

Characterization of Residue from EFB and Kenaf Core Fibres in the Liquefaction Process

(Pencirian Bahan Baki Hasil daripada Proses PENCECAIRAN EFB dan Serabut Teras Kenaf)

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ABSTRACT

Different type of fibers which is EFB and KC were liquefied in phenol with the presence of sulphuric acid as a catalyst. The liquefied residue was characterized by using Fourier transform infrared (FTIR) to determine the functional groups presents in both residues, X-ray diffraction (XRD) to determine the degree of crystallinity in the residue, thermogravimetric analysis (TGA) to analyze the thermal properties of the residue and scanning electron microscope (SEM) to investigate the structure and morphology of the residue. Phenol-to-EPB/KC ratio shows great effect on the amount of residue in the liquefaction process. Peak appearance can be observed in the FTIR analysis at 810 and 750 cm^{-1} which is attributed to the para and meta benzene, respectively or to be specific its associated to the p-alkyl phenol and m-alkyl phenol. In the XRD analysis, CrI of lignocellulosic materials increased after liquefaction process. Liquefaction process caused chemical penetration across the grain of the fiber, thus the fiber bundles started to separate into individual fibers shown in the SEM micrograph and the weights lost curve for both liquefied EFB and KC experienced three region decompositions.

Keywords: EFB; KC; lignocellulosic; liquefaction; residue

ABSTRAK

Pencecairan bahan berbeza iaitu serabut tandan kosong kelapa sawit (EPB) dan serabut teras kenaf (KC) telah dijalankan menggunakan fenol sebagai agen pencecairan dengan kehadiran asid sulfurik sebagai mangkin. Pencirian baki pencecairan dilakukan dengan menggunakan transformasi Fourier inframerah (FTIR) untuk menentukan kumpulan berfungsi yang hadir, pembelauan Sinar-X (XRD) untuk menentukan darjah kehabluran, analisis termogravimetri (TGA) untuk menganalisis sifat terma bahan baki) dan mikroskop elektron imbasan (SEM) untuk melihat struktur dan morfologi baki pencecairan. Nisbah fenol terhadap STKKS/TK memberikan kesan yang besar terhadap jumlah baki yang terhasil selepas proses pencecairan. Kemunculan puncak boleh diperhatikan dalam analisis FTIR pada 810 dan 750 cm^{-1} disebabkan oleh meta dan para benzena atau lebih spesifik berkaitan p-alkil dan m-alkil fenol. Dalam analisis XRD, darjah kehabluran bahan lignoselulosa meningkat selepas proses pencecairan. Proses pencecairan menyebabkan penembusan bahan kimia ke seluruh butiran serabut lalu menyebabkan berkas serabut terpisah kepada serabut individu seperti yang ditunjukkan pada mikrograf SEM. Manakala lengkung kehilangan berat untuk kedua-dua baki pencecairan STKKS dan TK mengalami tiga tahap penguraian dengan peningkatan suhu.

Kata kunci: Baki; EFB; KC; lignoselulosa; pencecairan

INTRODUCTION

Increasing interest in the production of wood adhesives made from renewable materials has been driven by the rising of phenol price and concerns over greenhouse gas emissions (Sulaiman et al. 2009). Originally, the raw materials such as phenol that has been used in the production of synthetic adhesives are from petrochemicals or its derivatives (Hui 2011; Sulaiman et al. 2009). In order to overcome this matter, many studies have been carried out by using lignocellulosic as an alternative starting materials to reduce the consumption of petroleum-based phenol (Ahmadzadeh et al. 2009; Alma & Basturk 2006). Lignocellulosic is well recognized as the world's most abundant and promising biomass to substitute petroleum-based chemicals due to its similarity in chemical

structure (El Mansouri et al. 2011; Hu et al. 2011). It can be categorized into three main components which are cellulose (40 – 50%), hemicellulose (20 – 30%) and lignin (20 – 30%) (Chai et al. 2009; Effendi et al. 2008). The existence of phenol derivatives and aromatics chemicals in lignin make them among the best candidates to substitute petroleum-based phenol in the production of phenolic resin (Effendi et al. 2008). Previous studies showed that liquefaction is a promising method to convert lignocellulosic biomass to phenolic compounds (Chai et al. 2009).

