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A Study on Glycerolysis of Oil Palm Empty Fruit Bunch Fiber

(Suatu Kajian tentang Gliserolisis Serabut Tandan Kosong Sawit)

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ABSTRACT

Lignocellulose from oil palm empty fruit bunch fiber (EFB) has been identified as another source for conversion into renewable energy or value added products. Cellulose, hemicellulose and lignin were extracted from EFB via a new treatment method using aqueous glycerol as a potential delignification agent. The aim of this study was to investigate the effect of treatment time and EFB to solvent ratio on the analytical compositions of EFB with or without further treatment with aqueous glycerol. The cooking time was varied at 3, 5 and 7 h with temperature fixed at 85°C. Three types of EFB were used; untreated fiber (UT-EFB), pretreated fiber with 5% (w/v) sodium hydroxide solution (N-EFB) and pretreated fiber with 5% (w/v) acetic acid solution (A-EFB). The analyses carried out were determination of extractives content, Klason Lignin, α-cellulose, hemicelluloses, holocellulose and ash content based on dry weight of the EFB. An increase in the glycerolysis time resulted in reduced content of Klason lignin and extractives but high percentages of holocellulose and α-cellulose for all EFB samples. Treatment of EFB with alkaline solution prior to glycerolysis resulted in reduction in cellulose content compared with holocellulose.

Keywords: Aqueous glycerol; cellulose; lignin; oil palm empty fruit bunch

ABSTRAK

Lignoselulosa daripada serabut tandan kosong sawit (EFB) telah dikenal pasti sebagai salah satu sumber berpotensi untuk ditukarkan kepada tenaga diperbaharui atau produk tambah nilai. Selulosa, hemiselulosa dan lignin diekstrak daripada EFB melalui kaedah rawatan baru menggunakan gliserol akues sebagai agen nyahlignin yang berpotensi. Kajian ini bertujuan untuk mengkaji kesan masa rawatan ke atas komposisi EFB secara analitikal dengan atau tanpa rawatan lanjutan dengan gliserol akues. Masa rawatan dipelbagaikan pada 3, 5 dan 7 jam dengan suhu ditetapkan pada 85°C. Tiga jenis EFB digunakan iaitu serabut tidak terawat (UT), serabut terawat larutan natrium hidroksida 5% (w/v)(N) dan serabut terawat larutan asid asetik 5% (w/v) (A). Analisis yang dijalankan adalah penentuan kandungan ekstraktif, Klason Lignin, α-selulosa, hemiselulosa, holoselulosa dan kandungan abu berdasarkan jisim kering EFB. Dengan peningkatan masa tindak balas gliserolisis memberikan kandungan Klason lignin dan ekstraktif yang berkurangan tetapi peratusan yang tinggi untuk holoselulosa dan α-selulosa untuk semua jenis sampel. Rawatan EFB dengan larutan alkali sebelum gliserolisis memberikan penyusutan dalam kandungan selulosa berbanding holoselulosa.

Kata kunci: Gliserol akues; lignin; selulosa; tandan kosong sawit

INTRODUCTION

A lot of efforts have been made by researchers all over the world to convert plant fibers to value-added products. Various pretreatments involving chemical, physical and biological treatments were conducted in extracting cellulose, hemicelluloses and lignin. Chemical treatments that have been commonly used are treatments with aqueous sodium hydroxide (Hamisan et al. 2009), silane (Sreekala et al. 1997), hydrogen peroxide (Run et al. 2000), acid (Tay & Rozman 2007), hot water (Borrega et al. 2011; Xiao et al. 2011) and ethanol (Aziz et al. 2002). Physical treatments are normally involved steam (Ruiz et al. 2008), ball-milling (Lin et al. 2010) and microwave (Binod et al. 2011). Biological approach is normally involved microorganisms such as enzyme like *celluclast* (Hamisan et al. 2009), enzyme cocktails (Amin et al. 2010) and some other microbes. Cellulose from fibers can be hydrolyzed to a single monomer such as glucose or xylose.

