

Article

Characteristics of Hydrothermal Carbonization Hydrochar Derived from Cattle Manure

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Abstract: The characteristics of hydrothermal carbonization hydrochar derived from cattle manure including excrements and lignocellulosic biomass were analyzed. The effects of hydrothermal carbonization were evaluated by varying the reaction temperatures in the range of 180–240 °C. The hydrochars were evaluated with respect to their usefulness as renewable fuels via physicochemical analysis and pyrolysis processes. As reaction temperatures increased, the fractions of fixed carbon in proximate analyses, carbon elements in ultimate analyses, and higher heating values of hydrothermally carbonized biochars increased in correlation with the primary reactions of coalification. Various correlations were derived with the characteristics of hydrochars in order to be utilized for operating and designing HTC reactors for cattle manure. The correlation between the O/C and H/C ratios was deduced on the basis of a van Krevelen diagram. The interaction equation was represented with the increased fraction of HHV compared to the reaction temperature of hydrothermal carbonization. The ultimate correlation for the estimation of higher heating values was suggested for HTC hydrochars. Moreover, the pyrolysis characteristics and kinetic parameters of the cattle manure and hydrochar were deduced by utilizing a multi-step kinetic model scheme. As the HTC reaction temperature increased, the global activation energy and the pre-exponential factors of hydrochars decreased in the low-temperature section and increased in the high-temperature section.



Citation: Song, E.; Park, S.; Han, S.; Lee, E.; Kim, H. Characteristics of Hydrothermal Carbonization Hydrochar Derived from Cattle Manure. *Energies* **2022**, *15*, 9195. <https://doi.org/10.3390/en15239195>

Academic Editor: Dimitrios Kalderis

Received: 17 October 2022

Accepted: 1 December 2022

Published: 4 December 2022

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Keywords: hydrothermal carbonization (HTC); cow manure; hydrochar; thermogravimetric analysis (TGA)

1. Introduction

In South Korea, cattle manure generation is estimated at 62,987 m³/day, which accounts for the highest ratio of 35.3% among total livestock manure (178,378 m³/day). Ninety-four percent (59,067 m³/day) of cattle manure is composted (self-treatment) [1]. The pollution of drinking water sources by cattle manure compost leads to serious social problems. In particular, investigations conducted by the government observe that severe algal blooms occur in Daecheong Lake every year in South Korea, caused by cattle manure. In many cattlesheds, particularly those upstream of the Daecheong Dam, cattle manure is sprayed on farmlands as fertilizer. Then, these are washed away by rainwater during rainy seasons, and the water flows into Daecheong Lake, causing algal blooms. In order to solve this problem, the government has been collecting cattle manure, producing composts with them, and supplying them to farms, but there is a lack of demand, and problems such as excessive nutrients in the soil persist [2]. Therefore, the fundamental treatment of cattle manure and a diversification of their treatment methods are urgently needed.

The South Korean government announced a policy to increase the share of renewable energy generation to 63.8 GW or 20% of total energy generation by 2030 [3]. Consequently, investments and research and development on wind, small hydro, hydrogen, and biomass power generation are actively made and conducted. The supply

cost of renewable energy is higher than fossil fuels and nuclear energy in general, and the competitiveness of renewable energy needs to be improved by increasing economic efficiency via research and development. Among the livestock manure and agricultural and livestock waste biomasses in South Korea, the energy potential of cattle manure is 780,000 toe/year, which accounts for 15.2%, and it is the second highest of all agricultural and livestock waste biomasses. In cases where energy is produced using cattle manure as a raw material, it is expected that up to 12% of the renewable energy goal of 20% could be met [4]. Several studies have been conducted to investigate the energy potential and usability of cattle manure [5–7].