Liquefaction is a technique to modify lignocellulosic materials for examples sawdust, empty fruit bunch (EPB) and kenaf core (KC) fibers in an organic solvent such as acetone, methyl alcohol, phenol and polyhydroxy

alcohols (Doh et al. 2005). These lignocellulosic materials which typically contain two or more hydroxyl groups will provide the sites for chemical modification to occur (Juhaida et al. 2010). Yield from the liquefaction process of lignocellulosic biomass in the presence of acid catalyst contains depolymerized product due to β 1 – 4 glucosidic bond cleavage (Kunaver et al. 2010). The complex structure in lignin will also break into smaller component namely phenol, guaiacyl and siringyl (Kleinert & Barth 2008).

One of the great and most important agricultural industrial in Malaysia is palm oil processing and its cultivated in large areas. The quantities of waste (EFB) generated from this processes are abundant and mostly are not fully utilized. In EFB fibres, lignocellulosic component comprises about 30.5% from their total weight. The rest are oil (2.5%) and water (67%). The compositions of major lignocellulosic components in EFB fibres are cellulose (45%), hemicellulose (32.8%) and lignin (20.5%) (Ridzuan et al. 2002). Another species of plant that received an increasing attention in Malaysia is kenaf. Capability of kenaf to grow over 3 m in three month has make Malaysian government keen to cultivate these plants as a fourth industrial crops in nation (Chan & Ismail 2009; Sajab et al. 2011). The percentages of major lignocellulosic components in kenaf core are cellulose (46.1%), hemicellulose (29.7%) and lignin (22.1%) (Ali et al. 2009).

In this study, we use two types of fibers which were EFB and KC in the liquefaction process. The liquefied residues were characterized by using Fourier transform infrared (FTIR) to determine the functional groups presents in both residues, X-ray diffraction (XRD) to determine the degree of crystallinity in the residues, thermogravimetric analysis (TGA) to analyze the thermal properties of the residues and scanning electron microscope (SEM) to investigate the structure and morphology of the residues.

EXPERIMENTAL DETAILS

EFB and kenaf core fibers used for the experiments were obtained from Sabutek Sdn. Bhd. Malaysia and Forest Research Institute Malaysia (FRIM), respectively. The EFB and kenaf core fibers were used as a substitute for phenol to reduce the consumption of petroleum-based phenol by using the phenolic derivatives from lignin in EFB and kenaf core fibers. Other chemicals such as industrial grade phenol (organic solvent), 98% sulphuric acid which act as the catalysts for liquefaction process and methanol (solvent) were all purchased from Sigma-Aldrich.

LIQUEFACTION PROCESS

Oven-dried EFB and kenaf core fibers (20 g), phenol (40, 50 and 60 g) and 98% H_2SO_4 (3% of phenol weight) were charged into a four-necked round bottom flask with capacity of 1000 mL equipped with thermometer and stirrer. The liquefaction reaction was set in an oil bath

at 150°C for 2 h. Liquefied mixture then dissolved with methanol to dilute the thick mixture and filtrated with filter paper (Whatman No. 1). After that the methanol-insoluble residue was dried in an oven and weighed.

DETERMINATION PERCENTAGE OF UNLIQUEFIED EFB AND KC FIBERS RESIDUE

In order to determine the percent of unliquefied EFB and KC fibers residue, methanol-insoluble residue (R) was calculated by using following equation:

$$\%R = (W_r / W_o) \times 100\%, \quad (1)$$

where W_o is the initial oven-dried EFB and KC fibers (g) and W_r is the oven-dried weight of the solid residue (g) after filtration of the liquefied mixture.

