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# Influence of heating rates on the products of high-temperature pyrolysis of waste wood pellets and biomass model compounds

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## ABSTRACT

The effect of heating rates ranging from 5 °C min<sup>-1</sup> to 350 °C min<sup>-1</sup> on the yields of pyrolysis products of wood and its main pseudo-components (cellulose, hemicellulose and lignin) have been investigated at a temperature of 800 °C in a horizontal fixed bed reactor. Results showed a successive dramatic increase and decrease in gas and liquid yields, respectively, while the yields of solid products showed a gradual decrease as heating rates increased. Increased gas formation and an increasingly aromatic oil/tar support the theory of rapid devolatilization of degradation products with increasing heating rate, leading to extensive cracking of primary pyrolysis vapours. Solid products with coal-like calorific value and large surface areas were obtained. CO became the dominant gas both on a mass and volume basis, at the heating rate of 350 °C min<sup>-1</sup> for all samples except xylan, which also produced a significant yield of CO<sub>2</sub> (20.3 wt% and 25.4 vol%) compared to the other samples. Cellulose produced a gas product with highest calorific value of 35 MJ kg<sup>-1</sup> at the highest heating rate. Results also indicate that the three main pseudo-components of biomass each exert a different influence on the products of high temperature pyrolysis of woody biomass.

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## 1. Introduction

Biomass pyrolysis is one of the most advanced thermochemical technologies for biomass conversion into renewable fuels and chemicals. Pyrolysis of biomass is generally characterized by both primary and secondary reactions (Mayes and Broadbelt, 2012; Mettler et al., 2012; Patwardhan et al., 2011b; Zhang et al., 2014). Primary reactions include mainly solid-phase processes such as drying, dehydration, thermal degradation, crosslinking and devolatilization, (Patwardhan et al., 2011b; Zhang et al., 2014). Secondary reactions involve mainly gas-phase as well as gas-solid reactions such as steam reforming, dry reforming, methanation and hydrogenation, water-gas shift/reverse water-gas shift, polymerization and condensation (Patwardhan et al., 2011a; Patwardhan et al., 2011b). Some named secondary reactions include Boudouard reaction, Diels-Alder reaction, Sabatier reaction, etc. A complex combination of these reactions results in the formation of liquid/tar, gaseous and solid products during biomass pyrolysis.

The predominant reactions and eventual products' distribution during the pyrolysis process are determined by nature of biomass

feedstock and process conditions including the type of reactor. The nature of biomass refers to its type, the thermal and physical properties as well as chemical compositions. In terms of pyrolysis process conditions, important parameters such as reaction temperature, heating rate, reaction pressure, residence times and presence of catalysts (Sun et al., 2010; Wang et al., 2008; Wei et al., 2006; Zanzi et al., 2002) play vital roles in influencing the relative yields and compositions of the pyrolysis products. Heating rate, final temperature and presence of a catalyst may be used to tune the distribution and composition of products. Depending on the reactor configuration, temperature, heating rate and vapour residence times have the greatest influence on the prevailing pyrolysis regime ranging from slow to ultra-fast pyrolysis (Wang et al., 2008). The distribution of pyrolysis products therefore depends on how these three parameters, in addition to feedstock type, are managed. In general for a given feedstock, heating rate and temperature influence the rate of biomass degradation and devolatilization, which influence the chemical properties of the initial pyrolysis intermediate species, from which eventual molecular pyrolysis products are formed. In a fluidised bed reactor, small particle sizes, fast heating rates and short residence times ensure that fast pyrolysis is achieved at different temperatures above 400 °C, leading to a majority liquid product via mainly primary reactions. In a fixed bed reactor, high temperatures and high heating rates

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**Nomenclature**

|               |                               |           |                              |
|---------------|-------------------------------|-----------|------------------------------|
| min           | minute                        | HHV       | higher heating value         |
| wt%           | weight percentage             | $Z_m$     | gas compressibility factor   |
| vol%          | volume percentage             | FTIR      | Fourier transforms infra-red |
| CV            | calorific value               | DCM       | dicloromethane               |
| $\mu\text{m}$ | micro metre                   | BET       | Brunauer, Emmett and Teller  |
| GC            | gas chromatography            | K         | kelvin temperature           |
| MS            | mass spectroscopy             | s         | second                       |
| TCD           | thermal conductivity detector | $\approx$ | approximately                |
| FID           | flame ionization detector     |           |                              |

can lead to high degradation and devolatilization rates, which may lead to the formation of highly reactive intermediate species (e.g. radicals). Even under short residence times, these devolatilized reactive species could react with each other to give different final pyrolysis products.

In the literature particular attention is paid to the study of pyrolysis for liquid fuel production leading to a wealth of data on studies of so-called fast and flash pyrolysis processes, where the aim is rapid heating rates and rapid volatile quenching; and slow pyrolysis (Duman et al., 2011; Elliott, 2013; Lam et al., 2017; Li et al., 2004; Luo et al., 2004; Onay and Kockar, 2003; Patwardhan et al., 2011a; Patwardhan et al., 2011b; Sun et al., 2010). However, pyrolysis is involved in any heat treatment of biomass particles, whether considered as the main step or part of a succession of steps in the process (Blondeau and Jeanmart, 2012), hence studies on high temperature pyrolysis which are also relevant to processes such as gasification and combustion, contribute to the understanding of thermochemical biomass conversion.

