



## Effect of feedstock water content and pyrolysis temperature on the structure and reactivity of spruce wood char produced in fixed bed pyrolysis

Luisa Burhenne <sup>\*</sup>, Marco Damiani, Thomas Aicher

Fraunhofer-Institute for Solar Energy Systems ISE, Heidenhofstr. 2, 79110 Freiburg, Germany

### HIGHLIGHTS

- ▶ Higher water content led to a higher liquid and a lower char yield.
- ▶ The specific char surface area increased with increasing initial water content.
- ▶ Increasing pyrolysis temperature up to 800 °C led to a 200 times smaller BET area.
- ▶ The micro-pores became about 10 times smaller at high pyrolysis temperatures.
- ▶ Reactivity in CO<sub>2</sub> significantly decreased with increasing pyrolysis temperature.

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### ABSTRACT

The influence of initial water content and temperature on the pyrolysis product distribution as well as on the structure and reactivity of the pyrolysis char was investigated. Spruce wood chips with 2.4%, 16.4%, and 55.4% initial water content were pyrolyzed in a tubular batch reactor at 500 and 800 °C with a heating rate between 4 and 12.6 °C/min. The structural features of the char samples were examined with scanning electron microscopy, Brunauer–Emmett–Teller (BET) method, and mercury porosimetry. The reactivity in CO<sub>2</sub> was investigated using thermo-gravimetric analysis and a fixed bed quartz reactor.

It could be seen that higher water content led to a higher yield of condensable products and a lower amount of char. At a pyrolysis temperature of 500 °C the CO-content of the product gas did increase significantly with increasing water content. Moreover, initial water content had no significant effect on the microscopic structure of wood chars.

The specific char surface area did increase with increasing initial water content up to the fiber saturation point. It was also observed that the specific char surface area was strongly influenced by the pyrolysis temperature. When the pyrolysis temperature increased from 500 to 800 °C, the BET surface area became at least 200 times smaller and the average size of micropores became about 10 times smaller. Most likely, pyrolysis at 800 °C induced more secondary reactions that were responsible for the occlusion of the micropores within the char [1].

Finally, it was found that reactivity in CO<sub>2</sub> significantly decreased with increasing pyrolysis temperature. However, initial wood water content did not have a significant effect on char reactivity in CO<sub>2</sub>.

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### 1. Introduction

Fixed bed gasification is recognized as a promising and effective way to upgrade biomass, such as wood, into a more valuable combustible gas. However, with the growing biomass needs for both bioenergy and biomaterials, the availability of biomass feedstock for gasification processes is becoming more and more limited, especially in highly populated regions. Therefore, technical processes need to be improved so that the biomass feedstock can be

converted completely into a high quality synthesis gas that can be used directly for heat and power production. In order to optimize any biomass gasification process and to fine-tune process parameters to achieve complete conversion of the feedstock, a detailed knowledge about the way in which the pyrolysis conditions influence the conversion behavior is important.

The complete process of thermochemical conversion can be divided into four overlapping steps, namely (i) drying, where water is removed from the feedstock; (ii) pyrolytic decomposition, where the main components of biomass, i.e. hemicellulose, cellulose and lignin, decompose to yield volatiles (CH<sub>4</sub>, H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>) and a variety of higher hydrocarbons (tars), and a solid fraction

<sup>\*</sup> Corresponding author.

E-mail address: [luisa.burhenne@ise.fraunhofer.de](mailto:luisa.burhenne@ise.fraunhofer.de) (L. Burhenne).

(char); (iii) reduction, in which the char undergoes further heterogeneous reactions; and (iv) combustion, an exothermal reaction of the residual char with oxygen. Drying usually precedes the pyrolytic decomposition, introducing a delay in particle heating and pyrolysis reactions [2]. Pyrolytic decomposition is the core reaction in all thermochemical conversion processes and is therefore crucial to the biomass decomposition into a gaseous and a solid fraction. Moreover, the process conditions during pyrolysis determine the char characteristics, e.g. structure, surface area and pore size distribution, which influence the char reactivity to gasifying agents. Char reduction is the slowest reaction of thermochemical conversion [3] and, in the case of fixed bed gasification, it is well known that energy efficiency, product distribution and stable operation of the process are strongly dependent on high reactivity and complete conversion of the pyrolysis chars [1,4].

The impact of pyrolysis conditions on the reactivity of conventional coal has long been recognized and studied. It is widely accepted that chars from wood are more reactive than chars from coal, mainly because wood char has a less ordered structure and a high content of oxygen [5]. However, only few studies investigate the impact of pyrolysis conditions on the biomass char structure and only recently studies were conducted to relate the char structure to the reactivity in CO<sub>2</sub>.

The effects of initial water content on the yields of total oily products from slow pyrolysis of spruce wood, hazelnut shell and wheat straw was studied by Demirbas [6]. His results indicate that higher feedstock moisture leads to a lower char yield and a higher yield of liquid products. Darmstadt et al. [7] found that the influence of feedstock moisture content is more pronounced in softwoods than hardwoods. They observed that char produced from softwood bark with high water content has a higher specific surface area; probably, the evolving steam creates voids in the remaining char. However, no prove has been given whether the initial feedstock water content has an influence on pyrolysis product distribution and pyrolysis char characteristics.

