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## Hydrothermal carbonization of waste biomass for energy generation

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### Abstract

In this study, hydrothermal carbonization was used to upgrade waste biomass at temperatures ranging from 150 to 375 °C and a residence time of 30 minutes. The kinetics of hydrothermal carbonization was investigated and fuel properties of produced hydrochars were evaluated. The kinetic study indicated that hydrothermal carbonization of biomass followed first-order reaction rate with the apparent activation energy of 67.41 and 179.54 kJ/mol for coconut fiber and 59.18 and 173.70 kJ/mol for eucalyptus leaves within the temperature ranges of 150-300 °C and 300-375 °C, respectively. Hydrothermal carbonization narrowed the differences in fuel properties among different biomass feedstocks. The fuel qualities of hydrochars were significantly improved: increased ignition temperatures and elevated combustion temperature regions compared to raw biomass feedstock. The present study showed that hydrothermal carbonization was a promising conversion process for the production of the hydrochars which had increased fuel qualities compared to raw biomass.

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### 1. Introduction

The application of biomass-derived energy is gaining much importance due to the decreased supply of fossil energy and growing environmental concerns. Among biomass-to-energy conversion methods, direct combustion and co-combustion with low rank coals are widely investigated, as these methods have less risk, are less expensive, and have the highest potential among short term options for realizing biomass

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energy utilization [1]. Several reviews on biomass combustion for heat generation conclude that direct combustion is not a satisfying option owing to inherent properties of biomass feedstocks such as high moisture and oxygen contents, and high alkaline earth metal content [1-3]. To overcome these problems, it is necessary to pre-treat or modify the biomass feedstock prior to combustion to homogenize different biomass feedstocks into a form similar to coal to accommodate existing coal-fired plants.

Hydrothermal treatment offers significant advantages for biomass conversion including the lack of an energy-extensive drying process, high conversion efficiency and relatively low operation temperature among thermal methods. In our previous study, the hydrochar has high energy density and its fuel quality was similar to that of lignite [4]. Realizing high-value application of hydrochar may provide some advantages and a viable option for biomass energy recovery.

The knowledge of reaction kinetics is vital to design and operate the reactors efficiently. Therefore kinetic analysis should be performed for better understandings of reaction characteristics of hydrothermal carbonization. However, the kinetics of HTC is scarcely reported [5-7]. In addition, as a solid fuel, only little information was available about combustion characteristics of the hydrochars [4,8].

In the present study, several hydrochars from waste biomass (coconut fiber and dead eucalyptus leaves) were produced under different carbonization conditions. The kinetics of the carbonization process was examined to better understand the conversion of biomass feedstocks and combustion characteristics of resultant hydrochars were investigated to evaluate the feasibility for solid fuel application.

## 2. Experimental

### 2.1. Materials

Coconut fiber and eucalyptus leaves were selected as the representative waste biomass due to their high production potential in Singapore. The biomass was crushed to less than 5 mm and then dried at 105 °C for 24 h for subsequent hydrothermal carbonization. The results of the ultimate and proximate analysis of coconut fiber and leaves are shown in Table 1.

Table 1. Proximate and ultimate analysis of coconut fiber and eucalyptus leaves

	Coconut fiber	Eucalyptus leaves
Ultimate analysis (db, %)		
C	47.75	46.96
H	5.61	6.22
N	0.90	1.23
S	0.23	0.77
O*	45.51	44.83
Proximate analysis (db, %)		
Volatile matter	80.9	79.2
Fixed carbon*	11.0	10.3
Ash	8.1	10.5

\*Calculated by difference.

