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Efika, CE, Onwudili, JA and Williams, PT orcid.org/0000-0003-0401-9326 (2018) Influence of heating rates on the products of high-temperature pyrolysis of waste wood pellets and biomass model compounds. Waste Management, 76. pp. 497-506. ISSN 0956-053X

https://doi.org/10.1016/j.wasman.2018.03.021

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 $\min^{-1}$ to 350 °C $\min^{-1}$ 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 $\min^{-1}$ for all samples except xylan, which also produced a significant yield of CO_2 (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^{-1} 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 wood pyrolysis.

Keywords: high-temperature pyrolysis, heating rate, woody biomass, high-CV gas products

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1.0 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 & 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 ºC, leading to a majority liquid product via mainly primary reactions. In a fixed bed reactor, high temperatures and high heating rates 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 & 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 & 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 & 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_2; evidenced by increased gas volumes due to enhanced cracking and devolatilization reactions (Çaglar & 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_2, CO and CH_4 and reduced CO_2 have been reported (Wei et al., 2006; Zanzi et al., 2002). Hydrogen, CO and CH_4 can be used directly as fuels or for making synthetic hydrocarbon fuels and chemicals. Gas heating values of above 18 MJ Nm^{-3} 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 °C to 1000 °C have been reported (Dupont et al., 2008). Concentrations of H_2 of above 28 mol% and combined H_2 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_2/CO ratio. However, high temperature also favours the cracking of tar (Zanzi et al., 2002) to hydrocarbon gases like CH_4 and C_2H_4, which tend to decompose into carbon (char) and H_2 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 & 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.

2.0 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 ≈ 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 µm. 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 Figure 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 heated zone of length 450 mm and can be easily controlled to provide the desired final temperature and heating rate. The sample was introduced to the reactor via a sample boat, which was a stainless steel cylindrical tube with a cup at its end for holding the sample. The sample boat was designed to be easily, horizontally inserted into and withdrawn from one end of the reactor. During experiments, the sample boat was placed at the centre of the reactor's heated zone for effective heating. A thermocouple was also integrated into the sample boat, designed to be placed concentric to the walls of the sample boat, thereby providing the temperature at the centre of the sample.

2.2 Procedure for pyrolysis

Experiments involving the effect of heating rates (5, 90 and 350 °C min^{-1}) were performed to a final temperature of 800 °C. All experiments were performed with 1.0 g of the each sample loaded unto the sample boat and inserted into the reactor which was continually swept with inert nitrogen gas at a flow rate of 100 mL min^{-1}. The pyrolysis vapour residence time within the reactor was estimated as 9 seconds based on the reactor volume and nitrogen flow rate. The actual sample heating rates were monitored with the thermocouple inserted at the centre of the sample boat and these were found to be very close to the reactor heating rate. Pyrolysis vapours were purged from the reactor by the nitrogen flow into two sets of glass condensers; the first was water-cooled and the second with a glass wool trap was immersed in dry ice. The non-condensable gases were collected in a sampling bag for off-line analysis by gas chromatography (GC). Solid products remained in the sample boat and were weighed and collected for analysis after the reactor cooled. Each experiment was carried out twice in order to determine repeatability and the reliability of the pyrolysis reactor, under identical conditions. Experimental results were reproducible within 3.5%, indicating that the reactor used in this work was reliable for pyrolysis investigations.

2.3 Analysis of pyrolysis products

2.3.1. Gas Analysis

Non-condensable gases which were collected in the sample gas bag were analysed by GC. A Varian 3380GC with dual packed columns and dual thermal conductivity detectors (GC/TCD) was used to analyse and determine the yields of permanent gases (H_2, CO, O_2, N_2 and CO_2). The column for CO_2 analysis was of 2 m length by 2 mm diameter with Haysep 80 – 100 mesh packing material. Analysis for H_2, CO, O_2 and N_2 was carried out in a second column of 2 m length by 2 mm diameter packed with 60 – 80 mesh molecular sieve. A second Varian 3380 GC with a flame ionization detector (GC/FID) was used to analyse and determine the yields of hydrocarbons gases (CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, C_4H_8 and C_4H_{10}) with nitrogen carrier gas. The column was 2 m length by 2mm diameter, packed with Haysep 80 – 100 mesh. The conditions used for the analysis have been detailed elsewhere (Efika et al., 2015). The higher heating value (HHV) of the gas products where calculated from the Equation 1 below;

$$HHV = CV_m / Z_m \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

Where CV_m is the sum of the products of the weight percent and the calorific values of the individual gases and Z_m is the compressibility factor of the gases.

2.3.2 Oil/Tar Analysis

Due to the high temperatures > 700 °C used in this work, the condensable volatiles would be referred to as a mixture of oil and tar. The condensed products collected in the condensers for each experiment were weighed and then sampled for qualitative analysis by gas chromatography/mass spectrometry (GC/MS) and Fourier transforms infra-red (FTIR). The product collected in the first condenser was brownish in colour and sticky while that collected in the second condenser was a mixture of water and a pale yellow liquid. The products from the two condensers were sampled with dichloromethane (DCM) and mixed together. Before analysis in the GC/MS/MS, the tar/oil product was passed through a packed column of anhydrous sodium sulphate to remove water. Appropriate dilutions of the prepared oil samples were made prior to GC/MS analysis. The DCM extract were then analysed semi-quantitatively on a GC/MS/MS instrument using external standard method. The GC/MS/MS system consisted of a Varian 3800-GC coupled to a Varian Saturn 2200 ion trap MS/MS equipment. The column used was a 30m x 0.25mm inner diameter Varian VF-5ms (DB-5 equivalent), while the carrier gas was helium, at a constant flow rate of 1 ml min^{-1}. The analytical conditions and detection have been detailed elsewhere (Efika et al., 2015). Spectral searches on the installed NIST2008 library were used to qualitatively identify the major ‘unknown’ compounds in the oil products. In addition, FTIR analysis of the raw liquid samples was carried out using a Thermoscientific, Nicolet iS10 spectrometer and the infrared bands recorded was compared with characteristic infrared bands of known organic functional groups in the database. Background correction for the DCM solvent was implemented during FTIR analysis.