Hydrothermal carbonization (HTC) is a thermochemical conversion process for transforming wet biomass feedstock into solid fuel as property of coal [8]. The HTC process originated from research studies to clarify the process of coal generation behavior [9]. It is mainly operated in a temperature range of 180–220 °C under subcritical water in saturated pressure conditions. HTC is one of the more promising processes for treating organic wastes, such as sludge, food wastes, and livestock manure, which have high moisture contents. It is a highly economical process because energy consumption is greatly reduced compared to dry processes [10]. The ionic constant of water increases greatly in the reaction condition of HTC. Water in this state behaves similarly to a non-polar solution or ion and acts as a natural acid or base catalyst. The main mechanisms of this process comprise hydrolysis, dehydration, decarboxylation, polymerization, aromatization, and condensation. By the dominant reactions, H₂O and CO₂ break away from hydroxyl, carboxyl, and carbonyl groups. The oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios of solid products decrease compared to feedstock, and as the hydrophilic groups decrease, the hydrophobicity increases and the heating value of hydrochar increases [11]. As a result, the physical dewaterability of HTC reaction products improves greatly. This subsequently lowers the energy consumption for removing water and significantly increases the energy density of hydrochar, thus greatly improving the value of hydrochar as a solid fuel.

In this study, the hydrochars of cattle manure were produced via HTC at different temperatures. The physicochemical characteristics of hydrochars were compared via ultimate analysis, proximate analysis, and heating values. The various correlations were derived with the characteristics of hydrochars to be utilized for operating and designing an HTC reactor for cattle manure. The correlation between the O/C and H/C ratios was deduced on the basis of a van Krevelen diagram. The interaction equation was represented with the increased fraction of HHV compared to the reaction temperature of hydrothermal carbonization. The ultimate correlation for the estimation of higher heating values was suggested for HTC hydrochars. The pyrolysis characteristics of hydrochar were investigated by thermogravimetric analyses. The kinetic analysis of the pyrolysis reaction was conducted using a global multi-step model, and major kinetic parameters were derived. The pyrolysis characteristics of hydrochars derived from cattle manure were fully utilized by applying the basic data on these to the fuel production system.

2. Materials and Methods

2.1. Cattle Manure

Cattle manure used in this work was collected from a cattleshed in Icheon-si, South Korea. The feedstock contains a substantial amount of bedding material, such as sawdust, straw, wood shavings, or spilled hay. Proximate, ultimate, and heating values of the raw material are presented in Table 1.

Table 1. Proximate, ultimate, and calorific analysis of feedstock and HTC samples.

Descriptions	Cattle Manure (Raw)	CM Hydrochar (180 °C)	CM Hydrochar (200 °C)	CM Hydrochar (220 °C)	CM Hydrochar (240 °C)
Proximate analysis (wt %, d.b. ¹)					
Moisture	0.50	0.17	0.17	0.15	0.13
Volatile matter	69.30	66.37	64.31	63.79	48.84
Fixed carbon	19.80	22.73	24.73	24.81	29.05
Ash	10.40	10.73	10.79	11.24	21.98
Ultimate analysis (wt %, d.b. ¹)					
Carbon	44.65	48.34	50.01	52.18	55.13
Hydrogen	5.62	5.61	5.52	5.52	5.28
Oxygen	34.39	33.85	32.15	30.96	21.03
Nitrogen	2.39	2.09	2.90	2.43	3.05
Sulfur	0.23	0.00	0.00	0.00	0.00
Calorific value (MJ/kg, d.b. ¹)					
HHV	18.91	20.13	22.34	22.76	24.14

¹ A dry basis.

