Desulfurization and in situ tar reduction within catalytic methanation of biogenous synthesis gas

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HIGHLIGHTS

▶ Ni-based catalysts can be used for methanation as well as to remove tars in the synthesis gas out of biomass gasifiers.
▶ In the present work, the influence of various factors on the deactivation of these catalysts is discussed.
▶ Besides the influence of temperature and flow-velocity in the gas-cleaning reactor, the effect of desulfurization is shown.
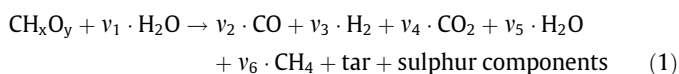
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ABSTRACT

For the production of Raw-SNG (Substitute Natural Gas) from synthesis gas of allothermal biomass gasification beside the methanation reactions, also tar-cleaning and desulfurization must be considered. In this work the tar and sulphur containing synthesis gas of an allothermal bench-scale gasifier is used to investigate a process in which the three mentioned steps are done in a simple way, suitable for decentralized application. Therefore, for the step of desulfurization the use of metal–oxides in a simple fixed-bed adsorber is investigated. For the second and third step Nickel is not only used to catalyze the methanation-reaction, it is also used as catalyst for high-temperature hydrocarbon reforming. Both steps are carried out in one apparatus: In a polytropic reactor (reactor just cooled by thermal losses), the exothermic methanation-reaction leads to a temperature-rise in the reactor of up to around 500 °C. It is investigated, whether this rise in temperature is sufficient to achieve an in situ tar conversion. Due to strong chemisorptive bondings of sulphur components, remaining in the gas after the MeO-adsorber, as well as a result of the biomass-tar, an increased Ni-catalyst deactivation turns out to be disadvantageous. This work replies to the question whether this catalyst consumption results from remaining sulphur in the synthesis gas, or from carbon-depositions resulting from biomass-tar. Parameter-studies are done with the aim to reduce the mentioned catalyst-deactivation to an economically feasible level. In order to reach a synthesis gas to Raw-SNG-conversion near to the theoretic thermodynamic equilibrium, the overall reaction kinetics must be considered. It is determined which gas residence times are needed in order to reach the expected synthesis gas conversion.

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1. Introduction

The production of Substitute Natural Gas (SNG) from solid biomass requires four process steps. In the first step the solid feedstock is converted into a hydrogen rich synthesis gas. For biomass fuelled, decentralized processes this step is preferentially done by means of allothermal gasification [1], whereas hydrogen contents up to 50 Vol% can be reached. Besides the permanent gases H_2, CO, CO_2, CH_4 and H_2O, sulphur components like H_2S, COS and thiophens as well as hi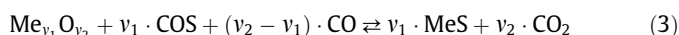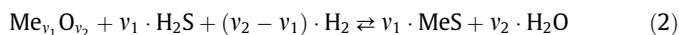gher hydrocarbons, referred as biomass-tar, are formed; cf. Eq. (1). Alkali-components like Na and K vaporise. The H_2O content in the gas depends on the gasification process and can roughly be estimated between 10 and 50 Vol%. [1–3].

$$CH_xO_y + v_1 \cdot H_2O \rightarrow v_2 \cdot CO + v_3 \cdot H_2 + v_4 \cdot CO_2 + v_5 \cdot H_2O$$
$$+ v_6 \cdot CH_4 + tar + sulphur\ components \quad (1)$$

In the gas-cleaning step subsequent to the gasification-step, the major gas impurities alkali-components, sulphur and tar must be removed. For decentralized biomass–SNG-production processes, due to efficiency reasons, gas-cleaning on a high temperature-level should be considered. Thereby sulphur removal can be achieved by adsorption on metal–oxides [4,5]. Cf. Eqs. (2) and (3).