In pulp and paper industry, organosolv pulping process involving mixture of water and organic solvents as delignifying components is of choice. These solvents are recovered by distillation after the pulping process. Organosolv pretreatment has attracted the attention of researchers to put an in depth study on types of organic solvents such as glycol, organic acid such as acetic acid or carboxylic acid and ester (Alriols et al. 2009; Rodríguez et al. 2008). Glycerol obtained from esterification of triacylglyceride is a potential delignification agent for lignin carbohydrate complex (LCC) but was not reported elsewhere. The carbohydrates in LCC are mainly xylan, the bond type in lignin include the β-O-4, β-β, 5-5, β-1 and β-5. The α-C=O and unsaturated α-β structure can also be found in the lignin of LCC. The linkage between lignin and

carbohydrates include ester bond, ether bond as well as acetal structure. The ester bond and the β-O-4 structures in LCC are stable in glycerol. The LCC can be further esterified and easily separated from the cellulosic compounds. The delignification rate is higher than the degradation of carbohydrates. Glycerolysis is a chemical process to break the glycosidic bonds between carbohydrates and act as an aid to increase both the delignification selectivity and the amount of delignification. The cooking process can be further accelerated by the addition of small amount of sulfuric acid or sodium hydroxide. However, to better understand the reactivity of EFB in glycerolysis, this study highlighted findings only on glycerolysis catalysed by 5% (w/v) of 1 M NaOH.

Malaysia is the second largest palm oil producer, after Indonesia. In the process of palm oil extraction, a large amount of oil palm empty fruit bunch (EFB) is generated as a waste product. Approximately 1.07 ton EFB is generated with every tonnage of palm oil production. To ensure the sustainability of the industry and protect the environment, more downstream processing of biomass waste into renewable energy or value added products would be beneficial to the palm oil industry to spur the production of renewable chemical feedstocks (Basiron 2007). Empty fruit bunch is the major waste of oil palm industry and is commonly being used to produce organic fertilizer, wood composite and fiber board (Deraman et al. 1999). However, most of this waste is burnt as an alternative to energy source resulted in thermal and potential air pollutions when treated unsystematically (Rahman et al. 2006).

The objective of this study was to determine the effect of cooking time and temperature as well as fiber to glycerol ratio on the compositional analysis of EFB undergone glycerolysis catalysed by 5% (w/v) 1 M NaOH. This involved determination of the percentage of extractive, Klason Lignin, α-cellulose, hemicellulose, holocellulose and ash content based on dry weight of EFB and correlate them to the processing parameters for optimization purpose.

Experimental Methods

MATERIALS

Treated (5% sodium hydroxide (N) and 5% acetic acid (A)) and untreated (UT) EFB were generously supplied by Malaysia Palm Oil Board (MPOB), Stesen Bangi Lama, Pekan Bangi Lama, Malaysia. Glycerol (anhydrous, 99%) was manufactured by R & M Ltd. Steinheim, Germany. Other chemicals for pulp characterization were benzene (~99% purity), ethanol (~99% purity), sulfuric acid (~95-98% purity) and sodium hydroxide pellet (~99% purity), supplied by Systerm Sdn Bhd, Petaling Jaya, Malaysia. Sodium chlorite (~80% purity, technical grade) was supplied by Sigma Aldrich, Shah Alam, Malaysia.

SAMPLE PREPARATION

The shredded EFB was further ground using a mechanical cutter and was then sieved using a sieve shaker to obtain a size of less than 250 μm. It was dried in the oven at 60°C for 24 h and then kept in an air-tight glass jar. Aqueous glycerol was prepared at 70% (v/v) concentration in distilled water. The EFB was mixed with the aqueous glycerol at a ratio of 1:20 (and compared to 1:10 and 1:30) in a 1 L four-neck flask. Then the mixture was refluxed in nitrogen gas at atmospheric pressure at varying cooking time of 3, 5 and 7 h. The temperature was varied in the range of 65°C to 85°C. Each hydrolysate was filtered using Büchner funnel and was divided into two parts. One part was dried at 60°C for pulp characterization. The other part was kept at 4°C before further analysis.

PULP CHARACTERIZATION

Characterization of pulp was carried out based on the Technical Association of Pulp and Paper (TAPPI) standard method. The tests were determination of moisture contents (TAPPI T264 om-97), ethanol-benzene extractives (TAPPI T204 om-97), Klason lignin (TAPPI T222 om-98), holocellulose (Wise Method), α-cellulose (TAPPI T203 om-99) and ash content (T211 om-7) based on oven dry basis.

