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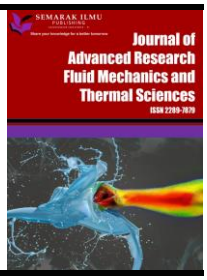

Synthesis of Hydrochars via Hydrothermal Carbonization of Zinc Chloride Activated Cotton Textile Waste

Ahmad Ikhwan Muaz Abd Rahman[1], Nur Alwani Ali Bashah[1], Wan Zuraida Wan Kamis[1,*], Norain Isa[1], Mohamed Syazwan Osman[1,2], Vicinisvarri Inderan[1], Moses Aderemi Olutoye[3], Azam Taufik Mohd Din[4]

[1] Chemical Engineering Studies, College of Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia
[2] EMZI-UiTM Nanoparticles Colloids & Interface Industrial Research Laboratory (NANO-CORE), Chemical Engineering Studies, Universiti Teknologi MARA, Cawangan Pulau Pinang, 13500 Permatang Pauh, Pulau Pinang, Malaysia
[3] Department of Chemical Engineering, Federal University of Technology Minna, Niger State, Nigeria
[4] School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

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ABSTRACT

Anthropogenic pollution from fossil fuel combustion due to increasing global populations and emerging industries poses a serious threat to the environment. Therefore, it is vital to explore alternative green energy sources. Hence, this study synthesized renewable solid fuel hydrochars by utilizing biomass of cotton textile waste (CTW) as feedstock. $ZnCl_2$ was selected as a catalyst due to its Lewis acid properties promoting hydrolysis and dehydration of raw materials towards hydrochar formation. The $ZnCl_2$-activated cotton textile waste ($ZnCl_2$-CTW) was prepared via the wet impregnation method at different $ZnCl_2$ loading. The hydrochars were synthesized via hydrothermal carbonization of $ZnCl_2$-CTW in a Parr batch reactor at the reaction temperature of 200 °C for 3 h. The hydrochars and CTW were characterized using a thermogravimetric analyser (TGA) to evaluate the proximate analysis, whereas an elemental analysis and determination of higher heating value (HHV) were conducted employing a CHNS analyser. The proximate analysis indicates the hydrochars volatile matter increases at higher catalyst loading, possibly due to the high content of bio-oil adsorbed on the hydrochars surface. The elemental analysis shows higher carbon and lower oxygen content for hydrochars compared to CTW, mainly due to the dehydration, decarboxylation, and aromatization reactions during HTC. Meanwhile, the HHV of hydrochars increases as catalyst loading increases to 1.5 g, which obtained the highest value of 18.41 MJ/kg, indicating good quality of solid fuel. This demonstrated that the $ZnCl_2$ catalyst was useful in improving the energy density of hydrochars. Overall, $ZnCl_2$ catalyst loading of 1.5 g has exhibited good performance in producing hydrochars via HTC of CTW. Thus, $ZnCl_2$-CTW has the potential to produce hydrochar suitable as solid fuel, contributing to the conversion of waste into energy and the preservation of the environmental.

* *Corresponding author.*
E-mail address: zuraida326@uitm.edu.my

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1. Introduction

The usage of fossil fuels has increased rapidly over the years due to the rise in global populations and anthropogenic activities, which result in the decline of energy resources [1]. Thus, suitable alternative energy is needed to offset declining natural resources. Biofuel, which can be produced from renewable resources, especially biomass, can provide similar energy to fossil fuels and positively influence climate change [2]. The biomass feedstock can be derived from many sources, such as plants, animals, and wastes. Over the years, due to population growth, improved quality of life, and the influence of fast-fashion, global fiber consumption is steadily increasing. This has resulted in an increased amount of textile waste, with the majority of the waste being disposed of [3]. Cotton textiles are among the most produced fiber-based-textile globally with annual production above 50 million tonnes. The textile products that become waste eventually end up in landfills or incinerated, causing environmental pollution. Cotton textile waste (CTW) mainly consists of cellulose with a small amount of pectin and protein, which constitutes a suitable feedstock for the production of biofuel. CTW can be utilized to produce hydrochars as a solid fuel that is renewable and environmentally friendly [4].

