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# Chemical Modifications of Torrefied Palm Kernel Shell Using COMB Method

N Rumbang[1], Karelius[2], M Dirgantara[3,*], K G Suastika[3]

[1]*Department of Agriculture Cultivation, University of Palangka Raya, Palangka Raya, Indonesia*
[2]*Department of Chemistry, University of Palangka Raya, Palangka Raya, Indonesia*
[3]*Department of Physics, University of Palangka Raya, Palangka Raya, Indonesia*
**Corresponding author. Email: dirgantaramade@mipa.upr.ac.id*

## ABSTRACT

Torrefaction is a thermochemical process to improve the properties of biomass as a solid fuel. In addition to solid fuel, the torrefaction process also produces a by-product in the form of liquid smoke from condensation results. In this study, an analysis of lignocellulose and Fourier Transform Infrared Spectroscopy (FTIR) on torrefied palm kernel shells with a particle size of 0.5 cm using the COMB (Counter Flow Multi-Baffle) reactor at a temperature of 250 ºC and a heat flow rate of 4 cm3/min. Liquid smoke was analyzed using GC-MS. Results showed that after torrefaction, hemicellulose decreased from 20.6% to 8.52%, cellulose 38.40% to 22.18%, and lignin from 20.75% to 18.36%. The results of lignocellulose analysis were supported by FTIR analysis showing that the torrefaction temperature of 250 ºC did not change the structure of lignocelluloses but reduced the content of lignocellulose. The GC-MS analysis of liquid smoke showed that volatile organic compounds (VOC) resulted from the torrefaction process was composed of acetic acid (62.16%), alkane (24.24%), phenol (10.41%), alcoholic compounds other than phenol (1.24%) and polysaccharides (1.95%). The levels of acetic acid, aldehyde, and phenol that were dominant in the condensate imply that the lignocellulose component, which was dominantly degraded during torrefaction at 250 ºC were hemicellulose, cellulose followed by lignin.

***Keywords:*** *Counter Flow Multi-Baffle, Liquid Smoke, Palm Kernel Shell, Torrefaction*

## 1. INTRODUCTION

The thermochemical process of torrefaction is an incomplete pyrolysis process, with the heating process between 200°Cand 300 °C in an inert atmosphere for improving the disadvantages of lignocellulosic biomass [1-2]. Biomass Torrefaction is gaining attention as an important preprocessing step to improve the quality of biomass in terms of physical properties and chemical composition [1]. In addition, torrefaction yield can vary between 24% and 95% of the original raw biomass weight [3]. Usually, the process caused degradation of mostly hemicelluloses. To a lesser extent, celluloses and lignin, it is mean that biomass with higher hemicellulose content will result in a lower yield. In contrast, biomass with lower hemicellulose gives higher yield value [3-4]. The torrefaction process also produces a by-product in the form of liquid smoke from condensation results.

Currently, available torrefaction technologies are basically designed and tested for woody biomass and utilization of the agricultural biomass as a fuel [5-6]. One of the latest torrefaction methods developed by the Korea Institute of Energy Research (KIER) is biomass torrefaction using counter flow multi-baffle (COMB) technology which currently also exists in Indonesia precisely at Lampung University. This technology has the advantage of low gas to solid ratio (G/S), short residence time (~5 min), constant difference (driving force) temperature along the column, simple, flexible and movable [7].

In this study an analysis of lignocellulose and Fourier Transform Infrared Spectroscopy (FTIR) before and after torrefaction process. One of the potential biomass in Indonesia is palm kernel shells prepare with a condition of passing 0.5 cm sieve using the COMB: Counter Flow Multi-Baffle method at a temperature of 250 ºC with a heat flow rate of 4 cm3/min. Beside that liquid smoke produced from this process is analyzed by GC-MS. Knowing the chemical modification of torrefied palm kernel shell can be parameters to determine the success of thermochemical process.

**Table 1.** FTIR-band assignment for the lignocellulosic component

| Wavenumbers ($cm^{-1}$) | | Functional group | Polymer |
|---|---|---|---|
| Torrefied Palm Shell | Raw Palm Shell | | |
| 1035,81 | 1033,88 | C-O groups (β-1,4-glycoside bonding) | Cellulose |
| 1163,11 | 1165,04 | C-O-C asymmetrical-stretching vibration | Cellulose and hemicellulose |
| 1329 | 1330,93 | $CH_3$ symmetrical angular vibration | Cellulose and hemicellulose |
| 1381,08 | 1377,22 | C–H deformation | Cellulose and hemicellulose |
| 1431,23 | 1431,23 | $CH_2$ bending vibration in olefin | Cellulose and hemicellulose |
| - | 1458,23 | $CH_3$ asymmetrical angular vibration<br>$CH_2$ bending vibration | Cellulose and hemicellulose |
| 1518,03 | 1510,31 | Aromatic skeleton vibration | Cellulose |
| 1612,04 | 1610,61 | C=C-stretching vibration<br>COOH groups stretching vibration in an aromatic ring | Cellulose, hemicellulose, lignin |
| 1710,92 | 1728,28 | C=O-stretching vibration in ester groups | hemicellulose |

## 2. METHOD

### *2.1. Raw Material Preparation*

The raw material for palm kernel shells was obtained from palm oil production of PT. Mulia Agro Permai Mill, Kotawaringin Timur Regency, Central Kalimantan. Samples were dried under the sun to reduce the moisture content until less than 5% and left in an airtight bag for 2 more weeks then sieved with a size of 0.5 cm [6, 8].

