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Research paper

Performance of a water gas shift pilot plant processing product gas from an industrial scale biomass steam gasification plant

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ABSTRACT

In this paper, the performance of a commercial Fe/Cr based catalyst for the water gas shift reaction was investigated. The catalyst was used in a water gas shift pilot plant which processed real product gas from a commercial biomass steam gasification plant with two different qualities: extracted before and extracted after scrubbing with a rapeseed methyl ester gas scrubber. The performance of the WGS pilot plant regarding these two different gas qualities was investigated. For this reason, extensive chemical analyses were carried out. CO, CO₂, CH₄, N₂, O₂, C₂H₆, C₂H₄, and C₂H₂ and H₂S, COS, and C₄H₄ S were measured. In addition, GCMS tar and NH₃ analyses were performed. Furthermore, the catalyst's activity was observed by measuring the temperature profiles along the reactors of the water gas shift pilot plant. During the 200 h of operation with both product gas qualities, no catalyst deactivation could be observed. A CO conversion up to 93% as well as a GCMS tar reduction (about 28%) along the water gas shift pilot plant was obtained. Furthermore, a specific H₂ production of 63 g H₂ per kg biomass (dry and ash free) was reached with both product gas qualities. No significant performance difference could be observed.

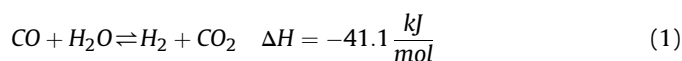
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1. Introduction

Today, hydrogen is an important resource for a wide range of applications in the chemical industry [1]. Steam reforming of natural gas and other processes with fossil fuels as feedstock produce more than 95% of the hydrogen which is needed in industry. Against a background of climate change, a CO₂ neutral method for hydrogen production should be established [2]. Biomass steam gasification is a proven technology and a CO₂ neutral alternative to steam reforming of natural gas [3].

A promising technology for biomass steam gasification is the dual fluidized bed (DFB) process [4,5]. The commercial biomass steam gasification plants in Guessing and Oberwart have been using this technology for several years. Both plants generate a product gas from woodchips with an high H₂ content ($\varphi_{H_2} \approx 40\%$, d.b.). The

other main components are CO ($\varphi_{CO} \approx 25\%$, d.b.), CO₂ ($\varphi_{CO_2} \approx 20\%$, d.b.), and CH₄ ($\varphi_{CH_4} \approx 10\%$, d.b.). In addition, it contains small amounts of N₂, O₂, higher hydrocarbons, and H₂S ($\varphi_{H_2S} \approx 100\text{ cm}^3 \cdot \text{m}^{-3}$, d.b.) and minor amounts of other sulfur components. The high H₂ content makes this product gas a promising CO₂ neutral H₂ source [6]. A process which can further increase the hydrogen content in the product gas is the water gas shift (WGS) reaction (see Equation (1)).



It converts carbon monoxide and steam to hydrogen and carbon dioxide. At the industrial scale, a WGS unit consists of a high temperature stage and a low temperature stage. In order to reach economic reaction rates, catalysts are necessary. A suitable catalyst for the high temperature stage is an Fe/Cr based catalyst. The high temperature stage operates adiabatically with a gas inlet temperature of 350–550 °C and space velocities from 400–1200 h^{−1}. The operating pressure depends on the plant requirements [1].

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Fe/Cr based catalysts seem to be robust against sulfur poisoning at the amounts of H_2S which are contained in the product gas of biomass steam gasification [7,8]. Catalysts for the low temperature stage (about 200 °C) are Co/Mo or Cu/Zn based catalysts. The Co/Mo catalyst is resistant to the presence of sulfur components but the amount of H_2S in the product gas of biomass steam gasification is too low for the Co/Mo catalyst (see Ref. [9]) to reach a high activity [8]. In contrast, Cu/Zn catalysts are sensitive to sulfur poisoning [1].

Several studies have been carried out regarding the H_2 production from biomass (see Ref. [10]). In Refs. [11] and [12], a high temperature and low temperature WGS unit was operated after a H_2O-O_2 gasifier and a steam reformer. In Ref. [13], synthetic gas mixtures which simulated the gas composition of pressurized oxygen gasification were used together with a high temperature WGS catalyst in order to achieve high H_2 yields. In Ref. [14], sawdust was gasified with mixtures of O_2 , N_2 , and H_2O in a fluidized bed gasifier. In Ref. [15], a model biogas was used with a steam reformer and a two-stage WGS reactor for increasing the H_2 yield. In addition, a lot of research in the field of gasification of biomass with supercritical water has been carried out (see Ref. [16]). For example, in Ref. [17], biomass was gasified in a heated batch reactor with supercritical water.

For this work, a WGS pilot plant applying a commercial Fe/Cr based catalyst was operated with product gas from the commercial biomass steam gasification plant in Oberwart, Austria. The WGS pilot plant was operated with product gas extracted before a rapeseed methyl ester (RME) gas scrubber for more than 100 h as well as with product gas extracted after a RME gas scrubber, again, for more than 100 h. Refs. [12] and [18] showed that an operation with product gas extracted after a RME gas scrubber with a low tar content is possible. The performance of the WGS pilot plant which processed the product gas extracted before the RME gas scrubber with a high content of tar is compared with the performance of the

WGS pilot plant which processed the product gas extracted after the RME gas scrubber with a low content of tar. The shifted product gas could be the basis for a simple polygeneration process which can generate valuable gases (H_2 and CH_4), electricity, and heat.

