



Research article

Catalytic decomposition of biomass tars: The impact of wood char surface characteristics on the catalytic performance for naphthalene removal



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ABSTRACT

Catalytic decomposition of naphthalene over four different wood chars has been investigated. The effect of the pyrolysis temperature and activation with CO₂ on the char structure and catalytic activity of the wood char has been studied in order to elucidate the tar decomposition rate and char stability towards deactivation. The wood char catalysts were produced by pyrolyzing spruce wood chips in a tubular batch reactor at 500 and 800 °C. Part of both char samples was further activated by purging CO₂ through a bed of the pyrolysis char at 800 °C. The wood char reactivity for naphthalene cracking was investigated using a fixed bed quartz reactor in a heated furnace with a constant inlet gas flow of naphthalene. Thermal decomposition was evaluated at temperatures between 700 and 1050 °C and taken into account when assessing the catalytic activity of each wood char at 850 and 1050 °C. The structural features of the char catalyst were examined before and after the tar cracking experiment by CO₂ and N₂ adsorption technique as well as scanning electron microscopy (SEM). Catalytic deactivation was studied by analyzing the surface structure of the char samples over exposure time to naphthalene. The self-produced wood char samples were compared to a commercial activated carbon to classify their structural and catalytic properties.

Catalytic tar cracking tests with all wood char catalysts confirmed that the activated char samples showed a high catalytic activity for naphthalene decomposition into carbon and hydrogen, whereas the non-activated char samples did not enhance the tar cracking reaction at 850 °C significantly.

N₂ adsorption revealed that deactivation of the char catalyst happens mainly due to coke deposition blocking the char active sites. The time evolution of the wood char's tar cracking activity was found to be proportional to the amount of micropores with a pore diameter smaller than 0.7 nm. SEM measurements visualized structural changes on the macroscopic char surface caused by naphthalene decomposition under an inert nitrogen atmosphere.

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1. Introduction

Biomass gasification is identified as one of the most promising renewable and CO₂ neutral technologies for the conversion of biomass into a combustible product gas. However, the high amount of tar in the product gas is still one of the main problems in biomass gasification systems [1] and hence, the removal of biomass-derived tars has been intensively studied over the last decades [1–3]. One of the most challenging technical barriers for the establishment of the gasification technology in the power market is considered to be developing a reliable and cost efficient tar removal process [4].

Tar removal processes are classified into physical, thermal or catalytic. Physical removal methods such as water washing and solid phase adsorption can easily remove tar from producer gases. However,

these waste management processes incur additional economic and environmental costs and have a negative impact on energy efficiency of the plant [5]. Therefore, it is ideal to treat the tars within the process while they are still present in the hot gas. Not only can thermal or catalytic gas treatment reduce tars, but also increase the heating value by boosting the hydrogen content in the product gas. Thermal processes require temperatures exceeding 1000 °C to remove tars and, therefore, thermally resistant reactor materials, large energy input, and long residence times [6]. Tar cracking through a catalytic process has the potential to be a simple and effective method for tar removal, while maintaining sensible heat in the producer gas [7,8]. As catalytic degradation of tars is possible at temperatures of 600–900 °C, expensive alloys are not required.

Thermal and catalytic treatment for tar removal has been investigated in numerous previous studies [1,2,9–11]. Carbon containing materials such as activated carbon or wood char were found by many researchers to show good catalytic activity for tar decomposition [9, 11,12]. Wood chars were determined to be more reactive than coal

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chars [13,14] and more resistant to poisoning [2,15] than other catalysts.

The structure of the wood char is determined during pyrolysis. The effect of pyrolysis conditions, e.g. temperature and presence of CO₂, on the microporous char structure and chemical surface properties has been discussed in our previous studies [14,16]. It was found that the microporous char surface area increases when increasing the pyrolysis temperature from 500 to 800 °C and that activation with CO₂ almost doubled the microporous surface area and pore volume. In addition, increasing the pyrolysis temperature leads to a higher structural ordering of the carbon resulting in a loss of catalytic activity [17,18]. The presence of alkali and alkaline earth metallic species (AAEM) on the char surface were found to increase the catalytic activity of wood char [15]. Although high heating temperatures and physical activation enable access to the earth metallic species, those active sites were found to be very sensitive to poisoning resulting in a fast catalytic deactivation of the wood char catalyst [19–22].

Hosokai et al. [15] found that tar conversion mechanisms over carbonaceous materials are similar to those occurring during the tar conversion over porous particles, i.e. deposition, dehydrogenation which leads to coke formation over the char surface, and gasification of the carbon deposits if H₂O or CO₂ are present. Fuentes-Cano et al. [2] stated that char deactivation is the main practical limitation for the use of any catalytic material and that it is therefore an important factor that has to be taken into account when assessing wood char as a possible catalyst for tar removal. In order to gain insight into the char deactivation we focus in this study on tar decomposition in a nitrogen–tar atmosphere without the reactivating agents CO₂ and H₂O usually present in a real gasifier product gas.

In view of the above mentioned studies, we expect that the surface of carbonized biomass, with sufficiently large surface area, would be capable to decompose tar to a significant conversion level [15] even at temperatures below 1000 °C. It is also assumed that the surface of micropores is the most influencing parameter on the char capability for the decomposition of light aromatic molecules, such as naphthalene [23].