DETERMINATION OF CRYSTALLINITY INDEX (CRI)

Determination of crystallinity index (CrI) for the native and liquefied residue of EFB and KC were calculated by the following equation which is obtained from X-Ray diffraction spectra.

$$CrI (\%) = [(I_{002} - I_{AM}) / I_{002}] \times 100\%. \quad (2)$$

RESULTS AND DISCUSSION

Phenol-to-wood/lignocellulosic ratio shows great effect on the amount of both residue and combined phenol in the liquefaction process (Alma 1996). Figure 1 shows the effect of phenol/EFB (P/E) and phenol/KC (P/K) ratio on the residue at a constant reaction temperature and amount of catalyst which is 150°C and 3% H_2SO_4 , respectively. The amount of residue decreases when the ratio of P/E and P/K increases from 2.0 to 2.5 and 3.0. For examples, a total amount of 32% and 31% residue reduction occur when the P/E and P/K ratio increase from 2 to 3, respectively. By increasing the ratio of liquefying reagent will grant sufficient amount of phenol to react and penetrate into the EFB and KC hence reduced the amount of residue. These results prove that increasing the P/E and P/K ratio has great influence on the liquefaction reaction. Besides that, the amount of residue produced by both raw materials showed that liquefaction of KC resulted higher residue compared to that of EFB fibres. This is because the lignin content in KC is higher than EFB. The residue of KC liquefaction is higher and this has attributed to the repolymerization of liquefaction products. The degradation of biomass into smaller products is mainly proceeds by depolymerization and deoxygenation. However, during these reactions, some condensation and repolymerization of intermediate products also proceed (Demirbas 2000). This caused higher amount of residue in KC than in EFB.

Figure 2(a) and 2(b) shows the FTIR absorption spectrum for the residue from liquefied EFB with phenol at 150°C in the presence of 3% H_2SO_4 as catalyst and

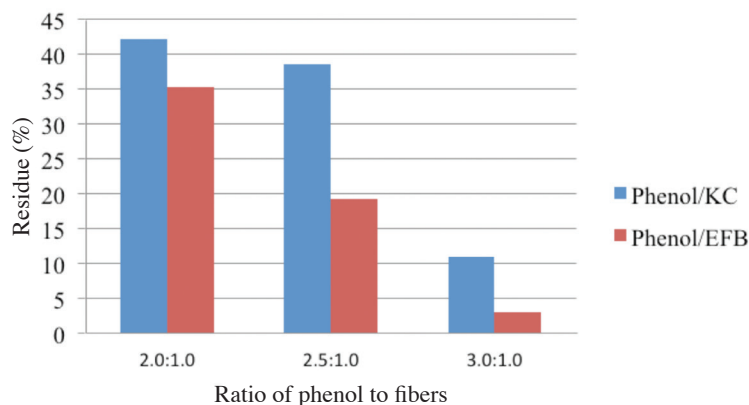


FIGURE 1. Effect of phenol/EFB and phenol/KC ratio on residue. Reaction time 120 min, temperature 150°C, catalyst 3%

