Thermal Characterization of Lignin from Extraction of Leucaena Leucocephala (LL) Pods by Formic Acid Fractionation Process

‘Aisyah Nadiah Binti Che Din, Noor Harliza Binti Abd Razak

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract*—Lignocellulose is one of the most abundant renewable sources of carbon that has been used for production of biofuel, chemical and polymers. Lignin is comprises of phenylpropane units linked together by various types of interunit linkages of which ether bonds are the widely recognized, represents 15–30 wt% in the lignocellulosic biomass and it is a key compound in the present and future biorefinery, rendering its valorization of great importance. This study investigated the highest yield amount of lignin with different aging of Leucaena Leucocephala Pods based on the length of their seeds and analyse the thermal characteristic of lignin properties from different aging of Leucaena Leucocephala Pods by using Thermogravimetric analysis (TGA). Fractionation process was used to extract the lignin with different aging of Leucaena Leucocephala Pods based on the length ofof their seeds was using a mixture of formic acid and hydrochloric acid as a catalyst by dissolving the samples with solution to retrieve the lignin. Lignin can obtain from black liquor after filtration process to separate the lignin from the solubilized hemicellulose. It was found that lignin obtained from sample 7mm length of seed provided the greatest yield of the various length size of raw materials. The length of LL pods was seen to affect the thermal properties. Overall, the lignin from sample 7mm had the highest yield lignin amount and greatest thermal stability.

***Keywords*—Characterization, Extraction, Leucaene Leucocephala, Lignin Degradation, Thermogravimetric Analysis**

I. INTRODUCTION

A component of plant cell walls known as lignocellulose is one of the most abundant renewable sources of carbon for production of biofuel , chemicals and polymers. Lignocellulose contains cellulose, hemicellulose and also lignin [1]. Cellulose is an unbranched homopolysaccharide consisting of D-glucopyranosyl units. Hemicelluloses are branched heteropolysaccharides consisting of both hexose and pentose sugar residues, which may also carry acetyl groups while the lignin, comprises of phenylpropane units linked together by various types of interunit linkages of which ether bonds are the widely recognized. Lignin represents 15–30 wt% in the lignocellulosic biomass and it is a key compound in the present and future biorefinery, rendering its valorization of great importance [2]. The function of lignin in the plant cell wall is to provide rigidity and resistance from compression and it is bound to cellulose and hemicellulose [3].

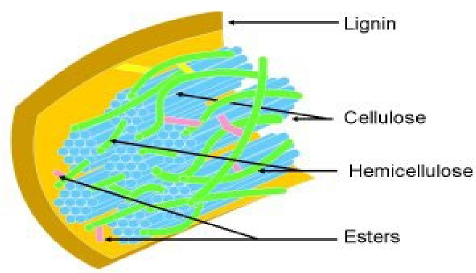

Fig. 1: The structure of lignocellulose

Leucaena Leucocephala (LL) is from family Mimosaceae and at least 14 other species recognised in the genus, for example, in Malaysia, LL tree is known as "Petai Belalang", and it customarily known to cure hypertension (Harliza et al., 2016). The trees additionally can be utilized as timber, firewood and soil disintegration control framework while the seeds can be utilized to treat diabetes [4]. The leaves of leucaena are exceptionally nutritious for ruminants and numerous brilliant creature generation information have been proved.

LL is an amazing kindling species with a particular gravity and high calorific value. Lignin can be gotten from specific parts of plant particularly in LL pods, leaves and seeds and it is abundant sources and easily to find this plants due to factor that it is quickly developing plant in Malaysia environment and weather. However, the application to produce the lignin by extracting from some part in LL plant as a sources lignin extraction is limited and no recent study about maximum amount of chitin that can be extracted from different age of pods in LL plant.

