



Influence of intraparticle secondary heterogeneous reactions on the reaction enthalpy of wood pyrolysis



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ABSTRACT

Despite the technical relevance of wood pyrolysis the reaction enthalpy of this conversion step remains a matter of controversy. In this work the slow pyrolysis of dry spherical beech wood particles with 25 mm diameter was investigated by means of Laser-Induced Fluorescence of the evolving volatiles together with macroscopic thermogravimetric analysis in a particle cell. It was observed that the reaction heat is correlated with the ratio of total fluorescence intensity versus conversion rate. In exothermic regimes of pyrolysis this ratio changes significantly, while it is relatively constant in endothermic regimes. Taking into account the results of differential scanning calorimetry and the char yields at different sample sizes the results of this study can be interpreted such that when heterogeneous secondary reactions of the pyrolysis volatiles are promoted, the production of char is enhanced together with the production of polyaromatic hydrocarbons, leading to a more exothermic global heat of reaction.

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1. Introduction

The energetic and chemical utilization of wood has become a prominent topic in the last decade. Among the different possible conversion processes pyrolysis is of major importance because it is not only a promising conversion process itself but also an important subprocess in other conversion processes like gasification, smouldering, combustion or hydrothermal carbonization.

Despite the technical relevance of wood pyrolysis the reaction enthalpy of this conversion step remains a matter of controversy, as has been pointed out recently by several authors [1–3]. In many studies in which models for slow pyrolysis of thermally thick wood particles have been developed, the reaction enthalpy of wood was considered to be constant (see Refs. [1,2]). Rath et al. [4] developed a correlation for the reaction enthalpy of wood pyrolysis based on Differential Scanning Calorimetry (DSC) experiments, assuming that there are two competitive reaction pathways which mainly contribute to the reaction enthalpy: the endothermic generation of volatiles and the exothermic generation of char. Depending on the final char yield the reaction enthalpy is considered to be either

endothermic or exothermic. In most cases, however, the final char yield is not known in the first place. Haseli et al. [2] suggested that the consideration of a temperature dependent heat of reaction may be required. In a subsequent work of that group [5], however, it was stated that the temperature dependent correlation did not accurately reflect the exo-/endothermic nature of the reactions involved. Park et al. [6] introduced a reaction network for wood pyrolysis which included endothermic primary pyrolysis as well as exothermic char formation reaction and exothermic homogeneous tar cracking. The char formation was postulated to occur through an intermediate solid species. The homogeneous tar cracking was found to be not relevant. It may also be possible that the exothermicity which can be observed in some pyrolysis experiments, is due to heterogeneous secondary reactions of volatiles that lead to generation of (secondary) char. In recent works [7,8] it has been pointed out that intraparticle heterogeneous secondary (cracking) reactions occurring during wood pyrolysis may have a significant impact on both the composition of the volatiles and the char yield. Furthermore, the DSC results obtained with lid by Rath et al. [4] may suggest that the exothermicity is not due to homogeneous reactions in the solid, but due to heterogeneous reactions in which the volatiles are involved. The general importance of intraparticle heterogeneous secondary reactions in wood pyrolysis has been pointed out by Schinkel [7]. In light of these findings it should be further noted that char formation in cellulose pyrolysis is not a

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primary step but a result of secondary reactions in the vapor and solid phases, as stated by the reviews of several authors [9–11]. Therefore it may not be possible to clearly distinguish between tar cracking and charring reactions, as tar cracking is a rather unspecific term that includes very different reactions. Therefore, tar cracking may be considered as one of the reactions involved in charring. It may be that the homogenous tar cracking reactions taking place at temperatures higher than 500 °C are of very different nature than the heterogeneous reactions at lower temperatures in which significantly more char is produced. In a most recent work, in which reaction heat effects of wood pyrolysis have been investigated [3], it was pointed out that it was difficult to attribute the reaction heat effects to either the activity of primary or secondary reactions. It is, therefore, the overall objective of this contribution to add some further experimental evidence to the question if the exothermicity in wood pyrolysis may be due to the occurrence of intraparticle heterogeneous secondary cracking reactions of volatiles.

With Laser-Induced Fluorescence (LIF) it is possible to characterize the volatiles leaving a pyrolyzing wood particle as has been done in previous works [12–14]. LIF will be used in this study together with macroscopic thermogravimetric analysis (macro-TGA) in a particle cell in order to find out if it is possible to correlate the exothermicity of wood pyrolysis to the observed LIF signal intensity. This will give further indications to the nature of the exothermic sub-processes in wood pyrolysis.

2. Experimental

The main components of the experimental setup have already been described previously [14]. Therefore, only a brief description is presented below.

