Effect of Temperature on Pyrolysis Products of a Pine Sawdust in an Indirectly Fired Rotary Kiln

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Abstract—**This work was aimed to investigate the effect of temperature on the gas composition and biochar characteristics of pyrolysis of a pine sawdust. The pyrolysis experiments were carried out in a large scale indirectly fired rotary kiln operating at 873K, 923K, 1023K and 1123K. The compositions of the pyrolysis gas were analysed using a gas chromatograph. The microstructure, specific surface area and oxidation reactivity of the resulting biochars were determined using scanning electron microscopy (SEM), Brenauer-Emmett-Teller (BET) analyser and thermogravimetric analysis (TGA), respectively. It was found that high temperatures favoured H_2 production while CO, CO_2 and CH_4 were dominant gas products at low temperatures. As the pyrolysis temperature increased, the yield, residual volatile matter content and specific surface area of biochar decreased while oxidation reactivity of the biochar was also reduced.**

Keywords-Biochar; Pyrolysis gas; Oxidation reactivity; Pyrolysis; Rotary kiln reactor

I. INTRODUCTION

Biomass pyrolysis is a complex thermo-chemical process in which biomass is converted to biochar, gas and liquid [1-3]. Biochar is composed of carbonaceous materials, which can be used as a fuel for heating and power generation or can be upgraded to activated carbon or slurry fuels [1-3]. Pyrolysis gas mainly contains carbon monoxide, hydrogen and methane, which is usually combusted to provide the heat for the pyrolysis or converted to high quality syngas or liquid [2, 3]. Pyrolysis liquid is a complex mixture of hydrocarbons, oxygenated hydrocarbons and water, which is usually upgraded to produce refined fuels or chemicals [2, 4, 5].

Indirectly fired rotary kiln reactor, such as the one owned and commercialised by Ansac Pty Ltd world widely, is one of the most promising pyrolysis techniques, offering many advantages in producing biochar and high heating value of gas over other types of reactors such as fluidised bed reactor [4, 6-9], moving bed reactor [10] and fixed bed reactor [11]. For instance, the rotation speed and solid retention time in the reactor can be easily adjusted to enable appropriate mixing of biomass and thus excellent heat and mass transfer rates. In addition, the rotary kiln reactor can adopt the biomass with various shapes, sizes and heating values continuously.

Temperature plays a crucial role in determining the yield and composition of the pyrolysis products. As a general trend, high pyrolysis temperatures favour the gas production while biochar and bio-oil are prone to form at low pyrolysis temperatures [11-16]. However, the effect of temperature on the compositions of gas and biochar reactivity produced is subject to the pyrolysis conditions and feedstock used [11, 14]. There have been various studies of the effect of temperature on pyrolysis products and biochar reactivity but to the best knowledge of the authors, studies of biomass pyrolysis using an indirectly fired rotary kiln reactor at industrial scale are scarce.

Against this backdrop, a series of experimental studies have been carried out with aims to investigate the effect of temperature on the pyrolysis products, gas compositions, biochar characteristics and reactivity of a pine sawdust, produced locally in Western Australia, in a pilot-scale indirectly fired kiln reactor at Ansac Pty Ltd in Bunbury. The results are expected to provide a mechanistic understanding of the pyrolysis process in the kiln reactor, which underpins widespread applications of this technology.

II. EXPERIMENTAL SETUP

A. Biomass Feedstock

The biomass feedstock used was a pine sawdust from a local pine plantation in southwest Western Australia, provided by WA & J King Pty Ltd. The proximate and ultimate analysis of the pine sawdust is shown in Table I.

