

Determination of Chemical Composition and Structural Changes of Torrefied *Leucaena leucocephala* (Petai Belalang) Pellets via TAPPI Method/FTIR

Nor Atiqah Nor Azizan, Dr. Siti Wahidah Puasa and Sharmeela Matali

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— Alternative energy from renewable resources such as biomass can be used as a substitution to fossil fuel for a greener energy option. However, utilization of biomass has some limitations such as high ash and moisture content, low energy density, low heating value, and high energy is required for size reduction. Torrefaction which is also known as a mild pyrolysis pre-treatment can be implemented to upgrade the physical and chemical properties of biomass. This pre-treatment involves a moderate temperature above 200°C in the absence of oxygen. Torrefaction offers advantages in overcoming the problem arise associated with raw biomass. In this study, a potential energy crop, *Leucaena leucocephala*, a woody biomass will be studied for its energy purposs as to identify their potential usage as bioenergy fuel. The purpose of this study was to determine the chemical composition and structural changes of torrefied *Leucaena leucocephala* pellets by using TAPPI method and FTIR. The torrefaction process of the sample was conducted in a horizontal tube furnace at five different temperatures with 60 min of holding time. The chemical compositions and structural changes of torrefied products were compared to its raw forms. The results obtained show a decrease in cellulose and hemicelluloses and an increase in lignin content as torrefaction temperature became severe. It was concluded that as torrefaction temperature increases, high quality of biomass with low moisture and volatiles content was produced. The results obtained prove that torrefaction as pretreatment process improves the biomass properties.

Keywords: *Biomass; Torrefaction; Leucaena leucocephala; TAPPI method; FTIR*

I. INTRODUCTION

The dependence on fossil fuels as our main source of energy supply has caused greenhouse gas emissions and depletion in fossil fuel reserves. Therefore, biomass as a renewable and sustainable energy source has increasingly become of more interest among researchers and engineers alike. Biomass promotes an environmental friendly fuel by reducing CO₂ and sulfur emissions when compared to that of fossil fuels [1]. It is the most abundant renewable feedstock and low cost raw materials. Thus, optimal utilization of biomass can lead to sustainable industrial progress and low-carbon economy. However, utilization of biomass as biofuels has some limitations such as high ash and moisture content, low energy density, low heating value, and high energy is required for size reduction [1]. Nevertheless, torrefaction as a pretreatment process can be carried out in order to overcome these

problems as well as to convert biomass into compatible energy fuels [2].

Torrefaction can be defined as a mild pyrolysis pre-treatment that involves a moderate temperature above 200°C in the absence of oxygen. By implementing torrefaction in the processing steps, the chemical and physical properties of biomass can be upgraded. The calorific values are also increased throughout torrefaction process. During torrefaction, hemicelluloses which is one of the main components that make up biomass and the most reactive component decomposes by evolving H₂O and light acid compound as a major product including CO₂ and CO [3]. Torrefaction can improve fuel volumetric energy density as well as increase its grindability. On top of that, torrefaction is also identified as a pretreatment step for entrained flow gasification due to its high energy density, less energy consumption for size reduction process and has spherical shaped particles during grinding [4].

The purposes of this research study to be conducted are to determine the chemical composition of torrefied *Leucaena leucocephala* (LL) pellets by using Technical Association of the Pulp and Paper Industry (TAPPI) method as well as to determine the structural changes of raw and torrefied LL by using Fourier Transform Infrared Spectroscopy (FTIR). LL which is also known as “Petai Belalang” is one of the plant species in Malaysia that has the potential as a bioenergy crop material. It is categorized as woody biomass with high biomass productivity. LL is considered an important plant for utilization of biomass as it is a very fast growing species, productive a multipurpose tree and can be grown in wide range of soil [5]. The compositions to be determined are extractive content (TAPPI T 204 cm-97 [6]), lignin content (TAPPI T 222 om-02 [7]), and cellulose and hemicelluloses content (Wise’s chlorite method and TAPPI T-203 om-99 [8]).

