Conversion of durian peel waste into chemicals and hydrochar by hydrothermal carbonization

Dewi Agustina Iryani[1,2,*], Satoshi Kumagai[3], Moriysu Nonaka[3], Tsuyoshi Hirajima[3]

[1]*Department of Chemical Engineering, University of Lampung, Bandar Lampung 35145, Indonesia*
[2]*Research and Development Center for Tropical Biomass, University of Lampung, Bandar Lampung 35145, Indonesia*
[3]*Department of Earth and Resources Engineering, Kyushu University, Fukuoka 819-0395, Japan*

Abstract:
Hydrothermal carbonization (HTC) of Durian peel waste was conducted in order to investigate the effect of reaction conditions such as temperature (200-300°C) and time (3-30 min) on the characteristics of liquid and solid product (hydrochars). The experiments were performed in a batch-type reactor containing slurry of 10 ml of water and 1.2 g of solids. Each fraction of products was analyzed to investigate the alteration of the main lignocellulosic polymers by hydrothermal carbonization using hot compressed water. The results showed that by increasing the temperature and reaction time, the main of lignocellulosic polymer such as hemicellulose and cellulose was completely dissolved in the water and gradually decomposed into simple sugars, which were then degraded and decomposed into furfural, 5-(hydroxymethyl) furfural (5-HMF) and organic acids, and leaving lignin in the solid (hydrochar) product. Thus, by increasing of reaction temperature and time both was able to decrease the yield of hydrochars, however its able to increase the carbon content, heating value, and energy density. Dehydration significantly decreased the oxygen content and slightly decreased the hydrogen content of the treated material and produced the hydrochar with composition comparable to typical solid fuels such as lignite (or low rank-coal) and sub-bituminous coal.

Keywords: *Hydrothermal carbonization; Durian peel; Hydrochar; Solid biofuel*

**Corresponding author. Tel.: +62-81293638980*
E-mail address: dewi.agustina@eng.unila.ac.id

1. Introduction

Durian (*Durio zibethinus*) is one of the most popular tropical fruits in the Southeast Asia countries particularly of Malaysia, Indonesia and Thailand. In this region, durian is also nown as "the king of fruits". This fruit has distinctive smell with spiky peel or hard outer shell (Chandra et al., 2009). Due to the high consumption of durians, huge amounts of the peels (as solid waste) are disposed, causing a serious problems in the environment.

The conversion of durian peel waste into chemicals and, solid biofuel as an energy sources could be a viable consideration and it is one of solution for suppressing the environmental pollution as well as reducing of fossil fuel consumption. Several technologies such as gasification, pyrolysis, (Zhang et al., 2010) and hydrothermal treatment (Iryani et al., 2014; Kruse and Dinjus, 2007; Yuliansyah et al., 2010) have been developed to convert agricultural biomass into chemicals and biofuel with a higher heating value. Compared with others thermochemical conversion technology, it has been acknowledged that the hydrothermal carbonization is an efficient technique to selectively decompose wet biomass. In the hydrothermal carbonization, the water (hot compressed water or HCW) acts as a solvent and can also be applied as a reactant, catalyst or product (Kruse and Dinjus, 2007). It enhances the hydrolysis, dehydration and decarboxylation reaction, decomposing the lignocellulosic polymer into valuable chemicals that dissolve into liquid products and remaining solid product (hydrochar) has high caloric value (Iryani et al., 2014; Iryani et al., 2016; Iryani et al., 2017; Sluiter et al., 2005; Yuliansyah et al., 2010).

In this study, we focus on the conversion of durian peel waste into valuable products by using hot compressed water as reactant medium at the temperature range of 200-300°C and reaction time of 3-30 min. The solid and liquid products obtained from hydrothermal carbonization were investigated and characterized in order to comprehensively understand the decomposition reaction. This study was also conducted in order to explore the possibility to obtain the best condition for production of hydrochar as a solid biofuel.

2. Material and methods

The durian peel as material which was used in this study collected from local durian processing industry in Bandar Lampung. The raw of durian peel had high water content (40-50%), hard texture with strong durian flavor. Prior the treatment, the durian peel was repeatedly washed with distilled water in order to remove dust and other inorganic impurities, then sun-dried for its moisture content. Subsequently, the durian peel was pulverized by using a cutting mill size into particle size of 1.0-1.5 mm, and then dried in an oven at 60°C for 24 h until less than 10%. The raw material was then stored into a desiccators for further use. The composition of durian peel was determined following the procedure recommended by the US National Renewable Energy Laboratory (NREL) (Sluiter et al., 2005).

