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(54) **A METHOD FOR METHANATION OF GASIFICATION DERIVED PRODUCER GAS ON METAL CATALYSTS IN THE PRESENCE OF SULFUR**

VERFAHREN ZUR METHANIERUNG DES AUS GASIFIZIERUNG ABGELEITETEN HERSTELLERGASES AUF METALLKATALYSATOREN IN GEGENWART VON SCHWEFEL

PROCÉDÉ DESTINÉ À PRODUIRE UN MÉLANGE GAZEUX RICHE EN MÉTHANE À PARTIR DE GAZ DE SYNTHÈSE CONTENANT DU SOUFRE PROVENANT D'UNE GAZÉIFICATION

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Description

[0001] Catalytic conversion of producer gases from gasification of solid feedstocks (such as coal or biomass) usually requires desulfurization in order to protect catalysts in downstream processes such as state-of the-art Fischer-Tropsch synthesis or methanation for production of Synthetic Natural Gas (SNG). Especially for methanation, the (higher) methane content in producer gas from low temperature gasification of coal / biomass (at 600 - 1000°C) allows energetically more efficient conversion, because the extent of exothermic reactions is decreased. However, low temperature gasification usually leads to organic sulfur compounds (e.g. thiophenes, mercaptanes), olefins and aromatic compounds in the resulting producer gas.

[0002] State of the art desulfurization is achieved by sequestration of sulfur species by scrubbing at low temperatures (< 50°C) and/or fixed bed adsorbers upstream of the synthesis (methanation), which takes place at temperatures above 300°C. This leads to a loss in overall efficiency, since not all heat can be recovered during the cooling and the subsequent heating. Further, in the low temperature scrubbing, all water in the producer gas (usually 25 - 40%) will condense while before the synthesis step, water again has to be added and evaporated to control carbon deposition in the catalytic conversion. Therefore, besides the high operation costs (heating, cooling, steam consumption for the regeneration of the scrubbing liquid), also the capital costs are high due to the required heat exchangers, condensers, evaporators etc.

[0003] Sulfur removal, which omits scrubbing and/or which is performed at temperature levels between that of the gasification and the temperature of the methanation, is desired for improvement of the overall efficiency.

[0004] Several processes or concepts that allow for methanation of sulfur containing producer gas without the need for scrubbing and water condensation are described in the literature: Rabou & Bos [1] describe the use of a commercial molybdenum based hydrodesulphurization (HDS) catalyst to convert thiophenes etc. to hydrogen sulfide (H_2S) which is followed by H_2S removal by means of a metal oxide bed (ZnO) and subsequent methanation over a nickel catalyst. However, the authors mention very high costs due to the low activity of the catalyst in their process chain.

[0005] Several authors and patents [e.g. 2] describe the use of sulfur tolerant methanation catalysts in fixed beds to convert mixtures from high temperature coal gasification containing carbon monoxide, hydrogen and sulfur compounds to methane. However, none of them showed that the catalyst would be active in the presence of olefins or even aromatic compounds in the feed gas. Such compounds are routinely found in synthesis gas from a low temperature gasifier. Catalysts for sulfur tolerant methanation are for instance molybdenum sulfide or vanadium sulfide [2b, 2c].

[0006] Seemann et al. [3] describe a process (see Fig. 1) in which organic sulfur compounds are nearly completely converted in a reactor that allows in parallel for partial or complete reforming/cracking of tars, hydrogenation reactions and partial or complete methanation. To avoid carbon deposition, a fluidised bed reactor allowing for internal regeneration is preferred. Downstream of this unit, nearly all sulfur is found in the form of H_2S and COS, which can either be removed in a fixed bed adsorber or in a scrubber, maybe together with CO_2. This process concept also allows for adding a nickel based methanation reactor to complete the methanation reaction downstream of the sulfur removal.

[0007] Some authors suggested high temperature sulfur removal by means of regenerative adsorber materials; other authors describe the regeneration of spent, sulfur poisoned catalysts:

Li et al. [4] describe the regenerative desulfurization of producer gas from coal or biomass gasification over metal based absorber materials. The desulfurization and regeneration of the absorber material are conducted at different temperatures (300°C and 500°C, respectively), and the desulfurization is separated from the (Fischer-Tropsch-) synthesis. Similarly, Kimura et al [5] describe a process for removal of H_2S from coal gas for gas turbine power generation over iron oxide catalysts and subsequent regeneration of the catalyst by oxidizing the FeS, and conversion of the formed SO_2 to elemental sulfur in a Claus process.

Katzer et al. [6] describe a process for regeneration of sulfur-poisoned metal catalysts by exposing the catalyst to a diluted oxygen/inert-gas mixture. They use very low oxygen concentrations of 1-10 ppm to regenerate a Ni catalyst at temperatures between 300°C and 500°C. The low oxygen content most probably shall help to avoid the formation of a nickel sulfate phase which is very stable and would deactivate the catalyst completely. However, the low oxygen content leads to very long regeneration times (several tens of hours). Johnson [7] describes a process for synthesis of hydrocarbons from natural-gas derived synthesis gas where a sulfur poisoned iron catalyst is regenerated in an oxidizer and reduced in a reducer, before being returned to the synthesis reactor.