Hydrothermal carbonization (HTC) is a thermochemical process to produce hydrochars from biomass through hydrolysis, dehydration, decarboxylation, aromatization, and polymerization in an aqueous environment [5,6]. HTC is conducted at temperature ranges between 180°C and 300°C [7,8]. HTC is more advantageous for biomass conversion than pyrolysis because it can use biomass with high moisture directly without drying or treatment [9,10]. The presence of moisture is considered a favorable condition for HTC primarily due to the role of liquid water as a reactant and solvent medium for biomass hydrolysis to create sugar monomers, followed by dehydration and decarboxylation [11,12]. At high temperatures, the water can be more reactive and act as a non-polar solvent for HTC [13].

Catalyst assisted HTC able to enhanced biomass conversion to hydrochars. $FeCl_3$-assisted HTC could significantly increase the conversion of CTW to hydrochars with greater energy yield, and it also improved hydrophobicity while lowering HTC temperature [4]. The HTC of cellulose can be achieved at a reduced temperature of 200 °C [14]. Thus, the conventional HTC process is insufficient without a catalyst to produce high-energy hydrochars at lower reaction temperatures, as suggested by previous studies. Cellulose was the common biomass component used to produce hydrochars via HTC [10,15]. Catalyst assisted HTC able to increase the energy yield and conversion rate of the hydrochars. Several catalysts that have been utilized for hydrothermal carbonization reactions are iron (II) chloride [14], iron (III) chloride [4], sulfuric acid [16], and aluminium oxides [15].

Moreover, Lewis's acids catalysts are a suitable alternative to mineral acids due to the simplicity of metal salt recovery, which resulted in the HTC process being more environmentally friendly [14]. Metal salts such as $ZnCl_2$ have been used to activate biomass suitable for water treatment [17-19]. However, limited studies have been reported on the hydrothermal carbonization of biomass utilizing $ZnCl_2$ as a Lewis acids catalyst and characterizations of the hydrochars produced. Therefore, an attempt has been made in the present paper to study the synthesis of hydrochars via $ZnCl_2$ catalyst-assisted HTC.

Therefore, this paper makes a significant contribution through its examination of the synthesis of hydrochars via hydrothermal carbonization of $ZnCl_2$-activated cotton textile waste ($ZnCl_2$ – CTW). The $ZnCl_2$-CTW was prepared via the wet impregnation method at different $ZnCl_2$ loading. The hydrothermal carbonization process was conducted in a Parr batch reactor and was characterized via a thermogravimetric analyzer (TGA) and CHNS analyzer to evaluate the proximate analysis, ultimate analysis, and determination of higher heating value (HHV).

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 $ZnCl_2$-CTW

Firstly, the CTW was cut into small pieces about 1 mm to 2 mm, as shown in Figure 1, followed by oven drying at 110 °C for 12 h to achieve constant weight. In a typical catalyst synthesis, the CTW and $ZnCl_2$ were weighed at 2.0 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 110 °C for 12 h. The samples were marked as $ZnCl_2$-CTW-x, where x is the weight (g) of impregnated $ZnCl_2$ (x = 0, 1, 1.5, 2).

Fig. 1. CTW after cut into small pieces

2.3 Hydrothermal Carbonization of $ZnCl_2$-CTW

Hydrothermal carbonization was performed based on the method Qi *et al.,* [4]. In a typical experiment, the sample $ZnCl_2$-CTW-1.5 was dispersed in 60 ml of deionized water and ultrasonically agitated for 10 min at a room temperature of 25 °C. Subsequently, the mixture was transferred to a 100 ml Parr batch reactor equipped with a heater and a programmable PID temperature controller. The reaction was conducted at 200 °C, employing a heating rate of 5 °C min^{-1} for 3 h with continuous stirring while at an autogenous pressure of 15-20 bar. At the end of the reaction, the heater was turned off, and the reactor was cooled to room temperature. The product mixture was poured into a beaker and was labeled as HC-$ZnCl_2$-CTW-1.5.

2.4 Hydrochars Purification

The product mixture was poured into a tube and centrifuged at 350 rpm for 10 min to separate the liquid and solid products. Next, the solid product hydrochars were soaked in 60 ml of diluted HCl solution in a beaker for 15 min to remove the residual $ZnCl_2$. The hydrochars were then centrifuged to separate the HCl solution from the solid product. Then, the HCl solution in the tubes was removed and replaced with fresh deionized water to wash the hydrochars from residual HCl. The process of the centrifuge and changing the liquid in the tubes was repeated several times until the pH of the

hydrochars sample achieved a neutral pH of 7. After the neutralization process, the hydrochars were placed on a petri dish. The drying process in an oven was conducted at 110 °C for 5 h. Lastly, the dried hydrochars were stored in a closed container, as in Figure 2, and kept for further analysis.

