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Experimental study on high temperature catalytic conversion of tars and organic sulfur compounds

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ABSTRACT

A 400 cpsi noble metal catalyst was used to test the conversion of tars and sulfur containing hydrocarbons in the presence of steam, hydrogen sulfide and ethene. In order to reproduce producer gas from biomass gasification, higher molecular hydrocarbons (toluene, naphthalene, phenanthrene, pyrene) and sulfur containing hydrocarbons (thiophene, benzothiophene, dibenzothiophene) were added to a syngas. The syngas consisted of H_2, CH_4, H_2O, CO, CO_2 and N_2. The catalyst was operated at temperatures between 620 °C and 750 °C and at gas hourly space velocity (GHSV) of 9000 h^{-1} and 18,000 h^{-1}.

Conversions of sulfur containing hydrocarbons (41—99.6%) were on average higher than conversions of sulfur free tars (0—47%). High temperature, low GHSV, low steam and sulfur content favored high conversions of tars and sulfur tars. As the catalyst was able to decompose sulfur tars under operating conditions close to a real wood gasification plant, it is possible to use it for hot gas cleaning in any process that includes sulfur sensitive catalysts such as fuel cells, liquid fuel synthesis or methanation processes. In such processes, H_2S produced by the reforming catalyst from sulfur tars can be captured downstream of the reformer in a metal oxide bed such as ZnO.

1. Introduction

An efficient and effective gas cleaning of producer gas from thermo-chemical conversion of biomass is needed to protect downstream equipment. Particulate matter, tars and contaminants reduce the performance of downstream equipment such as catalysts, internal combustion engines or turbines. Sulfur is known as poison for catalysts containing Ni, Cu, Co or Fe. The removal of sulfur species is therefore crucial for any process applying catalysts such as methanation, liquid fuel synthesis or fuel cells.

State of the art gas cleaning requires cooling of the producer gas below 400 °C in order to fulfill the temperature limits of the filtration system. Tars and steam will condensate in quenching columns operated at temperatures as low as 10 °C. Sulfur species will be captured in cold absorbers such as scrubbers (e.g. Selexol, Rectisol) or fixed beds (active carbon, metal oxide).

Depending on the technology, exit temperatures of biomass gasifiers can be as high as 850 °C supporting the application of hot gas cleaning (HGC). It has been shown by process modeling, that HGC allows significant efficiency improvements by avoiding cooling and reheating of the producer

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gas [1]. High exit temperatures of gasifiers enable the application of high temperature sorption materials upstream or inside of a hot gas filter to reduce the sulfur and alkali content of the producer gas [2]. At filtration temperatures above 400 °C, condensation of tars and steam can be avoided. Catalysts can be used downstream of a hot gas filter protected from particulate matter. In a dust free environment, catalyst structures, e.g. monolith channels, can be smaller allowing more compact process units. Catalysts are needed to convert tars and sulfur containing hydrocarbons to lower molecular hydrocarbons, CO, CO_2, H_2, H_2O and H_2S. So far, sulfur containing hydrocarbons cannot be captured by sorption materials but H_2S can be removed by high temperature sorption materials such as zinc oxide (ZnO) or zinc titanate (Zn_2TiO_4) [3].

The ability of the catalyst to decompose sulfur containing hydrocarbons is a precondition for the proposed process chain applying HGC in combination with a metal oxide bed to remove H_2S. The conversion of sulfur free tars has second priority. The catalyst activity regarding water gas shift (WGS) reaction and steam reforming of methane (SRM) has minor relevance regarding the desulfurization step. Tars and methane in the producer gas are unproblematic to some extent in case solid oxide fuel cells (SOFC) are used for electricity production. Tars can be considered as fuel and methane is used for internal cooling of the fuel cell [4].

Several studies cover the performance of catalytic conversion of tars in biomass gasification fuel gases [5–16]. Ni based catalysts show high activities but are prone to sulfur poisoning below 900 °C. Therefore, the performance of noble metal catalysts below 900 °C in the presence of sulfur is of special interest. Lower operating temperatures will better suit exit temperatures of biomass gasifiers. Additional heating of the producer gas to reach temperature around 900 °C can be avoided. However, noble metals such as Ir, Rh, Ru, Re and Pd are two to three orders of magnitude more expensive than Mo, W, Ni and Co.