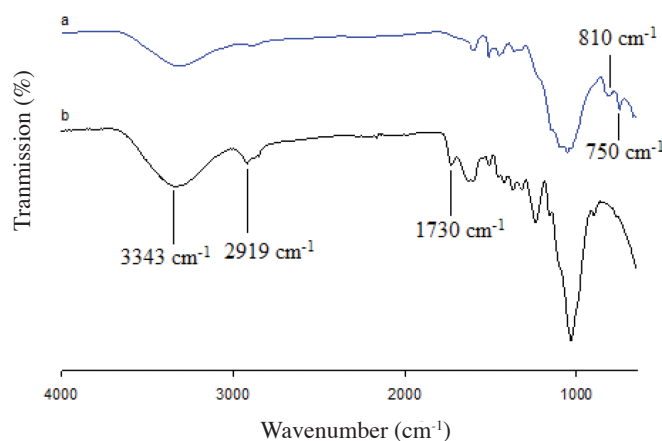


FIGURE 2. FTIR spectra (a) residue from liquefied EFB and (b) native EFB

native EFB, respectively. In general, FTIR spectra of lignocellulosic at the band 3600 – 3200 cm^{-1} attribute to the axial deformation of the O-H group. In this case, the peak is appeared at 3343 cm^{-1} for the native EFB but after the liquefaction process, the peak slightly shift to the right which is 3334 cm^{-1} due to the presence of other groups which affect the vibration of O-H. Absorption bands between 3200 and 1800 cm^{-1} corresponds to hydrocarbon stretching region (CH_2 and CH_3), which appeared at band 2919 cm^{-1} in this study. The carbon double bond region will appear around 1800 – 1500 cm^{-1} . This carbonyl bond is one of the most important peaks because the presence or absence of any carbonyl bond is a key future of a spectrum. This peak can be seen in the native EFB at 1730 cm^{-1} but absence after the liquefaction process due to the destruction of lignin network (Bakarudin et al. 2012). Peak appearance can be observed at 810 and 750 cm^{-1} . These peaks are attributed to the para and meta benzene, respectively or to be specific its associated to the p-alkyl phenol and m-alkyl phenol (Bakarudin et al. 2012).

The absorption spectrum for the liquefied KC and native KC, Figure 3(a) and 3(b), shows some similarities

with the EFB and liquefied EFB. A wide O-H band can be observed at 3450 cm^{-1} . The peak at 2940 cm^{-1} represents the axial deformation of C-H group due to the OH stretching in methyl and methylene groups. Decreasing intensity of peak related to carbonyl at 1726 cm^{-1} and appearance new peak at 830 and 755 cm^{-1} attributed to the para and meta benzene, respectively.

Figure 4(a) to 4(d) shows the XRD results for residue from liquefied EFB, native EFB, liquefied kenaf and native kenaf. From this figure we can observe that the shape of the 002 peak at $2\theta=22.6^\circ$ in all samples are asymmetric. According to Bakarudin et al. (2012), peak observed around 22.6° and 34.6° is assigned to the formation of oxidizable lignin. A sharp peak can also be observed around $\sim 26^\circ$ which is attributed to the formation of carbonaceous structure. Previous study shows that, CrI of lignocellulosic materials will increase after liquefaction process. The same result can be observed in this research which is shown in Table 1. Liquefaction of lignocellulosic normally carried out in the presence of acids as a catalyst. The presence of this acid will enhance the degradation process of cellulosic materials due to the hydrolytic cleavage of polymer