2.3.3. Analysis of solid residues

After each test, the weight of the solid residue remaining in the sample boat after pyrolysis was determined by subtracting the weight of the sample boat. The surface area of a selection of the recovered solid residues was measured to determine its suitability for further applications e.g. as catalyst supports. The surface area measurement was carried out with the Brunauer, Emmett and Teller (BET) method via nitrogen adsorption in a Quantachrome Corporation (FL, US) Autosorb 1-C instrument. In addition, the HHV of the recovered solid residue was determined using a bomb calorimeter (ASTM, 2000; ASTM D2015).

3.0. Results and Discussion

3.1 Effects of heating rate on Gas, Oil and Solid distribution

Table 2 shows the result of the effect of heating rate on the pyrolysis of waste wood, lignin, cellulose and hemicellulose at a final high temperature of 800 °C. Table 2 shows that three different major product fractions – solid residue, oil/tar and gas - were produced from the tests as expected (Balat, 2008; Bridgwater, 2003; Demirbas, 2001), at a final temperature of 800 °C, and at the chosen average heating rates of 5, 90 and 350 °C min^{-1}. It is clear from Table 2 that varying the heating rate of pyrolysis influenced the yields of the three major products from the four samples. For the wood pellets, gas yields increased from 14.5 wt% at a heating rate of 5 °C min^{-1} to 54.1 wt% at 350 °C min^{-1}, while solid residue yields decreased from 26.7 to 14.2 wt%, respectively. The oil/tar yields initially showed an increasing trend from 49.5 to 57.4 wt%, with the heating rate, from 5 °C min^{-1} through to 90 °C min^{-1}. However, when the heating rate was ramped up to 350 °C min^{-1}, a sharp reduction in the liquid yield to 27.4 wt% occurred, which corresponded to a sharp increase in the gas yield mentioned earlier (54.1 wt%). Similar results have been obtained from other researchers for the pyrolysis of different biomass feedstocks at high final temperatures of up to 900 °C. Williams et al. (Williams & Besler, 1996) reported that increasing the heating rate for pine wood pyrolysis from 5 to 80 °C min^{-1} resulted in increased production of oil and gas while reducing the yield of char. Becidan et al. (Becidan et al., 2007) showed that, compared to the low heating rate, a higher heating rate of 115 °C min^{-1} resulted in increased gas yield and reduced liquid and char yield during pyrolysis of waste biomass.

These results demonstrate how the combination of heating rate and temperature can be very influential for controlling the product yields from pyrolysis. The heating rate in combination with the particle size impacts pyrolysis by affecting how long it takes for the sample to get to the final pyrolysis temperature. More importantly, high heating rates should result in a more even and rapid heat transfer to the loaded sample in the fixed bed reactor, as a result of the relatively small particle size. Therefore, the increased gas yield during investigations at the heating rate of ≈ 350 °C min^{-1}, would have resulted from the relatively more uniform degradation of the covalent bonds in the biomass with the activation energy provided by the rapidly increasing temperature. Moreover, the high temperature environment within the reactor heated zone also meant the primary pyrolysis vapours were equally subjected to rapid secondary heating, which led to extensive so called secondary homogenous cracking reactions of the liberated primary pyrolysis products (Blondeau & Jeanmart, 2012), thus converting the biomass derived primary products to the simplest gas molecules. Furthermore, it is expected that although the average heating rate of the bulk sample as measured by the temperature sensor is relatively rapid (6 K s^{-1}), the condition in the reactor was non-isothermal as a result of the particle sizes being > 300µm (Blondeau & Jeanmart, 2011), as well as because of particle being packed into the cylindrical sample holder. This would have created both a temperature and heating rate gradient in the sample, with the particles at the outer layer initially experiencing both much higher heating rate than the bulk average as well as higher temperature than the particles at the centre. These sort of conditions, in addition to encouraging secondary homogenous cracking reactions for primary pyrolysis products, especially from the outer located particles, would have also promoted secondary intra-particle (heterogeneous) cracking reactions of the primary pyrolysis products of the particles located especially in the centre of the cylindrical arrangement (Di Blasi, 2008). This is more so for the most centrally located particles because it is argued that primary pyrolysis products from singular biomass particles would have been released into a somewhat porous wall of other biomass particles hence extending the volatiles-solid contact time as well as cracking effects.

The quantity of solid residues produced from waste wood pyrolysis declined with the increasing heating rate as shown in Table 2. This is in-line with previous literatures (Ayllón et al., 2006; Williams & Besler, 1996) which reported that low heating rates resulted in more char yield from the pyrolysis of biomass, and vice-versa. The increased char yield impacted by the low heating rate pyrolysis may be explained by the promotion of the cross-linking mechanisms for char formation by extending the time the sample spends at the "optimum char formation temperature region", (Hoekstra et al., 2012; Weinstetn & Broido, 1970), compared to pyrolysis at higher heating rate.

Figure 2 (a to c) shows plots with 2nd order polynomial trendlines, of product yields against heating rate for the different pyrolysed samples and their product fractions (gas, oil and solids) at a fixed final temperature of 800 °C, which shows a similar trends to the work of Di Blasi and co-workers (Di Blasi et al., 1999). This indicated that at the experimental conditions, increasing the heating rate resulted in an intensification of the high temperature effects. The plots also indicated that it was possible to estimate the product yields for pyrolysis at our experimental conditions for our samples using simple 2nd order polynomial equations.

The products of the separate pyrolysis of lignin, cellulose and hemicellulose exhibited a similar trend to the waste wood sample with increasing heating rate as shown in Table 2. As the heating rate was increased from 5 to 90 °C min^{-1}, the oil and gaseous products increased as a result of the release of volatiles from the solid structure of the samples, while the solid product yield decreased. Cellulose and xylan, behave essentially like the waste wood; at the heating rate of 5 °C min^{-1} oil was the product fraction of the highest yield for the cellulose and xylan while at 350 °C, gas production became dominant. On the other hand, lignin produced char as the main product at all heating rates. Pyrolysis of lignin has been reported to produce extensive char due to cross linking reactions from the phenolic fractions (Custodis et al., 2014; Kawamoto, 2017; Patwardhan et al., 2011a).