Results and Discussion

Untreated EFB (UT-EFB), NaOH-pretreated EFB (N-EFB) and acetic acid-pretreated EFB (A-EFB) samples were analysed prior to glycerolysis to determine their compositions and as summarised in Table 1. EFB contains 50.5% holocellulose (containing 36.7% α-cellulose), 23.2% Klason lignin (exclusion of soluble lignin) and 4.96% extractives. These are parallel to reports by researchers working on EFB (Amin et al. 2010; Aziz et al. 2002). However, N-EFB indicated lower Klason Lignin content but higher percentage of cellulose. The NaOH treatment has delignified the EFB, exposing more cellulose. This increased the hydrophilicity of EFB and creates greater tendency to absorb water molecules from the surrounding (higher moisture content at

TABLE 1. Pulp characterization of EFB before glycerolysis

Sample	Moisture content, %	Extractive, %	Klason lignin, %	Holocellulose, %	α-cellulose, %
UT-EFB	3.88±0.08	4.96±0.08	23.18±0.03	50.46±0.03	36.70±0.26
N-EFB	7.65±0.08	2.84±0.07	15.08±0.03	69.29±0.28	43.62±0.07
A-EFB	4.04±0.06	3.94±0.08	17.15±0.06	66.86±0.06	40.55±0.01

7.65±0.08%). The acetic acid treatment on the other hand, not only separated lignin but instantaneously hydrolysed cellulose to an extent, resulting in lesser cellulose content (due to scissoring) (Tay & Rozman 2007).

Treatment with alkaline solutions such as aqueous sodium hydroxide and aqueous glycerol are possible to enhanced delignification as described in the following mechanisms:

a) Fiber treated with alkaline solution (NaOH)

Fiber---OH (s) + Na+OH- (aq) → Fiber---O---Na (s) + H—O—H (liq).

b) Fiber treated with glycerol catalysed with 5% NaOH

Step 1. $\text{Fiber-O-Na(s)}+C_3H_5\text{–(OH)}_3\text{(aq)} \xrightarrow{Na^+OH^-(aq)} \text{Fiber–O–H+H–O–H+}Na^+OH^-\text{(aq)}.$

Step 2. $\text{Fiber-O}C_3H_5\text{(s)+H-O-H} \xrightarrow{Na^+OH^-(aq)} \text{Fiber–O–H(s)+}C_3H_5\text{–(OH)}_3\text{aq+}Na^+OH^-\text{(aq)}.$

Following these routes (a, b), performance of the reaction was monitored by mean of evaluating the reaction times and temperatures as well as the fiber to glycerol ratios (Step 1 and 2). The advantage of this pathway was the retrieval of glycerol (C_3H_5-$(OH)_3$ (aq)) at the end of the reaction (Step 2).

The ratio of solid to liquid studied were 1:10, 1:20 and 1:30 which was 1 g of dry EFB in 10 mL, 20 mL and 30 mL of aqueous glycerol, respectively. Table 2 summarized the data obtained from the compositional analysis of the glycerolysed EFB (of untreated (UTgly), NaOH treated (Ngly) and acetic acid treated (Agly)) at varying ratio of EFB to glycerol. Data in Table 2 indicated insignificant differences in the compositions between ratio of 1:20 and 1:30 for all three types of EFBs. The extraction of the main components in the fiber has reached its maximum level that an excess of glycerol at the ratio of 1:30 did not encourage further extraction. Glycerolysis of EFB at 1:10 ratio exhibited high recovery of Klason lignin and extractives. The trace of lignin was the insoluble part while the extractives could be pectin, wax or impurities present on the surface of fiber. Limitation in the amount/concentration of aqueous glycerol (1:10) restricting removal of the soluble lignin. Thus, 1:20 ratio was selected as optimum fiber to aqueous glycerol ratio. The reaction was then further studied at 85°C and varying cooking time at 3, 5 and 7 h. The compositional analysis was carried out to determine the optimum temperature and cooking time that best yield high recovery of holocellulose and α-cellulose. Figure 1 shows the trends in the percentage of extractives, Klason lignin, holocellulose and α-cellulose.

