Efficacy of Hydrothermal Treatment for Production of Solid Fuel from Oil Palm Wastes

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1. Introduction

Oil palm is a perennial crop that has higher productivity than other oil-producing crops. One hectare of oil palm plantation produces approximately 3.68 ton oil/year, which is much higher than for rapeseed (0.59 ton/year), soybean (0.36 ton/year), and sunflower (0.42 ton/ha) [1]. Crude palm oil (CPO) has become a more valuable commodity owing to recent price increases on international markets.

Until 2006, Malaysia was a leader in crude palm oil (CPO) production in the world. However, their limited land for expansion of plantation slows down the production rate. In contrast, Indonesia still has a huge amount of uncultivated land enabling extensive development of palm oil industry. Within 1995-2006, Indonesian plantation area jumped around three times into 6.6 million Ha. Such rapid expansion enhanced its annual CPO production. In 2008 Indonesia produced 19.33 million ton of CPO whereas Malaysia produced 17.63 million ton. Totally, both countries contributed around 85.9 % of world's palm oil production [2].

Despite its benefit, the palm oil industry generates a huge amount of biomass waste. As the continued growth of the industry, the amount of waste produced also significantly increases. Based on location where the waste is collected from, it can be divided into two types: waste from harvesting and replanting activity in plantation fields and waste from the milling process in palm oil mill.

Oil palm frond and trunk belong to first type of biomass waste. Zakaria [3] mentions that around 10.4 ton/ha of frond is generated annually from regular pruning, while around 14.4 ton/ha of frond and 75.5 ton/ha of trunk are obtained from replanting (once in 25 years). The second type of biomass waste are the empty fruit bunch (EFB), fiber, and shell, corresponding to approximately 22%, 11% and 8%, respectively, of the amount of fresh fruit bunch processed in a mill. In case of Indonesia, a total of 43.05 million ton of frond and 13.94 million ton of trunk

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were approximately generated in 2005 [4]. In addition, the Indonesian Oil Palm Research Institute (IOPRI) estimates that Indonesian mills generated approximately 15.9 million ton of EFB, 9.0 million ton of fiber and 4.8 million ton of shell during 2005.

In order to reduce negative impact of the waste into the environment, as well as to obtain more added values, extensive works have been conducted. For example, frond, trunk, and EFB are simply returned to plantation fields as an organic fertilizer, either directly or by pre-composted. In contrast, fiber and shell are used for boiler fuel in palm oil mill. However, such utilization methods face a common problem.

Decomposition of waste in plantation fields generates CO_2 and CH_4 (considered as green house gas) coupled with unpleasant smells, which can last for up to 1 year. In addition, high transportation and distribution cost, water pollution by the rest oil (in EFB), and its attractiveness for beetles and snake have been a number of obstacles that hardly are solved [5]. On the other hand, the direct use of shell and fiber in boiler is constrained by their relatively high moisture content which lowers the heating value. They also can not be stored for a long period of time due to decomposition. Since the amount of waste increases rapidly recently, a more effective technology to handle the waste is highly desired.

This chapter discusses on application of hydrothermal treatment for handling of oil palm waste at laboratory scale. Hydrothermal treatment refers to a thermochemical process for decomposing carbonaceous materials such as coal and biomass with water in a high temperature and high pressure condition. The use of such method for processing biomass was firstly developed by Bobleter and his co-workers [6] and had attracted much attention for hydrolysis of lignocellulosic materials since then.

This method relies on fact that water in subcritical/supercritical condition has outstanding characteristics. At ambient temperature, water is polar and it has an infinite network of H-bonding, and does not solubilize most organics. As water is heated, the H-bonds start weakening, allowing dissociation of water into hydronium ions (H_3O^+) and hydroxyl ions (OH^-). In the subcritical region, the ion product (K_w) of water increases with temperature and it is about 3 orders of magnitude higher than that of ambient water and the dielectric constant (ε) of water drops from 80 to 20. A low dielectric constant allows subcritical water to dissolve organic compounds, while a high ion product allows subcritical water to provide an acidic medium for the hydrolysis of biomass components. Although this dielectric constant of the subcritical region is low enough for organic to be soluble, it remains high enough to allow salt dissolution. In addition, the physical properties of water, such as viscosity, density, dielectric constant, and ion product, can be tuned by changes in temperature and/or pressure in the subcritical region [7].

Compared to other thermo-chemical conversion methods such as pyrolysis and gasification, the temperature for hydrothermal treatment is much lower (200–500°C for hydrothermal, compared with 450–550 °C for pyrolysis and 900–1200°C for gasification) [8,9]. In addition, biomass conversion takes place in a wet environment, so high moisture content of feed biomass is not an issue. The role of water in the treatment is not only as a medium, but also a chemical reactant on decomposition. A contrast situation is found on pyrolysis and gasification which have a limitation on moisture content of the feed [9,10]. Therefore, such method is suitable for treating biomass with high moisture content, such as agricultural wastes which contain more than 50 wt. % of moisture in fresh condition.

Many studies using hydrothermal treatment have been conducted, but most of these used the method as a biomass pretreatment step in bio-ethanol production [11–14]. Few studies have considered benefits of the resulting solid. The focus of the present chapter is experimental study on upgrading of oil palm waste into solid fuel by hydrothermal treatment.

2. Experimental

2.1. Materials

Oil palm waste is collected from an oil palm plantation and oil palm mill in southern Sumatra, Indonesia. Prior to use, each material is air-dried and is then pulverized to form powder with a maximum particle size of 1 mm by cutting-grinding (except for oil palm shell by impact-grinding) using IKA MF apparatus. The composition of the waste material is determined using a procedure recommended by the US National Renewable Energy Laboratory that is substantially similar to ASTM E1758-01. The detailed procedure of the chemical analysis will be explained further in section 2.3. The analysis results are listed in Table 1.

Component	Frond	Trunk	Fiber	Shell	EFB
Cellulose (wt. %, d.b)	31.0	39.9	19.0	14.7	35.8
Hemicellulose (wt. %, d.b)	17.1	21.2	15.2	16.4	21.9
Klason lignin (wt. %, d.b)	22.9	22.6	30.5	53.6	17.9
Wax (wt. %, d.b)	2.0	3.1	9.1	2.3	4.0
Ash (wt. %, d.b)	2.8	1.9	7.0	2.3	3.0
Others (by difference)	24.2	11.3	19.2	10.7	17.4

d.b, dry basis

Table 1. Composition of raw materials

2.2. Apparatus and experimental procedure

Experiments are carried out in a 500-mL batch-type autoclave (Taiatsu Techno MA 22) equipped with a stirrer and an automatic temperature controller. The autoclave has a maximum temperature of 400°C and a maximum pressure of 30 MPa. It is made from hastelloy with the dimension 6.0 cm ID x 20.6 cm L. A slurry of 300 mL of water and 30 g of waste material is loaded into the autoclave. A stream of N_2 gas is used to purge air from the autoclave and to maintain an initial internal pressure of 2.0 MPa. With stirring at 200 rpm, the autoclave is heated by an electric furnace to the target temperature at an average rate of 6.6°C/min. The target temperature, ranging from 200 to 380°C, is automatically adjusted. The reaction temperature is measured by K-thermocouple inserted into vessel of autoclave. Once the target temperature is reached, the sample is held for a further 30 min before the autoclave is cooled to ambient conditions by air blow using an electric blower.

