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Effects of $ZnCl_2$ Catalyst Loading in Hydrothermal Carbonization of Cotton Textile Waste to Produce Hydrochars

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ABSTRACT

Hydrothermal carbonization (HTC) is a thermochemical process that utilizes biomass as feedstocks to produce hydrochars as solid fuel. Cotton textile wastes (CTW) are abundant; most are landfilled or incinerated, causing environmental pollution. CTW is rich in cellulose, thus suitable as biomass feedstock. HTC at a moderate temperature below 230 °C yields low-value hydrochars with low carbon content; however, an acid catalyst enhances the reaction. In this study, zinc-activated cotton textile waste (Zn-CTW) was synthesized via incipient wetness impregnation and used as a catalyst in hydrothermal carbonization to produce hydrochars. The reactions were conducted in a batch reactor at a temperature of 200 °C for 3 h. The effects of $ZnCl_2$ catalyst loading on CTW were studied. The characteristics of hydrochars in terms of surface morphologies, hydrogen/carbon (H/C) and oxygen/carbon (O/C) ratios and surface functional groups were affected by the $ZnCl_2$ loading on CTW. The results show that the hydrothermal carbonization of Zn-CTW-1.5 obtained hydrochars with the lowest H/C and O/C ratio values of 1.286 and 0.614, respectively. The FTIR analysis indicates stretching vibration of the C-O bond, which are the carboxylic acids and esters formed in the hydrochars. The hydrochars' surface morphologies show irregular and rough surfaces. It is concluded that Zn-CTW has the potential as a heterogeneous catalyst to produce hydrochars via hydrothermal carbonization.

Keywords: *biomass; hydrothermal carbonization; hydrochars; heterogenous catalyst; solid fuel*

1. INTRODUCTION

The continuous growth of the world's population and urbanization has increased energy demand [1]. The detrimental effects on the environment, such as greenhouse gas pollution through the use of fossil fuels, warrant alternative energy sources [2]. Biomass, as a renewable and abundant resource, has the potential to be an excellent source of energy that may be transformed into various forms, such as solid, liquid or gaseous, via thermochemical processes [3]. Nevertheless, in order to be considered a viable long-term energy source, biomass has a number of drawbacks that must be addressed, such as high moisture and pollutants presence, low energy content, heterogeneity and low density. Pyrolysis and hydrothermal processes are among the biomass utilization technologies that have been explored in the past [4]. The hydrothermal carbonization (HTC) technique, without needing to dry the biomass, is more

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suitable than other thermal processes, such as gasification and pyrolysis, because biomass has a high moisture content [5]. Also, the HTC process is more energy-efficient since it uses lower temperatures between 150 °C to 300 °C compared to pyrolysis, which operates at 400 °C to 600 °C [6].

Hydrochar is a carbon-rich solid with greater energy and mass density, hydrophobicity, easier handling, and is more environmentally friendly [7]. The production of hydrochars via HTC is less harmful to the environment compared to pyrolysis, which generates dangerous chemical waste and by-products [8]. It is possible that utilizing hydrochars as solid fuel achieved via HTC would be more economical due to their increased qualities in terms of heating value and aromatic structure when compared to raw biomass [9]. Additionally, the hydrochars produced via the HTC process are suitable as fuel, thus lowering the need for fossil fuels and reducing CO_2 emissions. Hydrochars' advantages as solid fuel include high carbon content and high energy density [10]. Several biomass has been studied as the feedstock of HTC, such as oil palm shell [11], wheat straw [12] and rapeseed husk [13] that produces hydrochars with high carbon content and energy density.

Cotton textile waste (CTW) originated from textile mills, which are largely from the residual materials produced in the manufacturing process of cotton fabric. CTW consists of cellulose-rich cotton fibres, as well as pectin, protein, and other mixed impurities that can be used as a sustainable source of energy. CTW underwent a coalification reaction during the HTC process that produced hydrochars with low ash content, high heating values and energy density [14]. Qi et al. [15] reported that $FeCl_3$ assisted HTC has effectively improved the CTW conversion to hydrochars with a high energy yield. Xu et al. [16] obtained hydrochars with high energy density by using surfactant-assisted HTC of CTW. Thus, CTW is a viable biomass feedstock for use in the production of hydrochars and potential energy resources to generate clean solid fuel.

