Pyrolysis of sawdust in a horizontal tube furnace: Effects of temperature and heating rate on product composition

Vitiyaa Selva Kumar[1], *Zhi Hua* Lee[1,2*], *Kok Tat* Tan[3,4], and *Jia Huey* Sim[1,2]

[1]Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman (Sungai Long Campus), 43000 Kajang, Selangor, Malaysia
[2]Centre for Advanced and Sustainable Materials Research, Universiti Tunku Abdul Rahman (Sungai Long Campus), Bandar Sungai Long, Cheras, 43000 Kajang, Selangor Darul Ehsan, Malaysia
[3]Department of Petrochemical Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman (Kampar Campus) Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
[4]Centre for Environment and Green Technology, Universiti Tunku Abdul Rahman (Kampar Campus), Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

Abstract. The abundant sawdust waste from the timber production industries in Malaysia can be a potential biomass feedstock for pyrolysis process. However, the understanding of product composition and bio-oil quality from sawdust pyrolysis remains limited in Malaysian's context. In this study, pyrolysis of sawdust was conducted in a horizontal tube furnace to investigate the effects of temperatures (400-550 ℃) and heating rates (10-20 ℃/min) on the composition of products, quality and properties of bio-oil. According to Gas chromatography (GC) analysis, phenol group appears to be the major compound in the bio-oil. The chemical components of bio-oil were found to be richer at lower reaction temperatures (400-450 ℃), where it showcased the presence of phenols, ketones, carboxylic acids, furans, aldehydes, alkenes, alcohols, ether and amine. At increased reaction temperatures (500–550 ℃), the process favoured the production of catechol (17%). The yield of bio-char decreased with increasing temperatures and heating rates due to the loss of volatile matter, and 400 ℃ proved to be the optimum temperature for maximum biochar yield. The biochar also displays porous structure, with increased adsorption capacity. Since the pyrolysis of sawdust could produce phenolic compounds, it appears to be a potential feedstock for biomass pyrolysis.

1 Introduction

Pyrolysis is a thermochemical method that converts the biomass into valuable products such as liquid oils and chemicals [1-3] through thermal decomposition by heating the biomass in an oxygen-free atmosphere. The composition of pyrolytic products greatly depends on the biomass feedstocks and operating conditions [1]. Lignocellulosic biomass is a potential

*Corresponding author: leezh@utar.edu.my

feedstock of pyrolysis for bio-oil and high value-added chemicals production, while minimizing the waste generation. Found in various sources such as agricultural wastes, woods and industrial wastes, biomass mainly comprises of cellulose, hemicellulose and lignin. During pyrolysis, these components decomposed into primary and intermediate products during the first stage, followed by secondary reactions of intermediate products depending on the process conditions [1].

In Malaysia, sawdust is abundantly generated by timber production industries. It is considered a low-value product, often treated as waste or utilized in the production of low-quality plywood. Direct combustion of sawdust is inefficient and produces significant greenhouse gases. In this context, sawdust represents a potential feedstock for pyrolysis in Malaysia. However, there is a notable scarcity of studies focused on the composition of its pyrolytic products and the quality of the resulting bio-oil. Pyrolysis, a promising energy recovery technology, faces challenges due to high levels of oxygenated compounds in the bio-oil. These compounds increase the viscosity, lower heating value, and negatively impact pH and stability [4]. Several studies have focused on enhancing bio-oil quality through various approaches, including incorporation of catalysts [5], and configure of the reactor design [6]. Nonetheless, optimization of process conditions is the most significant and primary step to be carried out to minimize the undesired oxygenated compounds. Gupta et al. [7] found that bio-oil produced at high pyrolysis temperature has less oxygenated compounds. Varma et al. [8] found that 500 ℃ appeared to be the optimum temperature for maximum bio-oil yield with comparable characteristics to the petro diesel. In most of the studies, the main emphasize was only on the effects of process conditions on the product yields and the understanding on the influence of process conditions on the product composition is still lacking. Hence, it is very crucial to understand the relation on the effects of process condition towards the composition of valuable products. To address the concerns, the potential of sawdust as the feedstock of pyrolysis was evaluated and the influence of process conditions towards the product compositions and bio-oil quality was investigated.