Carr et al. [8] describe a method of regeneration of sulfur poisoned hydrocarbon cracking catalysts consisting of several cycles of oxidation and subsequent reduction. The catalyst used is based on Co, Ni, W, Cu, Mo, Cr, Mn, V or their oxides while the temperature for oxidation is between 900 - 1100 ° F.

Aguinaga & Montes [9] describe the regeneration of nickel catalysts by a sequence of oxidation- and re-

duction steps at constant temperature between 200°C and 500°C. The catalysts were poisoned by thiophene and the regeneration procedure with very low O_2 concentration (0.05 vol-%) removed up to 80% of the sulfur in 26 minutes.

Li et al [10] describe the regeneration of sulfur-poisoned nickel steam reforming catalysts with an oxidation- and a reduction step. The proposed temperatures are > 750°C for the oxidation in diluted oxygen, and > 850°C for the regeneration in inert gas and subsequent reduction in diluted hydrogen which is far above the temperature limit for a typical methanation catalyst.

[0008] Similar disclosure for a method for the catalytic production of a methane-rich gas mixture from sulfur-containing gasification-derived synthesis gas can be found in the US Patents Nos. 4,728,672 and 4,155,990.

[0009] It is therefore an objective of the present invention to provide a method for catalytic production of a methane-rich gas mixture from sulfur-containing gasification-derived synthesis gas wherein the energy efficiency is kept high and the usability of the methanation catalyst is maintained over a long period.

[0010] This objective is achieved according to the present invention by a method for catalytic production of a methane-rich gas mixture from sulfur-containing synthesis gas with simultaneous at least partial sulfur removal, comprising the steps of:

a) producing a synthesis gas mixture;
b) bringing said synthesis gas mixture into a contact with a methanation catalyst thereby continuously deactivating the methanation catalyst by sulfur and optionally carbon species comprised in the synthesis gas mixture in one part of the methanation process, while a part of said depleted methanation catalyst is simultaneously regenerated by oxidation in a different part of the process; wherein the methanation and the regeneration are performed at the same temperature between 300°C and 700°C, preferably in the range from 300°C and 450°C, and wherein the temperature in the catalytic methanation is controlled by means of internal heat exchangers or external heat exchange in a recycle stream or in a transfer line between methanation part and regeneration part;
c) the methanation catalyst is a metal, a metal oxide, a metal sulfide or a mixture of metals, metal oxides or metal sulfide/nitride/phosphide on a support;
d) said metal or metals are selected from a group comprising Ni, Ru, Mo, Co, Fe, Rh, Pd, Pt, Ir, Os, W, V, wherein the support is an oxide of a group comprising Al_2O_3, SiO_2, TiO_2, CeO_2, ZrO_2, carbides, nitrides, phosphides or a mixture thereof, wherein
e) the metal or metals are optionally promoted by one or more of the following elements: K, P, Na, Ba, Ni, Ru, Rh, Co, Pt, Pd, Ir, W, Os, V, Mn.

[0011] This method provides for the methanation of a producer gas proposing a simplified process as compared to the prior art. The method achieves a nearly complete methanation of CO in the presence of both organic and inorganic sulfur compounds, as well as olefins, tars etc., combined with an at least partial uptake of sulfur followed by a relatively fast oxidative regeneration of the methanation catalyst (bed material) and sulfur release while methanation and regeneration processes are performed at the same temperature level.

[0012] It is an advantageous feature of a preferred embodiment of the present invention when the sulfur species present in the synthesis gas mixture include, but are not limited to, one or more of the following compounds: hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), thiophene (C_4H_4S), Benzothiophene (C_8H_6S), Dibenzothiophene ($C_{12}H_8S$) and their derivates. This content in particular is quite typical to the producer gas derived from biomass gasification processes performed at lower temperatures in the range of 600 to 850°C.

[0013] In a further preferred embodiment, a fast regeneration of the methanation catalyst is achieved when the regeneration of the methanation catalyst is performed by oxidation of the methanation catalyst in the presence of an oxidizing agent, preferably when the regeneration of the methanation catalyst is performed by oxidation of the catalyst with a gaseous oxidizing agent. Preferably, said gaseous oxidizing agent may be air, air diluted with inert gas or air diluted with product gas after the methanation step.

[0014] A further preferred embodiment of the present invention can be achieved when a resulting product of the catalyst oxidation is separated from a resulting product of the catalytic methanation. This feature tremendously assists the efforts of removing the sulfur content originally contained in the synthesis gas mixture.

[0015] In order to develop a suitable strategy having the goal to maintain the selectivity and/or activity of the methanation catalyst as long as possible, the catalytic methanation can be performed in a fluidized bed reactor or an entrained flow reactor, from which a part of the catalyst can be conveyed to another fluidized bed reactor or another entrained flow reactor, in which the methanation catalyst can be oxidized and subsequently conveyed back to said methanation reactor.

[0016] Alternatively, the catalytic methanation can be performed in a fluidized bed reactor or an entrained flow reactor, from which a part of the catalyst can be conveyed to another fluidized bed reactor or another entrained flow reactor, in which the methanation catalyst can be oxidized and subsequently conveyed back to a reduction reduction or a first methanation reactor, from which it is further transferred to a second methanation reactor. Additionally, any further methanation reactor could be envisioned as well.