Table I Proximate and Ultimate Analysis (wt%) of the Pine Sawdust

Proximate analysis	wt%	Ultimate analysis	wt% (d.b)
Moisture (a.r)	10.9	Carbon	47.67
Volatiles Matters(d.b)	85.5	Hydrogen	3.32
Ash (d.b)	0.5	Sulphur	0.02
Fixed carbon (d.b, by difference)	13.96		
Low Heating Value (MJkg^{-1})	17.36		

B. Kiln Reactor

The experiments were conducted using a pilot-scale indirectly fired rotary kiln reactor, at ANSAC Pty Ltd in Western Australia, as schematically shown in Fig.1.

The rotary kiln reactor has a heat tube with a length of 3.98m and outer diameter of 0.51m. The rotation of the kiln reactor is driven by an electric motor and the rotation speed can be adjusted according to the need of retention time of biomass inside the reactor. The reactor is equipped with two start-up burners with burning diesel fuel and two off-gas burners with burning gases produced from biomass pyrolysis. The pine sawdust with the particle size around 25mm is continuously loaded in a hopper and then fed into the reactor by a screw feeder at a feeding rate of approximately 180kgh^{-1}. The biochar produced travels through a jacketed cooling screw conveyor and drops into a sealed collector. The biochar collector stands on the top of a digital balance with an accuracy of 0.01kg, allowing the weight of biochar to be measured and recorded. The gas produced is discharged from the top of a disengagement chamber at the end of the kiln reactor, part of which is drawn into the off-gas burners to be burned. A gas sampling point is located about half metre away from the end of the kiln, from which the gas samples were collected. Two thermocouples located on the outside surface of the heat tube measure the temperature of the kiln reactor. The temperature signals were acquired, recorded and monitored using a computer through a data taker.

The experiments were carried out at 873K, 923K, 1023K and 1123K. Each experiment was started with burning diesel to preheat the kiln with rotation for two to three hours till the heat tube reached the desired temperature prior to commencing the pine sawdust feeding. The pine sawdust was fed into the reactor continuously for eight hours. The total mass of biomass fed and biochar generated during the eight hours were recorded for the mass balance calculation. The kiln rotation speed was set to 2rpm, allowing the biomass to reside in the kiln reactor for approximately 25min. The gas was sampled periodically for analysis.

C. Data Analysis

Gas samples were collected and analysed using a Gas Chromatograph (GC) at the Centre for Energy at UWA. Nitrogen absorption and desorption technique were used to analyse the total surface area of biochar generated using a Brunauer-Emmett-Teller (BET) analyser (Trisrar II 3020).

The oxidation reactivity of biochar was determined using a thermogravimetric analyser (SDT Q600) operating under isothermal conditions. In a TGA experiment, approximately 5 mg biochar was placed in a ceramic crucible situated in the TGA furnace and a nitrogen flow of 150ml min^{-1} was introduced to the TGA during its heat-up from room temperature to a desired temperature at a heating rate of 60K min^{-1}. Upon reaching the desired temperature, the isothermal oxidation reaction of the char sample was initiated by switching the gas flow from nitrogen to air. The sample was then reacted with air to completion when its mass became invariant. The gas flow was switched to nitrogen again for cooling. In order to calculate the reaction kinetics, the TGA isothermal experiments were performed at temperatures from 623K to 773K with an interval of 50K, during which the reaction was in the kinetic-controlled regime based on our pre-screening tests. The reaction rate r and biochar conversion fraction x were then calculated using the following equations [12]:

$$r = -\frac{dm}{dt}(\frac{1}{m - m_{ash}}) \qquad (1)$$

$$x = \frac{m_0 - m}{m_0 - m_{ash}} \qquad (2)$$

where m is the instantaneous sample mass, m_0 the initial sample mass, and m_{ash} the ash content.

Assuming the first order reaction, the following rate equation is obtained:

$$r = P_{O_2} A \exp(-\frac{E}{RT}) \qquad (3)$$

where P_{O_2} is the oxygen partial pressure in air, A the pre-exponential factor (s^{-1}), E the activation energy ($kJmol^{-1}$). R is the universal gas constant and T is temperature.