### 2.2. Hydrochar preparation

The hydrochar was prepared in a laboratory scale semi-batch 500-ml Parr autoclave reactor (USA). Around 10 g of biomass (coconut fiber/eucalyptus leaves) was loaded with 100 ml de-ionized water into

the reactor and the autoclave was heated to desired temperature (150-375 oC). The reactor was held at final temperature for 30 min and then quickly cooled down to room temperature. The hydrochar was recovered as solid residue by vacuum filtration and dried in an oven at 105 oC for 24 h. The hydrochar sample was designated as “C-xxx” or “E-xxx”, where the C and E referred to respective hydrochars derived from coconut fiber and eucalyptus leaves and “xxx” shows centigrade temperature of hydrothermal carbonization.

### 2.3. Characterization

Elemental analysis (C, H, N and S) was determined on VarioMacro Cube Elementar (USA). The proximate analysis was conducted using 5E-MAG6600 Automatic Proximate Analyzer (China). Combustion analysis was conducted on a differential thermogravimetric analyzer TQ-500 (USA), with which weight loss and rate of weight loss of the sample as functions of time or temperature were recorded continuously in the range of room temperature to 800 oC. The experiments were carried out at atmospheric pressure, under air atmosphere at a linear heating rate of 20 oC/min. In order to eliminate mass and heat transfer effects, high air flow rate (150 ml/min) and small mass (around 10 mg with the particle size less than 150  $\mu\text{m}$ ) were used in combustion experiments.

## 3. Results and discussion

### 3.1. Hydrochar yield

Hydrochar yield as a function of hydrothermal temperature is shown in Fig. 1. Temperature plays a vital role in the hydrochar yield; similar trends of hydrochar yield vs. temperature were observed for coconut fiber and eucalyptus leaves. The hydrochar yield decreased rapidly with increasing temperature in the temperature range from 150 to 300 oC, followed by a further gradual decrease to 35.3% and 28.1% for coconut fiber and eucalyptus leaves up to 375 oC, respectively (C-220, 250, 300, 350 and 375 samples and E-200, 250, 300, 350 and 375 samples were selected for the following combustion analysis).

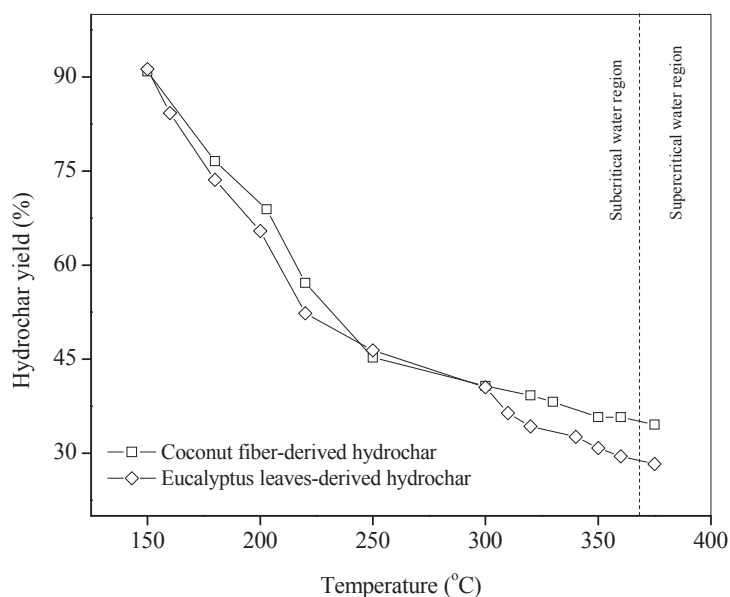


Fig. 1. Effect of hydrothermal temperature on the hydrochar yield of coconut fiber and eucalyptus leaves

### 3.2. Kinetic study of hydrothermal carbonization

A first-order kinetic reaction is the most frequently used assumption for solid fuel decomposition/combustion [6,9]. Therefore, in present study hydrothermal carbonization of biomass was fitted to first-order reactions. The reaction equation can be described by the following formula:

$$\frac{da}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-a) \quad (1)$$

where E is apparent activation energy; A is pre-exponential factor; T and t are absolute temperature and time respectively; R is the gas constant and a is weight loss which is calculated by

$$a = \frac{m_0 - m_t}{m_0 - m_f} \quad (2)$$

where  $m_0$  is the original weight of the biomass/biochar;  $m_t$  and  $m_f$  are the weight at time t and final temperature, respectively.