2.2. Hydrothermal Carbonization

The HTC experiments were performed in a custom-built 3 L, high-pressure batch reactor. The reactor is equipped with a magnetic drive agitator, thermometers, pressure gauges, a watt meter, a cooling system, and a programmable logic controller. In each experiment, 1000 g of feedstock and distilled water were loaded into the reactor with a mass ratio of 9:1. The reactant was stirred continuously at 250 rpm so that it could carry out uniform heat transfers from an external jacket on the batch vessel. The HTC process was performed at 180, 200, 220, and 240 °C. The reaction time was an hour and a half, including the temperature-rising step of an hour and the retention of the target temperature for 30 minutes. After processing, the reactor cooled to room temperature and the pressure decreased to ambient levels. For all the operating temperatures, the heating time was constant. The heat demand for the process was provided by a heating jacket, which consisted of electric resistance wire elements surrounded by ceramic fiber insulation and an outer steel cover. The required temperature inside the reactor during the period was maintained with a proportional integral derivative controller. The heating process was achieved by means of a programmable logic controller. Therefore, the heat-up time for different HTC temperatures was constant. Thus, the characteristics of reaction temperature could be investigated excluding the effect of heating rate. All experiments were conducted more than three times to achieve reproducibility. Thereafter, the HTC products of solid and liquid mixtures were separated using 5 µm filter paper. Finally, the solid product was dried in a drying oven at 105 °C for 24 h.

2.3. TG Run for Pyrolysis Analysis

The TG analysis of the pyrolysis behavior was carried out with a thermogravimetric analyzer (NETZSCH, STA 449 F5). For each run, 1 ± 0.2 mg of each sample was prepared. The TG results provided a function of temperature for the cattle manure and hydrochar samples with non-isothermal conditions, and a controlled heating program (10 min^{-1}) was used from room temperature up to 900 °C. The decomposition temperatures were measured under dynamic conditions in a nitrogen atmosphere with a total flow rate of 100 mL min^{-1} .

2.4. Non-Isothermal Kinetics

There are two main approaches to kinetic modeling pyrolysis. The first approach consists of network models such as chemical percolation devolatilization (CPD), FLASHCHAIN, and FG-DVC models, which have been developed to describe the complex process behavior of coal and biomass pyrolysis [12,13], but modeling the pyrolysis process takes a relatively

long period of time due to the composition of complicated mathematical models. The second approach consists of global models and has been practically utilized due to its computational simplicity. Accordingly, global pyrolysis kinetic models were adopted in this study. The global models can be sorted into two categories: one-step and multi-step models. The number of steps in the model presents the complexity of reaction kinetic pathways occurring during the entire process. The conversion (α) of the sample in the overall pyrolysis process can be calculated as follows:

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} \quad (1)$$

where W_0 , W , and W_∞ represent the instantaneous, initial, and final weights of the sample in the pyrolysis process, respectively.

The global kinetics model form can be described by the Arrhenius equation [14] as follows:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1 - \alpha)^n \quad (2)$$

where t is the given time (s), A is the pre-exponential factor (min^{-1}), E_a is the apparent activation energy (kJ mol^{-1}), R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature (K), and n is the order of reaction function. The cattle manure and hydrochars consist of mainly lignocellulosic biomass materials made up of cellulose, hemicellulose, lignin, and excrements (e.g., proteins, starches, lipids, sugars, etc.), as mentioned above. The multi-step model was employed to estimate the kinetic parameters to reflect the characteristics of the different components of the samples in this study. The conversion and kinetic equations of individual steps of the multi-step and global models are as follows:

$$\alpha_i = \frac{W_{i,0} - W_i}{W_{i,0} - W_{i,\infty}} \quad (3)$$

$$\alpha = \sum_i y_i \alpha_i \quad (4)$$

$$\frac{d\alpha_i}{dt} = A_i \exp\left(-\frac{E_i}{RT}\right) (1 - \alpha_i)^{n_i} \quad (5)$$

$$\frac{d\alpha}{dt} = \sum_i y_i \frac{d\alpha_i}{dt} \quad (6)$$

$$y_i = \frac{W_{i,0} - W_{i,\infty}}{W_0 - W_\infty} \quad (7)$$

$$\sum_i y_i = 1 \quad (8)$$

where subscript i indicates each step of the multi-step model and y_i represents the contribution of the individual process to the overall weight loss. The uncharted kinetic parameters and contribution factors were computed by estimating the experimental data using non-linear least-squares analyses. The optimization was performed in MATLAB to minimize the sum of squared residuals (S), and the deviations between the experimental data and the predicted values were calculated using the equations below.

