

Effects of Pretreatments on the Chemical Composition and Thermal Conversion of Oil Palm Empty Fruit Bunch

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The combustion of oil palm empty fruit bunch (OPEFB) can cause severe fouling, slagging, and ash melt-down problems, which originate from its non-organic components such as potassium, calcium, and silicon. To improve the usability of OPEFB as raw materials for combustion energy generation, the effects of pretreatments with various solution on the chemical composition and the thermal degradation were investigated. Soaking pretreatments with alkali, acidic, and neutral conditions were applied. The acid soaking pretreatments resulted in the reduction of the alkaline ash materials, although the silicon and the chlorine were effectively reduced by the alkali or the water soaking pretreatment. The changes in the ash composition by the different pretreatment conditions resulted in the changes of thermal properties. The pretreated OPEFB showed increased thermal degradation temperatures, indicating the improvement of the thermal stability by the pretreatment. The results of the various pretreatments showed that the water soaking pretreatment of OPEFB could be a promising pretreatment method to improve the applicability for combustion as a bio-fuel, in terms of economic viability and environmental sustainability.

DOI: 10.15376/biores.17.2.2727-2742

Keywords: Oil palm empty fruit bunch; Pretreatment; Ash; Thermal stability; Chlorine; Bio-fuel

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INTRODUCTION

Oil palm empty fruit bunch (OPEFB) is a by-product of the palm oil processing industry. The OPEFB has a low commercial value, and the large quantity of the continuously generated OPEFB bring disposal problems. Worldwide, approximately 15 million tons of OPEFB are annually generated by palm oil milling operations, in which a portion is burned in incinerators (Rahman *et al.* 2007). However, the combustion of OPEFB increases the propensity of sintering and slagging on furnace walls, as well as bed agglomeration, fouling, and corrosion of the combustion equipment, which further leads to environmental problems (Madhiyanon *et al.* 2012). Slagging and fouling propensity reduce the heat transfer of combustor surfaces and cause corrosion and erosion problems, which reduce the lifetime of the equipment (Liorente *et al.* 2008; Capablo *et al.* 2009; Konsomboon *et al.* 2011; Lindberg *et al.* 2013). These problems likely are due to the high ash content (3 to 10%) of OPEFB, which is a serious concern. Herbaceous fuels contain silicon and potassium as the principal ash-forming constituents. They are also rich in chlorine, relative to other biomass fuels, such as wood, straw, and grass (Bismarck *et al.* 2001). These properties indicate a potentially severe ash deposition problem at high temperatures. Alkali and alkaline earth metals, in combination with other fuel elements

such as silica, sulfur, and chlorine, are responsible for many undesirable reactions in combustion furnaces and power boilers (Jenkins *et al.* 1997). Pretreatment of biomass with acid, alkali, and water soaking has been reported to be a suitable method for reducing its organic and inorganic constituents (Mosier *et al.* 2005; Tan and Wang 2009; Izani *et al.* 2013; Nurhayati and Fauziah 2013; Karuna *et al.* 2014; Ying *et al.* 2014)

Thermal degradation of lignocellulosic materials is strongly influenced by their chemical compositions, such as cellulose, hemicellulose, and lignin (Channiwala and Parikh 2002). To facilitate the conversion of OPEFB into bio-fuel, understanding the relationship between the chemical compositions and thermal behavior is important.

In this study, the effect of pretreatment on the characteristics of the OPEFB as a bio-fuel for combustion process was evaluated. Identifying the relationship between the chemical compositions and thermal characteristics of the OPEFB was conducted by applying various pretreatments and by analysis of the thermal properties of the treated OPEFBs.

EXPERIMENTAL

Oil Palm Empty Fruit Bunch (OPEFB)

OPEFB were collected from PT Perkebunan Nusantara IV Riau (Indonesia). The samples were shredded into fibers, washed with flushed tap water to remove fats, dust, and oil, and then dried at 105 °C to a constant weight. Before pretreatment, the particle size for the OPEFB samples was reduced to less than 0.5 mm to ensure an even heat transfer rate.

OPEFB Pretreatment

The pretreatments of the OPEFB samples were conducted by soaking them in sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), or water. For the alkaline and acid pretreatments, the OPEFB samples were soaked in solutions of 1 or 2% NaOH and 10 or 20% H₂SO₄, respectively, at a ratio of 10:1 (v/w) at 20 ± 3 °C for 4 h. Then, the OPEFB samples were filtered by 200 mesh and washed several times with distilled water until a neutral pH was achieved. For water soaking pretreatment, 2000 mL solution was prepared by mixing the OPEFB samples with water at 20±3 °C (ratio of 50:1 (v/w)), and after stirring at 200 rpm for 2 h, it was left for 24 h. All samples were dried for 24 h at 105 °C to determine the remaining dry solids in the sample. Three measurements per sample were obtained and the average values were calculated.

Ash Contents and Higher Heating Value (HHV)

Ash contents were determined at 525 °C for 4h (TAPPI standard T 211). The higher heating values (HHV) were calculated from the elemental compositions using equation (1) from Channiwala and Parikh (T211 om-02),

$$HHV = 0.3491C + 1.1783H + 0.1005S - 0.1034O - 0.0151N - 0.0211A \quad (1)$$

where C, H, N, O, S, and A represent the carbon, hydrogen, nitrogen, oxygen, sulfur, and ash contents of the samples, respectively, expressed as dry weight percentages.

Chemical Composition Analysis

The chemical compositions of the OPEFB were determined by the respective TAPPI standards (T211 om-02; T207 cm-08; T204 cm-17; T222 om-2; T212 om-07; T428 om-10) as follows:

Table 1. Measurement Standards Used to Determine the Chemical Compositions of OPEFB

Chemical Composition Analysis	Analytical Method
Ash content	TAPPI standard T.211
Hot water extraction	TAPPI standard T.207
Solvent extraction	TAPPI standard T.204
Klason Lignin	TAPPI standard T.222
Holocellulose	TAPPI standard T.212
Alpha-cellulose	TAPPI standard T.429

Fourier-transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy was used to qualitatively analyze the functional groups of the chemical components in the untreated and pretreated OPEFB samples. IR was used in a scanning range of 4000 to 600 cm^{-1} .

Thermogravimetric Analyzer (TGA)

TGA was performed using a TGA Q500 series thermogravimetric analyzer (TA instruments, USA) to understand the thermal degradation behavior of the samples. The temperature was varied from 25 °C to 600 °C at a heating rate of 20 °C/min in a nitrogen atmosphere to prevent unwanted oxidative decomposition. The early-stage degradation temperature (T_o), maximum temperature for transition (T_m), and final temperature for transition (T_f) were evaluated based on the degradation curves. The degradation temperatures obtained in this study were the primary parameters of concern.

