

Identification of Compounds Released During Pyrolysis of Palm Kernel Shell (PKS) Using Pyrolysis-GC/MS

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Abstract

Pyrolysis is one of thermochemical conversion to convert biomass into bio-oil. The higher energy content in bio-oil suggests its potential as a raw material in the production of energy, bio-fuels, and other chemicals. Pyrolysis of PKS and the chemicals released were studied using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) at 400-600°C. Prior to pyrolysis, thermogravimetry experiments were carried out to monitor the degradation temperature of hemicellulose, cellulose, and lignin in the PKS. Degradation of hemicellulose occurred within a temperature range of 150-330°C, whereas the cellulose was degraded in temperatures range between 330-400°C. Degradation of lignin took place within a broad range of temperatures, which reached maximum at temperatures range of 200-500°C. Based on the Py-GC/MS results, pyrolysis of PKS at 400°C produced bio-oil that can be used as biofuel due to its high aromatic compounds but low carboxylic acids contents.

Keywords: *bio-oil; chemical; palm kernel shell; Py-GC/MS; thermogravimetry*

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INTRODUCTION

Biomass is widely recognized as one of the potential solutions to worldwide future energy problems. One of the largest biomass resources from agricultural residues in Indonesia is palm kernel shell (PKS). This idea is based on the fact that the Indonesia palm oil production growth is about 10% per year (Indonesia Investments, 2015). Palm oil production generated approximately 6-7% PKS based on fresh fruit bunch (Umikalsom *et al.*, 1997; Chiew *et al.*, 2011; Husain *et al.*, 2002). Indeed, the availability of PKS with high carbon content as source of biomass fuel can be sustained. PKS is a lignocellulosic biomass

composed mainly of cellulose, hemicelluloses, and lignin. Currently, PKS is used as fuel for boiler through combustion with low thermal conversion efficiency (Husain *et al.*, 2002; Kim *et al.*, 2010; Asadullah *et al.*, 2013). However, technological barrier and lack study and information on indigenous properties of PKS and the physico-chemical properties of bio-oil from PKS has slowed down the commercial uptake of PKS for advanced energy production (Asadullah *et al.*, 2013).

Pyrolysis is the chemical decomposition of organic material (biomass) through the application of heat in the absence of oxygen. During the pyrolysis

process, biomass is converted into a liquid product (bio-oil), a solid residue (bio-char) and gaseous compounds (Cordella *et al.*, 2012). Pyrolysis-based energy densification processes can be considered an interesting route for the energy valorization of residual biomass such as PKS (Faaij, 2006). Bio-oil is particularly attractive pyrolysis product because of its high energy content per volume as well as its potential use in the production of energy, bio-fuels, and chemicals (National Renewable Energy Laboratory, 2009).

Fundamental understanding of PKS pyrolysis behavior is essential to further PKS efficient thermochemical conversion. Several researchers have investigated the behavior and mechanism as well as characteristics of the products of PKS pyrolysis. They used single thermogravimetric analysis (TGA) and thermogravimetric characteristics of PKS in inert atmosphere (Kim *et al.*, 2010; Asadullah *et al.*, 2013; Lee *et al.*, 2013). Asadullah *et al.* (2013) observed that the thermal decomposition of PKS was slower than other biomass because of the higher lignin content. Quantitative pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was used to study the components involved in biomass pyrolysis (Gao *et al.*, 2013). Py-GC/MS technique involves the compositional information of the complex component macromolecules, as well as the characteristics of volatile products. This technique has been shown to be a reliable analytical technique for the characterization of biomass (Fahmi *et al.*, 2007; Qiang *et al.*, 2009).

Previous studies have examined the bio-oil composition obtained from Py-GC-MS of PKS. Chang *et al.* (2016a) focused their research in lignin conversion and reported that the phenol content of PKS bio-oil obtained from pyrolysis at 500°C was about 13.49%. Furthermore, they investigated the Py-GC/MS of PKS at higher temperature i.e. 600-800°C which yielded liquid product (bio-oil) of 36.8-50.9% (Chang *et al.* 2016b). Based on the previous studies, the main objective of the present study was to examine the pyrolysis of PKS at lower temperature and its PKS bio-oil characteristics.

