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Effect of Sequential Pre-treatment on the Thermal Behavior of Pre-treated Palm Empty Fruit Bunch using Thermal Gravimetric Analyzer

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ABSTRACT

Utilizing sequential pre-treatment of demineralization and torrefaction on biomass prior to pyrolysis has shown to be promising in enhancing the solid fuel feedstock properties. The aim of this study is to further investigate the suitable biomass feedstock for the pyrolysis process by monitoring the thermal degradation behaviors of different pre-treated palm empty fruit bunch (PEFB) prior to pyrolysis process. Thermal analyses of all samples were performed using a Mettler Toledo TGA at a heating rate of 20 °C·min^{-1} with nitrogen flow of 100 mL·min^{-1} from ambient temperature to 900 °C. The thermogravimetric analysis displayed that the torrefied demineralised palm empty fruit bunch (TDPEFB) has experienced major weight loss of 61.53% at its active degradation temperature. Meanwhile, torrefied palm empty fruit bunch (TPEFB) showed a lower amount of weight loss compared to TDPEFB since the presence of alkali and alkaline earth metal (AAEM) in TPEFB which inhibits the primary reaction, thus leading to the retention of mass in the biochar fraction. In comparison, the percent weight loss for untreated PEFB was recorded to be the lowest among the three samples which is about 33.9% during the active pyrolysis process. The results support the argument that the demineralization process has assisted

primary reactions by the removal of AAEM. This in turn contribute to higher weight loss of sample as more volatile matters and cellulose content could be released during thermal degradation of the TDPEFB. Subsequently, the quality and quantity of bio-oil produced could be enhanced. This sequential pre-treatment was suggested to be an effective approach for upgrading the quality of solid fuel feedstock for further thermal conversion processes such as pyrolysis.

Keywords: Thermal Degradation; Palm Empty Fruit Bunch; Torrefaction; Demineralization, Pyrolysis

INTRODUCTION

In the global energy system, fossil fuel has played a dominant role in the industrial revolution in producing chemical feedstock. Due to the scarcity of fossil fuel resources and crucial environmental pollution issues, new alternative energy resource from biomass has been utilized to reduce the dependency of replace petroleum and natural gas for sustaining the production of chemical feedstock [1]. The aim to reduce the carbon emission from the utilization of fossil fuel could be accomplished by aggressively searching and developing a method for generating fuel from renewable resources.

Recently, demineralization and torrefaction pre-treatments were found to be the promising pre-treatment methods by reducing the undesirable natural catalyst, AAEMs, moisture content, acetyl content and acid content of the biomass samples [2–5]. Therefore, a combination of demineralization and torrefaction process was used to reduce the oxygen content, carboxyl, water and ash content of biomass [4].

An approach of combining two processes of pre-treatment namely demineralization and torrefaction on biomass feedstocks have been intensively investigated [3,6,7]. Demineralization pre-treatment can be divided into water washing pre-treatment and acid or alkali hydrolysis that purposely to eliminate the inorganic material or AAEMs. Zhang et al., [3] studied the effect of water washing and torrefaction pre-treatment on rice husk pyrolysis by microwave heating. They concluded that this

pre-treatment is the significant method to improve the fuel characteristic of rice husk sample and the energy density to a certain extent by capably removed a large amount of troublesome inorganic species and eliminated oxygenated compound from the sample.

Similar results were observed by Wigley et al., [6] on the ability of pre-treatment to decrease the inorganic matter and oxygen content in the biomass feedstock for pyrolysis. For demineralization pre-treatment, mineral acid and organic acid (acetic acid and formic acid) were used to compare the effectiveness of inorganic removal of biomass. Second pre-treatment of torrefaction on the biomass indicated that 260 °C of torrefaction temperature for 20 min was the optimum condition to minimized biochar formation during thermal pyrolysis. Since the minimal oxygen was removed and reduced the mass yield as increased the torrefaction temperature to 280 °C, it is suggested that single torrefaction pre-treatment is not a suitable method to obtain bio-oil with a low oxygen content due to the low pyrolysis yields attainable.

Chen et al. [8] found the novel approach to improve the quality of biomass pyrolysis products by combining the washing and torrefaction pre-treatment. From their findings, the aqueous phase bio-oil washing pre-treatment can eliminate large amounts of metallic species in the biomass sample. Consequently, reduced the catalytic effects of these metals on the pyrolysis process. While torrefaction pre-treatment of demineralized biomass led to the disappearance of the first shoulder peak of hemicellulose due to degradation of hemicellulose during torrefaction pre-treatment. This combines pre-treatment affect the degradation peak of biomass that shift to a higher temperature compared to raw biomass [9].