2 Material and methods

Sawdust used in this study was collected from a timber processing factory in Kedah, Malaysia. The collected sawdust was crushed and sieved to particle size ≤ 300 μm before being dried at 100 ± 5 ℃ for 6 h in an oven. The proximate composition of biomass was analysed using the ASTM standard methods (ASTM E871 for moisture content, ASTM E1755 for ash, ASTM E872-82 for volatile matter and fixed carbon is calculated by difference) [8]. The elemental composition (carbon, hydrogen, nitrogen and oxygen) of sawdust was calculated using the formula of Nhuchhen [9]. The lignocellulosic components (hemicellulose, cellulose and lignin) of sawdust were determined using acid and alkaline chemical methods [10].

The biomass pyrolysis was performed in the horizontal tube furnace. The effect of process parameters on the process performance was investigated by manipulating the variable (pyrolysis temperature: 400 ℃, 450 ℃, 500 ℃ and 550 ℃; heating rate: 10, 15 and 20 ℃/min). Initially, high purity nitrogen gas flew into the furnace during the pre-treatment stage to produce an inert atmosphere and oxygen-free environment. For each run, 10g of dried biomass was used and the pyrolysis process was performed for 30 min. The thermal decomposition of sawdust was studied using thermogravimetric analyzer (TGA) under 20 ml/min nitrogen flow within the temperature range of 30-800 ℃. Gas chromatography (GC) was used to analyse the composition of bio-oil obtained. Gas chromatography-mass spectroscopy (GC/MS) analysis was carried out to identify the chemical compounds in the bio-oil. Fourier transformed infrared spectroscopy (FTIR) was used to determine the functional groups (bonds) presented in bio-oil. The surface morphology of biochar samples was observed using scanning electron microscope (SEM).

3 Results and discussions

3.1 Properties characteristics of sawdust

Based on the proximate analysis (Table 1), sawdust shows a high volatile matter of 73.47%. This implies high reactivity and easy devolatilization which is ideal for pyrolysis. The low ash content aligns with literature values [4,7-8], suggesting easier combustion as a fuel. Besides, the carbon and oxygen content in sawdust is higher as compared to the hydrogen and nitrogen contents. It also could be observed that the H/C and O/C ratio is low, which implies greater energy content in the biomass. These findings align with Elhenawy et al. [11], which also reported sawdust with high volatile content (73.4%), low ash content (5.2%), and lower H/C and O/C ratios. Throughout the thermal analysis (Figure 1), the biomass undergoes three stages of degradation. During the first stage, the moisture and light volatile matters evaporated up to 150°C, where around 8% of mass loss took place in this stage. In the second stage (180-500 °C), biopolymers like hemicellulose and cellulose undergo volatilization, breaking down into smaller molecules.

Table 1. Properties characterization of sawdust.

Proximate analysis (wt%)		**Elemental composition (wt%)**	
Moisture	25.03	Carbon (C)	52.41
Ash	2.77	Hydrogen (H)	5.69
Volatile matter (VM)	73.47	Oxygen (O)	37.92
Fixed carbon (FC)	23.76	Nitrogen (N)	1.20
Component analysis (wt%)		O/C molar proportion	0.54
Hemicellulose	34.46	H/C molar proportion	1.29
Lignin	25.51		
Cellulose	40.03		

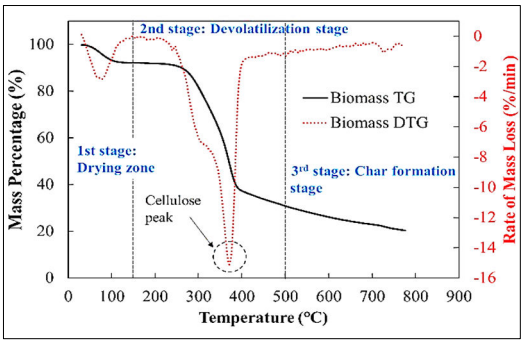

Fig. 1. Thermal degradation of sawdust.