After cooling, the gas products are fed into a gasometer (Shinagawa DC-1) to measure the volume. The gas is sampled using a microsyringe (ITO MS-GANX00) and its composition is determined by gas chromatography with thermal conductivity detection (Shimadzu GC-4C). The remaining slurry is filtered using an ADVANTEC 5C filter and a water aspirator. The solid part is dried to a constant weight in an oven at 105°C to yield the final solid product.

2.3. Analysis

The solid products are characterized using several techniques. The elemental composition is measured using Yanaco CHN Corder MT-5 and MT-6 elemental analyzer. The cellulose, hemicellulose, and lignin contents are measured using a procedure recommended by the US National Renewable Energy Laboratory [15]. In brief, the wax content is determined by a soxhlet extraction of 5.0 g of sample (particle size ≤0.5 mm) with ethanol. Approximately 150 mg of dewaxed and dried sample is then treated with 1.5 mL of 72 w/w% H_2SO_4 at 30°C for 1 h. Further, 42 mL of H_2O is added to the mixture followed by hydrolysis at 121°C for 1 h in an autoclave. The resulting mixture is washed several times using a hot water and filtered by a GP glass filter (pore size of 16 μm) in a vacuum condition. The obtained solid residue is dried at 105°C to a constant weight and its weigh is noted as klason lignin. Meanwhile, prior to being analyzed in HPLC, the filtrate is treated by an On Guard IIA column and 0.2 μm membrane filters to assure no residual solid and H_2SO_4 contained. The HPLC system is consisted of a KC-811column (JASCO) and refractive index (RI) detector (RI-2031, JASCO) and is operated under a 2 mM $HClO_4$ flowing at a rate of 0.7 ml/min and oven temperature of 50°C. The polysaccharide concentration is determined by measuring the corresponding sugar concentration with a correlation:

$$\text{cellulose (wt.\%)} = \text{glucose (wt.\%)} \times 0.9 \tag{1}$$

$$\text{hemicellulose (wt.\%)} = \text{(xylose + arabinose) (wt.\%)} \times 0.88 \tag{2}$$

Additionally, proximate, total sulfur and calorific analyses are carried out according to JIS M 8812, JIS M 8819, and JIS M 8814, respectively. The equilibrium moisture content (EMC) of raw materials and the corresponding solid products is determined according to JIS M 8811. Hence, an aliquot of the sample is placed in a desiccator containing saturated salt solution. The relative humidity inside desiccator is maintained at 75 %. After equilibrium is reached, it is quickly measured using a Sartorius MA 150 moisture content analyzer. Identification of the chemical structure and functional groups is performed on a Fourier-transform infrared (FTIR) spectrometer (JASCO 670 Plus) using the KBr disk technique. Cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra are measured on a solid-state spectrophotometer (JEOL CMX-300) with the following conditions: 10,000 scans; contact time, 2 ms; spinning speed, >12 kHz; pulse repetition time, 7 s. The spectrum is calibrated using hexamethyl benzene. Curve fitting analysis of the spectrum is performed using Grams/AI 32 ver. 8.0 software.

3. Results

3.1. Solid products and properties

The yield and properties of the solid products for different treatment temperatures are presented in Table 2 and 3. Due to the degradation reactions, the solid product yield decreases at elevated temperature, indicating the degradation reactions accomplish more completely. For instance, the solid yield at 200°C for all materials ranges from 58.3 to 67.7 wt.%. Meanwhile, their yields are only 31.7–37.3 wt.% at 380°C. Solid yield for oil palm shell and fiber are the highest among the oil palm wastes, particularly for ≥ 270°C treatments.

Properties	Raw	Treatment temperature (°C)						
(a) Frond		200	240	270	300	330	350	380
Solid yield (wt.%, db)		58.3	52.0	42.5	38.4	36.7	35.1	34.4
Fixed carbon (wt.%, daf)	17.5	20.5	29.7	45.9	48.1	52.3	54.8	62.6
Volatile matter (wt.%, daf)	82.5	79.5	70.3	54.1	51.9	47.7	45.2	37.4
Ash (wt.%, db)	1.8	1.3	1.3	1.2	1.0	0.7	0.8	1.8
Equilibrium Moisture (wt.%, ar)	14.7	7.6	6.4	5.5	5.2	5.0	5.2	5.0
Gross calorific value (MJ/kg, db)	18.4	20.2	22.6	26.3	27.1	28.8	29.4	30.9
(b) Trunk								
Solid yield (wt.%, db)		67.7	56.9	41.7	38.7	36.9	35.3	33.7
Fixed carbon (wt.%, daf)	16.1	16.2	26.6	45.1	48.8	52.8	55.0	63.6
Volatile matter (wt.%, daf)	83.9	83.8	73.4	54.9	51.2	47.2	45.0	36.4
Ash (wt.%, db)	2.2	1.8	1.8	2.2	2.1	1.9	2.1	2.9
Equilibrium Moisture (wt.%, ar)	13.6	7.5	6.5	5.1	4.8	4.6	4.5	4.1
Gross calorific value (MJ/kg, db)	18.3	19.5	22.1	26.4	27.4	28.9	29.0	30.0
(c) Fiber								
Solid yield (wt.%, db)		67.5	61.9	43.3	42.5	41.0	37.3	39.6
Fixed carbon (wt.%, daf)	17.8	23.8	28.5	37.4	36.8	37.2	46.6	48.2
Volatile matter (wt.%, daf)	82.2	76.2	71.5	62.6	63.2	62.8	53.4	51.8
Ash (wt.%, db)	7.0	6.5	6.4	9.7	9.0	10.2	11.0	8.6
Equilibrium Moisture (wt.%, ar)	13.0	6.9	6.4	5.1	5.1	4.2	4.3	3.6
Gross calorific value (MJ/kg, db)	19.8	22.1	23.7	27.4	29.4	29.9	30.0	30.6
(d) Shell								
Solid yield (wt.%, db)		63.2	57.6	48.3	45.6	39.6	38.9	37.3
Fixed carbon (wt.%, daf)	19.9	25.3	31.7	44.0	50.2	56.2	59.1	65.6
Volatile matter (wt.%, daf)	80.1	74.7	68.3	55.7	49.8	43.8	40.9	34.4
Ash (wt.%, db)	2.3	1.6	2.0	1.9	1.6	1.3	1.1	2.7
Equilibrium Moisture (wt.%, ar)	9.9	6.7	5.5	4.6	4.0	3.6	3.4	3.1
Gross calorific value (MJ/kg, db)	20.8	22.8	24.8	27.4	28.6	29.2	30.0	32.1
(e) EFB								
Solid yield (wt.%, db)		64.1	55.2	40.2	37.0	36.0	33.5	31.7
Fixed carbon (wt.%, daf)	18.6	17.3	26.0	42.8	42.5	49.3	51.7	59.8
Volatile matter (wt.%, daf)	81.4	82.7	80.0	57.2	57.5	50.7	48.3	40.2
Ash (wt.%, db)	3.0	2.6	2.4	2.9	3.5	2.7	3.1	4.2
Equilibrium Moisture (wt.%, ar)	11.8	8.1	5.8	5.2	4.1	4.0	3.5	3.2
Gross calorific value (MJ/kg, db)	18.4	20.1	22.6	26.8	28.9	30.0	30.8	31.1

db, dry basis; ar, as received basis; daf, dry ash-free basis

Table 2. Yield, proximate analysis and gross calorific value of the raw materials and solid products.

