Microwave Pretreatment of *Leucaena Leucocephala* using dilute sulphuric acid

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***Abstract*— Globally, the production of bioethanol from lignocellulosic biomass is in demand due to fossil fuels depletion and the effects of fossil fuels consumptions such as greenhouse gas emissions and climate change. As biomass sourced from natural forests is not favourable to avoid risks of deforestation, it is desirable to study the use of *Leucaena Leucocephala*, a fast-growing tropical tree, non-crop species to be a fuel supply for bioethanol production. However, it is necessary for lignocellulosic material, due to its recalcitrant structure to undergo pretreatment in order to increase the efficiency of its enzymatic hydrolysis of cellulose into simple sugars, before fermentation process to produce bioethanol. Therefore, the purpose of this study is to determine the effect of dilute sulphuric acid concentration and microwave pretreatment time on the functional groups, thermal degradation profiles and proximate analysis of *Leucaena Leucocephala*. The concentrations of dilute sulphuric acid used were 0.2M and 0.4M with microwave pretreatment time of 5 minutes and 10 minutes. Four types of pretreated samples (0.2M-5min, 0.2M-10min, 0.4M-5min, 0.4M-10min) were prepared with respective dilute sulphuric acid concentration and microwave pretreatment time. An untreated sample, which was not pretreated with dilute H_2SO_4 and microwave heating, was used as a basis of the pretreatment. FTIR results indicated that O-H absorption peak for each sample increased after respective pretreatment conditions. Increasing microwave pretreatment time did not necessarily remove C-H functional group of lignin. The disappearance of peak for C-O stretching in hemicellulose and lignin showed removal of major hemicellulose. No significant differences were observed for C-O-C, C-O, C-OH functional groups after pretreatment though small increased in band assignment in the region might indicate cellulose enhancement. Thermogravimetric analysis (TGA) results showed that during pyrolysis, the maximum degradation temperature and maximum mass rate loss obtained were 363.69°C and 2.76 mg min^{-1}, respectively. Increasing severity of microwave pretreatment time from 5 minutes to 10 minutes and dilute sulphuric acid concentration from 0.2M to 0.4M increased the biofuel properties of the sample as higher volatile matter were released with lower moisture and ash content were obtained for proximate analysis.**

***Keywords*— Dilute sulphuric acid, *Leucaena Leucocephala*, microwave pretreatment, lignocellulose**

I. INTRODUCTION

In recent years, technology for producing biofuels such as ethanol from lignocellulosic material is gaining serious attention due to rapid depletion of fossil fuels, which is still the major source of energy today. Diaz et al. (2015) reported that bioethanol has great potential as a renewable energy due to its compatibility with current infrastructure. *Leucaena Leucocephala*, an example of lignocellulosic biomass, has been considered as potential feedstock for bioethanol production (Ilham et al,2014). Various scientific studies on *Leucaena Leucocephala* had been done, due to its biofuel properties. *Leucaena Leucocephala* kernel oil can be blend directly with fossil fuel as the kernel contains fatty acids, potential source for inhibiting the bio-corrosion of metals (Nagendra et al.,2013). The seed oil can be converted into biodiesel via transesterification method. Studies on *Leucaena Leucocephala* as biochar fuel have been done as well. Anupam et al. (2016) studied upgradation of *Leucaena Leucocephala* bark to biochar fuel with high energy yielding, through slow pyrolysis, where biomass is heated in limited presence of air to break down the biomass into simpler substances such as solid biochar, pyrolytic gases and liquid bio-oil.