[0017] Another alternative can provide for the catalytic methanation being performed in one or more fixed bed

reactors, of which at least one is temporarily disconnected from a feed of the synthesis gas mixture thereby being subject to an exposure to a gaseous oxidizing agent.

[0018] With respect to the process efficiency, another advantageous feature of a preferred embodiment of the present invention provides for controlling the temperature in the catalytic methanation by means of internal heat exchangers or external heat exchange in a recycle stream or in a transfer line between methanation part and regeneration part. Alternatively or additionally, the temperature control for the catalytic methanation can be supported or achieved by controllable insertion of the reactant gases and/or by several feeding points and/or by cross flow and/or flow reversal.

[0019] In order to prolong the lifecycle of the methanation catalyst, the catalyst support can be modified to minimize the adsorption of sulfur or carbon species.

[0020] Preferred embodiments of the present invention are hereinafter explained in more detail with respect to the following drawings depicting in:

Fig. 1 a biomass methanation method as described by Seemann et al. [3];

Fig. 2 a simplified biomass methanation process with combined (partial) sulfur removal and methanation;

Fig. 3 a simplified scheme of the combined sulfur removal and methanation process; and

Fig. 4 measured signal at the outlet of the methanation reactor at constant temperature of 430°C versus time for diverse reactants.

[0021] Compared to the described state of art according to Fig. 1, the present invention for the process of the methanation of producer gas proposes a simplified process (see Fig. 2) with nearly complete methanation of CO in the presence of both organic and inorganic sulfur compounds, olefins, tars etc. combined with an at least partial uptake of sulfur followed by a relatively fast oxidative regeneration of the bed material and sulfur release at a temperature level near the methanation temperature. The present invention comprises continuous methanation, catalyst regeneration and sulfur removal and therefore leads to less unit operations. The catalyst regeneration can be performed at relatively high oxygen partial pressures, which allows performing the regeneration much faster. The catalyst reduction can be performed in the methanation reactor and does not require, but may have a specific reduction reactor.

[0022] The product gas, coming from a low temperature gasifier, is sent into a catalytic reactor, where H_2 and CO form CH_4 and H_2O. (see Fig. 2). The catalytic reactor comprises a synthesis part (i.e. methanation), and a regeneration part. (see Fig. 3). The sulfur species (e.g. H_2S, COS, C_4H_4S, thiophene-derivates, benzothiophenes, dibenzothiophenes) and possibly carbon species (e.g. C_2H_4, aromatics and other unsaturated hydrocarbons) slowly poison the catalyst at the beginning of the synthesis part of the reactor. The catalyst looses its activity for the synthesis, while sulfur and/or some carbon adsorb or deposit on the catalyst, thereby removing the sulfur and/or carbon species from the gas stream. The inactive catalyst is regenerated in the regeneration part of the reactor in presence of an oxidant such as diluted oxygen (e.g. air mixed with oxygen-depleted flue gas, but also peroxides, N2O or metal oxides). This oxidizes the adsorbed or deposited carbon and sulfur species on the catalyst surface and removes them in the form of SO_2 and CO_2 to the exhaust. With an appropriate regeneration temperature, the methanation activity can be restored. The regenerated catalyst is fed back to the synthesis part where it catalyses the desired reactions (methanation etc.) until the catalyst is deactivated again.

[0023] Both parts of the reactor can be operated at different temperatures, where the synthesis part is operated at preferentially around 300°C, and the temperature in the regeneration part is > 300°C (see Fig. 3). Both parts of the reactor can be operated at the same temperature, especially in the range of 400 - 450°C. The reactor can be designed as a circulating or bubbling fluidized bed or entrained flow, where the catalyst is fluidized and is continuously transported between the synthesis part and the regeneration part. Alternatively, the reactor can be designed as a swing reactor, where the fuel gas and the oxygen-containing gas are switched between two or more packed bed reactors, e.g. when the catalyst activity drops below a certain limit. Alternatively, the catalyst can be mechanically transported in a moving bed design between the synthesis reactor and the regeneration reactor. Alternatively, the regeneration of the catalyst may take place in a certain zone of a combined reactor.

[0024] Alternatively, the poisoned catalyst can be transported from a first methanation reactor where it is exposed to sulfur-laden synthesis gas to the regeneration reactor, and from said regeneration reactor to a second methanation reactor which is placed downstream of said first methanation reactor, where the catalyst is exposed to a sulfur-depleted synthesis gas which had been at least partially converted to methane. From said second methanation reactor, the catalyst can be then transported to said first methanation reactor or to said oxidation reactor.

[0025] Further, it is possible to introduce a solid adsorber bed such as ZnO between the first and the second methanation reactor to further deplete the gas in sulfur before it enters the second methanation reactor downstream.

[0026] Alternatively, the catalyst can be deposited on a solid substrate, such as a monolith, where one or more monoliths are exposed to sulfur-laden synthesis gas while one or more monoliths are exposed to oxidizing conditions, and the gas feeds (e.g. reducing/methanation/sulfur uptake/regeneration) change over time.