$$S = \sum_{j=1}^{N_d} \left(\left(\frac{d\alpha}{dt} \right)_j^e - \left(\frac{d\alpha}{dt} \right)_j^c \right)^2 \quad (9)$$

$$Devi.(%) = 100 \times \sqrt{\frac{S}{N_d - N_p}} \quad (10)$$

3. Results

3.1. Characteristics of Hydrothermal Carbonization Hydrochars with Reaction Temperature

The proximate, ultimate, and calorific analyses of cattle manure (raw material) and the hydrochar samples are presented in Table 1. The properties of the samples were analyzed after drying them at 105 °C for over 24 h. The volatile matters decreased, and the fixed carbons and ashes increased in general by the HTC reaction of cattle manure. As the HTC reaction temperature increased to 180–240 °C compared to the feedstock of cattle manure, the HTC solid content decreased to 66.37–48.84%. It is compared to the volatile matter content of cattle manure at 69.30%, while fixed carbons increased from 19.80% to 22.73–29.05%. Such a tendency is coincident with other findings [15]. In the range of 180 °C to 220 °C, the content of volatile matter and fixed carbons changed by 5% on average, whereas at 240 °C, the content of volatile matter and fixed carbons changed by 20% and 10%, respectively. A similar behavior was observed in previous studies [16,17], which concluded that hemicellulose started to decompose at about 175 °C and completely degraded at about 225 °C, while cellulose completely degraded above 250 °C.

The elemental carbon content of the hydrochar is considered as the energy content, which is a strong function of carbon content [18–20]. The elemental analysis showed that carbon content increased by more than 10% from 44.65% of the feedstock due to the HTC reaction. As the HTC reaction temperature increased to 180–240 °C, the carbon content increased to 48.34–55.13%. As the reaction temperature increased by 20 °C, the fixed carbons increased by 2% on average. The elemental carbon content of hydrochar increases in comparison to the cattle manure, whereas the carbon fraction of the hydrochar is lower than that of the hydrochar derived from lignocellulosic biomass with similar HTC conditions [21,22]. The hydrogen and oxygen content decreased by the HTC reaction and gradually decreased as the reaction temperature increased. This is due to the breakaway of the CO₂ and H₂O species by dehydration and decarboxylation reactions, which are the main reactions of HTC [23]. Furthermore, as nitrogen and sulfur were solubilized to the liquid phase by HTC reactions, the ratio of nitrogen to the feedstock decreased from 2.39% to 2.09–1.05%, while sulfur decreased from 0.23% to no detection within the error range. In terms of solid fuel, this result has the advantage of NO_x and SO_x reductions in the thermochemical process. Characteristics of the HTC hydrochar with nitrogen and sulfur based on the reaction temperature were identified, which were in agreement with previously reported findings [24,25]. On the other hand, as previously reported, the sulfur content is not relevant to temperature [26,27]. The nitrogen result presented a similar tendency. Figure 1 shows the degree of carbonization of the HTC solid content in the feedstock based on cattle manure using the van Krevelen diagram for the degree of carbonization of coal or biomass. The solid content generated by HTC reactions showed a clear decrease in O/C and H/C ratios due to the breakaway of the COOH functional group and H₂O by the dehydration and decarboxylation reaction compared to cattle manure [28–30]. This implies that the degree of carbonization increased. The correlation between the O/C and H/C ratios is expressed as follows.

$$\left(\frac{H}{C}\text{ratio}\right) = 2.64\left(\frac{O}{C}\text{ratio}\right)^2 - 1.03\left(\frac{O}{C}\text{ratio}\right) + 1.22 \quad (11)$$

The correlation equation showed highly consistent results, with $r^2 = 0.99$.