After rearranging (3), we have

$$\ln(\frac{dr}{dt}) = \ln(P_{O_2} A) - \frac{E}{RT} \qquad (4)$$

from which, the activation energy E and pre-exponential factor A can be obtained by plotting $\ln(\frac{dr}{dt})$ versus $1/T$.

III. RESULTS AND DISCUSSIONS

A. Effect of temperature on pyrolysis products yield

Figure 2 shows the effect of temperature on pyrolysis products yield of the pine sawdust. It is evident that there was a
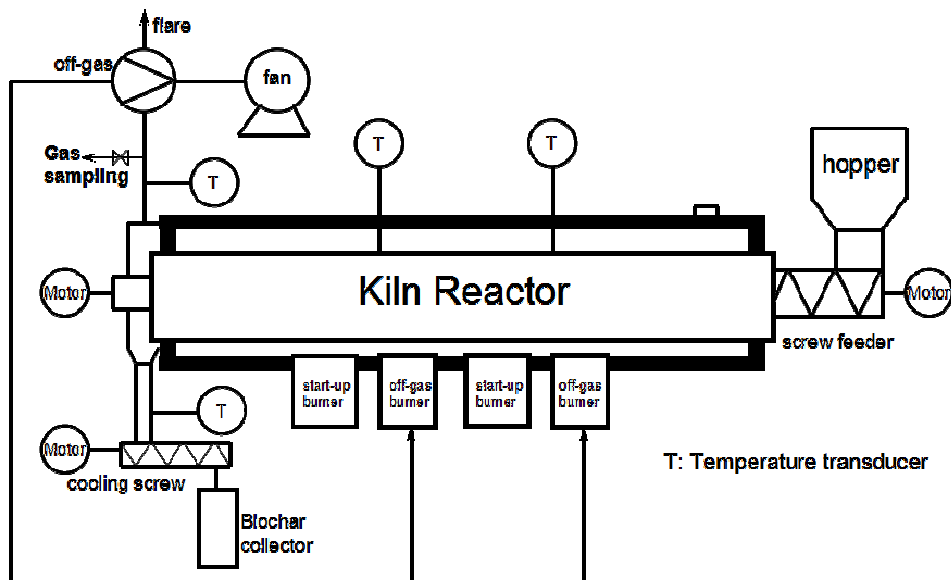
Figure 1. A schematic diagram of the indirectly fired rotary kiln pyrolysis system

significant decrease in the yield of biochar and a corresponding increase in the yield of gas and liquid as the temperature increased from 873K to 923K. However, both the yields of biochar and gas and liquid levelled off after 923K. Biochar has been found to be mainly composed of carbon and volatile matters [11]. Therefore, the increased yield of gas and liquid probably derived from the volatilisation of the volatile matters within the biochar as the temperature increased from 873K to 923K, leading to a decrease of biochar yield. However, the devolatilisation process became less significant when the temperature continued to increase from 923K to 1123K.

B. Effect of temperature on pyrolysis gas

Influence of temperature on the pyrolysis gas composition is shown in Fig.3. The main gases produced were hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). Small volumes of C_2H_2, C_2H_4, C_2H_6 and C_3H_8, were also detected. The results show that low temperatures favoured the formation of CO, CO_2 and CH_4 while high temperature favoured the formation of H_2. The trend is similar to the results found by William and Besler [11] in the fixed bed pyrolysis of a pine wood.

