Hydrothermal Carbonization Kinetics of Lignocellulosic Municipal Solid Waste

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ABSTRACT

Hydrothermal carbonization (HTC) is known as a thermochemical converting of wet biomass into a coal-like solid fuel (hydrochar). Hydrochar is easily crumbled. Because of hydrophobic properties, hydrochar is difficult to degrade by microorganisms. It has a calorific value comparable to lignite coal. In this study, hydrochar was made via converting the organic fraction of municipal solid waste through HTC at 190, 210, and 230°C for 30 min with feed to water ratio (FWR) 0.1, 0.2, 0.3. The feedstock processed includes food waste, paper, and wood waste, represented as a pseudo-component of the organic fraction of MSW. The high heating value (HHV), FTIR, as well as proximate and ultimate analyses were applied both to feedstock and hydrochar. The results showed that the energy density of hydrochar was elevated with increasing HTC temperature. The energy densification ratio and heating value increased by approximately 1.0–1.32 and 30%, respectively compared to raw feedstock. The lower yields of hydrochar were obtained at higher temperature. The typical char yields for lignocellulosic material range between 62–63 wt% at 190 °C and reduce to 54–57 wt% at 230 °C. Furthermore, a preliminary study of kinetic model for lignocellulose decomposition was conducted. This model was based on the mass loss rate of the lignocellulose compound in HTC of MSW. Three first-order reactions were given to illustrate the hydrochar yield at of 190, 210, and 230°C. The activation energy of lignocellulose decomposition was 76.26 kJ/mol, 51.86 kJ/mol, 12,23 kJ/mol for lignin, cellulose, and hemicellulose decomposition, respectively.

Keywords: activation energy, hydrothermal carbonization, lignocellulose, MSW

INTRODUCTION

After joining for more than 40 years, Indonesia has discontinued its membership of Organization of Petroleum Exporting Countries (OPEC) in 2009. The oil production in Indonesia reached its peak in the mid-1990s. However, along with population growth, the energy consumption continuously increases. The Indonesia's energy consumption increased by 5.9% in 2016, having doubled over the past two decades [BP, 2017]. Until now, oil is still primary choice in energy sources, followed by natural gases and coal. Unfortunately, these energies are non-renewable, so their supplies will be diminished soon.

Undeniably, apart from the energy crisis, Indonesia is still dealing with municipal solid waste management problem. Municipal solid waste (MSW) is one type of biomass which is enough to take more of our attention due to its potential for causing disaster and also its negative effects on human health. On the basis of the data of Indonesian Domestic Solid Waste Statistics for year 2008, the number of municipal solid waste

generation, coming from 154 cities/regencies in 33 provinces in Indonesia, almost reached 40 million tons/year [INSWA, 2008]. Around 50–70% of all generated MSW is handled and moved to the final disposal sites, and the unhandled MSW tends to be burned or open dumped [Damanhuri, 2005]. This fact can be witnessed in many large cities in Indonesia, including Bandung City, with the MSW management problems that are almost never solved. The high population and various activities towards a modern lifestyle that tends to be consumerist, in the end also influence the high waste generation.

In the past, MSW was considered as something that was not valuable. However, many people today realize that it has advantages and economical values due to its capability to be recycled as fuel, chemicals or even fertilizer [Matsakasa et al., 2017]. Unfortunately, the conversion of MSW directly into fuel is characterized by numerous difficulties. Unlike in the developed countries, the MSW in Indonesia is dominated by the organic fraction (about >60%) with high water content, low energy density, and heterogeneous material with varied shapes [Hrncic et al., 2016]. Organic fractions also take responsible of the waste odor and humidity along with sanitary issues. Thus, a good consideration is needed in order to select the appropriate technology. One of alternative technologies that can be chosen for converting waste into energy is hydrothermal carbonization (HTC).

Hydrothermal carbonization, also referred to as hydrothermal treatment [Indrawan et al., 2011; Yoshikawa, 2012], or even wet torrefaction [Bach et al., 2015; Yan et al, 2010], is a thermochemical conversion technique which uses liquid water as a reaction medium for conversion of wet feedstock [Ramke et al., 2009; Funke and Ziegler, 2010; Hoekman et al., 2011]. Thus, the pre-drying processes are not compulsory. During this process, commonly conducted at temperature 180–250°C, wet feedstock is converted into hydrochar, a coal-like material, through various chemical reactions such as hydrolysis, dehydration, decarboxylation, and polymerization/aromatization. [Sevilla and Fuertes, 2009; Titirici et al., 2007]. The produced hydrochar comprised higher carbon than its raw form. In addition, the calorific value and physical properties of hydrochar were quite similar to brown coals.

Water plays important role in this process, not only as solvent, but also as catalyst [Fang et al., 2018]. In order to avoid the phase change of water, high pressure was involved in the process. It results in that the required energy to heat the water in HTC is smaller than to evaporate water within the same amount in other thermochemical process. Despite all advantage of HTC over other thermochemical process with relation to handling of wet feedstock (such as MSW and sludge), a study on the kinetics and performance of the HTC process to convert MSW with high moisture content (>60%) into coal-like material have not been reported in open literature so far. In this study, the HTC experiments were focused on the effect of process condition (feed to water ratio (FWR), time, temperature) to the hydrochar properties in terms of calorific value, proximate and ultimate analysis. In addition, the approach model of HTC kinetic of organic fraction from MSW was investigated.