The higher heating values (HHV) increased from 18.91 MJ/kg of the feedstock to 20.13–24.14 MJ/kg of the hydrochars via HTC. The HHV increased with increasing temperatures. Such results confirm that the quality of the fuel was enhanced by the increase in the energy intensity via the HTC reaction [31]. Figure 2 shows the change in the increased fraction of HHV compared to the reaction temperature of HTC. As the reaction temperature increased, the fraction of HHV increased linearly. This correlation can be expressed as Equation (13), showing highly consistent results, with $r^2 = 0.94$.

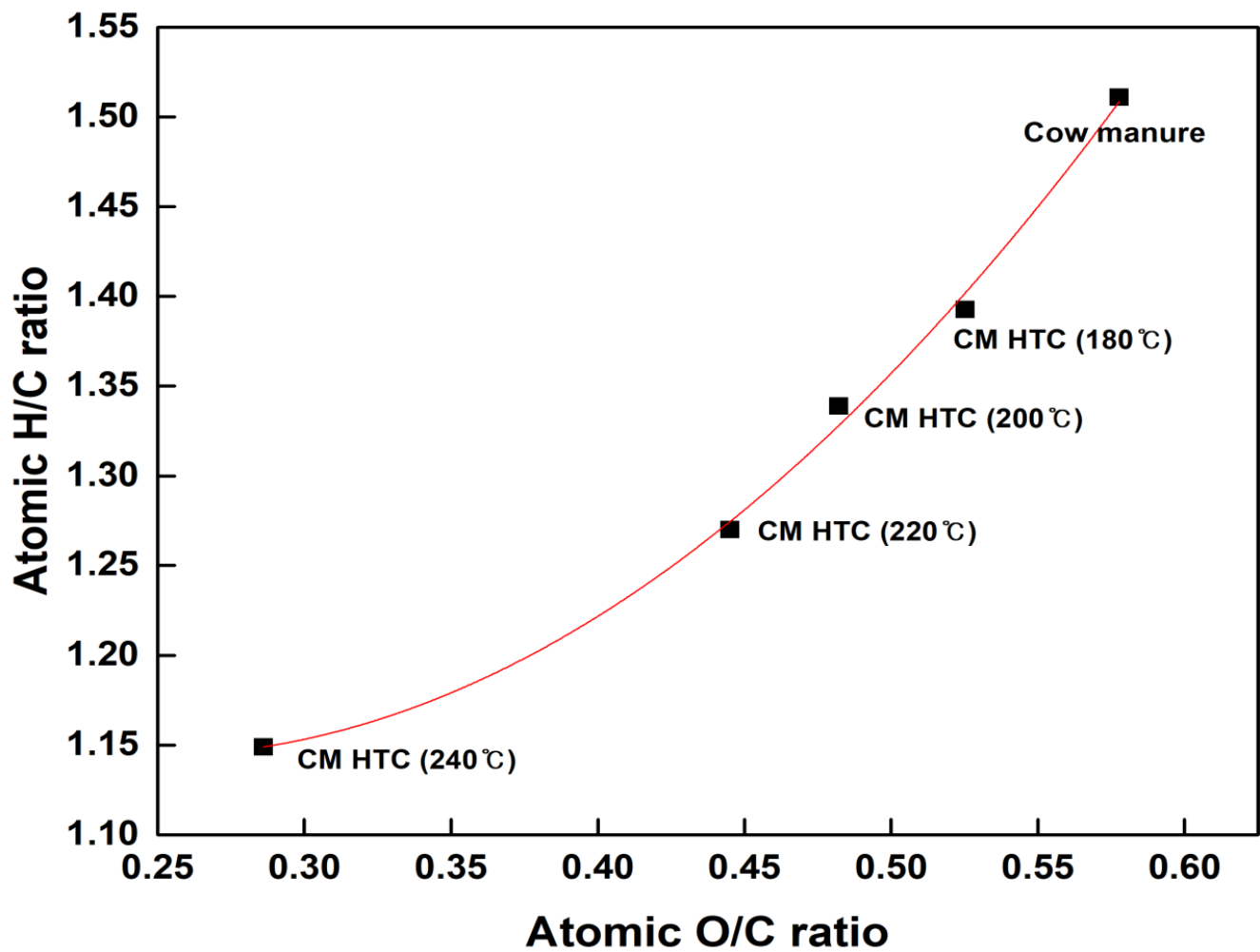


Figure 1. The van Krevelen diagram of cattle manure and the hydrochars with different HTC reaction temperatures.