The hydrothermal carbonization experiments were carried out in a 14 ml batch type reactor. The reactor was loaded with slurry made of 10 ml water and 1.2 g of fine durian peel waste. A stream of N_2 gas was used to purge air from the reactor and to maintain initial internal pressure of 0.5 MPa. The reactor was heated into the target temperature and reaction time, and afterward cooled in a water bath until room temperature. The treated slurry was collected and filtered using a GP 16 glass filter under vacuum to separate solid residue and liquid filtrate for further analysis.

The liquid product was analyzed by using High Performance Liquid Chromatography (HPLC) which was equipped with a KC-811 column (JASCO) and refractive index (RI) detector (RI-2031, JASCO). The HPLC operated under the following conditions: oven temperature 50°C, using 2 mM $HClO_4$ as the mobile phase, delivered at a flow rate of 0.7 ml/min. Moreover, the untreated and treated solid residue were further characterized using Yanaco CHN Corder MT-5 elemental analyzer. The elemental compositions or ultimate values were then used to calculate the higher heating value (HHV), energy density and energy yield according to Iryani et al. (2017).

3. Results and discussion

3.1 Solid product (hydrochar) composition

The analytical results of durian peel as a raw material presented in Table 1. While, the change of solid products composition after the treatment is presented in Fig. 1. The result shows that there are gradually changed of chemical composition of cellulose and hemicellulose content in the solid product with increasing in temperature and reaction time. Hemicellulose was easier to hydrolysis than other polymers due to its branched structure and lower degree of polymerization (DP) (Bobleter, 1994). Hemicellulose started to decompose at 200°C (5 min) and was completely degraded and undetectable at 200°C (20 min). Differ with hemicellulose, cellulose started to decompose at 240°C (10 min) and it was completely decomposed and undetected at 300°C (10 min). Cellulose has a greater thermal stability due to their structure which is consist of a long glucose polymer without branches, linked by strong β-(1,4)-glycoside bonds.

Table 1 Chemical composition, ultimate and heating value of durian peel as raw material

chemical component **(wt% d.b)**					ultimate values **(wt % d.a.f)**				Heating Value **(MJ/kg)**
cellulose	hemicellulose	acid insoluble compound	Wax	ash	C	H	O (diff.)	N	GCV
39,45	25,65	14,38	7,4	5,2	43,92	6,01	49,07	1,0	14,68

d.a.f dry ash free basis, *diff.* difference, *VM* volatile matter, *FC* fixed carbon, *GCV* gross caloric value

In the Fig. 1, it was also observed that at the high temperature (300°C) and long treatment time (20-30 min), the solid products were mainly dominated by lignin like or acid insoluble content. This occurred due to re-polymerization of solubilized lignin by breaking lignin–carbohydrate bonds in the presence of the organic acids released under hydrothermal. In addition, the sugar degradation products (such as furfural, 5-HMF) also react with lignin by condensation reactions and generate insoluble lignin (called 'pseudolignin'). As we mentioned in our previous studies that the recovery ratio of acid insoluble solid residue increases due to of char, re-polymerization products, condensation reactions, and saccharide decomposition products (Iryani et al., 2016; Iryani et al., 2017). All of those products were attached on the surface of the solid residue which leads dark solid color. This phenomena clearly observed in the Fig. 1 and Fig. 4, at the low temperature (200°C), before the furan-like compounds in liquid product decomposed, the content of acid insoluble solid content slightly increased. However, at mild and severe treatment conditions, the acid insoluble content likely to be affected by furan degradation products and making increased the content of acid insoluble solid content. Degradation of furan-like compounds occurred due to the high concentration of organic acids which leads to the reactivation of lignin polymerization which dissolved to the liquid, and it turned the lignin like content of solid product increased. This decomposition products deposited onto the surface of solid increased the content of the acid insoluble residue (klason lignin).

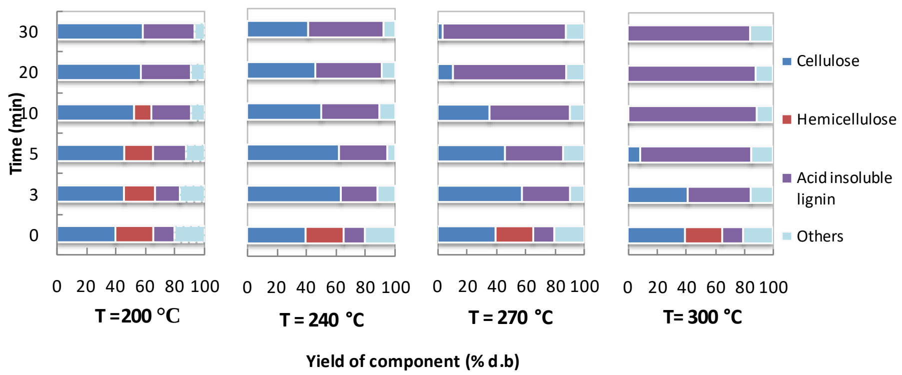

Fig. 1 Distribution of chemical composition of durian peel during hydrothermal carbonization

