A COMPARISON OF WOOD PYROLYSIS PRODUCTS OBTAINED BY THERMOGRAVIMETRY AND INTRA-PARTICLE MEASUREMENTS

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Abstract

The pyrolysis of birch wood was studied by thermogravimetry (TGA) and also by intra-particle measurements (IPM). During TGA, the wood samples were heated at a constant heating rate of 50 K/min and the pyrolysis gas which evolved from the bulk sample was analyzed by microGC. In the IPM, birch wood spheres were introduced into a preheated (500 °C) pyrolysis reactor and gas sampling was done from the particle center. The center temperature was measured by a thermocouple and the average heating rate was found to be close to 50 K/min. The major products were found to be CO, CO_2 and CH_4, while the C_2- and C_3-hydrocarbons and hydrogen were among the minor products with concentrations roughly an order of magnitude lower than the main products.

The results were analysed further by a 7-step reaction model, in which the pseudocomponents of the wood are decomposed in two parallel reactions, which lead to the permanent gases CO, CO_2, H_2, CH_4, to water vapor and char and, either to gas phase tar or to a condensed phase intermediate metaplast. At the time scales considered here, the gas phase tar is stable, while the metaplast is assumed to decompose into volatiles and char. The elemental compositions of the tar, metaplast and char species are variable input parameters and the stoichiometric coefficients are calculated automatically. This permits a fast adjustment and sensitivity analysis of the model parameters. In the present study, TGA and IPM results were interpreted in consistence with literature data about the pyrolysis of lignocellulosic biomass.

1- INTRODUCTION

Lignocellulosic biomass is widely used as renewable source of energy as well as raw material for the production of valuable chemicals. Due to the continued growth of energy demand, the interest in renewable energy development will continually increase. Biomass, in particular wood and forest residues, is one of the main renewable energy resources available, with 72 GW installed plant capacity in 2011 worldwide [1]. It can store large amounts of carbon and its use allows mitigation of the global CO_2 emissions. Furthermore, compared to other renewable resources, biomass is the only source of renewable liquid, gaseous and solid fuels [2]. Therefore, biomass is expected to be a suitable energy resource for future energy policies.

Amongst the treatment options for conversion of biomass into fuels, energy or valuable chemicals, thermal treatment processes have the highest conversion efficiencies. Furthermore, knowledge of the mechanisms occurring during the thermochemical conversion processes is fundamental for the optimal design of thermal treatment reactors. In the associated thermo-chemical conversion routes, pyrolysis is understood to be the first reaction step after drying and represents the early stage of other thermochemical processes such as gasification or combustion [3]. Understanding pyrolysis is imperative, if there is a desire to convert biomass into intermediate fuels with improved combustible properties. Therefore, understanding the pyrolysis kinetics is vital for the assessment of items including the feasibility, design, and scaling of industrial biomass conversion applications [4].

Wood pyrolysis is a complex physiochemical process in which yields and products are directly affected by several operating parameters. Despite continuing efforts to quantify the huge variety of pyrolysis products and to clarify the reaction pathways, many questions are still open. Due to the large variability of biomass composition and experimental procedures, there is a large scattering in the reported product compositions [5].

Although many experimental and modelling studies [4-8] focused on explaining the pyrolysis mechanisms to transform feedstock into valuable products, there still remains a number of aspects not fully understood. This is, because the pyrolysis process is not only determined by the chemical properties of the biomass: In addition, physical constraints like heating rate, particle size and total sample mass may also affect the pyrolysis kinetics and the product distribution. For an isolated chemical kinetic investigation of the pyrolysis process, it is therefore recommended to use the particle size and the sample mass as small as possible [9]. In addition, some experimental and theoretical work about the intra-particle heat and mass transfer is available in the literature [3,10-16]. In particular, the experimental setup and conditions in refs. [17-20] are comparable to those used here. Besides the horizontal reactor arrangement, the major novelty here is the gas sampling which was done from the interior of the particle directly. In previous studies, gas analysis was done from the bulk downstream gas flow which mainly represents pyrolysis products emerging from the particle surface. As prominent result of previous studies it was observed that the intra-particle contact of the volatiles with the developing char may facilitate the decomposition of tar. This effect is widely negligible here, because the pyrolysis gas was sampled directly from the particle center with a minimum of heterogeneous tar decomposition [21,22].

