

Chemical and Thermal Properties of Purified Kenaf Core and Oil Palm Empty Fruit Bunch Lignin

(Kajian Kimia dan Terma Lignin Tulen Teras Kenaf dan Serabut Tandan Kosong Kelapa Sawit)

SHARIFAH NURUL AIN SYED HASHIM, SARANI ZAKARIA*, CHIN HUA CHIA,
FEI LING PUA & SHARIFAH NABIHAH SYED JAAFAR

ABSTRACT

Chemical and thermal properties of pure lignin are depending on the plant origin, extraction method and type of lignocellulosic. In this study, lignin from oil palm empty fruit bunch (EFB) and kenaf core were recovered from soda black liquor by two steps of acid precipitation with hydrochloric acid and followed by soxhlet with n-hexane. The XRD analysis of purified EFB lignin (EAL) and purified kenaf core lignin (KAL) exhibited amorphous properties, similar to the standard alkali lignin (SAL). The FTIR and Raman spectra showed that all samples consist of HGS unit. In FTIR, the syringyl unit is assigned at (1125 cm^{-1}), (1327 and 1121 cm^{-1}) and (1326 and 1117 cm^{-1}) meanwhile the guaiacyl unit is assigned at (1263, 1212 and 1028 cm^{-1}), (1271, 1217 and 1028 cm^{-1}) and (1270, 1211 and 1030 cm^{-1}) for SAL, EAL and KAL, respectively. The peak around 1160 cm^{-1} represents C-O stretching of conjugated ester group present in HGS lignin. As for Raman, the HGS unit exists in the range of 1100-1400 cm^{-1} . Among the purified samples, the TGA result showed that KAL has a better thermal stability with the residue of 36.49% and higher T_g value which is 152.69°C.

Keywords: Acid precipitation; black liquor; HGS unit; soda lignin; soxhlet extraction

ABSTRAK

Sifat kimia dan terma lignin tulen bergantung kepada tumbuhan asal, kaedah pengekstrakan dan jenis lignoselulosa. Dalam kajian ini, lignin daripada serabut tandan kosong kelapa sawit (EFB) dan teras kenaf telah diasingkan daripada likor hitam soda dengan dua peringkat pemendakan asid menggunakan asid hidroklorik dan diikuti proses penulenan dengan n-heksana dalam sistem soxhlet. Berdasarkan kepada difraktogram sinar-X, didapati sampel lignin tulen EFB (EAL) dan sampel lignin kenaf teras (KAL) mempamerkan sifat amorfus sama seperti sampel SAL. Pencirian FTIR dan Raman pula membuktikan sampel lignin mempunyai kesemua unit monomer HGS. Dalam analisis FTIR, unit siringil ditemui pada (1125 cm^{-1}), (1327 dan 1121 cm^{-1}) dan (1326 dan 1117 cm^{-1}) manakala unit guaiasil ditemui pada (1263, 1212 dan 1028 cm^{-1}), (1271, 1217 dan 1028 cm^{-1}) dan (1270, 1211 dan 1030 cm^{-1}) masing-masing bagi SAL, EAL dan KAL. Puncak sekitar 1160 cm^{-1} mewakili regangan C-O bagi kumpulan ester berkonjugat yang hadir dalam lignin HGS. Bagi analisis Raman, unit HGS hadir dalam julat 1100-1400 cm^{-1} . Antara sampel yang dituliskan, KAL mempunyai kestabilan terma yang baik dengan baki 36.49% dan nilai T_g yang tinggi iaitu 152.69°C.