Sulfur in the form of H_2S was often considered in the studies mentioned before because sulfur free producer gases will hardly exist. It is important to consider steam content when evaluating performances of tar reforming catalysts since gasifiers using steam as gasification agent create producers gases with steam contents up to 50 vol% [17]. Most of the studies use merely toluene and naphthalene as model compounds. Sulfur containing hydrocarbons were usually not considered. The lack of appropriate analytical equipment and methods could be one reason for neglecting hydrocarbons containing more than one benzene ring and sulfur. The variety of sulfur containing hydrocarbons found in biomass gasifier gas was shown by Rechulski et al. [18]. Up to 41 different sulfur tars could be detected. The most abundant were thiophenes, followed by benzothiophenes and dibenzothiophenes. The amount of sulfur containing hydrocarbons in biomass producer gases can be above acceptable tolerance levels of the catalytic process.

In this study a 400 cpsi noble metal catalyst was used to test the conversion of tars and sulfur containing hydrocarbons in the presence of steam, H_2S and C_2H_4. In order to reproduce producer gas from biomass gasification, higher molecular hydrocarbons with up to four benzene rings and sulfur containing hydrocarbons with up to three rings were added to a

syngas. The results of this study built the basis for an applied kinetic model presented in a follow up study [19].

2. Materials and methods

2.1. Test rig

Fig. 1 shows the set-up of the reformer test rig consisting of two catalytic reactors, a mixing section in between the reactors and a flare to burn the gas at the end of the process.

Electric heating was used along the reactors and the mixing tube section to heat the system to desired temperatures and to compensate for heat losses. The whole set-up was insulated to reduce temperature losses. Temperatures were measured downstream of the catalytic partial oxidation (CPO) unit (T1), up- and downstream of the monolithic reformer (T2, T3). Thermocouples (Thermocoax, K-type, 1 mm) were positioned about 5 mm away from the catalytic monolith. The temperature measured after the catalytic monolith (T3) was defined as operating temperature. The maximum temperature that could be reached in the reformer unit was 750 °C during experiments with tar addition.

The system could be operated at atmospheric pressure only. Pressure sensors were installed up- and downstream of the reformer allowing recognizing blockages of monolith channels by soot. During the experiments no blockage could be measured by the installed pressure sensors. Visual inspections of the reformer monolith after experiments confirmed clean monolith channel entrances and exits. Some soot depositions could be observed downstream of the CPO unit by visual inspections. It was assumed that the CPO of methane and air without additional steam caused soot formation.

Syngas was produced in the first reactor by catalytic partial oxidation (CPO) out of methane and air. Thermal input of methane was 2.3 kW and 4.6 kW corresponding to gas hourly space velocities (GHSV) related to the reforming catalyst of 9000 h^{-1} and 18,000 h^{-1}. The lambda value was set at 0.29. Accordingly, 0.230 m_n^3/h of CH_4 and 0.637 m_n^3/h of air or twice the amounts were used to produce the syngas. Mass flow controllers (Bronkhorst, F–201C-FA-33-V) were used to regulate the gas flow of methane and air. CPO was operated at a constant temperature. Average temperatures of the syngas downstream of the CPO unit varied between 632 °C and 687 °C depending on the thermal input.

Downstream of the CPO unit, steam, H_2S, C_2H_4, tar model compounds and sulfur containing hydrocarbons were added
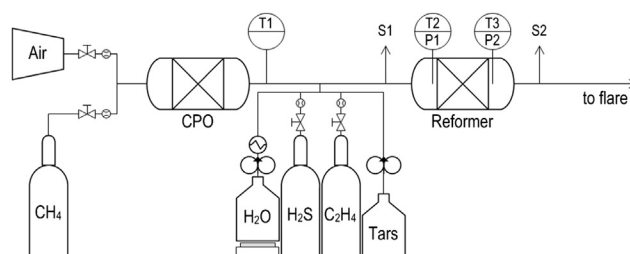

Fig. 1 – Experimental set up of catalytic reformer unit.