MATERIALS AND METHODS

MSW composition

This research consists of field observations in one of temporary disposal sites in Bandung City, precisely located at Gumuruh District. Gumuruh District represents an average densely populated district in Bandung which covers residential, business and traditional market and knitting industry. The waste sampling was performed for 8 consecutive days. It was followed with a laboratory analysis to obtain MSW composition and proximate analysis. There were several waste compositions: wet waste or organic waste, plastics, paper, rubber, etc. In order to give a clear image of waste composition both in Gumuruh District, Figure 1 shows the average composition of MSW and Table 1 gives the proximate and ultimate analysis from waste. The result was used as reference for the HTC experiment.

According to Table 1, only the organic fraction was utilized in the carbonization process. Wood waste (includes leaves and twigs), printing paper, and food waste (rice, bones, fruit peel) were used as representatives of pseudo-organic fraction of MSW. Its chemical properties were given in Table 2. All components were mixed and crushed into small size, below 10 mm. Before beingused in the HTC experiment, the feedstock was placed in open container to get air-dried prior first.

HTC Experiment

The HTC process of the organic fraction of MSW was carried out using a SS-304 stirred reactor (see Figure 2) This reactor was integrated with 2000 W heating mantle. In the experiment, 50 grams of feedstock was dispersed in distilled water with feed to water ratio (FWR) 0,1, 0,2, 0,3 and was blended for several minutes before the process. The mixer was set at 32 MHz. The mixture was placed inside the reactor. After making sure the reactor was closed tightly, nitrogen gas was passed through the reactor for several minutes to ensure no oxygen presence in the system. In order to analyze the effect of operating condition, the experiment was performed at the different temperature (T) 190, 210, 230 ℃. Temperature was held for 30 minutes. The treated products were unloaded from the reactor and the solids were separated from the liquids by using 2 mm mesh net. The separated solids were then dried and some were milled to pass the 60-mesh net for further heating value and physical composition analyses.

Feedstock and Products Analysis

The high heating value, ultimate and proximate analysis for both feedstock and products was performed. The analysis was supervised by TekMIRA Indonesia. Table 3 listed standard method that used for analysis. For the lignocellulosic content, an analysis from feedstock was performed by Center Pulp and Paper Indonesia. According to Channiwala and Parikh (2002), higher heating value (HHV) was determined by Eq. 1:

$$HHV = 0.3491\,C + 1.1783\,H + 0.1005\,S - {} - 0.1034\,O - 0.0151\,N - 0.021\,A \tag{1}$$

where: A is percentage of ash content, thus C, H, O, N, S is percentage of atomic weight of carbon, hydrogen, oxygen, nitrogen, and sulfur, respectively.

The parameters of mass yield (MY), energy densification ratio (ED), and energy yield (EY) were estimated by using formula as seen below:

$$mass\ yield = \frac{mass\ of\ dry\ hydrochar}{mass\ of\ dry\ feedstock} \times 100\% \tag{2}$$

$$energy\ densification\ ratio = {} = \frac{HHV\ of\ hydrochar}{HHV\ of\ feedstock} \tag{3}$$

$$energy\ yield = {} = mass\ yield\ \times energy\ densification \tag{4}$$

RESULTS AND DISCUSSION

Chemical composition of feedstock and hydrochar

Table 4 and Table 5 showed the HTC process of MSW under holding time 30. The composition of ash, carbon, and fixed carbon slightly elevated with widening temperature, whereas sulfur, oxygen, nitrogen and hydrogen decreased. It results clearly verified that a dehydration reaction occurred, so both oxygen and hydrogen were converted into smaller molecules in liquid and gas
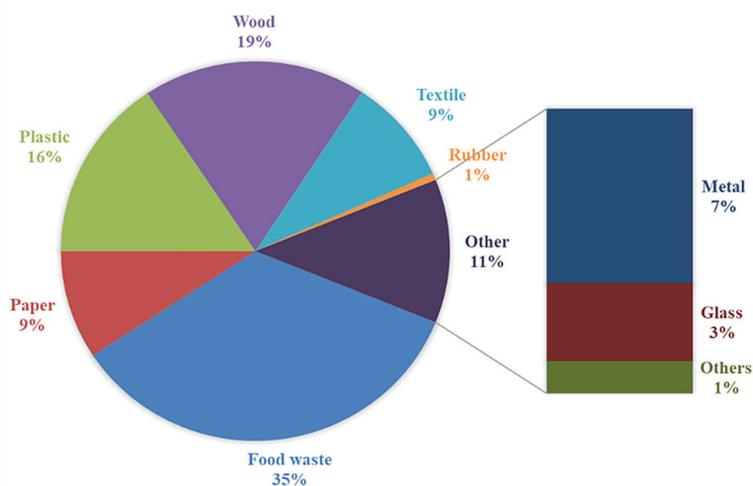

Figure 1. MSW composition at Gumuruh District

Table 1. Proximate and ultimate analysis of MSW

Parameters	Percentage
Moisture content	13.33
pH	6.13
Volatile Matter	54.21
Ash Content	15.03
Fixed Carbon	17.43
Carbon	48.21
Nitrogen	1.21
Oxygen	45.25
Hydrogen	5.12
Sulfur	0.21
Higher Heating Value/HHV (MJ/kg)	18.4