Kata kunci: Lignin soda; likor hitam; pemendakan asid; pengasingan soxhlet; unit HGS

INTRODUCTION

In Malaysia, kenaf and oil palm are well-known industrial crops which are largely cultivated due to world demand. Consequently, kenaf and EFB generate almost 12-30 tons ha^{-1} (Sumathi et al. 2008) and 15.8 million tons per year (Mossello et al. 2010) of waste, respectively. Plant fibers are one of lignocellulosic material and is comprises of three different chemical composition: cellulose, hemicellulose and lignin. Different plant gives dissimilar chemical composition and properties. The chemical composition of cellulose, hemicellulose and lignin in kenaf core fiber are 37-49%, 18-24% and 15-21% (Li et al. 2007), respectively. The chemical composition of cellulose, hemicellulose and lignin in EFB are 59.7%, 22.1% and 18.1% (Abdullah et al. 2011), respectively. Normally, this byproducts are disposed by dumping or open burning which lead to environmental

problem and hence affecting the human health (Carlos & Khang 2008). However, these chemical compositions are potential to be used in many applications due to its chemical group. For example, lignin can be used in the production of phenol formaldehyde resin (Mohamad Ibrahim et al. 2007), as corrosion inhibitor (Akbarzadeh et al. 2011) or in coating industry (Park et al. 2008).

Lignin can be recovered from waste black liquor, produced from pulp and paper industry. The color is dark brown which is rich in phenolic compounds (Garcia et al. 2009). It can also be conceived as complex aqueous solution due to the presence of organic (lignin, polysaccharides and resinous compound) and inorganic compounds (soluble salt ions). Alkaline pulping is one of the chemical processes for the production of pulp and paper which lead to the degradation of aryl-ether linkages.

It uses sodium hydroxide (NaOH) for cooking purposes to liberate the cellulosic fiber. Soda pulping is the most favorable alkaline pulping because of high quality pulp. Apart from that, it is more environmental friendly since it is not using any sulphur which leads to pollution (Jimenez et al. 2009).

Lignin is a phenolic macromolecule that exists in plant cells that made up of three monomers which are coniferyl alcohol, sinapyl alcohol and *p*-coumaryl alcohol (Figure 1). These monolignol produces *p*-hydroxyphenyl, guaiacyl and syringyl residues in the polymer. Usually softwood (gymnosperm) lignin is classified as guaiacyl lignin (Dence & Lin 1992) whereas hardwood (angiosperm) lignin contains a mixture of guaiacyl and syringyl residues. The previous research reported that EFB lignin S to G monomer ratio with 73:27 by Determination of Regiochemistry and Quantification (DFRC) (Lu et al. 2015). Meanwhile, for kenaf, some of previous research reported that kenaf core has all HGS units (Geronikaki et al. 1978; Seca et al. 1998) but some researcher reported that kenaf core has a mixture of only GS unit (Nishimura et al. 2002; Yan et al. 2009).

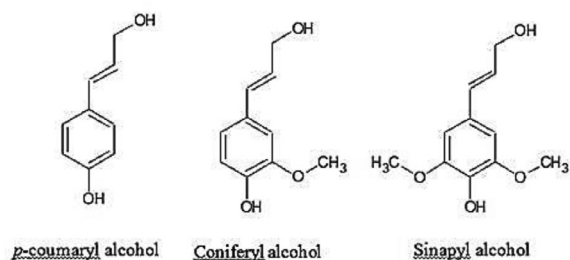


FIGURE 1. Monomer unit of lignin

Lignin has the tendency to be used as a starting material in various applications such as binder, bio-resin and natural fiber. Nowadays, the world interests on renewable materials are increasing. The purified lignin is possible to be used further for low cost carbon fiber production as an alternative for polyacrylonitrile-based carbon fiber since purity of lignin plays one of vital roles for carbon fiber production. Moreover, this preliminary study is important for the future utilization of lignin as raw material for new materials. The study on purification of kenaf and EFB lignins were done, in order to determine the chemical and thermal characterizations for both samples. Besides, the obtained characterizations were compared with standard alkali lignin (SAL) to discuss the difference between the lignins.

