Hydrothermal Pretreatment of Palm Oil Empty Fruit Bunch

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Abstract. Hydrothermal pretreatment methods in 2nd generation bioethanol production more profitable to be developed, since the conventional pretreatment, by using acids or alkalis, is associated with the serious economic and environmental constraints. The current studies investigate hydrothermal pretreatment of palm oil empty fruit bunch (EFB) in a batch tube reactor system with temperature and time range from 160 to 240 C and 15 to 30 min, respectively. The EFB were grinded and separated into 3 different particles sizes i.e. 10 mesh, 18 mesh and 40 mesh, prior to hydrothermal pretreatment. Solid yield and pH of the treated EFB slurries changed over treatment severities. The chemical composition of EFB was greatly affected by the hydrothermal pretreatment especially hemicellulose which decreased at higher severity factor as determined by HPLC. Both partial removal of hemicellulose and migration of lignin during hydrothermal pretreatment caused negatively affect for enzymatic hydrolysis. This studies provided important factors for maximizing hydrothermal pretreatment of EFB.

1. INTRODUCTION

Palm oil industry all over the world is dominated by Indonesia and Malaysia, for approximately 85% of the world oil palm production (Sulaiman et al., 2011). However, growth of palm oil industry create a new problem specifically waste generated. The palm oil industry produces large amounts of solid waste such as empty fruit bunches (EFB), kernels and fibres. If not utilized, the waste creates a disposal problem. Utilization of this biomass will improve the value of the by-products and contribute sustainability to the oil palm industry.

Palm empty fruit bunch (EFB) is a lignocellulosic material, currently is disposed through incineration, which incidentally causes air pollution problems for environment (Rahman et al., 2006). Meanwhile, EFB already reported as potential biomass for biochemicals and biomaterials application, since these materials are rich in carbohydrate and lignin, available throughout a year, renewable and sustainable (Ho et al., 2014; Zahari et al., 2014). For renewable energy sources, EFB can be utilized as a raw material for 2nd generation bioethanol production. Though it has drawbacks such as a slow reaction rate and a limited enzymatic accessibility to polysaccharides due to its recalcitrance (Kontinonkul et al., 2012). Therefore, pretreatment of EFB is required to open up its cell wall structure and, thereby, enhance its enzymatic accessibility during enzymatic hydrolysis (Jorgensen et al., 2007; Taherzadeh and Keikhosro, 2007).

The presence of hemicellulose and lignin hinders the access of the cellulase to cellulose, thus resulting in low efficiency of the hydrolysis (Sun and Cheng, 2012). An effective pretreatment should produce significant percent of cellulose supports, the lesser production of inhibitors and be cost effective (Sun and Cheng, 2012). Various types of pretreatment methods have been investigated. It was reported that the breakdown and loosening of the lignocellulosic structure in biomass was achieved by hydrothermal pretreatment and dilute acid or alkali at chosen treatment conditions (Zakaria et al., 2015). However, the conventional pretreatment, by using acids or alkalis, is associated with the serious economic and environmental constraints due to the heavy use of chemicals and chemical resistant materials (Diaz et al., 2010). Therefore, hydrothermal pretreatment more profitable to be developed.

Hydrothermal pretreatment, which is typically conducted in the range of 150-240°C has advantages over other pretreatments since the system only use water and the hydronium ion from water ionization act as catalyst in the reaction medium (Möller et al., 2011; Sabiha-Hanim et al., 2011). Moreover, water that used in this process is a non-toxic, environmental friendly and inexpensive media. Some study about hydrothermal pretreatment already published. Kumar et al., 2011 and Zakaria et al., 2015 investigated hydrothermal pretreatment of several biomass for production of bioethanol, but with limited range of temperature and reaction time. Successful fractionation of lignocellulosic biomass by hydrothermal pretreatments were greatly influenced by the combined reaction time and temperature. Therefore, the current study was to investigate wide range variation of temperature and reaction time as well as particle size effect on reducing hemicellulose and lignin during hydrothermal pretreatment of EFB.