METHOD

Materials

The PKS used in this study was supplied by palm oil mills of PTPN-IV located in Tombatu (North Sumatera-Indonesia). Prior to the experiment, PKS was firstly crushed and pulverized to a size 80–100 mesh. The cellulose (21.17 wt.%), hemicelluloses (16.13 wt.%), lignin (45.06 wt.%), ash (1.87 wt.%), and moisture (15.77 wt.%) contents in PKS were analyzed using NREL methods (Hyman *et al.*, 2008; Sluiter *et al.*, 2008a; Sluiter *et al.*, 2008b; Sluiter and Sluiter, 2008). Based on the ultimate analysis using elemental analyzer CHN 628 (Leco Corporation), the C, H, N, and O contents in PKS were found to be 48.60, 6.29, 0.48, and 44.63%, respectively.

Thermogravimetry (TG) Analysis

Thermogravimetric analysis was carried out on a Netzsch TG 209 F3 Tarsus. About 10-13 mg of PKS was placed in an alumina crucible and heated from room temperature (30°C) to 600°C under nitrogen atmosphere. The heating rate was controlled from 5-20°C/min.

Identification of Pyrolysis Products by Pyrolysis-GC/MS (Py-GC/MS)

Pyrolysis of PKS and volatile product identification was carried out by Py-GC/MS (Shimadzu, GC-2010, GCMS-QP2010). In the gas chromatography, a capillary type phase Rtx-5MS column with a length of 60 m, ID of 0.25 mm, and film thickness of 0.5 µm were used. The column temperature program was applied with a split ratio of 1:50 from 50 to 280°C.

The pyrolyzer was heated for 10 s from 30°C to the final temperature of 400-600°C with an interval of 50°C. Then, the vapor and aerosol were auto injected into the GC/MS for compounds analysis. The compounds were grouped into the same functional group and the concentration was based on percentage of peak area.

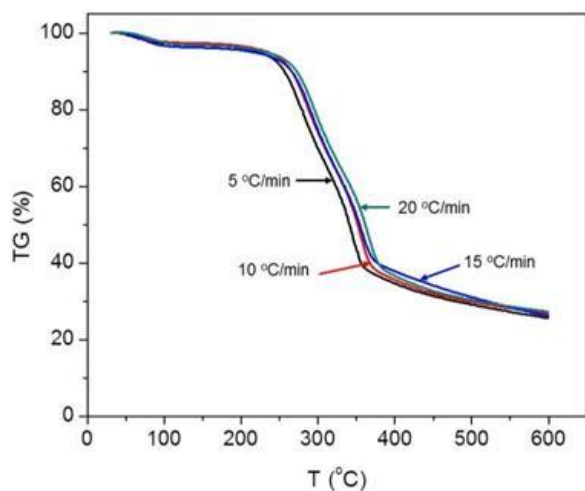
RESULTS AND DISCUSSION

Thermogravimetric Analysis of Palm Kernel Shells

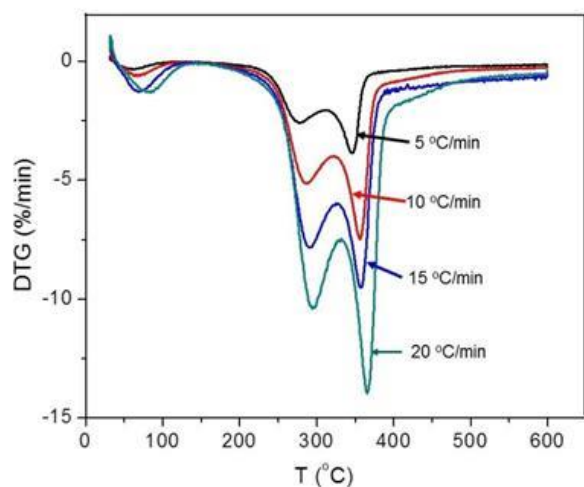
There are numerous applications of the TGA for material characterization such as through quantitative weight losses that occur in specified temperature regions of the TGA curve. This technique was applied to study the chemicals released during pyrolysis of PKS using Py-GC/MS until 600°C. The Py-GC/MS was operated at a maximum temperature of 600°C. The TGA and differential thermogravimetric (DTG) curves of PKS under 5, 10, 15, and 20°C/min of heating rates are shown in Figures 1 (a) and (b).