MATERIALS AND METHODS

ISOLATION AND PURIFICATION PROCESS

For the isolation process, the black liquor has undergone two steps of precipitation processes. The black liquor was acidified with 6M of hydrochloric acid (HCl) to pH6 for

neutralization purpose. Ethanol was added into the black liquor, to degrade the remaining polysaccharide. After that, the remained ethanols were removed using rotary evaporator. Again, HCl were added into the black liquor until the pH turn to 2. The precipitated lignin was filtered and washed with acidified water (pH2) to remove salt before dried for 24 h. For purification process, the lignins were extracted with n-hexane in Soxhlet apparatus for 6 h to remove non-lignin material such as wax or lipid. Before drying, the lignin fractions were washed with acidified water to remove an excess n-hexane. Lastly, the samples were washed with hot water and acidified water (pH2) to remove any residual sugar and again it was dried for another 24 h.

INSTRUMENTAL ANALYSIS

The functional groups and monomer unit of purified lignin were determined using FT-IR and was confirmed by Raman spectroscopy, respectively. The IR spectrum was recorded using Perkin-Elmer 2000 spectrophotometer at wavelength range 4000-650 cm^{-1} . The Raman spectrum was recorded using Bruker RFS 100 with 1064 nm diode laser, 100 scans, 200 mW power and 8 cm^{-1} resolution. The purity of lignin was determined by Bruker X-Ray diffractometer (XRD). Meanwhile, the thermal analyses were determined using TGA (TA model Q500) and DSC (TA model Q20). TGA analysis was carried out by heating 10 mg of lignin up to 800°C in a crucible with the heating rate of 10°C/min under nitrogen atmosphere. As for DSC, the lignin was heated up to 200°C with the 10°C/min under nitrogen atmosphere.

RESULTS AND DISCUSSION

XRD

Figure 2(a) shows the X-Ray diffraction spectrum of unpurified lignin for kenaf core (BKAL) and EFB (BEAL) meanwhile Figure 2(b) indicate the X-Ray diffraction spectrum for purified lignin for kenaf (KAL), EFB (EAL) and standard alkali lignin (SAL). BKAL and BEAL show a very sharp peaks around 31°, 45°, 56°, 66° and 75° which referred to impurities known as salt (NaCl). The appearance of this salt was due to the element of Na^+ from NaOH during pulping react with Cl^- from HCl during acid precipitation formed NaCl. After purification (EAL and KAL), the sharp peaks disappear and only diffused pattern, as SAL sample can be seen in the diffractogram. This result is similar as reported by Luo et al. (2011) and Sevastyanova et al. (2010). It approves that lignin is pure and exhibit amorphous behavior. The purity of lignin plays one of important roles for carbon fiber production instead of small molecular weight distribution (Baker & Rials 2013).

FTIR

Spectra of EAL and KAL have almost similar pattern with SAL as shown in Figure 2. A broad peak at around 3300

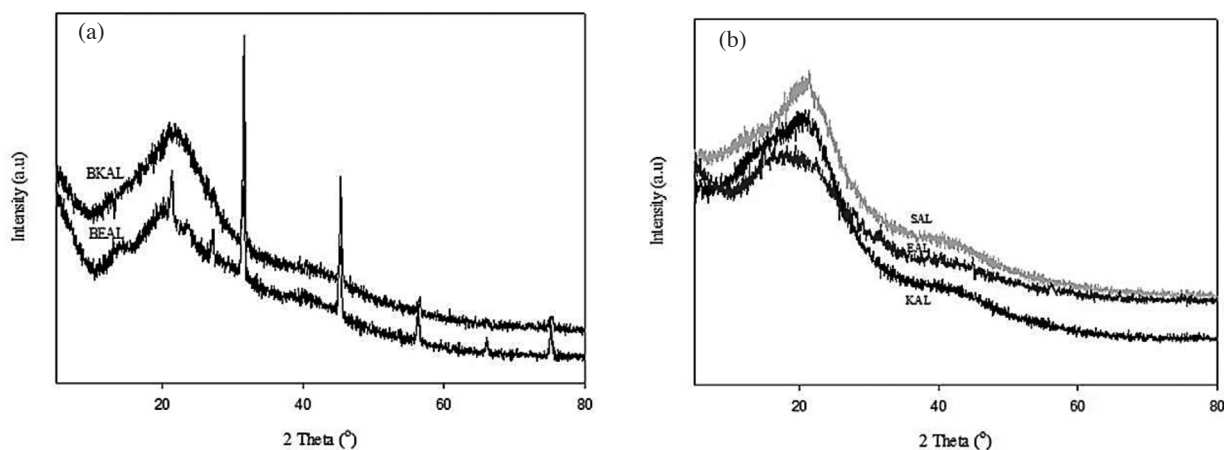


FIGURE 2. X-ray diffraction pattern of three lignins soda (a) unpurified lignin and (b) purified lignin