II. METHODOLOGY

A. Materials

Leucaena leucocephala sample was collected from open areas around Section 7, Shah Alam, Selangor, provided by a lecturer of Universiti Teknologi Mara (UiTM). The sample used is in the form of pellets. The pellets were grinded into coarse particle by using mortar grinder and sieved using a sieve shaker in order to obtain desired particle size of less than 212 µm.

B. Torrefaction experiments

Before starting the torrefaction experiment, purging was done by allowing nitrogen gas continuously flowed into a horizontal tube furnace (MTI Corp., USA) equipped with a 80 mm-ID quartz tube reactor which was attached to a precision temperature controller. Purging was done at a rate of 1 L/min for a period of 15

minutes as to provide inert condition within the reactor. 20 g of LL sample was subjected to torrefaction furnace with continuous nitrogen flow at 100 mL/min. The LL sample underwent torrefaction process with five different torrefaction temperatures which were 200°C, 225°C, 250°C, 275°C, and 300°C. Slow heating rate of 10°C/min was set to maintain the homogeneity of products [9]. 60 minutes of holding time was set as to held LL sample for continuous torrefaction once the torrefaction furnace reached the desired temperature. As torrefaction experiments completed, furnace was left to cool down to room temperature and the samples were removed from the furnace. The torrefied sample was weighed and the mass yield was calculated according to Eq. (1).

$$\text{Mass Yield, MY (wt\%)} = (m_{\text{torr}}/m_{\text{raw}}) \times 100\% \quad (1)$$

where m_{torr} refers to mass of the torrefied LL and m_{raw} is mass of the raw LL.

C. Characterization experiments

The extractives content of LL sample was determined according to TAPPI 204 cm-97 [6]. 21g of LL sample was subjected to extraction with ethanol-toluene solvent in a Soxhlet apparatus for 6 hrs. The dried LL sample to solvent ratio is 1:10 g/mL-1 (21g of LL in 210 mL solvent) and the ratio of toluene to ethanol is 2:1 (140 mL toluene and 70 mL ethanol). The sample is removed from Soxhlet apparatus and dried in the oven at 60°C for 24 hrs and reweighed. Then, the residues were subjected to extraction with 95% ethanol for 4 hrs and then with water at 100°C for 2 hrs. The sample is dried and reweighed again.

The lignin contents of LL sample were determined using Kappa number (K) method according to TAPPI T-222 om-02 [7]. 1 g of LL sample was mixed with 20 ml of 0.02 mol/l KMnO_4 and 5 ml of 2.0 M H_2SO_4 . The mixture was stirred at 200 rpm for about 3 minutes. Then, the mixture was filtered to separate the solid sample from the solution. The filtrate was measured by using UV spectrophotometer at wavelength 546 nm and the absorbent reading was recorded as A_e . A blank solution consists of a mixture of KMnO_4 and H_2SO_4 was used and the absorbent was recorded as A_o . The lignin content and lignin degradation of LL sample was calculated based on Eqs. (2)-(4).

$$\text{Kappa number, } K = a/w [1-(A_e/A_o)] \quad (2)$$

where K = Kappa number, a = volume of 0.02 mol/l KMnO_4 solution used, w = mass in grams of LL sample used in the experiment.

$$\text{Lignin content (wt\%)} = 0.15K \quad (3)$$

$$\text{Lignin degradation (wt\%)} = \frac{[\text{Lignin (raw)} - \text{Lignin (treated)}]}{[\text{Lignin (raw)}] \times 100\%} \quad (4)$$

Hollocellulose which is composed of cellulose and hemicelluloses were determined according to TAPPI T-203 om-99 and Wise's chlorite method [8]. 4 g of LL sample was mixed with 50 ml distilled water. The solution was then treated with 2 ml acetic acid and 5 g of sodium chlorite at 70°C for 4 hrs. Later, 2 g of hollocellulose produced was treated with 50 ml of 17.5% NaOH and 70 ml distilled water. This was to separate the hemicelluloses from hollocellulose, leaving the α -cellulose. Then, the insoluble α -cellulose was filtered and washed with 50 ml of 8.3% NaOH. The hemicelluloses content was calculated based on Eq. (5).

