Study on the Effect of Reaction Temperature, Time, and Solid Loading on Lignin from Oil Palm Frond (OPF) under Subcritical Phenol Conditions as a Precursor for Carbon Fiber Production

Khalidatul Athirah KHALID, Asimi Ana AHMAD, and Tau Len-Kelly YONG†

(Received August 17, 2018)

Carbon fiber is a well-established high value-added material. However, its price is considerably high. Lignin obtained from oil palm frond (OPF) is a compatible precursor for carbon fiber production. This study aims to determine the feasibility of OPF lignin obtained under subcritical phenol conditions by focusing on its fundamental properties (purity and particulate matter content) as a precursor for carbon fiber production. This study also focuses on the effect of temperature (260–300 °C), time (5–30 min), and solid loading (6 and 10 g) on these properties. From the results obtained, the highest lignin purity of 95.1% was obtained at 260 °C, 5 min, and 10 g solid loading. Meanwhile, the lowest particulate content of 15.6% was obtained at 300 °C, 30 min, and 6 g solid loading. It can be further concluded that at higher temperature and longer reaction time, the low molecular weight compounds are dissolved in the liquid product, resulting in a decrease in the lignin purity as well as the particulate matter content.

Key Words
Carbon fiber, Oil palm biomass, Subcritical phenol, Lignin, Biomass

1. Introduction
Carbon fiber is mainly used for high-end industries such as construction, aircraft, turbines, and sporting goods. Carbon fiber in automobiles and aerospace contributes to energy reduction through fuel savings because it is estimated that for every 10% mass saving in a vehicle leads to a 6–8% improvement in fuel economy. However, the limitation of carbon fiber usage in wider applications is mainly due to its high price, particularly its precursor and manufacturing process. Polyacrylonitrile (PAN) and pitch are the conventional feedstocks used in the production of carbon fiber. The demand of PAN for carbon fiber production is expected to grow at a compound growth annual rate of 12.9% or over 200 thousand tons in 2025. However, both feedstocks are derived from fossil fuels, which are finite. Furthermore, its pre-treatment steps and purification methods are complex and expensive. Considering its importance, the manufacture of low-cost carbon fiber with renewable, abundant, and low-cost precursors has been of great research interest.

An exponential growth of the palm oil industry in Malaysia has occurred over the past few decades. In 2017, Malaysia produced about 19.91 million tons of crude palm oil (CPO) in comparison to about 18.79 million tons in 2012. The increase in CPO production has led to the excessive generation of oil palm biomass. Oil palm fronds (OPFs) and oil palm trunk (OPT) are produced during harvesting and pruning from the plantation area. Meanwhile, empty fruit bunches (EFBs), palm kernel shells (PKSs), mesocarp fiber (MF), and palm oil mill effluent are generated from the mill site. The volume of oil palm biomass is predicted to increase along with the worldwide demand of CPO, posing waste management issues. Among all oil palm biomass, OPF has gained interest due to the massive quantities generated each year.

Since the fundamental principles of waste management are to reduce and recycle waste as well as to recover as much energy as possible, the excessive amount of OPF generated by a plantation site can be utilized efficiently and effectively to produce valued products such as carbon fiber due to the lignocellulosic components in OPF. All lignocellulosic biomass is built up by three important natural polymer compounds; cellulose, hemicellulose, and
lignin. Table 1 shows the chemical composition of oil palm biomass.

Lignin is a heterogeneous and amorphous polymer contained in the cell walls of vascular plants making it the second most abundant compound found in biomass after cellulose. Different plants may have different lignin structures, which are determined by the linkages formed between the phenylpropanoid lignin precursors; p-coumaryl, coniferyl, and sinapyl. Generally, coniferyl alcohol can be found in softwood lignin, while hardwood lignin consists of coniferyl and sinapyl alcohol. In contrast, p-coumaryl alcohol is mainly found in grass lignin. The existence of various oxygen functional groups such as phenolic, hydroxyl, carbonyl groups, and ether and ester bonds in lignin are major resources for the production of fuel and chemicals as well as precursors for carbon fiber production. However, the major challenge using lignin as a precursor for carbon fiber is to produce an equal or better precursor with mechanical properties comparable to the conventional precursor. To determine the viability of potential precursors for carbon fiber production, a set of specifications for lignin were developed by Oak Ridge National Laboratory (ORNL) as a reference (Table 2).