C. Effect of temperature on biochar characteristics

The effect of temperature on proximate, ultimate analysis and surface area of the resulting biochars is shown in Table II. It is clear that the biochar mainly consists of fixed carbon (FC) and volatile matters (VM) and the VM content within the biochars decreased as the temperature increased. The results imply that the temperature has a significant effect on the devolatilisation process. It is also evident that as the temperature increased, the surface area of the biochar was reduced, which could be due to the vanishing micropore structure when more volatile matters
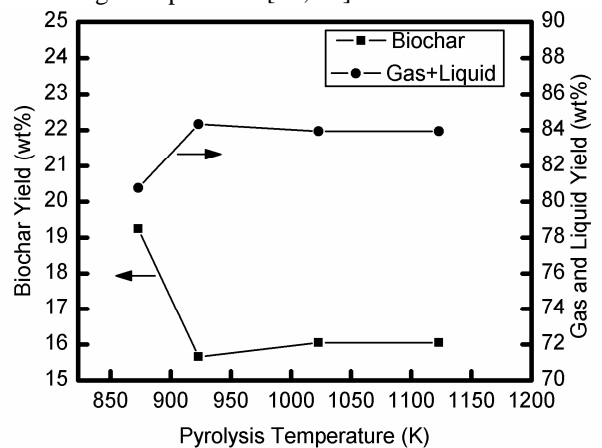
released at high temperatures[12, 14].

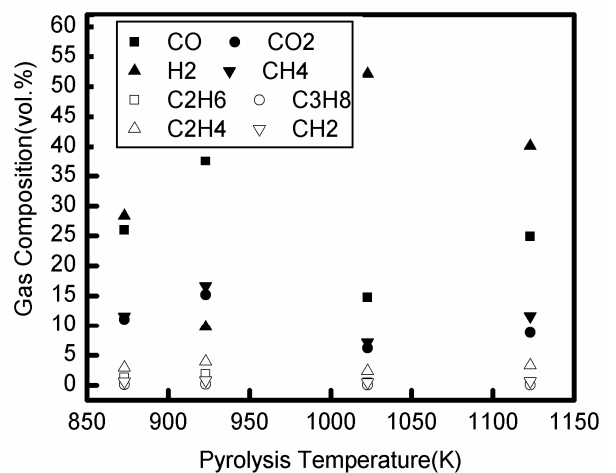Figure 2. Effect of temperature on pyrolysis products yield

Figure 3. Effect of temperature on pyrolysis gas composition

Table II Proximate (wt%), Ultimate analysis (wt%) and Surface area of the Biochars