Extractives in plant fiber could be wax, pectin and even simple sugar that are easily dissolved in solvent (ethanol-benzene mixture). Figure 1 indicate that all the treatments removed extractives from surface of EFB. However, N-EFB contains the lowest percentage of extractives followed by A-EFB and UT-EFB at 2.84%, 4.96% and 3.94%, respectively. These data were summarized in Table 3. Further treatment with aqueous glycerol dissolved more extractives. Percentage of extractives in UTgly, Ngly and Agly was lower compared with without glycerolysis. Swelling of the cellular structure increases the rate of diffusion out for the extractives during glycerolysis (Wertz et al. 2010). These extractives diffused out to the aqueous glycerol medium and created black liquor.

Holocellulose is a combination of cellulose and hemicelluloses and was determined by Wise method. Plant fiber normally contains around 65-70% holocellulose of wood dry weight (Rowell 2005). From Figure 1, the analyzed samples labeled as number 1, 5 and 9 were the untreated, pretreated NaOH and pretreated acetic acid EFB, respectively that have not undergone glycerolysis.

The percentage of holocellulose for UT-EFB was 50.46±0.05%. After treated with glycerol aqueous for 3,

TABLE 2. Data obtained from the compositional analysis of the glycerolysed EFB (of untreated (UTgly-), NaOH treated (Ngly-) and acetic acid treated (Agly-)) at varying ratio of EFB to glycerol

Sample	Moisture content, %	Extractive, %	Klason lignin, %	Holocellulose, %	α-cellulose, %
			UTgly		
1:10	3.86	5.02	23.10	50.28	36.73
1:20	6.94	3.77	16.53	79.58	45.3
1:30	6.96	3.78	16.54	79.64	45.4
			Ngly		
1:10	7.65	3.01	15.10	69.40	40.48
1:20	11.35	2.85	13.15	80.15	49.54
1:30	11.35	2.86	13.16	11.35	49.54
			Agly		
1:10	4.11	4.00	17.17	66.81	43.67
1:20	11.35	2.85	13.15	80.15	49.54
1:30	11.32	2.86	13.16	80.18	49.52

5 and 7 h, the yield of holocellulose increased with time but decreased insignificantly at 7 h producing 70.79±0.1%, 80.21±0.04% and 79.58±0.02%, respectively. The content of holocellulose in N-EFB was 69.29±0.28%. However, after glycerolysis the highest production of holocellulose was at 7 h treatment with 82.03±0.07% compared to 3 and 5 h at 75.92±0.08% and 79.23±0.09%, respectively. The A-EFB yielded 66.86±0.06% holocellulose. Once undergone glycerolysis, the percentage of holocellulose increased with treatment time with yields of 80.15±0.08%, 84.55±0.07% and 85.17±0.07% at 3, 5 and 7 h respectively. Higher temperature promoted opening of micro fibrils for access to glycerol to penetration (Demirbas 1998). The hemicellulose content was obtained by (1).

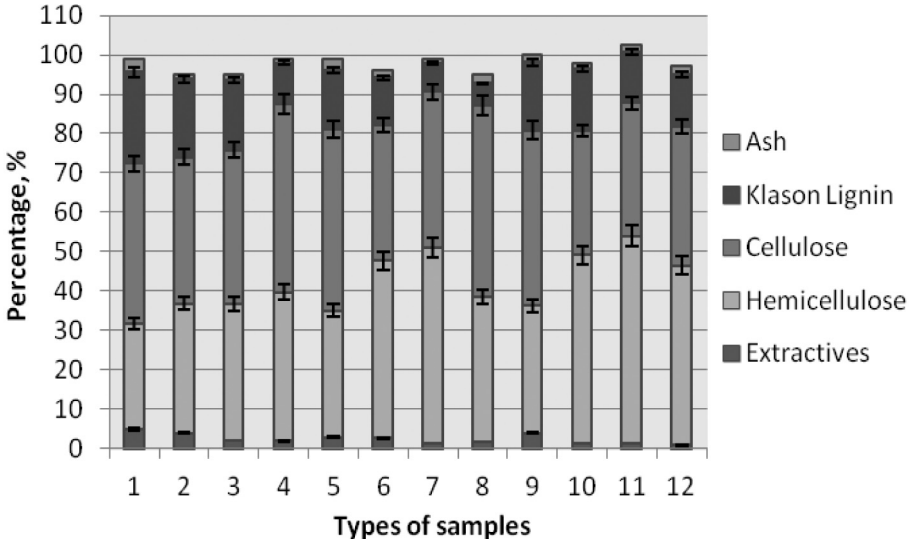
$$\text{Hemicellulose} = 100\% - [\text{Klason lignin (\%)} + \text{Cellulose (\%)}]. \quad (1)$$

