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Mass loss rates for wood chips at isothermal pyrolysis conditions: A comparison with low heating rate powder data

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ABSTRACT

Spruce chips of three different thicknesses were pyrolyzed isothermally in a vertical furnace macro-TGA at 574 to 676K, which is the temperature range relevant for char production. The measured mass loss data was analyzed in terms of mass loss rate, thermal lag and char yield as a function of chip size and pyrolysis temperature. The char yield decreased with increasing temperature and there was no significant difference in char yield as a function of sample thickness, ranging from 1mm to 7mm. Thermal lag was present for all chip sizes above 600K. At 574K the data suggests that chips below 1mm in thickness are decomposing at rates governed by reaction kinetics. An isoconversional kinetic model based on low heating rate data of spruce powder was adopted to analyze the data. The model predicted lower mass loss rates than those measured for the chips, suggesting that the pyrolysis process of wood proceeds through a network of parallel reactions. Despite this, the model could predict the final char yield of the wood chips with an accuracy above 80%. The predictive capability of the isoconversional reaction rate expression is promising since the procedure to derive such a rate expression is straight-forward, compared to the conventional model-fitting methods. The data and modeling approach presented in this work is important to the field of biomass pyrolysis as it covers the temperature range and chip sizes relevant for pyrolysis in multi-staged gasification plants which has been given little attention.

1. Introduction

Thermochemical conversion can convert biomass into gases, solids and liquids that can be used in commercial technology and thus enable a smooth transition from fossil fuels to renewable alternatives. Pyrolysis can be viewed as the most versatile among the thermal conversion processes since it can be used to produce solids, gas and liquids which may serve as fuels to, e.g. gasification and combustion. Pyrolysis of biomass is typically performed at temperatures between 200 and 700 ° C [1; 2]. The low temperature pyrolysis (200 and 350 ° C) is called torrefaction. It is a pretreatment method used to produce a brittle, hydrophobic solid of increased energy density that can be fed to gasifiers or combustors in a similar manner as coal [3]. At higher temperatures an increased part of the biomass will be transformed into gas and condensables. If the solid residue from such processes, called char, is gasified it will result in a gas stream with lower tar content, compared to conventional gasification of the raw biomass [4; 5]. Decreasing the tar content is a desirable outcome since tar is a nuisance in most gasification technologies, being a sign of low fuel conversion efficiency and leading to fouling and clogging of downstream equipment [6]. Another advantage resulting from the use of pyrolysis char as a gasification fuel is the brittle nature of char which makes milling much easier compared to raw biomass. Many of the available gasification technologies require fuels with small particle sizes [6]. Due to the high energy demand required for milling of fibrous biomass this limits the type of biomass that can be used efficiently. Pyrolysis reactors like rotary kilns are very versatile when it comes to fuel particle size [1; 7]. Due to relatively long vapor residence time and low heating rate these reactors are also suitable for maximizing the yield of char [1].

When using pyrolysis char as a gasification fuel, char properties like energy density and reactivity are important. In multi-stage gasification plants [4], the mass loss rate during pyrolysis will also be important, since the energy balance between the char and the evolved gases and tars will influence the balance between the integrated units. With this in mind, the present work aims at studying the mass loss rate of spruce chips at temperatures relevant for char production, namely 300 to 400 ° C, using a macro-TGA apparatus. As

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apparent from a literature review on wood pyrolysis at temperatures relevant for char production and with particle sizes above 1 mm [3; 8; 9; 10; 11; 12; 13; 14; 15; 16; 17; 18; 19; 20; 21; 22; 23], there are only a few studies that considered spruce wood [3; 12; 14; 21] among which only Reschmeier et al. [21] report temperatures above the torrefaction range. With respect to the present work, the latter considers wood pellets in a fluidized bed reactor. The current study thus provides new data of relevance when considering pyrolysis and production of char from spruce chips.

The experimental data from the macro-TGA are compared to the mass loss rates and char yields obtained from a purely kinetic model that is based on an isoconversional reaction rate expression developed in our previous work [24]. Although such a modeling approach does not account for heat and mass transfer limitations inside the wood chip, the simplicity and ease at which the model parameters can be derived make the approach attractive and motivates us to apply it for describing pyrolysis of wood chips. Comparing our modeling approach with other predictive pyrolysis models shows that the purely kinetic model adopted here is only marginally weaker than more sophisticated models that rely on various specific material parameters that are difficult to estimate. The modeling approach adopted here therefore presents a viable option for describing char production by pyrolysis.

2. Materials and methods

2.1. Sample characteristics

Norway Spruce (*Piceaabies*) chips free of bark and knots with three different shapes were used. Spruce was chosen since it is one of the most important wood species in the northern hemisphere [3]. A schematic of the dimensions of the chips is shown in Fig. 1. To get reproducible conditions all the chips were manufactured to have the fiber direction run parallel to the long axis of the chip as indicated in Fig. 1. The chips were manufactured to have three different thicknesses, hereafter referred to as thin, medium, thick. Table 1 summarizes the dimensions and masses of the samples. The wood chip pyrolysis data was compared to that for powder (40 mesh, corresponding to 0.4 mm), produced by grinding the wood chips in a ball mill. Lignin content, carbohydrate and proximate analysis for the wood chips can be found in our previous work [24].