cm^{-1} for all samples is assigned as aliphatic and aromatic of OH group. The two peaks at around $2900\text{--}2800\text{ cm}^{-1}$ is attributed to C-H vibration of methyl (CH_2) or methylene group (CH_3). The C=O stretching of carbonyl group lignin represent at around 1700 cm^{-1} . The peak of SAL samples is not pronounced as EAL and KAL. The three peaks that exist around $1590, 1510$ and 1425 cm^{-1} are due to aromatic ring vibration. Figure 3 shows that SAL, EAL and KAL consist of syringyl and quaiacyl unit. The syringyl unit is assigned at (1125 cm^{-1}), (1327 and 1121 cm^{-1}) and (1326 and 1117 cm^{-1}) (Mohamad Ibrahim et al. 2011) meanwhile the quaiacyl unit is assigned at ($1263, 1212$ and 1028 cm^{-1}), ($1271, 1217$ and 1028 cm^{-1}) and ($1270, 1211$ and 1030 cm^{-1}) (Garcia et al. 2012) for SAL, EAL and KAL, respectively. The peak around 1160 cm^{-1} represents C-O stretching of conjugated ester group that present in HGS lignin. The peaks around $900\text{--}700\text{ cm}^{-1}$ are contributed to C-H out of plane. This finding is slightly different from Jaafar et al. (2011) and Yan et al. (2009) who found only G and S unit in Kenaf and EFB lignin, respectively (Figure 4). This was due to the different extraction and pulping method that has been used. The properties and characterizations of lignin are dissimilar for different pulping, extraction and isolation process (Fitigau et al. 2013).

RAMAN

The HGS unit of SAL, EAL and KAL can be confirmed with Raman spectra. As shown in Figure 5, all lignin samples show peak at around 1600 cm^{-1} with shoulder or shorter peak at around 1660 cm^{-1} which act as main marker band for lignin determination (Gierlinger et al. 2012; Roder & Sixta 2004). The signal near 1660 cm^{-1} detected by the vibration of C=C bond which is assigned to ring deformation. Based on Raman spectra, EAL, KAL and SAL indicate a single broad peak at the range of $1100\text{--}1400\text{ cm}^{-1}$, representing of HGS type. The most convincing marker band for H type is $1213\text{--}1218\text{ cm}^{-1}$ where the signal is attributed to aryl OCH_3 and aryl OH. As for the G type of lignin, most promising marker band is around $1262\text{--}1275\text{ cm}^{-1}$. The marker band