The applications of lignin are mainly determined by its degradation to low molecular weight compounds or multifunctional micro-molecules. Lignin degradation produces three fractions: liquid products mainly including phenolic compounds, gaseous products including mostly CO2, CO, H2, CH4, and trace amounts of C2 and C3 hydrocarbons, and solid residues composed of condensed and unconverted lignin. This study focuses on the properties of solid lignin used as a carbon fiber precursor. The main concern in lignin extraction from biomass is its separation from other biomass constituents (cellulose, hemicellulose, and ash) so that high purity lignin can be obtained.

Recently, attention has been given to the depolymerization of biomass under sub- and supercritical conditions due to its capability of varying the fluid properties via manipulating the temperature and pressure. The dielectric constant decreases at high temperature causing the non-polar organic substances to dissolve, hence breaking the linkages between cellulose, hemicellulose, and lignin. Lignin separation under sub- and supercritical water conditions has been extensively studied because it is a clean reaction. However, the reaction under these conditions causes the repolymerization of monomers to produce char. Char formation hinders and decreases the quality of lignin as a carbon fiber precursor. Therefore, a new approach using subcritical phenol has been proposed. The critical point of phenol is 421.1°C and 6.13 MPa. Several studies have demonstrated that the addition of phenol may reduce the formation of char. This is because phenol inhibits cross-linking by reacting with the active sites in the decomposition fragments, which consequently suppresses char formation. In this study, the effect of temperature (260–300°C), time (5–30 min), and solid loading (6 and 10 g) on the lignin properties (purity and particulate matter content) were determined to study its viability as a precursor for carbon fiber production.

2. Experimental

2.1 Raw Materials and Chemicals

OPF was obtained from the Federal Land Development Authority plantation in Negeri Sembilan, Malaysia. Sample preparation followed standard procedures. The samples were ground and sieved to obtain particles in the size range of 210–500 µm. Subsequently, the samples were subjected to an extraction process using methanol and a Soxhlet extractor to remove any oil residues and extractives. After 6 h, the extracted samples were washed with water and dried in the oven for 48 h at 45°C.

2.2 Experiment

The reaction was conducted in an autoclave batch reactor with working volume of 100 mL. Weighed OPF (6 or 10 g) and 70 mL of phenol were mixed and loaded into the autoclave reactor and subjected to various experimental conditions (temperature, reaction time, and solid loading). The amount of phenol was chosen on the basis to maintain the reaction pressure under subcritical phenol conditions (6.13 MPa). The reaction time was recorded once the temperature inside the vessel reached the target temperature. When the reaction was completed, the reactor was immersed in a water bath to quench the reaction.

Table 1 Chemical composition of palm oil biomass

| Types of biomass | Chemical components (% dry wt.) | Cellulose | Hemicellulose | Lignin | Extractives | Ash |
|------------------|---------------------------------|-----------|---------------|--------|-------------|-----|
| OPF              |                                 | 30.4      | 40.4          | 21.7   | 1.7         | 5.8 |
| OPT              |                                 | 34.5      | 31.8          | 25.7   | 3.7         | 4.3 |
| EFB              |                                 | 38.3      | 35.3          | 22.1   | 2.7         | 1.6 |
| MF               |                                 | 33.9      | 26.1          | 27.7   | 6.9         | 3.5 |
| PKS              |                                 | 20.8      | 22.7          | 50.7   | 4.8         | 1.0 |

Table 2 Lignin specification as a carbon fiber precursor

| Criteria               | Value (wt.%) |
|------------------------|--------------|
| Lignin purity          | 99%          |
| Ash content            | <0.1         |
| Volatile matter        | <5.0         |
| Particulate matter     | 100% removal for matter >1 µm in diameter |
solid residue was separated from the liquid residue using vacuum filtration (Rocker 300, oil free 220 V). Subsequently, the solid residue was washed with methanol several times to ensure the removal of phenol. The washing was stopped when the color of the methanol filtrate was almost colorless and the refractive index (RI) of the methanol approached 1.33141. The solid residue was subsequently dried in an oven at 105 °C. The tube was placed in a water bath for 60 min at 100 ± 3 °C. The sample was filtered to obtain the insoluble particulate matter. The percentage of insoluble matter was determined based on the amount of remaining mass of solid and the mass of the original sample.