	Percentage component (wt.%, daf)							
(a) Frond	Raw	200°C	240°C	270°C	300°C	330°C	350°C	380°C
C	47.2	53.6	58.6	69.4	71.1	73.9	75.1	78.5
H	5.9	5.7	5.4	4.9	4.9	4.9	4.8	4.6
N	0.2	0.2	0.3	0.4	0.4	0.4	0.4	0.5
O (difference)	46.6	40.4	35.7	25.3	23.5	20.7	19.5	16.2
S	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
(b) Trunk								
C	47.5	51.4	57.5	69.3	71.4	73.4	75.3	78.2
H	5.9	5.9	5.6	5.1	5.0	4.9	4.9	4.5
N	0.5	0.4	0.6	0.8	0.8	1.0	1.0	1.1
O (difference)	45.9	42.1	36.2	24.6	22.6	20.6	18.6	16.1
S	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1
(c) Fiber								
C	50.7	59.2	61.0	71.9	73.0	76.1	77.0	80.0
H	6.9	6.6	6.4	6.6	7.1	7.3	6.7	5.9
N	2.5	1.3	1.2	1.6	2.2	2.4	2.7	1.5
O (difference)	39.2	32.7	31.3	19.8	17.5	13.9	13.4	12.5
S	0.6	0.1	0.1	0.2	0.2	0.2	0.2	0.2
(d) Shell								
C	50.6	57.1	62.2	70.8	72.4	72.2	74.3	80.9
H	5.9	5.7	5.6	5.4	5.0	4.7	4.5	4.8
N	0.4	0.4	0.4	0.6	0.5	0.6	0.6	0.7
O (difference)	43.0	36.8	31.8	23.1	22.1	22.5	20.5	13.5
S	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.1
(e) EFB								
C	46.9	51.6	57.1	70.5	71.8	74.1	77.0	79.9
H	6.3	6.3	6.0	5.6	5.4	5.7	5.7	5.1
N	0.5	0.5	0.5	0.8	0.8	0.9	1.0	1.1
O (difference)	46.2	41.6	36.3	23.0	22.0	19.2	16.2	13.8
S	0.1	0.0	0.0	0.1	0.0	0.1	0.1	0.1

daf, dry ash-free basis.

Table 3. Ultimate analysis of the raw materials and solid products.

The reaction has also changed both the physical and the chemical properties of the materials. Like other biomass materials, oil palm wastes have very high volatile content (between 80.1 and 83.9 wt.%), in contrast to the low fixed carbon (between 16.1 and 19.9 wt.%). Progressive decomposition reactions occur at higher temperature, leading to an increase in fixed carbon content and a decrease in volatile content. Treatment at 380°C increases the fixed carbon content to approximately 48.2–65.6 wt.% and decreases the volatile content to 34.4–51.8 wt.%. The data suggest that carbonization and devolatilization occur during treatment. This leads to an increase in gross calorific value of the solid product (Table 2). Among the products, solids obtained from treatment of shell have the highest fixed carbon and the lowest volatile content.

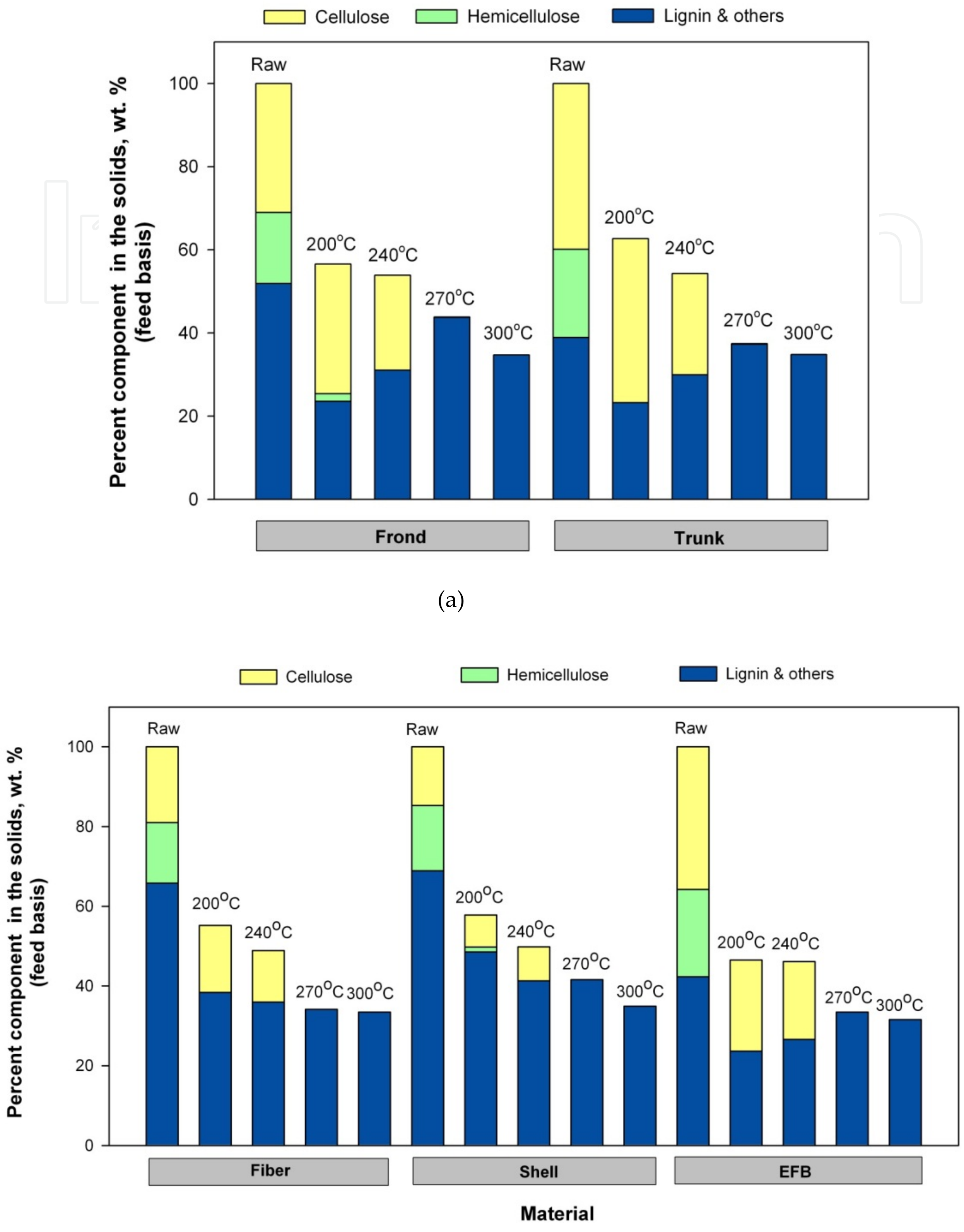
The calorific value is correlated with the elemental composition of a solid. The data in Table 2 show that an increase in calorific value is correlated with an increase in carbon content and a decrease in oxygen content (Table 3). Compared to the raw material, the solid produced at 380°C has approximately ~67% higher carbon content and ~65% lower oxygen content. These results suggest that components degraded and removed from the materials are mainly oxygen-rich compounds. The data in Tables 2 and 3 suggest that remarkable changes in solid properties occur in 200–270°C range. For instance, a 270°C treatment increases the gross calorific value of fiber from 19.8 to 27.4 MJ/kg, while additional heating process into 380°C only raises the gross calorific value to 30.6 MJ/kg. In other words, a 270°C treatment contributes ~70.4% of total change equivalent of gross calorific value. Similar trend is observed for other solid properties.