Fig. 2. The dried hydrochars

2.5 Thermogravimetric Analysis

The thermogravimetric analyser (TGA) was used to analyse the hydcrohars. A sample weighing 10 mg was placed in TGA under nitrogen gas with a flow rate of 10 ml/min and a heating rate of 10 °C/min. The temperature was ramped up from 30 °C to 110 °C and was held for 10 min. After that, it was proceeded by ramping up the temperature from 110 °C to 850 °C and was held for 10 min.

2.6 Elemental Analysis and Hydrochars Yield

The CHNSO analyser was used to determine the carbon (C), hydrogen (H), nitrogen (N), sulphur (S) and oxygen (O) content in the hydrochars and CTW. For this analysis, a small amount, 0.5 g of each sample, was used. The energy density was determined by using the higher heating value (HHV). HHV is one of the key characteristics of fuels that explains their greater energy content and determines the effective use of biomass [20]. HHV, mass yield, and energy yield were calculated using Eq. (1), Eq. (2) and Eq. (3) [4], respectively.

$$\mathrm{HHV} = 0.335\mathrm{C} + 1.423\mathrm{H} - 0.154\mathrm{O} - 0.14\mathrm{N} \quad (1)$$

$$\text{Mass yield} = \frac{\text{Dry hydrochar weight}}{\text{Dry CTW weight}} \times 100\% \quad (2)$$

$$\text{Energy yield} = \frac{\text{HHV hydrochar}}{\text{HHV CTW}} \times \text{Mass yield} \quad (3)$$

3. Results

3.1 Thermogravimetric Analysis of Hydrochars

Figure 3 shows the TGA of hydrochars at different $ZnCl_2$ loading. The dehydration stage occurs between 30 °C and 110 °C, whereby the moisture evaporates, thus decreasing the sample weight. The results show a similar trend of weight reduction for hydrochars obtained from HTC at different $ZnCl_2$ loading. However, the highest weight percentage due to moisture content was the hydrochars obtained from HTC without catalyst (HC-$ZnCl_2$-CTW-0). This could be due to the low dehydration reaction of the cellulose biomass, resulting in hydrochars having high moisture content [4].

Dehydration is one process that occurs during the HTC reaction to remove water from the cellulose [11].

The devolatilization stage occurs from 110 °C to 850 °C [21]. Figure 3 shows that HC-$ZnCl_2$-CTW-0 has the smallest weight reduction compared to the other samples of HC-$ZnCl_2$-CTW-1, HC-$ZnCl_2$-CTW-1.5, and HC-$ZnCl_2$-CTW-2.