Lignocellulosic biomass requires acid or enzymatic hydrolysis to convert its carbohydrates into simple sugars such as glucose, followed by the fermentation of sugars to produce ethanol and distillation of sugar solution to obtain pure ethanol in the final stage (Kallioinen et al,2013). However, enzymatic hydrolysis is inefficient due to recalcitrant lignocellulosic structure, in which complex lignin seal cellulose and hemicellulose structure, limits enzyme susceptibility to cellulose. Thus, a pretreatment is necessary before hydrolysis step to enhance enzymatic hydrolysis by breaking the hard lignin seal (Keshwani et al,2007). To convert lignocellulosic material into biofuel, enzymatic hydrolysis must be done to obtain fermentable sugars and ethanol. However, the hydrolysis efficiency is often reduced by complex lignin that seal cellulose and hemicellulose structure of biomass. Lignin complex limits susceptibility of enzymes to cellulose (Keshwani et al.,2007). Hence, it is necessary for lignocellulosic material to undergo pretreatment in order to increase the efficiency of enzymatic and chemical hydrolysis of cellulose and hemicellulose. Physical, chemical and physico-chemical pretreatments are examples of pretreatment methods that can be assayed for biomass pretreatment.

Physical pretreatment method such as microwave pretreatment is an alternative method to conventional pretreatments. Contrary to conventional heating, direct conversion of the electromagnetic field into heat in microwave induces heat at the molecular level (Bu et al., 2010). Microwave radiation effect on rice straw and bagasse immersed in water is one of the earliest known study involving microwave pretreatment (Nomanbhay et al.,2013). Microwave pretreatment can be facilitated with chemical pretreatment using alkali or acid such as NaOH and H_2SO_4 to improve enzymatic hydrolysis and glucose yield. To measure lignin and structural carbohydrate content, sulphuric acid H_2SO_4 has been used for more than 100 years (Sluiter et al.,2010). For a short reaction time, dilute acid pretreatment under temperature of 180°C can achieve high reaction rate such that almost all hemicellulose content can be removed while for a long reaction time of approximately between 30 to 90 minutes, hemicellulose removal is the most effective at 120°C (Fang,2013). Recent study such as microwave assisted NaOH and H_2SO_4 pretreatment of *Miscanthus* biomass by Zhu et al.(2015) shows that digestibility of *Miscanthus* sample pretreated with NaOH is 8 to 9 times higher than that of untreated sample. Nevertheless, H_2SO_4 gives better sugar yield than NaOH during the pretreatment. Feng et al.(2016) demonstrates that microwave formic acid pretreatment of beechwood enhance aromatic production.

Previous research on *Leucaena Leucocephala* has involves several pretreatment methods. For example, lignin isolation from *Leucaena Leucocephala* stems using acidic dioxane under nitrogen atmosphere has a dioxane lignin yield of 17.6 ± 0.7% (Yearla & Padmasree, 2016). Another study involves autohydrolysis, in which *Leucaena Leucoephala* wood sample is mixed with water and treated in a stainless steel reactor. The study was conducted to determine the influence of time and temperature of autohydrolysis process in order to obtain valuable liquor and suitable solid phase to produce energy by combustion. Optimum processing condition at 184ºC and for 30 minutes provided and acceptable liquor yield from 16 to 26%. Chemical characterization of *Leucaena Leucocephala* was conducted by acid hydrolysis using sulphuric acid at 121°C and 2 atm for 60 minutes. Results shows that *Leucaena Leucocephala* sample contains 37.2% cellulose,19.9% hemicellulose and 24.1% Klason lignin (Feria et al., 2011). Plus, slow pyrolysis of *Leucaena Leucocephala* bark under limited air in a cylindrical vessel at optimum temperature 367.47°C time of 135.38 minutes gave biochar yield of 47.29% (Anupam et al.,2016).

Microwave pretreatment facilitated by addition of chemicals is an energy saving method which requires shorter reaction times and improves sugar yields from lignocellulose (Lu et al.,2011). In this study, the effect of sulphuric acid concentration and microwave pretreatment time on the functional groups, thermal degradation profiles and proximate analysis of *Leucaena Leucocephala* were determined. Grinded wood samples were pretreated with dilute 0.2M and 0.4M sulphuric acid at microwave residence time of 5 and 10 minutes using a general laboratory microwave oven.

II. METHODOLOGY

A. Materials

Leucaena Leucocephala wood samples (stem) were obtained within the city of Shah Alam. Firstly, the wood samples were oven dried for 24h at 80 ºC to remove the moisture content. Later, dried wood samples were chopped and grinded using a constant speed mixer. A digital sieve shaker was used to obtain the wood sample size of ≤700 μm.