Due to thermal degradation, the content of cellulose, hemicellulose, and lignin in the solid decrease. Figure 1 shows the percentage of these components in the solid products after treatment at 200–300°C. The data suggest that hemicellulose and cellulose are relatively easier to degrade than lignin. The treatment significantly degrades both hemicellulose and cellulose to produce a more ligneous solid. Lignin identified in this analysis comprises not only original lignin from feed materials, but also precipitate derived from polymerization of water soluble compounds. This is obviously indicated from an increase in lignin content in 200–270°C range for solid products of frond, trunk, and EFB.

Slightly different behavior is observed for hemicellulose decomposition among materials. The frond and shell solid produced at 200°C still have a small amount of hemicellulose, which completely vanishes on treatment at 240°C. By contrast, no hemicellulose is found for the trunk, fiber and EFB products, even for treatment 200°C. This suggests that hemicellulose decomposition starts at temperatures <200°C. On the other hand, cellulose is gradually degraded at higher temperature and <0.5 wt.% of it (on a solid product basis) is remained after treatment at 270°C. This behavior is in agreement with other earlier reports [16,17].

3.2. Coal bands

Under hydrothermal treatment, all materials undergo a coalification-like process, as demonstrated in the van Krevelen diagram in Figure 2. The raw materials have high atomic H/C and O/C ratios, which both gradually decreases during treatment. The slope of the trajectories suggests that the O content decreases in proportion to the H content, probably due to dehydration. It is clear that the decrease in O and H content occurs mainly in the range 200–270°C. Less significant changes are observed at higher temperature. The products after treatment at ≥300°C have almost identical compositions with sub-bituminous and bituminous coals.



(a)

(b)

Figure 1. Percentage components in the products of low temperature treatment: (a) Frond and Trunk; (b) Fiber, Shell, and EFB

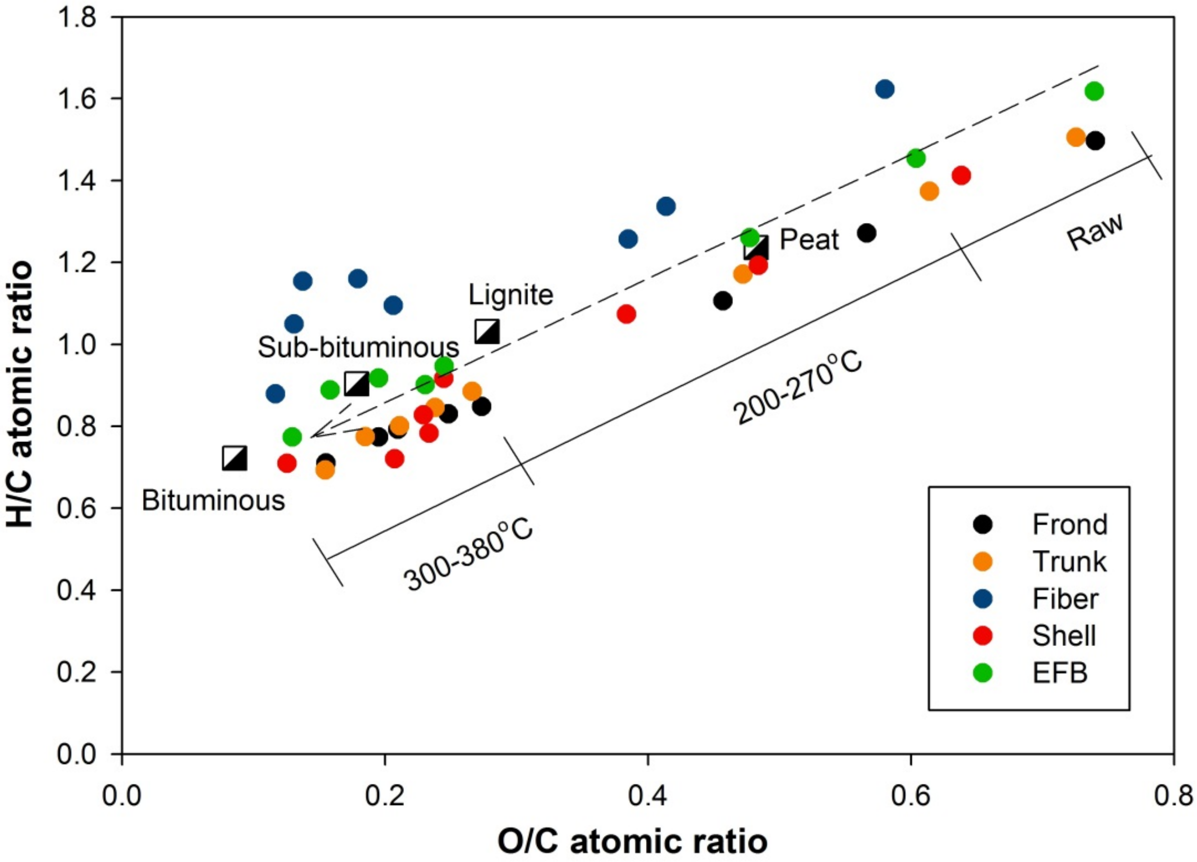


Figure 2. Van Krevelen diagram for materials and their corresponding products in comparison with some solid fuels

3.3. Fourier Transform Infrared (FT-IR) analysis

To understand changes in functional groups during hydrothermal treatment, FTIR analysis of the products is performed. Peaks are assigned based on literature data [18,19]. Figure 3–5 show spectra of the raw fiber, shell, EFB and the corresponding solid products. The intensity of the peak ~3500 cm^{-1} attributed to -OH groups decreases at elevated temperature, indicating that water molecules within the solids are gradually expelled. In other words, dehydration of the feed material occurs. The peak at ~2900 cm^{-1} attributed to aliphatic CH_n groups also weakens, indicating that several long aliphatic chains are broken down. More distinctive peaks are observed in the region below 2000 cm^{-1}. The peak at ~1700–1740 cm^{-1} represents carbonyl (C=O) stretching vibrations. The peak at ~1050 cm^{-1} attributed to glycosidic bonds, indicating the presence of cellulose, steadily weakens and completely disappears for temperatures >270°C, indicating that cellulose is totally degraded at this temperature. The decrease in intensity for both aromatic skeletal vibrations at ~1515 cm^{-1} and C-O-C aryl-alkyl ether linkages at ~1230 cm^{-1} suggest lignin decomposition. Conversely, solids derived from polymerization of intermediate compounds in the liquid phase increase the aromatic content, particularly at temperatures >300°C, as indicated by the increase in intensity for the peak at 1600 cm^{-1} attributed to aromatic skeletal vibrations and CO stretching.

