9-18-2020

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Recommended Citation

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Abstract

Hydrothermal treatment is a thermal conversion technology for processing high-moisture-content solid waste to coal-like materials. In this research, mixtures of sawdust and polyethylene terephthalate (PET) waste were treated in a 2000 mL hydrothermal reactor to produce hydrochar and a liquid product. The effects of zeolite addition and temperature variations during the treatment on the product characteristics were investigated. During the treatment, the utilized temperatures were 180, 200, and 220 °C, and the zeolite contents in the mixture were 10 and 20 wt%; the temperature and zeolite content were varied, while the other processing parameters were fixed, i.e., a biomass-to-PET ratio of 1:1, solid mixture-to-water ratio of 1:10, and processing time of 30 minutes at the targeted temperature. The product from each hydrothermal condition was characterized in terms of solid yield; liquid pH; chemical characteristics, determined using proximate analysis; and calorific value. The result shows that the addition of zeolite could increase the solid yield, while a higher treatment temperature led to a higher calorific value of the solid product.

Keywords: biomass waste, hydrothermal treatment, PET, zeolite

Introduction

Fossil fuels cannot be considered as renewable or sustainable energy resources because of their limited reserves and enormous gaseous emission [1]. Moreover, their unstable market price and limited supply are other reasons to shift from using fossil energy to alternative energy resources [2]. One of the accessible alternative resources is lignocellulosic biomass. In Indonesia, an abundant accumulation of lignocellulosic biomass exists in the form of agro-industrial wastes. The utilization of biomass waste as an alternative fuel provides several merits, such as a reduction in solid waste and the preservation of nonrenewable fuel resources.

In addition to biomass, another type of solid waste that is problematic to the environment is plastic waste. For example, polyethylene terephthalate (PET) is a common plastic that is extensively used in the packaging industry. It can be easily recycled and does not have any immediate environmental impact since it is relatively inert; however, it is commonly disposed in large volumes, which results in collection problems, and is poorly degradable in nature [3].

For treating high-moisture-content solid waste, conventional thermochemical processes such as combustion, gasification, and pyrolysis require a drying stage, which can make the whole process unreliable from the energy aspect. A newly developed method for the thermal treatment of waste called hydrothermal carbonization (HTC) method can be used for solids with high moisture content and operate at a much lower temperature (200 °C – 350 °C) than those of other thermal conversion methods such as pyrolysis (450 °C – 550 °C) and gasification (900°C – 1200 °C) [4]. It is called hydrothermal because it involves the heat treatment of carbonaceous solids soaked in water, whereby the water acts as a solvent as well as a reactant.

Hydrothermal treatment can be defined as a thermo-degradation process in which the material is contained in a vessel and exposed to an elevated temperature in a pressurized water suspension [5]. During the hydrothermal treatment process, the biomass component is hydrolyzed, and the organic component is broken down into unstable smaller portions and re-polymerized into oily compounds, and hydrochar is simultaneously

formed [6]. The less fibrous structure and high calorific value of the hydrochar product (coal-like materials) makes it a potential candidate for solid fuels [7].

Since the char is considered as the main hydrothermal product, several attempts had been made to increase the solid yield. Various alkali and alkali metal salts such as Na_2CO_3, K_2CO_3, KOH, and NaOH have been employed during the hydrothermal treatment to improve the solid product [8]. However, separating these soluble catalysts from the liquid product is difficult, and this hinders the recycling of the catalyst and the further utilization of the liquid product. On the other hand, if the additive is in the form of a non-degraded solid, separating it from the char after the thermal process will be much easier using mechanical sieves.

Zeolites are common natural-occurring catalysts for high-temperature reactions, and they possess valuable properties [9]. Its thermal stability permits its utilization as catalysts in many processes. However, it is rarely used in hydrothermal treatment [10]. Therefore, this study aims to investigate the effect of zeolite addition on the solid properties in the hydrothermal treatment of solid waste mixtures. A mixture of PET and sawdust is used to represent the organic and inorganic waste fractions in common municipal solid waste.