Table 2. Chemical properties of feedstock

Parameters	Percentage
Moisture content	9.47
Ash content	7.55
Volatile Matter	80.55
Fixed Carbon	11.90
Carbon	46.05
Hydrogen	5.70
Oxygen	0.70
Nitrogen	0.97
Cellulose	51.1
Hemicellulose	20.94
Lignocellulose	14.46
Water Extractive	6.04
Higher Heating Value/HHV (MJ/kg)	17.12

form. During HTC, the oxygen and hydrogen content decreases while the carbon content increases. Consequently, both O/C and H/C ratio of hydrochar is smaller than in raw material. This lower O/C and H/C ratios were affected by chemical reaction such as dehydration, demethylation and decarboxylation. With smaller O/C and H/C ratio, hydrochar becomes a coal-like material. During the HTC process, the O/C and H/C ratio of hydrochar reduced by 0.65 and 1.46 to 0.31 and 0.98, respectively.

Effect of process parameters on mass yield, energy yield, and high heating value of hydrochar

All the experiments in this investigation were conducted at autogenous pressure, adopted from our previous study [Putra et al., 2018]. Mass yield (hydrochar) is one of main indicator for hydrothermal carbonization process. It can be calculated according to Eq. (1). Figure 3 shows the effects of temperature and feed to water ratio

on mass yield. When the temperature is elevated from 190 to 230°C, the hydrochar yield decrease varies from 63.91 to 54.56%. On the other hand, the energy densification ratio and heating value increased by approximately 1.0–1.32 and 30% over raw feedstock, respectively (Figure 4). Specifically, for energy yield, the optimum condition for generating energy was at temperature of 210°C and FWR 0.1 (Figure 5). The highest yield was on temperature of 190°C at FWR 0.3 which is 63,91% and the lowest one is at 230°C at FWR 0.1 with 54.56%. In general, the mass yield decreased with increasing temperature and the feed to water ratio. A similar trend was also reported by Heilmann et al. (2010) and Yao et al. (2016).

Temperature and water play important role in every single thermochemical process. Water density decreased when water was heated up. Higher temperature also caused a dielectric constant and solvent polarity decrease. Thus, it has spurred the hydrolysis of lignocellulose (lignin,
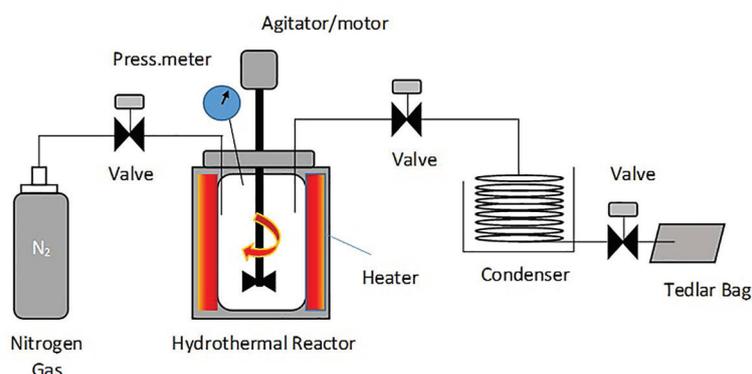

Figure 2. Experimental apparatus

Table 3. Standard method used by TekMIRA

Parameters	Standard Method
Volatile Matter	ISO 562
Ash content	ASTM D-3174
Fixed Carbon	100%-M-Ash-VM
Moisture content	ASTM D-3137
Carbon	ASTM-3178
Nitrogen	ASTM-3178
Oxygen	100%-C-H-N-S-Ash
Hydrogen	ASTM-3178

hemicellulose, and cellulose) content in feedstock. Kinetic decomposition of lignocellulose is reported in the next section. This suggests that the higher FWR, water will soak the entire surface of the feedstock, then certainly its decomposition reaction occurs perfectly. Conversely, if the water ratio is low, the surface of the biomass

is submerged only partially. As a result, decomposition occurs partly, but the resulting solid is high. At a temperature of hydrolysis between 160–180°C, more than 80% hemicellulose starts to be decomposed [Sevilla and Fuertes, 2009; Bobleter, 1994]. Unlike hemicellulose, cellulose was slowly decomposed and no more than 10% of lignin start to be decomposed at below 250°C [Funke and Ziegler, 2010; Bobleter, 1994; Yuliansyah et al., 2010].

Fourier Transform Infrared Spectroscopy

The parallel transmittances wavenumber of MSW and three hydrochar samples were demonstrated from 4000 to 500 cm^{-1}. Located at 3700 to 3000 cm^{-1}, the wide band was related with the-OH vibration in carboxyl or hydroxyl groups [Sevilla and Fuertes, 2009], and then shortened

Table 4. Proximate analysis of feedstock and hydrochar

Temperature	FWR	Time	Proximate Analysis			
			Ash	Volatile Matter	Fixed Carbon	Moisture Content
		minutes	%	%	%	%
Raw			7,55	70.43	11.90	10.12
190	0.3	30	8.53	74.30	17.17	5.70
	0.2	30	8.50	73.35	18.15	5.80
	0.1	30	8.52	72.58	18.90	5.97
210	0.3	30	8.18	72.18	19.64	6.42
	0.2	30	7.96	71.55	20.49	6.61
	0.1	30	8.21	70.10	21.68	6.57
230	0.3	30	8.04	70.32	21.64	7.04
	0.2	30	8.17	68.13	23.70	7.32
	0.1	30	8.52	66.32	25.16	7.60