RESULTS AND DISCUSSION

Effect of the Pretreatment on Ash Contents and Elemental Compositions

Figure 1 shows the ash contents of the untreated and pretreated OPEFB samples. The untreated samples showed higher ash contents than those of the pretreated samples.

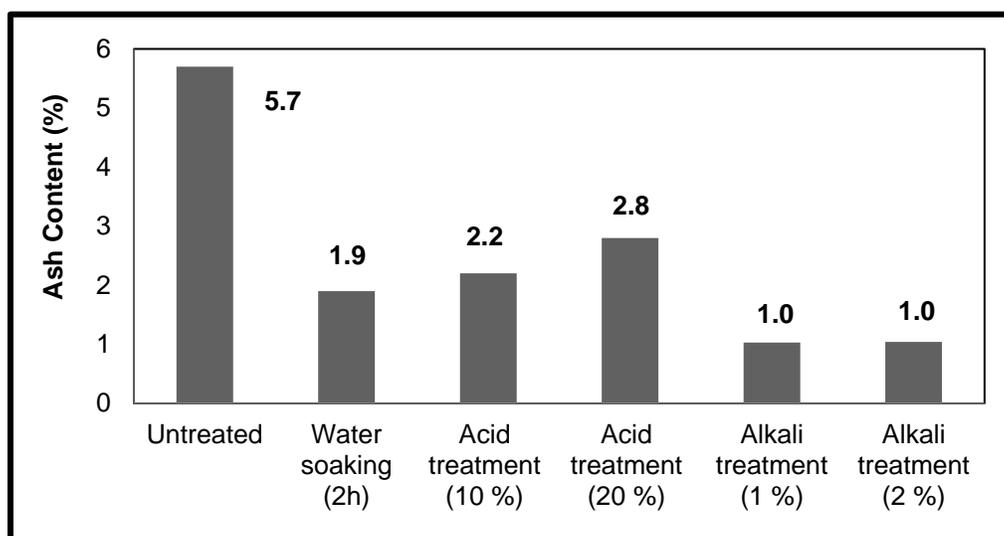


Fig. 1. Ash contents of untreated of OPEFB and treated OPEFB

The treatment with 1 or 2% NaOH reduced the ash contents by 82 to 83%, followed by the water-soaking treatment at a 65% reduction, and the acid treatment with 10% H₂SO₄ at 60.5% reduction and 20% H₂SO₄ at 50% reduction. The reason that the acid-treated samples showed higher residual ash contents than those of the alkali-treated samples was attributed to the decrease in total mass due to decomposition of organic matter by acid. (Fig. 3). Also, the application of the higher concentration of the acid or alkali had no noticeable influence on the reduction of the ash contents.

The ash contents of the water-pretreated OPEFB at various residence times are shown in Fig. 2. It was apparent that the water-soaking pretreatment effectively reduced the ash contents by more than approximately 50% regardless of the soaking times. These results indicated that the water-soaking pretreatment was the most suitable for ash removal in terms of economic feasibility.

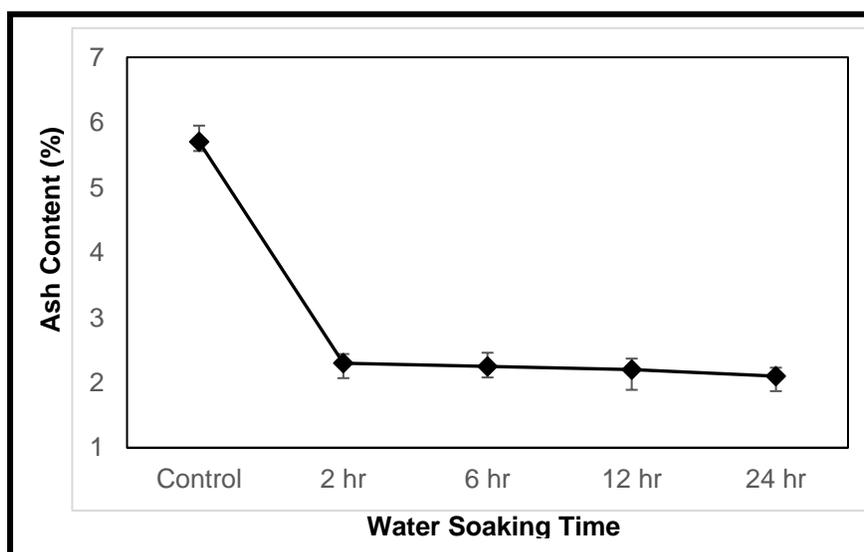


Fig. 2. The changes in the ash contents of water soaking pretreated of OPEFB at different soaking times

Table 2 compares the moisture contents, the volatile matter contents, the ash contents, the fixed carbon contents, and the compositions of carbon, hydrogen, nitrogen, and oxygen in the untreated and the pretreated OPEFB samples. The molecular mass of carbon is heavier than that of hydrogen; therefore, the H/C wt% ratio could be used to represent the amount of the hydrocarbon component in biomass (Lim *et al.* 2013). The removal of the hydrocarbon component during the pretreatment processes slightly increased the H/C wt% ratio. Furthermore, the increase in the contents of volatile compounds indicated the improvement in the fuel characteristics, such as the HHV. Ash removal can have a direct effect on the HHV (Asadieraghi and Daud 2014), as was evident by the higher HHVs of the pretreated OPEFB samples.

Table 2. Proximate and Ultimate Analysis of Untreated and Treated OPEFB; H/C: Hydrogen-to-Carbon Ratio; HHV: Higher Heating Value

	Untreated	Water soaking (2 h)	Acid treatment (H ₂ SO ₄ 10%)	Alkali treatment (NaOH 1%)
Proximate analysis (wt%)				
Moisture content	14.44	7.99	11.36	6.99
Volatile matter	70.42	78.8	82.15	79.29
Ash content	5.7	1.9	2.8	1.04
Fixed carbon	9.44	7.94	8.06	11.68
Ultimate analysis (wt%)				
Carbon	43.91	44.78	44.87	44.31
Hydrogen	5.62	5.77	5.74	5.83
Nitrogen	0.26	0.235	0.233	0.23
Oxygen	45.31	48.24	48.74	47.62
H/C	0.127	0.129	0.128	0.132
HHV (MJ/kg)	17.2	17.4	17.33	17.39

Reducing the ash content in biomass could also prevent the severe problems of slagging, agglomeration, deposition, and corrosion, associated with the high inorganics content (Jiang *et al.* 2013) during biomass combustion, in particular with silica, potassium, and chlorine (Jenkins *et al.* 1997). The elemental analysis indicated that the major inorganic constituents (Si, P, K, and Ca) varied after the three pretreatments (Table 3), the removal of which was associated with the solubility of the different metal oxides in water, alkali, and acid solutions. In particular, all pretreatments decreased the chlorine contents. Chlorine has been shown to be a major factor in deposit formation, and it plays a role in alkali transportation and vaporization, even when the alkali is bound as silicates (Kuchenbuch *et al.* 1986; Miles *et al.* 1996; Baxter *et al.* 1998).

