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Kinetic modeling of a combined tar removal and methanation reactor for biogenous synthesis gas at medium temperature conditions

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ABSTRACT

Combined tar steam reforming and methanation at relative low temperatures are an interesting gas cleaning option for decentralized, small-scale allothermal gasification plants. In the course of the work, a thermodynamic model for the tar removal reactor is developed, applying mass and energy balances, reaction kinetics and equilibrium equations. To describe the chemical reactions accurately, kinetic data, for the gas reactions and the steam reforming of tar, considered as two lumps (heterocyclic and polycyclic aromatics), is implemented into the model. The kinetic coefficients are obtained by regressing experimental data considering literature values. Since catalyst deactivation is a major obstacle especially at low temperature conditions, catalyst deactivation is implemented into the model by using the specific-catalyst-consumption, an empirically determined parameter, avoiding the data requirements of a kinetic model. The performance of the reactor model is evaluated and compared to experimental data, showing good agreement with the measured values.

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1. Introduction

High molecular weight polyaromatic hydrocarbons (tars) are a major technical obstacle in the implementation of the gasification technology because tar condensation and polymerization pose a serious threat to downstream equipment and end-user applications [1]. Since depending on type of gasifier and operational conditions biomass gasifiers produce a gas with tar content levels between 0.01 and 150 g/m^3 STP [2], the concentration of these contaminants has to be decreased to comply with the gas quality requirements for power generators which are under 100 mg/m^3 STP for internal combustion engines and gas turbines and as low as 0,1 mg/m^3 STP for methanol synthesis [3].

Several tar removal methods have been studied or are under investigation. These measures can be divided in primary measures inside the gasifier and secondary measures downstream of the gasifier. Since it would render expensive and complex downstream gas cleaning unnecessary, primary measures, which may achieve tar concentrations as low as 50 mg/m^3 [4], have gained much attention [5,6]. To obtain a sufficient syngas quality, required by most potential users, secondary measures have to be applied [7]. The most mature and commercially available option is tar removal by wet scrubbing. Many present industrial biomass gasification plants like the combined heat and power plant in Güssing , where syngas is produced through allothermal gasification in a dual fluidized bed reactor, use a product gas scrubber with rapeseed oil methyl ester (RME) to remove tar [8]. But wet methods have high investment costs and transfer the contaminants into a liquid phase which can lead to waste water problems. Catalytic hydrocarbon reforming seems to be a promising alternative considering the high gas purity and the increased fuel heat value. The conversion of the tar components is commonly performed at temperatures close to gasification temperature between 600–900 °C [9,10]. Although the operating temperature is considerably lower than for thermal cracking (1100–1300 °C), the process still leads to thermal losses and complex and large apparatuses especially under atmospheric pressure [4].

Various researchers showed that hydrocarbon steam reforming with conventional nickel catalysts is possible at temperatures in the range of 500 °C [10–12]. This is used in the so-called medium temperature gas cleaning process where methanation and hydrocarbon steam reforming occur simultaneously in one adiabatic reactor. The syngas enters the steam reforming reactor with a nickel containing catalytic bed at 300 °C, where the exothermic methanation reaction (2) leads to a temperature increase, which allows catalytic steam reforming of tar according to reaction (1).

$$C_xH_yO_z + (x-z)H_2O \rightarrow xCO + \left(\frac{y}{2} + x - z\right)H_2 \quad (1)$$

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Besides the methanation reaction (2), also the water-gas shift reaction (3) and the Boudouard reaction (4) are catalyzed by nickel and take place in the reforming reactor [13].

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \qquad \Delta H_R = -206\ \frac{kJ}{mol} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_R = -42\ \frac{kJ}{mol} \tag{3}$$

$$2CO \leftrightarrow C + CO_2 \qquad \Delta H_R = -172\ \frac{kJ}{mol} \tag{4}$$

The temperature increase in the reactor depends strongly on the syngas composition and other reaction conditions for example process pressure, which makes the combined tar removal and methanation process uniquely suitable for pressurized allothermal steam gasification plants due to the low nitrogen content in the produced syngas. Under the experimental conditions described in Section 2 a temperature rise of up to 500 °C was determined.

Since catalyst deactivation is a major issue for catalytic steam reforming at low temperatures, removal of particles and sulfur components is performed upstream of the catalytic tar removal reactor. Additionally a high water content in the syngas reduces coking [14] and hence deactivation of the catalytic bed.

This paper presents a relative simple but conclusive mathematic model of the methanation and tar removal reactor implemented in the software package IPSEpro. The necessary kinetic data is determined by using literature data and regressing the missing values in the software Aspen Plus on the basis of experimental data, obtained under conditions described in Section 2. Using this method the number and complexity of experiments, necessary for process simulation, is reduced significantly. The presented model calculates tar conversion rate, syngas composition, process conditions and catalyst deactivation and will be implemented into simulations of the overall gasification process in IPSEpro to facilitate classification, thermal integration and optimization of gasification plants.