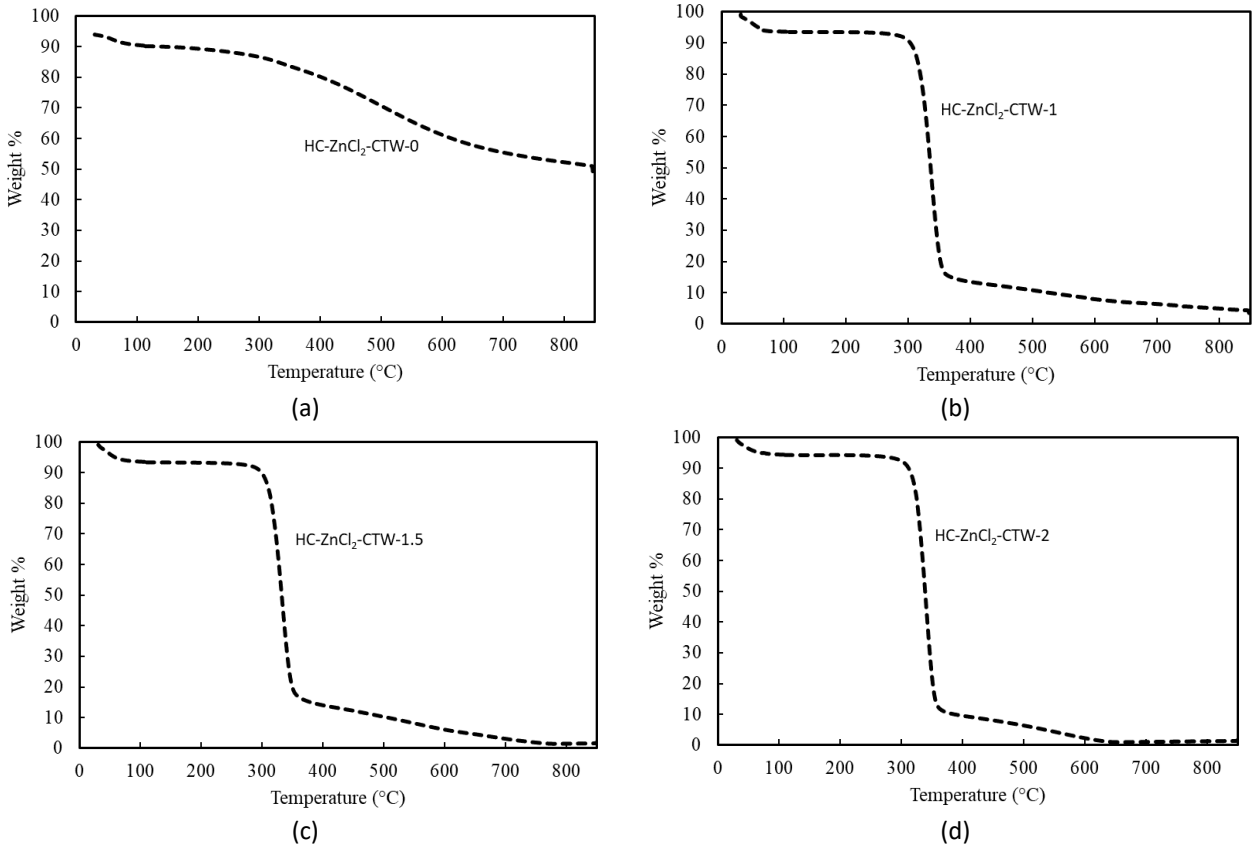

Fig. 3. Thermal gravimetric analysis of hydrochars (a) HC-$ZnCl_2$-CTW-0 (b) HC-$ZnCl_2$-CTW-1 (c) HC-$ZnCl_2$-CTW-1.5 (d) HC-$ZnCl_2$-CTW-2

As shown in Table 1, when $ZnCl_2$ loading increased, the volatile matter also increased. It was reported that with more catalyst loading, the volatile matter in hydrochars produced is decreased due to the hydrolysis and degradation processes of cellulose that occurred during the HTC process [15]. However, in this study, the increase in volatile matter is possibly due to traces of bio-oil produced during HTC with the $ZnCl_2$ catalyst. Some bio-oil that mainly consists of esters, fatty acids, and aromatic compounds may remain on the hydrochars surface, thus resulting in the high volatile matter [16]. At 850 °C and above, hydrochars combustion occurs where the fixed carbon content was studied [21]. The results show that with an increase in $ZnCl_2$ loading, the hydrochars decreased in fixed carbon content. Since the volatile matter content is high, the fixed carbon content is low for hydrochars produced from HTC.

Table 1
Moisture content, volatile matter, and fixed carbon of hydrochars

Sample	Moisture Content (%)	Volatile Matter (%)	Fixed Carbon (%)
HC-$ZnCl_2$-CTW-0	9.85	40.99	49.16
HC-$ZnCl_2$-CTW-1	6.53	90.06	3.41
HC-$ZnCl_2$-CTW-1.5	6.61	91.62	1.77
HC-$ZnCl_2$-CTW-2	5.73	92.74	1.54

3.2 Elemental Analysis

Table 2 shows the result of the CHNSO analysis on CTW and hydrochars at different $ZnCl_2$ loading. The findings indicate that the hydrochars have higher C content and lower O content than CTW. This is mainly due to the dehydration, decarboxylation, and aromatization reactions of cellulose in CTW during the HTC reaction [16]. Furthermore, as the $ZnCl_2$ loading increased from 0 g to 1.5 g, the C content in hydrochars also increased. The findings suggest that the $ZnCl_2$ catalyst can promote the degradation of cellulose during HTC. However, further increment of $ZnCl_2$ loading to 2 g (HC-$ZnCl_2$-CTW-2) caused further reaction of condensed carbon into organic acids, leading to decreased C content of hydrochars [4]. The sample HC-$ZnCl_2$-CTW-1.5 obtained the highest C content and the lowest O content at 51.78 % and 42.32 %, respectively. The finding indicates that 1.5 g of $ZnCl_2$ loading is the best condition to produce hydrochars. The increased C content in hydrochars with increased catalyst loading shows similar findings with other researchers [4,15,16]. Moreover, the hydrochars obtained in this study contain low N content at less than 1 %. The low N content in solid fuel is advantageous because it can lead to reduced emissions of NOx pollutants.