Further examination shows that cellulose yielded the highest oil product (54 wt%) at heating rate of 5 °C min^{-1}, and the highest gaseous product (73.1 wt%) at the heating rate of ≈ 350 °C min^{-1}. This is in agreement with the proximate analyses results in Table 1, which shows that cellulose has the highest volatile matter contents of all the three biomass components. Hence, the volatile content was converted mostly into condensable oil/tar during pyrolysis at 5 °C min^{-1}, and mostly into gases during pyrolysis at ≈ 350 °C min^{-1}. Compared to the cellulose, the xylan sample produced the higher gas and solids yields at the lower heating rates (5 and 90 °C min^{-1}), while it produced higher solid but lower gas yield at the heating rate of ≈ 350 °C min^{-1}. Shen et al. (Shen et al., 2010b) reported more char formation from xylan than cellulose during pyrolysis up to 750 °C, at fast heating rates.

Table 2 indicates that the increased gas yield noted for the cellulose and xylan samples at the heating rate of ≈ 350 °C min^{-1}, were as a result of the conversion of the oil products as well as the solid products, especially for cellulose. However, for the lignin sample the increased gas yield was mostly as a result of the cracking of oil products, as the solid residue remained mostly unchanged when the results of lignin pyrolysis at heating rates of 90 °C min^{-1} and at ≈ 350 °C min^{-1} are compared. Caballero et al. (Caballero et al., 1996) pyrolyzed lignin at high heating rate and temperatures up to 900 °C and found that the predominant product was char up to 800 °C and then gas followed by char above 800 °C. Again, considering the low volatile matter content of lignin, the low gas and oil yields was not a surprising result under the investigated conditions in this present study.

Considering the individual pyrolysis products from the wood, cellulose, xylan and lignin samples, the production of char noted for the wood sample can therefore be linked mostly to its content of lignin and partly from hemicellulose (Burhenne et al., 2013; Shen et al., 2010b). At the same time, the gaseous and oil/tar products from the wood pellet can be linked to the easily degradable volatile contents of mostly its cellulose fraction, with some contributions from the hemicellulose fraction (Burhenne et al., 2013).

3.2 Gas composition

Table 3 shows the detailed compositions and mass yields of components in the gas products from the four samples in relation to heating rate at 800 ºC. Clearly, the yields of the gas components increased with increasing heating rates. The highest gas mass yields were produced at the heating rate of ≈ 350 °C min^{-1} due to the promotion of enhanced cracking of the pyrolysis vapours. This is supported by the noted reduction in the quantity of oil/tar obtained from all the samples compared to the lower heating rate experiments. For all four samples , CO was the dominant gas component at the heating rate of 350 °C min^{-1}, and its formation could have resulted from rapid cracking of oxygenated primary volatiles (Duman et al., 2011) and possibly the Boudouard reaction (Radlein, 2002), equation 2. Possible reduced in-situ steam reforming reactions due to the low moisture content of the sample, as well as the presence of hydrogen containing species in the condensed liquid such as aromatics and alkenes, as shown in Table 4 may have contributed to the prevalence of CO in the gaseous product.

$C + CO_2 \rightarrow 2CO$ …………………………………………… (2)

For cellulose and xylan, CO formation has been attributed to decarbonylation of carbonyl functional groups in the biomass or the primary degradation products (Li et al., 2001; Shen et al., 2010a; Shen et al., 2010b). The CO_2 and CO products of lignin pyrolysis have been reported to be as a result of the degradation of carbonyl, carboxyl and ether groups while at high temperature CO production is mostly as a result of the cracking of diaryl ether groups (Wang et al., 2009). The high yields of CO from the samples at 350 °C min^{-1} suggests that the gas products have potential to be further reformed into hydrogen or used for the synthesis of hydrocarbon fuels.

However, CO_2 was a major gas component in the gas product from all samples at the lower heating rates of 5, 20 and 90 °C min^{-1}. Similar results have been achieved by other researchers (Beaumont & Schwob, 1984; Meesri & Moghtaderi, 2002) for the pyrolysis of wood. The higher yield of CO_2 at these conditions has been explained to be as a result of the primary decomposition of oxygen-containing functional groups, especially the decomposition of carboxylic compounds (Li et al., 2001; Meesri & Moghtaderi, 2002; Shen et al., 2010a; Shen et al., 2010b) due to their highly thermal unstable nature. Some researchers (Yang et al., 2007) compared the pyrolysis of cellulose, xylan and lignin and reported that xylan produced the highest CO_2 content as a result of higher carboxylic content. A comparison of the CO composition for the wood components at ≈ 350 °C min^{-1} heating rate indicates that most of the CO content of wood is likely contributed by cellulosic materials.

The HHV of the gas produced from the test at this heating rate of 350 °C min^{-1} was also noted to be the highest (18.8 MJ m^{-3}) as shown in Figure 3, compared to the other heating rates. This was as a result of the increased yield of CH_4 and the other hydrocarbon gases C_2 – C_4 in the product gas. For each of the samples, the HHV of the gases from the pyrolysis at ≈ 350 °C min^{-1}were the highest due to increased volume of gas produced and higher contents of hydrocarbon gases. Compared to the other wood components, lignin pyrolysis at ≈ 350 °C min^{-1} produced the lowest yield of gases, however the CV of its product gas was the highest among the wood components, due to its high content of hydrocarbons especially methane (Wang et al., 2009; Yang et al., 2007).

Table 3 shows that during pyrolysis at ≈ 350 °C min^{-1}, the cellulose gave the highest wt% of hydrogen but at low heating, lignin produced the highest wt% of hydrogen, which agrees with the work of others (Yang et al., 2007) during the slow pyrolysis of lignin, cellulose and hemicellulose at 900 °C. The authors attributed the yield of H_2 to the cracking of C-H aromatic bonds in the lignin and carbonized residues from the other three samples. This resulted from the release of molecular hydrogen during cross-liking polymerization of carbon atoms, which condense into polycyclic aromatic hydrocarbons and then to char.