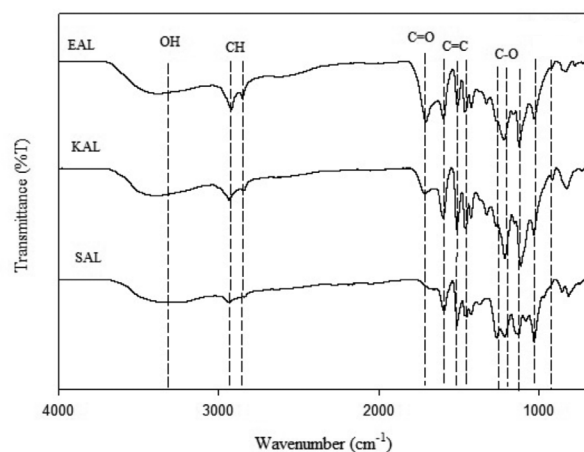


FIGURE 3. FTIR full spectrum of SAL, EAL and KAL

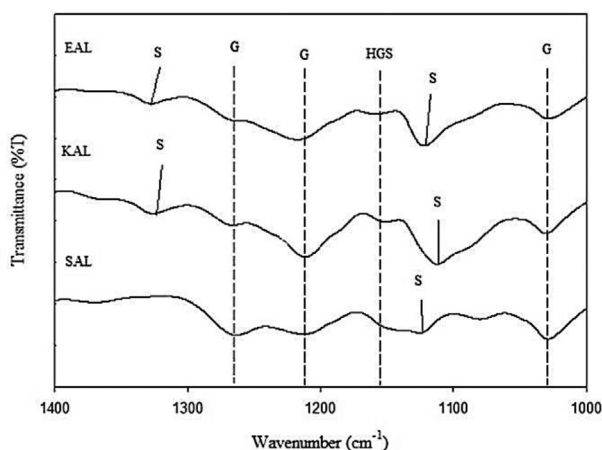


FIGURE 4. FTIR spectrum of SAL, EAL, and KAL at wavenumber $1400\text{--}1000\text{ cm}^{-1}$

for S is around $1331\text{--}1338\text{ cm}^{-1}$ where S signal is attributed to attach symmetric COC stretch of two OCH_3 groups that present at the position of 3 and 5. Due to the broad peak, we believe that these three lignin have all type of monomer units because the peaks exist is in the range of HGS type of lignin.

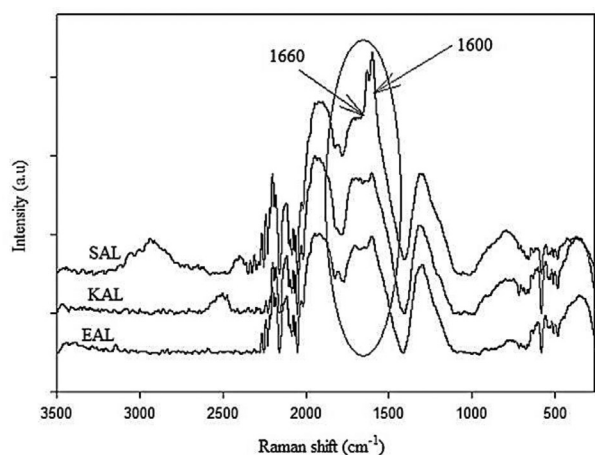


FIGURE 5. Raman spectra of alkaline lignin SAL, KAL and EAL

TGA

There are two degradation stages for all samples as shown in Figure 6. It was found that there were two degradation stages for all samples. The curve at the beginning was referred to the weight loss of water since boiling point of water is 100°C. The first stages of degradation referred to the weight loss of hemicellulose that was still remained in the lignin samples. According to Sun et al. (2000), hemicellulose will degrade at lower temperature which was 200-300°C. The second degradation stage referred to the weight loss of lignin occurred at differ range temperature which was within 250-680°C. Regarding to the temperature range, SAL exhibits the best thermal stability since the weight loss is 21.37% followed by EAL and KAL with 34.03 and 56.58%, respectively. The SAL has a good thermal stability due higher molecular weight. Greater molecular weight caused the sample SAL to have less mobility and hence make it more stable. The thermal degradation was due to the fragmentation of inter-unit linkages which releasing monoric phenols into the vapor phase (Mohamad Ibrahim et al. 2011). All lignin samples have residue started at the temperature above SAL, EAL and

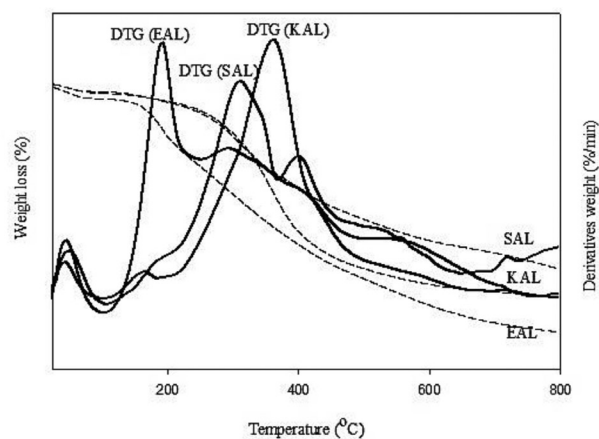


FIGURE 6. Thermogram of SAL, EAL and KAL samples

KAL and SAL have non-volatile residue 44.63, 36.49 and 25.86%, respectively.