2. Experimental setup

Section 2 gives a description of the experimental rig used to determine experimental data which was utilized to determine the kinetic data and describe the model, presented in this paper. To show the influence of catalyst deactivation long-term tests of 250 h have been performed. A more detailed description of the experimental setup of gasification, gas cleaning and analytic equipment can be found in [15] and [16].

2.1. Gasification setup

The syngas is produced in an allothermal, bench-scale fluidized-bed gasifier with a diameter of 80 mm, filled with olivine with a mean particle diameter of 250 μm. Although steam is used as a fluidization and gasification agent, the produced syngas has a relatively high N_2 content as the gasification rig is rinsed with N_2.

The gasifier is operated at 1.5 kW thermal input, which equals a biomass flow of 0.3 kg/h, using wood pellets according to [17] with a water content of 6% as feedstock, and produces 0.93 m^3 STP/h of syngas. The gasification reactor is externally heated to 820 °C by an electric tube furnace and is operated 1 bar above atmospheric pressure and with an excess steam ratio of 4. The excess steam ratio is defined as the quotient of fed steam to stoichiometric steam demand. Thereby the fed steam includes the steam, brought into the gasifier as fluidization and gasification agent, and the water content of the biomass feedstock. An excess steam ratio of 4 is necessary to prevent coking of the catalyst in the tar removal and methanation reactor R2.

2.2. Gas cleaning and methanation setup

Fig. 1 shows the setup of the gas cleaning test rig, which is connected to the gasification test plant and operated close to atmospheric pressure. After passing a filter cartridge to remove particles and aerosols, the syngas is cleaned in two reactors, which are not pressurized and can be heated to the desired temperature with heating tape. In Reactor R1 H_2S is adsorbed on ZnO at 300 °C. The Reactor R1 (layout: bed length 700 mm, diameter 44 mm) is filled with 1100 ml of commercially available ZnO-adsorbent in pelleted form and operated with a GHSV (gas hourly space velocity) of approximately 870 h^{-1}. Catalytic steam reforming of the tar in the syngas is performed in Reactor R2 (layout: bed length 120 mm, diameter 36 mm), filled with 350 g of commercial Ni-catalyst. The reactor is operated with a GHSV-value of approximately 2700 h^{-1}. The gas enters the reactor with 300 °C and is heated up to 510 °C due to the occurring exothermic methanation reaction. During operation the reactor is solely cooled by thermal losses. The temperature profile in the reactor is measured by twelve thermocouples, placed in intervals of 10 mm in a thermowell in the middle of the catalytic bed. These measurements are used to determine a distinctive temperature peak after the methanation reaction reaches equilibrium, which serves as a measure for the catalyst deactivation. Syngas with low tar content leaves the reactor at 500 °C and is cooled in a condenser to about 30 °C in the laboratory tests. The NH_4^+ content in the condensate is measured to determine the NH_3 content in the syngas.

The gas composition, the sulfur content as well as the tar content are measured at the three sampling points SP1, SP2 and SP3 in Fig. 1. The

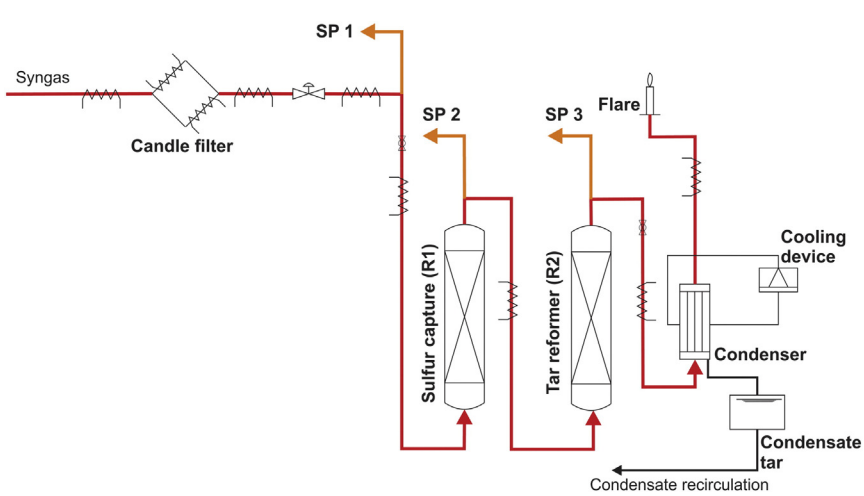

Fig. 1. Flow chart of the gas cleaning test rig.

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