During the pyrolysis test as shown in Figure 1, the thermal degradation of PKS took place within a wide range of 150-600°C, which consisted of three distinct decomposition regions: 150-330°C; 330-400°C, and 400-600°C. The thermal degradation was prefaced by the removal of bound and unbound moisture at room temperature until 150°C because the PKS was used without drying pre-treatment. The range temperatures of each decomposition region of PKS during thermogravimetric analysis were slightly different in each heating rate. The range temperature increased with faster heating rate. Ma *et al.* (2015) reported that during the thermogravimetric analysis of the three model components of lignocelluloses (cellulose, xylan-type hemicelluloses, and lignin) the hemicelluloses was decomposed at 100-365°C with the maximum weight loss occurring at 185-325°C. Degradation of cellulose occurred at 270-400°C. Moreover, lignin decomposed in a wide range temperature of 100-800°C with maximum weight loss occur at 200-500°C. Refer to that conditions, the first

region of PKS degradation in Figure 1 was hemicelluloses (150-330°C), the second region was cellulose (330-400°C), and then followed by lignin decomposition at around 200°C. PKS pyrolysis by TGA was also studied by Choi *et al.* (2015), Kim *et al.* (2010), and Asadullah *et al.* (2013) from room temperature until 800-1000°C. They found that, thermal decomposition of lignin after 600°C was very low and around such temperature, weight loss of PKS was between 60-70% and almost constant until 1000°C.



(a)



(b)

Figure 1. TG (a) and DTG (b) curves of PKS with heating rates at 5-20°C/min.

Based on the TGA and DTG curves shown in Figure 1, the minimum pyrolysis temperature of PKS for identification of chemicals released by Py-GC/MS was selected as 400°C and conducted until 600°C with a 50°C interval.

Pyrolysis-Gas Chromatography / Mass Spectrometry

PKS was pyrolyzed and analyzed by Py-GC/MS to investigate the chemicals released during

degradation of PKS structures from room temperature to final pyrolysis temperatures. The various final temperatures were 400–600°C with an interval of 50°C selected based on TGA and DTG curves as shown in Figure 1. The chemicals released from pyrolysis of PKS for each final temperature are shown in Figure 2.

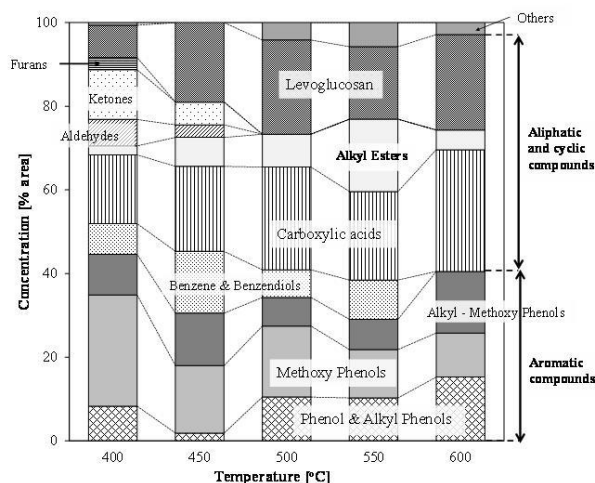


Figure 2. Chemicals released during pyrolysis of PKS using Py-GC/MS.

The chemicals released from pyrolysis of PKS shown in Figure 2 were grouped into phenol and alkyl phenols, methoxy phenols, alkyl-methoxy phenols, benzene and benzenediols, carboxylic acids, alkyl esters, aldehydes, ketones, furans, levoglucosan, and others. Some peaks appeared in chromatogram of GC/MS analysis are the other unknown chemicals. The detectable chemicals and their groups are shown in Table 1. The percentage area of chemical compounds after GC/MS analysis could be corresponded to the concentration of the chemicals released from PKS and described as chemical compositions of bio-oil.

