Turning Coconut Residue into Hydrochar using Hydrothermal Carbonization

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Abstract. The use of renewable and sustainable energy resources is critical, especially considering the scarcity of fossil fuels and the need to combat air pollution. Various types of biomass feedstock, including coconut husk, have been studied in the past to convert into useful forms of hydrochar. However, no one had attempted to use coconut residue to produce hydrochar through hydrothermal carbonization. The goal of this study is to investigate the properties of synthesised hydrochar from coconut residue under various operating conditions in order to determine the highest yield of hydrochar produced prior to methylene blue degradation. Hydrochar was created from coconut residue using hydrothermal carbonization (HTC). The hydrochar was synthesised over a range of residence times of 6 hours, 12 hours, 18 hours, 24 hours, and 48 hours at a constant temperature of 200°C. Prior to the degradation of methylene blue, the properties of hydrochar were investigated using elemental analysis. The oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios for all hydrochars were 0.36-0.16 and 1.78-1.17, respectively. For all concentrations, the highest rate of methylene blue removal was approximately 70-80 percent. Overall, residence time had a minor impact on the chemical properties of hydrochars.

1. Introduction

Hydrochar is a two-phased char that contains both solid and liquid phases, making it one of the most competitive biomass energy sources. It's a high-value-added carbonaceous material with a lot of oxygenated functional groups that's made from either dry or wet biomass utilising water as a solvent medium.[1,2]. Because carbon-rich solid hydrochar has a similar physical structure and chemical properties as lignite, it can be used as a fuel to replace traditional energy sources.

Hydrothermal carbonization is a low-temperature, wet thermal conversion technique that is gaining popularity for producing hydrochar. Compared to common carbonization methods such as pyrolysis and gasification, HTC is operated at mild temperatures (180 – 350 °C) and autogenous pressures. In recent years, many substrates have been used as feedstock to obtain solid products namely municipal solid waste, biomass and sewage sludge. However, the reported physicochemical properties (yield, fixed carbon content, etc) of the derived hydrochar are different with varies in feedstock type and processing variables including carbonization temperature, residence time, pressure, solid load and solid/water ratio[1].

Over the last few years, countless different types of biomasses such as woody biomass [3,4], herbaceous biomass [5] and fruit biomass [6-8] were used for HTC. It has shown that hydrochar characteristics highly depend not only on operating conditions but also on the types of feedstocks [1, 9-]
It was discovered that lignocellulose material feedstocks will experience HTC reactions pathways such as hydrolysis, dehydration, decarboxylation, polymerization, aromatization, and solid-solid reactions because all lignocellulose materials are primarily composed of cellulose, hemicellulose, lignins, and some extractives with only minor differences in composition [6]. These indicate that interrelationships in hydrochar properties may be detected using different feedstock types.

Earlier, a study on HTC of kernel babassu coconut bran was done by Costa et al. [7]. In the synthesis process, the temperature was around 120 - 180°C with tR of 48 h and biomass to ratio of 10%. Research showed that the content of C increases and that of O decreases when the temperature rises. A decrease in the O/C and H/C ratios is seen as a positive change, as it means less water vapor, smoke, and wasted energy during the combustion process [7]. An experimental study on carbonization of corn cob was done with operating conditions of 250°C with intervals of 0.5 to 6 hours and 10% biomass to water ratio [8]. It was discovered that as time progresses, O and H concentrations decline. This means that both elements are converted into liquid H2O and gas H2S, and dehydration is extensive. Hydrochar yield did decline slightly over time regardless of residence time as reported by Gao et al. [10].

Arellano et al. further investigated the potential of corn cob-based hydrochar as an adsorbate for methylene blue and discovered that the adsorption performance of HTC decreased as the temperature increased [8]. In contrast, hydrochar synthesised at low temperatures has a high capacity for methylene blue adsorption. At lower temperatures, carbonaceous materials have smaller pore sizes, resulting in low adsorption capacity. The presence of polar functional groups derived from corn cob, which is the source of hydrochar, may also contribute to the lower adsorption. This is due to the intermediate polarity of methylene blue, which causes repulsion [8].

Coconut residue is the selected biomass feedstock in this study whereas hydrochar was produced using it via hydrothermal carbonization technique. Several characterization has been done in order to determine the optimum parameters for hydrochar production. Also, the potential of hydrochar as an adsorbent for degrading methylene blue is also elucidated in this work.