$$Me_{v_1}O_{v_2} + v_1 \cdot H_2S + (v_2 - v_1) \cdot H_2 \rightleftarrows v_1 \cdot MeS + v_2 \cdot H_2O \qquad (2)$$

$$Me_{v_1}O_{v_2} + v_1 \cdot COS + (v_2 - v_1) \cdot CO \rightleftarrows v_1 \cdot MeS + v_2 \cdot CO_2 \qquad (3)$$
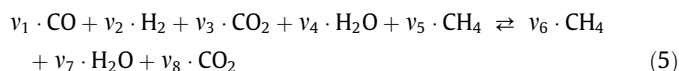
For high-temperature desulfurization applications temperatures of around 350 °C are commonly used. In this temperature range, especially with high H_2O contents in the gas, one must consider restrictions in the sulphur adsorption equilibrium [5]. The higher the water content is, the less H_2S can be adsorbed in the chemical equilibrium, Besides the main-reactions also unwanted side-reactions such as the Boudouard-reaction, the shift-reaction, the methanation reaction as well as Fischer–Tropsch-reactions occur [6]. The reason therefore is a certain catalytic effect of the ZnO-adsorbens.

In the mentioned temperature range, catalytic tar-removal can be done by steam-reforming on nickel-catalysts (4).

$$C_{v_1}H_{v_2} + v_1 \cdot H_2O \rightarrow \left(\frac{v_3}{2} + v_2\right) \cdot H_2 + v_3 \cdot CO \qquad (4)$$
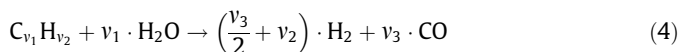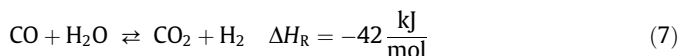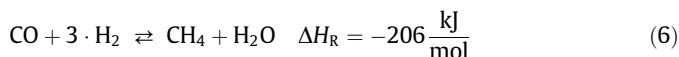
Various works show that tar reforming can be done at a temperature level higher than 800 °C [5,7–10]. Vosecky et al. [11] demonstrate that tar can also be converted at temperatures in the range of 500 °C.

The third step (Eq. (5)) represents the catalytic conversion of the synthesis gas to a methane-rich Raw-SNG [12]:

$$v_1 \cdot CO + v_2 \cdot H_2 + v_3 \cdot CO_2 + v_4 \cdot H_2O + v_5 \cdot CH_4 \rightleftarrows v_6 \cdot CH_4$$
$$+ v_7 \cdot H_2O + v_8 \cdot CO_2 \qquad (5)$$

As early as 1902 Sabatier and Senderens used nickel-catalysts in order to convert a gas consisting of three part of hydrogen and one part of carbon-monoxide to methane and water [13]. This so-called methanation-reaction (6), which is the reverse CH_4-reforming reaction, is highly exothermic and reduces the gas volume by half. If the synthesis gas from allothermal gasification should be converted, one can no longer assume the ideal conditions of Sabatier's research work: Generally the H_2 to CO-ratio does not meet the stoichiometric value of 3. Additionally there is CO_2 and steam in the gas. In order to reach a full H_2, respectively a full CO-conversion, the H_2-to-CO ratio must be adjusted to the stoichiometric value by means of the water gas shift (WGS) reaction (7). This reaction is only slightly exothermic and can also be catalyzed by nickel [14].

$$CO + 3 \cdot H_2 \rightleftarrows CH_4 + H_2O \quad \Delta H_R = -206 \frac{kJ}{mol} \qquad (6)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \Delta H_R = -42 \frac{kJ}{mol} \qquad (7)$$

If a synthesis gas, non-stoichiometric concerning to the methanation-reaction (6), is fed to a Nickel containing catalytic bed, the water gas shift reaction (7) takes place as a parallel reaction to the methanation-reaction (6). This implies that, if sufficient water and CO_2 is in the gas, for synthesis gas-compositions over- and under-stoichiometric regarding the methanation-reaction (6), a full H_2 and CO conversion can be reached without the need of a separate reactor for the WGS-reaction.