In this study, sequential pretreatment of demineralization and torrefaction on palm empty fruit bunch (PEFB) has been carried out and the thermal behavior profile of torrefied palm empty fruit bunch (TPEFB) and torrefied-demineralized palm empty fruit bunch (TDPEFB) were compared with that of the untreated palm empty fruit bunch (PEFB) using thermogravimetric analyzer (TGA).

EXPERIMENTAL

Biomass Sample

The palm empty fruit bunches (PEFB) were collected from United Oil Palm Industries Sdn. Bhd. located in Nibong Tebal, Pulau Pinang, Malaysia. The PEFB was rinsed with tap water to remove impurities and was dried in the oven at 105 °C for 24 h. It was ground using a hammer mill machine into small particle size and sieved to a particle size of 0.5-1 cm using the sieve shaker. The dried pulverized biomass was stored in air-tight containers until further use.

Demineralization of PEFB

Demineralization of EFB was carried out to eliminate AAEMs that reduced the ash content in the sample. About 100 g of EFB was placed in a flask containing 500 mL of 1 % nitric acid for acid leaching. The sample was sonicated for 10 min in ultrasonic bath at room temperature. After acid leaching, the sample was filtered and dried at 105 °C for 24 h to a constant mass.

Torrefaction of Demineralized PEFB (DPEFB)

The DPEFB sample was subjected to torrefaction process. Torrefaction experiments were performed in a vertical tube fixed bed reactor. Torrefaction of raw PEFB and demineralized PEFB were prepared in a vertical tubular reactor system. About 100 g of PEFB was placed into a steel container in the reactor. When the furnace reached the desired torrefaction temperature 240 °C, the temperature of the reactor was held for the desired residence time 30 min.

Thermogravimetric Analysis

Thermogravimetric analysis of PEFB, TPEFB and TDPEFB samples were carried out using a Mettler Toledo thermogravimetric analyzer to study the thermal behavior. About 10.0 mg of each PEFB samples were pyrolyzed at a heating rate of 293 K min^{-1} with nitrogen flow of 100 mL min^{-1} from ambient to 1173 K [10].

RESULTS AND DISCUSSION

Thermogravimetric analyser (TGA) revealed the thermal behaviour profile of the biomass samples based on thermogravimetric curve (TG) and derivative thermogravimetric (DTG) profiles that are illustrated in Figure 1 and Figure 2, respectively. From Figure 1, the first weight loss is identified at approximately 128 °C for untreated PEFB. This corresponds to the removal of water molecules which are adsorbed on the surface of untreated PEFB and is shown by the existence of first small peak in Figure 2. This initial peak is not prominent in both TPEFB 240 and TDPEFB 240 since torrefaction has successfully removed water molecules.

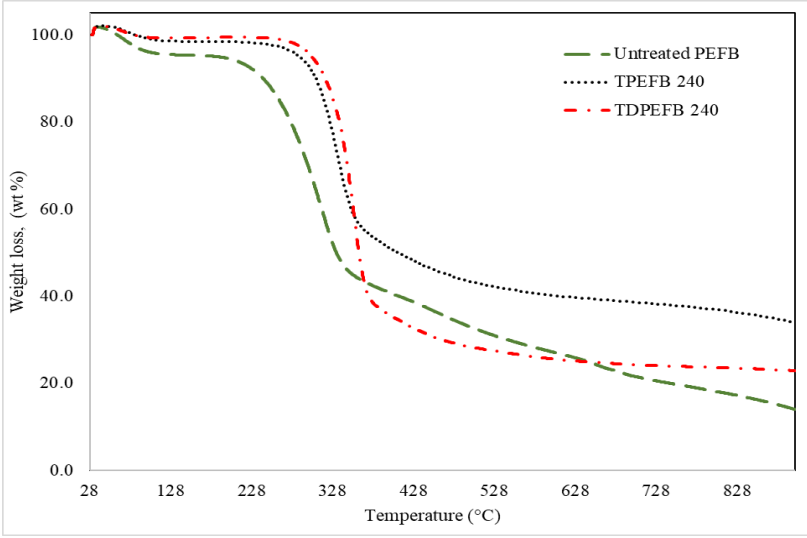

Figure 1: Thermogravimetric (TG) profiles of untreated PEFB, TPEFB 240 and TDPEFB 240 at a heating rate of 20 °C min^{-1} under inert condition