[0027] Alternatively, the catalyst may be suspended in

a liquid (e.g. ionic liquid), which may have additional useful absorption capacity for sulfur species, nitrogen species, ions, salts, tars, olefins and/or CO2. The reactions are then carried out in three phase flow such as a bubble column. The change of atmosphere around the catalyst material may then be achieved either by change of the gas composition fed, by addition of liquid or solid oxidants or by transporting the liquid phase with the suspended catalyst between one or more reactors fed with differing gas atmosphere (e.g. reducing/methanation/sulfur uptake/regeneration).

[0028] Alternatively, the catalyst may be connected to a moving part (similar to a recuperator, e.g. in form of a spinning monolith) which is moved or turned between reactors or reactor parts with the differing gas atmosphere.

Further, a combination of the above mentioned methods to achieve the change of atmosphere around the catalyst material can be applied.

[0029] The addition of the oxidant to the regeneration step may take place by addition of (diluted) air or oxygen containing (flue) gas, by addition of gaseous or liquid peroxides or other oxidizing species (e.g. hydrogen peroxide, N2O), by addition of solid oxidizing species (e.g. metal oxides), by transport of oxygen (e.g as ion or carbonate) through a membrane or by a combination of them. In the membrane case, either oxygen containing gases or species that may split off oxygen (e.g. by catalytic splitting upon external heating) are fed on the retention side of the membrane.

[0030] It is advantageous to avoid or control hot-spots in the methanation step due to the exothermic synthesis. This may be accomplished by active cooling by means of heat exchangers in the methanation reactor or in the transfer lines between methanation and/or reducing steps and the regeneration steps. Alternatively gas and/or liquid and/or solids may be taken out and cooled externally, followed by recycle to the methanation/reducing steps. Alternatively, cooling may be achieved by evaporation of a liquid in the reducing/methanation step or in the transfer lines, by latent heat uptake in a solid or liquid or by coupling with an endothermic reaction.

[0031] Further, temperature control may be achieved or supported by suitable addition of the reactant gases, e.g. several feeding points, cross flow, flow reversal etc. The catalyst is preferably a supported Ru catalyst or Ru containing catalyst, which may contain species supporting the sulfur uptake and/or the methanation reaction. Further, a combination or common transport of species or materials supporting the sulfur uptake and/or the methanation reaction may be applied.

[0032] It is advantageous to choose the support and the regeneration conditions such that adsorption of sulfur species (e.g. H2S, SO2) on the support and subsequent release and spill-over on the catalyst in any further step is minimized. Besides the choice of non-acidic supports (e.g. carbides, nitrides or phosphides), this may be accomplished or supported by modification of the (surface) properties of the support.

Example 1

[0033] Approx. 15 mg of a Ru catalyst supported on Al_2O_3 (Ru loading 2 wt-%) loaded into a fixed-bed reactor, where it was exposed to a gas mixture of 2.5 % H_2 and 0.125 % CO at 300°C. When 60 ppm of H_2S, 12 ppm of C_4H_4S and 6 ppm of COS were added to the feed, methanation activity decreased, until it reached eventually zero. Subsequently, the catalyst was exposed to 0.25% O_2 for 360 s at temperatures between 430°C and 600°C. After this regeneration treatment, the catalyst was again exposed to the H_2 / CO mixture where it showed again methanation activity at almost initial levels. This was repeated more than 30 times at various regeneration temperatures without significant decrease in methanation activity.

Example 2

[0034] Identical to example 1, only that the temperature was kept at 430°C at all times (methanation, sulfur poisoning and regeneration). Resulting mass spectrometer signals for one cycle are shown in Fig. 4. As in example 1, the cyclic process could be repeated several times.

[0035] Fig. 4 shows the measured signal at the outlet of the reactor at constant temperature of 430°C versus time. H_2 (m/z 2) starts flowing through the reactor at time t1. CO is added at time t2, which is reflected by the increasing methane signal (m/z 15). $H_2S/COS/C_4H_4S$/Ar are added at time t3. At time t3' COS (m/z 60) and C_4H_4S (m/z 84) are detected, which is accompanied by a decrease in CH_4 signal, which eventually drops to zero. After the reactive gases are stopped and the reactor is flushed, O_2 is added, which results in generation of SO_2 (m/z 64) in response to the regeneration the methanation catalyst.

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[0036]

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Claims

1. A method for catalytic production of a methane-rich gas mixture from sulfur-containing synthesis gas with simultaneous at least partial sulfur removal, comprising the steps of:

   a) producing a synthesis gas mixture;
   b) bringing said synthesis gas mixture into a contact with a methanation catalyst thereby continuously deactivating the methanation catalyst by sulfur and optionally carbon species comprised in the synthesis gas mixture in one part of the methanation process, while a part of said depleted methanation catalyst is simultaneously regenerated by oxidation in a different part of the process; wherein the methanation and the regeneration are performed at the same temperature between 300°C and 700°C, preferably in the range from 300°C and 450°C, and wherein the temperature in the catalytic methanation is controlled by means of internal heat exchangers or external heat exchange in a recycle stream or in a transfer line between methanation part and regeneration part;
   c) the methanation catalyst is a metal, a metal oxide, a metal sulfide or a mixture of metals, metal oxides or metal sulfide/nitride/phosphide on a support;
   d) said metal or metals are selected from a group comprising Ni, Ru, Mo, Co, Fe, Rh, Pd, Pt, Ir, Os, W, V, wherein the support is an oxide of a group comprising Al_2O_3, SiO_2, TiO_2, CeO_2, ZrO_2, carbides, nitrides, phosphides or a mixture thereof, wherein
   e) the metal or metals are optionally promoted by one or more of the following elements: K, P, Na, Ba, Ni, Ru, Rh, Co, Pt, Pd, Ir, W, Os, V, Mn.

