



## Full Length Article

# A comparison of the torrefaction behavior of wood, miscanthus and palm kernel shells: Measurements on single particles with geometries of technical relevance



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## ABSTRACT

A torrefaction test rig was designed to investigate large single biomass particles up to characteristic sizes of 25 mm, typical for industrial reactors. Time-resolved mass loss for such particles is measured with a magnetic suspension balance at well-defined torrefaction conditions (temperature, residence time, gas atmosphere). This paper comprises the results of woody and non-woody biomass: pine, a coniferous, and beech, a deciduous, wood, palm kernel shells and miscanthus. Influence of process temperature (240 to 320 °C), residence time (up to 1 h) and type of solid biomass on time-resolved mass loss is presented. Additional tests with oxygen in the process gas (0–15 vol%), typical for industrial torrefaction systems, are carried out for selected samples of beech wood. The differences in torrefaction behaviour of bark, sap- and heartwood of pine are evaluated. Finally, it is shown that the torrefaction reactor developed allows to derive kinetic parameters for mass loss. At temperatures up to 300 °C the mass loss for palm kern shells is highest followed by miscanthus, and pine. By examining pine, as an example, it is shown that heartwood is significantly more reactive than sapwood and bark. Finally, it is demonstrated, that for the particle sizes considered here heat and mass transfer limitations can be neglected for the determination of torrefaction kinetics. Kinetic data agree well with data from literature.

## 1. Introduction

Torrefaction, a thermal pre-treatment known as a “mild pyrolysis” at temperatures between approximately 200–320 °C in inert atmospheres [1], improves the key properties of biomass fuels. Dehydration, dihydroxylation and decarboxylation reactions occur during torrefaction and lead to a lower O/C and H/C ratio compared to the untreated biomass [2–5]. During torrefaction volatiles are released and the torrefied biomass remains as solid product. Product distribution is mainly influenced by temperature, residence time and biomass, with temperature being the dominating parameter. The torrefied solid product reveals a higher net calorific value and improved grindability properties [6–9]. Furthermore, thermal treatment reduces the hygroscopicity and diminishes the biological degradation tendency [10]. The effects mentioned above shift the properties of biomass closer to those of coal, which supports co-firing of biomass or complete substitution of coal. In comparison to untreated biomass, torrefied biomass is expected to lead to cost savings in terms of transport, storage and handling [5].

Biomass consists of the three major components cellulose, hemicellulose and lignin. Additionally, biomass contains a complex mixture

of organic compounds so called extractives, for example, resins, fats, terpenes and waxes. The composition and the thermal properties of hemicellulose, lignin and extractives vary from biomass to biomass. For example, the predominant hemicellulose in softwood is galacto-glucmannan and in hardwoods glucuronoxylan [11]. These differences can also occur between different parts of the same biomass, for example bark, sap- and heartwood. [12].

Biomass conversion under torrefaction conditions is mainly dominated by the degradation of hemicellulose which takes place in the range of 225–325 °C [1]. In comparison the degradation of cellulose occurs between 305 and 375 °C, and the thermal degradation of lignin decomposes gradually over the temperature range of 250–500 °C, with low mass loss rates in the lower temperature range [1]. Maximum torrefaction temperatures are limited to approximately 320 to 350 °C, since the mass loss rises significantly above 320 °C resulting in a reduction of the energy yield (see Eq. (3)).

Note that the envisaged properties of the torrefied product depend on the application area. Whereas the energy content (Lower Heating Value/Higher Heating Value) and the handling (grinding and conveying properties) are of main interest for power generation [13], more

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specific requirements, for example HHV > 20 MJ/kg, specific porosity, ash composition, may apply if torrefied biomass is considered to be used in blast furnaces [14].

The investigation of the torrefaction process was in the focus of several studies [1–3,5,15–17]. In particular, the influence of temperature and residence time, targeting the utilization of woody biomass as raw material, was investigated by different authors. Energy plants and residues from harvest and biomass related production processes became more important recently, and has been examined for example by [5,18,19]. Various studies examine the economic aspect of torrefaction [3,5,20]. In this context Sermiyagina et al. did prove the importance of careful heat integration and energetic use of the torrefaction gases to minimize costs for external fuel supply [21].

Although torrefaction is defined as mild pyrolysis in the absence of oxygen, the investigation of oxidizing atmospheres is in focus of studies published recently [22,23]. For example, Uemura et al. [22] investigated the influence of O<sub>2</sub> and CO<sub>2</sub> in N<sub>2</sub> on palm kernel shell torrefaction. The presence of oxygen as well as the presence of carbon dioxide increased the mass loss, in particular at higher torrefaction temperatures.

The influence of particle size has been examined by [15,22,24,25]. As expected, particle size influences the time scale until the particle reaches its terminal temperature. Tapasvi et al. investigated torrefaction of 10 mm and 40 mm spruce (softwood) and birch (hardwood) cubes and concluded that the (small) differences in mass loss for different geometries can be explained by the size-related limitations in heat and mass transfer during torrefaction [15]. However, because the time for heat-up is small for typical particle sizes in industrial reactors (cm range) compared to the time scales of the relatively slow torrefaction kinetics, the influence of particle shape and size on overall mass loss is limited.