$$IF_{HHV} = 0.0033(T) - 0.51 \quad (12)$$

where T is the reaction temperature of HTC and IF_{HHV} is the increased fraction of higher heating values compared to the feedstock, as follows:

$$IF_{HHV} = \frac{(HHV_{HTC} - HHV_{feedstock})}{HHV_{feedstock}} \quad (13)$$

where HHV_{HTC} and $HHV_{feedstock}$ are the higher heating values of the hydrochar and feedstock.

Among the HTC reaction temperatures, significant increases in the carbon content and heating value appeared at 240 °C. These are attributed to the HTC reaction of the lignocellulosic biomass, which is included in a significant amount, as mentioned above. The ultimate correlation for the estimation of HHV on cattle manure hydrochars was deduced following Equation (14), which is modified by the method of Sheng and Azevedo [32]:

$$HHV = 0.3795 C + 1.522 \left(H - \frac{O}{8} \right) \quad (14)$$

where HHV is a higher heating value (MJ/kg), and C , H , and O are the mass fractions of carbon, hydrogen, and oxygen. The average bias errors of the correlation drawn in this study are within 2%. They could be utilized for operating and designing the HTC reactor for cattle manure.

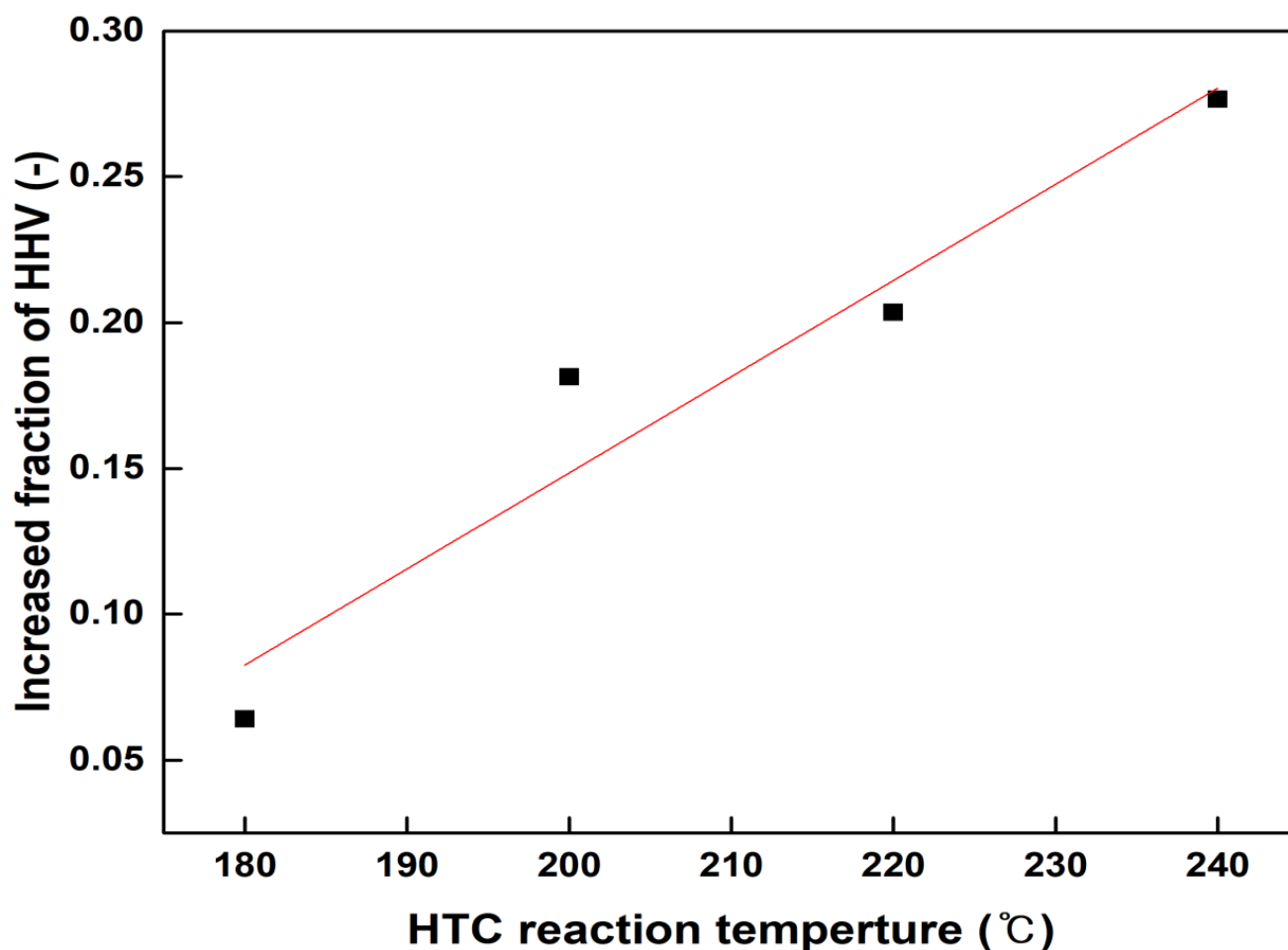


Figure 2. Increased fraction of higher heating values with HTC reaction temperatures for cattle manure.

3.2. Thermogravimetric Analysis of Cattle Manure and Hydrochars

The TG and DTG curves for the cattle manure and the hydrochars via the HTC samples in inert atmospheres are shown in Figure 3. The reaction indexes including characteristic temperatures, maximum mass loss rates, and residual mass fractions are summarized in Table 2. The kinetic parameters and mass fractions are estimated on the basis of residual mass dried samples attributed to the exclusion of the initial water content. Accordingly, the drying step is not considered in this work. The main thermal decomposition stages and corresponding mass losses of cattle manure and the hydrochars during the pyrolysis process occurred in a wide temperature range and presented