Liquefied Residue of Kenaf Core Wood Produced at Different Phenol-Kenaf Ratio

(Analisis Baki Pencecairan Kayu Teras Kenaf Terhasil pada Nisbah Fenol-Kenaf yang Berbeza)

SAIFUL BAHARI BAKARUDIN, SARANI ZAKARIA*
CHIN HUA CHIA & S. MOHD JANI

ABSTRACT

Liquefactions of kenaf core wood were carried out at different phenol-kenaf (P/k) ratios. Characterizations of kenaf core wood liquefied residue were carried out to measure the degree of liquefaction. This provides a new approach to understand some fundamental aspects of the liquefaction reaction. Functional groups on the raw kenaf core wood and liquefied residue were examined using Fourier transform infrared spectroscopy (FTIR). The crystallinity index of the kenaf wood liquefied residue, which represents crystallinity changes of the cellulose component after the liquefaction process, was studied using X-ray diffraction (XRD). The surface morphology of the wood residue was observed using scanning electron microscopy (SEM). The thermal behavior of the residues was analyzed using thermogravimetric analysis (TGA). Abroad peak around 3450-3400 cm^{-1} representing OH stretching in lignin start to disappear as P/K ratio increases. The results showed that the higher the P/K ratio the greater the liquefaction of the lignin component in the kenaf core wood. The crystallinity index (CrI) on the kenaf liquefied residues increased with the increase in P/K ratio. SEM images showed that the small fragments attached on the liquefied kenaf residue surface were gradually removed as the P/K ratio was increased from 1.5/1.0 to 2.5/1.0, which is mainly attributed to the greater chemical penetration toward reactive site of the kenaf fibres. Residue content decreased as the P/K ratio increased from 1.5/1.0 to 2.5/1.0. TGA results showed the increase of heat resistance in the residue as the P/K ratio was increased.

Keywords: Biomass; kenaf residue; liquefaction; phenol

ABSTRAK

Pencirian baki pencecairan teras kayu kenaf telah dilakukan untuk mengukur darjah pencecairan. Kajian ini menyediakan suatu pendekatan baru dalam memahami aspek teras tindak balas proses pencecairan. Perubahan kumpulan berfungsi di dalam baki pencecairan dianalisis dengan Spektroskopi Inframerah Transmisi Fourier (FTIR). Indeks penghabluran yang mewakili perubahan kehabluran selulosa dalam baki pencecairan telah dikaji melalui analisis pembelauan sinar-X (XRD). Morfologi permukaan baki pencecairan telah diperhatikan menggunakan mikroskop imbasan elektron (SEM). Sifat terma baki pencecairan dianalisis menggunakan analisis termogravimetri (TGA). Analisis menunjukkan suatu puncak lebar pada 3450-3400 cm^{-1}, merujuk kepada regangan OH di dalam lignin. Puncak ini mula menghilang dengan peningkatan nisbah fenol-kenaf (P/K). Ini menunjukkan lignin mengalami peningkatan kadar tindak balas dengan pertambahan nisbah fenol-kenaf (P/K). Indeks penghabluran (CrI) mewakili rantau berhablur selulosa mengalami peningkatan dengan pertambahan nisbah fenol-kenaf (P/K). Imej SEM menunjukkan serpihan halus yang melekat pada permukaan baki pencecairan kenaf. Fragmen ini mulai mengalami penyingkiran dari permukaan baki pencecairan apabila nisbah fenol-kenaf (P/K) meningkat daripada 1.5/1.0 ke 2.5/1.0 disebabkan peningkatan penusukan kimia ke atas tapak aktif serabut kenaf. Peratus baki pencecairan berkurangan dengan peningkatan nisbah fenol-kenaf daripada 1.5/1.0 ke 2.5/1.0. Analisis TGA menunjukkan peningkatan rintangan haba di dalam sampel baki pencecairan dengan peningkatan nisbah P/K.

Kata kunci: Baki kenaf; biojisim; fenol; pencecairan

INTRODUCTION

Conversions of lignocelluloses biomass, such as wood, bagasses and other agricultural by-products to fuel and useful chemicals, provide a long standing economic opportunity and technical challenge that has assumed different forms at different times according to the state of technology, economy and the demand for various products (Soltes 1983). Petroleum prices, feedstock supply and environmental issues are major concerns in the search for alternative renewable energy resources (Effendi et al. 2007). Lignocelluloses biomass has been proposed to be used as an alternative resource for producing phenolic chemicals by degradation/de-polymerization processes (Amen et al. 2001).