Table 5. Ultimate analysis of feedstock and hydrochar

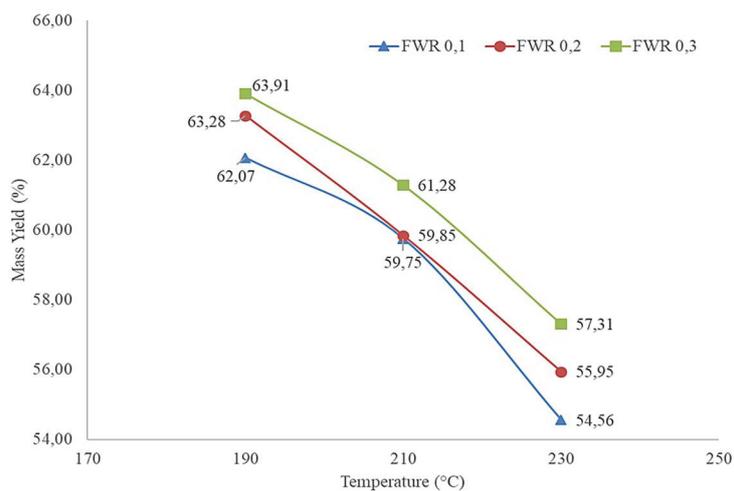| Temperature	FWR	Time	Ultimate Analysis				
			C	H	N	O	S
	g/ml	minutes	%	%	%	%	%
Raw			46.05	5.60	0.97	39.74	0.10
190	0.3	30	48.92	5.59	0.95	35.91	0.10
	0.2	30	51.74	5.52	0.87	33.38	0.00
	0.1	30	53.40	5.33	0.81	31.94	0.00
210	0.3	30	54.28	5.37	0.80	31.37	0.00
	0.2	30	56.56	5.24	0.77	29.48	0.00
	0.1	30	58.84	5.14	0.80	27.01	0.00
230	0.3	30	57.27	5.11	0.73	28.85	0.00
	0.2	30	59.07	5.00	0.72	27.04	0.00
	0.1	30	60.74	4.94	0.68	25.12	0.00

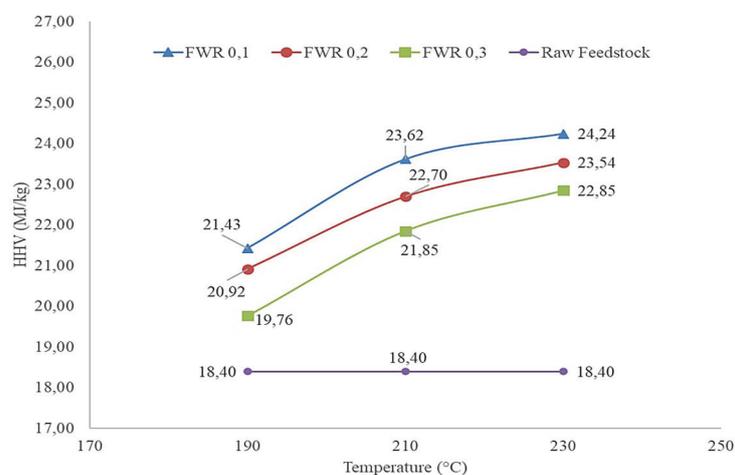**Figure 3**. Hydrochar (mass yield) at process temperature

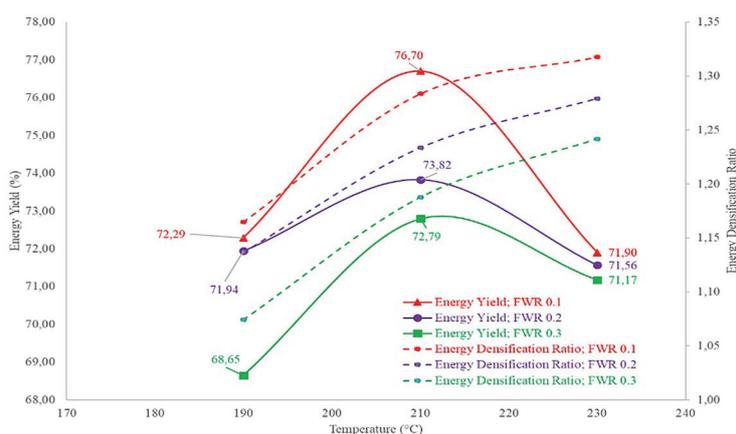**Figure 4**. High heating value (HHV) of hydrochar

Figure 5. Energy yield from HTC process

after HT might be contributed to the dehydration. The bands located at 2965 and 2850 cm^{-1} were associated with aliphatic -CH stretching vibration and deforming vibration. The wavenumber at 1750 cm^{-1} and 1460 to 1000 cm^{-1} were associated to carbonyl groups C=O [Calucci et al., 2012] and β-glycosidic bond in cellulose and hemicellulose [Liu et al, 2013], respectively. The

reduction in these bands indicates that carbon dioxide (CO_2) was formed. The wavenumber from 890 to 750 cm^{-1} represented the aromatic group C-H [Kim et al., 2014]. By the increasing of these bands, it can be described that an aromatization/polimerization reaction arose during HTC. Besides, during the decarboxylation reactions, the functional groups were also converted.