B. Microwave Pretreatment of Leucaena Leucocephala using dilute sulphuric acid

The microwave pretreatment of *Leucaena Leucocephala* wood samples were conducted using a general laboratory microwave, purged with nitrogen gas which was supplied through inlet tube at the top of the microwave oven to avoid any reaction of H_2SO_4 fume with air. 0.2M and 0.4M of sulphuric acid solution were prepared in a fume chamber by diluting concentrated H_2SO_4 with distilled water. Approximately 7.5 g of *Leucaena Leucocephala* wood sample and 300ml of 0.2 M of sulphuric acid solution were added into a 500 ml laboratory glass bottle, and placed in the microwave, with the cap of the bottle removed. The microwave time was set to 5 minutes under constant power at 200 W. After 5 minutes, the samples and acid mixture were taken out from the microwave and left to cool at room temperature. The pretreatment methods were repeated by pretreatment conditions; 0.2M H_2SO_4-10 min, 0.4 M H_2SO_4-5 min and 0.4M H_2SO_4-10 min respectively. After pretreatment, a Buchner funnel was used to filter the mixture. Solid residues obtained were washed thoroughly with distilled water and sodium hydroxide until the pH reached approximately 7. The washed solid residues were then dried at 40ºC overnight in a universal oven (Feng et al.,2016).

C. FTIR analysis

The FTIR analysis of solid samples were done using a Perkin Elmer Spectrophotometer Spectrum One in the region of 515-4000cm-^{1} to determine the structural properties of *Leucaena Leucocephala* wood samples before and after pretreatment. About 0.1g of solid sample were compressed to make flat discs and placed on the ATR crystal device. Later, an absorption spectrum of the sample was obtained in the computer (Diaz et al.,2015).

D. Thermogravimetric analysis

The thermogravimetric analyses of solid samples were conducted using a thermogravimetric analyzer (Mettler Toledo TGA/DSC 1 Stare System). Approximately 20 mg of samples were placed in alumina crucibles (150μl). For each thermogravimetric analysis, the heating rate was kept constant at 20°C min^{-1}. Nitrogen gas at 100ml min^{-1} was used as the carrier gas for the pyrolysis of sample from 30°C to 950°C, while the combustion of residues occurred between 950°C until 1100°C in air flowrate of 100 ml min^{-1}.

III. RESULTS AND DISCUSSION

Pretreatment method in which is the primary stage of bioethanol production, is necessary for lignin, the component that seal hemicellulose and cellulose structure of biomass to be removed so as to increase the efficiency of enzymatic and chemical hydrolysis of cellulose and hemicellulose. According to Senthilkumar et al. (2015), *Leucaena Leucocephala* wood samples contain 40.19% of cellulose, 34.29% of hemicellulose and 24.23% of lignin. Hence, cellulose content is the highest in *Leucaena Leucocephala*, followed by hemicellulose, while lignin content is the least. The pretreatment method used in this study is by microwave heating of biomass combined with dilute sulphuric acid. Accesibility of cellulose in biomass can be increased by mixing biomass with dilute sulphuric acid as hemicellulose is solubilized (Agbhor et al,2011). Plus, previous studies reported that microwave pretreatment with acid extraction can disrupt the recalcitrant structure of biomass and thus increase the efficiency of biomass conversion to sugars (Feng et al.,2016).