Methods

Experiments were conducted in a 2000 mL batch stainless steel autoclave reactor equipped with a mixer and an automatic temperature controller (Figure 1). The use of organic and inorganic solid (sawdust and PET) is quite unique but essential for representing common municipal solid waste (MSW). The high component variety inside the MSW will create a high fluctuation of HTC product characteristics; thus, an ideal mixture substitution is necessary. Before used, sawdust was collected from a local market then oven dried, while PET bottle was cleaned and crushed to form 3 – 5 mm flakes. The pretreatment of biomass was following other report [11]. In this study, a mixture of 25 g of sawdust, 25 g of PET, and 500 mL of water was loaded into an autoclave, and the autoclave was tightly closed. The autoclave was heated up to the maximum temperature, ranging from 180 °C to 220 °C. Once the targeted temperature was reached, the sample was held for 30 minutes before the autoclave was cooled down. The slurry of the product was filtered. The residue was dried in an oven at 105 °C for 3 hours to obtain the final solid product (hydrochar). The solid product heating value was measured using a bomb calorimeter.

The natural zeolite particles (5 – 10 mesh) used in this experiment were obtained from the Klaten Region of Central Java, Indonesia. The main zeolite crystal structure is Mordenite that has been reported previously [12]. They were calcined at 350 °C for 3 hours. The prepared zeolite was mixed with the solid feed (biomass and PET) before being heated and was then separated after the process. The zeolite contents in the mixture were 10 and 20 wt%. The pH of the liquid product after the process was measured using a portable pH meter. The composition of zeolite and the treated materials can be seen in Table 1. Elemental analysis of zeolite has been done using Shimadzu EDS while the composition of sawdust was determined by thermogravimetry analysis using TG-DTA.
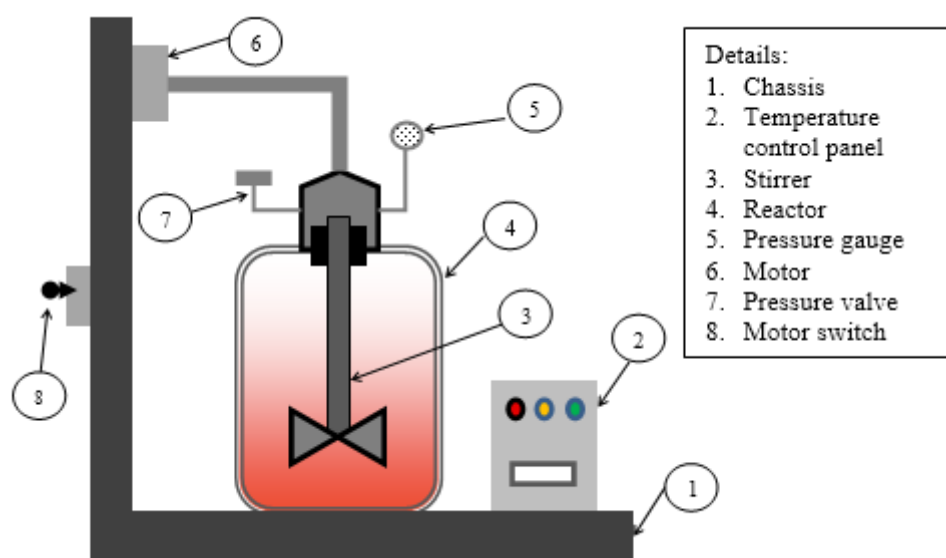

Figure 1. Apparatus of Small-scale Hydrothermal Reactor

Table 1. Composition of Solid Materials for Hydrothermal Carbonization

Components	Sawdust	Zeolite
Hemicellulose (%, d.b)	5.11	-
Cellulose (%, d.b)	49.33	-
Lignin (%, d.b)	29.49	-
Si	-	70.750
Al	-	12.381
Ca	-	7.385
Fe	-	4.127
K	-	2.919
S	-	1.131
Ti	-	0.552

The chemical characteristics of the hydrothermal treatment products, including ash content, water content, volatile matter content, and fixed carbon content, were determined using proximate analysis. The calorific value of the products was also evaluated as higher heating value (HHV), which is significantly higher under air-dried conditions and indicates that the products can act as fuel.

