenols.

19. The process according to claim 16, which comprises carrying out the process in a fluidized bed reactor with catalytic particles having a size in a range from 20 to 2000 μm.

20. The process according to claim 19, which comprises controlling a temperature with heat transfer means.

21. The process according to claim 19, which comprises controlling a temperature of the process with heat transfer means in the fluidized bed reactor.

22. The process according to claim 16, which comprises feeding additional hydrogen into the process.

23. The process according to claim 22, which comprises feeding the additional hydrogen from a recycle stream at the top of the reactor, at the bottom of the reactor, and/or in between.

24. The process according to claim 22, which comprises feeding the additional hydrogen into the process as secondary injection into a fluidized bed.

25. The process according to claim 16, which comprises feeding additional steam into the process, by feeding at the top of the reactor, at the bottom of the reactor, and/or in between.

26. The process according to claim 25, which comprises feeding the additional steam into the process as secondary injection into a fluidized bed.

27. The process according to claim 16, which comprises feeding additional steam into the process, by feeding at the top of the reactor, at the bottom of the reactor, and/or in between.

28. The process according to claim 27, which comprises feeding additional steam into the process, by feeding at the top of the reactor, at the bottom of the reactor, and/or in between.

29. The process according to claim 16, which comprises feeding additional hydrogen into the process, by feeding at the top of the reactor, at the bottom of the reactor, and/or in between.

30. The process according to claim 16, which comprises feeding additional hydrogen into the process, by feeding at the top of the reactor, at the bottom of the reactor, and/or in between.

31. The process according to claim 16, which comprises feeding additional hydrogen into the process, by feeding at the top of the reactor, at the bottom of the reactor, and/or in between.

32. The process according to claim 30, which comprises additionally removing carbon dioxide.

33. The process according to claim 30, which comprises additionally removing carbon dioxide.

34. The process according to claim 30, which comprises additionally removing water.

35. The process according to claim 34, which comprises returning the hydrogen removed in the additional removal step in a recycle stream fed into the first methanation unit.

36. A method for converting a raw gas into a methane-rich and/or hydrogen-rich gas, which comprises the following steps.

a) providing raw gas originating from a coal and/or biomass gasification process, the raw gas including a content of methane and hydrogen and a content of carbon monoxide, carbon dioxide, alkanes, alkenes, alkynes, tar,
COS, hydrogen sulfide, and organic sulfur compounds; wherein a ratio of hydrogen to carbon monoxide ranges from 0.2 to 5;
b) bringing the raw gas into contact with a catalyst arranged as a fluidized bed reactor at temperatures above 200° C. and at pressures equal or larger than 1 bar in order to convert the raw gas into a first product gas, thereby simultaneously converting organic sulfur components into hydrogen sulfide, reform tars, generating water/gas shift reaction, and generating methane from the hydrogen/carbon monoxide content;
c) introducing the first product gas into a sulfur absorption process to generate a second product gas, thereby reducing a content of hydrogen sulfide and COS from 100 to 1000 ppm down to 1000 ppb or less;
d) optionally bringing the second product gas into a carbon dioxide removal process to generate a third product gas substantially or completely free of carbon dioxide;
e) introducing the third product gas into a second methanation process to generate a fourth product gas having a methane content above 5 vol.%;
f) optionally bringing the fourth product gas into a carbon dioxide removal process to generate a fifth product gas substantially or completely free of carbon dioxide; and
g) introducing the fifth product gas into an hydrogen separation process in order to separate a hydrogen rich gas from a remaining methane-rich gas (substitute natural gas).

37. The method according to claim 36, wherein the raw gas contains at least one of benzole, naphthalene, and thiophenes.

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