Several catalysts, such as iron (II) chloride [17], iron (III) chloride [15], sulfuric acid [16] and aluminium oxides [18], were used in hydrothermal carbonization reaction. HTC supported by aluminium catalysts produced hydrochar with increased carbon content compared to raw biomass cellulose [18]. Sulfuric acid was effective as a catalyst to facilitate the hydrolysis of CTW into soluble intermediates that were further converted to hydrochars with a high energy density [16]. Lewis acids catalysts have been used as an alternative to mineral acids due to the simplicity of metal salt recovery, making the catalyzed carbonization process more ecologically friendly [17]. $ZnCl_2$ is a common metal salt that has been used to activate biomass to produce porous sorbents suitable for water treatment [19-21]. However, there have been limited studies on the utilization of $ZnCl_2$ as a Lewis acids catalyst in the hydrothermal carbonization of biomass from CTW and the characterizations of the hydrochars produced. In this work, $ZnCl_2$-activated cotton textile waste (Zn-CTW) was synthesized via incipient wetness impregnation at various $ZnCl_2$ loading and used as a catalyst in hydrothermal carbonization to produce hydrochars. The effects of synthesis condition of Zn-CTW were investigated based on the hydrochars obtained in terms of surface morphologies, hydrogen/carbon (H/C), oxygen/carbon (O/C) ratios and surface functional groups.

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2. METHODOLOGY

2.1 Materials and chemicals

Cotton textile waste (CTW) was obtained from the local textile mill. $ZnCl_2$ (98 % purity) and HCl (37 % purity) were purchased from Qrec (Asia) Sdn. Bhd. All the chemicals used were analytical reagent grade.

2.2 Preparation of Zn-CTW

Firstly, the CTW was cut into small pieces about 1mm to 2 mm sizes and followed by oven drying at 150 °C for 12 h to achieve constant weight. In a typical catalyst synthesis via incipient wetness impregnation method, the CTW and $ZnCl_2$ were weighed at 2 g and 1.5 g, respectively. Then, CTW and $ZnCl_2$ were mixed in the 250 ml beaker with 100 ml of deionized water. The mixtures were stirred by a magnetic stirrer for 4 h and then placed in a drying oven at 120 °C for 12 h. The samples were marked as Zn-CTW-x, where x is the weight of impregnated $ZnCl_2$ (x = 0.0 g, 1.0 g, 1.5 g, 2.0 g).

2.3 Hydrothermal carbonization of Zn-CTW

Hydrothermal carbonization was performed based on the method Qi et al. [15]. In a typical experiment, the sample Zn-CTW-1.5 were dispersed in 60 mL of deionized water and ultrasonically agitated for 10 min at a room temperature of 25 °C. The mixture was then transferred to a 100 mL Parr batch reactor equipped with a heater and a programmable PID temperature controller. The reaction was carried out at 200 °C at a heating rate of 5 °Cmin^{-1} for 3 h with continuous stirring and self-pressurized at 15 -20 bar. At the end of the reaction, the heater was turned off, and the reactor was cooled to room temperature. The reaction mixture was then centrifuged to separate the liquid phase from the solid product. The solid black product, the hydrochars, was soaked in HCl solution (10 wt%) for 15 min to remove the residual metal salt and subsequently filtered through a 0.45 mm filter. The resultant hydrochars were repeatedly washed with deionized water until a neutral pH was obtained, followed by oven drying at 110 °C for 12 h. The hydrochars were marked as HC-Zn-CTW-1.5. The experiments were repeated for $ZnCl_2$ loading of x = 0.0 g, 1.0 g, 2.0 g. The parameter conditions for HTC reaction are selected based on reported works in the production of hydrochars, as shown in Table 1.

Table 1: Parameter conditions for HTC [15, 19]

Parameter Conditions	Value
Reaction Temperature (°C)	200
Residence Time (h)	3
Catalyst loading (g)	0-2

2.4 Characterizations of hydrochars

The elemental compositions (carbon, hydrogen, nitrogen) of hydrochars were determined by the elemental analyzer (Perkin Elmer Series, 2400). The oxygen content was calculated based on the difference in total compositions. The surface chemistry of hydrochars in terms of the presence of functional groups was qualitatively identified by fourier transforms infrared (FTIR) spectroscopy (Thermo Scientific Nicolet 6700) from 4000 cm^{-1} to 400 cm^{-1} with a resolution of

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4 cm^{-1}. Surface morphologies of hydrochars derived at different HTC conditions were examined by scanning electron microscope (SEM) FEI QuantaTM. Samples were placed in the sample grid, coated with gold-palladium for electron reflection and vacuumed prior to analysis.