2. The method according to claim 1, wherein the synthesis gas mixture is derived from a gasification process and the sulfur species present include, but are not limited to, one or more of the following compounds: hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon disulfide (CS_2), thiophene (C_4H_4S), Benzothiophene (C_8H_6S), Dibenzothiophene ($C_{12}H_8S$) and their derivates.

3. The method according to claim 1 or 2, wherein the regeneration of the methanation catalyst is performed by oxidation of the methanation catalyst in the presence of an oxidizing agent.

4. The method according to claim 3, wherein the regeneration of the methanation catalyst is performed by oxidation of the catalyst with a gaseous oxidizing agent.

5. The method according to claim 4, wherein said gaseous oxidizing agent is air, air diluted with inert gas or air diluted with product gas after the methanation step or air diluted with flue gas.

6. The method according to any of the preceding claims, wherein a resulting product of the catalyst oxidation is separated from a resulting product of the catalytic methanation.

7. The method according to any of the preceding claims, wherein the catalytic methanation is performed in a fluidized bed reactor or an entrained flow reactor, from which a part of the catalyst is conveyed to another fluidized bed reactor or another entrained flow reactor, in which the methanation catalyst is oxidized and subsequently conveyed back to said methanation reactor.

8. The method according to any of the preceding claims 1 to 6, wherein the catalytic methanation is performed in a fluidized bed reactor or an entrained flow reactor, from which a part of the catalyst is conveyed to another fluidized bed reactor or another entrained flow reactor, in which the methanation catalyst is oxidized and subsequently conveyed back to a reduction or a first methanation reactor, from which it is further transferred to a second methanation reactor.

9. The method according to any of the preceding claims 1 to 6, wherein the catalytic methanation is performed one or more fixed bed reactors, of which at least one is temporarily disconnected from a feed of the synthesis gas mixture thereby being subject to an exposure to a gaseous oxidizing agent.

10. The method according to any of the preceding claims, wherein the temperature control for the catalytic methanation is supported or achieved by controllable insertion of the reactant gases and/or by several feeding points and/or by cross flow and/or flow reversal.

11. The method according to any of the preceding claims, wherein the catalyst support is modified to minimize the adsorption of sulfur or carbon species.

Patentansprüche

1. Ein Verfahren zur katalytischen Herstellung einer methanreichen Gasmischung aus einem Methan enthaltendem Synthesegas gleichzeitig mit der zumindest teilweisen Entfernung von Schwefel umfasst folgende Schritte:

   a) Herstellung einer Mischung aus Synthesegas
   b) in Kontakt bringen von besagter Mischung aus Synthesegas mit einem Katalysator zur Methanisierung, wodurch gleichzeitig der Katalysator zur Methanisierung durch in der Mischung aus Synthesegas enthaltende Schwefel und wahlweise Kohlenstoff-Spezies in einem Teil des Methanisierungsprozesses deaktiviert wird, während ein Teil dieses besagten erschöpften Katalysators zur Methanisierung gleichzeitig durch Oxidation in einem anderen Teil des Prozesses regeneriert wird; wobei die Methanisierung und die Regeneration bei derselben Temperatur zwischen 300° und 700°, vorzugsweise im Bereich von 300° und 450°, ausgeführt werden, und wobei die Temperatur in der katalytischen Methanisierung durch interne Wärmeaustauscher oder externe Wärmeaustauscher in einem Strang der Wiederverwertung oder in einem Transferpfad zwischen dem Methanisierungsteil und dem Regenerationsteil geregelt wird;
   c) der Katalysator zur Methanisierung ist ein Metall, ein Metall-Oxid, ein Metall-Sulfid oder eine Mischung aus Metallen, Metall-Oxiden oder Metall-Sulfiden/Nitriden/Phosphiden auf einem Trägermaterial;
   d) besagtes Metall oder Metalle werden aus einer Ni, Ru, Mo, Co, Fe, Rh, Pd, Pt, Ir, Os, W, V enthaltenden Gruppe ausgewählt, wobei das Trägermaterial ein Oxid aus einer Al_2O_3, SiO_2, TiO_2, CeO_2, ZrO_2, Carbiden, Nitriden, Phosphiden oder einer Mischung davon enthaltenden Gruppe ist, wobei
   e) das Metall oder die Metalle wahlweise von einem oder mehreren der folgenden Elemente gefördert werden: K, P, Na, Ba, Ni, Ru, Rh, Co, Pt, Pd, Ir, W, Os, V, Mn.

2. Das Verfahren gemäss Anspruch 1, wobei die Mischung aus Synthesegas aus einem Prozess zur Vergasung stammt und wobei die vorliegende Schwefelspezies einen oder mehrere der folgenden Komponenten enthält, jedoch nicht auf diese beschränkt ist: Schwefelwasserstoff (H_2S), Carbonylsulfide (COS), Schwefelkohlenstoff (Cs_2), Thiophene (C_4H_4S, Benzothiophene (C_8H_6S), Dibenzothiophene ($C_{12}H_8S$) und deren Derivate.