In this study, the FTIR analysis and thermogravimetric analysis (TGA) of *Leucaena Leucocephala* wood were discussed. For the FTIR analysis, the effect of microwave pretreatment time and dilute sulphuric acid concentration on the chemical structure (functional groups) of samples were determined. On the other hand, thermogravimetric analysis was done to study the effects of pretreatment on the thermal degradation profiles and proximate analysis of *Leucaena Leucocephala.*

A. The effects of pretreatment on the functional groups of Leucaena Leucocephala

Figure 1 shows the combined FTIR spectra of the untreated and pretreated samples of *Leucaena Leucocephala* wood samples. The absorption peaks for O-H stretching of phenolic, alcoholic and carboxylic functional groups of lignin were in the region 3289.01 cm^{-1} to 3341.38cm^{-1}. From observation, the O-H absorption peak of lignin for each sample increases after respective pretreatment conditions. Lignin subunits such as p-hydroxyphenylpropene (p-coumaryl alcohol), guaiacyl (coniferyl alcohol) and (sinapyl alcohol) syringyl are bonded by network of aryl ether bonds, β-O-4 and α-O-4 linkages (Inwood, 2014). High O-H absorption peak after pretreatment is due to the cleavage of β-O-4 linkages under harsh conditions such as longer pretreatment time and higher acid concentration (Sun et al., 2014).

The absorption peaks between 2916.50cm^{-1} to 2917.18cm^{-1} represents the C-H stretching of methyl and methylene groups in lignin. After pretreatment, no absorption peaks indicating C-H stretching available for sample (0.2M-5min) and (0.4M-5min) respectively. Thus, some parts of lignin composition had been removed during pretreatment for both samples, as the C-H stretching indicating the presence of lignin compound had diminished. This could be due the removal of methyl and methylene groups as biomass degraded (Sun et al.,2014). However, the absorption peak for C-H stretching was still available and shifted from 2917.18cm^{-1} to 2916.50cm^{-1} for the sample (0.4M-10 min) and (2917.18cm^{-1} to 2916.58cm^{-1}) for sample (0.2M-10 min). From observation, increasing microwave heating time from 5 minutes to 10 minutes did not necessarily remove C-H functional groups of lignin. Kumar et al. (2016) reported that longer pretreatment time is not associated with the removal of lignin. It was mentioned that the amount of lignin removed is dependent on the amount of hydrogen ion in the reaction liquid, such as dilute sulphuric acid. Hence, acid concentration is more significant in compared to pretreatment time for lignin removal.

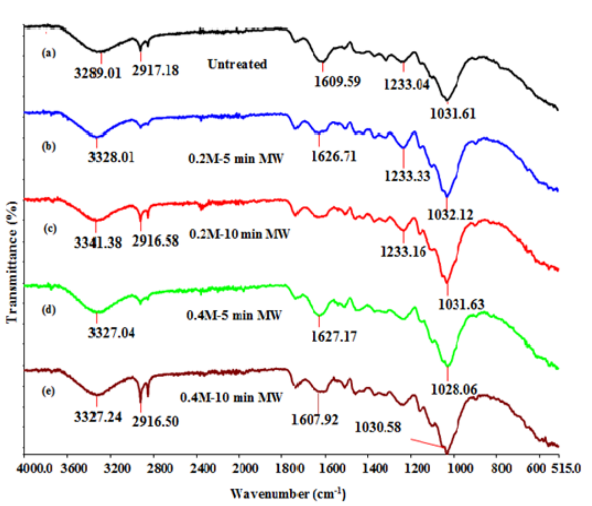


Fig.1: Combined FTIR spectra of the untreated sample and pretreated samples. (a) Untreated (b) 0.2M-5min MW (c) 0.2M-10min MW (d) 0.4M-5min MW (e) 0.4M-10min MW

On the other hand, the absorption peaks attributed to C=C stretching vibration of aromatic lignin were found in all samples after pretreatment, except for the (0.2M-10min) sample. The missing absorption band for C=C stretching is caused by significant modification or breakage of lignin aromatic lignin (Li et al., 2010). On the other hand, stronger peak was obtained for (0.2M-5min) and (0.4M-5min) sample, at 1626.71cm^{-1} and 1627.17cm^{-1} respectively after pretreatment. This is likely due to the replacement of C-H bonds by C=C bonds during condensation reaction (Chen et al.,2016). Under acidic condition, condensations of lignin occur, in which prevent lignin solubilisation in acidic medium (Candido et al.,2012).