DSC

Table 1 shows the T_g value of SAL, EAL and KAL. SAL has the highest T_g followed by EAL and KAL. Among the purified samples, KAL gave the highest T_g compared to EAL with the difference of 29.06°C. The T_g value of SAL, EAL and KAL are different from 80-180°C because it is depend on the origin, condition or method of isolation (Garcia et al. 2012). Normally, the sample with good thermal stability has high T_g as well (Mohamed et al. 2011). The DSC result was compatible with TGA where the T_g of SAL, EAL and KAL were below than 200°C. It proves that lignin start to degrade at respective T_g value as in Table 1 due to the degradation of hemicellulose in lignin as discussed in TGA.

TABLE 1. T_g value of lignin

Samples	T_g (°C)
SAL	161.35
EAL	123.63
KAL	152.69

CONCLUSION

The lignin from black liquor was successfully been extracted and purified. The purified samples exhibited amorphous behavior of HGS monomer similar as standard sample. The thermal properties showed that SAL showed the best thermal stability and highest T_g value. Among purified samples, KAL showed the best thermal stability and highest T_g value compared to EAL.

ACKNOWLEDGEMENTS

We would like to acknowledge the financial support from the Ministry of Higher Education (MOHE), Malaysia through the ERGS/1/2012/STG05/UKM/4 grant and Centre for Research and Instrumentation (CRIM) for the testing services.

REFERENCES

- Abdullah, N., Sulaiman, F. & Gerhauser, F. 2011. Characterisation of oil palm empty fruit bunches for fuel application. *Journal of Physical Science* 22(1): 1-24.
- Akbarzadeh, E., Mohamad Ibrahim, M.N. & Rahim, A.A. 2011. Corrosion inhibition of mild steel in near neutral solution by Kraft and soda lignins extracted from oil palm empty fruit bunch. *Int. J. Electrochem. Sci.* 6: 5396-5416.
- Baker, D.A. & Rials, T.G. 2013. Recent advances in low-cost carbon fiber manufacture from lignin. *Journal of Applied Polymer Science* 130(2): 713-728.
- Carlos, R.M. & Khang, D.B. 2008. Characterization of biomass energy projects in Southeast Asia. *Biomass and Bioenergy* 32: 525-532.