Lignin and chitin are basically a similar pattern of molecule arrangement but with a solitary contrast they are differences in their property and vary in their position they occupied in earth. Plant cell wall material is comprised of cellulose, while chitin is found in exo-skeleton, fungal cell wall and so on. The research is focusing on plant material which is in aging of LL pods based on length of seeds on characterization the lignin properties from extraction by using thermogravimetric analysis (TGA) method.

The objectives of this study were therefore : (1) to determine the highest yield amount of lignin with different aging of Leucaena Leucocephala Pods based on the length of their seeds; (2) To analyse the thermal characteristic of lignin properties from different aging of Leucaena Leucocephala Pods by using Thermogravimetric analysis (TGA).

II. METHODOLOGY

A. Raw material

Leucaena Leucochepala (LL) pods was collected in area Padang Jawa, Shah Alam with different sizes and aging start from young pods until brown pods.The samples was washed by using pure water to make sure there is no impurities left that will affecting the result of experiment and then the samples was dried in the oven dryer to remove moisture content at temperature of 60^{o}C for 24 hours to make sure there is no moisture content that may affected the efficiency of samples during experiment. After drying process, the pods was grinded and sieved using 911MPECM100 (911Metallurgy Corp, Canada) cutting mill to pass through a 0.5 micron sieve plate and the grinded samples was weighted. Then, the samples was dried in oven for 24 hours and weighted again until constant value of samples before stored in closed container with using silica gel from ChemPur to keep the samples dry before proceed to next procedure. The value of weighted samples before and after are shown in the Table 1.

Table 1: Weight of samples before and after dry

Samples (mm)	Before Dry (g)	After Dry (g)
Matured	17.86	16.14
10	26.86	24.35
9	15.25	14.46
8	14.37	12.77
7	24.22	22.07
6	19.59	17.79
5	17.48	16.04
4	19.57	17.09

B. Formic acid (FA) treatment

Approximately 3 g of dried LL samples was placed in conical flask and 85% of formic acid (FA) from ChemPur was poured into it with 0.2% HCl as a catalyst at a ratio 10:1 of liquid to solid. The mixture was heated in a water bath at 150 rpm by maintained the temperature of the mixture in the conical flask at 60^{o}C as shown in Fig. 2a. The mixture was filtered after 6 hours heating (Fig. 2b).

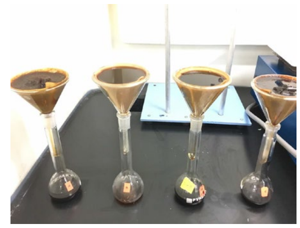

Fig. 2a) Heating process of mixture using water bath, b) Filtration process of LL samples

The solid residue was washed with 85% FA followed by washing with distilled water until obtained neutral pH. Finally, the neutral pH of solid residue was oven dried and weighed.

C. Isolation of lignin and sugar

The black liquor from filtration of mixture was evaporated using rotary evaporator to release formic acid and the solids composed of lignin and hemicellulose sugars remained in the evaporator were washed with distilled water until obtained around pH 2 of solubilized hemicellulose sugars with lignin and then filtered as shown in Fig. 3a below to separate lignin (Fig. 3b) from solubilized hemicellulose sugars as described in Zhang, et al. [5].

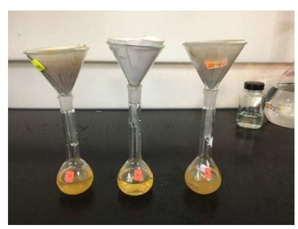

Fig. 3a Filtration process of solubilized hemicellulose sugars with lignin, b) Solid residue of lignin

Fig. 4 below shows the flow diagram for lignocellulose fractionation of LL pods by formic acid treatment and isolation of lignin and sugar.