The absorption peaks (1233.04cm^{-1}, 1233.16cm^{-1}, 1233.33cm^{-1}) were associated with C-O-C, C-O, C-OH functional groups, attributed to celluloses, hemicelluloses and lignin component (Asadieraghi & Daud.,2014). Nevertheless, the peak at 1233.04cm^{-1} had diminished for both (0.4M-5min) and (0.4M-10min) samples. The disappearance of peak for C-O stretching in hemicellulose and lignin is caused by the removal of major hemicellulose after dilute acid pretreatment. (Li et al.,2009). Similar results were reported by Zhu et al. (2015), in which the peak indicating acetyl C-O stretching of hemicellulose disappears after *Miscanthus* pretreatment with dilute sulphuric acid, suggesting that hemicellulose is deacetylated by pretreatment. Hydronium ions released by acid during dilute acid pretreatment cause depolymerisation of hemicellulose by selective hydrolysis of glycosidic linkages, releasing O-acetyl group to form uronic acid and acetic acid. (Pu et al.,2013).

Lastly, the peaks at 1031.61cm^{-1} for untreated sample, 1028.06 cm^{-1}, 1031.63 cm^{-1}, 1032.12 cm^{-1} and 1030.58cm^{-1} respectively for pretreated samples are linked with the presence of C-O-C, C-O, C-OH functional groups of lignocelluloses as well. (Asadieraghi & Daud.,2014). These region are attributed to aromatic C-H deformations in plane, non-conjugated C=O stretching and C-O deformation in primary alcohols (Vallejos et al., 2011). The primary alcohols are belong to the guaiacyl type found in lignin (J.Z. Mao et al.,2011). Other than that, the FTIR spectra in the region are associated with the C-O vibration in cellulose. In this study, no significant differences were observed on the FTIR spectra for C-O-C, C-O, C-OH functional groups after pretreatment as no disappearance of related peak had occurred. Candido et al. (2012) reported that cellulose structure is not easily broken by low concentration mineral acid due to its high crystallinity. However, small increase in band assignment from 1031.61cm^{-1} before pretreatment to 1032.12cm^{-1} and 1031.63cm^{-1} respectively after 0.2M of dilute sulphuric acid pretreatment might indicate the enhancement of cellulose content in the samples (Nomanbhay et al.,2013).

B. The effects of pretreatment on the thermal degradation profiles of Leucaena Leucocephala

Thermogravimetric analysis was done to determine the thermal degradation profiles and proximate analysis data of each sample after pretreatment. According to Montesino et al. (2015), in the study of pyrolytic degradation *Acacia mangium* wood, a type of softwood lignocellulose, there are three distinct stages of thermal degradation of biomass. The first stage is moisture content removal, followed by the second stage, in which most volatiles mainly cellulose and hemicellulose are decomposed, accounting up to 70 percent of the total mass. The third stage corresponds to decomposition of lignin, cellulose and residual char at up to 800°C. In this stage, 90 percent of the sample original mass had been lost. The second and third stages are related to the higher volume of volatiles released from the biomass. Another study by Shrestha et al. (2015) on combustion characteristic of *Leucaena Leucocephala* wood pellet reported there are four stages of combustion profile. The first stage is moisture content removal from the pellet at temperature less than 110°C. The second stage is for devolatilization of volatile matters at 197°C to 350°C, followed by char combustion stage at the temperature between 360°C to 600°C. The last stage is at the temperature of more than 600°C, corresponding to the decomposition of residue. Based on these references, the thermal degradation profile of *Leucaena Leucocephala* wood in this study were determined. The thermal degradation stages of cellulose, hemicellulose and lignin were highlighted to determine the efficiency of the dilute H_2SO_4 and microwave prtreatment in each sample, based on the responds of each lignocellulose component to combustion.