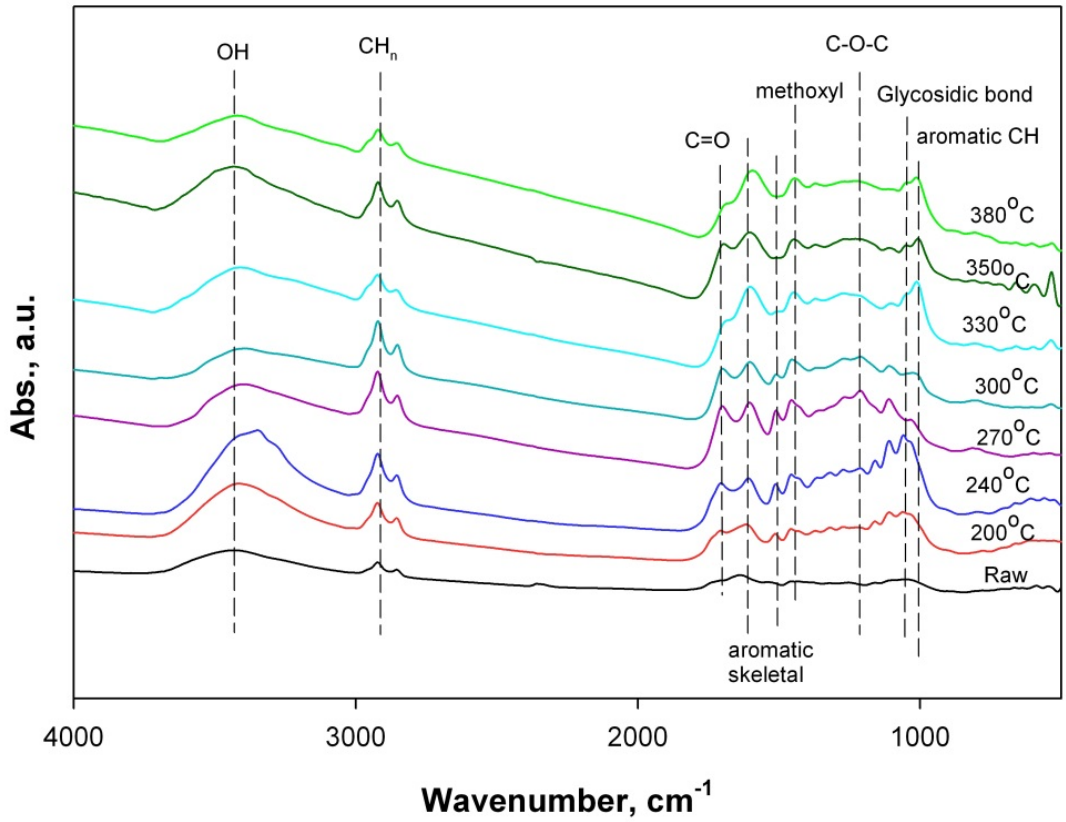


Figure 3. FT-IR spectra for raw fiber and solid products obtained at various temperatures

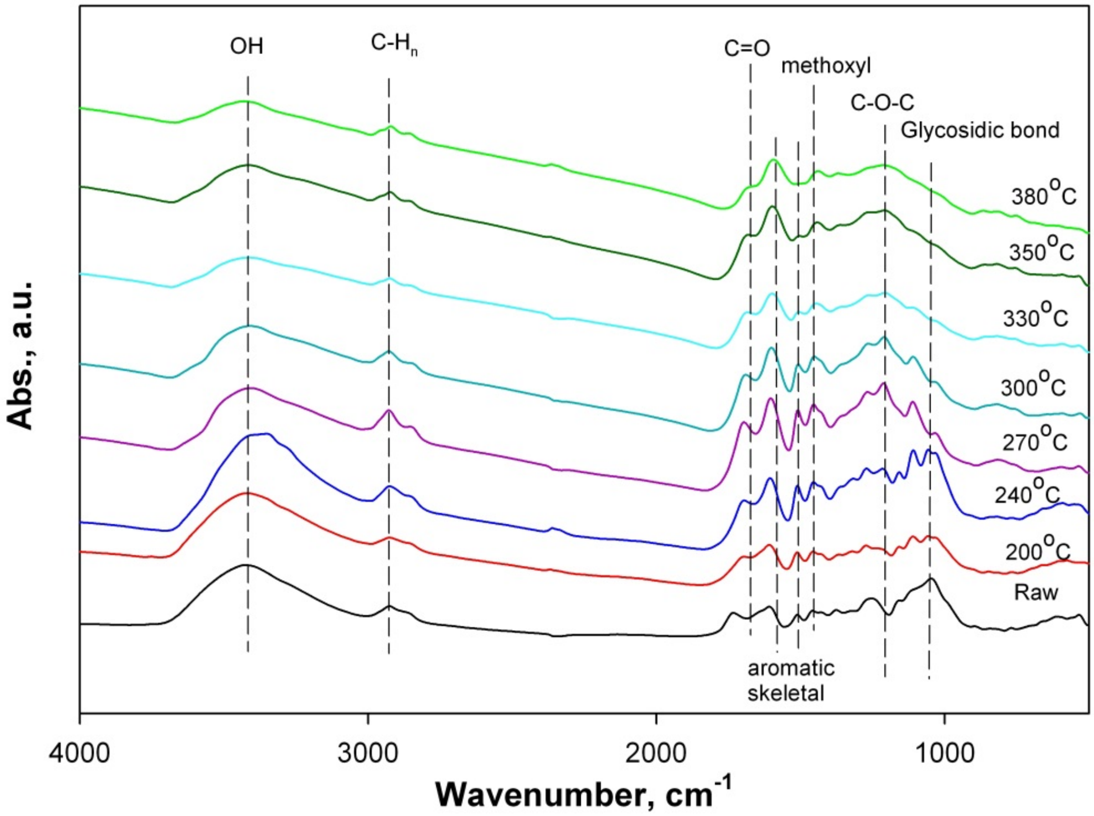


Figure 4. FT-IR spectra for raw shell and solid products obtained at various temperatures

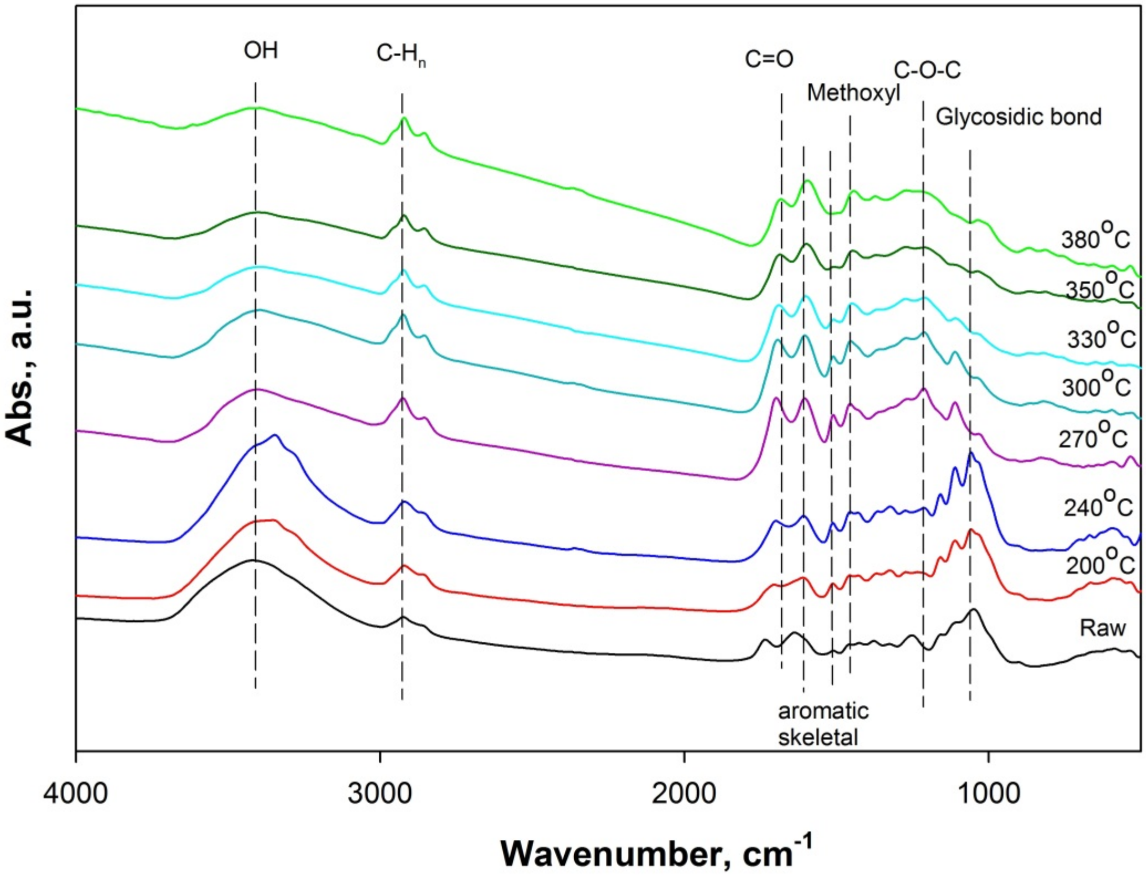


Figure 5. FT-IR spectra for raw EFB and solid products obtained at various temperatures