The percentages of hemicellulose obtained were consistent with the recovery of Klason lignin from each type of EFB. The optimum yield of hemicellulose from UT-EFBgly was at 7 h treatment with yield of about 37% compared with UT-EFB at just about 28%. Sample of A-EFBgly gave optimum yield at 5 h (~52%) while 49% recovery by sample of N-EFBgly at 5 h.

Klason lignin is the insoluble residues retrieved after hydrolysis with 72% sulfuric acid as per required by TAPPI T222 om-98. The data summarized in Table 3 and plotted in Figure 1 indicated that UT-EFB contained the highest percentage of lignin followed by A-EFB and N-EFB at 23.18±0.03%, 15.08±0.03% and 17.15±0.06%, respectively. Mercerization with NaOH has extracted partial portion of lignin (Sreekala et al. 1997).

However, upon glycerolysis of UT-EFB, lignin has also been removed from the fiber. Increasing cooking time from 3 to 7 h resulted in reduction of the Klason lignin content in the EFB to 16.53±0.02%, 13.43±0.02% and 9.67±0.07%, respectively. The same effect was encountered by the N-EFB when exposed to glycerolysis with lignin content reduction to 11.54±0.13%, 7.9±0.05% and 5.06±0.14% at cooking time of 3, 5 and 7 h, respectively. The A-EFB when glycerolized at 3, 5 and 7 h contained 13.15±0.07%, 10.74±0.06% and 7.36±0.06%, respectively. Pretreatment of EFB with NaOH and acetic acid prior to glycerolysis were able to extract more lignin from the EFB and were much affected by the cooking time. EFB pretreated with NaOH (N-EFB) achieved reduction of up to 70.3% when undergone glycerolysis for 7 h compared with 55.1% and 51.0% of the UT-EFB and A-EFB, respectively. Conventionally, sodium hydroxide solution has been used as a solvent for pulping to remove lignin from cellulosic fiber. Hydroxide anions from sodium hydroxide form linkages with lignin and cleave the bonding. Carbohydrates degradation is minimized during alkaline delignification (Chakar & Ragauskas 2004).

The extraction of α-cellulose as a white residue remained after hydrolysis with sodium hydroxide 17.5% (w/w) was carried out following TAPPI T203 om-99. Total percentage of α-cellulose contributed to total percentage of holocellulose. Low efficiency in treatment yields low content of α-cellulose through high holocellulose content. The α-cellulose content in UT-EFB and A-EFB



Note:
1: Untreated EFB (UT-EFB); 2: Untreated EFB treat with glycerol aqueous at 3 h (UT-EFBgly 3H); 3: Untreated EFB treated with glycerol aqueous at 5 h (UT-EFBgly 5H); 4: Untreated EFB treat with glycerol aqueous at 7 h (UT-EFBgly 7H); 5: Pre-alkaline EFB treated (N-EFB); 6: Alkaline EFB treated glycerol aqueous at 3 h (N-EFBgly 3H); 7: Alkaline EFB treated glycerol aqueous at 5 h (N-EFBgly 5H); 8: Alkaline EFB treated glycerol aqueous at 7 h (N-EFBgly 7H); 9: Pre treated acetic acid (A-EFB); 10: Acetic acid EFB treat with glycerol aqueous at 3 h (A-EFBgly 3H); 11:Acetic acid EFB treated glycerol aqueous at 5 h (A-EFBgly 5H); 12: Acetic acid EFB treated glycerol aqueous treat at 7 h (A-EFBgly 7H)