Figure 2 combines the thermogravimetric (TG) profiles (thermal degradation) of untreated and pretreated samples. The untreated sample served as basis for the comparison with the TG profiles of pretreated samples. For the untreated sample, the combustion starts at about 30°C and ends at 1100°C. The first stage of the combustion is the moisture content removal stage, between 30°C to 147°C. At this stage, the mass percentage of the sample had decreased from originally 100% to about 94%. The second stage (284°C to 375°C) recorded 43.7% of mass loss from the sample, possibly corresponds to devolatilization of hemicellulose and cellulose in which leads to formation of char. The combustion of char is the third stage of the combustion occurred between 376°C to 936°C .In this stage, the decomposition of lignin and cellulose might have taken place as well (Montesino et al.,2015). The profile above 964°C is associated with ash content and inorganic matter (Shrestha et al., 2015). About 41.2 % of the sample original mass had remained after pretreatment.

After pretreatment with 0.2M of sulphuric acid and 5 minutes microwave heating (0.2M-5min), the moisture from the sample was removed between the temperatures 39°C to 68°C, about 4.7% of the original mass was loss. The devolatilization stage starts at 322°C until 404°C, contributing to 40.6 % of mass loss. Combustion of char occurred between 405°C to 932°C, for the decomposition of lignin and cellulose .The last stage which is the degradation of residues begins at about 941°C until 945°C, leaving only 46.21% of the original mass.

From observation, the thermal degradation profile for the sample after pretreatment with 0.2M of dilute sulphuric acid and 10 minutes of microwave heating time (0.2M-10min), drying process results in 9.1% of mass loss at the temperature between 35°C to 106°C. Devolatilization of hemicellulose and cellulose observed from 312°C to 400°C, corresponding to almost 50% of mass loss from the sample. Char formed due to devolatilization undergone combustion from 400°C to 923°C. Degradation of residues begins at about 945°C. About 23.02 % of residues (ash content) were recovered at the end of combustion.

As can be seen from Figure 2, there is almost no moisture content being removed from the sample, after pretreatment with 0.4 M dilute sulphuric acid and 5 minutes of microwave heating (0.4M-5min), indicating that higher acid concentration at 0.4M had released more moisture content from the sample after pretreatment. However, devolatilization of hemicellulose and cellulose occurred between 313°C to 404°C, resulting in about 51% of weight loss from the sample. Char combustion stage begins at about 405°C until 934°C. Residue degradation occurred between 946°C to 1017°C, leaving only ash and inorganic matter content at 36.79 % of the original mass.

Only about 3.07 % of mass loss from sample due to the drying of moisture content at the temperature from about 43°C until 149°C, after pretreatment with 0.4M of dilute sulphuric acid and 10 minutes of microwave heating time (0.4M-10min). Volatile matter such as hemicellulose and cellulose started to devolatilize from 303°C until 390°C, corresponds to about 56.77 % of mass loss. The combustion of char started from 390°C until about 942°C. Lastly, the combustion of residue started at 942°C until 945°C, leaving about 21.17 % of ash and inorganic matter. Only 21.17 % (ash content) of the original mass were recovered from the sample at the end of combustion.

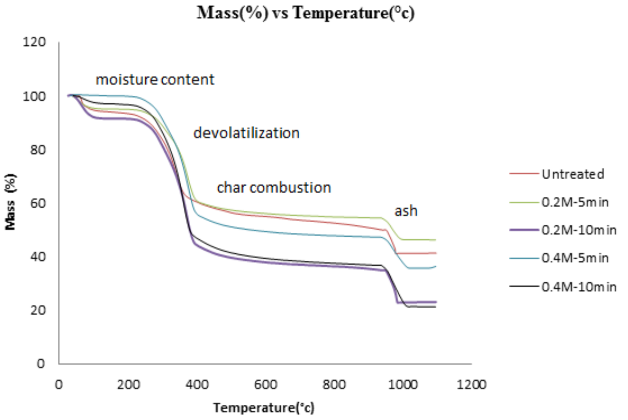


Fig.2: Thermogravimetric profiles of untreated and pretreated samples at constant heating rate 20°C min^{-1}

All pretreated samples, except for samples pretreated with 0.2M H_2SO_4 and 5 minutes of microwave heating, have lower mass percentage at the end of TGA pyrolysis (~1100°C) than the untreated sample. Moreover, it is noticed that the ash content decreased generally with the increase in microwave residence time, which is from 5 minutes to 10 minutes. Hence, increasing microwave residence time can enhance the thermal conversion of biomass to volatile products, thus reducing ash content during biomass thermal decomposition (Feng et al., 2016).