3. RESULTS AND DISCUSSION

3.1 Effects of $ZnCl_2$ loading on H/C and O/C ratios of hydrochars

Figure 1 shows that hydrochars obtained at 1.5 g $ZnCl_2$ loading (HC-Zn-CTW-1.5) have the lowest hydrogen to carbon (H/C) ratio of 1.239, while the hydrochars obtained without $ZnCl_2$ loading (HC-Zn-CTW-0.0) has the highest value of H/C ratio of 1.638. Additionally, HC-Zn-CTW-2.0 and HC-Zn-CTW-1.0 have slightly lower H/C ratios compared to HC-Zn-CTW-0.0, which is at 1.620 and 1.624, respectively. Figure 2 indicates that HC-Zn-CTW-1.5 also has the lowest oxygen-to-carbon (O/C) ratio of 0.614, whereas HC-Zn-CTW-2.0 exhibits the highest O/C ratio of 0.925. Meanwhile, HC-Zn-CTW-1.0 dan HC-Zn-CTW-0.0 have slightly lower O/C ratios compared to HC-Zn-CTW-2.0, which is at 0.832 and 0.894, respectively. The findings suggest that 1.5 g $ZnCl_2$ loading produces hydrochars that are more suitable for solid fuel because low H/C and low O/C ratio are advantageous due to reduced energy loss, less smoke, and water vapor during burning. This is a result of the energy density of biomass feedstock being enhanced, where there were fewer low-energy H-C and O-C bonds and more high-energy C-C bonds [22]. Ameen et al. [23] stated that lower H/C and O/C ratios imply superior fuel attributes, whereas higher H/C and O/C ratios would produce more water vapor and smoke during burning, thus leading to more energy loss. The reduction in the H and O contents of hydrochars is mostly due to dehydration and decarboxylation reactions, while condensation and aromatization reactions result in the enrichment of C content [24]. Thus, when the C content increases, whereas the H and O content decreases, this results in a low value of the H/C and O/C ratio.

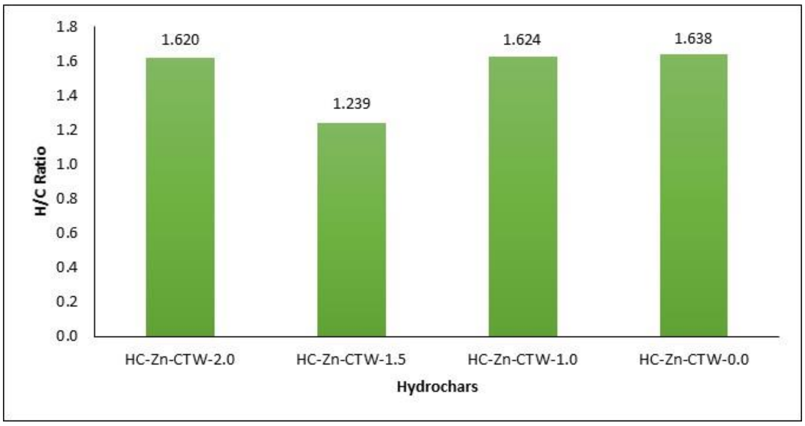

Figure 1: H/C ratio for hydrochars obtained at different $ZnCl_2$ loading

Dehydration and decarboxylation are the physical and chemical reactions that occur immediately after hydrolysis and entail the removal of water and carbon dioxide from the biomass matrix. The carbonization of biomass is then caused by the creation of hydronium ions from the developed acids, which lowers the H/C and O/C ratios [10]. The H/C and O/C ratios are important in determining the level of deoxygenation and the aromatic content during the hydrothermal carbonization reaction [4]. The increased H/C ratio indicates a reduced aromatic

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concentration in the hydrochars. This shows that 1.5 g of catalyst loading is better than the other catalyst loading because a lower O/C and H/C ratio is more favorable for generating a clean solid fuel.