3. Das Verfahren gemäss Anspruch 1 oder 2, wobei die Regeneration des Katalysators zur Methanisierung durch die Oxidation des Katalysators zur Methanisierung in der Gegenwart eines Oxidationsmittels ausgeführt wird.

4. Das Verfahren gemäss Anspruch 3, wobei die Regeneration des Katalysators zur Methanisierung durch die Oxidation des Katalysators mit einem gasförmigen Oxidationsmittel ausgeführt wird.

5. Das Verfahren gemäss Anspruch 4, wobei besagtes gasförmiges Oxidationsmittel entweder Luft, mit Edelgas verdünnte Luft, oder nach dem Schritt der Methanisierung mit Gasprodukten verdünnte Luft oder mit Abgasen verdünnte Luft ist.

6. Das Verfahren gemäss irgendeinem der vorherigen Ansprüche, wobei das resultierende Produkt der katalytischen Oxidation von einem resultierenden Produkt der katalytischen Methanisierung getrennt wird.

7. Das Verfahren gemäss irgendeinem der vorherigen Ansprüche, wobei die katalytische Methanisierung in einem Wirbelschichtreaktor oder einem Flugstromreaktor durchgeführt wird, von dem ein Teil des Katalysators zu einem anderen Wirbelschichtreaktor oder einem anderen Flugstromreaktor übertragen wird, in dem der Katalysator zur Methanisierung oxidiert wird und anschliessend zurück zu besagtem Methanisierungsreaktor übertragen wird.

8. Das Verfahren gemäss irgendeinem der vorherigen Ansprüche 1 bis 6, wobei die katalytische Methanisierung in einem Wirbelschichtreaktor oder einem Flugstromreaktor ausgeführt wird, von dem ein Teil des Katalysators zu einem anderen Wirbelschichtreaktor oder einem anderen Flugstromreaktor übertragen wird, in dem der Katalysator zur Methanisierung oxidiert wird und anschliessend zurück zu einem Reduktions-oder einem ersten Methanisierungsreaktor übertragen wird, von dem es weiter zu einem zweiten Methanisierungsreaktor übertragen wird.

9. Das Verfahren gemäss irgendeinem der vorherigen Ansprüche 1 bis 6, wobei die katalytische Methanisierung in einem oder mehreren Festbettreaktoren,

von denen mindestens einer zeitweise von einer Zufuhr der Mischung aus Synthesegas getrennt ist, wodurch diese einem gasförmigen Oxidationsmittel ausgesetzt sind.

10. Das Verfahren gemäss irgendeinem der vorherigen Ansprüche, wobei die Regelung der Temperatur für die katalytische Methanisierung von einer regulierbaren Einspeisung der Reaktionsgase und/oder durch mehrere Einspeisepunkte und/oder durch eine Querströmung und/oder eine Strömungsumkehr unterstützt oder erreicht wird.

11. Das Verfahren gemäss irgendeinem der vorherigen Ansprüche, wobei der Katalysatorträger abgewandelt ist um die Absorption von Schwefel- oder Kohlenstoffspezies zu minimieren.

Revendications

1. Procédé pour la production catalytique d'un mélange gazeux riche en méthane à partir d'un gaz de synthèse contenant du soufre avec élimination simultanée au moins partielle du soufre, comprenant les étapes :

a) de production d'un mélange gazeux de synthèse ;
b) de mise en contact dudit mélange gazeux de synthèse avec un catalyseur de méthanation tout en désactivant en continu le catalyseur de méthanation par des espèces soufrées et éventuellement carbonées comprises dans le mélange gazeux de synthèse dans une partie du procédé de méthanation alors qu'une partie dudit catalyseur de méthanation épuisé est régénérée simultanément par oxydation dans une partie différente du procédé ; la méthanation et la régénération étant réalisées à la même température entre 300°C et 700°C, de préférence dans la plage de 300°C à 450°C et la température dans la méthanation catalytique étant régulée au moyen d'échangeurs thermiques internes ou d'un échange thermique externe dans un flux de recyclage ou dans une ligne de transfert entre la partie de méthanation et la partie de régénération ;
c) le catalyseur de méthanation étant un métal, un oxyde métallique, un sulfure métallique ou un mélange de métaux, d'oxydes métalliques ou de sulfure/nitrure/phosphure métalliques sur un support ;
d) ledit métal ou lesdits métaux étant choisi(s) dans un groupe comprenant Ni, Ru, Mo, Co, Fe, Rh, Pd, Pt, Ir, Os, W, V, le support étant un oxyde d'un groupe comprenant Al_2O_3, SiO_2, TiO_2, CeO_2, ZrO_2, des carbures, des nitrures, des phosphures ou un mélange correspondant,
e) le métal ou les métaux étant éventuellement activé(s) par un ou plusieurs des éléments suivants : K, P, Na, Ba, Ni, Ru, Rh, Co, Pt, Pd, Ir, W, Os, V, Mn.

2. Procédé selon la revendication 1, le mélange gazeux de synthèse étant dérivé d'un procédé de gazéification et les espèces soufrées présentes comprenant, mais sans s'y limiter, un ou plusieurs des composés suivants : sulfure d'hydrogène (H_2S), sulfure de carbonyle (COS), disulfure de carbone (CS_2), thiophène (C_4H_4S), benzothiophène (C_8H_6S), dibenzothiophène ($C_{12}H_8S$) et leurs dérivés.