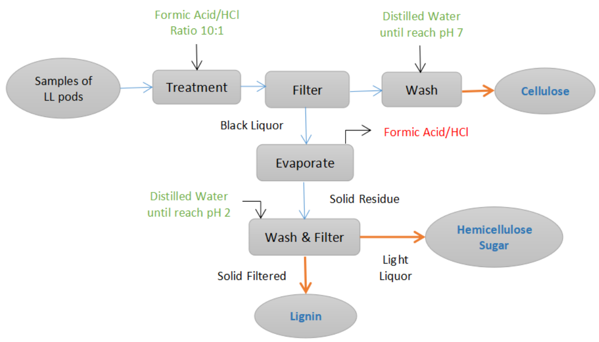

Fig. 4 Flow diagram for lignocelluloses fractionation of Leucaena Leocephala pods by formic acid

D. *Characterization via thermogravimetric analysis*

All the samples was characterized via thermogravimetric analyses to determine the thermal stability by using a TGA analyzer unit (Mettler Toledo) under operating in nitrogen atmosphere with about 20mg for each sample was heated starting from 25^{0}C up to 800^{0}C at a heating rate of 10^{0}C /min.

III. RESULTS AND DISCUSSION

A. *Yield of lignin in LL pods*

Table 2: The percentage lignin yield after extraction

Samples (mm)	Weight of solid residue (g)	Lignin yield (%)
4	0.711	23.65
5	0.803	26.72
6	0.587	19.55
7	1.042	34.64
8	0.871	29.00
9	0.918	30.58
10	0.749	24.93
Matured	0.961	31.98

Extraction of lignin with different aging of Leucaena Leucocephala Pods based on the length of their seeds was carried out using a mixture of formic acid and hydrochloric acid as a catalyst by dissolving the samples with solution to retrieve the lignin and observe the highest yield amount of samples. Lignin can obtain from black liquor after filtration process to separate the lignin from the solubilized hemicellulose. Percent yield of lignin from each samples after formic acid treatment was recorded and the result are presented in Table 2. The results indicate that the 7mm of LL pods sample obtained the highest yield of lignin content of 34.64% followed by samples of matured, 9mm, 8mm,5mm, 10mm, 4mm and 6mm with lignin content of 31.98%, 30.58%, 29.00%, 26.72%, 24.93%, 23.65% and 19.55% respectively.

B. *Thermogravimetric analysis*

Thermal characterization and decomposition of lignin occur slowly throughout the pyrolysis process using TGA under nitrogen environment. The result from TGA curves shows the percentage of weight loss from the samples with respect to the temperature of thermal degradation. Besides, the first derivative (DTG) from the TGA analysis indicates the corresponding rate of weight loss. From the peak of this curve (DTG_{max}) can be presented as a measure of thermal decomposition and can be used as a means to compare thermal stability characteristics of different samples [6]. Yang, et al. [7] stated that the molecular structure of lignin is composed of mostly aromatic rings having different branching which lead to a wide range of degradation temperature from 20ºC to 800ºC. Fig.5 shows TGA plots of lignin from LL pods samples with different length of seeds under nitrogen atmosphere at heating rate 10ºC/min.

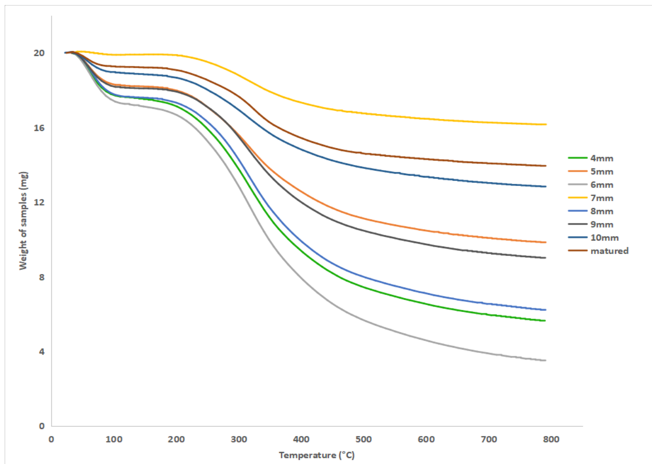

Fig. 5 TGA plots of lignin from LL pods samples with different length of seeds under nitrogen atmosphere at heating rate 10ºC/min.