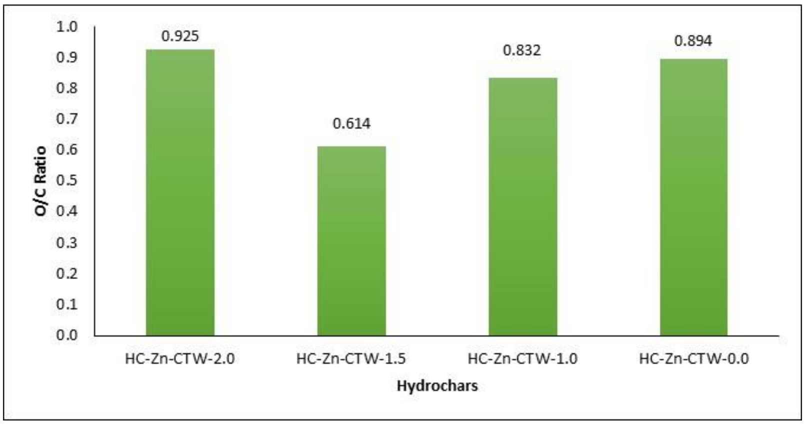

Figure 2: O/C ratio for hydrochars obtained at different $ZnCl_2$ loading

3.2 Surface functional groups of hydrochars obtained at different $ZnCl_2$ loading

Figure 3 shows the spectrum characteristics bands of organic compounds present in the hydrochars obtained at different $ZnCl_2$ catalyst loading, which are associated with the C-H and C-C bond stretching and bending vibrations. The bands at 1109 cm^{-1} and 1053 cm^{-1} are the stretching vibration of the C-O bond in the carbonyl group, which indicates the presence of carboxylic acids and esters formed in the hydrochars. Xu et al. [16] reported similar characteristics bands of C-O stretching in the carbonyl group from the hydrochars obtained via the hydrothermal carbonization process. Figure 3 also indicates distinct bands in the wavenumber regions 3300-3500 cm^{-1} that correspond to the O-H stretching vibrations, which include hydrogen bonding in water molecules [25]. The bands for HC-Zn-CTW-2.0 are less intense in contrast to HC-Zn-CTW-1.5, possibly due to the dehydration reaction occurring during the HTC process [25]. This agrees with the elemental results, whereby HC-Zn-CTW-2.0 has a higher H/C and O/C ratio compared to HC-Zn-CTW-1.5. Other than that, the spectrum shows no significant difference between the different catalyst loading.

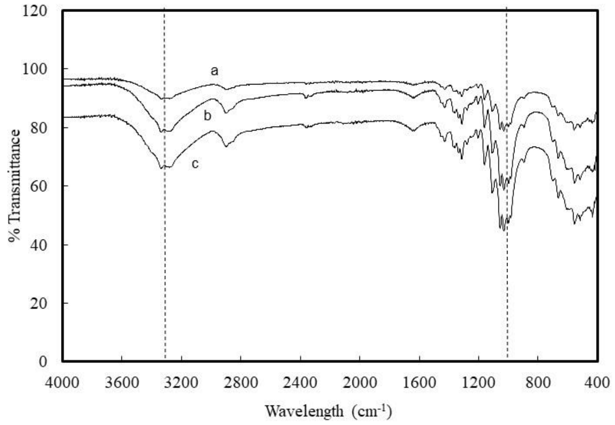

Figure 3: FTIR spectra for hydrochars obtained at different $ZnCl_2$ loading (a) HC-Zn-CTW-2.0, (b) HC-Zn-CTW-1.0, (c) HC-Zn-CTW-1.5