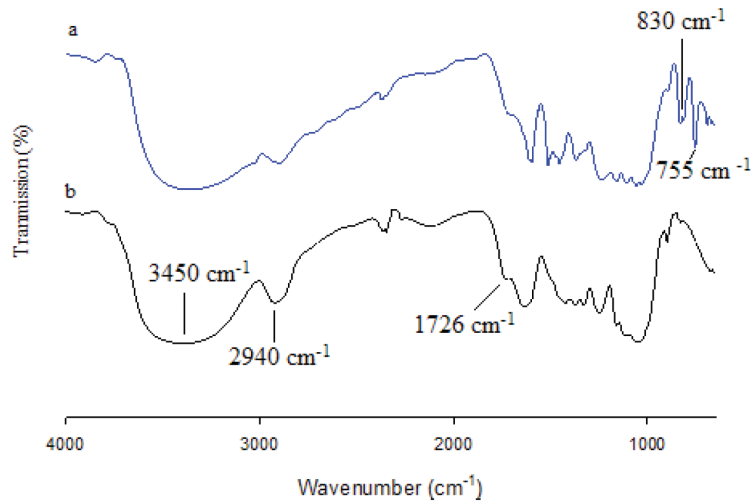


FIGURE 3. FTIR spectra (a) residue from liquefied KC and (b) native KC

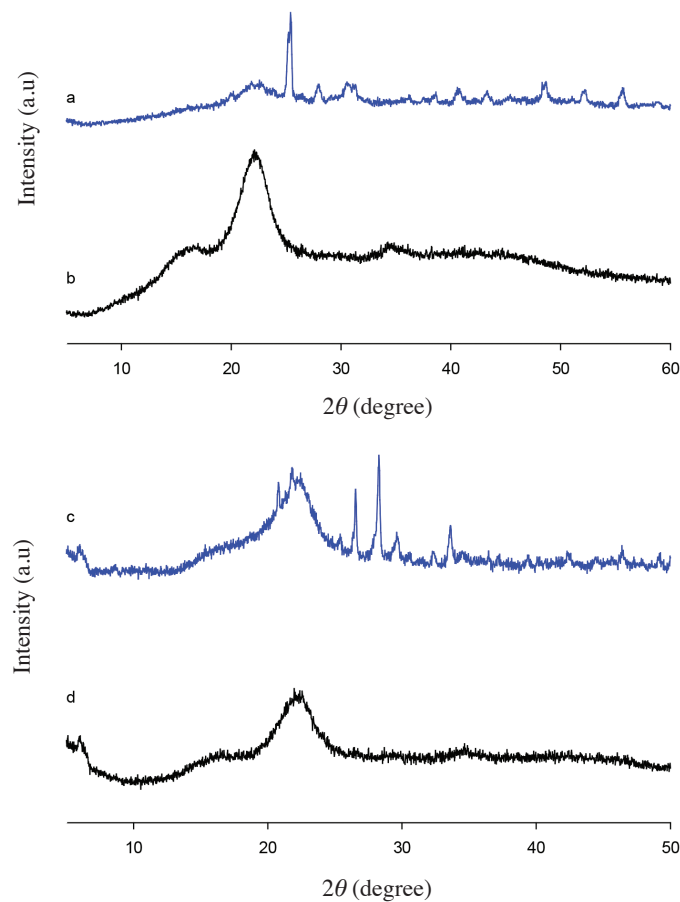


FIGURE 4. XRD Deffractograms (a) residue from liquefied EFB, (b) native EFB, (c) residue from liquefied KC and (d) native KC

glycosidic linkage within nearby molecule hence increase the crystallinity index (Adel et al. 2010). Moreover, the increasing of these CrI also affected by the removal of lignin from the amorphous region thus resulting in the relative portion of the crystalline region of cellulose increased (Bakarudin et al. 2012; Pan et al. 2007).

The SEM images of the native and liquefied residue for EFB and KC at different ratio of P/E and P/K are shown in Figure 5(a) to 5(h). From Figure 5(a) to 5(b), EFB and KC fibers surface appear rough. The silica on the EFB fiber is clearly seen and also small fraction of cell wall element can be observed in KC fibers due to the milling

TABLE 1. Crystallinity index of liquefied EFB and Kenaf residue

	I_{002}	I_{AM}	Crystallinity Index (CrI) %
Native EFB	2303	1099	52
L 3:1	1436	548	61
Native Kenaf	63	34	46
L 3:1	77	35	54