As shown in Figure 2 and Table 1, the chemicals released from pyrolysis of PKS consist of aromatics, cyclic, and aliphatic compounds. The aromatics were derived mainly from the decomposition of lignin because it composed of an aromatic ring with three primary phenyl propane monomers namely coumaryl, coniferyl, and sinapyl alcohols. Moreover, lignin has various functional groups of methoxyl, phenolic hydroxyl, aliphatic hydroxyl, benzyl alcohol, noncyclic benzyl ether, and carbonyl groups (Azadi *et al.*, 2013). Therefore, groups of phenol, alkyl phenols, methoxy phenols, alkyl-methoxy phenols, benzenes, and benzenediols were produced from decomposition of lignin in the PKS structure. In addition, groups of carboxylic acids, alkyl esters, aldehydes, ketones, furans, and levoglucosan that mainly comprise cyclic and aliphatic compounds were derived from cellulose and hemicelluloses. The prediction was supported by results of Liaw *et al.* (2014) that hydroxy-ketone, cyclopentene and levoglucosan were derived from

cellulose depolymerization reaction. While the acetic acid and furan were the derivative products of hemicelluloses decomposition.

Table 1. Chemical compounds in volatile products of PKS pyrolysis

Group	Chemicals
1. Phenol & Alkyl phenols	Phenol
	Phenol,2-methyl-
	Phenol, 3-methyl-
2. Methoxy phenols	Phenol, 3-undecyl-
	Phenol, 2-methoxy-
	Phenol, 4-methoxy-
	Phenol, 2,6-dimethoxy-
	Phenol, 3,4-dimethoxy-
	Phenol, 2-methoxy-4-(2-propenyl)-
	Phenol, 2-methoxy-4-(1-propenyl)-,
	(E)-
	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-
	Phenol,2,6-dimethoxy-4-(2-propenyl)-
3. Alkyl-methoxy phenols	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
	Phenol, 2,6-dimethoxy-4-(2-propenyl)-
	Ethanone,1-(4-hydroxy-3,5-dimethoxyphenyl)-
	2-Methoxy-4-methylphenol
4. Benzenes & Benzenediols	Phenol,4-ethyl-2-methoxy-
	Phenol, 4-ethenyl-2-methoxy
	Phenol, (1,1-dimethylethyl)-4-methoxy-
5. Carboxylic acids	1,2-Benzenediol
	3-Methoxy-pyrocatechol
	Benzenemethanol,4-methoxy-
	Benzene,1,2,3-trimethoxy-
	Benzaldehyde,4-hydroxy-3,5-dimethoxy-
	Ethanedioic acid
	Acetic acid
	Benzoic acid
6. Alkyl esters	Dodecanoic acid
	Tetradecanoic acid
	Hexadecanoic acid
	Oleic acid
	Stearic acid
7. Aldehydes	Benzoic acid, 4-hydroxy-, methyl ester
	Benzenepropanoic acid, 2-methoxy-, methyl ester
	Benzenepropanoic acid,2-methoxy-, methyl ester
	2,4-Hexadienedioic acid, 3,4-diethyl, dimethyl ester, (E,Z)-
8. Ketones	Dodecanoic acid, ethenyl ester
	Acetaldehyde
	Pentanal
9. Furans	2-Butanone
	2-Propanone, 1-hydroxy-
	Acetone
	Cyclopentanone, 2-methyl-
10. Levoglucosan	Cyclohexanone
	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-

The increase in pyrolysis temperature of PKS from 400-600°C, vary the concentration of chemical in the volatile product. The concentration of the aromatics reduced as the pyrolysis temperature increased up to 550°C. However, the concentration of the aromatics was higher at 600°C than at 550°C where benzene and benzenediol compound groups were undetectable. High concentrations of benzenes, benzenediols and methoxy phenols were produced at low temperatures. These types of compounds are derived from guaiacyl-type compounds of lignin that had ether bond such as β -O-4. It was reported that the β -O-4 had lower thermal stability and decomposed easily at low temperatures (Xu and Ferdosian, 2017; Chang *et al.*, 2016a). However, at high temperatures, the production of phenol, alkyl phenols, alkyl-methoxy phenols, carboxylic acids and levoglucosan were high. These indicated that decomposition of lignin structure mainly occur at high temperature to produce phenolic compounds. On the other hand, aldehydes, ketones, and furans were formed at low temperatures. Formation of aldehydes, ketones, organic acids were derived from decomposition of sugar ring in celluloses and hemicelluloses which occur in a range temperature 150-400°C as shown in Figure 1 (Chang *et al.*, 2016a; Rasmussen *et al.*, 2014). Then, the production of alkyl ester as one of the volatile products of PKS pyrolysis was higher at 550°C than at other temperatures that are supposed to be derived from cellulose and hemicelluloses.