As for a constant heating rate  $\beta = dT/dt$ , the equation (1) can be rearranged as

$$\ln\left[-\frac{\ln(1-a)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (3)$$

As mentioned, the hydrochar yield decreased significantly with elevated temperature in the range of 150-300 oC, and further decreased up to 375 oC. According to the different reaction rates above or below 300 oC, the temperature range was divided into range 1 (150-300 oC) and range 2 (300-375 oC) and the kinetic parameters were calculated separately within these ranges.

If hydrothermal carbonization of biomass follows a first-order reaction mechanism, then the plot of  $\ln[-\ln(1-a)/T^2]$  versus  $1/T$  will give a straight line. From the slope, E/R, the apparent activation energy can be obtained and by taking the absolute temperature at which  $m_t = (m_0 - m_f)/2$  in the intercept of equation (3), the pre-exponential factor A can be calculated.

Plots of  $\ln[-\ln(1-a)/T^2]$  against  $1/T$  are shown in Fig. 2; the regression functions are obtained by a linear fitting method. The high correlation coefficients ( $R^2$ , presented in Table 2) indicate that the first-order reaction mechanism can well describe hydrothermal carbonization of coconut fiber and eucalyptus leaves within both temperature ranges. However, there are significant differences in the apparent activation energies for hydrothermal carbonization in the different temperature ranges for both coconut fiber and eucalyptus leaves. The coconut fiber had activation energies of 67.5 and 179.5 kJ/mol while the leaves had 59.2 and 173.7 kJ/mol for temperature ranges 1 and 2 respectively. Consistent with the FT-IR and  $^{13}C$  NMR analyses, the hemicellulose was decomposed first at lower temperatures (less than 250 oC) followed by cellulose which decomposed completely at 300 oC under hydrothermal conditions. For the lignin, at temperatures lower than 300 oC, only melting would occur instead of degradation. In the present study, decomposition of hemicellulose and cellulose, and carbonization of lignin occurred primarily at lower temperatures (temperature range 1). Therefore the apparent activation energy of temperature range 1 was the combined activation energy of hemicellulose and cellulose, while the activation energy of temperature range 2 was mainly for lignin. Due to the large difference between carbohydrates (hemicellulose and cellulose) and lignin, the reactions that occurred were quite different between temperature ranges 1 and 2, resulting in different apparent activation energies. In addition, the difference

of apparent activation energies could also be due to decrease in the dielectric constant of water as it approaches the supercritical point, where water behaves more like a non-polar solvent.

Competing reactions such as condensation, depolymerization, and polymerization during hydrothermal treatment of biomass also occur. Depolymerization reactions are believed to dominate at low temperature, while polymerization and aromatization reactions dominate at high temperatures [10,11]. As a consequence, different apparent activation energies result from the different reactions in these two temperature ranges.

The apparent activation energies obtained in the present study in temperature 1 were lower than those in previous reports [6,7]. This is possibly due to different properties of the hot-pressurized water, which are highly dependant upon the exact temperature and pressure being used [12]. Also, use of different biomass feedstocks may be a reason for the difference in activation energies [7].