3. Results and Discussions

3.1 Lignin Purity

Lignin purity is the degree by which the sample after phenol extraction is free from compounds other than lignin. In this study, the lignin purity was determined by adding the AIL and ASL fractions. Based on NREL specification, the percentage of AIL is defined as the ratio of weight of AIL recovered to ODW of the recovered solid residue in phenol extraction, using the average total solid content. The percentage of ASL is defined as the ratio of weight of ASL recovered to ODW of the recovered solid residue in phenol extraction, using the average total solid content. Based on Table 2, the lignin purity needs to be >99% for it to be viable as a carbon fiber precursor.

Theoretically, the decrease in the dielectric constant at high temperature subsequently decreases the polarity of phenol, which has the ability to dissolve non-polar organic compounds and break the linkages between cellulose, hemicellulose, and lignin. Under these conditions, cellulose, hemicellulose and lignin undergoes marked structural changes where the bonds start to decompose to form low molecular compounds, which are found dominantly in the liquid product compared to the solid phase. The solid residue consisted of mainly cellulose with lignin and hemicellulose. This is because, the degradation of hemicellulose occurred at 200–320 °C, lignin over a wider range of 140–600 °C. Meanwhile cellulose degradation occurred at the range of 280–360 °C. On the other hand, this study is at the range of 260–300 °C. This can be observed in the percentage of solid residues recovered decreased with temperature and reaction time.

Table 4 shows the percentage of AIL recovered to weight of solid residue recovered and the percentage of acid insoluble ash to AIR. This an important indicator of the mass balance of the solid residue composition. In addition, Table 5 shows the percentage of AIL, ASL and total lignin purity. The lignin recovered in this study are mainly as

### Table 3 Experimental conditions

| Condition                  | Experimental range |
|----------------------------|--------------------|
| Reaction temperature (°C)  | 260, 280, and 300  |
| Reaction time (min)        | 5, 10, and 30      |
| Solid loading (g)          | 6 and 10           |
| Raw material               | OPF                |
| Solvent                    | Phenol             |

#### 2.4 Analysis

2.4.1 Lignin Purity

Lignin purity analysis was carried out in accordance with the NREL specification (Determination of Structural Carbohydrates and Lignin in Biomass). The AIR were placed inside a muffle furnace at 575 ± 25 °C for 24 h. This is to determine the amount of acid insoluble ash. The acid insoluble lignin (AIL) is obtained by subtracting the acid insoluble ash from the AIR. Meanwhile, the acid soluble lignin (ASL) content was determined using ultraviolet spectroscopy of sulfuric acid after extraction at 205 nm with an absorptivity coefficient of 110 g. L⁻¹cm⁻¹. Lignin purity was determined by adding the AIL and ASL fractions.
Fig. 2 (a) and (b) show the effect of temperature (260–300 °C), reaction time (5–30 min), and solid loading (6 and 10 g) on lignin purity. It can be observed that higher lignin purity was obtained at low temperature (260 °C). Furthermore, the purity decreased upon increasing the temperature (280–300 °C).

Fig. 2 (a) and (b) show the highest lignin purities of 64.0% and 64.8% were obtained at 260 °C and 5 min reaction time at a 6 and 10 g solid loading, respectively. It can be concluded that the range of lignin purity was higher at lower temperature for all the reaction times and solid loadings studied.