Aromatic compounds are expected to be applied as bio-oil for liquid fuel production. Bio-oil with higher aromatic compound content are derived from PKS as shown in Figure 2, being produced at 53% after pyrolysis at 400°C. Moreover, the bio-oil consisted of lower carboxylic acids than those produced at other pyrolysis temperatures. Bio-oil is highly valuable as fuel because with low acidity of oil would slow down the corrosion of combustion engine. In addition, the carboxylic acids can be further converted into diesel or jet fuels by hydrotreating process (Rabaev *et al.*, 2015). Based on the type of compounds released from pyrolysis of PKS, the potential bio-oil for liquid fuel application was that produced at 400°C. The bio-oil can be further being hydrotreated with a suitable catalyst. The composition of aromatics and carboxylic acids after pyrolysis at 400°C are shown in Table 2.

As mentioned above, the production of new compounds such as phenol and alkyl phenols, alkyl-methoxy phenols, carboxylic acids, and levoglucosan increased at higher pyrolysis temperature. Phenols and alkyl phenols are used in production of phenolic resin. Moreover, in the carboxylic acids group, decanoic, tetradecanoic, hexadecanoic and oleic acids were the dominant chemicals, which can be used as emulsifier or surfactant. It is also clear that the production of levoglucosan also increased at higher. Levoglucosan chemically is stable in the atmosphere (Hennigan *et al.*, 2010) and can be hydrolyzed into glucose by an

acid catalyst that can be converted biochemically into bioethanol (Li *et al.*, 2013).

Table 2. Compositions of aromatics and carboxylic acids after pyrolysis at 400°C

Group	Chemicals	Concentration (% area)
Phenol & Alkyl Phenols	Phenol	8.28
	Phenol, 4-methoxy-	5.47
Methoxy phenols	Phenol, 2,6-dimethoxy-	6.10
	Phenol, 3,4-dimethoxy-	0.95
	Phenol, 2-methoxy-4-(2-propenyl)-	0.61
	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-	7.10
	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	1.93
	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	4.44
Alkyl, Methoxy Phenols	2-Methoxy-4-methylphenol	3.75
	Phenol, 4-ethenyl-2-methoxy	3.31
	Phenol, (1,1-dimethylethyl)-4-methoxy-	2.65
Benzenes & Benzenediols	1,2-Benzenediol	7.33
	Acetic acid	6.04
Carboxylic acids	Benzoic acid	0.64
	Dodecanoic acid	2.16
	Tetradecanoic acid	1.09
	Hexadecanoic acid	3.16
	Oleic acid	3.37

CONCLUSION

Thermal degradation of PKS was performed through TGA and Py-GC/MS to identify the compounds released. During TG analysis, thermal degradation of PKS occurred in three stages of hemicelluloses, cellulose, and lignin that started by moisture removal. The degradation of PKS mainly occurred at temperatures range of 200-450°C and produced 53% of aromatic compounds at 400°C. Bio-oil of PKS that produced at 400°C had the potential to be used as liquid fuels. Bio-oil obtained from pyrolysis of PKS at 600°C has the potential as a source of chemical derivatives due to its higher phenol and alkyl phenols, alkyl-methoxy phenols, carboxylic acids, and levoglucosan content. However, methoxy phenols, benzenes, and benzenediols were produced in higher concentration under low temperature of PKS pyrolysis.

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REFERENCES

Asadullah, M., Rasid, N.S.A., Kadir, S.A.S.A., and Azdarpour, A., (2013), Production and Detailed

Characterization of Bio-Oil from Fast Pyrolysis of Palm Kernel Shell, *Biomass and Bioenergy*, 59, pp. 316-324.