Because of the heterogeneity of biomass and the large number of ongoing reactions during pyrolysis simplified global kinetic models are common. Basis of the models is the decomposition of the main components of biomass –cellulose, hemicellulose and lignin. Considering the temperature range of the torrefaction process (200 to approximately 320 °C) the dominating reactions are drying and decomposition of hemicellulose. Degradation of cellulose and lignin play a minor role. The models range from simple single step to multi step models. An overview over the models from different authors is given by Chew et al. [2] and Klinger et al. [26]. Very common are models based on the suggestion of Di Blasi and Lanzetta [27] which is originally based on the pyrolysis of xylan. They suggested a two-step mechanism with parallel reactions (see Appendix A). The Di Blasi-Lanzetta model was used by several authors to derive kinetics for torrefaction of biomass, for example by Prins [17], Repellin [28] and Shang [29].

The current paper introduces a single particle reactor which allows a fast characterization of the torrefaction behaviour of solid biomass under realistic heating rates and particle sizes typical for industrial scale systems. Data processing allows to derive mass yield, energy yield and kinetic parameters. This paper compares beech wood, pine wood, palm kernel shells and miscanthus. Special attention is paid on the influence of oxygen in the process gas (beech wood) by analysing CO and CO<sub>2</sub> concentrations of torrefaction gases in addition to mass loss. Differences in the torrefaction behaviour of bark, sap- and heartwood (pine) is presented. By fitting the di Blasi-Lanzetta pyrolysis model to mass loss curves kinetic parameters are derived.

## 2. Experimental

### 2.1. Fuel analysis

This paper comprises the results of woody and non-woody biomass: pine, a coniferous, (origin: Netherlands) and beech, a deciduous, wood (origin: Germany), palm kernel shells (PKS) (origin: Ghana) as a residual agriculture material from the palm oil production and miscanthus (origin: Germany), as an example for an energy crop. After receiving the biomass samples, they were dried in air and stored in

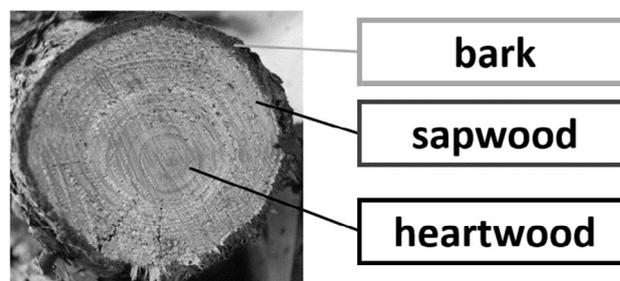


Fig. 1. Cross section of a trunk, pine [33].

absence of light in sample containers.

Wood samples with defined geometry were used for the tests. Variations in dimensions are less than  $\pm 0.5$  mm. The annual growth rings were chosen to be on the smallest surface of the wood cuboid for all samples. Bark, sap- and heartwood pine samples were taken from the same trunk. Pine was selected because it belongs to the heartwood tree family with pronounced differences between the sap- and heartwood (see Fig. 1). The carbon content (see Table 2) of the untreated pine material varies, bark shows the highest amount of carbon with 58.3 m%, followed by heartwood (54.3 m%) and sapwood (51.3 m%). Also, the HHV shows the same trend with highest value for bark (22.7 MJ/kg) and the lowest value for sapwood (19.3 MJ/kg). Whereas the moisture content is typically lower in heartwood, the content of extractives is higher compared to the sapwood. Not only the content of the extractives but also the composition of extractives is different between heart- and sapwood. For more details see [11].

Colour of the bark, sap- and heartwood samples is different, as can be seen from Table 1. While samples size is identical (20 mm  $\times$  10 mm  $\times$  5 mm), sample masses vary from 0.50 g for the sapwood sample to 0.64 g for the heartwood sample.

Miscanthus is cut into particles with an almost cylindrical geometry, the average diameter ranges between 7 and 8.5 mm with a length between 23 and 27 mm. Due to the irregular shape of the palm kernel shells, a single universal particle size is hard to define. Therefore, particles longest, widest and thickest axis is given in Table 1. Particle size, average mass and its standard deviation are given in Table 1.

Photos taken before and after the tests document all samples. An example for the untreated sample is given in Table 1. Changes in dimensions and mass caused by the thermal treatment were measured and documented as well.

Table 2 summarizes the results of ultimate and proximate analysis as well as higher heating value for the biomass samples on a dry basis.

Fig. 2 presents the results of the fiber analysis. The content of cellulose, hemicellulose, lignin and extractives varies between the different biomass samples. The content of hemicellulose, which typically dominates torrefaction, increases from pine, to beech, to miscanthus. It is noteworthy that the composition of PKS is significantly different with a high content of lignin as well as extractives.

### 2.2. Single particle oven

The oven, shown in Fig. 3, is designed for examining the mass loss – time relation of single particles from 2 up to 25 mm at temperatures up to 400 °C. The basic concept of the test rig consists of two major elements, a magnetic suspension balance and a preheated oven. The magnetic suspension balance is installed on a vibration-free rack, whereas the oven is mounted on a table moveable by an electrical guide unit. The oven is preheated until the desired temperature is reached. Note that during the heat-up phase of the oven, the biomass particle is not placed inside the oven.

As soon as the desired process settings are obtained and stable, the suspension balance and the oven are disconnected for sample insertion. After positioning the sample at the balance, the oven and the

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