$$\text{Hemicellulose (wt\%)} = 100\% - [\text{lignin (\%)} + \text{Cellulose(\%)}] \quad (5)$$

D. FTIR Analysis

FTIR was used to investigate the changes in the chemical structure of the solid torrefied biomass in terms characteristics of

functional groups as raw biomass was subjected to torrefaction process [10]. Spectrum One Spectrometer (Perkin Elmer, USA) (Plate 36) in accordance with ASTM E-1252 was used to determine the FTIR spectrum. 1 mg of LL sample was placed on a diamond surface. To ensure good contact, LL sample was pressed against it using stainless steel press rod with sufficient pressure in the range of 50 to 60 psi. LL sample was bombarded with infrared beam where the FTIR spectrum data obtained was measured and analyzed by the instrument's software. Wavenumber in the range from 4000 to 650 cm^{-1} with a standard solution of 4 cm^{-1} was used to record each of the spectrum. The absorption frequency spectra obtained were recorded and plotted and the existence of functional groups was compared against the standard IR-spectra of hydrocarbons.

III. RESULTS AND DISCUSSION

A. The effects of torrefaction on Mass Yield and Color Changes

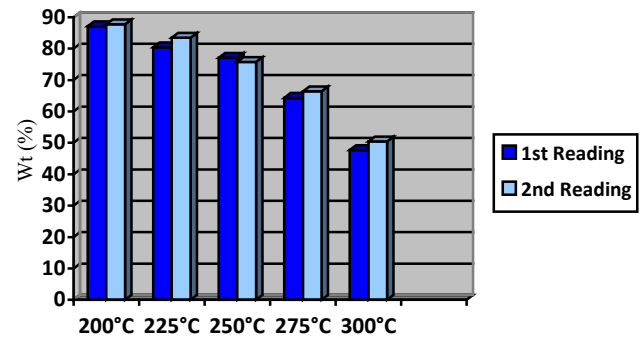


Figure 1: Effect of Torrefaction on Mass Yield

Figure 1 and Table 1 shows the effect of torrefaction on percentage of mass yield of LL. Mass yields refer to the solid remain after torrefaction process. From Figure 1, it can be observed that the mass yield for torrefied LL decrease as torrefaction temperature increase. The typical mass yield for torrefied biomass are in the range of 50 to 90wt% [11]. The loss of mass during torrefaction process was majorly caused by the thermal degradation of hemicelluloses and some short-chain lignin compound [12]. The highest mass yield of torrefied LL was at torrefaction temperature of 200°C, whereas the lowest mass yield of torrefied LL was at temperature 300°C where about half of its initial mass was lost. The mass loss implies to the moisture removal and volatiles (thermally unstable) [2].



Figure 2: The Effect of Torrefaction on Colour of the Torrefied Biomass

On the other hand, the observation also includes the colour of the torrefied LL. The colour of the torrefied LL sample became darker when torrefaction temperature increases. This was primarily due to the increase of the torrefaction temperature as well as the removal of moisture content during thermal treatment [2]. It can be concluded that as torrefaction temperature increase, the mass yield decrease and the colour of the torrefied LL sample became darker.