Kinetics of lignocellulosic materials

A simplified kinetics model was developed by Reza et al based on the data obtained from the mass yield of hydrochar [Reza et al., 2013]. That model neglected lignin decomposition at the treated temperatures. In this study, a kinetic model was developed by modifying the previous model [Reza et al., 2013]. The first step involved the hydrothermal reaction of the basic biomass components in the order of hemicellulose, cellulose, extractive and lignin. The Microsoft Excel Solver software was applied to establish the kinetic parameters such as pre-exponential factor and activation energy. This method assumes all reaction first-order reactions order reaction and employs the general rate equation and Arrhenius equation. All the assumptions of reactions and equations were summarized in Table 6.

If M_t represents total mass of non-reacted biomass and hydrochar at reaction time (t), M_t can be interpreted as Eq. 5 below:

$$M_t = C_t + H_t + Hc_t + L_t \qquad (5)$$

If the mass yield of hydrochar is Y(t), thus formula (5) possibly modified as below.

$$Y_t = \frac{M_t}{M_0} = Y_{C_O}e^{-k_3 t} + Y_{H_O}e^{-k_2 t} + \beta C_0(1 - e^{-k_3 t}) + $$
$$+ \gamma L_0(1 - e^{-k_1 t}) + Y_{L0}e^{-k_1 t} \qquad (6)$$

where: Y_{C0}, Y_{H0}, and Y_{L0} were initial mass fraction of cellulose, hemicellulose, and lignin, respectively. In order to calculate Y_t by Eq. (6), the value of β and γ were required in vary time. If time t tends to unlimited then equation (6) can be rewritten as Eq. (7), where extractives were ignored:

$$Y_t = \frac{M_t}{M_0} = Y_{C0}e^{-k_3 t} + Y_{H0}e^{-k_2 t} + $$
$$+ \beta C_0(1 - e^{-k_3 t}) + \gamma L_0(1 - e^{-k_1 t}) + \qquad (7)$$
$$+ Y_{L0}e^{-k_1 t} \lim_{t \to \infty} Y_t = \beta C_0 + \gamma L_0$$

where: H_o is sum of hemicellulose and initial extractive. Figure 7 showed the result of HTC process at all three temperatures within extended reaction time (1800, 3600, and 7200 seconds) in order to evaluate value β and γ. The HTC process with three different temperature gave quite similar of mass yield around 49% after 2 hours. If only 10% of lignin is decomposed, then substituting all the collected values gives a single value for evaluation of β and γ, equal to 0.49. After that the parameters k_1, k_2 and k_3 are still unknown in Eq. (6). By minimizing the objective function F(k1, k2, k3), the rate constants can be obtained as shown in Eq. (8).

$$F(k_1, k_2, k_3) \equiv$$
$$\equiv \sum_{i=1}^{10} \left(Y_{i^{eksperimen}} - Y_{i^{model}}(k_1, k_2, k_3)\right)^2 \qquad (8)$$

where: $Y_i eksperimen$ is the experimental mass yield,
$Y_i model$ is the estimated mass yield using Eq. (6),
and i represents each of 10 reaction times.

By using the conjugate gradient method in Microsoft Excel solver, the function F was minimized with respect to k_1, k_2, k_3. Table 7 reported the value of rate constant, while Arrhenius plot for k_1, k_2, and k_3 was given in Figure 8. The activation energies and pre-exponential factors are obtained from the slopes of Figure 8; the calculated activation energies (E1, E2, E3) are 12.23 kJ/mol for hemicellulose (k_1), 51.86 kJ/mol for cellulose (k_2), and 76.26 kJ/mol for lignin. This result is preliminary study which still requires further investigation. Table 8 summarized the activation energies from the present and previous studies.

CONCLUSION

The present study relates to a hydrothermal carbonization process for the preparation of coal-like material using a pseudo-component of MSW (food waste, paper, and wood waste) as feedstock. It can be concluded that the hydrochar yields for lignocellulosic typically range from between 50% and 65% at the lower process

Table 6. Assumptions of reactions, and equations that used in present study

No.	Biomass Component	Percentage	Reaction Order	Reaction and Formula
1	Extractive (E)	5,16	instantaneous reaction [Peterson et al., 2008]	Components such as starch, sugar, and proteins are very reactive in compressed hot water [Sasaki et al., 2000]. Extractive is decomposed into chemicals (C_h) and Gas (G) $$E \rightarrow C_h + G$$ $$\frac{dE_t}{dt} = \infty$$
2	Lignin (L)	21,94	order 1	Not more than 10% of lignin is slowly decomposed t 180-220 °C [Kim et al., 2012]. The mass yield of solid products from lignin is denoted by the parameter γ $$L \rightarrow \gamma H_c + (1 - \gamma) G$$ $$\frac{dL_t}{dt} = -k_1 L_t$$ $$L_t = L_0 e^{-k_1 t}$$
2	Hemicellulose (H)	19,92	order 1	Hemicellulose starts to be easily decomposed at 160 °C. $$H \rightarrow C_h + G$$ $$\frac{dH_t}{dt} = -k_2 H_t$$ $$H_t = H_0 e^{-k_2 t}$$
3	Cellulose (C)	47,84	order 1	Cellulose is decomposed into hydrochar, chemical, and gas. Parameter β is denoted for mass yield of solid products from cellulose $$C \rightarrow \beta H_c + (1 - \beta)(C_h + G)$$ $$\frac{dC_t}{dt} = -k_3 C_t$$ $$C_t = C_0 e^{-k_3 t}$$
4	Hydrochar (Hc)	Mass Hc at reaction time t	order 1	Hydrochar is resulted from partly decomposition of cellulose and small amount of lignin. $$Hc(t) = \beta C_0 (1 - e^{-k_3 t}) + \gamma L_0 (1 - e^{-k_1 t})$$

temperature (190–230 °C) and at feed to water ratio around 0.1, 0.2, 0.3. When the temperature is elevated from 190 to 230 °C, the hydrochar yield decreased vary from 63.91 to 54.56%. On the other hand, the energy densification ratio and heating value increased by approximately