This paper aims to compare the intra-particle measurements (IPM) with relevant thermo-gravimetric (TGA) results and with corresponding kinetic model calculations.

2- MATERIALS AND METHODS

Experimental procedure

Two different diameters have been chosen for the birch wooden spheres: 19.0 mm and 31.8 mm, (tolerance: ±0.8 mm). The operating temperature of 500 °C was chosen based on litera-ture review which showed optimum operating temperatures for wood biomass and unclear energy change between 320-480 °C temperature ranges. The primary difference in using particles of different diameters is in terms of the different heating rates at the particle centers.

The thermogravimetric experiments were performed under argon atmosphere with a Netzsch STA409 PC Luxx analyzer using milled (~ 200 µm) particle birch wood samples of 20 mg total mass. The gas analysis was done by microGC as described below.
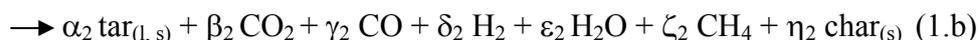
The IPM were performed by inserting the spherical wood particles into a tubular (internal diameter: 38 mm; length: 305 mm) stainless steel reactor surrounded by an electrically heated furnace. The temperature inside the furnace was maintained at 500 °C using a temperature controller (CN7800, Omega), connected to a K-type thermocouple placed on the external wall of the reactor. To establish a non-oxidant environment inside the reactor, a helium flow of 340 mL/min was supplied and kept constant using a mass flow controller (GFC17, Aalborg). Helium has been chosen as the inert gas to enable detection of nitrogen in the event of air leakage into the system.

The particles were heated mainly by radiant heat from the reactor walls and the evolving pyrolysis gases were mixed into the helium purge gas and rapidly fed to the Inficon 3000 microGC analyzer. The residence time in the gas sampling line was around 50 msec only. The microGC was equipped with two columns (Molsieve and PLOT U) for the simultaneous detection of $C_1 - C_3$ hydrocarbons as well as CO, CO_2, H_2 and the carrier gas. More details about the experimental procedure were reported earlier [21].

In addition, the temperatures at the center and at the surface of the particles have been measured by means of closed bead K-type thermocouples. The insertion point for the thermocouple at the center of the particle has been drilled to three quarter of the radius (i.e. 7.1 mm and 11.9 mm for the small, respectively large particle) to avoid impacting the sampling probe.

Kinetic Model

The kinetic model is an extension of earlier model developments [23,24]. Therein, the bio-mass composition is described by the mass fractions of the monomeric pseudocomponents cellulose ($C_6H_{10}O_5$), hemicellulose ($C_5H_8O_4$) and lignin ($C_{10}H_{10}O_4$). These are assumed to decompose according to two parallel reaction channels, one of which leads to gas phase $tar_{(g)}$ and the other one to a condensed phase intermediate $tar_{(l, s)}$ ("metaplast") besides the water gas compounds, methane and char:

$$\text{pseudocomponent} \longrightarrow \alpha_1 \, tar_{(g)} + \beta_1 \, CO_2 + \gamma_1 \, CO + \delta_1 \, H_2 + \varepsilon_1 \, H_2O + \zeta_1 \, CH_4 + \eta_1 \, char_{(s)} \quad (1.a)$$

$$\longrightarrow \alpha_2 \, tar_{(l, s)} + \beta_2 \, CO_2 + \gamma_2 \, CO + \delta_2 \, H_2 + \varepsilon_2 \, H_2O + \zeta_2 \, CH_4 + \eta_2 \, char_{(s)} \quad (1.b)$$