Table 2
Elemental analysis of CTW and hydrochars at different $ZnCl_2$ loading

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Sulfur (%)	Oxygen (%)
CTW	42.61	5.88	0.46	0.00	51.05
HC-$ZnCl_2$-CTW-0	43.91	5.90	0.08	0.00	50.11
HC-$ZnCl_2$-CTW-1	47.22	5.75	0.11	0.00	46.92
HC-$ZnCl_2$-CTW-1.5	51.78	5.38	0.52	0.00	42.32
HC-$ZnCl_2$-CTW-2	46.93	5.73	0.13	0.00	47.21

3.3 Energy density

Figure 4 shows the HHV for CTW and hydrochars obtained at different $ZnCl_2$ loading during HTC. HHV represents the heat generated by fully combusting a unit quantity of solid fuel. HHV can be described as energy density, which is the amount of energy released by a specific mass or volume of fuel [20]. The findings indicate that the HHV of hydrochar is higher than CTW; thus, producing solid fuel via HTC is feasible. As the $ZnCl_2$ loading increased from 0 g to 1.5 g, the HHV for the hydrochars also increased from 15.37 MJ/kg to 18.41 MJ/kg. This demonstrated that the $ZnCl_2$ catalyst was effective in improving the hydrochars fuel quality. However, HC-$ZnCl_2$-CTW-2 shows a decrease in HHV at 16.59 MJ/kg, possibly due to the further degradation of condensed carbon into organic acids, which decreased the C content [4]. The sample HC-$ZnCl_2$-CTW-1.5 gives the highest HHV of 18.41 MJ/kg, indicating that 1.5 g of $ZnCl_2$ loading is the best condition to produce hydrochars. The increase in catalyst loading enhanced the dehydration, decarboxylation, and aromatization reactions of cellulose in CTW during the HTC process [16].