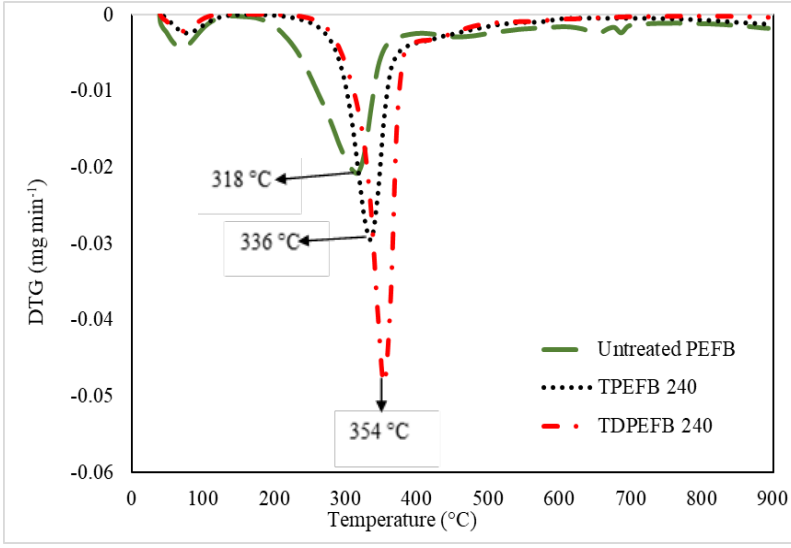

Figure 2: Derivative thermogravimetric (DTG) profiles of untreated PEFB, TPEFB 240 and TDPEFB 240 at a heating rate of 20 °C min^{-1} under inert condition

The second peak shows that the significant weight loss occurs from 200 °C to 350 °C for untreated PEFB and from 290 °C to 350 °C, 290 °C to 400 °C for TPEFB 240 and TDPEFB 240, respectively. From the results, it indicates that TDPEFB 240 has experienced major weight loss of 61.53 % at its active degradation temperature. This is followed by TPEFB 240 at 49.01 % of percent weight loss and the lowest percentage of weight loss recorded by untreated PEFB, which is about 33.9 % occur during the active pyrolysis process. This resembles the degradation of lignocellulosic content in the samples of untreated PEFB and the remaining lignocellulosic components after the pre-treatment process for TPEFB 240 and TDPEFB 240. The different thermal degradation of the pre-treated PEFB could be attributed to the various contents of cellulose, hemicellulose and lignin [11].

TPEFB 240 shows a lower amount of weight loss compared to TDPEFB 240 since the presence of AAEMs in TPEFB inhibits the primary reaction, thus leads to the retention of mass in biochar fraction. It also supports the argument that the demineralization process has assisted primary reactions by the removal of AAEMs, thus contribute to higher weight loss by

converting into more volatile components [12,13]. Therefore, this indirectly could be highlighted the positive effect of the biomass demineralization pre-treatment on the pyrolysis process. The highest weight loss in TDPEFB 240 could be an indication of more volatile matters and cellulose content in the biomass samples.

It is known from the literature that hemicellulose is degraded at a peak temperature of 300 °C to 325 °C, while cellulose decomposes at the peak temperature in the range of 365 °C to 371 °C [14–17]. As can be seen in Figure 2, the untreated PEFB shows the lowest peak temperature in the DTG curve that could indicate it has the highest content of hemicellulose and exhibits the catalytic effect of AAEMs that moved cellulose degradation to the lower temperature of pyrolysis. Therefore, the active pyrolysis process began at a much lower temperature for untreated PEFB compared to TPEFB 240 and TDPEFB 240. This devolatilization stage of untreated PEFB resulted in changes via the occurrence of simultaneous reactions such as depolymerization, decarboxylation, dehydration and decarbonylation [18,19].

However, the peak temperatures of the DTG curves for TPEFB 240 and TDPEFB 240 have shifted to 336 °C and 354 °C, respectively. In this case, TPEFB 240 had underwent single pre-treatment of torrefaction. In contrast, the TDPEFB 240 sample had experienced sequential demineralization and torrefaction during the pre-treatment stage, which resulted in the decomposition of hemicelluloses during torrefaction pre-treatment. Thus, increase the composition of cellulosic content of both pre-treated PEFB.