The decrease in potassium was directly related to the decrease in ash content, as previously reported (Jenkins *et al.* 1996; Das *et al.* 2004). Biomass with a high alkali metal content, especially potassium, is dissolved by washing it with water (Fahmi *et al.* 2007; Yang *et al.* 2006). When potassium is present as KCl, it can easily vaporize and participate in the slagging mechanism (Masiá *et al.* 2007; Kuchenbuch *et al.* 1986). Water-soaking, as the most economical treatment, could remove silica and chlorine. Although the chemical treatment processes are very effective in removing inorganic materials, they could be expensive and may have a negative impact on the physiochemical structure of the biomass.

Therefore, in terms of economic and environmental sustainability, water pretreatment can be the most promising and moderately effective method for mineral control.

Table 3. Elemental Composition of Untreated and Treated OPEFB

Elemental	Untreated	Water Soaking (2 h)	Acid Treatment (H ₂ SO ₄ 10%)	Alkali Treatment (NaOH 1%)
Na	0.02	0.01	0.02	10.04
Mg	1.89	5.09	3.52	6.79
Si	32.18	26.86	44.1	24.31
P	6.72	6.67	6.73	5.27
S	4.58	11.62	30.86	8.61
Cl	4.44	7.63	0.36	0.03
K	39.67	30.31	1.82	3.6
Ca	10.52	9.25	12.79	41.39

The alkali-pretreated OPEFB samples contained the higher amounts of Ca, Mg, and Na compared to the other pretreated OPEFB samples (Table 3). In ash, Ca, Mg, and Na were present in the form of oxides with high melting points. Based on the chemical abstract service (CAS), the melting points of sodium oxide, calcium oxide, and magnesium oxide are 1132 °C, 2899 °C, and 2582 °C, respectively (Table 4).

Table 4. Melting Temperature of the Elemental Ash Components

No	Elemental Component	Ash Compound	CAS	Chemical Formula	Melting Temperature (°C)
1	Phosphorus	Phosphorus oxide	1314-56-3	P ₂ O ₅	562
2	Sodium	Sodium Oxide	1313-59-3	Na ₂ O	1132
3	Potassium	Potassium oxide	12136-45-7	K ₂ O	350
4	Magnesium	Magnesium oxide	130948-4	MgO	2582
5	Calcium	Calcium oxide	1305-78-8	CaO	2899
6	Silica	Silica dioxide-alpha	14808-60-7	SiO ₂	573
		Silica dioxide-beta	14808-60-7	SiO ₂	867
		Silica dioxide-gamma	15468-32-3	SiO ₂	1470
7	Iron	Iron oxide	1309-37-1	Fe ₂ O ₃	1565
8	Manganese	Manganese oxide	1344-43-0	MnO	1840

Chemical Composition and Structural Analysis

The chemical compositions of the OPEFB samples before and after pretreatment are presented in Table 5. The OPEFB samples contained high amounts of holocellulose, approximately 80%, similar to other non-woody biomass. The α -cellulose contents increased from 65% to >67%. The highest increase in the α -cellulose content was observed in case of the alkali pretreatment. This suggested that under alkaline conditions, the OPEFB samples could be successfully fractionated and the crystallinity of cellulose increased, as previously reported (Yu *et al.* 2009).

Alkali pretreatment of biomass has been widely used in the pulp and paper industries, as well as for lactic acid and bioethanol production (Azzam 1989; Silverstein *et al.* 2007; Chen *et al.* 2014). Furthermore, the removal of the different types of extractives

was expected to affect the thermal stability of the OPEFB fibers (Mark *et al.* 1971). Since the thermal stability of different wood species was dependent on the variations in chemical composition (Ishola and Taherzadeh 2014), it could be expected that thermal degradation of the OPEFB were related to its chemical composition.

Table 5. Chemical Composition of the Untreated and Treated OPEFB

Samples	Chemical Composition (wt%)							
	Ash content	Hot water extraction	Alcohol-benzene Extraction	Klason Lignin	Holo-cellulose	α - cellulose	β - cellulose	Weight Loss
Untreated Samples	5.7	14.9	6.15	23.4	81.32	68.01	31.99	-
Water soaking (2 h)	1.9	8.21	6.65	17.5	84.68	67.54	32.46	9
Alkali treatment (NaOH 1%)	1.04	3.93	6.06	21.3	78.63	75.132	24.868	17
Acid treatment (H ₂ SO ₄ 10%)	2.8	4.49	6.46	26.4	81.50	78.57	21.43	28

The loss in total solids after the three pretreatment processes was also determined (Fig. 3). Only 9% and 17% loss of total solids was observed after the water-soaking and the alkali pretreatments, respectively, compared to the 28% after the acid pretreatment. The high loss in total solids after the acid pretreatment resulted in the highest mass reduction. This could have originated from the overall reduction of organic matter as well as the removal of inorganic elements. Thus, the alkali pretreatment could be useful method for achieving an appropriate amount of total solids lost (Izani *et al.* 2013).