Lignocellulosic biomass is derived from three main components, i.e., hemicelluloses, cellulose and lignin. Due to the phenolic nature of the lignocellulosic biomass, a wide variety of phenols, phenol derivatives and aromatic chemicals can be produced. The fact that high lignin content of biomass is widely available, often at low cost and in large quantities, enhanced the efforts to replace the petroleum-based phenol partially with lignocelluloses biomass. Direct liquefaction of lignocellulosic biomass has proven to be a promising process to convert lignocellulosic material into valuable chemicals (Wang et al. 2008).

Kenaf (*Hibiscus cannabinus* L.) is an annual herbaceous crop of the Malvaceae family. Due to environmental and feedstock supply problem, researchers start to study the potential applications of kenaf in various field including pulp and paper industry. In Malaysia, realizing the diverse possibilities of commercially exploitable derived products from kenaf, the National Kenaf Research and Development Program has been formed to develop kenaf as a new industrial crop in Malaysia (Edeerozey et al. 2006). Large in quantity, renewable and high lignin content (Khristova et al. 2002), biomass kenaf has been proposed to be used as an alternative phenolic source instead of using petroleum base phenol in the synthesis of phenolic resin using thermochemical conversion such as pyrolysis and liquefaction (Lee & Ohkita 2003; Tymchyshyn & Xu 2010).

Liquefaction of kenaf, particularly on pyrolysis study of lignin (Guaiacylglycerol-β-guaiacyl ether) with special reference to the production of phenol derivative precursor (liquefied kenaf) with several parameters was investigated. Guaiacylglycerol-β-guaiacyl ether has been proposed as model compound in place of lignin in order to demonstrate the reaction mechanism of lignin during liquefaction process (Kobayashi et al. 2004; Wang et al. 2009a; Wang et al. 2009b). Liquefaction parameters that yield the highest value of biomass kenaf conversions to phenolic derivative precursor (liquefied kenaf) were chosen. Then liquefied kenaf was prepared as feedstocks for the synthesis of phenol formaldehyde resole resin. The properties of phenolic resin and liquefied kenaf residue obtained were investigated. In this study, liquefied kenaf residue obtained from liquefaction of kenaf core which represents the extent of wood liquefaction process were characterized by chemical, morphology and physical analyses. The aim of this research is to investigate the liquefaction of kenaf core using sulfuric acid as catalyst for the preparation of liquefied kenaf/phenol formaldehyde resin. Also, the effect of phenol/kenaf ratio on the liquefaction reaction and properties of resulting liquefied kenaf residue were examined.

EXPERIMENTAL DETAILS

Kenaf core fibers were obtained from the Forest Research Institute of Malaysia (FRIM). The kenaf core fibers were milled into powder (20-200 mesh) and dried in an oven at 150°C for 24 h. The chemicals used in this study were as follow: phenol (solvent reagent), sulfuric acid (catalyst), and methanol (diluting agent). Phenol used in the liquefaction process was liquid industrial grade (90% concentration) and all the other chemicals are ACS reagent-grade chemicals (methanol and sulfuric acid) supplied by Systerms and were used as received.

LIQUEFACTION KENAF WOOD CORE

Kenaf powder, 3% sulfuric acid (based on total amount of phenol) and phenol at room temperature were loaded into the three necks round bottom flask with a capacity 500 mL, set in an oil bath equipped with reflux condenser, thermocouple and electrical stirrer. The oil bath was heated up to the desired temperature for a specified reaction time. The experimental parameters are listed in Table 1. The liquefied kenaf was diluted with methanol and filtered with Whattman grade 1 filter paper. The percentage of methanol insoluble residue (R) was calculated based on following equation:

$$\%R = (W_i / W_o) \times 100\% \qquad (1)$$

where W_o is the weight of oven-dried initial input kenaf (g) and W_i is the oven-dried of the solid residue (g).

FTIR spectrum was obtained using a Perkin-Elmer G-X spectrometer. Small amount of sample powder was mixed with KBr powder and then pressed into disk for FTIR analysis. The transmittance spectra were measured in the wavelengths ranging from 4000 to 500 cm^{-1} at a resolution of 1 cm^{-1}.