### *2.2. Torrefaction*

The torrefaction process was carried out at the Integrated Agriculture Laboratory, Tropical Biomass Research and Development Centre, Lampung University. The torrefaction reactor used in this experiment was COMBTM (Counter Flow Multi-Baffle) with the principle of heating work on raw materials using hot air which was blown with a blower with a certain flow rate so that it occurred in contact with raw materials in certain holding time [7].

In previous research had shown that at a temperature of 300 °C there was a high increase in calories in biomass, there was going to be a large mass loss in the process. At a temperature of 200 °C, the increase in calorific value was not significant, the temperature of 250 °C becomes the optimum temperature for the biomass faction process such as pine wood and corn cobs [16]. The torrefaction processing this study was using palm shell biomass with particle size passed 0.5 cm, at a temperature of 250 °C with a heat flow rate of 4 cm3/minute.

### *2.3. Lignocellulosic, FTIR, and GC-MS Analysis*

Lignocellulose analysis was performed using gravimetric methods to determine hemicellulose, cellulose and lignin levels. FTIR analysis aims to see changes in functional groups due to the torrefaction process. The samples are analyzed before and after torrefaction. The Torrefaction process has a by-product in the form of condensate, which generally can be used in various applications such as latex thickener. GC-MS is used to analyze condensate content from the torrefaction process.

## 3. RESULTS AND DISCUSSION

Lignocellulosic analysis shows after torrefaction, hemicellulose decreased from 20.6% to 8.52%, cellulose 38.40% to 22.18% and lignin 20.75% to 18.36%. These results indicated that there was a decrease in lignocellulose content due to thermal degradation during the torrefaction process. The changes in the chemical properties of palm shells before and after torrefaction of palm shells resulting from torrefaction process, analysis was carried out using FTIR [9], and GC-MS analysis was also applied on liquid smoke as a by-product of torrefaction to see what compounds are formed and condensed as a result of thermal degradation during the torrefaction process took place. Figure 1 show the spectra of FTIR raw palm shell and torrefied palm shell.

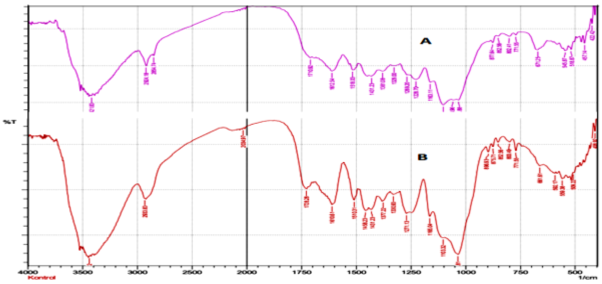

**Figure 1** Spectra IR (A) Torrefied Palm Shells; (B) Palm Shells

In general, there is no significant difference in the FTIR uptake pattern in raw palm shells and torrefied palm shells (Figures 1A and 1B). What generally occurs is a decrease in absorption intensity especially in the absorption area that is a characteristic for cellulose and hemicellulose [10]–[12]which shows no structural changes to lignocellulose after torrefaction, but only a reduction in the percentage of lignocellulose during the torrefaction process. FTIR-band assignment for the lignocellulosic component is shown in Table 1.

Nevertheless, the FTIR spectrum shown in Figures 1A and 1B show the difference in absorption patterns and loss of absorption in some wavenumbers. As in the wavenumber of 3417.86 cm-1 shows the existence of a stretching vibration OH experiencing a shift towards the wavenumber 3425.58 cm-1. Shifting towards this larger wavenumber indicates that the OH stretching vibration is in a more rigid state (affected by hydrogen bonds), as well as the loss of uptake of 2034.97 cm-1 is a vibration absorption from a combination of CH and OH stretching [13] (Figure A) caused by the reduction of hydrogen-bonded molecules or compounds with the -OH group belonging to cellulose. In addition, the uptake that appeared on the palm shell FTIR spectra at wavenumber 1458.23 cm-1 showed CH3 asymmetrical angular vibration and CH2 bending vibration for cellulose and hemicellulose are no longer seen in the FTIR spectra of the torrefied palm shell, which shows there has been a thermal degradation of lignocellulose in the palm shell especially hemicellulose.

In order to support the FTIR data, GC-MS analysis was carried out on the liquid smoke from the torrefaction. GC chromatograms and MS results of chemical compounds in liquid acids can be seen in Figure 2 and Table 2.