The important parameters include solid yield, energy yield, and energy densification, which are defined below [5]:

$$Y = \frac{w_{db}\ product}{w_{db}\ feed} \times 100\%$$ (1)

$$E_d = \frac{HHV\ of\ product}{HHV\ of\ feed}$$ (2)

$$E_Y = Y \times E_d$$ (3)

where
Y = Solid yield (%)
w_{db} = mass of dried solid basis (g)
E_d = Energy densification
E_Y = Energy yield
HHV = Higher heating value

Results and Discussion

Hydrothermal processes utilize subcritical water as the solvent as well as a reactant. Subcritical water is water pressurized at temperatures above its boiling point, under ambient pressure, and below the critical point. Within a region closer to the critical conditions, the water properties become more sensitive to pressure and temperature changes. The higher the temperature, the lower the density of the liquid phase and the vapor density, which causes the water properties to be closer to that of supercritical water [13]. Ionized water molecules are also formed when the temperature is elevated. Hydrolysis is a primary reaction in the hydrothermal treatment, whereby hemicellulose or cellulose is attacked by ionized water molecules and the β-(1-4) glycosidic bonds

of ester and ether are disintegrated. This bond breakage yields a wide range of products, including dissolved oligomers such as (oligo-)saccharides from hemicellulose and cellulose [14].

This mechanism leads to the thermal degradation of the feed material. Some of the chemical bonds in the material are broken, so that long-chain compounds such as cellulose, hemicellulose, and lignin become decomposed into smaller and simpler molecules. Furthermore, some solid materials are dissolved in the solvent, while some others are degraded to become gases. The remaining solid material after the heat treatment is recovered as solid residue with a high calorific value [5].

Based on the material composition in Table 1, sawdust has a high cellulose content (49.33%), followed by lignin, and then hemicelluloses. Through analysis, the lignocellulosic composition was found to correlate with the product properties after the treatment. Meanwhile, a hydrolysis reaction also occurred in PET depolymerization, in which the ionized water molecules attacked the long-chain polymer then broke it down into smaller oligomers. On the other hand, the performance of zeolite as a catalyst is strongly influenced by the Si-to-Al ratio. A higher ratio will enhance the acid sites contained in the natural zeolite, thus increasing the cracking possibility of the compounds in the solid waste.

Proximate analysis was conducted to determine the hydrochar quality as a fuel, which is mostly represented by the carbon content. The data in Table 2 show that the temperature affected the hydrochar properties. The higher

Table 2. Proximate Analysis Results of Solid Products

Properties	Non-Catalytic		
	180 ºC	200 ºC	220 ºC
Ash Content (%, d.b.)	1,013	1,158	0,467
Water Content (%, d.b.)	4,483	3,862	2,557
Volatile Matter (%, d.b.)	66,549	71,284	50,033
Fixed Carbon	24,539	27,401	23,205

Properties	Catalytic 10%		
	180 ºC	200 ºC	220 ºC
Ash Content (%, d.b.)	3,677	3,121	1,398
Water Content (%, d.b.)	3,662	3,732	3,712
Volatile Matter (%, d.b.)	64,724	71,778	69,966
Fixed Carbon	26,508	26,599	23,607