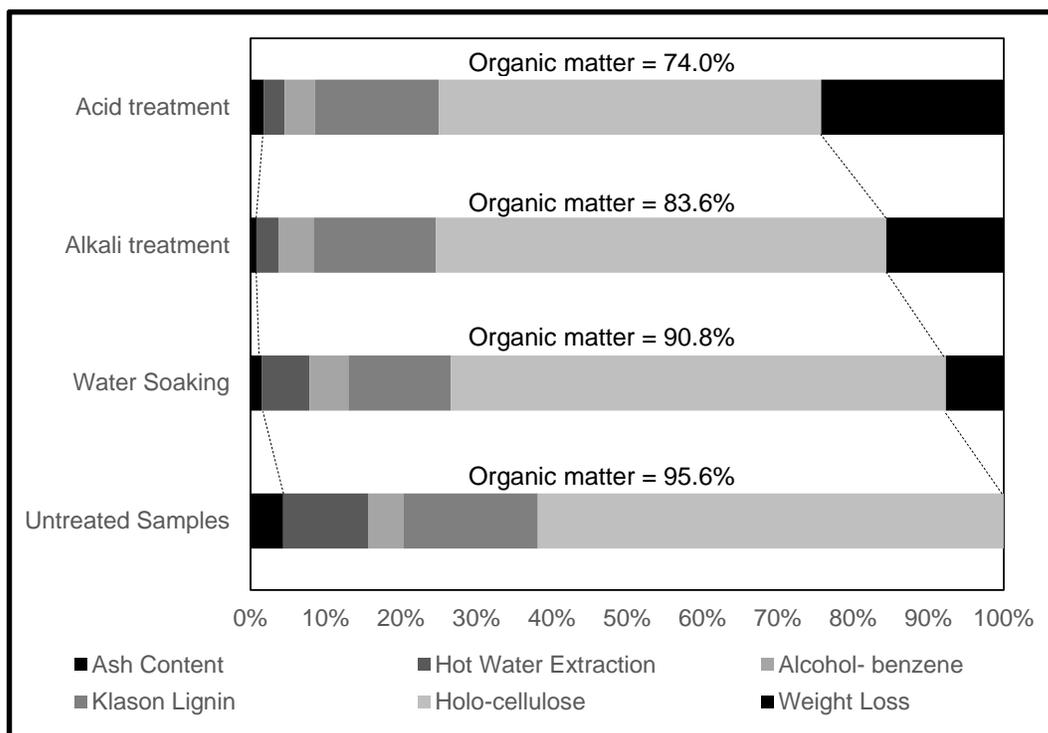


Fig. 3. Changes in the chemical component ratio of OPEFB samples depending on the pretreatment methods

The chemical groups in the untreated and the pretreated OPEFB samples were analyzed by using FTIR to determine the functional groups and the composition of the structural changes based on their specific transmittance (Fig. 4). The band assignments and displacements corresponding to the literature are listed in Table 6. Fourteen bands were observed in the ranges of 2800 to 3700 cm^{-1} (Fig. 5(a)) and 600 to 1800 cm^{-1} (Fig. 5(b)). The broad O-H stretching vibration between 3200 and 3600 cm^{-1} indicated the presence of alcohols and cellulose. The decrease in the intensity of the peak in this range after pretreatment was attributed to the partial removal of hemicellulose. The highest cellulose loss was observed with the water-soaking and alkali pretreatments, indicated by the lowest intensity of the O-H stretching absorption.

Table 6. Assignments of the Infrared Band Maxima to the Various Components of the OPEFB Samples Depending on the Pretreatment Methods

Un-treated	Acid pretreatment	Alkali pretreatment	Water soaking	Assignment	Source	Reference
665	669	668	670	C-O out-of-plane bending mode	Cellulose	Fackler <i>et al.</i> 2011
898	896	898	902	C(1)-H deformation, ring valence vibration	Polysaccharides	Faix <i>et al.</i> 1991; Etoegni <i>et al.</i> 1991
1031	1029	1028	1029	Deformation in primary alcohols; plus C=O stretch (unconj.)	Lignin	Fackler <i>et al.</i> 2011
1159	1156	1161	1166	C-O-C asymmetric valence vibration	Polysaccharides	Faix <i>et al.</i> 1991
1239	1235	-	-	C=O stretch, OH ip. bending		Faix <i>et al.</i> 1991
1275	1274	1275	1275	G-ring plus C=O stretch	G-Lignin	Fackler <i>et al.</i> 2011
1323	1323	1324	1324	O-H blending of alcohol groups	Carbohydrate	Faix <i>et al.</i> 1991
1381	1371	1375	-	C-H deformation vibration	Cellulose	Etoegni <i>et al.</i> 1991
1459	1459	1460	1465	OH plane deformation vibration	Cellulose	Etoegni <i>et al.</i> 1991
1540	-	1581	1584	C=O stretch; S > G; G condensed > G etherified	Lignin	Faix <i>et al.</i> 1991
1635	1632	1421	-	C O stretch in conjugated p-substituted aryl ketones	Lignin	Etoegni <i>et al.</i> 1991
2851	2850	2850	2849	Asymmetric CH ₂ valence vibration	Extractives	Fackler <i>et al.</i> 2011
2918	2917	2917	2917	Symmetric CH ₂ valence vibration Hydrogen bonded		Fackler <i>et al.</i> 2011
3280	3294	3288	3281	O-H valence vibration; O(3)H--O(3) Intermolecular in cellulose	Cellulose	Fackler <i>et al.</i> 2011