According to Watkins, et al. [6], degradation of the lignin samples divided into three stages. The first stage, the weight loss occurred caused by the moisture which the weight loss due to the water evaporation in the samples. Based on the graph above indicates that the temperature for first stage around 20 ºC-120 ºC. The next stage shows the temperature take place at range between 125ºC-440 ºC which it is assign to the degradation of components of carbohydrates in the lignin samples, which are converted to volatile gases such as CO, CO_2, and CH_4. The last stage presented the degradation occured at wide range at the temperature 440 ºC and above which at this stage, the derivation of degradation volatile products from lignin along with the gas formation are getting removed be suggested that the lignin’s thermal properties are dependent on their source[6]. The weight loss is slow due to the decomposition of carbonaceous material retained in the char residue through aromatization reaction and cracking of carbon-hydrogen or carbon-oxygen bonding

[8]. From all the samples that was extracted, the lignin from sample 7mm had the greatest thermal stability and highest char yield of 83.06% followed by matured (71.94%), 10mm (65.12%), 5mm (51.10%), 9mm (46.44%), 8mm (33.24%), 4mm (30.41%), and lastly 6mm (18.95%).

Table 3: Value of maximum of thermal decomposition temperature (DTG_{max}) and unvolatized weight fraction at 800ºC

Lignin Samples (mm)	DTG (ºC)	Lignin residue (%) at 800ºC
4	315.12	30.41
5	318.11	51.10
6	318.50	18.95
7	317.27	83.06
8	316.21	33.24
9	315.51	46.44
10	315.17	65.12
Matured	326.41	71.94

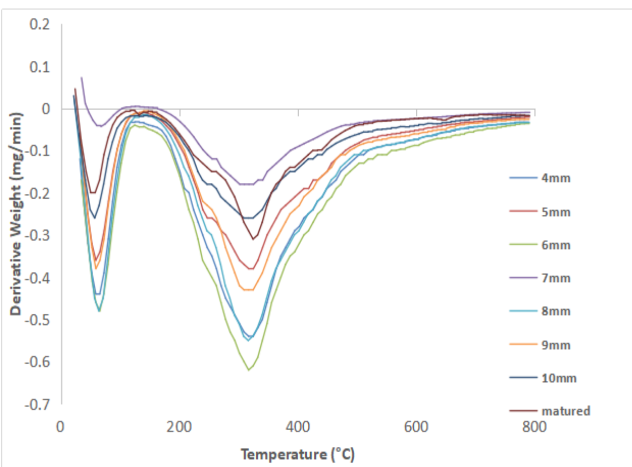

Fig. 6 Derivative TGA curves of lignin from LL pods samples with different length of seeds under nitrogen atmosphere at heating rate 10ºC/min.

Around 20%-80% of lignin samples still remained unvolatized at 800ºC due to the formation of highly condensed aromatic structures which have the ability to form char as shown in Table 3 and Fig. 6. DTG_{max} appeared between 315 and 330ºC for all lignin. In this region, pyrolytic degradation is expected to occur. This degradation process involves fragmentation of inter-unit linkages, releasing of monomers and derivatives of phenol into the vapor phase. Two visible peaks are observed in the range of temperature between 20 ºC-800 ºC. The first peak is mainly associated to the cleavage of the glycosidic bonds and the second peak is associated to fragmentation of other depolymerized units [8].

IV. CONCLUSION

In the present study, after extraction of Leucaena Leucocephala pods by using formic acid fractionation process, the result of dried samples was obtained, which is the sample of 7mm length of seed had the highest lignin yield of 34.64% while the lowest lignin yield from sample 6mm contain only 19.55%. Thermal characterization of lignin are analysed using pyrolysis process using thermogravimetric analysis equipment. Overall, lignin extracted from sample 7mm also had the greatest thermal stability and highest char yield of 83.06% and sample 6mm indicate the lowest yield of lignin.

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