The activity of char for tar decomposition varies with the nature of the tar compound [2]. Biomass tars can be classified as primary - produced during pyrolysis; secondary - those produced from primary tars in oxidizing environments; and tertiary - not present in biomass feed, but produced from the recombination of lighter tars at elevated temperatures. Naphthalene, a tertiary tar, is considered one of most stable and difficult to reform tar components [24]. Naphthalene also represents the major fraction of two ringed aromatics in gasification tars [24] and thus, is often used as model tar [25,26]. Therefore, naphthalene was selected as the model compound for the experiments in this study.

The aim of this study was to assess four different kinds of wood char catalyst produced via pyrolysis and activation with CO₂ for the removal of light aromatic molecules using naphthalene as model compound.

This aim was achieved by first quantifying the contribution of thermal naphthalene decomposition to gain an undistorted consideration of the catalytic activity of the chars. Then, naphthalene cracking over different wood char catalysts was studied in a fixed bed reactor. The results were compared to the decomposition behavior of benzene over wood char which was found in one of our earlier studies [16]. In a final step, the internal structure of all char catalysts was analyzed using CO₂ and N₂ adsorption measurements as well as scanning electron microscopy in order to examine the impact of structural differences on the char reactivity and in particular on the deactivation of the char catalyst.

2. Materials and methods

2.1. Char sample preparation

Wood chips of Norway spruce without bark (*Picea abies* (L.) Karst.) were used in this study. The wood chips were provided by the Institute of Forest Utilization and Work Science (FoBaWi) of the University of

Freiburg with an initial width between 10 mm and 20 mm and a length of approx. 30 mm. The wood char catalysts were prepared by drying the wood chips in an oven at 115 °C for 24 h until a relative moisture of less than 2% was achieved. Then, 75 g of the dried wood was pyrolyzed in a metal tubular reactor placed inside a furnace. The samples were heated up to 500 °C and 800 °C under a continuous pure nitrogen flow of 1.5 l/min at a heating rate of 10 °C/min and denoted hereafter as "Py500" and "Py800", respectively. The final pyrolysis temperature was held for one hour. Further information regarding pyrolysis procedure are given in one of our previous studies [14]. The wood char samples were cooled down to room temperature and then crushed and sieved to achieve a catalyst with a particle size between 0.5 and 2.0 mm diameter. Part of the samples was additionally activated with CO₂ at a N₂ to CO₂ ratio of 55:45. For activation, 10 g of the char were placed inside the quartz glass reactor and heated up to 500 (Py500) and 800 °C (Py800), respectively, under a nitrogen flow of 1 l/min at a heating rate of 17 °C/min (Fig. 1(a)). Once this temperature was reached the nitrogen flow was reduced to 0.2 l/min and 0.166 l/min of carbon dioxide were added. The Py800 sample was activated for 1 h. The Py500 sample was heated from 500 to 800 °C with enabled CO₂ flow at a heating rate of 10 °C/min and then further activated for additional 30 min. Hence, the total time exposed to CO₂ activation for both samples was 1 h, the gas residence time in the char bed was about 5.7 s. The activated Py500 and Py800 char catalysts are hereafter called "Py500a" and "Py800a", respectively.

2.2. Tar decomposition

2.2.1. Experimental set up

The tar supply for the tar cracking experiments consisted of a saturator filled with naphthalene under a continuous nitrogen flow. For this study, naphthalene at a mass concentration of 0.57 g/Nm³ (volumetric concentration: 100 ppmV) was chosen, controlled by leading 0.09 l/min of nitrogen through the naphthalene saturator at a temperature of 52 °C and then mixing the flow with a pure nitrogen stream of 1 l/min (Fig. 1(a)).

The feed gas was passed through a tubular quartz reactor with an inner diameter of 21 mm placed inside an electrical furnace (Fig. 1(b)). In the middle of the uniform heating zone the inner reactor diameter was reduced to 18 mm by means of a circumferential flute. A porous quartz glass support disk was placed on top of the flute in order to hold the catalyst bed in position for catalytic cracking.

Naphthalene as the key component was continuously measured during the experiments using a gas chromatograph (Agilent 5890 N) with a thermal conductivity detector (GC TCD) positioned downstream of the reactor (Fig. 1(a)). In an additional GC measurement, the gas chromatograph monitored the amount of non-condensable gases, i.e. H₂, CH₄, C₂H₂, C₂H₄, C₂H₆, CO₂ and CO to determine the cracking products.

2.2.2. Thermal tar conversion

The thermal influence on tar decomposition was evaluated by leading naphthalene through the previously described reactor set-up without char catalyst present in the reactor tube. The naphthalene concentration and volumetric flow rate are listed together with the parameters for naphthalene cracking in Table 1. In order to evaluate the impact of the bed temperature on the average thermal tar conversion, the temperature in the quartz glass reactor was increased from 700 °C to 1050 °C in steps of 50 °C. Residence time of the gas in the heating zone of the reactor with the determined temperature was about 5 s. Naphthalene conversion was measured three times at each temperature level at an interval of 10 min between the GC measurements.

2.2.3. Catalytic tar conversion

The reactivity of each char catalyst (Py500, Py800, Py500a and Py800a) for naphthalene decomposition was investigated by leading

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