1.0–1.32 and 30% over raw feedstock. The lower yields of hydrochar were obtained at higher temperature. It means that the decarboxylation and dehydration reactions occur. Thus, the level of oxygen becomes significantly reduced at the higher temperature. Decarboxylation and
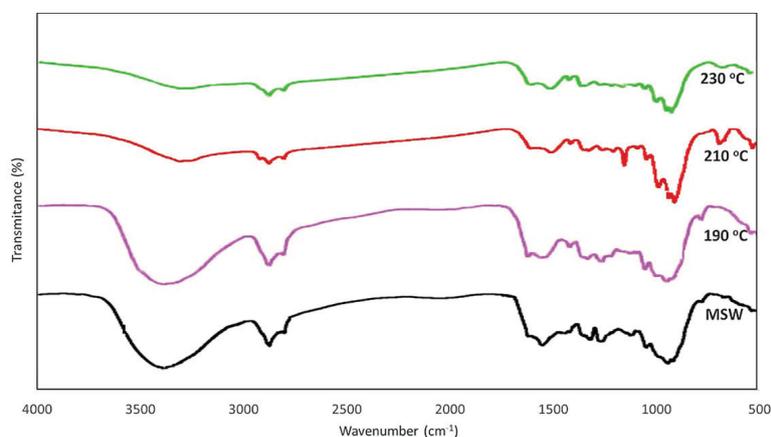
Figure 6. Fourier transform infrared (FTIR) spectra of MSW and hydrochar
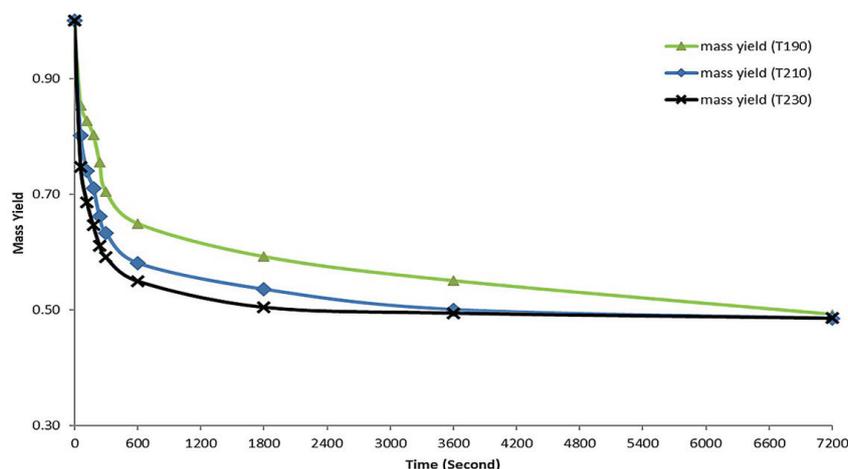
Figure 7. Mass yield as a function of time at three reaction temperatures

dehydration reactions tend to increase the energy content (HHV) of the hydrochars. The highest HHV is 24.24 MJ/kg.

Furthermore, a preliminary study of kinetic model for lignocellulose decomposition was conducted. This model was based on the rate of mass loss of lignocellulose compound (lignin, cellulose, hemicellulose) in hydrothermal carbonization of MSW. Three parallel first-order reactions were shown to accurately describe the mass yield for temperatures at 190, 210, and 230°C. Lignocellulose degradation is described by a first order rate constant with activation energy 76.26 kJ/mol, 51.86 kJ/mol, 12,23 kJ/mol for lignin, cellulose, and hemicellulose decomposition, respectively.

Table 7. 1st order rate constants determined by minimizing the objective function

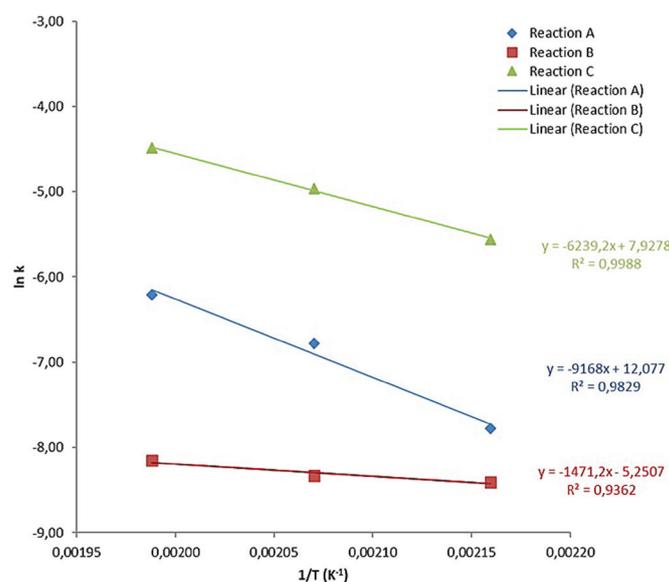| Function	HTC 190 °C	HTC 210 °C	HTC 230 °C
k_1 (s^{-1})	0,0004172	0,0011309	0,0020048
k_2 (s^{-1})	0,0002226	0,0002400	0,0002871
k_3 (s^{-1})	0,0038565	0,0069537	0,0112515
objective	0,0024	0,0017	0,0015

Acknowledgement

Figure 8. Arrhenius plot for k1, k2, k3, first-order rate const ants for degradation of Lignin, hemicellulose and cellulose, respectively.