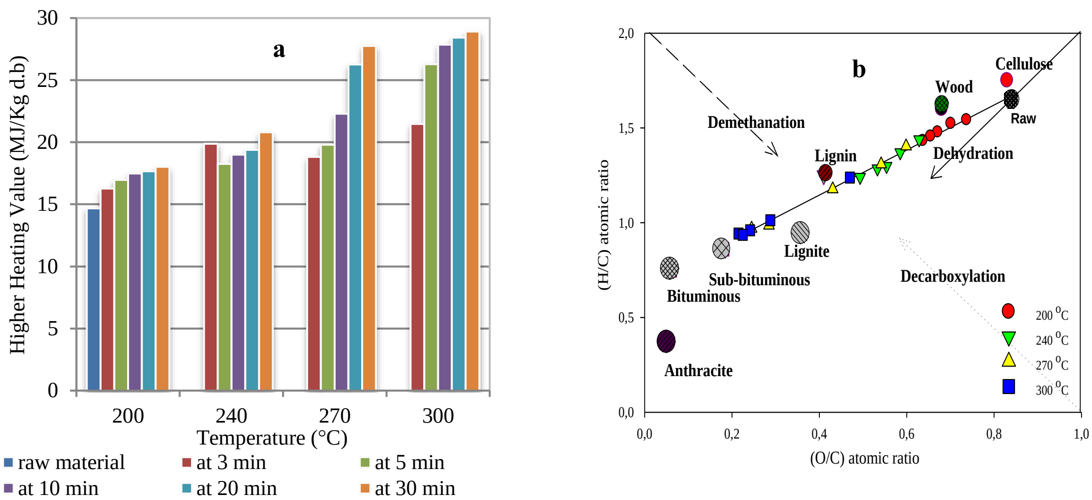

Fig. 2 Thermal Characterization of untreated and treated durian peel: (a) Higher heating value (HHV); (b) Atomic H/C and O/C ratios in the different treatment conditions

The effect of hydrothermal carbonization of durian peel can be clearly observed from elemental analysis (Fig. 2a and 2b). The carbon content in raw durian peel is 43.92 wt.% and it can be increased up into 72.27 wt.% at temperature 300°C (30 min). This result suggests that the dehydration and polymerization reactions occurred during the treatment removing H and O, thus with significantly increases the higher heating value (HHV) of solid products. The highest HHV was obtained at temperatures of 300°C (30 min). Compared with the raw durian peel of 14.68 MJ/kg-dry feed base, the higher heating value of the solid product at optimum conditions increased to 28.91 MJ/kg-dry base feed.

In Fig. 2b, the values of atomic H/C and O/C ratios in raw sample were 1.64 and 0.84, respectively. After the treatment, they were in the ranges of 0.96–1.54 and 0.21–0.74, respectively. This result implies that the H/C and O/C values decreased with increasing treatment temperature and time from which the most significant change occurs in the temperature range of 240–300 °C has trajectory slope is parallel and strong linier correlation (r = 0.989), reflects that the dehydration reaction occurs during the hydrothermal carbonization. Further, it was also observed that a slight carboxylation occurred at 270–300°C (>10 min). Apparently, the atomic ratios of H/C and O/C of durian peel are closer to that of lignite and sub-bituminous coal. The loss of H and O from hydrothermal carbonization occured due to the reactions of dehydrogenation, de-oxygenation and dehydration processes.