Table 1: Mass Yield of Torrefied LL

Sample	Initial Mass (g)	Final Mass (g)		Mass Yield (wt%)		Average Mass Yield (wt%)
		1 st	2 nd	1 st	2 nd	
Raw LLP	-	-	-	-	-	-
TLLP200	20	17.43	17.54	87.15	87.72	87.44
TLLP225	20	16.08	16.69	80.39	83.45	81.92
TLLP250	20	15.41	15.14	77.05	75.72	76.39
TLLP275	20	12.86	13.28	64.31	66.42	65.37
TLLP300	20	9.54	10.08	47.70	50.41	49.06

B. The effects of Torrefaction on Chemical Composition of LL

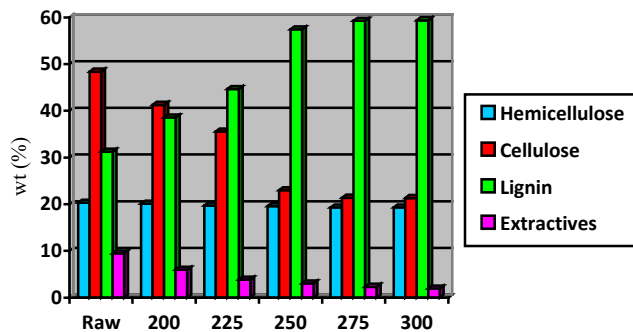


Figure 3: Effect of Torrefaction on Chemical Composition

Figure 3 and Table 2 show the effect of torrefaction on chemical composition of LL. For composition of extractives content, as torrefaction temperature increases the percentage of extractives content decreases. This behavior was caused by the reduction of the amount of tannins, gums, starches, sugars, dyes or pigments in the torrefied biomass [13]. The loss of these components was caused by thermal treatment of the biomass. Raw LL contains the highest amount of extractive content due to their nature of chemicals that present in the raw form. Besides that, the percentages of extractives content also affect the decomposition temperatures of cellulose and hemicelluloses. In this concern, a greater amount of extractives content will decrease the degradation temperature of the biomass components [14]. Biomass with high percentage of extractive content is not suitable for bioenergy application for thermal power. Thus, torrefied biomass at torrefaction temperature of 300°C is the most suitable to be used as biofuels.

Table 2: Chemical Composition of LL

Sample	Extractives (%)	Lignin (%)	Cellulose (%)	Hemicellulose (%)
Raw LL	9.46	31.25	48.40	20.35
TLLP200°C	5.96	38.60	41.27	20.13
TLLP225°C	3.84	44.68	35.59	19.72
TLLP250°C	3.03	57.45	22.99	19.56
TLLP275°C	2.32	59.30	21.38	19.32
TLLP300°C	1.93	59.39	21.32	19.29

Torrefaction also increases the lignin content of *Leucaena leucocephala*. As torrefaction temperature increases, the percentage of lignin content increases. This behavior was caused by increase in thermal decomposition of hemicelluloses and cellulose. Cellulose and hemicelluloses are the main component in biomass and they generally begin to decompose at temperature ranging from 250°C to 300°C [15]. Moreover, lignin is said to be the most difficult component to be degraded thermally. Nevertheless, high lignin content also improved and higher the energy value of the torrefied biomass [16].

Furthermore, as torrefaction temperature increases, the cellulose and hemicelluloses content decreases. During torrefaction process,

cellulose and hemicelluloses are the most affected as they are the main component in the biomass [13]. Cellulose and hemicelluloses are thermally unstable compared to lignin and thus, decompose at lower temperature. The decrease of cellulose and hemicellulose also caused by the reduction of volatiles [15]. Moreover, cellulose and hemicelluloses degrade in large amount at temperature 250°C to 300°C. High degradation of cellulose and hemicelluloses content in biomass will results in char-like material that is rich in lignin [12]. Thus, as cellulose and hemicelluloses decrease with increasing temperature, the lignin content increases. From Figure 3, raw biomass contains the highest cellulose and hemicelluloses compound. Meanwhile, torrefied biomass at 300°C has the lowest cellulose and hemicelluloses content.

These finding are close to the previous research that prove when torrefaction temperature became more severe, the mass yield, extractives, cellulose and hemicellulose contents decrease and lignin content increases. The removal of moisture content in torrefied biomass indicates the reduction in hydroxyl group during thermal treatment and thus, provides hydrophobic condition which can avoids decaying problem in wet condition [17]. The loss of extractives, cellulose and hemicelluloses during torrefaction process provide new structure of the biochar that is easy to grind [13]. The structure of the torrefied sample became brittle and improves the grindability [18]. In addition, high lignin content implies high energy density. The high lignin content at high torrefaction temperature results in higher energy value [16]. To conclude, torrefaction improves biomass properties by reducing the extractives, cellulose and hemicelluloses contents as well as increasing the lignin content.