The liquefied kenaf residues crystallinity index (CrI) and degree of crystallinity were measured using XRD. Liquefied kenaf residues were pressed into disk and analysed with an X-ray diffractometer (D5000, Siemen). The X-ray diffractograms were recorded from $2\theta = 5°$ to 50°. The X-ray diffractograms of all samples were analysed

TABLE 1. Parameter of kenaf liquefaction

	Liquefaction temperature (°C)	Phenol/kenaf (P/K) ratio	Time (minute)
1	170	1.5/1.0	90
2	170	2.0/1.0	90
3	170	2.5/1.0	90

using Segal method (Segal 1959). The crystallinity index calculation followed:

$$CrI(\%) = [\ (I_{002} - I_{am})/\ I_{002}\ ] \times 100\ \%\qquad(2)$$

where I_{002} is the intensity of the diffraction from the (002) plane at $2\theta = 22.58°$ and I_{am} is the intensity of the amorphous background scatter measured at $2\theta = 17.18°$.

Liquefied kenaf residue after the liquefaction process was analyzed using a Philips XL 30 Oxford 6650 scanning electron microscope with acceleration voltage 20.0 KV. Samples were sputter coated with a thin layer of gold, using a vacuum sputter coater to avoid electrostatic charging before subjected to the SEM.

Thermogravimetric analysis and differential thermogravimetry (DTG) were carried out using a Mettler Toledo SDTA 851e thermal analyzer at a heating rate of 10°C/min. The analysis temperature ranged from 30°C subsequent to 700°C in a static atmosphere. Samples (about 1 mg) were loaded into alumina crucible for analyses.

RESULTS AND DISCUSSION

The effect of phenol-kenaf ratio (P/K) at the liquefaction temperature of 170°C is shown in Figure 1. This figure shows the decrease in residue content as the P/K ratio increases for the liquefaction process. The residue content decreased from ~8.62% to 71.36% as the P/K ratio was increased from 1.5/1.0 to 2.5/1.0. This can be attributed to the increase of chemical penetration toward the reaction

sites on the kenaf wood powder as the increase of phenol dosage. The higher the phenol concentration the greater of the liquefaction reaction during liquefaction process (Pan et al. 2007).

The SEM images of raw kenaf fibres and liquefied kenaf residues with P/K ratio 1.5/1.0 to 2.5/1.0 are shown in Figure 2(a) - 2(d). The SEM images illustrate that raw kenaf core powder possesses a rough surface and consists of many small fragments on the cell wall which were formed during the milling process (Figure 2(a)). Raw kenaf fibres generally consist of coarse bundles of single fibre held together by lignin and pectin Keshk et al. (2006). Fibre bundles are broken down to individual fibres, due to the removal of lignin during liquefaction process (Alma & Basturk 2006). This effect starts from the outer layer of fibre bundles and progresses to the inner fiber bundles which is clearly shown in Figure 2(a) to 2(d). As the P/K ratio increased from 1.5/1.0 to 2.5/1.0, most small fragments attached on the surface of wood residues were removed.

Figure 3 shows the spectra of raw kenaf and liquefied kenaf residues obtained using different P/K ratios. A broad peak around 3450-3400 cm^{-1} is attributed to the OH stretching which is caused by the moisture (water) in the fibers and hydroxyl group in lignin, cellulose and hemicelluloses. The peak around 2940-2820 cm^{-1} represent the OH stretching in methyl and methylene groups (Fengel 1989). These two peaks are attributed to the absorption bands of lignin which are presented in the spectra of raw kenaf and liquefied kenaf residue. The reduction of the

TABLE 2. Crystallinity Index of liquefied kenaf residue

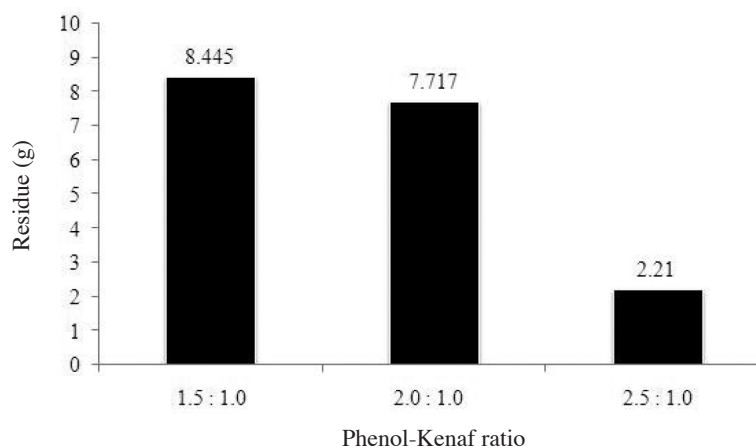|	I_{002}	I_{am}	Crystallinity Index (CrI)
Raw kenaf	22.58	17.18	23.91
P/K: 1.5/1.0	21.94	16.16	26.34
P/K: 2.0/1.0	21.84	15.56	28.75
P/K: 2.5/1.0	21.69	15.06	30.57