High temperature pyrolysis of biomass, when combined with appropriate heating rates can be used to obtain high yields of high calorific value gas products and tars with consistent chemical compositions (Blondeau and Jeanmart, 2012; Zanzi et al., 1996). In this case, high temperatures would provide the activation energies required to break most covalent bonds in biomass, leading to formation of light molecular weight species. Researchers have reported that higher temperatures promote the production of gaseous process products comprising of hydrogen, methane, CO and CO<sub>2</sub>; evidenced by increased gas volumes due to enhanced cracking and devolatilization reactions (Çaglar and Demirbas, 2002; Demirbas, 2002; Dufour et al., 2009; Williams, 2005; Zanzi et al., 2002). High temperature pyrolysis of biomass to obtain increased yields of H<sub>2</sub>, CO and CH<sub>4</sub> and reduced CO<sub>2</sub> have been reported (Wei et al., 2006; Zanzi et al., 2002). Hydrogen, CO and CH<sub>4</sub> can be used directly as fuels or for making synthetic hydrocarbon fuels and chemicals. Gas heating values of above 18 MJ Nm<sup>-3</sup> have been reported for pyrolysis temperatures above 750 °C up to 900 °C (Fagbemi et al., 2001). Biomass conversions to gas of up to 87 wt % for temperatures above 800–1000 °C have been reported (Dupont et al., 2008). Concentrations of H<sub>2</sub> of above 28 mol% and combined H<sub>2</sub> and CO of above 65 mol% (Li et al., 2004) and 70–80 vol% (Sun et al., 2010) have been reported for the pyrolysis of biomass at high temperatures (800 °C) without catalysts resulting in an increased H<sub>2</sub>/CO ratio. However, high temperature also favours the cracking of tar (Zanzi et al., 2002) to hydrocarbon gases like CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>, which tend to decompose into carbon (char) and H<sub>2</sub> when the temperature is high enough (Dufour et al., 2009; Guoxin et al., 2009; Kantarelis et al., 2009; Sun et al., 2010). In addition, the same factors that favour increased pyrolysis gas formation may inadvertently lead to simplification of components of oil/tar products into organic compounds with simple structures, which are often useful. Therefore, further cracking and condensation of hydrocarbon gases can lead to the production of simple

but highly stable aromatic hydrocarbons (Kantarelis et al., 2009). Furthermore, increased volatile yields have been reported (Beis et al., 2002; Meesri and Moghtaderi, 2002; Seebauer et al., 1997) at high heating rates compared to lower heating rate pyrolysis at the same temperature. This resulted from enhanced process severity impacted by rapid formation and evolution of small volatile molecules during pyrolysis. Such rapid volatile mass losses due to high heating rates could leave behind a solid residue with tuneable pore structure (Cetin et al., 2005; Zanzi et al., 1996), which may be advantageous for further applications e.g. as catalyst supports, water treatment or tar cracking.

In this present study, a lignocellulosic biomass sample in the form of waste wood pellets and the three main biochemical components of biomass (lignin, cellulose and hemicellulose) have been separately subjected to high temperature pyrolysis under different heating rates. A detailed analysis of the reaction products may shed some light on whether the three components interact during biomass pyrolysis. This will contribute to the understanding of the effects of temperature and heating rates on yields and composition of products from biomass and its components under the pyrolysis conditions used in this work. The novelty of this study is to provide experimental data as a basis for evaluating and applying this type of pyrolysis process as a biomass pre-processing technology for subsequent biomass valorisation into liquid fuels and chemicals. The main focus of this work will be on the gaseous and liquid products, which are useful for liquid fuels and chemicals production.

**2. Materials and methods****2.1. Materials**

Waste wood pellets with dimensions of 6 mm diameter and 14 mm length, were originally made from pinewood sawdust. For this study, the wood pellets were ground and sieved to  $\approx$  1 mm particle size. The biomass components in the form of cellulose (microcrystalline), lignin (Kraft alkali) and hemicellulose (xylan) samples used were each of particle size <180  $\mu\text{m}$ . The cellulose was supplied by Avocado Research Chemicals, UK, while lignin and hemicellulose samples were obtained from Sigma-Aldrich, UK. These were used as is without further treatment. The proximate and ultimate compositions of the samples were determined using a Stanton-Redcroft Thermogravimetric analyser (TGA) and a Carlo Erba Flash EA 112 elemental analyser, respectively. The results of these analyses are presented in Table 1. The moisture contents of the samples determined by TGA analysis were 6.4, 4.7, 4.1 and 6.7 wt% for wood, cellulose, lignin and xylan, respectively.

Pyrolysis experiments were carried out in a purpose-built horizontal fixed bed reactor, shown in Fig. 1. The reactor was made up of a horizontal stainless steel cylindrical tube of length 650 mm and internal diameter of 11 mm. The reactor was heated externally by a Carbolite electrical tube furnace which provides a

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