This study is in agreement with a few previously reported studies that concluded the solid product and lignin purity decrease considerably upon increasing the temperature. Ko et al. (2014) observed that lignin purity increases with temperature under a hot water pre-treatment process. The lignin purity obtained in their study was 40.3% at 220 °C. On the other hand, Laurenco et al. (2014) observed that lignin purity decreases with temperature for both softwood and hardwood. The lignin purity obtained in their study were 21.9% for softwood and 23.0% for hardwood at 170 °C. Furthermore, Saisu et al. (2003) observed that low

Table 5 Percentage of AIL, ASL and total lignin purity

| Temperature (°C) | Solid Loading (g) | Reaction Time (min) | AIL (%) | ASL (%) | Total (%) |
|-----------------|------------------|---------------------|---------|---------|-----------|
| 260             | 6                | 5                   | 62.3    | 17      | 63.9      |
|                 |                  | 10                  | 62.0    | 18      | 63.8      |
|                 |                  | 30                  | 61.1    | 19      | 63.0      |
|                 | 10               | 5                   | 64.2    | 0.6     | 64.7      |
|                 |                  | 10                  | 64.0    | 0.6     | 64.6      |
|                 |                  | 30                  | 63.0    | 0.8     | 63.8      |
| 280             | 6                | 5                   | 61.5    | 1.5     | 63.1      |
|                 |                  | 10                  | 61.2    | 1.6     | 62.8      |
|                 |                  | 30                  | 60.8    | 1.8     | 62.6      |
|                 | 10               | 5                   | 63.7    | 1.0     | 64.6      |
|                 |                  | 10                  | 62.8    | 1.0     | 63.8      |
|                 |                  | 30                  | 62.0    | 1.1     | 63.0      |
| 300             | 6                | 5                   | 61.1    | 1.6     | 62.7      |
|                 |                  | 10                  | 60.7    | 1.7     | 62.4      |
|                 |                  | 30                  | 59.8    | 1.8     | 61.6      |
|                 | 10               | 5                   | 62.8    | 1.2     | 63.9      |
|                 |                  | 10                  | 61.4    | 1.2     | 62.6      |
|                 |                  | 30                  | 60.7    | 1.4     | 62.1      |

AIL.

Fig. 2 (a) and (b) show the effect of temperature (260–300 °C), reaction time (5–30 min), and solid loading (6 and 10 g) on lignin purity. It can be observed that higher lignin purity was obtained at low temperature (260 °C). Furthermore, the purity decreased upon increasing the temperature (280–300 °C).

This study is in agreement with a few previously reported studies that concluded the solid product and lignin purity decrease considerably upon increasing the temperature. Ko et al. (2014) observed that lignin purity increases with temperature under a hot water pre-treatment process. The lignin purity obtained in their study was 40.3% at 220 °C. On the other hand, Laurenco et al. (2014) observed that lignin purity decreases with temperature for both softwood and hardwood. The lignin purity obtained in their study were 21.9% for softwood and 23.0% for hardwood at 170 °C. Furthermore, Saisu et al. (2003) observed that low
molecular weight lignin fragments undergo cross-linking at 400 °C, which subsequently produce high molecular weight fragments of residual lignin and char. As a result, char formation decreased the lignin purity 30).

From this study, it can be concluded that subcritical phenol produces lignin with good purity with minimal formation of char over the temperature range used in our study. It is also vital to note that higher lignin purities were obtained using much milder conditions under subcritical phenol conditions.

The effect of the reaction time towards lignin purity under subcritical phenol conditions showed a similar trend where the lignin purity decreased with reaction time (Fig. 2 (a) and (b)). As the reaction time increased, a higher amount of delignification occurred, which was subsequently dissolved with little remaining as an insoluble residue after 30 min. Tao et al. (2016) 31) focused on the effect of the organosolv fractionation time on the thermal and chemical properties of lignin. The highest lignin purity obtained in their study was 94.6% at 120 min. This study indicated that the lignin purity can be improved using a shorter reaction time under subcritical phenol conditions.

The result obtained was similar to that of Takada et al. (2016) 32) in their study on the delignification of Japanese beech using subcritical phenol. In their study, they observed that almost 50% of lignin was obtained as the liquid product in 5 min. Meanwhile at 30 min, 90% of lignin was removed, leaving only 10% unconverted lignin in the solid residue.