3. Procédé selon la revendication 1 ou 2, la régénération du catalyseur de méthanation étant effectuée par oxydation du catalyseur de méthanation en présence d'un agent oxydant.

4. Procédé selon la revendication 3, la régénération du catalyseur de méthanation étant effectuée par oxydation du catalyseur de méthanation à l'aide d'un agent oxydant gazeux.

5. Procédé selon la revendication 4, ledit agent oxydant gazeux étant de l'air, de l'air dilué par un gaz inerte ou de l'air dilué par un gaz produit après l'étape de méthanation ou de l'air dilué avec du gaz de carneau.

6. Procédé selon l'une quelconque des revendications précédentes, un produit résultant de l'oxydation du catalyseur étant séparé d'un produit résultant de la méthanation catalytique.

7. Procédé selon l'une quelconque des revendications précédentes, la méthanation catalytique étant effectuée dans un réacteur à lit fluidisé ou un réacteur à flux entraîné à partir duquel une partie du catalyseur est transportée vers un autre réacteur à lit fluidisé ou un autre réacteur à flux entraîné, dans lequel le catalyseur de méthanation est oxydé et ensuite transporté en retour vers le réacteur de méthanation.

8. Procédé selon l'une quelconque des revendications précédentes 1 à 6, la méthanation catalytique étant effectuée dans un réacteur à lit fluidisé ou un réacteur à flux entraîné à partir duquel une partie du catalyseur est transportée vers un autre réacteur à lit fluidisé ou un autre réacteur à flux entraîné, dans lequel le catalyseur de méthanation est oxydé et ensuite transporté en retour vers une réduction ou un premier réacteur de méthanation, à partir de laquelle/duquel il est transféré plus loin vers un deuxième réacteur de méthanation.

9. Procédé selon l'une quelconque des revendications précédentes 1 à 6, la méthanation catalytique étant

effectuée dans un ou plusieurs réacteurs à lit fixe dont au moins l'un est temporairement déconnecté d'une alimentation en mélange gazeux de synthèse et ainsi soumis à l'action d'un agent oxydant gazeux.

10. Procédé selon l'une quelconque des revendications précédentes, la régulation de la température pour la méthanation catalytique étant supportée ou réalisée par l'introduction régulable des gaz réactifs et/ou par différents points d'alimentation et/ou par un flux croisé et/ou par une inversion de flux.

11. Procédé selon l'une quelconque des revendications précédentes, le support catalytique étant modifié pour minimaliser l'adsorption des espèces soufrées ou carbonées.

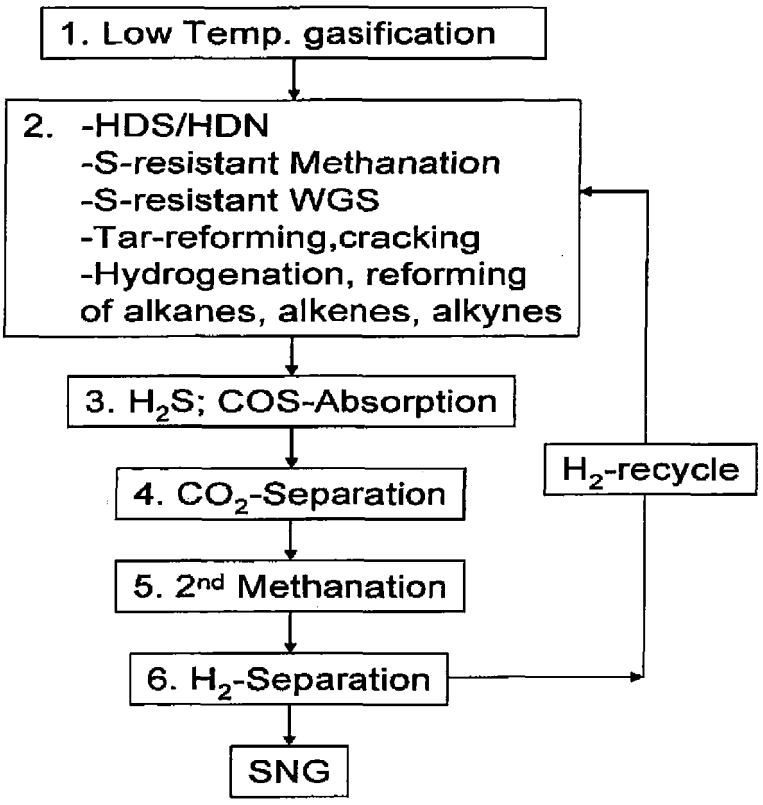
1. Low Temp. gasification
2. -HDS/HDN
-S-resistant Methanation
-S-resistant WGS
-Tar-reforming,cracking
-Hydrogenation, reforming of alkanes, alkenes, alkynes
3. H_2S; COS-Absorption
4. CO_2-Separation
5. 2nd Methanation
6. H_2-Separation
SNG
H_2-recycle