Also with CO_2 and H_2 as educt-gases, methane can be synthesized by means of the "Sabatier-reaction" (8).

$$CO_2 + 4 \cdot H_2 \rightleftarrows CH_4 + 2 \cdot H_2O \quad \Delta H_R = -165 \frac{kJ}{mol} \qquad (8)$$
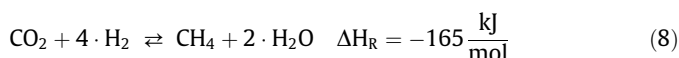
However, the Sabatier-reaction seems not to be an independent reaction [14,15]. Rather the parallel reaction of methanation- (6) and water gas shift reaction (7), takes place. Hereby via the water gas shift reaction (7) CO_2 and one mole H_2 is converted to CO and water. This results in a stoichiometric composition in relation to the methanation-reaction (6).

In the last process-step, the methane-rich Raw-SNG with CH_4-concentrations up to 50 Vol%, must be after-treated in order to reach the regulations for feeding the gas into the natural-gas grid [16]. Therefore the H_2O content of the gas has to be condensed, the CO_2 in the gas removed. The latter is normally done via absorptive processes. If H_2 remains in the gas, it also has to be settled out, for example by means of membrane technology. However, this work does not deal with the step of gas-after-treatment.

The present work discusses the influence of two synthesis gas impurities (tar and sulphur-containing species) on the process of catalytic methanation, in order to propose a simplified process that integrates the gas-cleaning step of tar-removal within the step of methanation. For desulfurization a simple fixed-bed adsorber, based on metal–oxide is connected upstream to the methanation-reactor. The tests shown here use a particle-free synthesis gas contaminated with tar and sulphur, directly from an allothermal fluidized bed gasifier. By means of a polytropic (only cooled by thermal losses) fixed-bed methanation reactor, it is studied whether the temperature-peak reached in the reactor, which is caused by the exothermic methanation, is sufficient to allow reforming of the biomass-tar (4) simultanously to the methanation-reactions (6) and (7). Concerning the combined process of methanation and tar-refoming, it is determined how the tar influences the gas residence times, given as gas hourly space velocity (GHSV)-values, needed to reach the equilibrium of the methanation reactions on the reactor outlet. Due to the strong chemisorptive bonds [17,18] of the sulphur compounds in the gas with the nickel-catalyst, those components cause a loss in catalytic activity. Not only the sulphur components cause deactivation, also higher hydrocarbons referred as tar can deactivate the catalyst by coking. Czekaj et al. [19] show the on-going surface processes during the methanation of synthesis gas containing hydrocarbons. In the present work, tests were done in order to separate the deactivation phenomena resulting from the sulphur in the synthesis gas from the deactivation due to the tar fraction in the synthesis gas. It is also determined how the water- as well as the tar-content of the synthesis gas influences the catalysts coke-related deactivation.

2. Experimental setup

Fig. 1 shows the flow chart of the experimental plant used for the present work. The plant consists of an allothermal, bench-scale fluidized-bed gasifier, connected to a fixed-bed sulphur adsorber and a double-stage-fixed-bed methanation-reactor. For measuring the permanent-gas components, the sulphur content as well as the tar content, appropriate analytic-equipment (cf. Section 2.3) is used.

2.1. Gasification setup

The allothermal gasification system, depicted in Fig. 2, has a maximal thermal input capacity, appropriate for lab-use, of 5 kW. For the experiments described in the present work, the gasifier was operated at 1.5 kW thermal input, that is equivalent to a bio-mass flow of 0.3 kg/h. This leads to a time-range of operation of around 250 h. As fuel, in all the tests shown here, wood pellets according to Austrian National Standard; OENORM M 7135 [20] are used. The synthesis gas is produced in a bubbling fluidized bed-reactor with a diameter of 80 mm. In order to reduce the particle rejection, a freeboard-enlargement with a diameter of 240 mm is applied. Steam acts as fluidization medium, as well as gasification agent. In order to supply the heat for the allothermal operation, an electric tube furnace with a capacity of 4 kW_{el} is installed. Through a flexible applicable electric heat supply, it is possible to control the gasification temperature in a range from 700 °C