C. FTIR Analysis

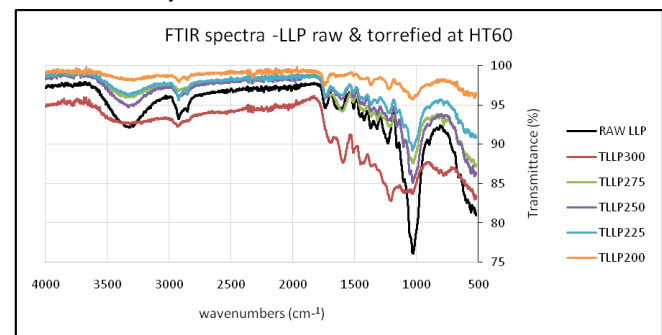


Figure 4: FTIR Spectra of Raw and Torrefied LL

In order to investigate the changes in chemical structure of the torrefied LL, FTIR spectroscopy was used. Figure 4 shows the FTIR spectra of raw and torrefied LL at holding time of 60 minutes. The structural changes occur were majorly due to the degradation of hemicelluloses in the biomass [19]. Through FTIR analysis, different types of functional groups contained in LL sample can be determined. From Figure 4, the FTIR spectroscopy of raw and torrefied LL were obtained in the range 4000 to 500 cm^{-1} .

Via FTIR plots, higher percentage of transmittance will signify less energy is being absorbed by the chemical bond. On the contrary, the lower the percentage of transmittance, the greater the energy is absorbed. Also, as the wavenumber increases, the frequency increases and the energy of the oscillating chemical bond also increases. Therefore, the bonds located at higher wavenumber are the stronger bond, whereas the bonds located at lower wavenumber are the weaker bonds. Various bonds of spectrum were identified with functional group O-H (3650-3200 cm^{-1} [12]), C-H (2960-2850 cm^{-1} [17]), C=O (1705-1750 cm^{-1} [13]), C-O-C (1150-1300 cm^{-1} [19]) and C-O (1000-1100 cm^{-1} [17]) groups. From Figure 4, it can be observed that the torrefied biomass have their functional group vibrations shifted towards lower wavenumbers. There are also changes in the intensity of each of the torrefied LL sample.

The strong and very broad peaks in the range of 3650 to 3200

cm^{-1} , which represent the O-H stretching frequency, were smaller for torrefied biomass compared to that of raw biomass. The changes of the intensity were because of the evolution of water [20]. For torrefied LL, lower water vapor was evolved as compared to the raw sample. Furthermore, the presence of O-H bonds also indicates the stability of phenols and alcohols in the sample [21]. Phenolic compound relates to lignin content that present in biomass [22]. This shows that lignin structure was not affected by torrefaction, however became relatively concentrated due to the increasing of carbon content [17].

Next, at peaks within 2960 to 2850 cm^{-1} represents the C-H stretching vibrations that are assigned to aliphatic groups. The spectral peaks were smaller for torrefied biomass than raw biomass. It can be observed from Figure 4 that the bands became flatter as torrefaction temperature increase. This is due to the reduction of H/C atomic in the torrefied biomass [12]. Moreover, these peaks also imply the evolution of carbon dioxide and methane [20].

As for peaks ranging from 1705 to 1750 cm^{-1} , they are related to the stretching vibrations of the C=O. These bands are related to oxygen functionalities in non-conjugated and conjugated system which is carbonyl or carboxyl group of hemicelluloses [19]. Likewise, the spectral peaks at this region were smaller for torrefied biomass compared to the raw biomass. This behavior is caused by the thermal degradation of hemicelluloses [12]. This thermal degradation of hemicelluloses is caused by deacetylation during the thermal treatment of the biomass [10]. This situation also depends on torrefaction process condition such as temperature, particle size, biomass type, and etc.