3.3 Semi-quantitative composition of the oil/tar products

Figure 4 shows the spectra from the FTIR analysis of waste wood pyrolysis oil, which indicates the functional group characteristics of the pyrolysis oil from wood slow heating (5 °C min^{-1}) and from fast heating (≈ 350 °C min^{-1}) to 800 °C. A comparison of both spectra clearly shows differences in the peak intensities which are representative of the different functional groups present in the liquid products. The spectra demonstrate the differences in the composition of the pyrolysis oils as a result of the different heating rates. The presence of polycyclic, monocyclic and substituted aromatic groups is indicated in the absorption peaks between 675 to 900 cm^{-1} and 1572 to 1625 cm^{-1}. The peaks from 950 to 1325 cm^{-1} represent C-O stretching and O-H deformation, indicating the presence of alcohols and phenols (Efika et al., 2015). Peaks between 1350 to 1475 cm^{-1} and 2800 to 3000 cm^{-1} represent C-H deformation and indicates the presence of alkanes or alkyl groups. The presence of alkenes is indicated by the C=C stretching vibrations between peaks 1625 and 1675 cm^{-1}. C=O stretching vibrations are indicated by the peaks between 1650 and 1850 cm^{-1}, while O-H vibrations are indicated by the broad peaks between 3050 and 3600 cm^{-1}, and a combination of these peaks suggests the presence of carboxylic acids and their derivatives.

Table 4 shows the detected compounds from the GC/MS analysis of the oil products from wood, cellulose, xylan and lignin, and with reference to pyrolysis at the different heating rates investigated. The relative abundance of the detected compounds are indicated by asterisks, so that more asterisks in Table 4 indicates increasing weight percent yields of the identified compound. For simplicity, the compounds in the oil/tar have been classified into oxygenates, phenolics, aliphatic hydrocarbons and aromatic hydrocarbons. Table 4 shows that for the oil product from wood pyrolysis, there was a decrease in oxygenates, while aromatic compounds increased with increasing heating rate. As an indication of the effects of heating rate on the yields of the different classes of organic compounds in the oil/tar, a selection of compounds detected in the oil/tar; representing oxygenates, phenols aliphatic and aromatic hydrocarbons have been made. Figure 5 showed the weight percent yields of cyclopentanone, phenol, indane and naphthalene in the pyrolysis oils from waste wood. Clearly, the yields of naphthalene increased from 0.1 – 3.2 wt%, with increasing heating rate from 5 to ≈ 350 °C min^{-1} for the pyrolysis of wood. In contrast, the yields of cyclopentanone and phenol showed a decreasing trend. As the heating rate was increased, the high temperature effects were intensified, which resulted in the cracking of products such as the oxygenates and other simple aliphatic compounds, into gases as well into the more thermally stable aromatics via Diels-Alder reactions. Such cyclization and aromatization processes led to increased refining of the oil and loss of sides groups resulting from cleavage of weaker bonds. Such refining reactions at the molecular level would increase aromatic content of the liquid products and also increase the formation in the gas products as seen in Tables 2 and 3.

The GC/MS results are in agreement with the FTIR spectra presented in Figure 4 which shows an increase in the intensity of the indicative peaks for the monocyclic, polycyclic and substituted aromatic groups, in the spectra for the liquid from pyrolysis at heating rate of 350 °C min^{-1} compared to that at 5 °C min^{-1}. As an illustration, the GC/MS chromatograms of the oils/tars obtained from waste wood pyrolysis at heating rates of 5 °C min^{-1} and 350 °C min^{-1} have been presented in Supplementary Information File (S11). The chromatograms clearly shows the transition from majority oxygenated and aliphatic compounds at the lower heating rate to a majority lower molecular-weight aromatic hydrocarbons at the higher heating rate. This transition corroborates the FTIR spectra in Figure 4, which shows higher peak intensities for peaks between 1350 to 1475 cm^{-1}, 1625 to 1675 cm^{-1}, 2800 to 3000 cm^{-1} and between peaks 950 to 1325 cm^{-1}, corresponding to the presence of aliphatic compounds (alkanes and oxygenates) in the liquid products, for the pyrolysis at 5 °C min^{-1} compared to the pyrolysis at

350 °C min^{-1},. (Yu et al., 1997) reported an increase in the aromatic content and a decrease in the oxygenate content of oil from wood pyrolysis with increasing temperature from 700 to 900 °C. Other researchers (Xianwen et al., 2000) reported that the most abundant hydrocarbons detected from the pyrolysis of wood at 500 °C were alkanes, while (Tsai et al., 2007) reported the presence of many of aromatic compounds as well as oxygenated compounds for the pyrolysis of rise husk to 500 °C, at a heating rate of at 400 °C min^{-1}. The GC/MS chromatograms obtained from the analysis of the liquid products from the biomass model compounds at heating rates of 5 °C min^{-1} and 350 °C min^{-1} have been provided in the Supplementary Information [SI1].

The results of the analysis of the oil products from the pyrolysis of cellulose, xylan and lignin at 5 and ≈ 350 °C min^{-1} are also shown in Table 4, showing similar trends to those obtained from the waste wood sample. For pyrolysis at 5 °C min^{-1}, the most abundant compounds detected for the cellulose, xylan and lignin were oxygenated and aliphatic compounds. The presence of long-chain alkanes (hexadecane and pentadecane) from slow pyrolysis of lignin was reported by (de Wild et al., 2009) during pyrolysis of lignin. The authors reported further increase in the yields of these compounds during the hydro-treatment of the pyrolysis oils, as a result of hydrodeoxygenation reaction of the lignin-derived bio-oil. While during pyrolysis ≈ 350 °C min^{-1}, the most abundant compounds detected in the oil products from cellulose, xylan and lignin were aromatics. Others have investigated the pyrolysis of lignin to 800 °C, at slow and fast heating rates, and reported increased aromatics at the fast heating conditions while an abundance of oxygenates were detected at the slow heating rate (Windt et al., 2009). Mono-aromatic compounds are also primary decomposition products of lignin (Asmadi et al., 2011), and this explains its relatively higher content in the lignin derived oil at 5 °C min^{-1}. (Shen et al., 2010a) reported an increase in the production of ringed hydrocarbons and a decrease in oxygenates content of the pyrolysis oil with increasing pyrolysis temperature from hemicellulose.