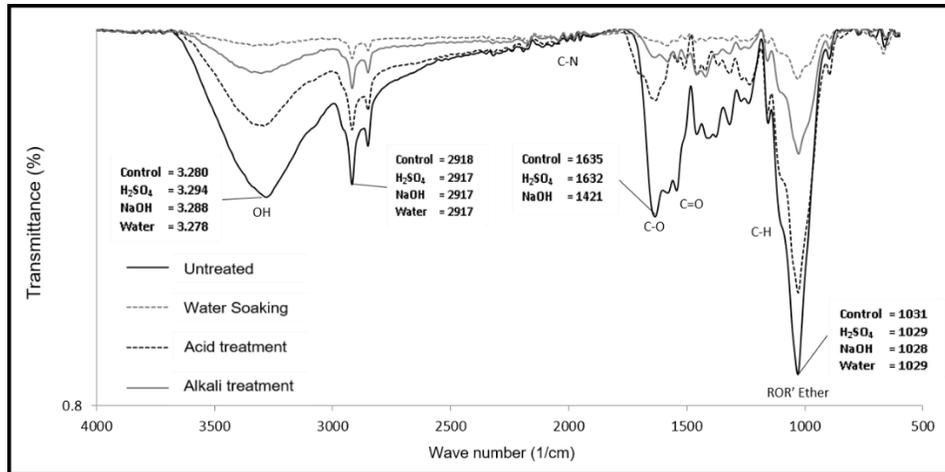
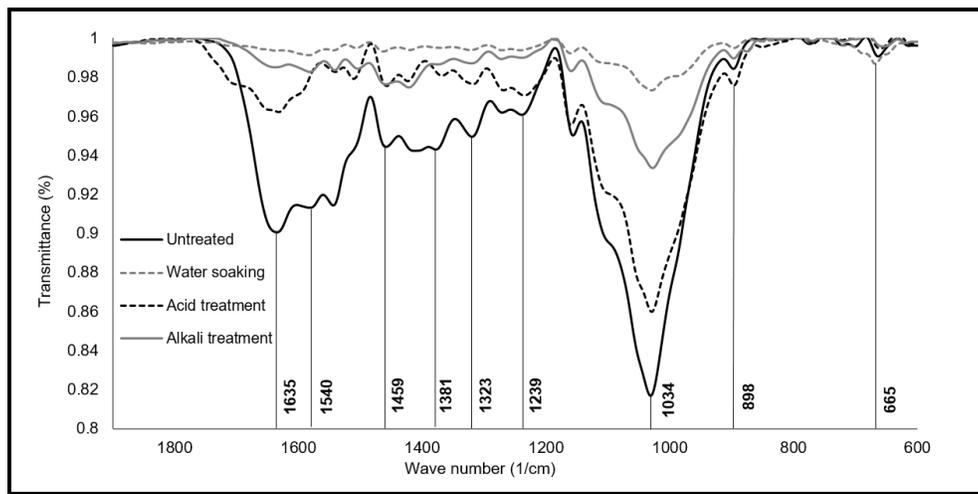
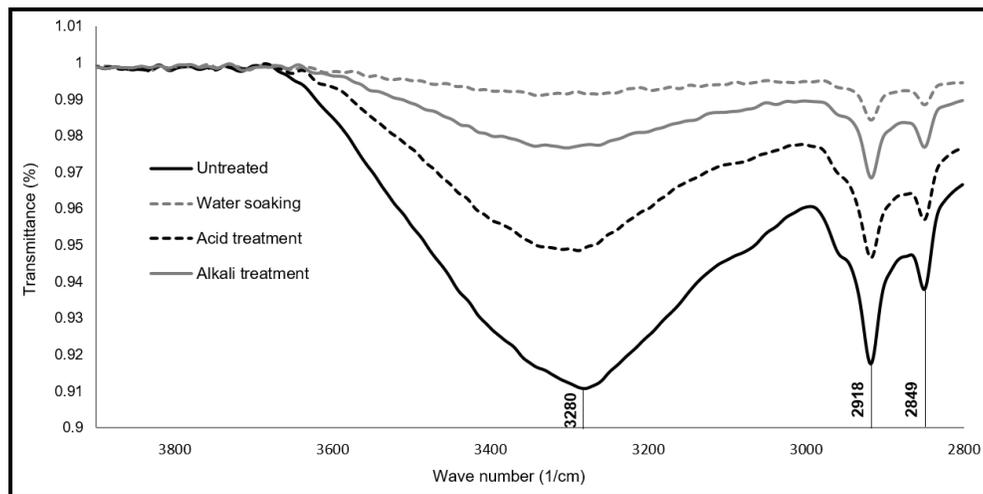


Fig. 4. Fourier transform infrared spectroscopy analysis of OPEFB samples depending on the pretreatment methods



(a)



(b)

Fig. 5. Fourier-transform infrared spectra of OPEFB samples within the wavenumber ranges of 2800~3800 cm⁻¹ (a) and 600~1800 cm⁻¹ (b)

The strong intensity bands observed in the OPEFB samples within the region of 2900~3000 cm^{-1} were typical bands of the C-H stretching vibrations found in CH_2 and CH_3 . The band at 2918 cm^{-1} was more prominent in the untreated OPEFB samples, which might be attributed to the higher extractive content, since some compounds in organic extractives, such as fatty acid methyl esters and phenolic acid methyl esters, contained methyl and methylene groups (Schwanninger *et al.* 2004; Nordin *et al.* 2013). A strong intensity was also observed near 1635 cm^{-1} , which originated from the symmetric vibration of the CH_2 group.

The band at 1381 cm^{-1} was assigned to the C-H deformations in cellulose and hemicellulose. The intensity of this band slightly decreased after pretreatment, indicating a slight decrease in the cellulose and hemicellulose contents. A greater decrease in intensity was found after the acid pretreatment, which could be attributed to the higher hemicellulose removal. Decreasing intensities for all the pretreated OPEFB samples were also observed in the band at 1159 cm^{-1} , which was assigned to the C-O-O- > C-O-C asymmetric vibration of cellulose and hemicellulose. These results indicated that the pretreatments affected the chemical structure of the OPEFB.

Thermal Stability Analysis

The changes in the thermal behavior depending on the pretreatment methods were evaluated. The thermal degradation increased with increasing temperature at a heating rate of 20 $^{\circ}\text{C}/\text{min}$ (Fig. 6); the corresponding thermal degradation rates were presented in Table 4. The thermal behavior of the untreated and the pretreated OPEFB samples followed a similar trend with three stages of weight loss; the transition began at approximately 230 $^{\circ}\text{C}$ and was nearly complete at approximately 500 $^{\circ}\text{C}$.

The thermal degradation of the OPEFB samples could be divided into three stages: the first stage for the moisture evaporation, the second stage for the main devolatilization, and the final stage for the continuous slight devolatilization. The mass loss due to the water vaporization stage began 20 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$. The primary thermal decomposition of the cellulosic component occurs between 200 and 400 $^{\circ}\text{C}$. (Olanders and Steenari 1995) The untreated and the acid-treated samples exhibited small DTG peaks at around 200 $^{\circ}\text{C}$, which might indicate the presence of extractives. In addition, two peaks were observed in the DTG curve of the OPEFB sample. The small peaks observed from 50 to 120 $^{\circ}\text{C}$ denoted the water evaporation process of the reaction, while the second peak between 210 and 520 $^{\circ}\text{C}$ signified the devolatilization of the samples.

As stated above, the chemical composition of the OPEFB affected the thermal stability. Cellulose is a crystalline polymer, which contributes to its high thermal stability, while the amorphous hemicelluloses and the lignin tend to degrade at lower temperatures. (Etegni and Campbell 1991). In the DTG spectra (Fig. 6(b)) of the pretreated OPEFB samples, there was a slight peak at around 310 $^{\circ}\text{C}$, which was absent in the DTG curve of the untreated sample. It was generally assumed that the changes in the degradation temperature could have originated from the catalytic effects of ash, as well as the degradation of hemicelluloses (Konsomboon *et al.* 2011).