2. METHODS

2.1. Raw materials

The palm oil empty fruit bunch (EFB) as raw materials on the experiment was collected from PTPN-VII, Lampung - Indonesia. The EFB were grinded and separated into 3 different particle sizes i.e. 10 mesh, 18 mesh and 40 mesh. Here in after, the grinded EFB then dried in an electrical oven for 24 h to reach moisture content below 10% prior to hydrothermal pretreatment.

2.2. Hydrothermal pretreatment

Process hydrothermal pretreatment was carried out in an autoclave made of 304 stainless steel grade with 280 ml of volume and inside diameter of 5.4 cm as shown in Fig. 1. About 100 mL of distilled water and 10 mg of EFB (equivalent to 1:10, solid: liquid ratio) was fed into the autoclave and covered tightly. The tightened reactor was flushing three times by inert gas (Nitrogen), then pressurized with nitrogen gas until the reactor pressure reach 7 bar. The reactor was agitated at 60 rpm in order to provide homogenize mixing of the sample in the vessel reactor. The reactor heated from room temperature to desired temperature, and the final temperature was maintained as long as designed reaction time. Pretreatment process was carried out by 15 and 30 minutes reaction time under variation of temperatures (160 - 240 °C) for each particle size of EFB. After completed the reaction time, the reactor was cooled down to 30°C by electric fan. The pH values of the hydrothermally treated samples were measured using a digital pH meter (pH 700, EUTECH - Instruments). The pretreated samples were filtered and subsequently oven dried at 105°C for 24 h prior to solid yield measurements and component analysis. The intensity of the hydrothermal treatment was expressed as severity factor (log Ro). The severity factor corresponding to different hydrothermal pretreatment conditions are calculated as in Eq. (1), for t is the reaction time (min), and T is the process temperature (°C) (Overend and Chornet, 1989).

$$R_0 = t \exp\left[(T - 100)/14.75\right] \quad \text{.........................} \quad (1)$$

2.3. Analytical procedures

EFB were characterized prior to and after hydrothermal pretreatment. Characterization of components containing in the biomass (i.e. cellulose, hemicellulose, and lignin) was analyzed base on National Renewable Energy Laboratory (NREL) (Ruiz and Ehrman, 1996). Acid hydrolysis was conducted to ±300 mg of dried EFB for lignin, hemmicellulose and cellulose content analysis. Afterwards, the weight of acid insoluble lignin (AIL) was weighed by Sartorius BS224S, whereas acid soluble lignin (ASL) measured by Spectrophotometry UV/Vis at 205 nm (Spectrophotometer Optizen 2120 UV). Sum of AIL and ASL obtained the total lignin content of the sample. Moreover, the filtrate also analyzed by HPLC Waters e2965 using Aminex HPX-87H column at 65°C with 0.6 ml min^{-1} eluent of 5mM sulfuric acid for xylose and glucose analysis. Afterward the xylose and glucose were converted into hemicellulose and cellulose content in the sample, respectively.

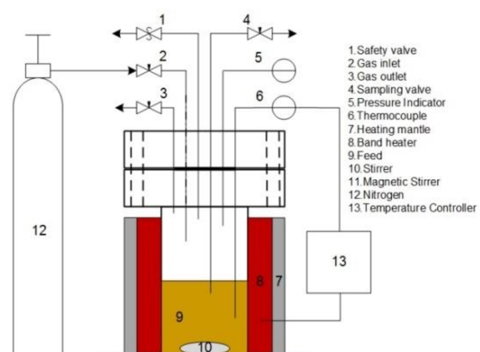


FIGURE 1. Hydrothermal pretreatment reactor

3. RESULTS AND DISCUSSION

3.1. Chemical composition and properties of untreated EFB

Component analysis of untreated EFB for each particle size is listed in Table 1. The major component of untreated EFB is lignin, followed by cellulose and hemicellulose. Particle size effect of untreated EFB shows insignificant differences on component percentage.