Properties	Catalytic 20%		
	180 ºC	200 ºC	220 ºC
Ash Content (%, d.b.)	3,442	4,727	1,874
Water Content (%, d.b.)	25,079	3,550	3,717
Volatile Matter (%, d.b.)	67,854	73,772	66,173
Fixed Carbon	21,447	27,000	22,632

the reaction temperature, the higher the values of most properties. However, the highest fixed carbon content value was obtained at a temperature of 200 °C for all the treatment conditions. This is probably due to the more intense loss of oxygen- and hydrogen-rich volatile materials from the solid to the solvent at higher temperatures, leaving carbon-rich materials at the end of the process. However, at the highest temperature, the further degradation of organic compounds accelerated the breakage of chemical bonds in the materials. Thus, the long-chain molecules were degraded into shorter chains in the forms of gaseous and liquid phases, causing a significant loss of carbon content inside the solid product. The temperature increase is also correlated with the water content in the chars. Under the non-catalytic treatment, the water content decreased gradually as the temperature increased, leading to an increase in the net calorific value of the product.

In terms of the ash content, the increase in temperature and pressure will further dissolve minerals from the solid [15]. This observation agrees with that of a previous report that suggests a high-temperature condition for obtaining hydrochar with less ash content for better fuel quality [16]. Decreasing the water and ash contents while increasing the calorific value absolutely upgrades the hydrochar properties [17]. The calorific value of the solid products is provided in Figure 2.

The HTC method increases the heating value of the solid due to the occurrence of complex chemical reactions during the process. The degradation reaction involves depolymerization, degradation of monomers (cleavage, dehydration, and decarboxylation reactions), and recombination of fragmented components [18]. The fixed carbon content on the treated hydrochar was increased due to the energy densification process during the hydrothermal treatment. The reaction temperature had significant effects on the solid yield, energy densification
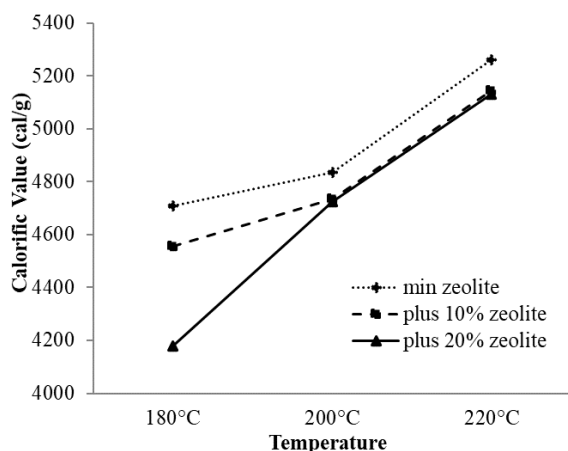

Figure 2. Calorific Value of Solid Products, with Zeolite addition (plus) and without Zeolite (min)

ratio, and energy yield of the solid products [5]. The higher the temperature, the higher the energy densification ratio, and the lower the solid yield and energy yield. Mustaqim *et al.* [19] found that the higher temperature employed in the hydrothermal process could dissolve and disintegrate the solid structure into soluble distributed components and generate a small amount of solid residue. However, the current research revealed a contrary result regarding the solid yield of hydrochar, due to the zeolite addition, as shown in Figure 3.

As indicated in Figure 3, due to the zeolite addition, the calorific value of the char was slightly reduced, especially in higher treatment temperatures. This result may be correlated with the solid yield shown in Figure 3, which significantly increased in the presence of zeolite, as also found by Abidin *et al.* [20]. It can be considered that at the highest temperature, the highest solid yield of hydrochar was obtained in the presence of 20 wt.% zeolite. This finding indicates that the addition of zeolite increases the solid yield without trading off much of the heating value of the solid products.
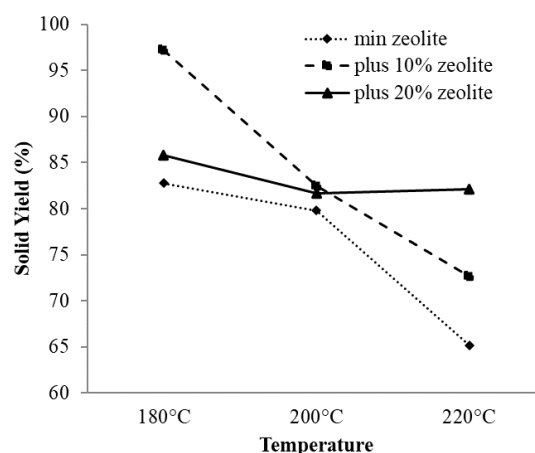