Azadi, P., Inderwildi, O.R., Farnood, R., and King, D.A., (2013), Liquid Fuels, Hydrogen and Chemicals from Lignin: A Critical Review, *Renewable and Sustainable Energy Reviews*, 21, pp. 506-523.

Chang, G., Huang, Y., Xie, J., Yang, H., Liu, H., Yin, X., and Wu, C., (2016a), The Lignin Pyrolysis Composition and Pyrolysis Products of Palm Kernel Shell, Wheat Straw, and Pine Sawdust, *Energy Conversion and Management*, 124, pp. 587-597.

Chang, G., Huang, Y., Xie, J., Yin, X., and Wu, C., (2016b), Kinetic Analysis of Palm Kernel Shell during Pyrolysis Reaction, *Chemistry and Industry of Forest Products*, 36 (4), pp. 31-40.

Chiew, Y.L., Iwata, T., and Shimada, S., (2011), System Analysis for Effective Use of Palm Oil Waste as Energy Resources, *Biomass and Bioenergy*, 35, pp. 2925-2935.

Choi, G.-G., Oh, S.-J., Lee, S.-J., and Kim, J.-S., (2015), Production of Bio-based Phenolic Resin and Activated Carbon from Bio-oil and Biochar Derived from Fast Pyrolysis of Palm Kernel Shells, *Bioresour. Technology*, 178, pp. 99-107.

Cordella, M., Torri, C., Adamiano, A., Fabbri, D., Barontini, F., and Cozzani, V., (2012), Bio-oils from Biomass Slow Pyrolysis: A Chemical and Toxicological Screening, *Journal of Hazardous Materials*, 231-232, pp. 26-35.

Faaij, A., (2006), Modern Biomass Conversion Technologies. *Mitigation and Adaptation Strategies for Global Changes*, 11, pp. 343-375.

Fahmi, R., Bridgwater, A.V., Thain, S.C., Donnison, I.S., Morris, P.M., and Yates, N., (2007), Prediction of Klason Lignin and Lignin Thermal Degradation Products by Py-GC/MS in a Collection of Lolium and Festuca Grasses, *Journal of Analytical Applied Pyrolysis*, 80, pp. 16-23.

Gao, N., Li, A., Quan, C., Du, L., and Duan, Y., (2013), TG-FTIR and Py-GC/MS Analysis on Pyrolysis and Combustion of Pine Sawdust, *Journal of Analytical Applied Pyrolysis*, 100, pp. 26-32.

Hennigan, C.J., Sullivan, A.P., Collett, J.L., and Robinson, A.L., (2010), Levoglucosan Stability in Biomass Burning Particles Exposed to Hydroxyl Radicals, *Geophysical Research Letter*, 37, pp. 2-5.

Husain, Z., Zainal, Z.A., and Abdullah, M.Z., (2002), Analysis of Biomass-Residue-Based Cogeneration

System in Palm Oil Mills, *Biomass and Bioenergy*, 24, pp. 117-124.

Hyman, D., Sluiter, A., Crocker, D., Johnson, D., Sluiter, J., Black, S., and Scarlata, C., (2008), Determination of Acid Soluble Lignin Concentration Curve by UV-Vis Spectroscopy: Laboratory Analytical Procedure (LAP), Issue date 06/01/2007/. National Renewable Energy Laboratory, <http://permanent.access.gpo.gov/lps94095/42617.pdf>. Download date: November 3rd 2015.

Indonesia Investments, (2015), Crude Palm Oil Indonesia Update Limited Production Growth in 2015, <http://www.indonesia-investments.com/news/todays-headlines/crude-palm-oil-indonesia-update-limited-production-growth-in-2015/item5184>. Download date: November 3rd 2015.

Kim, S.J., Jung, S.H., and Kim, J.S., (2010), Fast Pyrolysis of Palm Kernel Shells: Influence of Operation Parameters on the Bio-oil Yield and the Yield of Phenol and Phenolic Compounds, *Bioresource Technology*, 101, pp. 9294-9300.