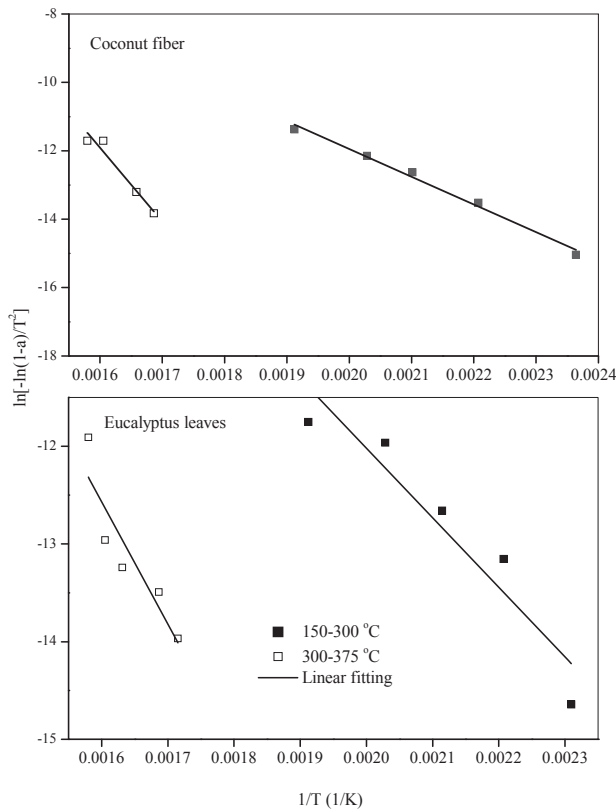


Fig. 2. Linear fitted plots for hydrothermal carbonization using first-order kinetics model at temperature ranges of 150-300 °C and 300-375 °C

### 3.3. Combustion behaviour of hydrochar

Fig. 3 shows the DTG curves for the coconut fiber, eucalyptus leaves and their derived hydrochars, with the combustion parameters summarized in Table 3. From the curves, it can be seen that the combustion behaviour of the biomass changed significantly after hydrothermal carbonization, especially

for the coconut fiber. For coconut fiber, a sharp DTG peak was observed centered at about 295 oC and a weight loss of 82% was measured at 326 oC, where significant weight loss was no longer detected. The combustion of coconut fiber involves mainly volatile matter combustion, which was ignited at a low temperature of 273 oC due to the high reactivity of volatile matter. The rapid weight loss of coconut fiber within a short time at the lower temperature range implies that there was incomplete combustion with low efficiency and high pollutant emission (CO and PAH) [1].

Table 2. Kinetic parameters for hydrothermal carbonization of coconut fiber and eucalyptus leaves.

Biomass	Temperature (°C)	Equation	R <sup>2</sup>	E (kJ/mol)	A
Coconut fiber	150-300	Y = -8107.5 x + 4.27	0.9908	67.5	4.08E+12
	300-375	Y = -21595x + 22.64	0.9549	179.5	1.23E+21
	150-300	Y = -7118.1x + 2.22	0.9026	59.2	4.38E+11
Eucalyptus leaves	300-375	Y = -20893x + 21.37	0.9924	173.7	2.05E+20

Compared to coconut fiber, the reactivity of the hydrochar decreased, resulting in a higher ignition temperature and combustion in a wider temperature range. The elevated combustion temperature with high weight loss rate implies improved combustion safety, increased combustion efficiency and decreased pollutant emission. These combustion characteristics are significant improvements over raw biomass feedstock as a fuel [1-3].

Among all coconut fiber-derived hydrochars, C-375 (produced from supercritical water) was unique with the lowest maximum weight loss rate and burnout and the highest ash content. In the DTG curve of C-375, a wide peak with maximum weight loss rate (0.47 %/oC) was observed at 505 oC and a minor weight loss was also present at 728 oC which was attributed to the decomposition of the ash content. Similar results were also observed for eucalyptus leaves and leaves-derived hydrochars. For the raw eucalyptus leaves, two separated peaks were observed due to the large differences in reactivities of the components. Around 60% weight loss was observed to occur at 360 oC due to the high reactivity. After hydrothermal treatment, the height of the first peak in the DTG curve decreased and the maximum weight loss rate shifted to the second peak (0.82 %/ oC for leaves and higher than 0.98 %/oC for the biochars except L-375). Among all leaves-derived hydrochars, the maximum weight loss rate was achieved in E-250 (similar to C-250). E-375 has the lowest burnout and widest combustion range beyond temperature 605 oC.