As indicated by the subscripts l and s, the metaplast may be a mixture of liquid and solid semi-volatile compounds [13,25] which are assumed to decompose in a way similar to eq. (1.a). A particular feature of the model is that the elemental compositions of $tar_{(g)}$, $tar_{(l, s)}$ and $char_{(s)}$ can be chosen deliberately in iterative runs until satisfactory agreement with measured

data of the remaining gas compounds is achieved. This is greatly facilitated by an automatic calculation of the stoichiometric coefficients α - η for given input values. The gas phase tar is taken to be stable under the present experimental conditions, hence no extensive data base for the gas phase kinetics is needed here in contrast to other studies [25]. While in TGA studies the temperature distribution is taken to be uniform within the sample volume, this is not applicable to the IPM experiments. Therefore, the calculations were performed for the limiting case of high heating rate which is experienced at the particle surface and for the case of low heating rate which is applicable at the particle center. The heating rates were obtained from differentiation of the measured temperature profiles [21].

3- RESULTS AND DISCUSSION

Compared to TGA experiments, the temperature history experienced by the large particles during IPM is more complicated, hence the thermal decomposition pathways and the product composition may also be expected to be different. During IPM, the particle surface is heated primarily by radiation from the reactor walls. The surface heating rate therefore is very high and after the onset of pyrolysis, the surface becomes covered by a char layer which acts as a radiation shielding to some extent. The heat is then conducted radially to the interior of the spherical particle and the pyrolysis front proceeds in the same direction. During this process, the particle porosity is likely to increase and the heating rate decreases until finally, the particle center will pyrolyze at a heating rate which is much lower than the surface heating rate. Fig. 1 shows the measured temperature histories of the two tested particles (19 and 31.8 mm i.d.) at the surface and at the center as well as the corresponding heating rates.
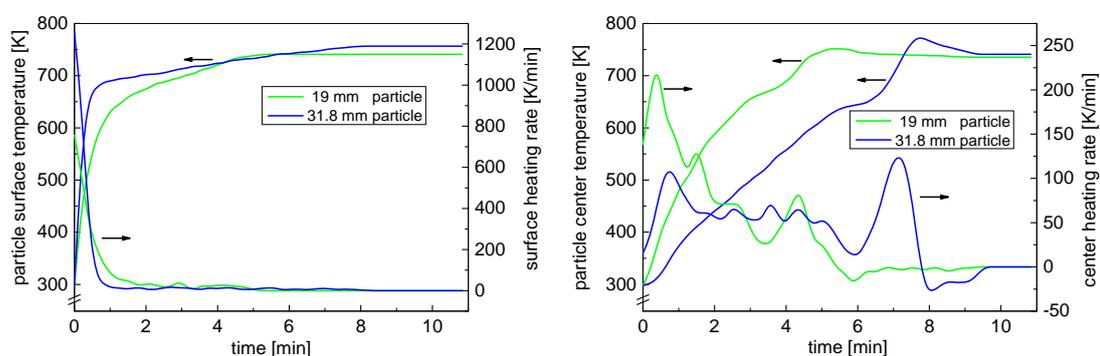

Figure 1: Measured temperatures [21] and heating rates at particle surface and center.

Quite obviously, the surface conditions are not much different for particles of different size with maximum heating rates between 600 and 1200 K/min, hence most of the temperature rise is finished within less than 1 min. At the particle center, the heating rates are comparable also for the two particle sizes, but they are only around 50 K/min on the average, hence it takes between 4 and 8 min to reach the final temperature there. Note the secondary temperature rise between 650 and 750 K which is often attributed to the exothermic decomposition of cellulose [18]. It is quite likely that this temperature peak corresponds to the major decomposition peak of TGA studies [21] which occurs close to the end of the pyrolysis process. This view coincides with the reported particle conversion times being 4 – 6 min for the 19 mm particle and 8 – 10 min for the 31.8 mm particle [21].