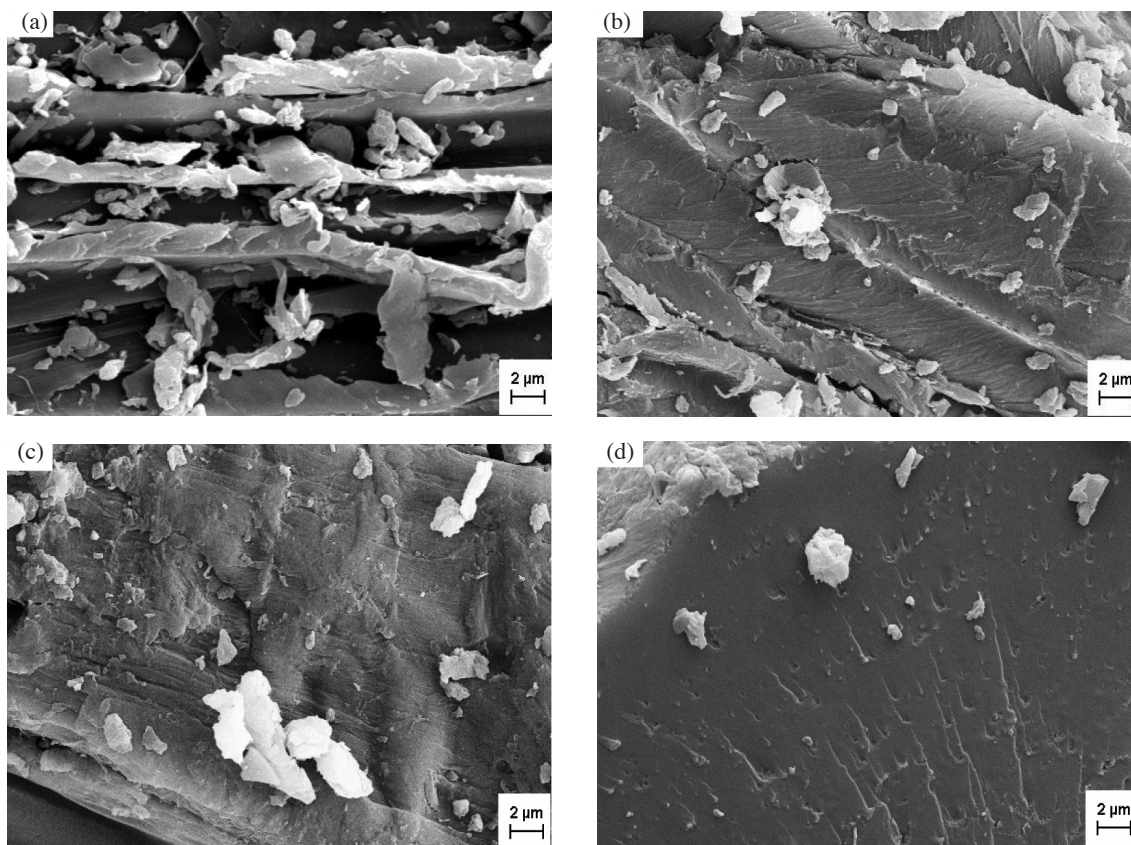FIGURE 1. Liquefied kenaf residue content versus phenol-kenaf ratio at 170°C