In order to study the effect of the solid loading on lignin purity, two different OPF solid loadings (6 and 10 g) were chosen. The results are shown in Fig. 2 (a) and (b), which demonstrate that a higher solid loading produced a higher lignin purity for all reaction temperatures and times studied. Both purities were obtained at 260 °C and 5 min.

Overall the lignin purity showed a minimal increase with solid loading. Several studies have reported that the effect of biomass loading is less significant when compared to temperature and reaction time 33) 34). Awaluddin et al. (2016) 35) have shown similar trends in their study.

Based on the results demonstrated above, the highest lignin purity obtained in this study was 64.0% and 64.8% at 260 °C, 5 min and solid loading of 6 g and 10 g respectively. This result also indicates that the lignin purity achieved in this study did not achieve the specifications stated by the ONRL (Table 2). The low purity of lignin obtained in this study can be attributed to the incomplete hydrolysis of carbohydrate or condensation of the carbohydrate degradation products with lignin.

3.2 Analysis of the Particulate Matter Content

Lignin as a carbon fiber precursor needs to be free from solid particles larger than 1 μ in diameter. Particulate matter is the amount of solid particles trapped in the lignin sample, also known as inclusions. Inclusions are typically natural particulates such as sand, clay, or cellulose, which are the major cause of defects to the structure of carbon fiber 30). These defects are known to decrease the mechanical properties of carbon fiber, such as its modulus and tensile strength, resulting in the initiation point for fiber breakage 39). Very limited studies have reported on the particulate content in lignin extraction 22). Therefore, this study aims to determine the effect of the reaction parameters (temperature, solid loading, and reaction time) on the particulate matter content.

Fig. 3 (a) and (b) show the effect of temperature (260–300 °C), reaction time (5–30 min), and solid loading (6 and 10 g) on the particulate matter content. It is vital to obtain lignin with the lowest particulate matter content as possible.

The lowest particulate matter contents of 15.6% and 19.0% were obtained at 300 °C and 30 min for 6 and 10 g solid loading, respectively. It can be concluded that the particulate matter content decreases with temperature for all the reaction times and solid loadings studied.
The higher particulate matter content at low temperature (260 °C) obtained in this study can be attributed to the incomplete degradation of cellulose. Cellulose degraded at temperatures between 280–360 °C due to the stability and homogenous unbranched crystalline structure of its linked D-glucose units. Meanwhile, hemicellulose and lignin decompose at lower temperatures between 200–320 °C and 140–600 °C, respectively. This is consistent with the results obtained, in which a higher particulate matter content was observed at low temperature (260 °C) when compared to high temperature (300 °C).

Furthermore, under subcritical conditions and at high temperature, the high molecular weight compounds are mainly in the solid residue while the low molecular weight compounds are mainly in the liquid residue. This contributes to the high amount of particulate matter. It can be concluded that a higher temperature range is desirable to obtain lignin with a low particulate matter content.

The effect of the reaction time on the particulate matter content shows a similar trend to that observed for the lignin purity. A decreasing trend in the particulate matter content was observed with reaction time (Fig. 3 (a) and (b)).

Moreover, the reaction temperature plays a crucial role in the particulate matter content. A longer reaction time was preferable to obtain lignin with a low particulate matter content.

The particulate matter content in lignin obtained using supercritical phenol is affected by the different decomposition behavior of the compounds found in biomass (cellulose, hemicellulose, and lignin). Cellulose requires a longer reaction time to degrade into low molecular weight fragments when compared to hemicellulose and lignin, even at high temperature. The incomplete degradation of cellulose increases the amount of high molecular weight compounds in the solid residue, which explains the high particulate matter content in lignin obtained in this study under a short reaction time. This result is in agreement with Mishra and Saka (2011). Furthermore, subcritical phenol causes the low molecular weight compounds to be solubilized into the liquid product. A longer reaction time allows a longer time to break the lignin linkages into low molecular weight lignin fragments, which can be dissolved into the liquid product leaving a solid product with high molecular weight lignin.