3.4. The ^{13}C NMR analysis

^{13}C NMR measurements are conducted to complement FTIR in characterizing the molecular structure of the solid products. NMR is useful for making comparisons without the need for peak ratios. Each resonance peak can be measured relative to the total resonance intensity to give the relative amount of individual molecular groups. Typical ^{13}C NMR spectra for raw biomass with peak assignment can be found in the literature [20–24].

In brief, resonance peaks in spectra for raw oil palm wastes are assigned to CH_3 in acetyl groups (21 ppm), methoxyl groups in lignin (56 ppm), C-6 carbon atoms in cellulose (62–65 ppm), C-2/C-3/C-5 atoms in cellulose (72–75 ppm), C-4 atoms in cellulose (84–89 ppm), C-1 atoms in hemicellulose (102 ppm), C-1 atoms in cellulose (105 ppm), unsubstituted olefinic or aromatic carbon atoms (110–127 ppm), quaternary olefinic or aromatic carbon atoms (127–143 ppm), olefinic or aromatic carbon atoms with OH or OR substituents (143–167 ppm), esters and carboxylic acids (169–195 ppm) including acetyl groups in hemicellulose (173 ppm), and carbonyl groups in lignin (195–225 ppm). Despite the various resonance peaks observed, for semi-quantitative analysis Wikberg and Maunu [21] and Wooten et al. [22] simply classify spectra into aliphatic (0–59 ppm), carbohydrate (59–110 ppm), aromatic (110–160 ppm), carboxyl (160–188 ppm) and carbonyl (188–225 ppm) regions.

Data for raw and treated fiber reveal that the peak resonance for hemicellulose and cellulose progressively decrease (Figure 6). A similar pattern is observed for other oil palm wastes (Figure 7–8). The spectra suggest that peaks corresponding to CH_3 (21 ppm) and COOH (173 ppm) in acetyl groups of hemicellulose are eliminated at 200°C. Carbon atoms in cellulose and hemicellulose (62–105 ppm) progressively decrease at 200–270°C. Thus, neither cellulose nor hemicellulose carbon atoms remain after treatment at ≥270°C. Lignin decomposition is indicated by a gradual decrease in methoxyl lignin (56 ppm) along the temperature range. Treatment at ≥270°C leads to extreme spectral changes to a more aromatic nature. Hence, aromatic carbon atoms from lignin structures (31 and 110–160 ppm) dominated the entire spectra. This is in good agreement with the component analysis, which suggests that lignin is the predominant component for treatment at ≥270°C (Figure 1).

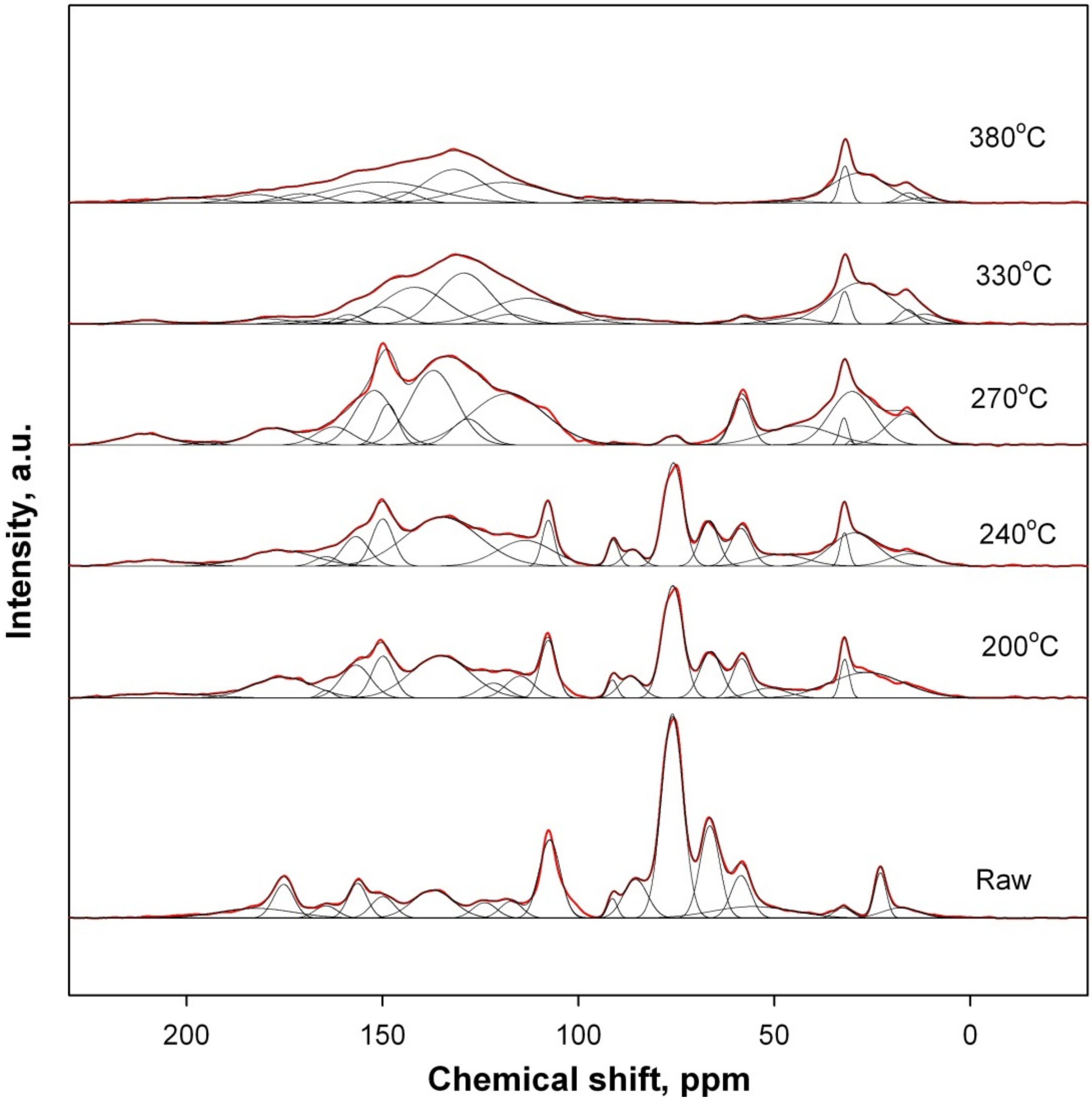


Figure 6. ^{13}C NMR spectra for raw fiber and its treated products.