2. Materials and methods

The experimental work was carried out at the plant site of the biomass steam gasification plant in Oberwart, Austria, where the WGS pilot plant is located. The pilot plant consisted of three reactors in series which applied an Fe/Cr based catalyst. The gas composition and the steam content were measured before and after each reactor. GCMS tar and NH_3 analyses were performed by the Test Laboratory for Combustion Systems at the Vienna University of Technology. The temperature profile along each reactor was recorded. This allowed judging the activity of the applied Fe/Cr based catalyst.

2.1. The biomass gasification plant

The WGS pilot plant processed product gas from the combined heat and power (CHP) plant in Oberwart. Fig. 1 shows a simplified flowchart of the CHP plant.

The plant is based on the DFB steam gasification technology described in detail in Refs. [4] and [5]. The CHP plant generates district heat and electricity with biomass (woodchips) as feedstock. Table 1 shows the main operating parameters of the CHP plant.

Biomass is fed into the biomass dryer. The dried biomass is transported into the gasifier by a screw conveyor. In the gasifier, the biomass reacts with steam and is in contact with the bed material (olivine) at about 850 °C at ambient pressure. The result is a product gas with a high hydrogen content ($\varphi_{H_2} \approx 40\%$, d.b.). Then, the product gas is cooled and cleaned in a bag house filter and in an RME gas scrubber. In the RME gas scrubber, tar, NH_3 , and other

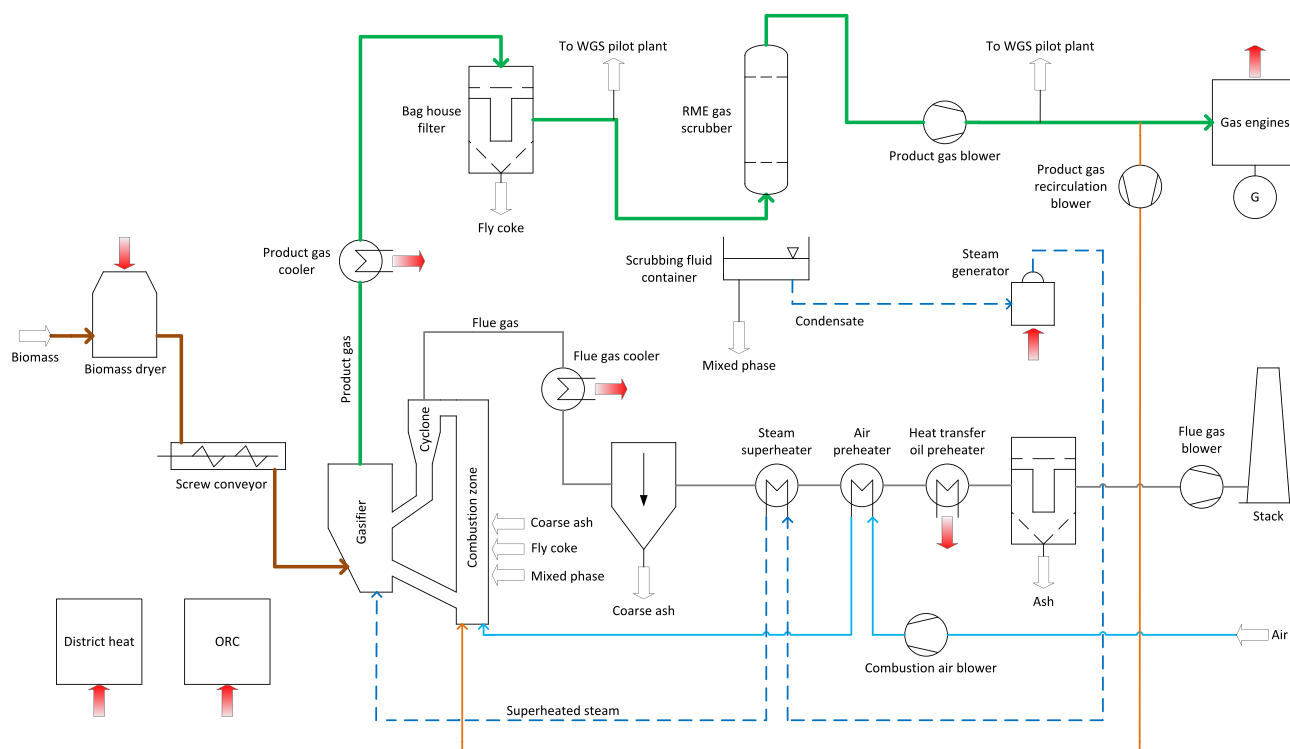


Fig. 1. Simplified flowchart of the CHP plant in Oberwart, Austria. Heat sources and heat sinks of the process are indicated by arrows. The flowchart also shows the extraction points for experimental work before and after the RME gas scrubber of the CHP plant.

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