The effect of particle size, heating rate and temperature on the structure of mallee wood char, produced in a fluidized-bed reactor, was investigated by Asadullah et al. [1] using Raman spectroscopy. They found that the temperature had a significant influence on the char structure. With increasing pyrolysis temperature the total Raman peak area was indicating an increasing aromatization of all chars. By pyrolysing particles with seven different sizes between 0.18 and 4.75 mm, they found that in the biomass particles with a diameter larger than 3.35 mm, the heating rate had no influence on the char structure. The present study focuses on fixed bed processes only, where large particles and slow heating rates occur. It is assumed that heating rate has no impact on the char structure under these condition. Therefore, we investigated only the influence of temperature at one slow heating rate in the present study.

By comparing two different biomass feedstocks Guerrero et al. [8] observed that for char produced at low heating rates, the surface area for both biomass chars reached a maximum value at around 700–800 °C. At temperatures above 800 °C, the specific surface area dropped significantly, probably due to thermal annealing. In a review about charcoal production and properties, Antal and Gronli [9] summarized that the maximal pyrolysis temperature has a strong impact on the surface area, pore structure, and adsorption properties of the charcoal. A study of Mermoud et al. [10] about steam gasification of large char particles (10–30 mm) at different temperatures confirms that pyrolysis temperature is the most influencing parameter on gasification kinetics. However, in none of the studies above, a correlation between pyrolysis temperature and pore size distribution was found.

It was stated that the surface area developed by mesopores and macropores is a better indicator for the reactive surface than the total surface area also including the contribution of micropores

(<2 nm). It is well known that micropores do not participate in heterogeneous char oxidation and methane or tar conversion reactions due to diffusion limitation. Similar results are found by Moliner et al. [11] studying the effect of carbon structure on thermochemical decomposition of methane for the production of hydrogen. In their study with different activated carbons they have shown that the initial reaction rate of methane decomposition is related to the surface chemistry and that the long-term behaviour is related to the surface area and the pore size distribution, in particular to the area in mesopores. In this way, microporous carbons exhibit high initial conversion rates but they become rapidly deactivated. In contrast, mesoporous carbons with high surface area provide more stable and sustainable methane decomposition [11].

So far, literature does not provide an understandable relationship between pyrolysis conditions and char structure. In addition, the impact of surface area and pore size distribution on char reactivity to gasifying agents is not yet well understood.

The overall aim of this study was to (i) investigate whether the initial feedstock water content does influence the yield of pyrolysis products after slow pyrolysis; (ii) elucidate the effect of the initial feedstock water and pyrolysis temperature on the physical structure of spruce wood char; and (iii) examine the impact of structural differences on the char reactivity in CO<sub>2</sub>.

This aim was achieved by first pyrolysing spruce wood chips at 2.4%, 16.4%, and 55.4% initial water content at both 500 and 800 °C and analyzing the amount of gaseous, solid and liquid products. Then, the physical structure was investigated with scanning electron microscopy, Brunauer–Emmett–Teller (BET) method, and mercury porosimetry. In a last step, the reactivity in CO<sub>2</sub> was investigated using thermo-gravimetric analysis and a fixed bed quartz reactor.

## 2. Materials and methods

### 2.1. Biomass

Wood chips of Norway spruce without bark (*Picea abies* (L.) Karst.) were used in this study. The wood chip samples were provided by the Institute of Forest Utilization and Work Science (FoB-aWi) of the University of Freiburg and were stored in sealed plastic bags. The samples had an initial width between 10 and 20 mm and a length of 30 mm. The water content was indicated to be close to 0% (oven dry wood), 18% (air dry wood), and >30% (green wood, i.e. freshly harvested). The samples were oven dried at 105 °C for 24 h in order to estimate the actual mean wood water content  $w$  which was calculated as follows:

$$w = \frac{m_{\text{H}_2\text{O},I}}{m_{\text{wood}} + m_{\text{H}_2\text{O},I}} \times 100\% \quad (1)$$

with  $m_{\text{H}_2\text{O},I}$  and  $m_{\text{wood}}$  being the mass of water in the wood and the mass of the dry wood, respectively. The actual wood water contents of the wood chips were 2.4%, 16.4%, and 55.4% with a standard deviation of 2.2%, 0.9%, and 0.6% respectively.

The ash content in the wood was found after burning a wood sample with 2.4% initial water content in an oven, where the sample was kept at 850 °C for 8 h. The unburned material was considered the ash weight, which was 0.2% on an oven dry basis.

Ultimate analysis of the spruce wood chips was carried out by courtesy of the TEER institute of RWTH Aachen according to the standard DIN 51732 (Table 1).

### 2.2. Pyrolysis

Pyrolysis and char production for characterization was performed in a vertical batch reactor, placed in an electrical oven

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