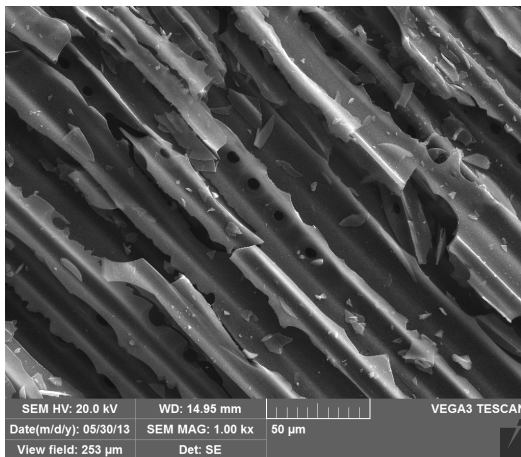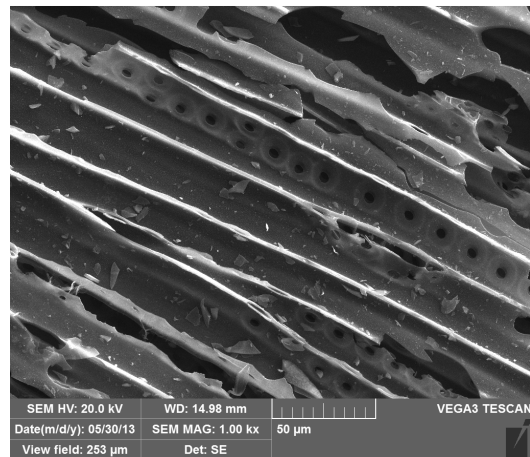|	Proximate Analysis (d.b)			Ultimate Analysis (d.b)			Surface area (m²g⁻¹)
	FC	VM	A	C	H	S	
Biochar at 873K	88.6	9.7	1.7	85.77	1.73	0.05	308
Biochar at 923K	86.8	9.8	3.4	88.59	1.04	0.09	232
Biochar at 1023K	89.2	7.2	3.6	88.82	1.47	0.03	260
Biochar at 1123K	94.2	4.2	1.6	90.01	1.04	0.06	65
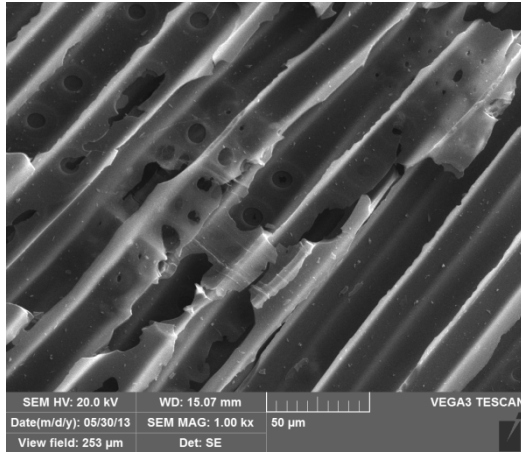
(a)
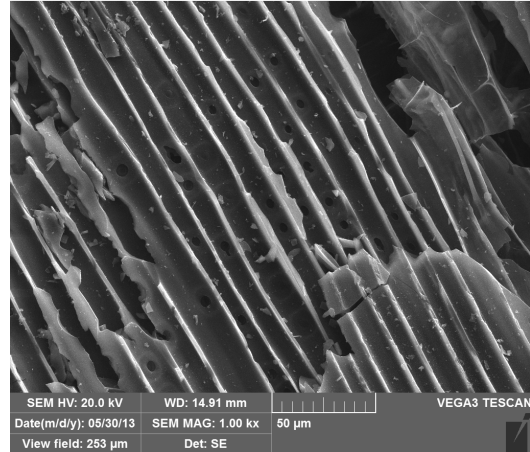
(b)

(c)

(d)

Figure 4. SEM images of the pine sawdust chars produced under different temperatures: (a) 873K; (b) 923K; (c) 1023K and (d) 1123K

Fig. 4 shows the SEM images of the pine sawdust chars produced under different temperatures. It is clear that the biochars from different temperatures have similar fibrous structure and circular bordered pits on the wall. As a coniferous tree, pine has most features of conifer tracheids and one of the most known characters is the circular bordered pits on the radial walls of the tracheids [17] . The results from Fig.3 suggest that under the tested conditions, the volatile matters escaped from natural porosity within the pine such as the open end of the tracheid channels and circular bordered pits on the walls of tracheid. This is probably due to the low heating rates in the kiln [9, 15]. At a low heating rate, the volatile matters are prone to leave from the natural porosity of the pine, leaving the major morphological structures of the pine unaffected [12].