Table 8. Activation energies from present and other previous studies

Ref.	Components	Temp. (°C)	Activation Energy (KJ/mol)
Reza et al (2013)	Hemicellulose and cellulose from wood	200, 230, 260	29 (hemicellulose), 77 (cellulose)
Sasaki et al. (2000)	Microcystalline cellulose	290–400	145.9 (290 °C), 547.9 (400 °C)
Prins et al. (2006)	Lignocellulose	torrefaction	76 (hemicellulose), 152 (cellulose)
Jatzwauck and Schumpe (2015)	Soft rush (Juncus effusus)	180, 240	141 (A-B), 75 (B-C), 74,3 (B-D)
Iryani et al. (2016)	Sugarcane baggase	200–300	88,1 (hydrolysis), 129, (dehydration)
Peterson et al. (2008); Grénman et al. (2011)	Pure hemicellulose and cellulose		129–215
Present study	MSW	190–230	12.23 (hemicellulose), 51.86 (cellulose), 76.26 (lignin)

REFERENCES

1. Bach, Q.V., Tran, K.Q., Øyvind, S., Trinh, T.T., 2015. Effects of wet torrefaction on pyrolysis of woody biomass fuels. Energy, 88, 443–456. DOI: http://doi.org/10.1016/j.energy.2015.05.062

2. Bobleter, O., 1994. Hydrothermal degradation of polymers derived from plants. Progress in polymer science 19(5), 797–841. DOI: http://doi.org/10.1016/00796700(94)90033–7

3. BP Statistical Review of World Energy, Indonesia Insights, From BP, Publication (June 2017).https://www.bp.com/content/dam/bp/en/corporate/pdf/energy-conomics/statistical-review-2017/bp-statistical-review-of-world-energy-2017-indonesia-insights.pdf (accessed on January 10, 2018)

4. Calucci, L., Rasse, D. P., Forte, C., 2012. Solid-state nuclear magnetic resonance characterization of chars obtained from hydrothermal carbonization of corncob and Miscanthus. Energ. Fuel., 27(1), 303–309. DOI: http://doi.org/10.1021/ef3017128

5. Channiwala, S., Parikh, P., 2002. A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel 81(8), 1051–1063. DOI: http://doi.org/10.1016/S0016–2361(01)00131–4

6. Damanhuri, E., 2005. Some principal issues on municipal solid waste management in Indonesia. Expert Meeting on Waste Management in Asia-Pacific Islands, Oct 27–29, Tokyo. www.kuliah.ftsl.itb.ac.id/wp-content/uploads/2008/08/tokyo-271005.pdf

7. Fang, J., Zhan, L., Ok, Y.S., Gao, B., 2018. Minireview of potential applications of hydrochar derived from hydrothermal carbonization of biomass. J. Ind. Eng. Chem., 57, 15–21. http://doi.org/10.1016/j.jiec.2017.08.026

8. Funke, A., Ziegler, F., 2010. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. Biofuels Bioproducts & Biorefining-Biofpr, 4, 160–177. http://doi.org/10.1002/bbb.198

9. Grénman, H., Eränen, K., Krogell, J., Willför, S., Salmi, T., Murzin, D.Y., 2011. The kinetics of aqueous extraction of hemicelluloses from spruce in an intensified reactor system. Ind. Eng. Chem. Res. 50, 3818–3828. DOI: http://doi.org/10.1021/ie101946c

10. Heilmann, S.M., Davis, H.T., Jaden, L.R., Lefebvre, P.A, Sadowsky, M.J., Schendel, F.J., von Keitz, M.G., Valentas, K.J., 2010. Hydrothermal carbonization of microalgae. Biomass and Bioenergy, 34(6): 875–882. DOI: http://doi.org/10.1016/j.biombioe.2010.01.032

11. Hoekman, S.K., Broch, A., Robbins, C., 2011. Hydrothermal carbonization (HTC) of lgnocellulosic biomass. Energy Fuels, 25 (4), 1802–1810. DOI: http://doi.org/10.1021/ef101745n

12. Hrncic, M.K., Kravanja, G., Knez, Z., 2016. Hydrothermal treatment of biomass for energy and chemicals. Energy, 116(2), 1312–1322. DOI: http://doi.org/10.1016/j.energy.2016.06.148

13. Indonesian domestic solid waste statistics year 2008. https://inswa.or.id/wp-content/.../07/Indonesian-Domestic-Solid-Waste-Statistics-20082.pdf Accessed on March 12, 2018.