Peaks were found at 305 °C and 370 °C correspond to mass loss rates of 6.9 %/min and 15 %/min, respectively, represents hemicellulose decomposition at the first peak and cellulose at the second. These two components are the main contributor of bio-oil during the pyrolysis. F-X. Collard et al. [12] and Zhou et al. [13] also reported that maximum decomposition rate of cellulose takes place between 330–370 °C. Slow degradation of lignin also occurs during the second stage. The less significant weight loss at high temperature is attributed by the existence of hydroxyl phenolic groups, which indicate the decomposition of lignin. Cellulose more readily transforms into volatile compounds compared to hemicellulose and lignin. Hemicellulose degrades at lower temperatures, while lignin, being more thermally stable, degrades at higher temperatures. Higher lignin content results in more solid biochar after pyrolysis. The decomposition temperatures of cellulose and hemicellulose indicate that 370 - 500 °C is optimal for pyrolysis. High cellulose and hemicellulose content makes

sawdust an ideal feedstock for biomass pyrolysis to generate value-added products.

3.2 Analysis of bio-oil and biochar

From the experiment, it was found that the bio-oil produced from pyrolysis process at different process conditions were dark brown in colour, as shown in Figure 2 (a). There were large number of compounds identified through qualitative GC/MS analysis of the bio-oil. Due to the complexity of bio-oil, only major compounds were identified as shown in Figure 2 (b). It could be observed that 2,6-dimethoxyphenol is the main phenolic compound of bio-oil. The methylated and methoxylated phenolic compounds were formed from lignin decomposition [1]. Bio-oil compositions produced under various pyrolysis temperatures and heating rates were analyzed using GC (Figure 3 (a)). The bio-oil contained phenols, ketones, carboxylic acids, furans, aldehydes, alkenes, alcohols, ether, and amines. Phenolic compounds were the major components (>80%) regardless of temperature. They were derived from the decomposition of lignin, by cracking the phenyl-propane units of lignin in sawdust [3]. More ketones and furans were produced below 500℃, with 3-ethyl-2-cyclopenten-1-one and 5-methyl-2(3H)-furanone yielding up to 44% and 95%, respectively.

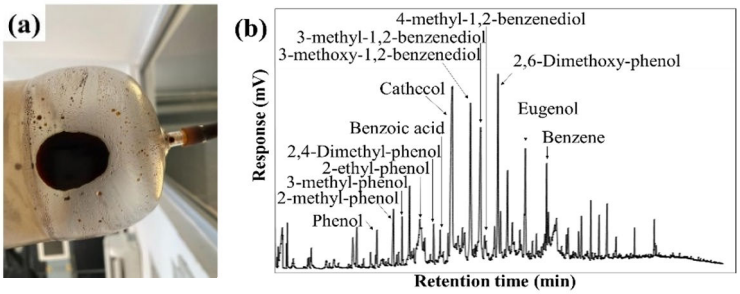

Fig. 2. (a) Bio-oil produced during pyrolysis process; **(b)** GC/MS analysis of bio-oil produced at pyrolysis temperature of 450 ℃ at heating rate of 10 ℃/min, respectively.