TABLE 1. Component analysis of untreated EFB for each particle size

Particle Size (mesh)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
10	27.11	15.28	34.95
18	25.95	11.46	31.13
40	19.31	8.49	34.04

3.2. Chemical composition and properties of hydrothermally pretreated EFB

Table 2 shows the calculation results of severity factor (log R_0) for each variations of process temperature and reaction time. Those severity factor were applied as hydrothermal pretreatment conditions of EFB for each particle size.

TABLE 2. Severity factor calculation

T (°C)	t (min)	Severity factor (log R_0)
160	15	2.94
160	30	3.24
180	15	3.53
180	30	3.83
200	15	4.12
200	30	4.42
220	15	4.71
220	30	5.01
240	15	5.30
240	30	5.60

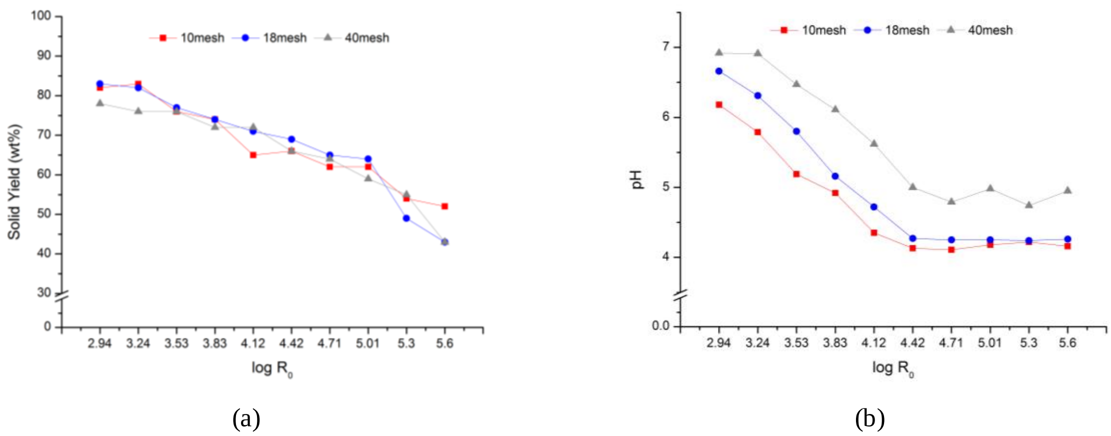
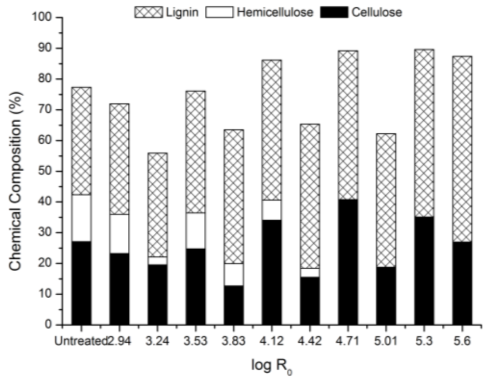
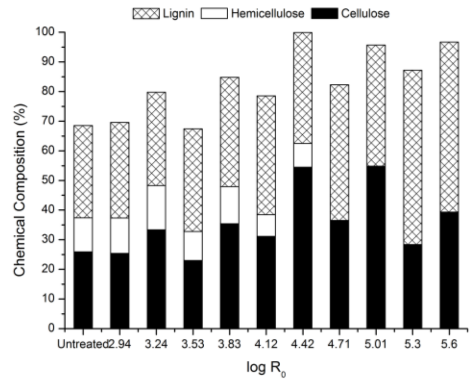


FIGURE 2. Hydrothermal pretreatment product parameters changed over severity factor, (a). Solid Yield, (b). pH.