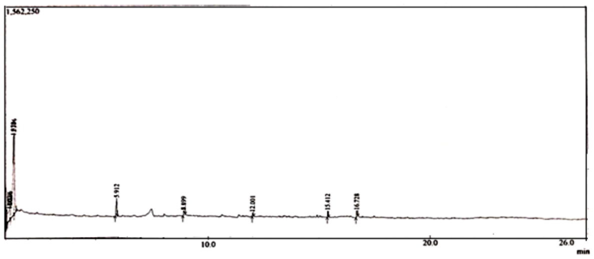

**Figure 2** Chromatogram (GC)of Liquid Smoke

The GC-MS analysis of liquid smoke, which is one of the results of torrefaction aims to find out what compounds are formed from the results of the thermal degradation of the palm shell in the torrefaction process. In addition, GC-MS analysis was carried out to predict the bonding process that occurs in the chemical components of the palm shell, both hemicellulose, cellulose, and lignin. Based on the results of GC-MS analysis, it can be seen that at a temperature of 250 oC volatile organic compounds (VOC) produced then condensed as liquid smoke mostly are acetic acid (62.16%), alkanal or aldehyde compounds (24.24%), Phenol (10.41%), alcohol compounds other than phenol (1.24%) and polysaccharides (1.95%).

**Table2**. The result of GC-MS Chemical Compounds in Liquid Smoke

| No | Compound Name | Ret Tim (Min) | m/z | Concentration (%) |
|---|---|---|---|---|
| 1. | n-octanal<br>Acetic Acid | 1,059 | 44 | 19,59 % |
| 2. | Acetic Acid | 1,372 | 60 | 62,16 % |
| 3. | Phenol | 5,912 | 94 | 10,41% |
| 4. | n-Fentanyl | 8,901 | 44 | 2,87% |
| 5. | 5-hydroxy-2,7 dimethyl-4-octanol | 12,003 | 69 | 1,24% |
| 6. | 4-hydroxy-3-methoxy-benzaldehyde | 15,412 | 151 | 1,78% |
| 7. | 1,6-anhydrous-beta-D-Glucopyranosa | 16,724 | 60 | 1,95% |

Thermal degradation in the torrefaction process occurs gradually. At temperatures of 200-240 °C, the decomposition of hemicellulose and cellulose begins to become a solution of pyrolignite (low boiling organic acids such as acetic acid, formic acid, and methanol, wood gas (CO and CO2)), a little tar. At 240-400 °C, depolymerization occurs and the CO and CC bonds break. In this temperature range cellulose is degraded, lignin begins to decompose to produce tar, pyrolignite solution, and CO gas decrease, whereas CO, CH4, and H2 gases increase [14].

Hemiselulosa polymers are degraded first compared to lignin and cellulose because hemicellulose has the lowest molecular weight among other lignocelluloses. Chemical compounds resulting from thermal degradation of hemicellulose are mostly acetic acid, alkanal or aldehyde, and ketone.

The mechanism of the formation of acetic acid chemically resulted from the rearrangement of carbon both originating from hemicellulose begins with the process of breaking and breaking the chain of chemical bonds that produce unstable radical compounds such as CHO*, CH2OH*, OH*, H*, O*, and C *

For an instance, the reaction between CHO* and CH2OH* will form mutually reaction to form stable new compounds such as CH3COOH and other carbonyl compounds such as aldehydes and ketones. Other radicals such as carbon atom radicals will experience rearrangement to form aromatic compounds [15].The decomposition of lignin is characterized by the formation of phenol compounds in torrefaction liquids. The content of phenols in torrefaction liquids is influenced by the lignin content of the material and the temperature of the torrefaction. Lignin does not have repeat units like hemicellulose and cellulose but consists of complex phenolate units which are very stable and difficult to separate and have various shapes, so that they will only decompose at high temperatures [16]. The 1,6-anhydrous-beta-D-Glucopyranosa compound is probably the result of degradation of the cellulose (there is a pyran ring). While other more complex compounds such as 5-hydroxy-2,7 dimethyl-4-octanol, 4-hydroxy-3-methoxy-benzaldehyde are other compounds resulting from thermal degradation of torrefaction.

## 4. CONCLUSIONS

Torrefaction palm kernel shells using the COMB reactor at a temperature of 250 ºC and 4 cm3/minute flow rate, do not change the structure of lignocellulose but cause a decrease in lignocellulose composition due to thermal degradation. Volatile organic compounds (VOC) resulted from the torrefaction process condensed as liquid smoke that is mostly acetic acid (62.16%), alkanes (24.24%), phenols (10.41%), alcoholic compounds other than phenol (1.24%) and polysaccharides (1.95%) %). The level of acetic acid, aldehydes, and phenols that are dominant in the condensate of torrefaction showing that the lignocellulose component which is dominantly degraded during torrefaction at a temperature of 250 ºC is hemicellulose, cellulose followed by lignin degradation.

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