FIGURE 2. SEM micrograph of (a) raw kenaf fibres, residue of the kenaf fibres after the liquefaction process with
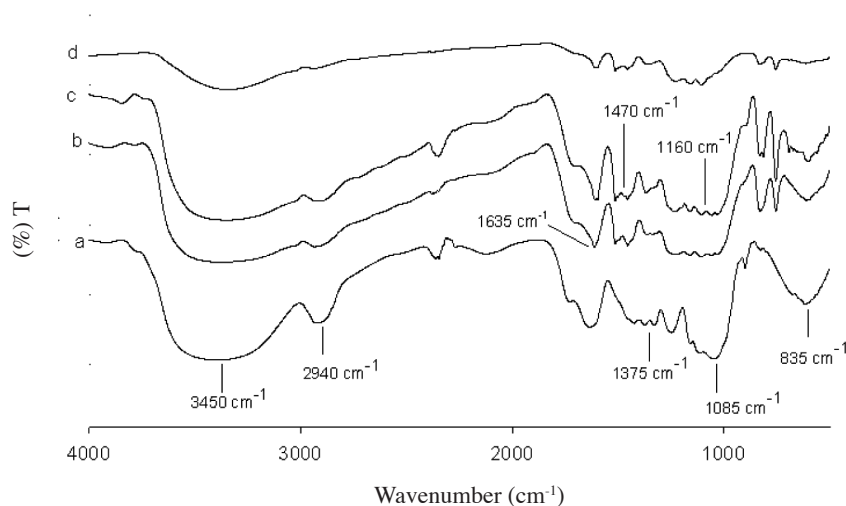(b) P/K ratio 1.5/1.0, (c) P/K ratio 2.0/1.0 and (d) P/K ratio 2.5/1.0

FIGURE 3. FTIR spectra (a) raw kenaf, (b) residue P/K ratio 1.5/1.0, (c) residue P/K
ratio 2.0/1.0, (d) residue P/K ratio 2.5/1.0

peak's intensity might be due to the loss of phenolic or alcoholic groups when P/K ratio increased from 1.5/1.0 to 2.5/1.0 (Wahyudiono et al. 2008) . Therefore, it can be concluded that the intensity of OH stretching in methyl and methylene group decreased with the increase of the P/K ratio during liquefaction process. It can also be noted that the peak's intensity at 3450-3400 cm^{-1} also reduced due

to the chemical modification of cellulose and cracking of lignin during the liquefaction reaction which resulted in the reduction of free hydroxyl group in cellulose and therefore reduced the moisture content in the fibre (residue).

An intense absorbance is observed around 1085-1030, 1370-1365, 1470-1460 and 1635-1600 cm^{-1} in the spectrum of raw kenaf. The spectrum band around 1085-1030 cm^{-1} is

due to C-H, C-O deformation, while band around 1370-1365 cm^{-1} corresponds to C-H deformations (symmetric), 1470-1460 cm^{-1} corresponds to C-H deformations (asymmetric) and 1635-1600 cm^{-1} OH deformation vibration. The intensities band at 1085-1030, 1370-1365, 1470-1460 cm^{-1} and 1635-1600 cm^{-1} (Socrates 2001) starts to disappear as P/K ratio increases from 1.5/1.0 to 2.5/1.0, suggesting that lignin might react to a greater extent of reaction (degradation) as P/K ratio increases. The peak absence (3450, 2940 cm^{-1}) represents the damage of the lignin network in the liquefied kenaf residues, thus suggesting lignin was liquefied rapidly among three major components in kenaf as P/K ratio increased during liquefaction process (Ahmadzadeh & Zakaria 2009). While the wide peak at 835-815, 1175-1165 cm^{-1} and 1160-1150, 820-770 cm^{-1} each associate with *p*-Alkyl phenol and *m*-Alkyl phenol (Socrates 2001) respectively occur in all spectrums except in the raw kenaf spectrum. This finding indicates that the phenolic characteristic presence in liquefied kenaf residue was due to the phenolation reaction towards kenaf during liquefaction. The phenolic characteristic is attributed to the condensation reaction of fragment residue via phenols to produce a new high molecular weight insoluble residue (Zhang et al. 2006).

Figure 4 represents XRD diffractograms of raw kenaf and liquefied kenaf residues. The peak at 22.3° and 34.6° which assigned to diffraction planes of cellulose are presented in diffractograms of liquefied kenaf residues (Kobayashi et al. 2004). The major diffraction of cellulose in liquefied kenaf residue diffractogram is similar to the diffractogram plane of nature cellulose, which is at 22.6° (Segal et al. 1959). The peak present around 30.0° in the diffractograms of liquefied kenaf residues is assigned to the formation of oxidizable lignin (Keshk et al. 2006). The formation of sharp peak at ~26° is attributed to the formation of carbonaceous structure as degradation product of the liquefaction process.