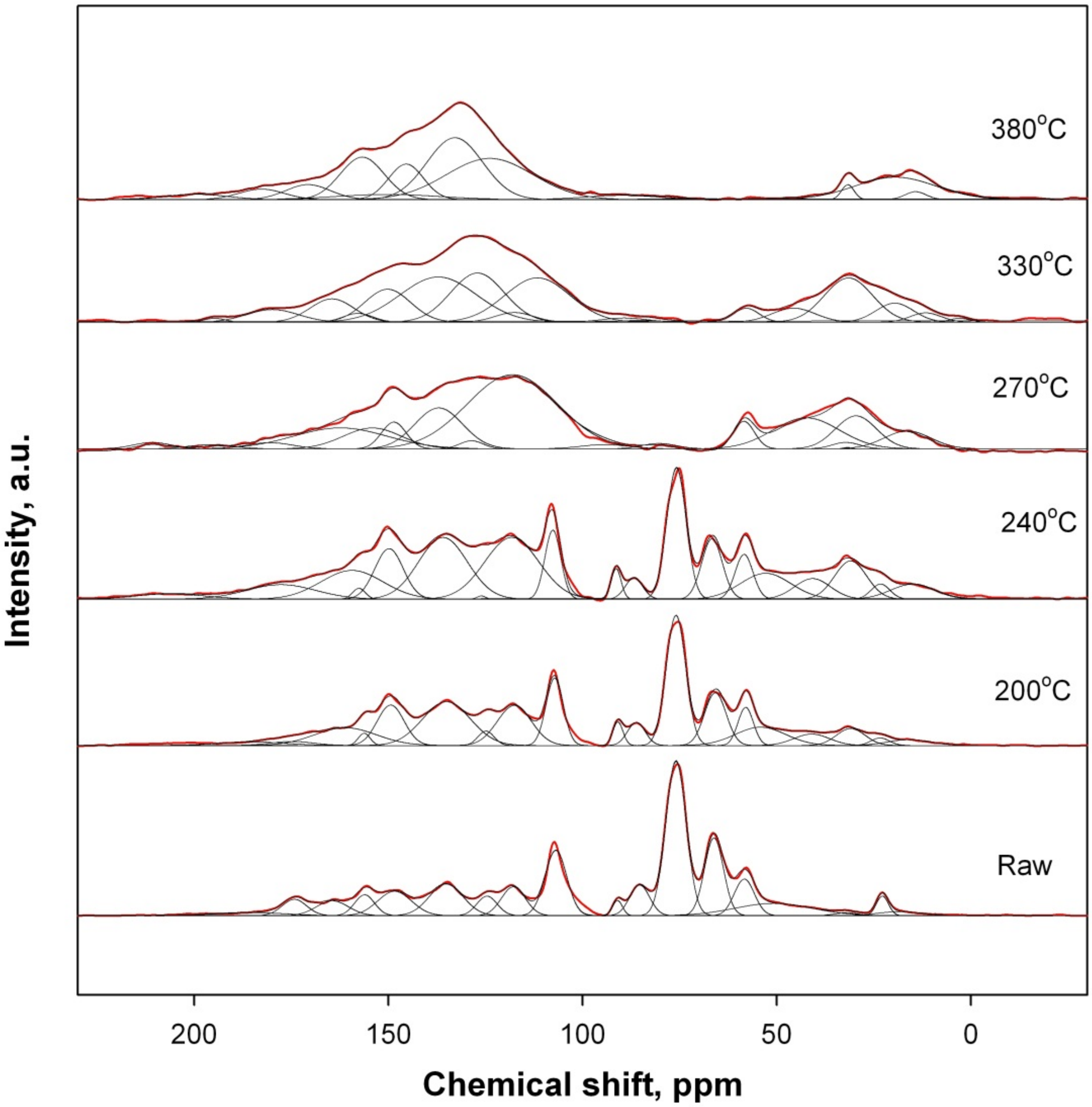


Figure 7. ^{13}C NMR spectra for raw shell and its treated products

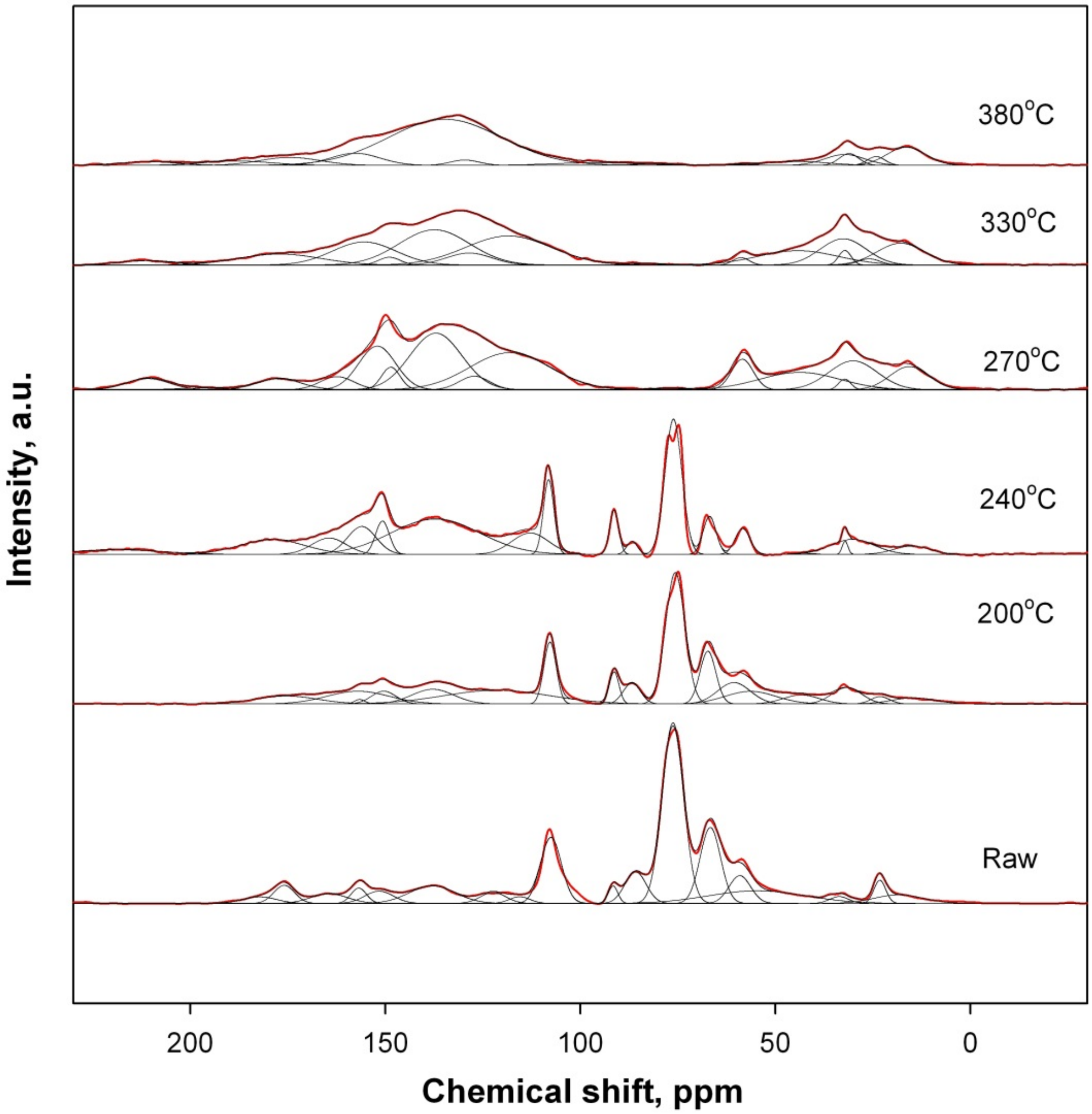


Figure 8. ^{13}C NMR spectra for raw EFB and its treated products.