Table 7 lists the decomposition temperatures of all samples (untreated and pretreated). The alkali and the water pretreated OPEFB samples showed an initial degradation at approximately 272 and 265 $^{\circ}\text{C}$, respectively, whereas the untreated samples started to decompose at 237 $^{\circ}\text{C}$. The alkali pretreatment sample had the highest final degradation at 351 $^{\circ}\text{C}$, which could be resulted from the reduction of hemicelluloses and lignin during the chemical pretreatment, and the increase of the crystallinity in the alkali

pretreated OPEFB samples. The alkaline conditions facilitated the degradation of the amorphous regions in cellulose and could increase its degree of crystallinity (Khan *et al.* 2009).

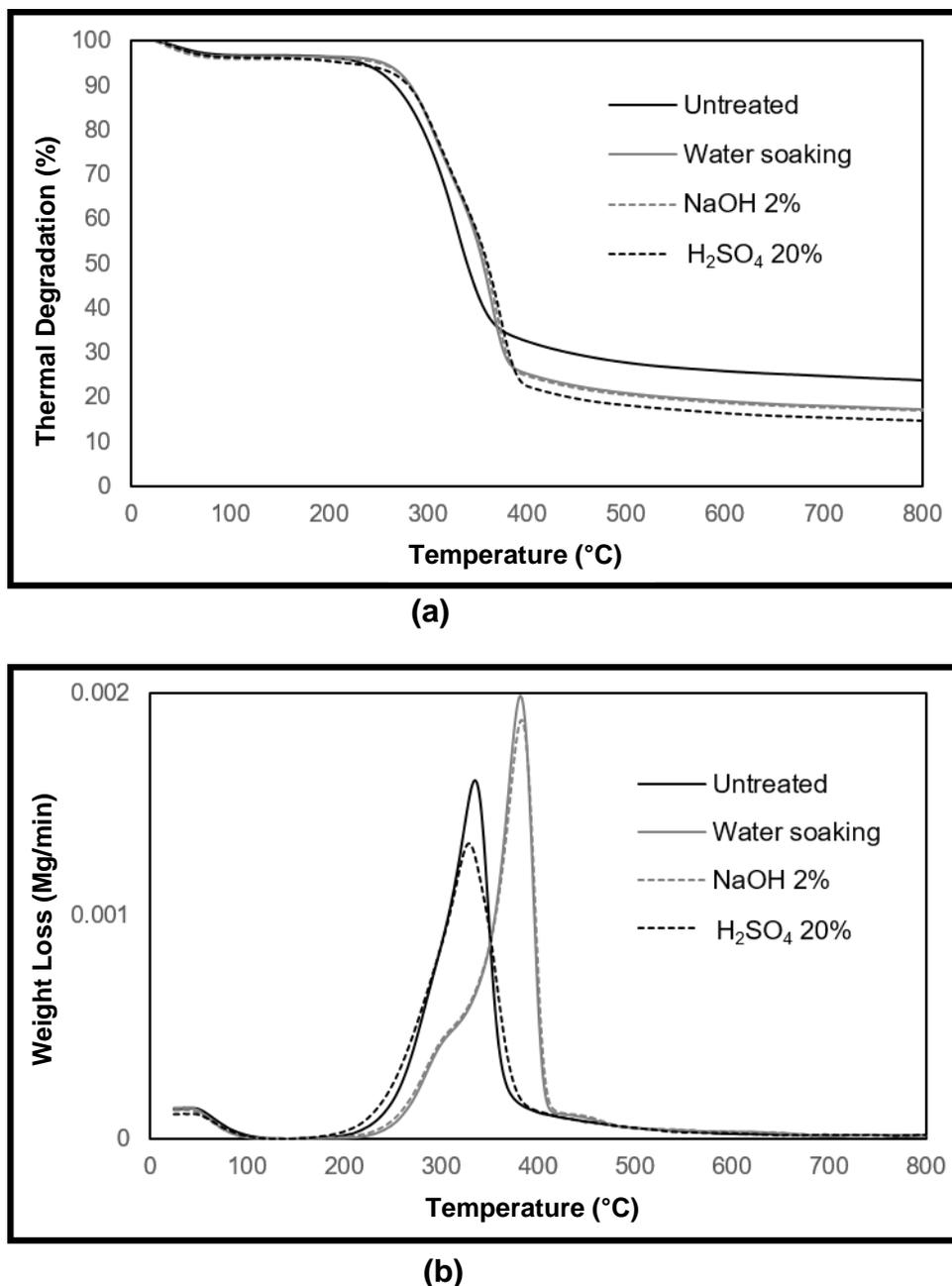


Fig. 6. The thermogravimetry curve (a) and the derivative thermogravimetry curve (b) OPEFB samples before and after pretreatment

The total weight loss in the temperature range between 100 °C and 450 °C was 80.8% after alkali pretreatment, 79.7% after water-soaking pretreatment, and 82.8% after acid pretreatment, compared to the 71.8% for the untreated sample. This result could be due to two possible reasons: First, the ash itself would largely not volatilize; therefore, it contributed to the char yield. Second, the ash could contribute to the greater char

production through its catalytic activity. The low char yield in the pretreated samples might be due to the removal of hemicelluloses and lignin, providing the better accessibility to cellulose in the finer-treated samples (Khan *et al.* 2009). This also indicated the effectiveness loss of the degradation rate, and a faster degradation rate resulted in a higher residual weight.

Table 7. Degradation Temperature from Thermogravimetric Analysis of Untreated and Treated OPEFB Samples

OPEFB Sample	Transition Temperature			Weight Loss (%)	Residual Weight (%)
	T_0 (°C)	T_m (°C)	T_f (°C)		
Untreated	237	261	311	71.76	28.19
Water soaking	265	282	342	79.66	20.29
Alkali pretreatment	272	289	351	80.82	19.13
Acid pretreatment	248	266	315	82.79	17.17

The thermal stability of the OPEFB samples improved owing to the chemical degradation of hemicelluloses, lignin, and some portion of silica during the different pretreatments. Those results led to the increase in the main degradation temperature, especially for the alkali-pretreated samples (Bismarck *et al.* 2001).

CONCLUSIONS

In this study, the OPEFB samples were pretreated with water, sodium hydroxide, and sulfuric acid to evaluate the effects of the pretreatment methods on the ash control and the chemical compositions. The main conclusions were as follows:

1. The pretreatment (acid, alkali, and water-soaking) had a remarkable effect on ash removal, and it was noted that the mineral elemental composition of the OPEFB fibers could be controlled.
2. The chemical and the structural compositions of the OPEFB could be changed by the pretreatment, which resulted in the changes in thermal degradation properties.
3. The differences in thermal stability could be attributed to variations in the chemical compositions after the pretreatment. The pretreatment of OPEFB samples decreased the char yield after the thermal degradation and increased the thermal stability by increasing the main thermal degradation temperature.