The crystallinity index (CrI) of liquefied kenaf residue at P/K ratio 1.5/1.0, 2.0/1.0 and 2.5/1.0 are 26.34, 28.75 and 30.57, respectively. The increasing pattern in CrI values by 9.14 % and 6.30 % were observed as P/K ratio increases from 1.5/1.0 to 2.5/1.0. This finding is in agreement with the report that low lignin content sample possesses higher crystallinity of cellulose (Deraman & Zakaria 1999). According to Oujai and Shanks (2005), cellulose is known as a crystalline structure attributed to linear structure and multiple intermolecular hydrogen bonds. Thus the increase in the CrI values can be elucidated by the increase in cellulose crystalline region as a result from the removal of lignin from amorphous region of liquefied kenaf residue at higher P/K ratio (Pan et al. 2007). While Cheng et al. (2009) suggested that the shift of amorphous and semi-crystalline region into crystalline region and arrangement of semi-crystalline region at crystalline surface plane are responsible for the increasing of CrI values. Crystalline cellulose undergoes slower liquefaction rate than that of amorphous lignin which is due to resistant crystalline structure toward the liquefaction condition (Ahmadzadeh & Zakaria 2009).

Figure 5 illustrates the TG thermogram for the thermal degradation behaviour of kenaf residue after liquefaction. Small weight loss was observed around 100°C in the TGA curves which assign to the lost of moisture in the samples (Singh et al. 1996; Spinace et al. 2009). TGA curves ~ 236-297°C with maximum decomposition peak at 268°C represents decomposition of hemicelluloses. Second decomposition process occurred at ~ 298-366°C, with maximum decomposition peak at 335°C. Comparison of thermal decomposition rate shows that lignin possesses low decomposition rate at low temperature and underwent maximum decomposition at 437°C. This finding is in agreement with Spinace et al. (2009), who proposed that lignin de-polymerization are dominant than that of hemicelluloses/cellulose in this range of temperature.
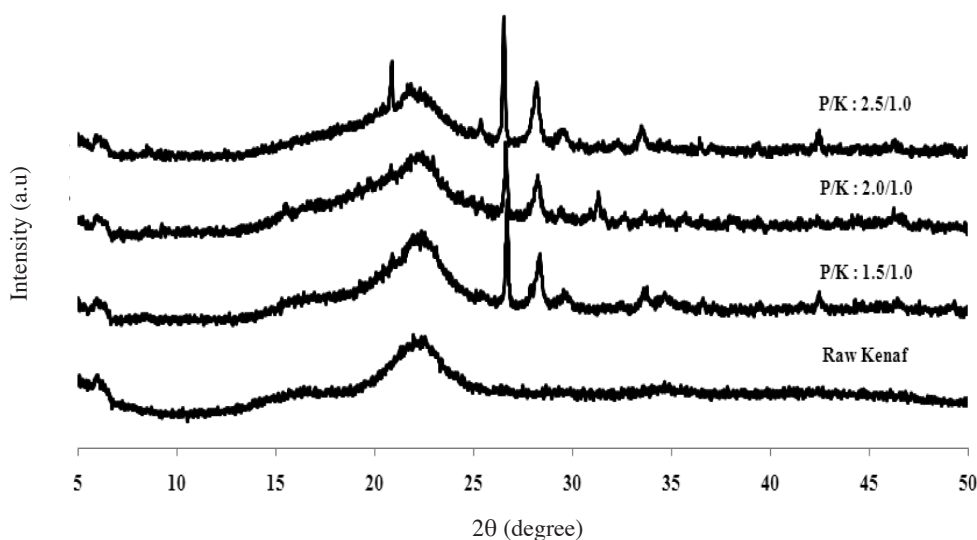

FIGURE 4. Diffractogram of raw kenaf and liquefied kenaf residue

Figure 6 illustrates the weight loss of liquefaction residue up to 450°C. The results obtained demonstrate the increase in heat resistance of liquefied kenaf residue as the P/K ratio was increased from 1.5/1.0 to 2.0/1.0. This increasing pattern can be explained from chemical reactivity between chemical components in kenaf and phenol, thus improved the thermal resistance properties in liquefied kenaf residue (Ahmadzadeh & Zakaria 2009). Other explanation for the increase of heat thermal resistance is due to the phenolation of decomposed wood component. In other words, the formation of thermally stable high molecular weight residue from the decomposition and recombination reaction of cellulose degraded derivatives (cello-oligosacharide and glucose) pyranose ring structure with phenol occurred during liquefaction process (Zhang et al. 2006). As P/K ratio increased from 2.0/1.0 to 2.5/1.0, the heat resistance decreased due to the increase in the amount of thermally stable structure of lignin which has been thermally degraded in this range of temperature.