Figure 3 (b) displays the effect of pyrolysis temperature (400–550 ℃) and heating rate (10-20 ℃/min) on the biochar yield. It is evident from Fig. 3 (b) that the mass of biochar decreased with increasing temperature, where low temperature favors the formation of biochar due to slow pyrolysis. This directly indicates that high pyrolysis temperature leads to more bio-oil production. The biochar yield is the lowest at 550 ℃ regardless of the heating rates. Moreover, at high pyrolysis temperature, maximum level of degradation would take place, where the biochar and vapour were converted into bio-oil and gaseous products due to the secondary cracking reactions of high molecular weight hydrocarbons. It has been previously reported that maximum bio-oil yields were attained at temperature range of 500 – 550 ℃ [8]. Low pyrolysis temperature is not sufficient enough to complete the pyrolysis process, hence the biochar yield is high due to the partial decomposition of sawdust [14]. Moreover, the ring opening of the tricomponent monomers and the cleavage of the C-C bond in the components ring are not complete [15]. Hence, the amount of biochar started to reduce and the rate of volatile formation enhanced at high pyrolysis temperature. Similar findings were reported in the research conducted by Ahmed et al. [4] and Varma et al. [8]. In overall, the factor of temperature outweighed the impact of heating rate on the biochar yield. The mild effects of heating rate on biochar formation were observed at low heating temperature of 400 ℃ and the impact can be neglected when the temperature approach 450 ℃ and beyond. According to the Fig. 3 (b), the pyrolysis temperature of 400 ℃ favors the production of biochar with reported highest yield. The thermal analysis of sawdust also proves that rapid mass loss occurs till 400 ℃, hence temperature lower than 400 ℃ is preferable to maximize

the biochar production.

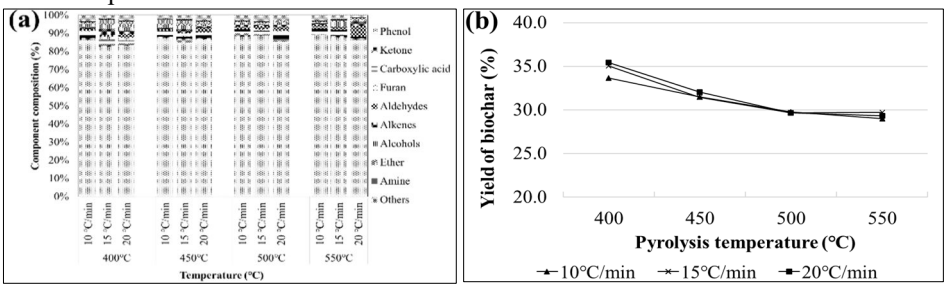

Fig. 3. (a) Effect of pyrolysis temperatures and heating rates on the bio-oil compositions; **(b)** Effect of pyrolysis temperatures and heating rates on biochar yield.

During the pyrolysis process, different chemical bonds were broken, which results in removal of volatiles and rearrangement reaction within the structure of residue. This stage is considered as primary mechanisms. After this structure reformation, some volatiles are still unstable, which can undergo additional conversion known as secondary reactions [12]. In the primary stage, the biomass components undergo few reaction pathways such as char formation, depolymerization and fragmentation. In the following stage, cracking and recombination takes place between the unstable volatile compounds. The hemicellulose and cellulose components undergo transglycosylation to produce anhydrosugars. This anhydrosugars transforms into furanic compounds through the dehydration and cyclization reactions [16]. Based on Figure 3 (a), more furanic compounds were presents in bio-oil produced at temperature below 500 °C, and this temperature range is in line with the TGA degradation profile of hemicellulose and cellulose, where it takes place at temperature range of 180 – 500 °C. Moreover, lignin is the contributor to the phenolic compounds in bio-oil, where it undergoes several reactions such as dehydration, demethylation, demethoxylation and ether bond breakage. Usually, lignin is pyrolyzed at a wide temperature range during the pyrolysis process. At low heating rate, the weakest chemical bonds will break and others will remain stable, hence the structure is just slightly affected, which leads to more char formation. At a very high heating rate, more chemical bonds were broken simultaneously, results in more volatiles removal and inhibits the char formation [12]. Furthermore, the distribution of volatile compounds also depends on the process temperature and optimum liquid oil yield is reported at temperature range of 450 – 550 °C [12]. The depolymerization and fragmentation reactions of chemical bonds usually takes place at this temperature range.