The reduction of the potential risk materials such as chlorine, silicon, and minerals could prevent the severe problems generated during the OPEFB combustion and could improve the combustion efficiency. In terms of economic and environmental feasibility, the water soaking pretreatment effectively improved the characteristics of the OPEFB, thereby upgraded the OPEFB qualities as bio fuel for various thermal conversion processes such as combustion energy production.

ACKNOWLEDGMENTS

This work was supported by the research fund of Chung-nam National University.

REFERENCES CITED

- Asadieraghi, M., and Daud, W. M. A. W. (2014). "Characterization of lignocellulosic biomass thermal degradation and physicochemical structure: Effects of demineralization by diverse acid solutions," *Energy Conversion and Management* 82, 71-82. DOI: 10.1016/j.enconman.2014.03.007
- Azzam, A. M. (1989). "Pretreatment of cane bagasse with alkaline hydrogen peroxide for enzymatic hydrolysis of cellulose and ethanol fermentation," *J. Environmental Science & Health Part B* 24(4), 421-433.
- Baxter, L. L., Miles, T. R., Miles Jr, T. R., Jenkins, B. M., Milne, T., Dayton, D., and Oden, L. L. (1998). "The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences," *Fuel processing Technology* 54(1-3), 47-78. DOI: 10.1016/S0378-3820(97)00060-X
- Bismarck, A., Mohanty, A.K., Askargora, I., Czaplá, S., Misra, M., and Spingera, J. (2001). "Surface characteristic of natural fibers: Surface properties as the water uptake behavior of modified sisal and coir fibers," *Green Chemical* 3, 100-107, DOI: 10.1039/B100365H
- Capablo, J., Jensen, P.A., Pedersen, K.H., Hjuler, K., Nikolaisen, L., Backman, R., and Frandsen, F. (2009). "Ash Properties of Alternative Biomass," *Energy and Fuels* 23, 1965-1976, DOI: 10.1021/ef8008426
- Channiwala, S. A., and Parikh, P. P. (2002). "A unified correlation for estimating HHV of solid, liquid and gaseous fuels," *Fuel* 81(8), 1051-1063. DOI: 10.1016/S0016-2361(01)00131-4
- Chen, Y., Tshabalala, M. A., Gao, J., Stark, N. M., Fan, Y., and Ibach, R. E. (2014). "Thermal behavior of extracted and delignified pine wood flour," *Thermochimica Acta* 591, 40-44. DOI: 10.1016/j.tca.2014.06.012
- Das, P., Ganesh, A., and Wangikar, P. (2004). "Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products," *Biomass and Bioenergy* 27(5), 445-457, DOI: 10.1016/j.biombioe.2004.04.002
- Etiegni, L., and Campbell, A. G. (1991). "Physical and chemical characteristics of wood ash," *Bioresource Technology*, 37(2), 173-178. DOI: 10.1016/0960-8524(91)90207-Z
- Fackler, K., Stevanic, J. S., Ters, T., Hinterstoisser, B., Schwanninger, M., and Salmén, L. (2011). "FT-IR imaging microscopy to localise and characterise simultaneous and selective white-rot decay within spruce wood cells," *Holzforschung* 65, 411-420, DOI: 10.1515/hf.2011.048
- Fahmi, R., Bridgwater, A. V., Darvell, L. I., Jones, J. M., Yates, N., Thain, S., and Donnison, I. S. (2007). "The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow," *Fuel* 86(10-11), 1560-1569, DOI: 10.1016/j.fuel.2006.11.030
- Faix, O., Bremer, J., Schmidt, O., and Tatjana, S. J. (1991). "Monitoring of chemical changes in white-rot degraded beech wood by pyrolysis—Gas chromatography and Fourier-transform infrared spectroscopy," *J. Analytical and Applied Pyrolysis*, 21(1-2), 147-162. DOI: 10.1016/0165-2370(91)80022-Z

- Ishola, M. M., and Taherzadeh, M. J. (2014). "Effect of fungal and phosphoric acid pretreatment on ethanol production from oil palm empty fruit bunches (OPEFB)," *Bioresource Technology* 165, 9-12. DOI: 10.1016/j.biortech.2014.02.053
- Izani, M. N., Paridah, M. T., Anwar, U. M. K., Nor, M. M., and H'ng, P. S. (2013). "Effects of fiber treatment on morphology, tensile and thermogravimetric analysis of oil palm empty fruit bunches fibers," *Composites Part B: Engineering*, 45(1), 1251-1257. DOI: 10.1016/j.compositesb.2012.07.027
- Jenkins, B. M., Bakker, R. R., Baxter, L. L., Gilmer, J. H., and Wei, J. B. (1997). "Combustion characteristics of leached biomass," in: *Developments in Thermochemical Biomass Conversion*, pp. 1316-1330.
- Jenkins, B. M., Bakker, R. R., and Wei, J. B. (1996). "On the properties of washed straw," *Biomass and Bioenergy* 10(4), 177-200. DOI:10.1016/0961-9534(95)00058-5
- Jiang, L., Hu, S., Sun, L. S., Su, S., Xu, K., He, L. M., and Xiang, J. (2013). "Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass," *Bioresource Technology* 146, 254-260. DOI: 10.1016/j.biortech.2013.07.063
- Karuna, N., Zhang, L., Walton, J. H., Couturier, M., Oztop, M. H., Master, E. R., McCarthy, M. J., and Jeoh, T. (2014). "The impact of alkali pretreatment and post-pretreatment conditioning on the surface properties of rice straw affecting cellulose accessibility to cellulases," *Bioresource Technology* 167, 232-240. DOI: 10.1016/j.biortech.2014.05.122
- Khan, A. A., de Jong, W., Jansens, P. J., and Spliethoff, H. (2009). "Biomass combustion in fluidized bed boilers: Potential problems and remedies," *Fuel Processing Technology* 90(1), 21-50, DOI: 10.1016/j.fuproc.2008.07.012
- Konsomboon, S., Pipatmanomai, S., Madhiyanon, T., and Tia, S. (2011). "Effect of kaolin addition on ash characteristic of palm empty fruit bunch (EFB) upon combustion," *J. Applied Energy* 88, 298-305. DOI: 10.1016/j.apenergy.2010.07.008
- Kuchenbuch, R., Claassen, N., and Jungk, A. (1986). "Potassium availability in relation to soil moisture," *Plant and Soil* 95(2), 233-243.
- Lim, W. S., Kim, J. Y., Kim, H. Y., Choi, J. W., Choi, I. G., and Lee, J. W. (2013). "Structural properties of pretreated biomass from different acid pretreatment and their effects on simultaneous saccharification and ethanol fermentation," *Bioresource Technology* 139, 214-219. DOI: 10.1016/S0016-2361(01)00131-4
- Lindberg, D. K., Backmann, R., Chartrand, P., and Hupa, M. (2013). "Towards a comprehensive thermodynamic database for ash-forming element in biomass and waste combustion – Current situation and future development," *Fuel Processing Technology* 105, 129-141. DOI: 10.1016/j.fuproc.2011.08.008
- Liorente, M. J. F., Arocas, P. D., Nebot, L. G., and García, J. E. C. (2008). "The effect of the addition of chemical materials on the sintering of biomass ash," *Fuel* 87(12), 2651-2658. DOI: 10.1016/j.fuel.2008.02.019
- Madhiyanon, T., Sathitruangsak, P., Sungworagarn, S., Pipatmanomai, S., and Tia, S. (2012). "A pilot scale investigation of ash and deposition during oil palm empty fruit bunch (OPEFB) combustion," *Fuel Processing Technology* 96, 250-264, DOI: 10.1016/j.fuproc.2011.12.020
- Mark, H., Galord, N., and Bikales, N. (eds.) (1971). *Encyclopedia of Polymer Science and Technology*, First Ed., John Wiley & Sons 15(28), USA.