The effect of demineralization and torrefaction pre-treatment can be seen on percentage weight loss and the degradation rate of both pre-treated PEFB. Therefore, the active pyrolysis processes of TPEFB 240 and TDPEFB 240 are contributed by the remaining lignocellulosic and AAEMs content of pre-treated PEFB that shifts the process to a higher temperature region compared to untreated PEFB. This trend is similar to a previous study [20], where the primary weight loss was observed in the range from 250 °C to 450 °C with the corresponding DTG curve appearing from 350 °C to 390 °C and this showed the decomposition temperature regions represented by hemicellulose, cellulose and lignin.

Besides, the results imply that the sequential application of demineralization and torrefaction on untreated PEFB reduced the ash content, allowed the removal of AAEMs and offset the negative impact on the increase of ash content and the presence of AAEMs due to torrefaction [21]. Our Previous study on the sequential pretreatment of demineralization and torrefaction on PEFB found that ash content reduced while volatile matter increased for pre-treated PEFB [22]. This observation might be due to the extensive decomposition of hemicellulose into volatiles and solid products that took place at more severe torrefaction conditions [23].

The third stage is observed at a temperature range from 350 °C to 600 °C in Figure 1. It is a slow weight loss taking place over a wide range of temperatures and is due to the decomposition of lignin in the samples. In summary, three temperature regions are indicated for the decomposition of lignocellulosic of untreated PEFB, TPEFB 240 and TDPEFB 240. These results indicate that demineralization pre-treatment influenced the degradation of lignocellulosic components in PEFB and facilitates the decomposition of hemicellulose and cellulose at different temperatures during torrefaction pre-treatment.

CONCLUSION

From the thermal behavior results, TDPEFB 240 was identified the suitable solid biofuel for further thermal conversions such as combustion, pyrolysis, gasification and other applications. Thus, this sequential pre-treatment was suggested to be the most effective approach for upgrading the quality of solid fuel feedstock for further thermal conversion processes for the future.

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REFERENCES

[1] Y. X. Seow, Y. H. Tan, N.M. Mubarak, J. Kansedo, M. Khalid, M. L. Ibrahim, M. Ghasemi, 2022. A review on biochar production from different biomass wastes by recent carbonization technologies and its sustainable applications, *J. Environ. Chem. Eng*., vol.10, pp. 1-21.

[2] R. Ahmad, M. A. M. Ishak, K. Ismail, and N. N. Kasim, 2019. Influence of microwave pre-treated Palm Kernel Shell and Mukah Balingian coal on co-gasification, *J. Mech. Eng. Sci.*, vol. 13, no. 4, pp. 5791-5803.

[3] S. Zhang, Q. Dong, L. Zhang, Y. Xiong, X. Liu, and S. Zhu, 2015. Effects of water washing and torrefaction pretreatments on rice husk pyrolysis by microwave heating, Bioresour. *Technol.,* vol. 193, pp. 442-448.

[4] J. J. Chew, V. Doshi, S. T. Yong, and S. Bhattacharya, 2016. Kinetic study of torrefaction of oil palm shell, mesocarp and empty fruit bunch, *J. Therm. Anal. Calorim*., vol. 126, no. 2, pp. 709-715.

[5] N. H. Mohamad Hassan and A. H. Abdul Razik, 2021. Optimal Technological Selection for Biomass Torrefaction, *Int. J. Eng. Technol. Sci,* vol. 7, no.1 pp. 105-112.

[6] T. Wigley, A. C. K. Yip, and S. Pang, 2015. The use of demineralisation and torrefaction to improve the properties of biomass intended as a feedstock for fast pyrolysis, *J. Anal. Appl. Pyrolysis,* vol. 113, pp. 296-306.

[7] J. M. Reckamp, R. A. Garrido, and J. A. Satrio, 2014. Selective pyrolysis of paper mill sludge by using pretreatment processes to enhance the quality of bio-oil and biochar products, *Biomass Bioenergy,* vol. 71, pp. 235-244.