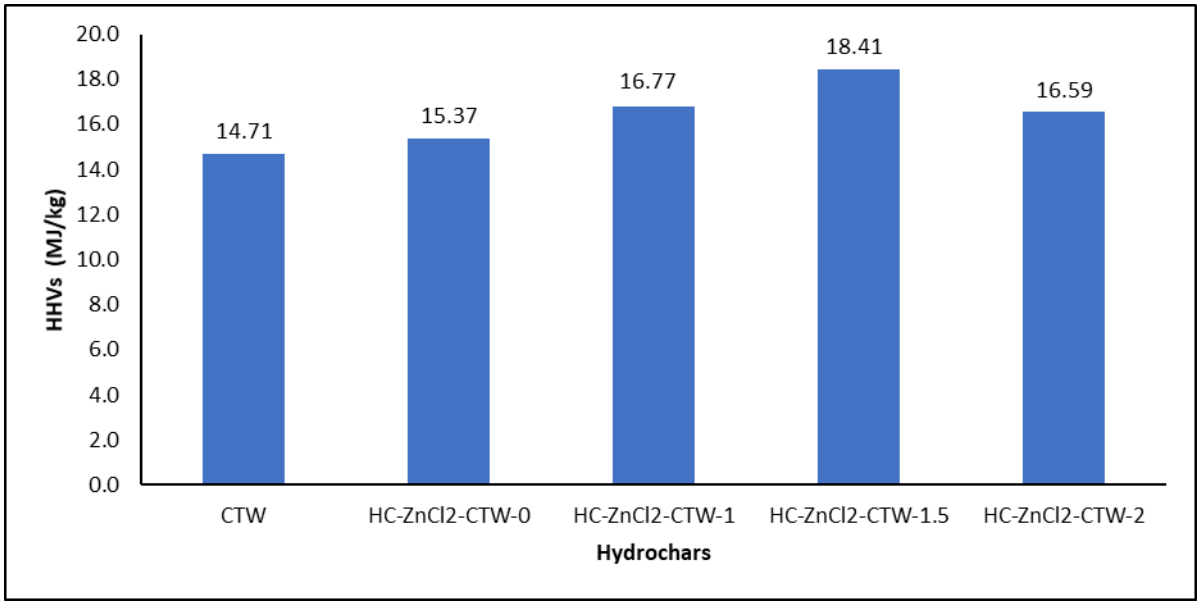

Fig. 4. HHV of CTW and hydrochars obtained at different $ZnCl_2$ loading

3.4 Mass Yield and Energy Yield

Figure 5 shows the mass yield and energy yield of the hydrochars. The mass yield of hydrochars decreased with increased $ZnCl_2$ loading. The decrease in mass yield could be attributed to the $ZnCl_2$ catalyst being added to the HTC process, which accelerated the degradation of cellulose in CTW and produced a large number of small molecules that were then condensed and polymerized to create high aromatic carbon ring structures. The highest mass yield is acquired from hydrochars obtained from HTC without catalyst loading. The finding indicates that 200°C is not a sufficient temperature for the uncatalyzed HTC process to degrade cellulose, and the structure remains in the hydrochars, thus causing the high mass yield. The sample HC-$ZnCl_2$-CTW-2 has the lowest mass yield, with 55.5%, because of the cellulose degradation and further condensation into organic acids during the HTC process [4]. The trends of energy yield and mass yield are similar, whereby the yield decreased with increased $ZnCl_2$ loading. The partial degradation of the condensed components of biomass could lead to a decrease in mass yield and a reduction in energy yield [16]. Furthermore, the difference between energy yield and mass yield was higher in hydrochars obtained from HTC with $ZnCl_2$ catalyst compared to uncatalyzed HTC. This suggests that the $ZnCl_2$ catalyst can promote the HTC process to produce hydrochars with higher energy density.

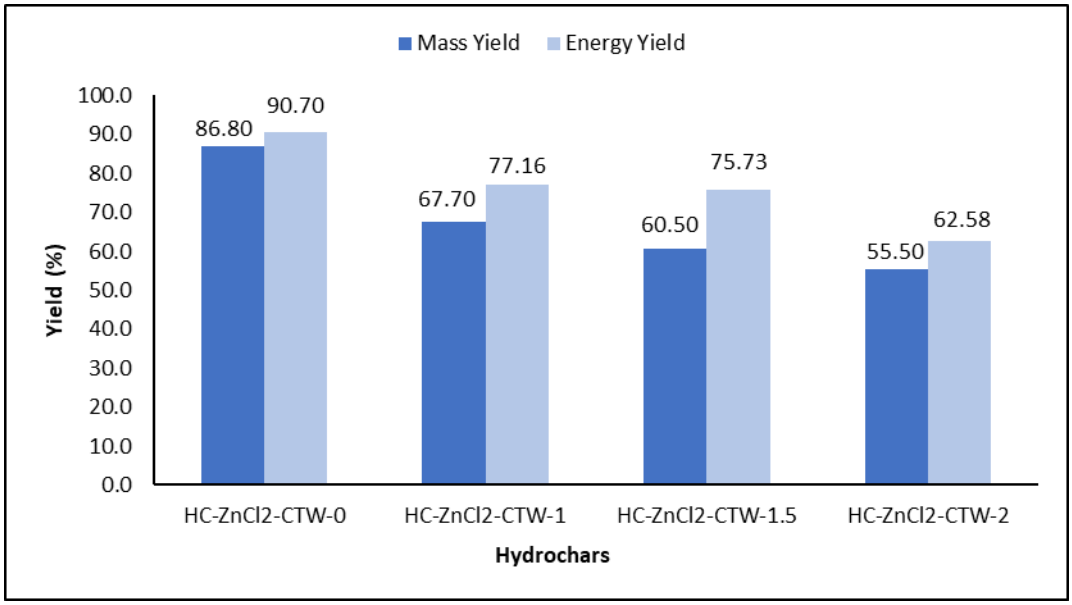

Fig. 5. Mass yield and energy yield of hydrochars obtained at different $ZnCl_2$ loading

4. Conclusions

Hydrothermal carbonization is one of the effective ways to convert waste from biomass into value-added product hydrochars. The study on the effects of $ZnCl_2$ catalyst loading on HTC of CTW shows that Zn-CTW-1.5 obtained hydrochars with the highest energy density with HHV of 18.41 MJ/kg, which is a good indication of solid fuel. Moreover, the highest C content and the lowest O content was HC-Zn-CTW-1.5, with a percentage of 51.78% and 42.32%, respectively. The results show higher carbon and lower oxygen content for hydrochars compared to CTW, indicating successful dehydration, decarboxylation, and aromatization reactions during HTC. Overall, $ZnCl_2$ catalyst loading of 1.5 g has exhibited good performance in producing hydrochars via HTC of CTW. The significance of this study is that waste from biomass sources such as CTW can be converted to hydrochars, thus contributing towards waste to energy recovery efforts and environmental preservation. The future recommendations are to study other fabric wastes than CTW as the biomass feedstock and effects of HTC parameters such as temperature and time.

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