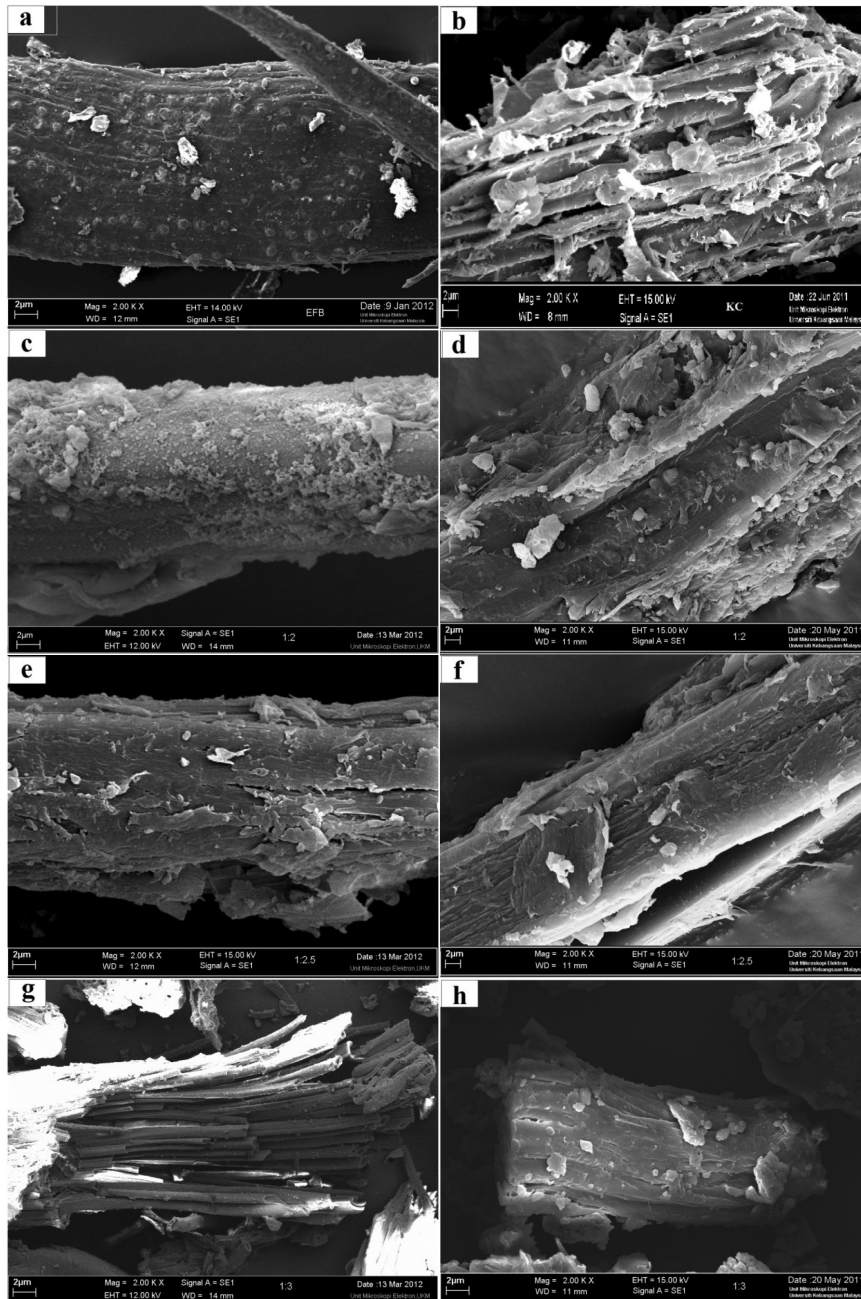


FIGURE 5. SEM images of the native and liquefied residue for EFB and KC at different ratio of P/E and P/K. (a) native EFB, (b) native KC, (c) liquefied EFB ratio 2:1, (d) liquefied KC ratio 2:1, (e) liquefied EFB ratio 2.5:1, (f) liquefied KC ratio 2.5:1, (g) liquefied EFB ratio 3:1 and (h) liquefied KC ratio 3:1

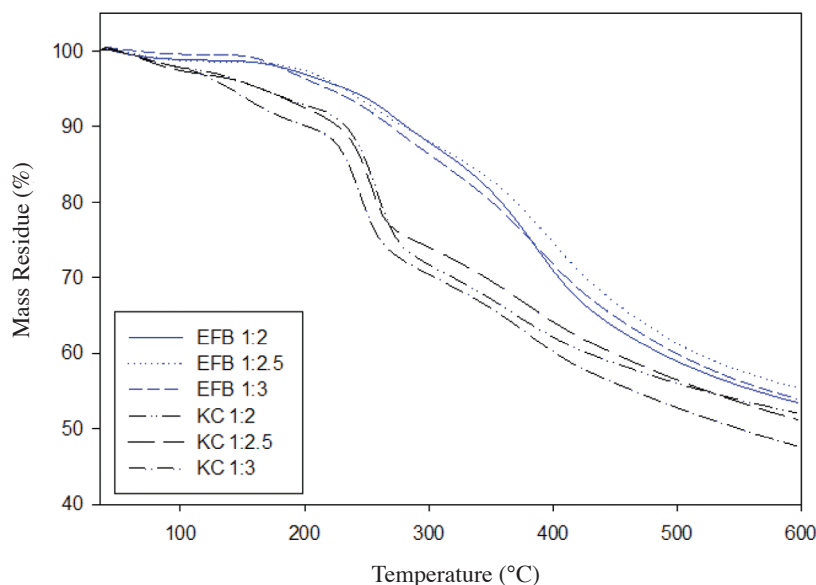


FIGURE 6. TGA weights lost curve for the liquefied EFB and KC at different ratio of P/E and P/K