2. Materials and Method

Coconut residue was obtained from a local market, whereas methylene blue was obtained from Sigma Aldrich and used without further purification.

2.1. Biomass Feedstock Preparation

The coconut residue was dried at room temperature until it reached a constant weight before being stored in a sealed container for use in the next hydrochar synthesis.

2.2. Hydrothermal Carbonization Experiment

Hydrothermal carbonization was carried out through Hydrothermal Autoclave Reactor. 5g of coconut residue was weighed into a 100mL Teflon vessel with 50 mL of deionized water (DI water) filled in the vessel. The Teflon vessel was sealed airtight in the autoclave reactor. Then, the reactor was heated for 6 hours with temperature of 200°C and heating rate of 5°C/min. The reactor was cooled down to room temperature once the reaction is completed. The hydrochar produced was recovered by filtration using 0.45μm filter paper. The hydrochar was then washed for several times with DI water to remove the water-soluble volatile matter and oven-dried at 100°C for 24 hours. The experiment was repeated for 9,12, 18, 24 and 48 hours.

2.3. Methylene Blue Solution Preparation

A stock solution with 1000 M of methylene blue was prepared by mixing 1 g of methylene blue in 1 L of distilled water. Concentration of methylene blue was analysed using UV- Visible spectrometer (Cary 60, Agilent Technologies, USA) at the characteristic wavelength (λmax = 668 nm) for calibration purpose.
2.4. Characterization of Hydrochar

2.4.1. Determination of Hydrochar Yield

Hydrochar yield was calculated using Eq. 1 [11],

$$\text{Hydrochar yield (\%) = } \frac{\text{Mass of Dried Hydrochar}}{\text{Mass of Dried Coconut Residue}} \times 100\%$$

Eq. 1

Apart from that, determination of hydrothermal severity, \( R_0 \) is done for estimation of biomass degradation and conversion. The higher the \( R_0 \) indicates lower yield of hydrochar due to hydrolysis and degradation of hydrochar of cellulose and hemicellulose in biomass as suggested by Falco et al. [9]. The calculation is a function of combined effect of processing temperature, \( T \) and residence time, \( t_R \) based on Eq. 2 [9].

$$R_0 = t_R \times \exp\left[\frac{(T-100)}{14.75}\right]$$

Eq. 2

2.4.2. Determination of Hydrochar Chemical Composition

The chemical composition of yielded hydrochar was analysed via CHN Elemental Analyzer (Perkin Elmer 2400 Series II) to determine the contents of carbon, hydrogen and nitrogen in hydrochar. Elemental O content was calculated by subtracting \((100 - \text{C (percent) - H (percent) - N (percent) - S (percent) - Ash (percent)})\) on a dry-mass basis, with a maximum of 0.1g of each hydrochar required for the analysis.

2.4.3. Determination of Hydrochar as Adsorbate for Methylene Blue Removal

Hydrochar had a remarkable feature as an adsorbent for environmental contaminant due to substantial oxygen-containing functional groups on its surface as reported previously [13]. However, no previous studies on the adsorption of methylene blue by hydrochar produced from coconut residue have been conducted. As a result, an investigation into the rate of removal of methylene blue by hydrochar was carried out. In this study, four different concentrations of methylene blue were used, which were 50M, 100M, 150M, and 200M, respectively. All methylene blue concentrations were prepared using the dilution method in a volumetric flask to obtain a more accurate concentration of diluted methylene blue solution. The dilution calculation can be calculated using Eq. 3.

$$M_1V_1 = M_2V_2$$

Eq. 3

Where \( M_1 \) and \( V_1 \) is the concentration and volume of methylene blue stock solution while \( M_2 \) and \( V_2 \) is concentration and volume of desired concentration of methylene blue solution.

3. Results and Discussions

This study was solely focused on the effect of residence time, \( t_R \) namely 6, 12, 18, 24 and 48 hours, on the properties of hydrochar. The biomass-to-water ratio is set at 10%, and the temperature is set at 200°C. It was discovered that the coconut residue only decomposed into hydrochar after the sixth hour. This is because coconut residue requires a temperature greater than 200°C to break the bond and thus convert it to hydrochar.