CONCLUSION

In this study kenaf powder was successfully liquefied with phenol in the presence of sulfuric acid as catalyst at 170°C. The liquefied kenaf residue characterization demonstrated that the residue content decrease in liquefaction process was attributed from the efficient chemical penetration toward reactive site of kenaf powder. The TG curves showed that liquefied kenaf residue underwent several decomposition states and experienced improved thermal resistance as P/K ratio increased. The changes in the FTIR spectrum and the removal of small fragment attached on the surface of kenaf residue confirm the effect of P/K ratio on kenaf liquefaction and liquefied kenaf residue. XRD diffractograms showed that cellulosic crystalline component was the most resistant component toward liquefaction process. The results obtained suggested that the following; liquefaction time: 90 min, temperature: 170°C, P/K ratio: 2.5/1.0 and catalyst concentration: 3% (based on weight phenol) are sufficient for the liquefaction reaction of kenaf powder.
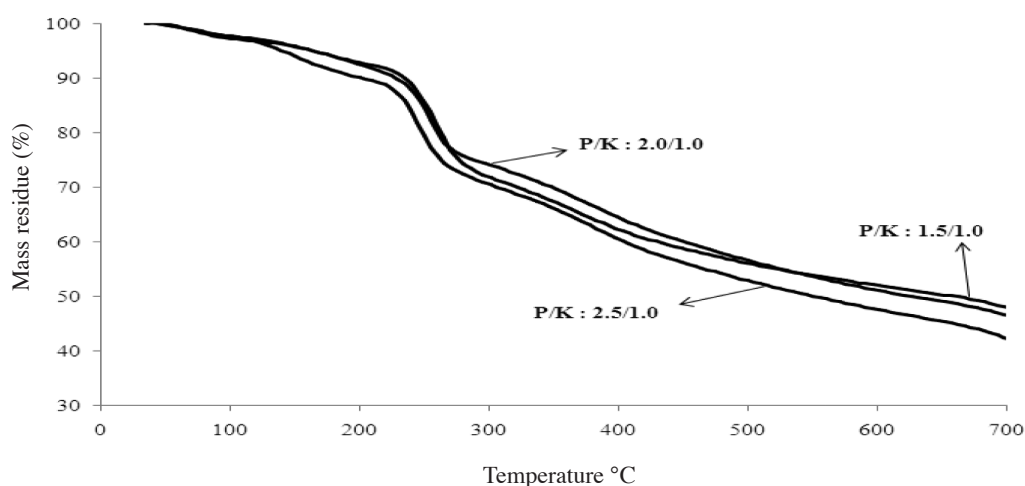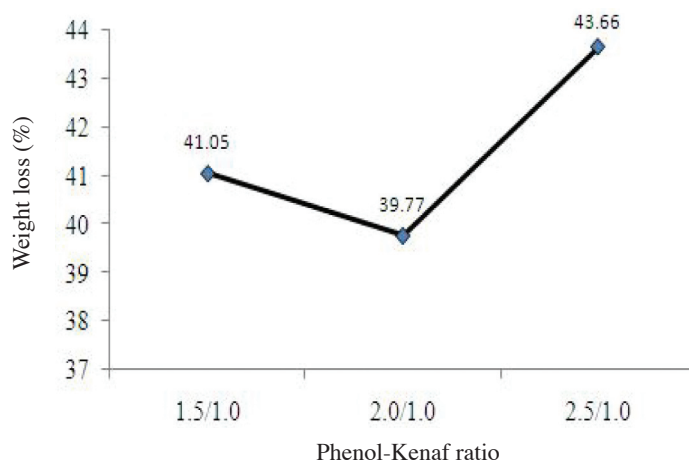

FIGURE 5. TGA curve of liquefied kenaf residue

FIGURE 6. Weight loss of liquefied kenaf residue up to 450ºC

REFERENCES

Ahmadzadeh, A. & Zakaria, S. 2009. Preparation of novolak resin by liquefaction of oil palm empty fruit bunch (EFB) and characterization of EFB residue. *Polymer-Plastics Technology and Engineering* 48: 10-16.

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: 171-176

Amen, C.C., Pakdel, H. & Roy, C. 2001. Production of monomeric phenols by thermochemical conversion of biomass: a review. *Bioresource Technology* 79: 99-277.

Cheng, Y., Wang, Y., Wan, J. & Ma, Y. 2009. Crystal and pore structure of wheat straw cellulose fiber during recycling. *Cellulose* 17: 1-10.