- Dence, C.W. & Lin, S.Y. 1992. *Methods in Lignin Chemistry*. Springer-Verlag: Berlin Heidelberg.
- Fitigau, I.F., Peter, F. & Boeriu, C.G. 2013. Structural analysis of lignin from different sources. *International Science Index* 7(4): 98-103.
- Garcia, A., Alriols, M.G., Spigno, G. & Labidi, J. 2012. Lignin as natural radical scavenger. Effect of the obtaining and purification processes on the antioxidant behaviour of lignin. *Biochemical Engineering Journal* 67: 173-185.
- Garcia, A., Toledano, A., Serrano, L., Egues, I., Gonzalez, M., Marin, F. & Labidi, J. 2009. Characterization of lignins obtained by selective preprecipitation. *Separation and Purification Technology* 68: 193-198.
- Geronikaki, A.A., Dalimova, G.N., Ya, N., Kul'chik & Abduazimov, K.A. 1978. A study of the structure of kenaf lignins by alkaline nitrobenzene oxidation. *Chemistry of Natural Compounds* 14(5): 551-554.
- Gierlinger, N., Keplinger, T. & Harrington, M. 2012. Imaging of plant cell walls by confocal Raman microscopy. *Nature Protocols* 7(9): 1694-1708.
- Jaafar, S.N.S., Haimer, E., Liebner, F., Bohmdorfer, S., Potthast, A. & Rosenau, T. 2011. Empty palm fruit bunches—a CO₂-based biorefinery concept. *Journal of Biobased Materials and Bioenergy* 5: 1-9.
- Jimenez, L., Serrano, L., Rodriguez, A. & Sanchez, R. 2009. Soda-anthraquinone pulping of palm oil empty fruit bunches and beating of the resulting pulp. *Bioresource Technology* 100: 1262-1267.
- Li, X., Tabil, L.G. & Panigrahi, S. 2007. Chemical treatments of natural fiber for use in natural fiber-reinforced composites: A review. *J. Polym. Environ.* 15: 25-33.
- Lu, F., Karlen, S.D., Regner, M., Kim, H., Ralph, S.A., Sun, R., Kuroda, K., Augustin, M.A., Mawson, M., Sabarez, H., Singh, T., Jimenez-Monteon, G., Zakaria, S., Hill, S., Harris, P.J., Boerjan, W., Wilkerson, C.G., Mansfield, S.D. & Ralph, J. 2015. Naturally P-hydroxybenzoylated lignins in palms. *Bioenerg. Res.* 8: 934.
- Luo, J., Genco, J., Cole, B. & Fort, R. 2011. Lignin recovered from the near-neutral hemicellulose extraction process as a precursor for carbon fiber. *BioResource* 6(4): 4566-4593.
- Mohamad Ibrahim, M.N., Zakaria, N., Sipaut, C.S., Sulaiman, O. & Hashim, R. 2011. Chemical and thermal properties of lignin from oil palm biomass as a substitute for phenol in a phenol formaldehyde resin production. *Carbohydrate Polymer* 86: 112-119.
- Mohamad Ibrahim, M.N., Md Ghani, A. & Nen, N. 2007. Formulation of lignin phenol formaldehyde resins as a wood adhesive. *The Malaysian Journal of Analytical Sciences* 11(1): 213-218.
- Mossello, A.A., Harun, J., Shamsi, S.R.F., Resalati, H., Md Tahir, P., Ibrahim, R. & Mohmamed, A.Z. 2010. A review of literatures related of using kenaf for pulp production (beating, fractionation, and recycled fiber). *Modern Applied Science* 4(9): 131-138.
- Nishimura, N., Izumi, A. & Kuroda, K. 2002. Structural characterization of kenaf lignin: Differences among kenaf varieties. *Industrial Crops and Products* 15: 115-122.
- Park, Y., Doherty, W.O.S. & Halley, P.J. 2008. Developing lignin-based resin coatings and composites. *Industrial Crops and Products* 27: 163-167.
- Roder, T. & Sixta, H. 2004. Confocal Raman spectroscopy-applications on wood samples. *Lenzinger Berichte* 83: 13-16.
- Seca, A.M.L., Cavaleiro, J.a.S., Domingues, F.M.J., Silverstre, A.J.D., Evtuguin, D. & Neto, C.P. 1998. Structural characterization of the bark and core lignins from kenaf (*Hibiscus cannabinus*) *J. Agric. Food Chem.* 46: 3100-3108.
- Sevastyanova, O., Qin, W. & Kadla, J.F. 2010. Effect of nanofillers as reinforcement agents for lignin composite fibers. *Journal of Applied Polymer Science* 117: 2877-2881.
- Sumathi, G.A., Chai, S.P. & Mohamed, A.R. 2008. Utilization of oil palm as a source of renewable energy in Malaysia. *Renewable and Sustainable Energy Reviews* 12: 2404-2421.
- Sun, R., Tomkinson, J. & Jones, G.L. 2000. Fractional characterization of Ash-Aq lignin by successive extraction with organic solvents from oil palm EFB fibre. *Polymer Degradation and Stability* 68: 11-119.
- Yan, T., Xu, Y. & Yu, C. 2009. The isolation and characterization of lignin of kenaf fiber. *Journal of Applied Polymer Science* 114: 1896-1901.

School of Applied Physics
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor Darul Ehsan
Malaysia

*Corresponding author; email: szakaria@ukm.edu.my

Received: 28 March 2015

Accepted: 26 January 2016