



Test of a hydrodesulfurization catalyst in a biomass tar removal process with catalytic steam reforming



Christian Zuber^{a,*}, Christoph Hochenauer^b, Thomas Kienberger^a

^a agnion Highterm Research GesmbH, Conrad-von-Hötzendorfstrasse 103a, 8010 Graz, Austria

^b Graz University of Technology, Institute of Thermal Engineering, Inffeldgasse 25B, 8010 Graz, Austria

ARTICLE INFO

Article history:

Received 16 December 2013

Received in revised form 24 February 2014

Accepted 4 March 2014

Available online 13 March 2014

Keywords:

Allothermal gasification

Tar reforming

Desulfurization

Hydrodesulfurization

Catalyst deactivation

ABSTRACT

In order to remove tars from a synthesis-gas produced with an allothermal, pressurized fluidized-bed biomass gasifier, a catalytic gas-cleaning-process is used. The tars are removed by means of catalytic steam reforming on a commercial nickel catalyst at temperatures of around 500 °C in a packed bed reactor. The synthesis-gas enters the reforming reactor at 300 °C. Due to the strongly exothermic methanation-reaction the catalyst bed heats up to temperatures high enough to achieve sufficient catalyst activity for tar reforming. Ni-catalysts are sensitive for sulfur poisoning, therefore the main sulfur component in the hydrogen-rich synthesis-gas, hydrogen sulfide (H₂S), is adsorbed in a packed bed reactor, filled with ZnO, upstream the tar reformer. Beside H₂S there are further sulfur compounds in the gas stream which cannot be removed efficiently by means of ZnO. The aim of this work is to investigate whether it is possible to use a commercially available Co–Mo catalyst for hydrodesulfurization (HDS) upstream the ZnO-bed in order to convert organic sulfur compounds into H₂S. Hydrodesulfurization processes are state-of-the-art in large-scale petrochemistry. The process-conditions in this common use-case differ from these in the application discussed within this work. To examine the ability of HDS in the process discussed here, specific HDS-tests and overall system tests were carried out with a synthesis-gas from a laboratory gasifier. The used synthesis-gas was produced with an allothermal fluidized bed gasifier with wood pellets as fuel. The HDS-catalyst started to show activity for hydrogenation of thiophene at a temperature of 350 °C under atmospheric pressure. The use of hydrodesulfurization showed a positive influence on the catalyst deactivation of the subsequent Ni-catalyst.

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1. Introduction

Because of the expected tremendous impact of climate change, caused by the utilization of fossil fuels, and the fact that the availability of these fuels is limited, it is necessary to change the ways of global energy production [1]. Therefore the usage of renewable energy sources becomes necessary. Biomass and agricultural waste are one of the renewable energy sources that should not only be used for heat supply like in most cases nowadays, but also for generating electricity or second generation bio fuels. In this regard, the gasification of biomass seems to be promising, especially due to the high process-efficiency and the suitability for decentralized energy production [2]. For thermochemical gasification various technologies can be taken into account. The allothermal fluidized bed steam

gasification of biomass which this paper deals with produces a high caloric synthesis-gas that mainly contains H₂, CO, CO₂, CH₄ and H₂O. Beside these main components, the gas also includes unwanted byproducts like particles, tars (C₆+ hydrocarbons), sulfur compounds, ammonia and alkali metal condensates [3].

Before the usage of the synthesis-gas in a gas engine or the processing into other fuels, the gas has to be cleaned from the main impurities. Especially the removal of the biomass tar is crucial, because the condensation of tars causes severe fouling in unheated plant components downstream the gasifier. Along with other methods, like for instance FAME-scrubbing, tar removal can be carried out by means of catalytic steam reforming on a Ni-catalyst at temperatures of about 500 °C [4–6].

The simplified catalytic tar removal method described here is especially suitable for decentralized small scale plants. In this process, after leaving the gasifier, the synthesis-gas is cooled down to 300 °C for filtration. At this temperature beside the coke-particles, also already condensed alkali-metal and other ash-particles can be removed. Almost the total tar load is in gaseous state.

* Corresponding author. Tel.: +43 699 1422 4701.

E-mail addresses: christian.zuber@agnion.de, christian.zuber@gmx.at (C. Zuber).

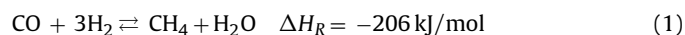


Fig. 1. Scheme of the discussed gas cleaning process.

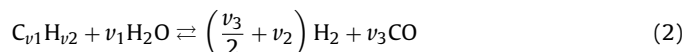
Fig. 1 shows the scheme of the here described gas cleaning process. The first reactor downstream the gasifier and the filtration of the synthesis-gas is the HDS Co–Mo catalyst. There hydrogenation and hydrodesulfurization reactions take place. Subsequent to this the H_2S -concentration in the synthesis-gas is reduced with ZnO in the second reactor. The aim of these first two steps is to reduce the total sulfur-load in the synthesis-gas, before entering the steam reforming nickel catalyst in the third reactor. In the following sections the single steps of the process are described in detail, beginning with the steam reforming of the biomass tars.