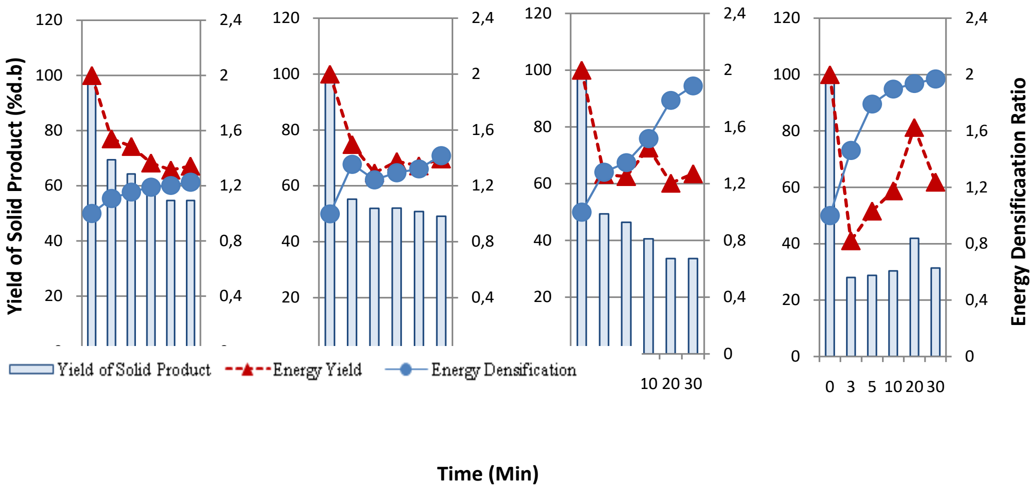

Fig. 3 Distributions of higher heating value, energy density ratio, yield of solid products, and energy yield undergoing hydrohermal carbonization

By increasing the heating values, the hydrothermal carbonization increased the energy density of the solid product. The energy density increased with temperature and time of reaction from as low as of 1.1 at 200°C (3 min) to as high as of 1.97 at 300°C (30 min). This data is consistent with the observation by Chen et al. (2012) indicated that the energy density of sugarcane bagasse after wet torefaction lift up to 20%.

This trend was reversed when concerning to the energy yield and mass yield, the hydrothermal carbonization leaded to reducing of solid product and energy yields. Solid and energy yields are defined as the mass ratio of dried treated material to untreated dried raw, and the energy yield is defined as their energy ratio. Fig. 3 depicts that both of solid and energy yields go down with increasing temperature reaction and reaction time. And, the solid yield tend to always lower than the energy yield. However, at temperature 300°C, there was some difference which due to condensation reaction.

3.2 Chemical analysis of liquid products

Fig. 4 presented only the chemical compounds from decomposition product of hemicellulose and cellulose. The analysis of the liquid product suggested that the sugars from hemicelluloses were produced at lower temperatures. The hydrothemal carbonization decomposed hemicellulose into xylose and arabinose. Hemicellulose starts to degrade at 200°C (5 min) into furfural and acetic acid. Hemicellose was then completely degraded and undetected at 200°C (20 min).

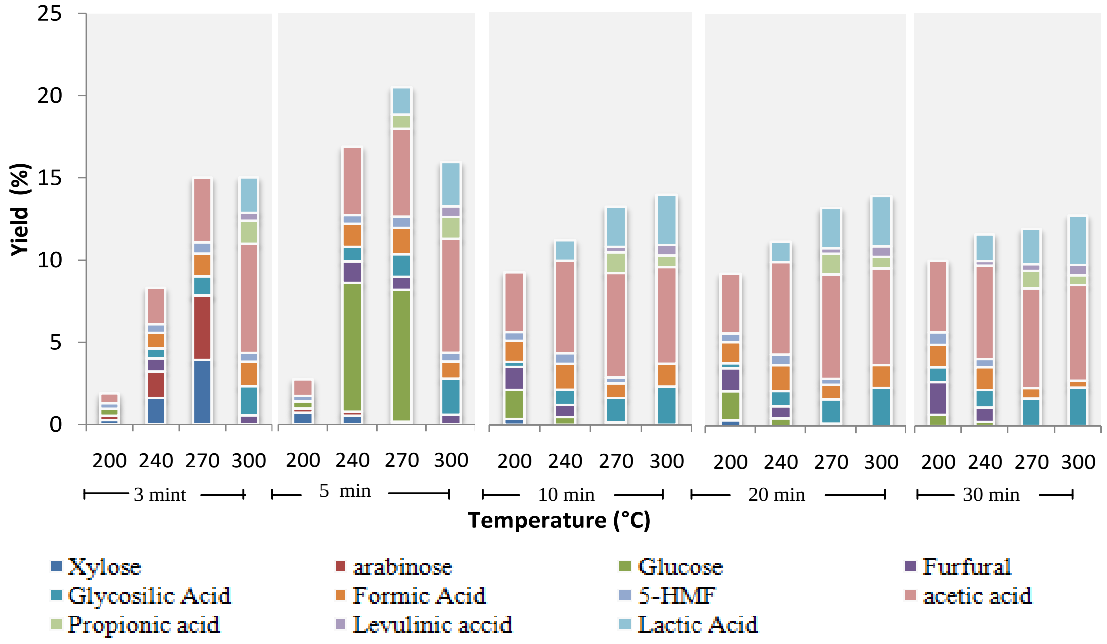

Fig. 4 Composition of liquid products obtained in varied temperature and reaction time