14. Indrawan, B., Prawisudha, P., Yoshikawa, K., 2011. Chlorine-free solid fuel production from municipal solid waste by hydrothermal process. Journal of the Japan Institute of Energy, 90, 1177–1182

15. Iryani, D.A., Kumagai, S., Nonaka, M., Sasaki, K., Hirajima, T., 2016. Hydrothermal carbonization kinetics of sugarcane bagasse treated by hot compressed water under variabel temperature conditions. ARPN Journal of Engineering and Applied Sciences 11(7): 4833–4839.

16. Jatzwauck, M., Schumpe, A., 2015. Kinetics of hydrothermal carbonization (HTC) of soft rush. Biomass and Bioenergy, 75, 94–100. DOI: http://doi.org/10.1016/j.biombioe.2015.02.006

17. Kim, D., Lee, K., Park, K.Y., 2014. Hydrothermal carbonization of anaerobically digested sludge for solid fuel production and energy recovery.

Fuel 130, 120–125. DOI: http://doi.org/10.1016/j.fuel.2014.04.030

18. Kim, D., Prawisudha, P., Yoshikawa, K., 2012. Hydrothermal upgrading of Korean MSW for solid fuel production: effect of MSW composition. Journal of Combustion, 1–8. DOI: http://doi.org/10.1155/2012/781659

19. Liu, Z. G., Quek, A., Hoekman, S. K., Balasubramanian, R., 2013. Production of solid biochar fuel from waste biomass by hydrothermal carbonization. Fuel 103, 943–949. DOI: http://doi.org/10.1016/j.fuel.2012.07.069

20. Matsakasa, L., Gaob, Q., Janssonb, S., Rovaa, U., Christakopoulos, P., 2017. Green conversion of municipal solid wastes into fuels and chemicals. Electronic Journal of Biotechnology, 26, 69–83. DOI: http://doi.org/10.1016/j.ejbt.2017.01.004

21. Peterson, A.A., Vogel, F., Lachance, R.P., Froling, M., Antal, M.J., Tester, J.W., 2008. Thermochemical biofuel production in hydrothermal media: a review of suband supercritical water technologies. Energy Environ. Sci. 1, 32–65. DOI: http://doi.org/10.1039/b810100k

22. Prins, M.J., Ptasinski, K.J., Janssen, J.J.G.F., 2006. Torrefaction of wood: part 1. Weightloss kinetics. J. Anal. Appl. Pyrolysis 77, 28–34. DOI: http://doi.org/10.1016/j.jaap.2006.01.002

23. Putra, H.E., Dewi, K., Pasek, A.D., Damanhuri, E., 2018. Hydrothermal carbonization of biomass waste under low temperature condition. MATEC Web of Conferences 154, 01025. DOI: http://doi.org/10.1051/matecconf/201815401025

24. Ramke, H.G., Blohse, D., Lehmann, H.J., Fettig, J., 2009. Hydrothermal carbonization of organic waste. Twelfth International Waste Management and Landfill Symposium, International Waste Working Group (IWWG). Available online: www.hs-owl.de/fb8/fachgebiete/abfallwirtschaft/.../Sardinia_2009_HTC_Internet.pdf

25. Reza, M.T., Yan, W., Uddin, M.H., Lynam, J.G., Hoekman, S.K., Coronella, C.J., Vásquez, V.R., 2013. Reaction kinetics of hydrothermal carbonization of loblolly pine. Bioresource Technology, 139C, 161–169. DOI: http://doi.org/10.1016/j.biotech.2013.04.028

26. Sasaki, M., Fang, Z., Fukushima, Y., Adschiri, T., Arai, K., 2000. Dissolution and hydrolysis of cellulose in subcritical and supercritical water. Ind. Eng. Chem. Res., 39 (8), 2883–2890. DOI: http://doi.org/10.1021/ie990690j

27. Sevilla, M., Fuertes, A.B., 2009. The production of carbon materials by hydrothermal carbonization of cellulose. Carbon, 47, 2281–2289. DOI: http://doi.org/10.1016/j.carbon.2009.04.026

28. Titirici, M.M., Thomas, A., Yu, S.H., Müller, J., Antonietti, M., 2007. A dire ct synthesis of mesoporous carbons with bicontinuous pore morphology from crude plant material by hydrothermal carbonization. Chemistry of Materials, 19(17), 4205–4212. http://doi.org/10.1021/cm0707408

29. Yan, W., Hastings, J.T., Acharjee, T.C., Coronella, C.J., Vásquez, V.R., 2010. Mass and energy balances of wet torrefaction of lignocellulosic biomass. Energy Fuels, 24 (9), 4738–4742. DOI: http://doi.org/10.1021/ef901273n

30. Yao, Z., Ma, X., Lin, Y., 2016. Effects of hydrothermal treatment temperature and residence time on characteristics and combustion behaviors of green waste. Applied Thermal Engineering, 104, 678–686. DOI: http://doi.org/10.1016/j.applthermaleng.2016.05.111

31. Yoshikawa, K. Hydrothermal treatment of municipal solid waste to produce solid fuel. 7th International Energy Conversion Engineering Conference, International Energy Conversion Engineering Conference (IECEC), https://doi.org/10.2514/6.2009–4606

32. Yuliansyah, A.T., Hirajima, T., Kumagai, S., Sasaki, K., 2010. Production of solid biofuel from agricultural wastes of the palm oil industry by hydrothermal treatment. Waste and biomass valorization, 1(4), 395–405. DOI: http://doi.org/10.1007/s12649–010–9045–3