[8] D. Chen, K. Cen, X. Jing, J. Gao, C. Li, and Z. Ma, 2017. An approach for upgrading biomass and pyrolysis product quality using a combination of aqueous phase bio-oil washing and torrefaction

pretreatment, Bioresour. *Technol.*, vol. 233, pp. 150-158.

[9] F. Abnisa, A. Arami-Niya, W. M. A. Wan Daud, J. N. Sahu, and I. M. Noor, 2013. Utilization of oil palm tree residues to produce bio-oil and bio-char via pyrolysis, *Energy Convers. Manag.*, vol. 76, pp. 1073-1082, doi: 10.1016/j.enconman.2013.08.038.

[10] M. A. Aziz, K. M. Sabil, Y. Uemura, and L. Ismail, 2012. A study on torrefaction of oil palm biomass, *J. Appl. Sci.*, vol. 12, no. 11. pp. 1130-1135.

[11] L. Richa, B. Colin, A. Pétrissans, C. Wallace, A. Hulette, R. L. Quirino, W. Chen, M. Pétrissans, 2023. Catalytic and char-promoting effects of potassium on lignocellulosic biomass torrefaction and pyrolysis, *Environ. Technol. Innov,* vol.31, pp. 1-16.

[12] W. H. Chen and P. C. Kuo, 2010. Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass, *Energy,* vol. 36, no. 2, pp. 803-811.

[13] W. Vercruysse, C. L. Gomes, D. Bleus, M. Pappa, B. Joos, A. Hardy, W. Marchal, D. Vandamme, 2023. Demineralization of common ivy-derived biomass and biochar and its effect on the resulting activated carbon properties, Sep. *Purif. Technol*, vol, 319, pp. 1-9.

[14] L. Burhenne, J. Messmer, T. Aicher, and M.-P. Laborie, 2013. The effect of the biomass components lignin, cellulose and hemicellulose on TGA and fixed bed pyrolysis, *J. Anal. Appl. Pyrolysis*, vol. 101, pp. 177-184.

[15] M. Asadieraghi and W. M. A. Wan Daud, 2014. Characterization of lignocellulosic biomass thermal degradation and physiochemical structure: Effects of demineralization by diverse acid solutions, *Energy Convers. Manag.*, vol. 82, pp. 71-82.

[16] J. Y. Cui, N. Zhang, and J. C. Jiang, 2022. Effects of Microwave-Assisted Liquid Hot Water Pretreatment on Chemical Composition and Structure of Moso Bamboo, Front. Bioeng. *Biotechnol,* vol.9, pp. 1-7.

[17] P. J. Weimer, 2022. Degradation of Cellulose and Hemicellulose by Ruminal Microorganisms, *Microorganisms*, vol.10, pp.1-30.

[18] X. Y. Lim and J. M. Andrésen, 2011. Pyro-catalytic deoxgenated bio-oil from palm oil empty fruit bunch and fronds with boric oxide in a fixed-bed reactor, *Fuel Process. Technol.,* vol. 92, no. 9, pp. 1796-1804.

[19] Y. Joshi, M. Di Marcello, and W. de Jong, 2015. Torrefaction: Mechanistic study of constituent transformations in herbaceous biomass, *J. Anal. Appl. Pyrolysis*, vol. 115, pp. 353-361.

[20] L. Cao, X. Yuan, L. Jiang, C. Li, Z. Xiao, Z. Huang, X. Chen, G. Zeng, H. Li, 2016. Thermogravimetric characteristics and kinetics analysis of oil cake and torrefied biomass blends, *Fuel,* vol. 175, pp. 129-136.

[21] D. Chen, J. Mei, H. Li, Y. Li, M. Lu, T. Ma, Z. Ma, 2017. Combined pretreatment with torrefaction and washing using torrefaction liquid products to yield upgraded biomass and pyrolysis products, Bioresour. *Technol.,* vol. 228, pp. 62-68.

[22] N. N. Kasim, K. Ismail, A. R. Mohamed, M. A. M. Ishak, R. Ahmad, and W. I. N. W. Ismail, 2018. Characteristic, thermochemical behaviors and kinetic of demineralized and torrefied empty fruit bunches (EFB), *Adv. Sci. Technol. Eng. Syst.,* vol. 3, no. 5. pp. 365-373.

[23] P. Indum and C. Mueanmas, 2019. Screening the factors affecting torrefaction of palm kernel shell by using Plackett-Burman Design, *IOP Conf. Series: Earth and Environmental Science* 268, pp. 1-7.