3.1. Hydrochar Yield

According to Figure 1, it was observed that the yield of hydrochar was slightly reduced with longer residence time, \( t_R \). This demonstrated that hydrochar did not significantly affected by residence time as the yield was only drop approximately 4.6% from 6-48 hours. Reason of this is that at higher residence time, \( t_R \) lighter organic compounds and permanent gases are formed contributed to decline of hydrochar yield and escalate the carbon’s porosity [17].
This trend was also observed by Kalderis et al, who found that hydrochar produced after 6 hours of residence time showed only a slight decrease in hydrochar yield. [14]. This indicates that, the structural rearrangement only occurs in the first 6 hours and turn out to be a stable structure afterwards. Apart from that, hydrothermal severity $R_0$, was calculated and plotted in Figure 1 in the form of logarithmic. The purpose of defining $R_0$ was to evaluate the degree of degradation and conversion of biomass. Base from the figure, log $R_0$ was inversely proportional to hydrochar yield where log $R_0$ increased with residence time while the yield decreased which was same trend as suggested by Wang et al. 2018 [12]. Gao et al. reported that hydrochar yield is monotonically reduced with rising of severity factor which was due to hydrolysis and degradation of cellulose and hemicellulose in biomass [11]. As a conclusion, longer residence time, $t_R$ insignificantly affected the hydrochar yield as compared to elevating the temperature which is parallel with Zhang et al. where hydrochar produced from HTC of corn corb with different residence time (0.5-6 hours) does not shows significant effect on the yield of hydrochar with only 1.1% reduction was observed [6]. Besides that, long residence time at lower temperature also does not indicate that biomass is fully carbonized. However, the rate of carbonization can be elevated at longer residence time which means complete carbonization can be achieved by elevating the residence time at lower temperature but may took days as compared to elevating the temperature.

![Comparison of $R_0$ and Yield of Hydrochar](image1.png)

**Figure 1.** Severity factor vs. hydrochar mass yield at different residence times

![Van Krevelen Diagram](image2.png)

**Figure 2.** The O/C and H/C ratios for all hydrochars was plotted on Van Krevelen Diagram that adopted from Kambo & Dutta [2]

### 3.2. Chemical Composition of Hydrochar

Elemental analysis is a method to define the elemental composition of unknown substance. Determination of H and O content is crucial in order to obtain the elemental ratios of H/C and O/C. Both ratios are useful to identify the chemical transformation of coconut residue during hydrothermal carbonization (HTC). According to the results of table 1, the carbon content increases significantly from 6 to 18 hours and then slightly from 18 to 48 hours. The uptrend of carbon content is resulting from reactions occurred during HTC which is dehydration and decarboxylation reactions [7-9]. The slight increment may due to current temperature was insufficient to cease the bond of macromolecules of biomass to be degraded [12]. Thus, higher temperature or longer residence time may be needed to increase the carbon content of hydrochar. Besides that, it was observed that oxygen content was decreased when residence time, $t_R$ is increased. This phenomenon was also due to both dehydration and decarboxylation reactions during HTC as the combination of the two reactions brought to deoxygenating reactions [3]. As a result, the oxygen content of hydrochar decreased as the residence time increased.

Besides that, increment in nitrogen content was observed with increasing residence time. Supposedly, nitrogen content was decreased due to dissolution into processing liquid. Yet, the increment
of nitrogen content with residence time can be due to nitrogen content of coconut residue is removed by dissolution into hot water but it is retained in hydrochar due to longer reaction time. On the other hand, hydrogen content was inversely proportional to residence time. This can be explained by the occurrence of dehydration and decarboxylation reactions which removes both hydrogen (H) and oxygen (O) form coconut residue in the form of water [4].

| Table 1. Elemental Composition of Hydrochar at Different t_R |
|------------------------------------------------------------|
| Residence Time, t_R | 6 h | 12 h | 18 h | 24 h | 48 h |
| C (%)             | 60.76±0.01 | 65.20±0.01 | 67.32±0.01 | 67.52±0.01 | 67.47±0.01 |
| H (%)             | 9.00±0.01 | 7.53±0.01 | 7.02±0.01 | 6.83±0.01 | 6.57±0.01 |
| N (%)             | 1.09±0.01 | 1.10±0.01 | 1.18±0.01 | 1.23±0.01 | 1.30±0.01 |
| O (%)             | 29.15 | 26.17 | 24.48 | 24.42 | 24.66 |
| H/C               | 1.78 | 1.39 | 1.25 | 1.21 | 1.17 |
| O/C               | 0.36 | 0.30 | 0.27 | 0.27 | 0.27 |