Lee, Y., Park, J., Ryu, C., Gang, K.S., Yang, W., Park, Y.K., Jung, J., and Hyun, S., (2013), Comparison of Biochar Properties from Biomass Residues Produced by Slow Pyrolysis at 500°C, *Bioresource Technology*, 148, pp. 196-201.

Li, Q., Steele, P.H., Mitchell, B., Ingram, L.L., and Yu, F., (2013), The Addition of Water to Extract Maximum Levoglucosan from the Bio-oil Produced via Fast Pyrolysis of Pretreated Loblolly Pinewood, *Bioresources*, 8, pp. 1868-1880.

Liaw, S.-S., Perez, V.H., Zhou, S., Rodriguez-Justo, O., and Garcia-Perez, M., (2014), Py-GC/MS Studies and Principal Component Analysis to Evaluate the Impact of Feedstock and Temperature on the Distribution of Products during Fast Pyrolysis, *Journal of Analytical Applied Pyrolysis*, 109, pp. 140-151.

Ma, Z., Chen, D., Gu, J., Bao, B., and Zhang, Q., (2015), Determination of Pyrolysis Characteristics and Kinetics of Palm Kernel Shell using TGA-FTIR and model-free integral methods, *Energy Conversion Management*, 89, pp. 251-259.

National Renewable Energy Laboratory, (2009), Biomass Research - What Is a Biorefinery?,

<http://www.nrel.gov/biomass/biorefinery.html>. Download date: November 12, 2015.

Qiang, L., Wen-zhi, L., Dong, Z., and Xi-feng, Z., (2009), Analytical Pyrolysis – Gas Chromatography / Mass Spectrometry (Py-GC/MS) of Sawdust with Al/SBA-15 catalysts, *Journal of Analytical Applied Pyrolysis*, 84, pp. 131-138.

Rabaev, M., Landau, M.V., Vidruk-Nehemya, R., Koukouliev, V., Zarchin, R., and Herskowitz, M., (2015), Conversion of Vegetable Oils on Pt/Al₂O₃/SAPO-11 to Diesel and Jet Fuels Containing Aromatics, *Fuel*, 161, pp. 287-294.

Rasmussen, H., Sørensen, H.R., and Meyer, A.S., (2014), Formation of Degradation Compounds from Lignocellulosic Biomass in the Bio-refinery: Sugar Reaction Mechanisms, *Carbohydrate Research*, 385, pp. 45-57.

Sluiter, A., Hames, B., Ruiz, R.O., Scarlata, C., Sluiter, J., and Templeton, D., (2008), Determination of ash in biomass: Laboratory Analytical Procedure (LAP), Issue date 07/17/2005/. National Renewable Energy Laboratory, <http://www.nrel.gov/biomass/pdfs/42622.pdf>. Download date: November 3rd 2015.

Sluiter, A., Hyman, D., Payne, C., and Wolfe, J., (2008a), Determination of Insoluble Solids of Pretreated Biomass Material: Laboratory Analytical Procedure (LAP), Issue date 03/21/2008/, National Renewable Energy Laboratory, <http://www.nrel.gov/biomass/pdfs/42627.pdf>. Download date: November 3rd 2015.

Sluiter, A. and Sluiter, J., (2008b), Determination of Starch in Solid Biomass Samples by HPLC: Laboratory Analytical Procedure (LAP), Issue date 07/17/2005/. National Renewable Energy Laboratory, <http://www.nrel.gov/biomass/pdfs/42624.pdf>. Download date: November 3rd 2015.

Umikalsom, M.S., Ariff, B., Zulkifli, H.S., Tong, C.C., Hassan, M.A., and Karim, M.I.A., (1997), The Treatment of Oil Palm Empty Fruit Bunch Fibre for Subsequent Use as Substrate for Cellulase Production by *Chaetomium Globosum* Kunze, *Bioresource Technology*, 62, pp. 1-9.

Xu, C. and Ferdosian, F., (2017), Conversion of Lignin into Bio-Based Chemicals and Materials, *Green Chemistry and Sustainable Technology*, Springer-Verlag GmbH, Germany, pp.15-19.