The pyrolysis of the wood, cellulose, xylan and lignin samples at the heating rate of ≈ 350 °C min^{-1} intensified the effect of the high pyrolysis temperature resulting in secondary heating which promoted vapour phase cracking and condensation reactions, leading to the formation of gases and aromatic compounds. However at the heating rate of 5 °C min^{-1}, the heating effect was minimized as volatiles were gradually released and swept out of the reactor before its temperature could increase to temperatures at which secondary reactions were encouraged, leading to the formation of mostly oxygenated and aliphatic compounds.

3.4 Solid residue characteristics

The BET surface area for the solid residues from wood pyrolysis at the lowest and highest heating rates were measured, and indicated that the solids from the pyrolysis at 5 °C min^{-1}, had a higher surface area (219 m^2g^{-1}) than that for the solids from pyrolysis at ≈ 350 °C min^{-1} (123 m^2g^{-1}). This indicated that during pyrolysis at ≈ 350 °C min^{-1}, the thermal shock impacted on the wood sample would have caused the volatiles to be violently released from the wood structure, thereby destroying the internal pore structure (Zanzi et al., 1996) of the solid product. In contrast, during pyrolysis at slow heating rate, the volatiles gradually exited the structure of the wood sample. The HHV of the solid residues from both heating rates were similar. For instance, the solid residue obtained at a heating rate of 5 °C min^{-1} had a HHV of 33.9 MJ kg^{-1}, while at a heating rate of 350 °C min^{-1} it was 33.1 MJ kg^{-1}. Hence, these results demonstrate that high-temperature pyrolysis can be a source of carbonaceous solid materials with large surface areas and coal-like calorific values from biomass.

4.0 Conclusions

Overall, this study provided some understanding of high temperature pyrolysis of biomass both as an advanced technology platform for biomass conversion and as pre-processing step for biomass gasification. The pyrolysis of waste wood and its major biochemical components (cellulose, xylan and lignin) were carried out in a fixed bed reactor at three different heating rates and to a final temperature of 800 ºC. A combination of heating rate and high temperature gave profound influence on the yields and compositions of solid residue, gas and liquid products as follows, and in no particular order;

Firstly, promoted secondary cracking of volatiles and resulted in increased yields of product gases with high calorific values from all four samples. Secondly, Oil/tar products became more aromatic with increasing heating rate from all samples, due to thermal refinement leading to production of highly stable molecules. Finally, Char product with relatively surface areas and coal-like CVs were obtained due to rapid devolatilization of smaller molecules from within particles leading to a char of a highly porous nature.

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List of Figures

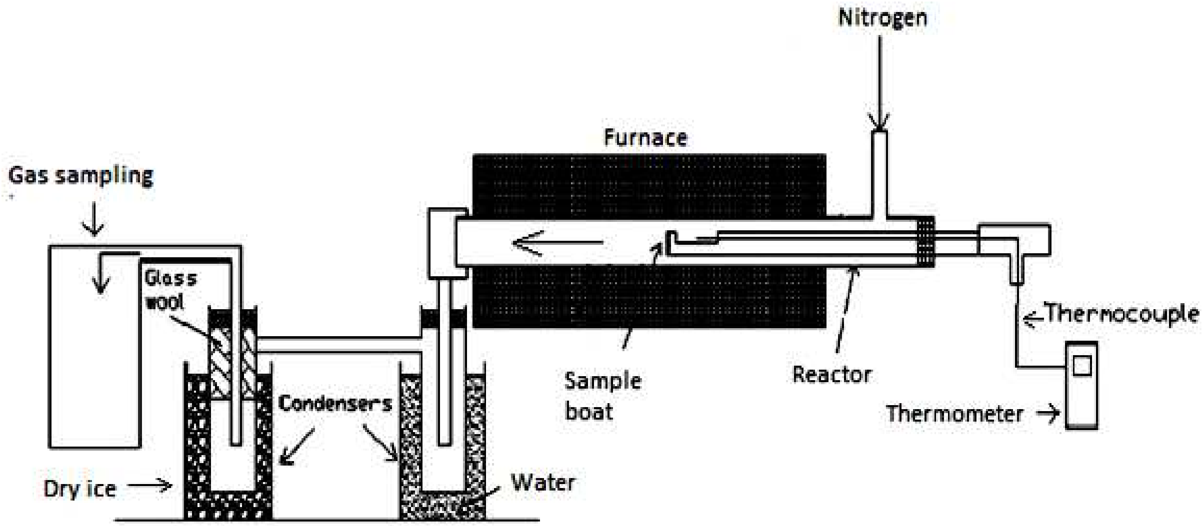

Nitrogen
Furnace
Gas sampling
Glass wool
Condensers
Sample boat
Reactor
Thermocouple
Thermometer
Dry ice
Water