processes (Bakarudin et al. 2012). When EFB and KC fiber undergoes liquefaction at the ratio of 2:1, the silica and fraction of cell wall on the surface were slightly removed (Figure 5(c) and 5(d)). As the P/E and P/K ratio increased from 2.5:1 to 3:1, all the silica and fraction of cell wall are totally eliminated. The elimination of these silica and fraction of cell wall on the surface of the fiber lead to the chemical penetration across the grain of the fiber hence cause the fiber bundles started to separate into individual fibers as shown in Figure 5(e) – 5(h) (Pan et al. 2007).

Figure 6 represents the TGA results for the liquefied EFB and KC at different ratio of P/E and P/K, respectively. Both weights lost curve experienced in three region decompositions. The first region started around 100°C is due to the removal of water or moisture. After that, decomposition observed around 230–350°C in the P/E samples and 236–297°C in P/K samples which is correspond to the decomposition of hemicelluloses and cellulose. In the last region, which occur beyond 350°C for P/E and 298°C for P/K samples coincides to the degradation of lignin. Lignin is a highly cross-linked, three-dimensional aromatic polymer and also consists of phenyl propane units linked together by C-C bonds. The complex structure and properties of lignin makes its decomposition rate slow compared to other polysaccharides components (Spinacé et al. 2009). The thermal analysis studies on lignocellulosic fiber shows different results by using different type of fibers. Even though lignocellulosic materials primarily consists of three main components which are cellulose, hemicelluloses and lignin but other factors will also affect the results such as heating rate and initial fiber condition (Tomczak et al. 2007).

CONCLUSION

Both fibers, EFB and KC fibers are successfully liquefied in phenol at 150°C in the presence of 3% H₂SO₄ as catalyst. The amount of residue decreases when the ratio of P/E and P/K increases from 2.0 to 3.0. The total amount of 32 and 31% residue reduction occur when the P/E and P/K ratio increase from 2.0 to 3.0, respectively. These results proved that increasing the P/E and P/K ratio has great influenced on the liquefaction reaction. FTIR characterization showed that characteristic of natural fibre differed after undergone the liquefaction process. Band intensities, appearance and disappearance occur depend on type of modification. Despite lignocellulosic materials primarily consists of three main components which are cellulose, hemicelluloses and lignin but other factors will also effected the results such as initial fiber condition.

REFERENCES

- Adel, A.M., El-Wahab, Z.H.A., Ibrahim, A.A. & Al-Shemy, M.T. 2010. Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part I. Acid catalyzed hydrolysis. *Bioresource Technology* 101(12): 4446-4455.
- Ahmadzadeh, A., Zakaria, S. & Rashid, R. 2009. Liquefaction of oil palm empty fruit bunch (EFB) into phenol and characterization of phenolated EFB resin. *Industrial Crops and Products* 30(1): 54-58.
- Ali, I.S., Sapuan, S.M., Zainudin, E.S. & Abdan, K. 2009. Kenaf fibres as reinforced for polymeric composites: A review. *International Journal of Mechanical and Materials Engineering* 4: 239-248.
- Alma, M.H. 1996. Several acid-catalyzed phenolated of wood and its application to molding material. PhD Thesis. Kyoto University, Kyoto, Japan (unpublished).
- Alma, M.H. & Basturk, M.A. 2006. Liquefaction of grapevine cane (*Vitis vinisera* L.) waste and its application to phenol-