The heating rate β is an important input parameter for the model calculation, because it is needed to calculate the temperature T as function of time, $T = T_0 + β \cdot t$ ($T_0 \approx 298$ K, t = time) and, according to Fig. 1, β itself is dependent on time during the IPM experiments. Hence the Arrhenius rate constants k of the decomposition reactions take the form

$$k = k_0 \times \exp(-E_a / R \cdot [T_0 + \beta t]) \tag{2}$$

where k_0 is the pre-exponential factor, E_a is the activation energy and R is the universal gas constant. Therefore, the rate constants are time dependent themselves and, the system of differential equations defined by the pyrolysis model has no analytical solution and needs to be solved by numerical integration. In the present study, a FORTRAN 90 version of the LSODE package [26] was used for this purpose and the two limiting cases were considered as mentioned above: pyrolysis under particle surface heating conditions and pyrolysis under particle center heating conditions.
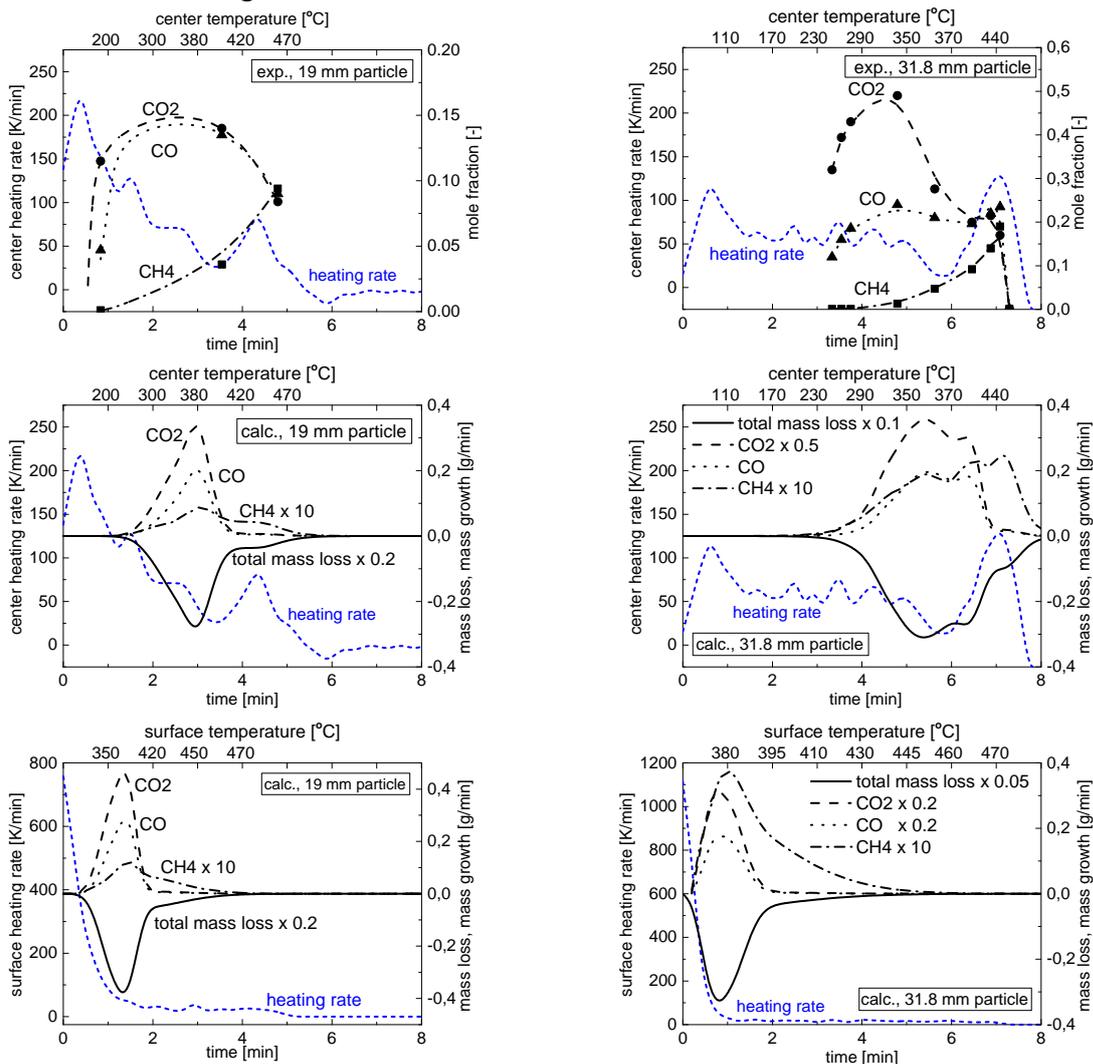