Figure 1

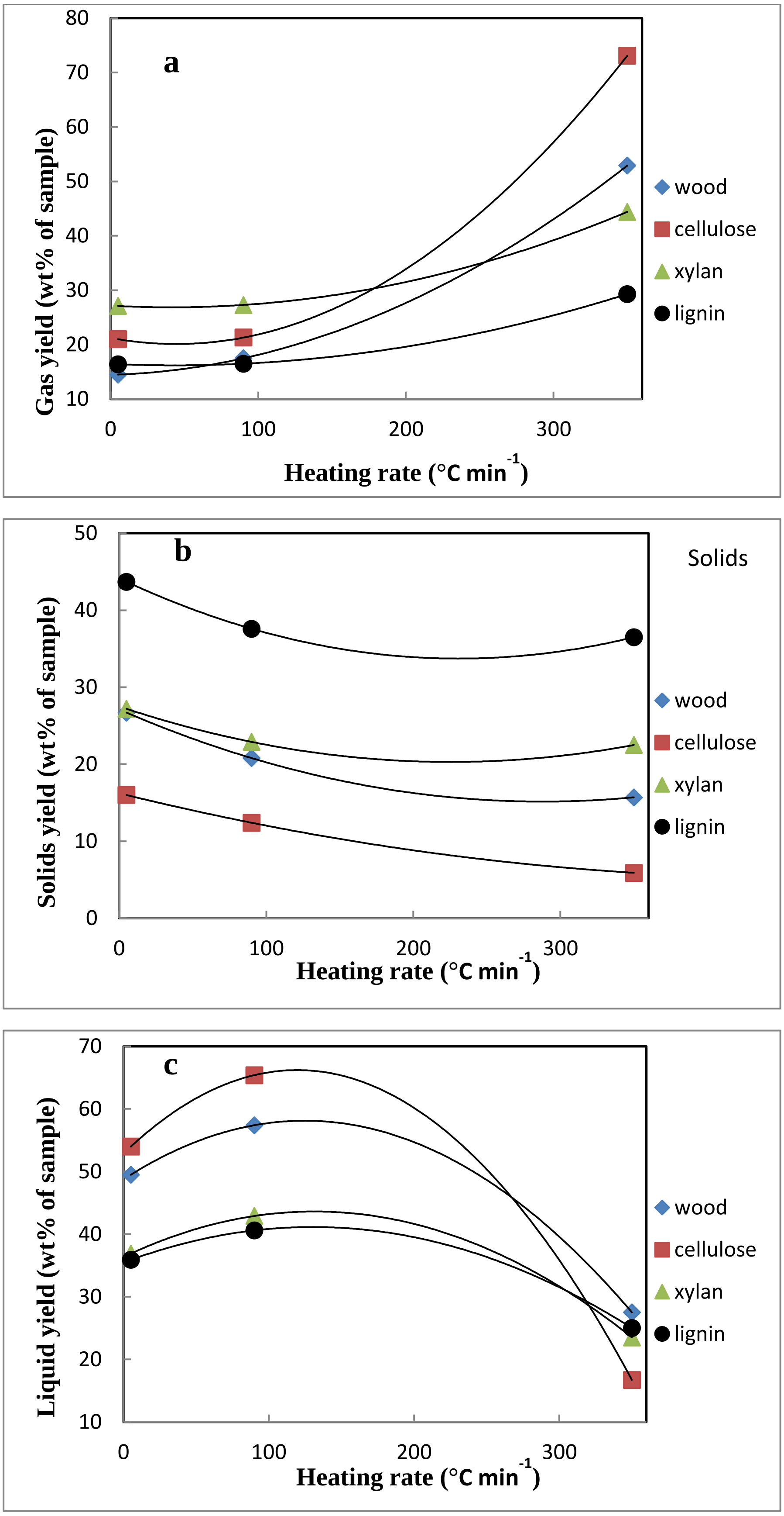

a
Gas yield (wt% of sample)
80
70
60
50
40
30
20
10
0
100
200
300
Heating rate (°C min-1)
wood
cellulose
xylan
lignin
b
Solids
Solids yield (wt% of sample)
50
40
30
20
10
0
0
100
200
300
Heating rate (°C min-1)
wood
cellulose
xylan
lignin
c
Liquid yield (wt% of sample)
70
60
50
40
30
20
10
0
100
200
300
Heating rate (°C min-1)
wood
cellulose
xylan
lignin

Figure 2

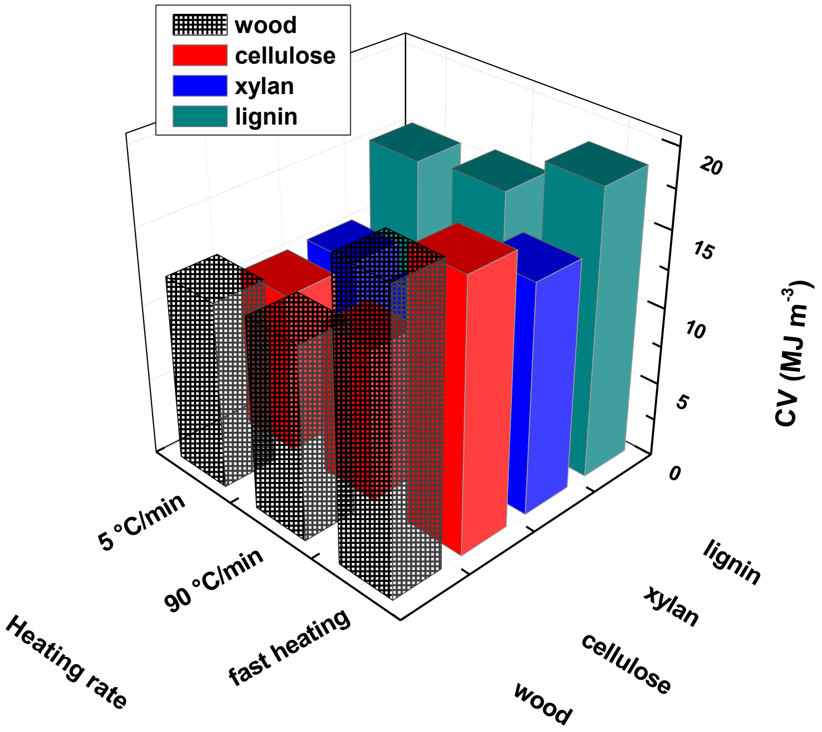

wood
cellulose
xylan
lignin
20
15
10
5
0
CV (MJ m^{-3})
5 °C/min
90 °C/min
fast heating
Heating rate
lignin
xylan
cellulose
wood