Laser-Induced Fluorescence measurements were carried out using the third harmonic of a Nd:YAG laser (Type QuantaRay by Spectra-Physics, USA), corresponding to a wavelength of 355 nm. A repetition rate of 10 Hz with a pulse energy of 2 mJ was applied. The fluorescence was detected at an angle of 90° with a spectrograph (type SpectraPro 2300i by Princeton Instruments, USA) using a grating with 300 grooves/mm. An ICCD camera (NanoStar by LaVision GmbH, Goettingen, Germany) was coupled to the spectrograph. The particle cell is made of a hollow tailored stainless steel (1.4841) cube which houses the biomass particle during pyrolysis and which allows optical access for both the laser beam and the camera. For details regarding the design of the particle cell the reader is referred to the previous publication [14]. In a first set of experiments the wood particle is held inside the chamber by a wire connected to a balance to measure the mass loss over time. The balance (Type BP 121S by Sartorius AG, Goettingen, Germany) has a precision of 0.1 mg. In a second set of experiments the temperature of the particle during pyrolysis is measured with a type K thermocouple of 1 mm thickness which is surrounded by a ceramic tube of 2.5 mm outer diameter. The tip of the thermocouple is positioned at the particle center. In both sets of experiments the fluorescence signal is monitored. Furthermore, a second thermocouple measures the temperature in the chamber at approximately 30 mm distance from the particle surface. The laser beam passes through the cell at a distance of approximately 20 mm below the bottom of the spherical wood particle. A carrier gas flow of nitrogen is guided through the reaction chamber. The nitrogen flow of 3.5 Nl/min is provided by a mass flow controller and is preheated to approximately 500 °C in a coiled tube inside an electrical oven before it enters the particle cell. With this setup a maximum heating rate of approximately 0.3 K/s is possible which is in the range of the heating rates which are typical for pyrolysis zones in downdraft gasifiers [15,16].

Table 1
Properties of the materials used

	Reference Beech wood	Leached Beech wood
Proximate analysis, wt.% (d.b.)		
Fixed carbon	13.98 ± 0.20	12.01 ± 0.15
Ash	0.41 ± 0.01	0.16 ± 0.06
Volatile matter	85.60 ± 0.20	87.83 ± 0.21
Ultimate analysis, wt.% (d.b.)		
C	48.35 ± 0.14	48.24 ± 0.21
H	6.87 ± 0.04	6.73 ± 0.11
N	0.09 ± 0.00	0.08 ± 0.01
S	0.04 ± 0.01	0.10 ± 0.04
O (by difference)	44.65 ± 0.15	44.86 ± 0.22
Apparent density, g/cm ³	0.687 ± 0.074	0.657 ± 0.042

2.1. Materials

The beech wood spheres with 25 mm diameter were provided by Meyer & Weigand GmbH, Nordlingen, Germany. The spheres have neither been milled nor compacted during their production, which means that their physical structure remained unchanged by the production process. The particles were dried in an oven at 106 °C for 90 min prior to the experiments. Results of proximate and ultimate analysis of the material are presented in Table 1. The nitrogen used has 99.999 mol% purity (ALPHAGAZ™ provided by Air Liquide, Germany).

In order to investigate the impact of minerals (especially alkalis) on the extent of secondary reactions and their potential influence on the exothermicity of the pyrolysis process, some beech wood particles have been pretreated by a leaching procedure to reduce the mineral content: The beech wood spheres have been put in a distilled water bath, which was placed in a vacuum oven. By means of a vacuum pump an absolute pressure of approximately 100 mbar was generated to remove the air from the particle pores and let the distilled water penetrate into the pores. The particles stayed under vacuum for approximately 12 h. After the evacuation the pressure was set back to ambient conditions under which the particles remained in the distilled water for another 24 h. The particles that have been pretreated in this manner have also been subjected to proximate and ultimate analyses. The results are also shown in Table 1. It can be observed that both fixed carbon and volatile matter content are not changed significantly by the leaching procedure. Hence, one can reasonably assume that the leaching procedure does not change the chemical nature of the organic matrix of the wood. This is further supported by the observation that the ultimate analyses of leached and reference material do not differ significantly, either. However, the ash content is significantly reduced by the leaching procedure, showing that the purpose of the pretreatment is fulfilled.

3. Results and discussion

The results will be presented and discussed in the following manner: at first the results of the macro-thermogravimetric analysis (macro-TGA) of both reference and leached particles will be analysed to examine the exothermic regimes during pyrolysis of a thermally thick wood particle possessing a Biot number of approximately 1.2 (Figs. 1–3). After that the fluorescence emitted by the volatiles leaving the pyrolyzing particle will be examined (Figs. 4–6). This will be done by analysing the evolution of the total fluorescence intensity (reflecting the total amount of secondary and/or tertiary pyrolysis products). The combined analysis of both macro-TGA and fluorescence data (Figs. 3 and 6) will show to what extent exothermic behaviour during pyrolysis is correlated to the LIF signal intensity.

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