D. Effect of temperature on biochar reaction rate

Fig.5 shows the oxidation reaction rate of the biochars produced under different pyrolysis temperatures as a function of biochar conversion under the temperature of 723K. It is
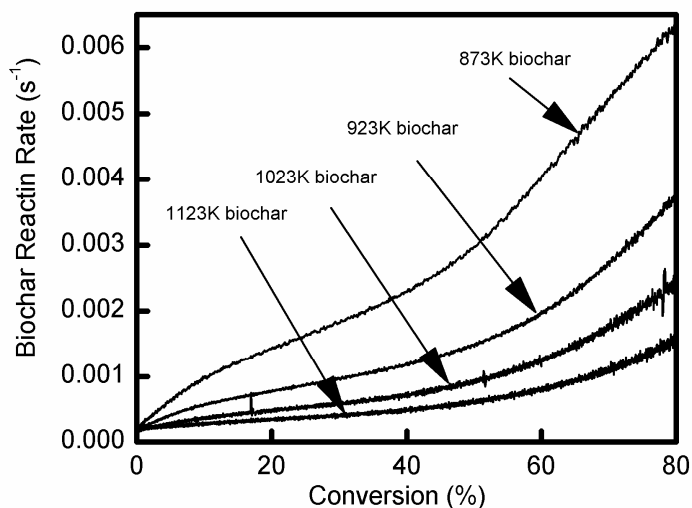
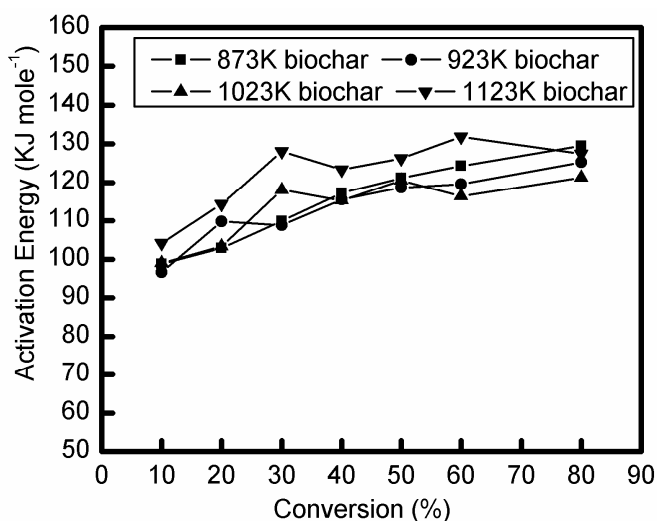Figure 5. Effect of pyrolysis temperature on biochar reactivity

Figure 6. Effect of pyrolysis temperature on biochar activation energy

seen that the biochar oxidation reaction rate decreased as pyrolysis temperature increased at the same biochar conversion. This could be due to the smaller surface areas of biochars at high pyrolysis temperature shown in Tab.2. Fig.4 also illustrates that the oxidation reaction rate of the biochars increased as the biochar conversion increased. As the reaction between the biochar and oxygen proceeded, more pores may form inside the biochars, leading to higher reaction rate. However, this needs to be further verified.

Fig.6 illustrates the effect of the temperature on the activation energy of biochar oxidation as a function of biochar conversion. It is evident that the activation energy of biochars produced from different pyrolysis temperatures had little variation at the same biochar conversion. The main component of biochar has been found to be carbon and the same activation energy of biochars under different pyrolysis temperatures suggests that the pyrolysis temperature tested has little effect on the carbon structure in the biochars. In fact, it is amorphous carbon in all biochars produced based on our examinations using XRD. It is also shown that the activation energy increased for all biochars as the biochar conversion was below 30% and then levelled off. With the progress of oxidation, the volatile matter or hydrocarbon molecules deposited on the surface of the biochars was oxidised and released and the carbon structure became more ordered reflected by the increased activation energy. However, the carbon structure did not change significantly after 30% conversion reflected by a constant activation energy around 120-130kJmole^{-1}.

CONCLUSIONS

The effect of temperature on pyrolysis products and biochar morphology and reactivity of a pine sawdust in a pilot-scale indirectly fired kiln reactor was investigated. The following conclusions can be drawn from the current study:

1. The biochar production rate decreased as the pyrolysis temperature increased.

2. The major pyrolysis products were CO, CO_2, H_2 and CH_4. High pyrolysis temperatures favoured the production of H_2 while CO, CO_2 and CH_4 were dominant gas products at low pyrolysis temperatures.

3. The volatile matter residues in biochar and biochar surface areas decreased as the pyrolysis temperature increased. The volatile matters released from natural porosity of the pine sawdust under the tested conditions, leaving the major morphological structures of the pine unaffected.

4. Biochars produced at low pyrolysis temperatures had higher oxidation reactivity than that produced at high pyrolysis temperatures.

5. The pyrolysis temperature had little effect on the activation energy of biochar oxidation, which suggests that the carbon structure in the biochars produced under the tested pyrolysis temperatures were the same.

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