Microwave pretreatment with dilute H_2SO_4 has a significant influence on pyrolysis temperature of *Leucaena Leucocephala* wood, as the temperature at which maximum weight loss occur for each of the sample increases after pretreatment. Referring to Table 1, the maximum pyrolysis temperature for sample (0.4M-10min) is at 363.69°C in compared to untreated sample which is at 340.23 °C. Asadieraghi and Daud (2014) reported that cellulose is decomposed at ~365°C and that the increase in degradation rate of acid pretreated samples is associated with cellulose structure and crystallinity. Plus, FTIR spectra of sample (0.4M-10min) in Figure 4.5 shows the absent of peak at 1233 cm^{-1} for cellulose component. Feng et al. (2016) also reported a similar result, in which the pyrolysis of beech wood from 320 °C to 390°C could be related to decomposition of cellulose and hemicellulose components. Thus, it can be concluded that the maximum temperature for mass loss per minute of sample to occur (363.69°C) is possibly related to the decomposition of cellulose and hemicellulose.

Other than that, it can be observed that higher microwave heating time (10 minutes) resulting in higher maximum mass loss per minute of the sample. For example, in Table 1, the highest maximum mass loss per minute is obtained for sample (0.4M-10min), which is 2.76 mg min^{-1}, followed by sample (0.2M-10min) which is 2.42 mg min^{-1}. The maximum mass rate loss could possibly correspond to cellulose and volatile matters content in biomass (Asadieraghi & Daud,2014). However, less maximum mass loss per minute were obtained for samples heated in microwave for 5 minutes (0.2M-5min and 0.4M-5min) , with maximum mass loss of 1.92 mg min^{-1} and 2.31 mg min^{-1} respectively. Thus, higher microwave pretreatment time (10 minutes) results in greater mass loss from biomass.

Table 1: The temperature (°C) at which maximum mass loss occurs and maximum mass loss (mg/min) of each sample

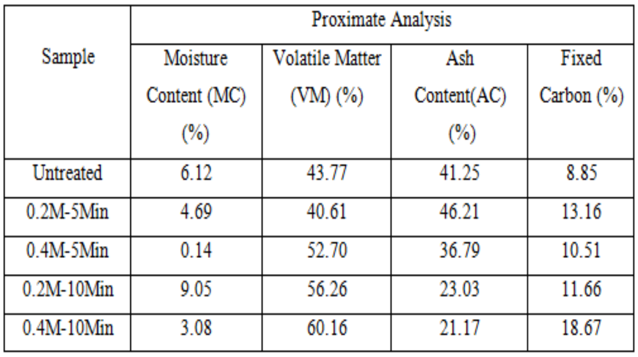
Sample	Temperature (°C) at which maximum mass loss occur	Maximum mass loss (mg/min)
Untreated	340.23	1.66
0.2M-5min	376.04	1.92
0.2M-10min	377.36	2.31
0.4M-5min	373.22	2.42
0.4M-10min	363.69	2.76

C. *Proximate analysis data of Leucaena Leucocephala*

One of the proximate analysis data to be observed after pretreatment is moisture content. Moisture content influences the heating value of a biomass. A biomass can produce more heat per unit mass when the moisture content is less. Hence, sample with the least moisture content is preferable as it can increase the heating value of sample (Rasat et al, 2016). When the moisture content is high, the suitability for the biomass to be used in thermo-chemical conversion process such as combustion is reduced (Shukla & Vyas,.2015) .From Table 2, the lowest amount of moisture content obtained is 0.14 % after pretreatment with 0.4M H_2SO_4 and 5 minutes microwave heating, while the highest amount of moisture content obtained is 9.05 % after pretreatment with 0.2M H_2SO_4 and 10 minutes of microwave heating. However, the amount of moisture content after pretreatment might not suitable for the determination of the best acid concentration and microwave residence time for pretreatment. Surrounding factors such as exposure to atmospheric air or uneven drying in oven during sample preparation might have affected the moisture content of each sample before pyrolysis.