(a)



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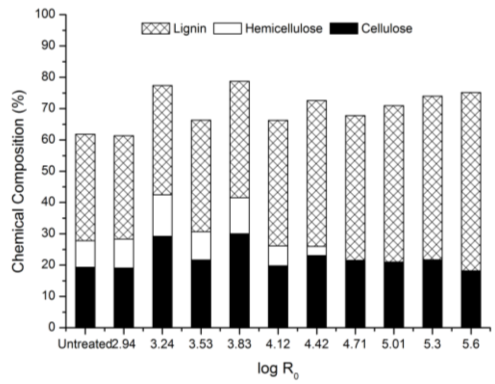

(c)

FIGURE 3. Component analysis of hydrothermally pretreated EFB for each particle size,

(a). 10 mesh, (b). 18 mesh, (c). 40 mesh.

Fig. 2 represents the hydrothermal pretreatment product parameters (solid yield and pH) for every particle size changed over severity factor. As shown in Fig. 2.(a), about 43–53% of solids yield were obtained from EFB samples at the highest severity factor (temperature and time). For every particle sizes, the yield of the solid decreased as the severity factor ascended from 2.94 to 5.30, which indicated that the yield of solids declined with the increase of pretreatment temperature. Meantime, for reaction time effect obviously described on smallest particle size (40 mesh), which is yield of solids declined with the prolonging of reaction time. When the pretreatment temperature was at 240°C, the solid yield declined from 55% to 43% with the prolonging of time from 15 to 30 min (the severity factor increase form 5.30 to 5.60). This result clarified the severity factor in Eq. 1, which the main parameter in hydrothermal pretreatment are process temperature and reation time. Zakaria et al., 2015 described the dissolution of soluble components of EFB occurred and correlated well with severity factor resulting in decreased solid recovery yield. Meanwhile, pH of pretreated EFB slurries decreased from neutral to acidic toward higher severity factor (Fig. 2.b). It occur due to accumulation of acetic acid from de-acetylation of hemicellulose degradation (Sabiha-Hanim et al., 2011; Ho et al., 2014). On the other way, Kumar et al., 2011 explained the pH of liquid hydrolyzate decreases with an increase in process temperature due to the increased formation of organic acids.

This study obtained that the chemical composition of EFB was greatly affected by the hydrothermal pretreatment especially hemicellulose which decreased at higher severity factor (Fig. 3). It explained that the degradation of hemicelluloses was not obvious for a relatively mild treatment, while it became more serious with the increase of temperature and prolongation of time. Xiao et al., 2014 also reported the reduction of hemicellulose in bamboo was occured in high severity factor. The removal of hemicelluloses was the goal of pretreatment since xylan was a inhibitor of enzymatic hydrolysis (Zhang et al., 2012).

As shown in Fig. 3, about 2-fold increase of lignin content was recorded toward higher severity factor from each particle size. This can be explained by the fact that most of the lignin was solubilized at selected treatment temperature range (200 - 240°C) and recondensation of this material took place upon cooling process. The current finding is in agreement with other studies which reported accumulation of lignin under acidic environments (Goh et al., 2010; Sabiha-Hanim et al., 2011; Pu et al., 2013; Zakaria et al., 2015). Additionaly, cellulose and hemicelluloses in biomass might be partially converted into pseudo lignin under the hydrothermal conditions given, which resulted in the increase of acid-insoluble lignin (Xiao et al., 2014). The chemical structure of lignin seemed to be redistributed, and it may be a crucial role on the enzymatic hydrolysis. Meanwhile, one and a half increase of cellulose content was noted at log R_0 = 5.01 and 4.42, with the highest is 54.85% at severity 5.01 (Fig. 3.b). The explanation about this result is the dissolution of hemicellulose and relocation or migration of lignin resulted in higher cellulose content (Zakaria et al., 2015).

4. CONCLUSION

Hydrothermal pretreatment appropriated to remove hemicelluloses and to break up the cellulosic structure of lignocellulosic biomass. The relocation of lignin during the hydrothermal pretreatment may negatively affect enzymatic hydrolysis and reduce the yield of glucose because of its redeposition on the surface of biomass residues as well as high affinity and capacity for enzyme. Therefore, It be required the next phase of pretreatment to remove the lignin, after hydothermally pretreated. There is insignificant effect on component percentage of untreated and pretreated EFB, due to differences of particle size.

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