- Masiá, A. T., Buhre, B. J. P., Gupta, R. P., and Wall, T. F. (2007). "Characterising ash of biomass and waste," *Fuel Processing Technology*, 88(11-12), 1071-1081, DOI: 10.1016/j.fuproc.2007.06.011
- Miles, T. R., Miles Jr, T. R., Baxter, L. L., Bryers, R. W., Jenkins, B. M., and Oden, L. L. (1996). Boiler deposits from firing biomass fuels. *Biomass and Bioenergy* 10(2-3), 125-138. DOI: 10.1016/0961-9534(95)00067-4
- Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Hotzapple, M., and Ladisch, M. (2005). "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresources Technology* 96, 673-686. DOI: 10.1016/j.biortech.2004.06.025
- Nordin, N. I. A. A., Ariffin, H., Andou, Y., Hassan, M. A., Shirai, Y., Nishida, H., and Ibrahim, N. A. (2013). "Modification of oil palm mesocarp fiber characteristics using superheated steam treatment," *Molecules* 18(8), 9132-9146. DOI: 10.3390/molecules18089132
- Nurhayati, A., and Fauziah, S. (2013). "The properties of the washed empty fruit bunches of oil palm," *Physical Science* 24(2), 117-137.
- Olanders, B., and Steenari, B. M. (1995). "Characterization of ashes from wood and straw," *Biomass and Bioenergy* 8(2), 105-115. DOI: 10.1016/0961-9534(95)00004-Q
- Rahman, S. H., Choudhury, J. P., Ahmad, A. L., and Kamaruddin, A. H. (2007). "Optimization studies on acid hydrolysis of oil palm empty fruit bunch fiber for production of xylose," *Bioresour. Technol.* 98, 554-559. DOI: 10.1016/j.biortech.2006.02.016
- Schwanninger, M. J. C. R., Rodrigues, J. C., Pereira, H., and Hinterstoisser, B. (2004). "Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose," *Vibrational Spectroscopy* 36(1), 23-40. DOI: 10.1016/j.vibspec.2004.02.003
- Silverstein, R. A., Chen, Y., Sharma-Shivappa, R. R., Boyette, M. D., and Osborne, J. (2007). "A comparison of chemical pretreatment methods for improving saccharification of cotton stalks," *Bioresource Technology* 98(16), 3000-3011, DOI: 10.1016/j.biortech.2006.10.022
- Tan, H., and Wang, S. (2009). "Experimental study of the effect of acid washing pretreatment on biomass pyrolysis," *Chemical Technology* 37, 668-672, DOI: 10.1016/S1872-5813(10)60014-X
- TAPPI T211 om-02. (2007). "Ash in wood, paper and paperboard combustion at 525 °C," TAPPI Press, Atlanta, GA.
- TAPPI T207 cm-08. (2008). "Water solubility of wood and pulp," TAPPI Press, Atlanta, GA.
- TAPPI T204 cm-17. (2007). "Solvent extractive of wood and pulp," TAPPI Press, Atlanta, GA.
- TAPPI T222 om-2. (2006). "Acid insoluble lignin in wood and pulp," TAPPI Press, Atlanta, GA.
- TAPPI T212 om-07, (2012). "One percent sodium hydroxide solubility of wood and pulp," TAPPI Press, Atlanta, GA.
- TAPPI T429 om-10, "Alpha cellulose in paper," TAPPI Press, Atlanta, GA.
- Xu, Z., Wang, Q., Jiang, Z., Yang, X. X., and Ji, Y. (2007). "Enzymatic hydrolysis of pretreated soybean straw," *Biomass and Bioenergy* 31(2-3), 162-167, DOI: 10.1016/j.biombioe.2006.06.015

- Yang, C. Y., Lu, X. S., Lin, W. G., Yang, X. M., and Yao, J. Z. (2006). "TG-FTIR study on corn straw pyrolysis-influence of minerals," *Chemical Research in Chinese Universities* 22(4), 524-532, DOI: 10.1016/S1005-9040(06)60155-4
- Ying, T. Y., Teong, L. K., Abdullah, W. N. W., and Peng, L. C. (2014). "The effect of various pretreatment methods on oil palm empty fruit bunch (EFB) and kenaf core fibers for sugar production," *Procedia Environmental Sciences*, 20, 328-335, DOI: 10.1016/j.proenv.2014.03.041
- Yu, C. T., Chen, W. H., Men, L. C., and Hwang, W. S. (2009). "Microscopic structure features changes of rice straw treated by boiled acid solution," *Industrial Crops and Products* 29(2-3), 308-315. DOI: 10.1016/j.indcrop.2008.06.005

Article submitted: February 2, 2022; Peer review completed: February 26, 2022; Revised version received and accepted: March 21, 22; Published: March 28, 2022.
DOI: 10.15376/biores.17.2.2727-2742