On the other hand, peaks ranging from 1150 to 1300 cm^{-1} represent the C-O-C asymmetric stretching vibrations. These bands are associated with the content of cellulose and hemicelluloses that are present in the biomass [12]. As can be observed from Figure 4, the intensity of bands in this region decrease for the torrefied biomass compared to raw biomass. As the severity of the torrefaction conditions increases, the intensity of these bands decreases. These show that as torrefaction temperature increase, the content of cellulose and hemicelluloses decrease.

Finally, the peaks in the range of 1000 to 1100 cm^{-1} represent the C-O stretching vibrations. These bands show the highest peak intensity for all samples. These bands also related to the content of cellulose and hemicelluloses in the biomass. Similarly, the spectral peaks were smaller for torrefied biomass compared to raw biomass. This is due to degradation of cellulose and hemicelluloses as torrefaction condition became more severe. These bands also can be associated to aromatic skeletal vibrations. Aromaticity refers to lignin as lignin is the only aromatic ingredient of biomass [10].

D. Recommendation

One of the recommendations to improve the research in the future is to analyze the chemical composition of LL by using other method such as through Thermogravimetric Analysis (TGA) or using microwave heating. Through this method, a comparison can be made between TAPPI method and the other methods used. The content of extractives, lignin, cellulose and hemicelluloses can also be obtained.

Besides that, further characterization research on LL can be done by using X-Ray Diffraction (XRD) analysis and Scanning Electron Microscopy (SEM). The energy properties of the raw and torrefied LL also should be investigated. Also, the optimal conditions for the torrefaction of LL can be investigated by using response surface methodology.

Lastly, it is suggested that the performance of torrefied *Leucaena leucocephala* when undergoing pyrolysis, gasification or combustion to be studied further. The effect of torrefaction on the yield of biomass pyrolysis, gasification or combustion can be analyzed. Other types of biomass also can be used such as corn stover/stalk, oil palm mill waste and etc.

IV. CONCLUSION

In this research study, LL was torrefied at various temperatures and the effect of torrefaction on the chemical composition and structural changes of the torrefied LL was examined in detail by using TAPPI method and FT-IR analysis, respectively. The raw LL was also characterized to study the chemical composition and structural changes of the raw sample. The raw LL was compared to the torrefied LL to study their potential usage as bioenergy fuel. As agreed by various previous researches, mass yield of the torrefied LL decreases as torrefaction temperature decreases. This is primarily caused by the loss of moisture content and volatiles such as hemicelluloses, partial cellulose and some short-chain lignin compounds during the torrefaction process. For chemical composition analysis, as torrefaction temperature increases the percentage of extractives content decreases. This behavior was due to the reduction of the amount of tannins, gums, starches, sugars, dyes or pigments in the torrefied biomass during thermal treatment. On the other hand, torrefaction increase the lignin content of LL which is due to increased thermal decomposition of hemicelluloses and cellulose. Besides that, as torrefaction temperature increases, the cellulose and hemicelluloses content decreases as these components are the main component in the biomass and thermally unstable, thus most affected due to higher temperature exposure during heating. Lastly, for FTIR analysis, various bonds of spectrum have been identified with various functional groups. Lignin content that is related to phenolic compound was observed around O-H stretching vibrations region. Cellulose and hemicelluloses contents are observed around C-O-C and C-O spectrum vibrations. It is observed that at higher torrefaction temperature, the intensity of the peaks for torrefied biomass decrease. As a conclusion, torrefaction of LL has been successfully done and the effect of the torrefaction on chemical composition and structural changes has been investigated. The results obtained prove that torrefaction process improves the biomass properties. Through torrefaction process, high quality biochar can be produced and thus, LL has high potential to be used as a bioenergy feedstock.

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