Fig. 1

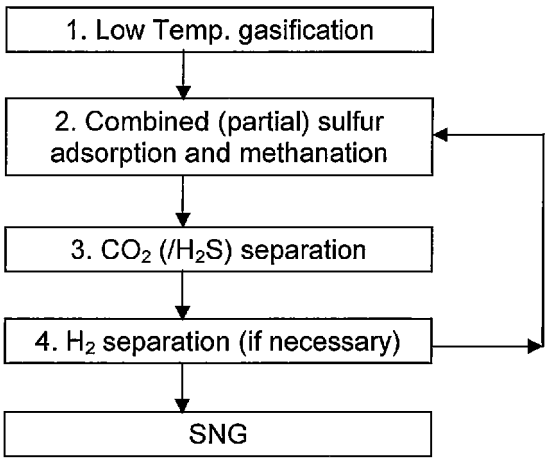
1. Low Temp. gasification
2. Combined (partial) sulfur adsorption and methanation
3. CO_2 (/H_2S) separation
4. H_2 separation (if necessary)
SNG

Fig. 2

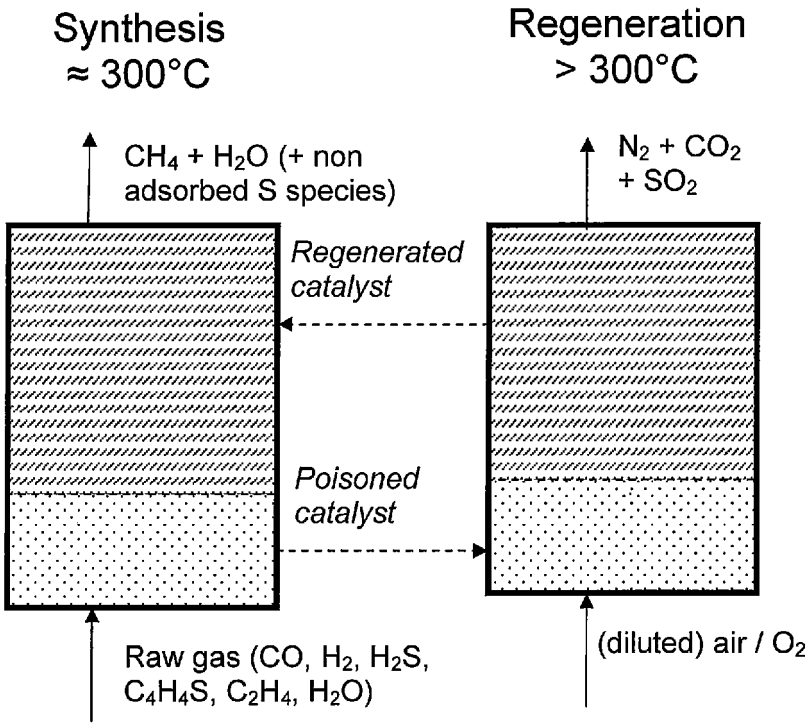
Synthesis
≈ 300°C
Regeneration
> 300°C
CH4 + H2O (+ non adsorbed S species)
N2 + CO2 + SO2
Regenerated catalyst
Poisoned catalyst
Raw gas (CO, H2, H2S, C4H4S, C2H4, H2O)
(diluted) air / O2

Fig. 3

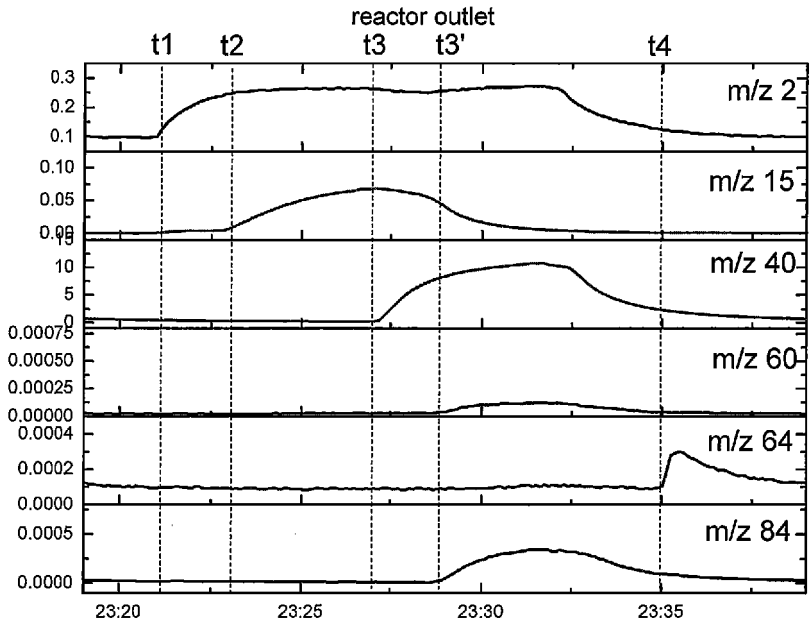
reactor outlet
t1
t2
t3
t3'
t4
m/z 2
m/z 15
m/z 40
m/z 60
m/z 64
m/z 84
0.3
0.2
0.1
0.10
0.05
0.00
15
10
5
0
0.00075
0.00050
0.00025
0.00000
0.0004
0.0002
0.0000
0.0005
0.0000
23:20
23:25
23:30
23:35

Fig. 4

REFERENCES CITED IN THE DESCRIPTION

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