FIGURE 1. Compositional analysis of the EFB samples

TABLE 3. Pulp characterization of EFB glycerolysi

Sample	UTgly-EFB			Ngly-EFB			Agly-EFB		
Time, H	3	5	7	3	5	7	3	5	7
Moisture content, %	6.94±0.08	7.23±0.07	8.55±0.07	13.11±0.12	13.93±0.08	14.96±0.1	11.35±0.07	13.04±0.07	14.07±0.09
Ethanol-benzene, %	3.89±0.12	3.11±0.01	2.68±0.09	2.14±0.07	1.55±0.07	1.09±0.07	2.85±0.06	2.23±0.05	1.34±0.07
Holocellulose, %	70.79±0.1	80.21±0.04	79.58±0.02	75.92±0.08	79.23±0.09	82.03±0.07	80.15±0.08	84.55±0.07	85.17±0.07
α-cellulose, %	45.3±0.02	55.0±0.07	60.68±0.1	41.39±0.12	46.01±0.09	43.77±0.09	49.6±0.05	51.2±0.06	56.00±0.07
Klason lignin, %	16.53±0.02	13.43±0.02	9.67±0.07	11.54±0.13	7.9±0.05	5.06±0.14	13.15±0.07	10.74±0.06	7.36±0.06

increased with increasing cooking time when it underwent glycerolysis (Table 3) up to about 60%. However, glycerolized N-EFB (Ngly-EFB) showed reduction in the percentage of α-cellulose (from 41.39±0.12% to 43.77±0.09%) after 5 h cooking (46.01±0.09%). In addition, the α-cellulose content was the lowest compared with both from UTgly-EFB and Agly-EFB. Delignification involved scissoring of the carbohydrate. Excessive treatment (alkaline treatment followed by glycerolysis) and heat exposure when not optimized might be able to degrade the molecular chains of the lignocelluloses. As a result, these polymeric chains were cut off to monomers (reduced sugars). Glycerol as a delignification solvent was more efficient in the presence of acid or alkaline where the ratio of glycerol in pretreatment solvent mixture was higher and pretreated at higher temperature as suggested by Novo et al. (2011) and Demirbas (1998). According to Demirbas (1998), delignification with the aid of aqueous glycerol minimized sugar loss but retarded further lignin removal. On the other hand, addition of alkaline catalyst such as sodium hydroxide promoted delignification but encouraged sugar loss.

The ash content was determined following T211 om-7 method. The value obtained indicated content of inorganic matters exclusive of mineral salts and other organic matters in the fiber after combustion at 575±25°C for 24 h. The ash content for UT-EFB was found higher (~3.44%) compared with N-EFB (~1.96%) and A-EFB (~2.84%). After glycerolysis, the ash content of each EFBs decreased with cooking time at 1.22 %, 1.50% and 1.05% (UTgly-EFB at 3, 5 and 7 h, respectively), 1.87%, 1.50%, and 1.03% (Ngly-EFB at 3, 5 and 7 h, respectively) and 1.66%, 1.55% 1.08% (Agly-EFB at 3, 5 and 7 h, respectively).

Conclusion

Glycerol is possible to work as delignification agent for plant fiber in the presence of 1 M NaOH as catalyst. The rate of delignification was much influenced by the cooking time and the EFB to glycerol ratio. The percentage of Klason lignin in the glycerolized UT-EFB was the lowest with a reduction of more than 70% but the highest cellulose content of up to 60%. However, N-EFB was suspected to have experienced degradation due to low cellulose content compared with UTgly-EFB. An increase in the cooking time from 3 to 7 h increased the cellulose content in UTgly-EFB and Agly-EFB and reduced the Klason lignin in both. Alternative approach for delignification to alkaline treatment for future work on enzymatic hydrolysis for instance might be more efficient if glycerolysis is considered.

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References

Alriols, M.G., Tejado, A., Blanco, M., Mondragon, I. & Labidi, J. 2009. Agricultural palm oil tree residues as raw material for cellulose, lignin and hemicelluloses production by Ethylene glycol pulping process. *Journal of Chemical Engineering* 148: 106-114.

Amin, N.A.S., Ya'ini, N., Misson, M., Haron, R. & Mohamed, M. 2010. Enzymed pretreated empty fruit bunch for Biofuel production. *Journal of Applied Sciences* 10(12): 1181-1186.

Aziz, A.A., Husin, M. & Mokhtar, A. 2002. Preparation of cellulose from oil palm empty fruit bunches via ethanol digestion: Effect of acid and alkali catalysts. *Journal of Oil Palm Research* 14(1): 9-14.