Moreover, the infrared spectra of bio-oil produced at 450 °C at heating rate of 10 °C/min is presented in Figure 4 (a). The functional groups observed between 3500-3000 cm^{-1} and 1750-1000 cm^{-1} indicated the presence of phenols, acids and alcohols in bio-oil. The obtained FTIR spectra is comparable to the results reported in literature [8, 17]. The broad bands at 3600-3200 cm^{-1} are the characteristic of hydrogen bonds, which indicates the presence of phenols, carboxylic acids, and alcohols. The appearance of band at 2950-2850 cm^{-1} represents the alkyl C-H stretching, which shows the presence of alkanes. Besides that, it also can be observed that the absorption bands at 1800-1600 cm^{-1} (C=O stretching; aldehydes and ketone) and 1300-900 cm^{-1} (C-O stretching; oxygenated compounds) were found in all bio-oil samples. The stretching vibration at 1515 cm^{-1} denotes the existence of aromatics and alkenes [8]. Figure 4 (b) shows the SEM images of bio-char produced at pyrolysis temperatures of 400–550 °C. It can be observed that the biochar displays porous structure, which is due to the devolatilization reactions that occur during the pyrolysis process [17]. Similarly, Gupta et al. [7] also reported on the pores formation after the thermochemical process. During the pyrolysis process, the volatiles escaped from the sawdust leaving a porous structure with rough appearance. It is also obvious that a honeycomb-like structure

can be observed in all the biochar samples. Ahmed et al. [4] also reported that the pores and cracks were more obvious on the biochar surface as the temperature increased from 400 to 600°C. This is due to the enhanced rate of decomposition and devolatilization at higher pyrolysis temperature, which results in prominent surface roughness, pores and eventually improving the reactivity and adsorption capacity of biochar.

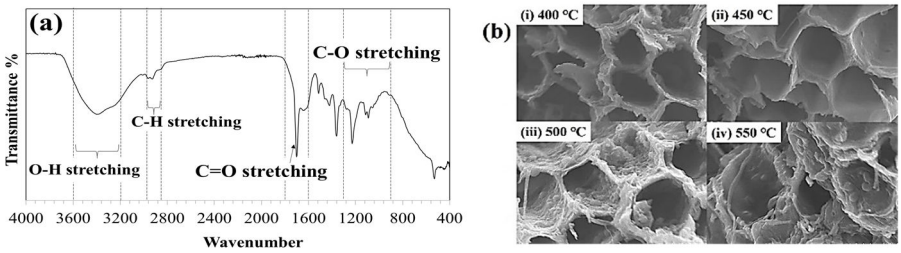

Fig. 4. (a) FTIR spectra of bio-oil produced at 450 °C with heating rate of 10 °C/min; **(b)** SEM images of biochar obtained at different pyrolysis temperatures: (i) 400°C; (ii) 450°C; (iii) 500°C; (iv) 550°C.

4 Conclusions

The sawdust is proved to be a feasible feedstock for the biomass pyrolysis with its good properties such as high volatile matter, low ash content, low H/O and O/C ratios. It was observed that the pyrolysis temperature has great influence on the product composition. The yield of biochar decreased with increased pyrolysis temperature. Based on the results, the optimum condition for maximum biochar yield (35.41%) is at 400 °C with heating rate of 20°C/min. The main compounds discovered in the bio-oil produced from sawdust pyrolysis were 2,6-dimethoxyphenol, 3-methyl-1,2-benzenediol, cathecol and benzene. In overall, phenolic compounds showcased the highest composition in all the tested conditions (82-90 area%). The biochar has porous structure and can be possibly utilized as adsorbent. Since the pyrolysis of sawdust could produce phenolic compounds, it appears to be a potential alternative to replace the fossil phenols, which is highly desirable. The utilization of sawdust in the pyrolysis process is proven to be effective in waste minimization and energy production.

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