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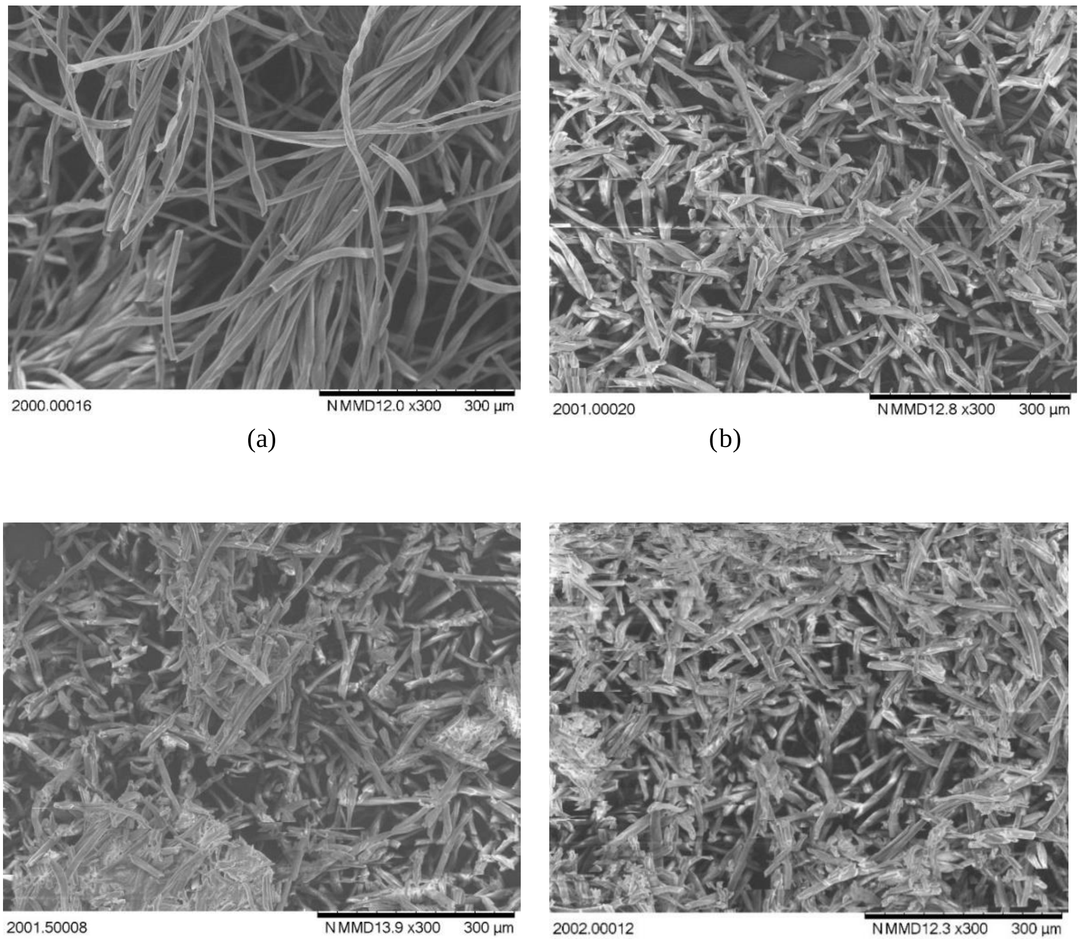
3.3 Surface morphologies of hydrochars obtained at different $ZnCl_2$ loading

Figure 4 (a) shows that the surface morphologies of the hydrochars obtained via HTC reaction without $ZnCl_2$ loading (HC-Zn-CTW-0.0) exhibit fine and smooth structures. However, the surface morphologies of hydrochars obtained via HTC reaction with various $ZnCl_2$ loading in Figure 4 (b), (c) and (d) reveal more irregular and rougher surfaces. The findings suggest that $ZnCl_2$ loading during the HTC reaction is important for the conversion of CTW biomass to hydrochars. Xu et al. [16] reported that the hydrochars surface became rough, which generally reflected the conversion of CTW during the HTC reaction. The raw biomass had generally flat, continuous surfaces, while the hydrochars surface had uneven, rougher surfaces and new microsphere formations that took varied forms and sizes [4]. Figure 4 (b), (c) and (d) also shows the formation of aggregated particles and reveal the breakdown of cellulose content in the CTW. The findings indicate distinct oligomers such as cellobiose, cellotriose, cellotetraose, and HMF were produced on the surface of the hydrochars as a result of the hydrolysis and dehydration reactions that occurred. Different particle-size hydrochar microspheres were generated with varying degrees of polymerization of these oligomers [18]. The morphologies show rougher surfaces for HC-Zn-CTW-1.5, which also correlate with the result on H/C and O/C ratio being the lowest among the obtained hydrochars.



(c) (d)

Figure 4: SEM images of (a) HC-Zn-CTW-0.0 at 300X magnifications, (b) HC-Zn-CTW-1.0 at 300X magnifications, (c) HC-Zn-CTW-1.5 at 300X magnifications, (d) HC-Zn-CTW-2.0 at 300X magnifications

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4. CONCLUSION

Hydrothermal carbonization (HTC) is one of the effective ways to convert waste from biomass into hydrochars, which is a value-added product. The study on the effects of $ZnCl_2$ catalyst loading on HTC of CTW shows that Zn-CTW-1.5 obtained hydrochars with the lowest H/C and O/C ratio values of 1.239 and 0.614, respectively, which are a good indication of solid fuel. The FTIR analysis indicates stretching vibration of the C-O bond, which are the carboxylic acids and esters formed in the hydrochars. The SEM analysis indicates irregular and rough surfaces, which are characteristics of hydrochars as opposed to smooth surfaces. It is concluded that Zn-CTW has the potential as a heterogeneous catalyst to produce hydrochars via hydrothermal carbonization. The significance of this study is that waste from biomass sources such as CTW can be converted to hydrochars, thus contributing towards waste to the energy recovery effort. It is recommended for further study on the other biomass sources utilizing $ZnCl_2$ as a catalyst in the HTC reaction.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this paper.

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