Basiron, Y. 2007. Palm oil production through sustainable plantations. *European Journal of Lipid Science and Technology* 4(2): 289-295.

Binod, P., Satyanagalakshmi, K., Sindhu, R., Janu, K.U., Sukumaran, R.K. & Pandey, A. 2012. Short duration microwave assisted pretreatment enhances the enzymatic saccharification and fermentable sugar yield from sugarcane bagasse. *Renewable Energy* 37(1): 109-116.

Borrega, M., Nieminen, K. & Sixta, H. 2011. Effects of hot water extraction in a batch reactor on the delignification of Birch wood. *BioResources* 6(2): 1890-1903.

Chakar, F.S. & Ragauskas, A.J. 2004. Review of current and future softwood Kraft lignin process chemistry. *Industrial Crops and Products* 20: 131-141.

Deraman, M., Zakaria, S., Husin, A., Aziz, A.A., Ramli, R., Mokhtar, A., Yusof, M.N.M. & S, M.H. 1999. X-ray diffraction studies on fiber of oil palm oil empty fruit bunch and rubber wood for medium density fiberboard. *Journal of Materials Science Letters* 18: 249-253.

Demirbas, A. 1998. Aqueous glycerol delignification of woods chips and ground wood. *Bioresource Technology* 63: 179-185.

Hamisan, A.F., Abd-Aziz, S., Kamaruddin, K., Shah, U.K.M., Shahab, N. & Hassan, M.A. 2009. Delignification of Oil Palm empty fruit bunch using chemical and microbial methods. *International Journal of Agricultural Research* 4(8): 250-256.

Lin, Z., Huang, H., Zhang, H., Zhang, L., Yan, L. & Chen, J. 2010. Ball milling pretreatment of corn stover for enhancing the efficiency of Enzymatic hydrolysis. *Applied Biochemistry and Biotechnology* 162(7): 1872-1880.

Novo, L.P., Gurgel, L.V.A., Marabezi, K. & Curvelo, A.A.S. 2011. Delignification of sugarcane bagasse using glycerol-water mixtures to produce pulps for saccharification. *Bioresource Technology* 102(21): 10040-10046.

Rahman, S.H.A., Choudhury, J.P., Ahmad, A.L. & Kamaruddin, A.H. 2006. Optimization studies on acid hydrolysis of oil palm empty fruit bunch fiber for production of xylose. *Bioresource Technology* 98(3): 554-559.

Rodríguez, A., Serrano, A., Moral, A., Pérez, A. & Jiménez, L. 2008. Use of high-boiling point organic solvents for pulping Oil Palm empty fruit bunches. *Bioresource Technology* 99(6): 1743-1749.

Rowell, R.M. 2005. *Handbook of Wood Chemistry and Wood Composite*. Madison: CRC Press/Taylor & Francis.

Ruiz, E., Cara, C., Manzanares, P., Ballesteros, M. & Castro, E. 2008. Evaluation of steam explosion pre-treatment for enzymatic hydrolysis of sunflower stalks. *Enzyme and Microbial Technology* 42: 160-166.

Run, C.S., Fang J.M. & Tomkinson, J. 2000. Delignification of rye straw using hydrogen peroxide. *Industrial Crops and Products* 12: 71-83.

Sreekala, M.S., Kumaran, M.G. & Thomas, S. 1997. Oil Palm fibers: Morphology, chemical composition, surface modification and mechanical properties. *Journal of Applied Polymer Science* 66: 821-835.

Tay, G.S. & Rozman, H.D. 2007. Chemical modification of oil palm empty fruit bunch: Determination of optimum condition and characterization. *Journal of Applied Polymer Science* 106: 1697-1706.

Wertz, J.L., Bédué, O. & Mercier, J.P. 2010. *Cellulose Science and Technology. Fundamental Sciences*. Boca Raton, Florida: Taylor and Francis Group.

Xiao, L.P., Sun, Z.J., Shi, Z.J., Xu, F. & Sun, R.C. 2011. Impact of hot compressed water pretreatment on the structural changes of woody biomass for Bioethanol production. *BioResources* 6(2): 1576-1598.

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