2.2. Pyrolysis experiments

The wood chips were pyrolyzed in an inhouse-built isothermal macro-TGA. The macro-TGA consists of a tubular furnace (inner diameter 100 mm) into which a metal wire basket (801 mg, Ni-Cr wire), connected to a balance (model FZ-120i, A&D weighing) with a wire, can be inserted. For a small enough sample mass, of negligible moisture, this setup enables practically isothermal pyrolysis conditions. An illustration of the system is shown in Fig. 2. The purge gas flow rate is 5 normal L/min and the shield gas flow rate is 7 normal L/min. Nitrogen of 99.997 % purity was used for both of these streams. For each experiment a pre-dried (12–24 h at 377 K) chip was put in an upright position in the wire basket and lowered down into the purge zone to remove oxygen. After a minimum of two minutes the sample basket was manually lowered down from the purge zone into the furnace. The time that elapsed from the start of the sample insertion into the heated zone to the start of the sampling mass logging was 5–10 s. The mass was sampled every 2 s with an accuracy of 1 mg. The pyrolysis temperature, measured with a thermocouple (accuracy ±2 K) placed 1.5 cm below the sample basked and 2 cm off center, was sampled once per second and varied on average with a standard deviation below 4 K from the isothermal temperature. After each pyrolysis experiment the sample basket was withdrawn from the furnace and placed in the purge zone to cool down before removing the char from the basket. The mass of the pre-dried sample chip and the resulting char was measured in an external balance (LPW-723, VWR). For all chip thicknesses the sample mass measured in the external balance varied by less than 10 mg from the value measured in the macro-TGA. A number of 3–5 repetitions were performed at each isothermal temperature, i.e. at 574, 597, 615, 637 and 676 K. For the medium thickness chips the minimum dwelling time was 44 min and the longest time was 240 min. A similar range of dwelling times was applied for the thin and thick chips at 574 K, while shorter dwelling times were used 676 K.

The mass loss data from the macro-TGA was compared to pyrolysis runs of spruce powders published previously [24]. In short, a Mettler Toledo TGA/DSC 1 STAR System was used to perform dynamic runs at heating rates of 1, 2, 5, 7 and 10 K/min from room temperature to 1000 K. The sample mass of the 40 mesh spruce powders was 4 mg. The experimental procedure is described in our previous study [24].

Table 1
Sample dimensions and sample masses.

Sample	Dimensions [mm]			Mass [mg]
	Width (A)	Thickness (B)	Length (C)	
Thin chip	13–15	≤ 1	15–20	163±10
Medium chip	14–15	1–2	20–24	301±9
Thick chip	13–15	4–7	20–24	691±65

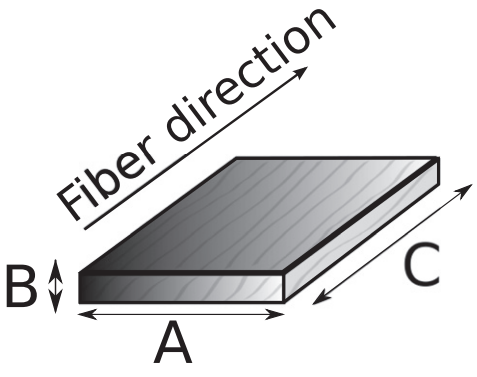

Fig. 1. Schematic of the dimensions of the chips. The chip thickness (B) is perpendicular to the fiber direction.

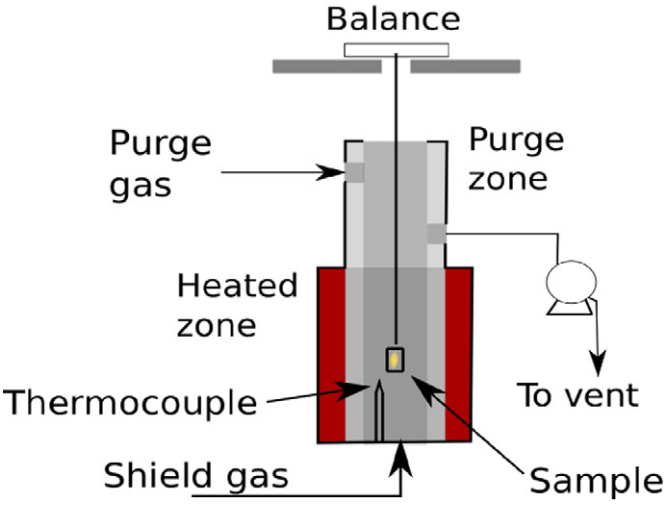

Fig. 2. The isothermal macro-TGA setup.