O = 100 – (C+H+N)

Both H/C and O/C ratios of hydrochars decreased with increasing residence time. The decrease of H/C and O/C ratios was mainly because of dehydration and decarboxylation reaction during HTC [6, 10]. Reduction of H/C and O/C ratios indicate elimination of -CH3 and CO2 from biomass. High O/C ratio prompt to production of low carbonization rates of hydrochar and presence of polar functional group on hydrochars [10]. To visualized the degree of carbonization of hydrochar, a Van Krevelen diagram with H/C against O/C ratio was plotted (Figure 2). This diagram will function as an indicator where high ratio indicates presence of macromolecules (cellulose) while low ratio indicates presence of more condensed (aromatic) structure [3].

Corresponding to Figure 2, even though H/C was quite high, the result showed a decrease in H/C trend. Thus, lower H/C ratios and lower O/C ratios at longer residence times indicated an increase in condensed structure as well as the presence of macromolecules in the hydrochar. Aside from that, the coal band of all hydrochars except hydrochars at 6 hours was found to be like lignite, with H/C and O/C atomic ratios of lignite being typically 0.8-1.3 and 0.2-0.38, respectively, [18]. Hence, it was concluded that all hydrochars except the one produced at 6 hours were a low rank coal which is comparable to lignite. Thus, a good performance of co-combustion of hydrochars blended with coal can be achieved as these hydrochars has good compatibility with lignite. The trends of hydrochars produced is similar as the trend of hydrochar formed from Babassu kernel bran [7], corn cob [8] and bamboo [13] where all hydrochars shows reduction in both O/C and H/C atomic ratios due to deoxygenating reactions which is in parallel with results obtained from HTC of coconut residue.

3.3. Removal of Methylene Blue by Hydrochar

The results of the 50M hydrochar methylene blue removal produced during the 6-48 hour residence were studied. Figure 3 shows the results of dyes removed by hydrochar in 6 different time of residence from 6 - 48 hours with a 50 M methylene blue concentration, respectively. It was observed that the rate of removal was decreased with time which indicates that the methylene blue dye particles were capture
by active site of hydrochar. Based on the plotted graph, the highest rate of removal of all concentration was hydrochar produced at 24 hours. This may due to the carbon content of hydrochar at 24 hours was the highest which was approximately 67.52%.

Although the hydrochar produced after 48 hours is longer than that produced after 24 hours, the rate of removal was lower. This could be because hydrochar produced at 24 hours was in powder form, whereas hydrochar produced at 48 hours was in small granular form, as was done for the study of hydrochar structure. As a result, the adsorbent capacity was reduced because the smaller surface area of granular hydrochar at 48 hours reduced the adsorbent capacity.

On the other hand, it was observed that the dye removal rate was significantly increased at first few hours before reach equilibrium after approximately 5 h. This phenomena suggested that the high rate of adsorption in the beginning as adsorbents site is all vacant initially while decreasing adsorption rate might ascribed to diminish in magnitude of adsorbent’s vacant sites and dye concentration. Arellano et al. reported that, the mark down on rate of adsorption near the end of experiments denotes that monolayer formation of methylene blue onto adsorbent surface was possible to happened [8]. This occurrence may lessen the available active sites requisite for further adsorption after acquiring equilibrium.

**Figure 3.** Methylene Blue Removal at 50M Concentration against Time

**Conclusions**

In this research study of production of hydrochar at different residence time, the average yield of hydrochar was approximately 50% where the mass yield of hydrochar did not show significant changes with longer $t_R$ where the difference between mass yield of hydrochar with $t_R$ at 6 hours and 48 hours was around 4.6%. However, the hydrothermal severity, $R_0$ shows an uptrend with increasing $t_R$ which was accurate as $R_0$ increase would cause diminished on mass yield of hydrochar. In this study, the C content of hydrochars increased with longer $t_R$ due to dehydration and decarboxylation reactions in the autoclave reactors. The C content was increased significantly at first 18 hours but then increased slightly after 18 hours may due to operating condition was insufficient to break the macromolecules. Overall, the highest MB removal was hydrochar produced at 24 hours which was approximately 80% with C content of 67.52%.

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