1.1. Catalytic steam reforming

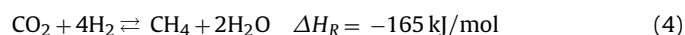
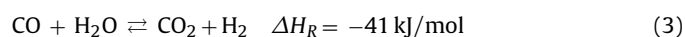
The gas enters the steam reforming reactor at 300°C , where the methanation reaction (1) and steam reforming of biomass tar take place on a nickel-based catalyst simultaneously. The occurring methanation-reaction (1) is strongly exothermic and heats up the gas to temperatures over 500°C [7].



This rise in temperature enables steam reforming of biomass tar, in order to generate hydrogen and carbon monoxide according to Eq. (2) [8].



Beside the two mentioned reactions, also the water-gas shift reaction (3) and the Sabatier reaction (4) for reasons of balance, take place [8].



Catalytic reactions always lead to a certain deactivation of the catalyst used for the process. According to Bartholomew [9], there are different types of catalyst deactivation in general. In the catalytic process discussed in this paper, two mechanisms appear: Beside the deactivation by means of sulfur poisoning the Ni-catalyst, fouling of the catalyst caused by carbon or coke occurs.

1.2. Removal of hydrogen sulfide with ZnO

In order to reduce sulfur poisoning of the Ni-catalyst, it is reasonable to reduce the sulfur load upstream the steam reforming Ni-catalyst. In the raw synthesis-gas produced with an allothermal steam gasifier, hydrogen sulfide (H_2S) is the main sulfur component [10]. Various metal oxides are appropriate for desulfurization of biomass-based synthesis-gas [10–12]. For reasons of stability against the reducing atmosphere, the reachable desulfurization-concentration in equilibrium and the adsorption capacity, zinc oxide (ZnO) seems to be suitable for this process [8]. The adsorption of H_2S on ZnO is a chemisorptive process and described by Eq. (5), where * is the active surface site of ZnO.



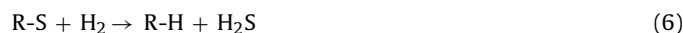
The reachable equilibrium sulfur-concentration downstream the desulfurization-reactor strongly depends on the temperature of

the adsorbent. At 300°C , which is the catalyst's inlet temperature, it is possible to reach H_2S -contents far below 1 ppm_v, downstream the zinc oxide bed.

1.3. Hydrogenation and hydrodesulfurization

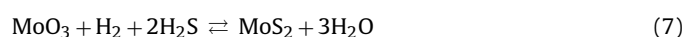
As mentioned above, H_2S is the main sulfur-component in the synthesis-gas. Besides H_2S , the gas also contains small amounts of other, mainly organic, sulfur components as carbonyl sulfide (COS), carbon disulfide (CS_2), thiophene ($\text{C}_4\text{H}_4\text{S}$) and benzothiophene ($\text{C}_8\text{H}_6\text{S}$). These cannot be removed effectively by ZnO. Sasaoka et al. [13] reported that COS can be partly converted to H_2S on ZnO at 500°C , but also the reverse reaction can occur. The organic sulfur species cause analog to H_2S deactivation of the Ni-catalyst in the downstream tar-reformer. To counteract this sulfur-related deactivation, a hydrogenation of the organic sulfur components seems to be possible. The HDS Co–Mo catalyst has to be integrated in the process upstream the H_2S -adsorption with ZnO. So the H_2S produced by the HDS Co–Mo catalyst can be removed with the ZnO-adsorbent.

Hydrodesulfurization is commercially used in large scale in oil refineries in order to convert organic sulfur compounds like mercaptanes or thiophenes to hydrocarbons and H_2S by means of hydrogen as reactant (Eq. (6)) [14,15].

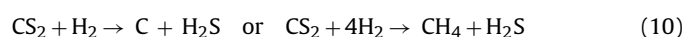
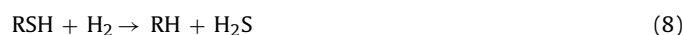


This process is carried out at temperatures between 300 and 425°C and medium to high pressures from 10 to 200 bar [14]. The used catalysts are based on molybdenum (Mo) with nickel (Ni) or cobalt (Co) as promoter (Co–Mo, Ni–Mo), mostly supported on Al_2O_3 , TiO_2 or $\text{SiO}_2\text{-Al}_2\text{O}_3$ [16–20].

The HDS-reaction needs two main catalyst functions. First, the hydrogenation of C=C double bonds and following this the hydrogenolysis of C–S bonds, both reactions occur on the active MoS_2 sites. The HDS Co–Mo catalyst becomes active only in the sulfided state. Sulfidation of molybdenum oxide is described in Eq. (7) [16]. Whether the catalyst is pre-sulfided before use or not, has no influence on the maximum reachable activity, which is only determined by the sulfidation equilibrium [16,21]. Of course the hydrogen and H_2S in the feed gas can be used to sulfide the HDS Co–Mo catalyst.



The reactions to be catalyzed by HDS-catalysts are the hydrodesulfurization reactions of thiols like methanethiol or ethanethiol (8), thiophene (9), carbon disulfide (10), carbon oxy-sulfide (11) as well as the hydrogenation of olefins like ethene (12) [16].



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