Cellulose starts to decompose at 240°C (20 min) and completely degraded at 300°C (10 min). The cellulose decomposed to form glucose, which further decomposed to form 5-(hydroxymethyl) furfural (5-HMF) and organic acids by hydrolysis, dehydration and decarboxylation reaction. Increase temperature and reaction time gradually increase 5-HMF yield. However, at the elevated temperature (300°C) and longer reaction time, 5-HMF decomposed into organis acids. The organic acids are decomposition product of xylose and glucose such as acetic acid, formic acid, lactic acid, levulenic acid and propionic acid, from which at first increases with the treatment temperature. However, after extended treatment time, the organic acids such as formic acid content tend to decrease.

4. Conclusion

The change of physicochemical of durian peel occurred during the hydrothermal carbonization processes. The treated solid products by using hydrothermal carbonization treatment were varied depending on temperature and treatment time. The hydrothermal carbonization the durian peel decomposed into the water and produced the liquid product which consist of some valuable and important chemical products for chemical industries and biofuel feedstock. The chemical composition analysis of solid products showed that the cellulose and hemicellulose content gradually decreased. Hemicellulose starts to degrade at 200°C (5 min) into furfural, glycosilic acid, and acetic acid. Cellulose starts to decompose at 240°C (20 min) and completely degrades at 300°C (10 min). The cellulose decomposed to form glucose, which further decomposed to form 5-(hydroxymethyl) furfural (5-HMF) and organic acids by hydrolysis, dehydration and decarboxylation reaction. The dehydration reaction occurred during the hydrothermal carbonization processes. This reaction was then could be significantly decreased the oxygen content and slightly decreased the hydrogen content of the treated material. The Optimum conditions was found at 300°C for the production of a solid product with high caloric value with the products had a composition comparable with typical solid fuels such as lignite (or low rank-coal). The hydrothermal carbonization could be one of solution to reduce environmental pollution caused by the combustion of wet durian peel.

Acknowledgement

The authors are grateful for the financial support of The Global COE Program (Novel Carbon Resources Sciences, Kyushu University).

References

Bobleter, O. 1994. Hydrothermal degradation of polymer derived from plants. Progress in Polymer Science, 19, 797–841.

Chandra, T.C., Mirna, M.M., Sunarso, J., Sudaryanto, Y. and Ismadji, S. 2009. Activated carbon from durian shell: Preparation and characterization. Journal of the Taiwan Institute of Chemical Engineers, 40, 457–462.

Chen, W.H., Ye, S.C. and Sheen, H.K. 2012. Hydrothermal carbonization of sugarcane bagasse via torrefaction in association with microwave heating. Bioresour. Technol., 118, 195–203.

Iryani, D.A., Kumagai, S., Nonaka, M., Nagashima, Y., Sasaki, K. and Hirajima, T. 2014. The hot compressed water treatment of solid waste material from the sugar industry for valuable chemical production. Int. J. Green Energy, 11, 577–588.

Iryani, D.A., Kumagai, S., Nonaka, M., Sasaki, K. and Hirajima, T. 2016. Hydrothermal carbonization kinetics of sugarcane bagasse treated by hot compressed water under variabel temperature conditions. ARPN J. Eng. Appl. Sci., 11(7), 4833–4839.

Iryani, D.A., Kumagai, S., Nonaka, M., Sasaki, K. and Hirajima, T. 2017. Characterization and production of solid biofuel from sugarcane bagasse by hydrothermal carbonization.Waste Biomass Valor, 8, 1941–1951.

Kruse, A. and Dinjus, E. 2007. Hot compressed water as reaction medium and reactant. I. Properties and synthesis reaction. J. Supercrit. Fluids, 39, 363–380.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D. and Crocker, D. 2005. Determination of structural carbohydrates and lignin in biomass, in: The US National Renewable Energy Laboratory Technical Report, US National Renewable Energy Laboratory.

Yuliansyah, A.T., Hirajima, T., Kumagai, S. and Sasaki, K. 2010. Production of solid from agricultural waste of the palm oil industry by hydrothermal treatment. Waste Biomass Valor J., 1, 395–405.

Zhang L., Xu C. and Champagne P. 2010. Overview of recent advances in thermo-chemical conversion of biomass. Energy Conversion and Management, 51, 969–982.