Deraman, M. & Zakaria, S. 1999. X-ray diffraction studies on fiber of oil palm empty fruit bunch and rubberwood for medium-density fiberboard. *Journal of Material Science Letters* 18: 249-253.

Edeerozey, A.M.M., Akil, H.M., Azhar, A.B. & Ariffin, M.I.Z. 2006. Chemical modification of kenaf fibers. *Materials Letters* 61: 2023-2025.

Effendi, A., Gerhauser, H. & Bridgwater, A.V. 2007. Production of renewable phenolic resins by thermochemical conversions of biomass: A review. *Renewable and Sustainable Energy Review* 12: 2092-2116.

Fengel, D. 1989. *Wood, Chemistry, Ultrastructure, Reactions*. Berlin: Walter de Gruyter.

Keshk, S., Suwinarti, W. & Sameshima, K. 2006. Physicochemical characterization of different treatment sequences on kenaf bast fiber. *Carbohydrate Polymers* 65: 202-206.

Kobayashi, M., Asano, T., Kajiyama, M. & Tomita, B. 2004. Analysis on residue formation during wood liquefaction with polyhydric alcohol. *Journal Wood Science* 50: 407-414.

Khristova, P., Kordsachia, O., Patt, R., Khider., T. & Karrar, I. 2002. Alkaline pulping with additives of kenaf from Sudan. *Industrial Crops and Products* 15: 229-235.

Lee, S.H. & Ohkita, T. 2003. Rapid wood liquefaction by supercritical phenol. *Wood. Sci. Technol.* 37: 29-38.

Oujai, S. & Shanks, R. 2005. Composition, structural and thermal degradation of hemp cellulose after chemical treatments. *Polym. Degrad. Stab*. 89: 327-335

Pan, H., Shupe, T.F. & Hse, C.Y. 2007. Characterization of liquefied kenaf residues from different liquefaction conditions. *Journal of Applied Polymer Science* 105: 3739-3746.

Segal, L., Creely, J.J., Martin, A.E. & Conrad, C.M. 1959. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffreactometer. *Text Res. J.* 29: 786-794.

Singh, R., Arora, S. & Lal, K. 1996. Thermal and spectral studies on cellulose modified with various cresyldichlorothiophosphates. *Thermochimia Acta* 289: 9-21.

Socrates, G. 2001. *Infrared and Raman Characteristic Group Frequencies Tables and Charts*. England: Academic Press.

Soltes, E.J. 1983. *Wood and Agricultural Residues*. New York: Academic Press.

Spinace, M.A.S., Lambert, C.S., Fermoselli, K.K.G. & De Paoli, M.A. 2009. Characterization of lignocellulosic curaua fibres. *Carbohydrate Polymers* 77: 47-53.

Tymchyshyn, M. & Xu, C. 2010. Liquefaction of bio-mass in hot-compressed water for the production of phenolic compounds. *Bioresource Technology* 101: 2483-2490.

Wahyudiono., Sasaki, M. & Goto, M. 2008. Recovery of phenolic compounds through the decomposition of lignin in near and supercritical water. *Chemical Engineering and Processing* 47: 1609-1619.

Wang, M., Xu, C. & Leitch, M. 2008. Liquefaction of cornstalk in hot compressed phenol-water medium to phenolic feedstock for the synthesis of phenol-formaldehyde resin. *Bioresource Technology* 100: 2305-2307.

Wang, M., Leitch, M. & Xu, C. 2009a. Synthesis of phenol-formaldehyde resol resins using organosolv pine lignins. *European Polymer Journal* 45: 3380-3388.

Wang, M., Leitch, M. & Xu, C. 2009b. Synthesis of phenolic resol resins using cornstalk-derived bio-oil produced by direct liquefaction in hot-compressed phenol-water. *Journal of Industrial and Engineering Chemistry* 15: 870-875.

Zhang, Y., Ikeda, A., Hori, N., Takemura, A., Ono, H. & Yamada, T. 2006. Characterization of liquefied product from cellulose with phenol in the presence of sulfuric acid. *Bioresource Technology* 97: 313-321.

Saiful Bahari Bakarudin, Sarani Zakaria* & Chin Hua Chia
School of Applied Physics
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor D.E.
Malaysia

S. Mohd Jani
Rice and Industrial Crops Research Center
Malaysian Agricultural Research and Development Institute (MARDI)
Persiaran Mardi-UPM
43400 Serdang, Selangor D.E.
Malaysia

*Corresponding author; email: sarani@ukm.my