Table 3. Combustion parameters of biomass feedstocks and their derived hydrochars.

Sample	T <sub>i</sub> (°C)	T <sub>m</sub> (°C)	T <sub>b</sub> (°C)	R <sub>max</sub> (%/°C)
Coconut fiber	273	295	326	2.39
C-220	295	450	472	1.64
C-250	372	436	472	1.71
C-300	400	458	478	1.67
C-350	410	451	512	0.94
C-375	393	505	580	0.47
Eucalyptus leaves	253	312	456	0.82
E-200	288	414	449	1.59
E-250	288	423	445	1.97
E-300	374	417	449	1.15

E-350	369	410	470	0.98
E-375	428	522	581	0.55

Ti = ignition temperature; Tb = burnout temperature; Di = ignition index.

Additionally, by comparing the combustion behaviors of the hydrochars, similar combustion behaviors were observed. Hydrothermal carbonization has the ability to homogenize the different biomass feedstocks considerably, which increases the potential for biomass utilization. At supercritical conditions, the low combustion reactivity together and low hydrochar yield showed that very high temperatures and pressures were not favorable for hydrochar biofuel production from biomass [12].

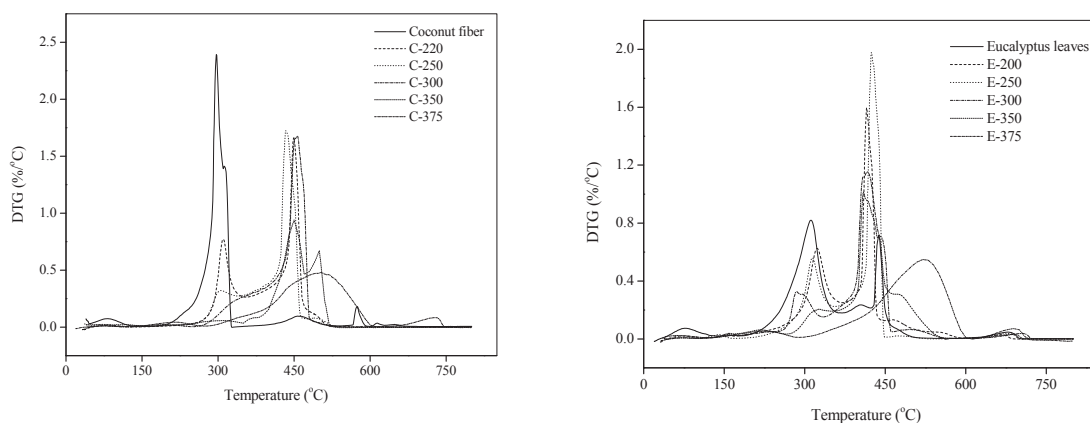


Fig. 3. DTG curves of coconut fiber, eucalyptus leaves and their derived hydrochars.

#### 4. Conclusions

Hydrothermal carbonization was able to homogenize biomass feedstocks of different origins and hydrochars with improved fuel qualities were successfully produced from hydrothermal carbonization of waste biomass. The hydrothermal carbonization of both coconut fiber and eucalyptus leaves was well described by first-order kinetics. Large differences in apparent activation energies in temperature ranges of 150-300 °C and 300-375 °C were ascribed to different carbonization reactions occurring in these ranges. For coconut fiber, apparent activation energies of 67.5 and 179.5 kJ/mol were obtained over the 150-300 °C and 300-375 °C ranges. For eucalyptus leaves, the apparent activation energies were 59.2 and 173.7 kJ/mol.

The combustion behaviours of hydrochars were distinct from raw biomass, with increased maximum weight loss rate, elevated ignition temperature and wide combustion ranges at higher temperatures. This combustion behaviour suggests that the produced hydrochars are appropriate for combustion or co-combustion with lignite in existing coal-fired boilers for heat generation.

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