The combustion behavior of biomass is strongly influenced by the amount of volatile matter. Higher amount of volatile matter indicates lower time for combustion of biomass (Shukla & Vyas.,2015). In this study, the highest volatile matter released after pretreatment is 60.16 %, for the sample with 0.4M H_2SO_4 and 10 minutes microwave residence time, followed by 56.26 % for sample with 0.2M H_2SO_4 and 10 minutes microwave residence time. However, lesser volatile matter is produced, which is 40.61% and 52.70% when samples were microwave heated for 5 minutes respectively. Hence, longer microwave residence time produces more volatile matters, and lower time is needed for combustion.

Table 2: Proximate analysis results of one untreated and four pretreated *Leucaena Leucocephala* wood samples by mass percentage, with constant heating rate of 20°C min $^{-1}$



Sample	Proximate Analysis			
	Moisture Content (MC) (%)	Volatile Matter (VM) (%)	Ash Content(AC) (%)	Fixed Carbon (%)
Untreated	6.12	43.77	41.25	8.85
0.2M-5Min	4.69	40.61	46.21	13.16
0.4M-5Min	0.14	52.70	36.79	10.51
0.2M-10Min	9.05	56.26	23.03	11.66
0.4M-10Min	3.08	60.16	21.17	18.67

Moreover, thermogravimetric results also shows that the ash content of the sample pretreated with 0.4M H_2SO_4 and 10 minutes microwave residence time shows the lowest amount of ash content, which is 21.17%. Sample pretreated with 0.2M H_2SO_4 and 5 minutes of microwave heating has the highest amount of ash content, which is 46.21 % and is least favourable. Similar result was obtained in softwood pretreatment by Feng et al. (2016) for microwave assisted formic acid pretreatment beech wood. In the study, it was reported that with increase in the intensity and duration of microwave-assisted formic acid pretreatment, char yields (ash content) had generally decreased. Plus, high ash content could be related to higher amount of lignin in the sample. Yearla and Padmasree (2015) reported that, high amount of residue is due to the presence of aromatic lignin. From observation, it can be concluded that higher H_2SO_4 concentration and longer microwave residence time might be the best for reducing the ash content of sample.

Fixed carbon, excluding moisture and ash content, is the mass left after the release of volatiles (Garcia et al.,2012). According to Syukla and Vyas (2015), the amount of fixed carbon corresponds to the calorific energy of the biomass. Plus, Ismaila et al. (2013) also reported that the higher amount of carbon content in plant biomass, the higher is the energy for useful work. In this study, the amount of fixed carbon content had increased for each sample after pretreatment. As can be seen, the sample (0.4M-10min) has the highest amount of fixed carbon (18.67 %) while the least amount of fixed carbon is for the sample (0.4M-5min) which is 10.51 %. Thus, sample (0.4M-10min) is the most preferable biomass sample.

IV. CONCLUSION

The O-H absorption peak for each sample increases after respective pretreatment conditions. Increasing MW pretreatment time did not necessarily remove C-H functional group of lignin. The disappearance of peak for C-O stretching in hemicellulose and lignin attributed to removal of major hemicellulose. Small increase in band assignment for C-O-C, C-H and C-O stretch indicate cellulose enhancement. High mass rate loss (2.76 mg/min) for the sample 0.4M-10min showed high decomposition of hemicellulose. Therefore, it can be concluded that increasing severity of MW-H_2SO_4 pretreatment could enhance the biofuel properties of samples and cellulose accessibility for enzymatic hydrolysis to simple sugars in bioethanol production.

ACKNOWLEDGMENT

Thank you to my supervisor, Mdm. Nor Sharliza Mohd. Safaai and Universiti Teknologi Mara.

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