Figure 3. Solid Yield (Y) in Different Temperatures and Zeolite addition Amounts (min: minus/without; plus: with addition)
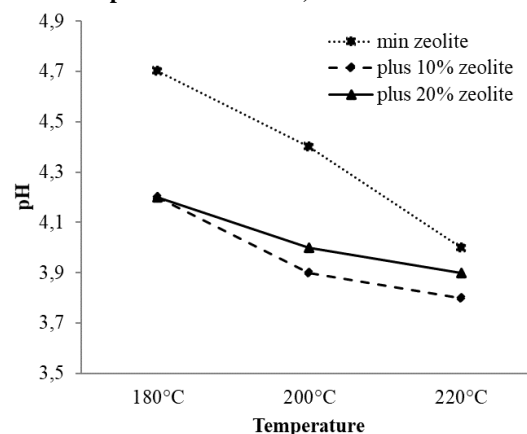

Figure 4. Temperature and pH of the Liquid Product with Different Zeolite addition Amounts (min: without; plus: with addition)

From the data illustrated in Figure 4, the pH of the liquid product had a strong correlation with the temperature and the amount of zeolite added. The higher the temperature, the lower the pH of the liquid; this is due to the intense dissolution of organic acids from the degraded solid. Meanwhile, the zeolite addition further reduced the pH and promoted the release of organic acids from the solid to the liquid product, and this contributed to the cracking process of hydrocarbon compounds and promoted the recombination of the fragmented products to form a new solid product. By zeolite addition, it provides active sites on the surface for enhancing radical molecules concentration in the liquid phase within subcritical temperature in order to split macromolecule structure of biomass into smaller molecules. The radicals will strip off oxygen functional groups on the char into the solution that will lead into organic acid production. This finding was confirmed by FTIR analysis of char in which increasing the zeolite content will further removed oxygenated group spectra [10].

From the E_d data in Table 3, it can be confirmed that the hydrothermal process could increase the energy content in the solid. In general, the densification energy of the solid product treated with zeolite was slightly less than that of the product without zeolite. However, the energy yield of the product treated with zeolite (10%) was higher than those of the other products without zeolite. This finding emphasizes the role of zeolite in increasing the solid yield while only slightly reducing the energy content. It can be said that the role of zeolite is as a directing agent (catalyst) for organic acid production from waste decomposition in the liquid product during hydrothermal treatment. As reported earlier that addition of zeolite will produce more acid molecules as shown by GCMS results of the liquid product [10]. More production of acid molecules will lead to pH reduction. The effect of heat treatment using acidic solution is better energy yield content in the final solid product since oxygen content is highly eliminated from the char surface.

Table 3. Energy Densification Ratio and Energy Yield of Treated Hydrochar

Hydrochar	E_d	E_Y
min zeolite, 180 °C	1.102	91.218
min zeolite, 200 °C	1.132	90.341
min zeolite, 220 °C	1.232	80.242
plus 10% zeolite, 180 °C	1.067	103.700
plus 10% zeolite, 200 °C	1.108	91.354
plus 10% zeolite, 220 °C	1.204	87.487
plus 20% zeolite, 180 °C	0.978	83.933
plus 20% zeolite, 200 °C	1.106	90.316
plus 20% zeolite, 220 °C	1.201	98.657

Conclusion

Due to the hydrothermal treatment, approximately 65 wt.% to 97 wt.% of the waste mixture was recovered in the form of char that can be used as solid fuel. The addition of zeolite elevated the solid yield without a significant decrease in the calorific value of the char. It also gradually enhanced the acidity of the hydrothermal solutions, which helps in the simultaneous degradation and recombination process.

Acknowledgements

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