To study the effect of the solid loading towards particulate matter content, two different OPF solid loadings (6 and 10 g) were chosen under the same reaction temperature and reaction time. The results shown in Fig. 3 indicate that a 6 g solid loading produced lignin with a lower particulate matter content when compared to the 10 g solid loading, which is desirable as a precursor for carbon fiber production. The highest particulate matter content obtained at a 6 g solid loading was 15.6%. Meanwhile, the lowest content obtained at 10 g was 19.0%. Both were obtained at 300 °C and 30 min.

Overall the particulate matter content shows a significant decrease with the solid loading at all the reaction temperatures and reaction times studied. From these results, it can be concluded that a lower solid loading causes a decrease in the particulate matter content. A higher solid loading leads to a higher particulate matter content due to the increased inclusions in the sample. This is in agreement with Baker et al. (2005).

Based on the results shown above, the particulate matter content obtained in this study are in the range of 15.6–34.0%. The results obtained are above the requirements of the ORNL, where 100% removal is needed for particulate matter >1 µ in size. The presence of undesirable substances due to the incomplete reaction of the other compounds found in biomass such as cellulose may increase the amount of particulate matter content in the lignin product. Furthermore, the reaction is subjected to the solvent properties. During the reaction, an increase in temperature reduces the dielectric permittivity of phenol.
and makes it less polar. This facilitates the dissolution of part of lignin as low molecular weight compounds. Incomplete washing during OPF preparation may be another factor that causes the high amount of particulate matter.

4. Conclusion

Studies on the effect of temperature, reaction time, and solid loading to produce lignin from OPF under subcritical phenol conditions have been successfully conducted. Two analyses (lignin purity and particulate content) have given information on the viability of lignin from oil palm biomass as a carbon fiber precursor. High purity lignin with a low particulate matter content is needed as a precursor for carbon fiber. There is a correlation between these two analyses. Temperature, reaction time, and solid loading are crucial parameters to be considered in order to obtain high lignin purity and reduce the presence of particulate matter. Based on the results obtained, it can be concluded that temperature, reaction time, and solid loading are important parameters that may affect the quality of lignin produced as a carbon fiber precursor under subcritical phenol conditions.

Acknowledgements

The authors would like to acknowledge the grant provided by the Malaysia Ministry of Higher Education through Fundamental Research Grant Scheme (FRGS) that has made this research possible.