Figure 3

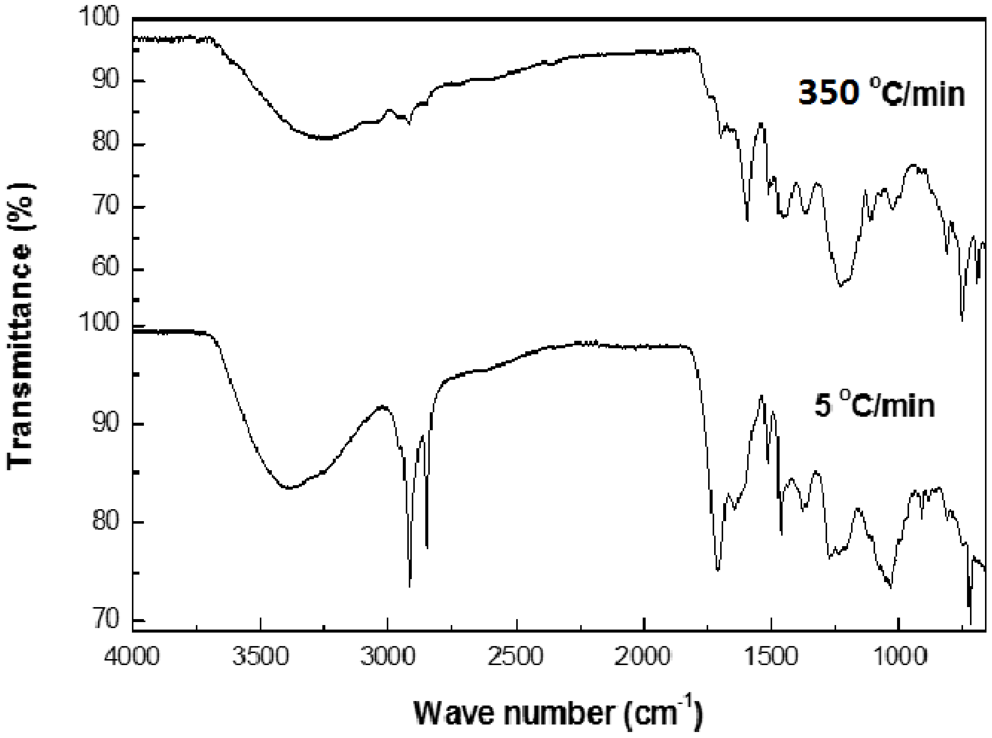
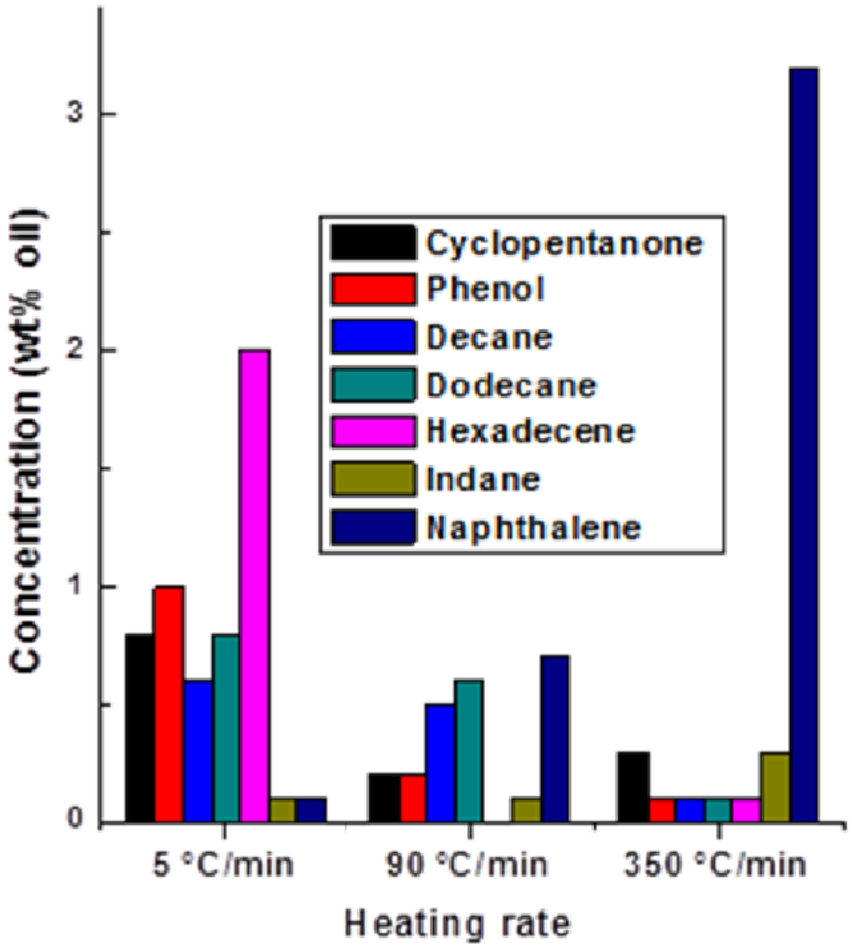

350 °C/min
5 °C/min
Transmittance (%)
Wave number (cm^{-1})
100
90
80
70
60
100
90
80
70
4000
3500
3000
2500
2000
1500
1000

Figure 4



Concentration (wt% oil)
0
1
2
3
Cyclopentanone
Phenol
Decane
Dodecane
Hexadecene
Indane
Naphthalene
5 °C/min
90 °C/min
350 °C/min
Heating rate

Figure 5

Nomenclature

min	Minute
wt%	Weight percentage
vol%	Volume percentage
CV	Calorific value
µm	Micro metre
GC	Gas chromatography
MS	Mass spectroscopy
TCD	Thermal conductivity detector
FID	Flame ionization detector
HHV	higher heating value
Z_m	Gas compressibility factor
FTIR	Fourier transforms infra-red
DCM	Dicloromethane
BET	Brunauer, Emmett and Teller
K	Kelvin temperature
s	Second
≈	Approximately

List of Tables

Table 1: Proximate and Ultimate compositions of waste wood sample and biomass model compounds used in this work

	Waste wood	Cellulose	Xylan	Lignin
Ultimate analysis (wt%)				
C	46.6	41.7	40.3	61.3
H	5.8	5.9	5.5	5.1
N	0.40	0.41	0.41	1.1
S	nd	nd	nd	0.7
O (by diff, ash free)	38.2	52	49.8	27.7
Proximate analysis (wt%)				
Moisture	7.0	5.0	6.0	4.0
Ash	2.0	-	4.0	4.0
Volatile Matter	76	82	73	56
Fixed carbon	15	13	17	36

nd: not detected

Heating rates	5 ^{o}C min^{-1}				90 ^{o}C min^{-1}				≈ 350 ^{o}C min^{-1}			
Results wt% of sample	wood	cellulose	xylan	lignin	wood	cellulose	xylan	lignin	wood	cellulose	xylan	lignin
Gas	14.5	21.0	27.1	16.4	17.5	21.3	27.3	16.5	52.9	73.1	44.4	29.3
solid	26.7	16.0	27.2	43.7	20.8	12.4	22.9	37.6	15.7	5.9	22.5	36.5
Oil	49.5	54.0	36.9	35.9	57.4	65.4	42.9	40.6	27.5	16.7	23.5	25.0
Mass Balance	90.8	91.0	91.2	96.0	95.7	99.0	93.0	94.7	96.1	95.6	90.5	90.8