- formaldehyde type adhesive. *Industrial Crops and Products* 24(2): 171-176.
- Bakarudin, S.B., Zakaria, S., Chia, C.H. & Jani, S.M. 2012. Liquefied residue of kenaf core wood produced at different phenol-kenaf ratio. *Sains Malaysiana* 41(2): 225-231.
- Chai, L.L., Zakaria, S., Chia, C.H., Nabihah, S. & Rashid, R. 2009. Physico-mechanical properties of PF composite board from EFB fibres using liquefaction technique. *Iranian Polymer Journal* 18(11): 917-923.
- Chan, K.W. & Ismail, M. 2009. Supercritical carbon dioxide fluid extraction of Hibiscus cannabinus L. seed oil: A potential solvent-free and high antioxidative edible oil. *Food Chemistry* 114(3): 970-975.
- Demirbas, A. 2000. Mechanism of liquefaction and pyrolysis reactions of biomass. *Energy Conversion and Management* 41: 633-646.
- Doh, G.H., Lee, S.Y., Kang, I.A. & Kong, Y.T. 2005. Thermal behavior of liquefied wood polymer composites (LWPC). *Composite Structures* 68(1): 103-108.
- Effendi, A., Gerhauserm, H. & Bridgwater, A.V. 2008. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renewable and Sustainable Energy Reviews* 12(8): 2092-2116.
- El Mansouri, N.E., Yuan, Q. & Huang, F. 2011. Study of chemical modification of alkaline lignin by the glyoxalation reaction. *BioResources* 6(4): 4523-4536.
- Hu, L., Pan, H., Zhou, Y. & Zhang, M. 2011. Methods to improve Lignin's reactivity as a phenol substitute and as replacement for other phenolic compounds: A brief review. *BioResources* 6(3): 3515-3525.
- Hui, P. 2011. Synthesis of polymers from organic solvent liquefied biomass: A review. *Renewable and Sustainable Energy Reviews* 15(7): 3454-3463.
- Juhaida, M.F., Paridah, M.T., Mohd. Hilmi, M., Sarani, Z., Jalaluddin, H. & Mohamad Zaki, A.R. 2010. Liquefaction of kenaf (*Hibiscus cannabinus* L.) core for wood laminating adhesive. *Bioresource Technology* 101(4): 1355-1360.
- Kleinert, M. & Barth, T. 2008. Phenols from Lignin. *Chemical Engineering & Technology* 31(5): 736-745.
- Kunaver, M., Medved, S., Čuk, N., Jasiukaitytė, E., Poljanšek, I. & Strnad, T. 2010. Application of liquefied wood as a new particle board adhesive system. *Bioresource Technology* 101(4): 1361-1368.
- Pan, H., Shupe, T.F. & Hse, C.Y. 2007. Characterization of liquefied wood residues from different liquefaction conditions. *Journal of Applied Polymer Science* 105(6): 3740-3746.
- Ridzuan, R., Stephen, S. & Mohd, A.J. 2002. Properties of medium density fiberboard from oil palm empty fruit bunch fiber. *Journal of Oil Palm Research* 14(2): 34-40.
- Sajab, M.S., Chia, C.H., Zakaria, S., Jani, S.M., Ayob, M.K., Chee, K.L., Khiew, P.S. & Chiu, W.S. 2011. Citric acid modified kenaf core fibres for removal of methylene blue from aqueous solution. *Bioresource Technology* 102(15): 7237-7243.
- Spinacé, M.A.S., Lambert, C.S., Feroselli, K.K.G. & De Paoli, M.A. 2009. Characterization of lignocellulosic curaua fibres. *Carbohydrate Polymers* 77(1): 47-53.
- Sulaiman, O., Salim, N., Hashim, R., Yusof, L.H.M., Razak, W., Yunus, N.Y.M., Hashim, W.S. & Azmy, M.H. 2009. Evaluation on the suitability of some adhesives for laminated veneer lumber from oil palm trunks. *Materials & Design* 30(9): 3572-3580.
- Tomczak, F., Sydenstricker, T.H.D. & Satyanarayana, K.G. 2007. Studies on lignocellulosic fibers of Brazil. Part II: Morphology and properties of Brazilian coconut fibers. *Composites Part A: Applied Science and Manufacturing* 38(7): 1710-1721.

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