References

1. National Renewable Energy Laboratory Website, https://www.nrel.gov/docs/ fy16osti/66071.pdf (Last access: 2018.5.14)
2. Grand View Research Website, https://www. grandviewresearch.com/industry-analysis/carbon-fiber- market-analysis (Last access: 2018.5.14)
3. Malaysian Palm Oil Board, http://bepi.mpob.gov.my/index.php/en/ (Last access: 2018.5.14)
4. Aljuboori, A. H. R., International Journal of biomass & renewables, 2, 13-18 (2013)
5. Kong, S. H.; Loh, S. K.; Bachman, R. T.; Rahim, S. A.; Salimon, J., Renewable and Sustainable Energy Reviews, 39, 729-739 (2014)
6. Graglia, M.; Kanna, N.; Esposito, D., ChemBioEng Reviews, 2, 377-392 (2015)
7. Kai, D.; Tan, M. J.; Chee, P. L.; Chuay, Y. K.; Yap, Y. L.; Loh, X. J., Green Chemistry, 18, 1175-1200 (2016)
8. Neata, G.; Campeanu, G.; Popescu, M. I.; Popa, O.; Babeau, N.; Basaraba, A.; Popescu, D. D., Romania
9. Park, S. J.; Kim, B. J., in Carbon fibers, Springer, Dordrecht, p. 275-317 (2015)
10. Baker, F. S.; Griffith, W. L.; Compere, A. L., in Process Report, Oak Ridge National Laboratory, p. 188-196 (2005)
11. Stewart, D., Industrial Crops and Products, 27, 202-207 (2008)
12. Nguyen, T. D. H.; Maschietti, M.; Amand, L. E.; Vamling, L.; Olausson, L.; Andersson, S. I.; Thelander, H., Bioresource Technology, 170, 196-203 (2014)
13. Zhu, Z.; Toor, S. S.; Rosendahl, L.; Yu, D.; Guanyi, C., Energy, 80, 284-292 (2015)
14. Sun, P.; Heng, M.; Sun, S.; Junwu, C., Energy, 35, 5421-5429 (2010)
15. Carr, A., G.; Mammucari, R.; Foster, N., R., Chemical Engineering Journal, 172, 1-17 (2011)
16. Saisu, M.; Sato, T.; Watanabe, M.; Adschiri, T.; Arai, K., Energy & Fuels, 17, 922-928 (2003)
17. Xu, C.; Ferdosian, F., in Conversion of Lignin into Bio-Based Chemicals Materials (Green Chemical and Sustainable Technology), Springer-Verlag Berlin Heidelberg, Germany, p.1-152 (2017)
18. Takada, M.; Tanaka, Y.; Minami, E.; Saka, S., Holzforschung, 70, 1047-1053 (2016)
19. Pandey, M. P.; Kim, C. S., Chemical Engineering & Technology, 34, 29-41 (2011)
20. Hames, B.; Ruiz, R.; Sluiter, S. A.; Sluiter, J.; Templeton, D., Laboratory analytical procedure (LAP), 1617 (2008)
21. Sluiter, A.; Hames, B.; Ruiz, R.; Scarlata, C.; Sluiter, J.; Templeton, D.; Crocker, D., Laboratory analytical procedure, 1617, 1-16, (2008)
22. Luo, J.; Genco, J.; Cole, B.; Fort, R., BioResources, 6, 4566-4592 (2011)
23. Mohamad, N.; Mohamad, N. N.; Yong, T. L. K., J. Jpn. Inst. Energy, 96(8), 279-284 (2017)
24. Stefanidis, S. D.; Kalogiannis, K. G.; Iliopoulou, E. F., Journal of Analytical and Applied Pyrolysis, 105, 143-150 (2013)
25. Zhao, Y. Y.; Li, X. H.; Wu, S. B.; Li, Y. M., BioResources, 11, 21-32 (2016)
26. Mishra, G.; Saka, S., in Zero-Carbon Energy Kyoto 2010, Springer, Tokyo, p. 147-152 (2011)
27. Ko, J. K.; Kim, Y.; Ximenes, E.; Ladisch, M. R., Bioresource Technology, 112, 252-262 (2015)
28. Lourenço, A.; Gominho, J.; Marques, A. V.; Pereira, H., BioResources, 8(2), 2967-2980 (2013).
29. Saisu, M.; Sato, T.; Watanabe, M.; Adschiri, T.; Arai, K., Energy and Fuels, 17, 922-928 (2003)
30. Oliveux, G.; Dandy, L. O.; Leeka, G. A., Progress in Material Science, 72, 61-99 (2015)
31) Tao, J.; Hosseini, O.; Delbeck, L.; Kim, P.; Harper, D. P.; Bozell, J. J.; Rials, T. G.; Labbe, N., *RSC Advances*, **6**, 79228-79235 (2016)
32) Takada, M.; Tanaka, Y.; Minami, E.; Saka, S., *Holzforschung*, **70**, 1047-1053 (2016)
33) Roque, R. M. N., Doctoral dissertation, University of Birmingham, (2014)
34) Wunna, K.; Nakasaki, K.; Auresenia, J. L; Abella, L. C.; Gaspillo, P. D., *Chemical Engineering Transactions*, **56**, 1831-1836 (2017)
35) Awaluddin, S. A.; Thiruvenkadam, S.; Izhar, S.; Hiroyuki, Y.; Danquah, M. K.; Harun, R., *BioMed Research International*, **11**, 1-11 (2016)
36) Compere, A. L., Griffith, W. L., Leitzen Jr, C. F.; Petrovan, S., Proceedings of the 36th International SAMPE Technical Conference, p. 2246-2254 (2004)
37) Belkheiri, T.; Andre0rsson, S.; Mattsson, C.; Olausson, L.; Theliander, H.; Vaming, L., *Energy Fuels*, **32**, 5923-5932 (2018)
38) Yoon, S. Y.; Han, S. H.; Shin, S. J., *Energy*, **77**, 19-24 (2014)
39) Marcus, Y., *Separations*, **5**, 4 (2018)