Table 2: Product yields and mass balances from the high temperature pyrolysis of waste wood and biomass components in relation to heating rates

Table 3: Compositional yields of gas products (in wt% and volume %) from high temperature pyrolysis of waste wood and biomass components in relation to heating rates (nitrogen-free)

Heating rates	5 ^{o}C min^{-1}				90 ^{o}C min^{-1}				≈ 350 ^{o}C min^{-1}			
Yields, wt% of sample	wood	cellulose	xylan	lignin	wood	cellulose	xylan	lignin	wood	cellulose	xylan	lignin
H_2	0.4	0.4	0.6	1.0	0.4	0.3	0.6	0.7	0.8	1.4	1.0	0.8
CO	5.6	6.3	7.1	6.1	6.3	6.7	9.0	6.9	30.3	44.5	16.8	15.9
CO_2	7.2	13.0	17.5	6.2	9.2	13.1	16.0	5.8	10.9	14.7	20.3	5.7
CH_4	1.0	0.8	0.7	2.6	1.2	0.7	0.8	2.6	4.8	5.0	2.7	4.4
C_2 - C_4	0.3	0.6	1.2	0.5	0.4	0.5	0.9	0.5	6.1	7.3	3.7	2.4
Yields, volume % of sample												
H_2	32.7	25.7	30.3	47.7	24.8	21.3	27.8	38.8	18.1	22.0	26.3	28.4
CO	31.0	28.4	24.4	21.4	33.3	31.5	30.6	27.1	48.7	50.2	32.9	39.0

CO_2	25.5	37.6	38.0	13.7	28.8	39.3	34.6	14.5	11.2	10.6	25.4	9.0
CH_4	9.6	6.6	4.4	16.0	11.2	6.0	4.5	18.2	13.6	9.9	9.1	18.9
C_2H_4	0.4	0.4	0.4	0.2	0.6	0.5	0.4	0.3	5.7	4.7	3.9	2.5
C_2H_6	0.5	0.5	1.4	0.5	0.7	0.6	1.2	0.6	0.8	1.3	1.2	0.8
C_3H_6	0.2	0.3	0.3	0.1	0.3	0.5	0.3	0.1	1.1	0.8	0.6	0.6
C_3H_8	0.1	nd	0.3	0.1	0.1	0.0	0.4	0.4	0.2	0.1	0.2	0.2
C_4H_8 & C_4H_6	nd	0.4	0.2	0.1	0.1	0.1	0.1	0.0	0.6	0.2	0.4	0.6
C_4H_{10}	nd	0.2	0.4	0.2	0.0	0.1	0.1	0.0	0.0	0.3	0.0	0.0
Gross Calorific values (MJ/kg)	8.1	9.2	13.4	13.0	8.0	8.0	12.7	11.3	24.1	35.8	25.4	16.7

nd: not detected

Table 4: List and indicative concentrations of different classes of compounds detected from GC/MS analysis of oil/tar products derived from high temperature pyrolysis of waste wood and biomass components in relation to heating rates

Heating rate	**5 ℃ min^{-1}**				**≈ 350 ℃ min^{-1}**			
	wood	**cellulose**	**xylan**	**lignin**	**wood**	**cellulose**	**xylan**	**lignin**
Identified compounds	**Oxygenates**							
Cyclopentanone	***	****	****	****	**	*		
Furfural								
Anisole	*	*	**	**				
Phenol	***				*		*	*

Acetophenone		***	****	**				
	Phenolics							
2,4-Dimethylphenol			****					
1,2-Benzenediol								
2,3,5-Trimethylphenol	**	****			***		****	
4-Isopropylphenol	****	**						
Dibenzofuran		****		*				
	Aromatic hydrocarbons							
Styrene	*	*				****		
o-Xylene	*	*						
Alphamethylstyrene	***		*		**	*	**	*
Betamethylstyrene	*		*	*	***	***	****	**
Indane	*	*	**	*	***	*	*	*
Indene	*	*	*	*	***	***	***	
1,2,3,4-Tetramethylbenze								
Naphthalene	*	**	**	*	****	****	****	****
2-Methylnaphthalene			**	*		****		
1-Methylnaphthalene		***	**					****
Biphenyl	***	*	*	*	*	****	****	****
2-Ethylnaphthalene				*				
1-Ethylnaphthalene						***		
2,6-Dimethylnaphthalene	*	*	*	***				
1,4-Dimethylnaphthalene	**	*	**	***	***			****
Fluorene	***	*	*	*			****	
1,3-Diphenylpropane							**	
Phenanthrene		*		*			***	
1-Phenylnaphthalene	**							
o-Terphenyl		**						

Fluoranthene		*			*			*
Pyrene	*		*		**		*	*
m-Terphenyl			*					
1,3,5-Triphenylbenzene	***		**	*	***	**	****	****
	Alkanes							
Octane, C8		***	***	***		*	*	*
Decane, C10	***	**	**	**	*			
Undecane, C11	**	***	***	***	*	*	*	*
Dodecane, C12	***	***		***	*	*	*	*
Tridecane, C13	**				*	*	*	
Tetradecane, C14			***				*	
Pentadecane, C15				***			*	
Hexadecane, C16			*				*	*
Phytane			*	*		*		
Heptadecane, C17			*	*			*	*
Pristane			***			*	*	*
Octadecane, C18					*		*	*
Eicosane, C20							*	*
	Alkenes							
Octene, C8		**					****	*
Nonene, C9						***	**	
Decene, C10		****		***			**	
Undecene, C11			***					***
Dodecene, C12				***				**
Tridecene, C13				*				
Tetradecene, C14								
Pentadecene, C15					***			*