3.5. Equilibrium moisture content analysis

Hydrothermal treatment greatly reduces the EMC of materials. As shown in Table 2.2, treatments at 200°C reduces the EMC from 14.7 to 7.6 wt.% for frond, and from 13.6 to 7.5 wt.% for trunk. Similarly, the EMC of fiber, shell, and EFB decrease from 13.0 to 6.9 wt.%, from 9.9 to 6.7 wt.%, from 11.8 to 8.1 wt.%, respectively after treatment at 200°C. Further treatment at 380°C leads to EMC as low as 5.0 wt.% (frond), 4.1 wt.% (trunk), 3.6 wt.% (fiber), 3.1 wt.% (shell), and 3.2 wt.% (EFB), respectively. However, the decrease in EMC mainly occurrs in the range 200–270°C, with only small changes observed at higher temperatures. These results correspond to the changes in solid components shown in Figure 1.

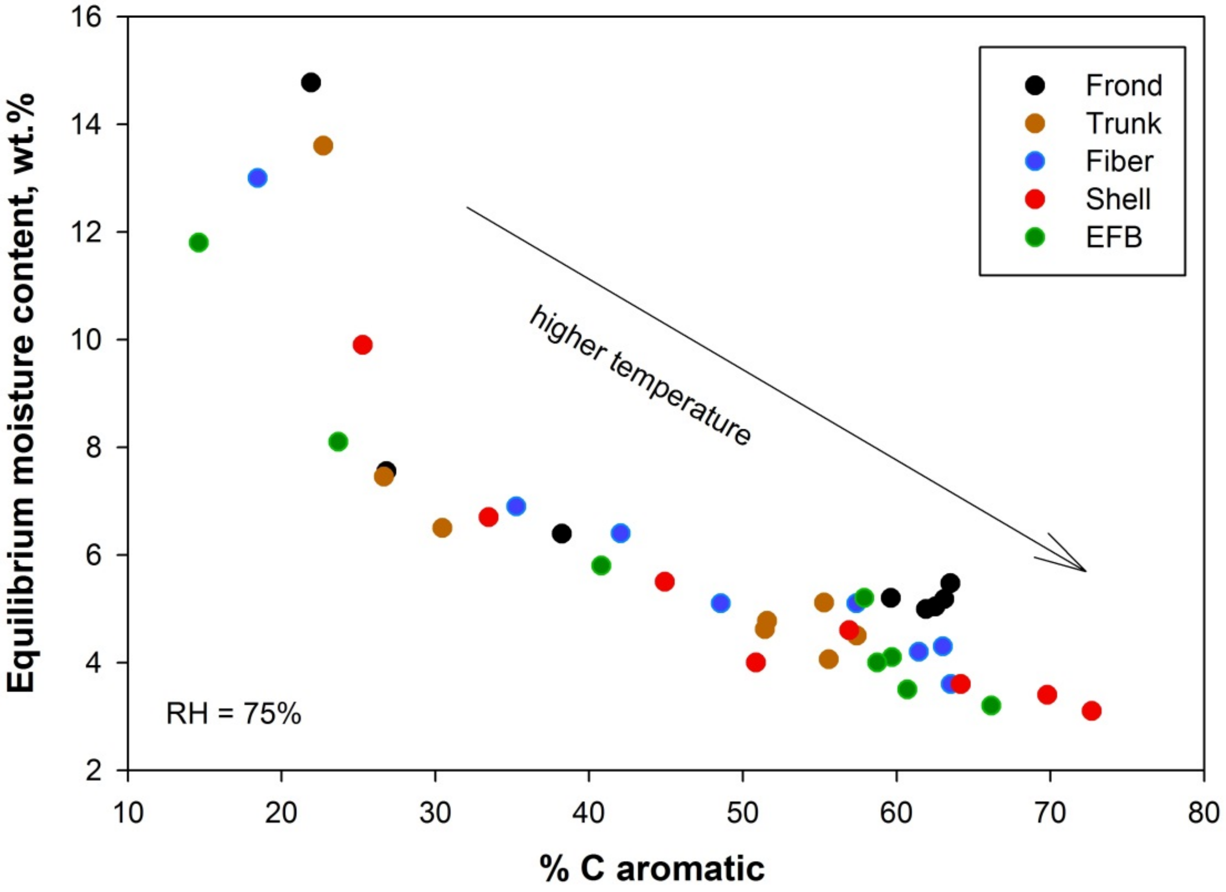


Figure 9. Relationship between percentage aromatic carbon and equilibrium moisture content

Based on the component characteristic on water adsorption, hemicellulose is the strongest, followed by cellulose and lignin [25]. Since hemicellulose is removed first from the solid at low temperature, it is reasonable that the EMC of the material dramatically decreases in this range. By contrast, solids with high lignin content adsorb only a small amount of moisture.

The EMC results are confirmed by NMR results demonstrating an increase in aromatic content in the solid material. The presence of aromatic compounds, which are hydrophobic, results in resistance to humidity and water adsorption from air. Therefore, a higher aromatic content is correlated with lower EMC. The relationship between the relative amount of aromatic carbon and the EMC is presented in Figure 9.

EMC and calorific value are two important properties of solid fuels. When material is burned, some of the energy released by combustion is consumed to vaporize the water contained in the material. Material with a higher EMC will require more energy for moisture evaporation. Thus, a good solid fuel should have a high calorific value and a low EMC. Our experiments demonstrate that both properties are improved by hydrothermal treatment

4. Conclusions

Upgrading of oil palm waste is investigated for hydrothermal treatment at 200–380°C and initial pressure of 2.0 MPa for a residence time 30 min. Approximately 30–60 wt.% of the original material is recovered after the process. The very high oxygen and volatile matter content of the original material are significantly reduced. By contrast, the fixed carbon content increases sharply due to carbonization. A van Krevelen diagram reveals that solids resulting from treatment at >330°C have a composition comparable to that of sub-bituminous and bituminous coals. FTIR analysis confirms that oxygen elimination due to dehydration in conjunction with decomposition of hemicellulose and cellulose occurr at 200–270°C. At temperatures >270°C, the structure of the solid dramatically changes and is dominated by lignin. This is indicated by an increase in aromatic compounds, as determined by ^{13}C NMR spectroscopy.

Hydrothermal treatment progressively changes the calorific value and EMC of materials. Treatment at 380°C produces solid with a gross calorific value of 30.0–32.1 MJ/kg and EMC of 3.1–5.0 wt.%. However, approximately 65% of the total increase in calorific value and 92% of the total decrease in EMC take place within the range 200–270°C, which can be attributed to complete removal of hemicellulose and cellulose. Presence of hydrophobic aromatic compounds in these solids rejects moisture adsorption from atmosphere that potentially reduces the net energy produced. In addition, as solid fuel, which may be transported from one location to other, their higher energy density will affect on reduction of storage, as well as transportation cost. Based on these results, it is proposed that hydrothermal treatment could become an advantageous technology for producing solid fuel from biomass wastes. Among the wastes treated, solid products of oil palm shell demonstrate the best results.

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