Figure 2: Measured [21] and calculated gas evolution during IPM.

The validity of the model calculation was tested by comparison with experimental results from beech wood pyrolysis [27]. In the present study, the particle decomposition and the corresponding gas evolution was calculated for the two limiting cases of the heating rates at the center and at the surface of the particles.

Fig. 2 compares the measured and calculated gas release as function of time and temperature.

Note that the experimental gas evolution is given in relative units (mole fractions), while the calculated gas evolution is given in absolute units (g/min). Therefore, only a qualitative comparison is possible with respect to the curve pattern. A quantification of the absolute amounts measured from the pyrolysis reactions is currently in progress. This will enable a further model validation in the future.

The measured data show that the center gas evolution starts 1 min after introducing the 19 mm particle into the reactor. In case of the 31.8 mm particle, the gas evolution starts later, approx. 3 min after insertion (top row in Fig. 2). It is further seen from the experimental data that the gas evolution is widely uncorrelated to the heating rate. However, in case of the 31.8 mm particle, it appears that the secondary temperature peak is accompanied by a corresponding peak of the gas evolution. These findings are confirmed qualitatively by calculations which employ the temperature history at the particle center (middle row in Fig. 2). However, the calculations predict the gas evolution to start a little later than measured and, at least for the 19 mm particle, the gas evolution peak is predicted to be sharper than measured. Quite interestingly, in case of the 31.8 mm particle, the gas evolution is calculated to exhibit a double peak pattern in agreement with the experimental data. If the surface heating rate is applied, very sharp and early gas evolution peaks are calculated (bottom row in Fig. 2). In case of the 19 mm particle, it cannot be excluded definitely that a small amount of the sampled pyrolysis gas had its origin in regions close to the particle surface. For the 31.8 mm particle, a similar situation appears unlikely [22]. Still, concerning the onset of the pyrolysis gas evolution, it may well be that some amount of pyrolysis gas reaches the center sampling probe from locations which are a little outside the center, because of a notable pressure drop which is generated by the microGC pump in regions $\pm$ 0.25 particle radii around the particle center [22]. While the calculated CO and CO_2 evolution profiles are in reasonable agreement, this is not the case for CH_4: While the CH_4 release appears to increase continuously during the IPM, the model calculation predicts evolution profiles similar to CO and CO_2, just shifted to later times and at much smaller absolute levels, of course.

4- CONCLUSIONS

Temperature measurements at the surface and at the center of cm-sized pyrolyzing birch wood spheres were used to calculate the evolution of some permanent pyrolysis gases (CO, CO_2 and CH_4). The temperature conditions at the particle center dominate the pyrolysis gas composition sampled from the center. The sampling probe appears to average the pyrolysis gas from an interior region of approx. $\pm$ 0.25 particle radii around the particle center, hence the measured pyrolysis gas evolution starts a little bit earlier than the calculated gas evolution. The measured CH_4 evolution profile appears to be quite different from the calculated CH_4 profile which needs further investigation.

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