asymmetrical DTG curves, which are mainly verified by materials of a heterogeneous nature such as other biomasses between 178 °C and 696 °C, resulting from the decomposition of cattle manure including general lignocellulosic biomass materials and extractives [33]. For the cattle manures, the hemicellulose, cellulose, and lignin content is higher than in swine and chicken manure [34,35]. Accordingly, the main components of cattle manure consist of cellulose, hemicellulose, lignin, and partially undigested organic matter. As can be shown in the mass loss profiles of the raw materials, those hydrochars show different behaviors. For the raw material sample, the main weight loss occurred from 224 °C to 684 °C with about 70% of weight loss, and the maximum weight loss rate is 0.0081 min⁻¹ at approximately 316 °C. On the other hand, the main degradation of the hydrochars of the cattle manure produced via HTC appears to start at approximately 178 °C. As the temperature increased to 328 °C, fractional weight loss rates increased and showed maximum values of 0.0033–0.0077 min⁻¹. With increasing reaction temperatures, the maximum weight loss rates decreased gradually. After the

pyrolysis process, residual weight fractions are analyzed to be 0.29 and 0.30–0.44 for raw materials and hydrochars, respectively. The observed data are in accordance with the fixed carbon and ash yield analyzed by proximate analyses in Table 1. For the characteristics of solid fuels, the hydrochars of cattle manure upgraded by the HTC process show that the initial temperature, maximum weight loss, and the amount of volatile matter are lower than those of the raw materials during the pyrolysis process. This could be primarily attributed to the breaking of weak bonds and then the coalification process that resulted from a series of reactions during the HTC process [36–38]. The effect of the reaction temperature of the HTC process indicates that as reaction temperature increases, the maximum weight loss rates and the fraction of volatiles decrease.

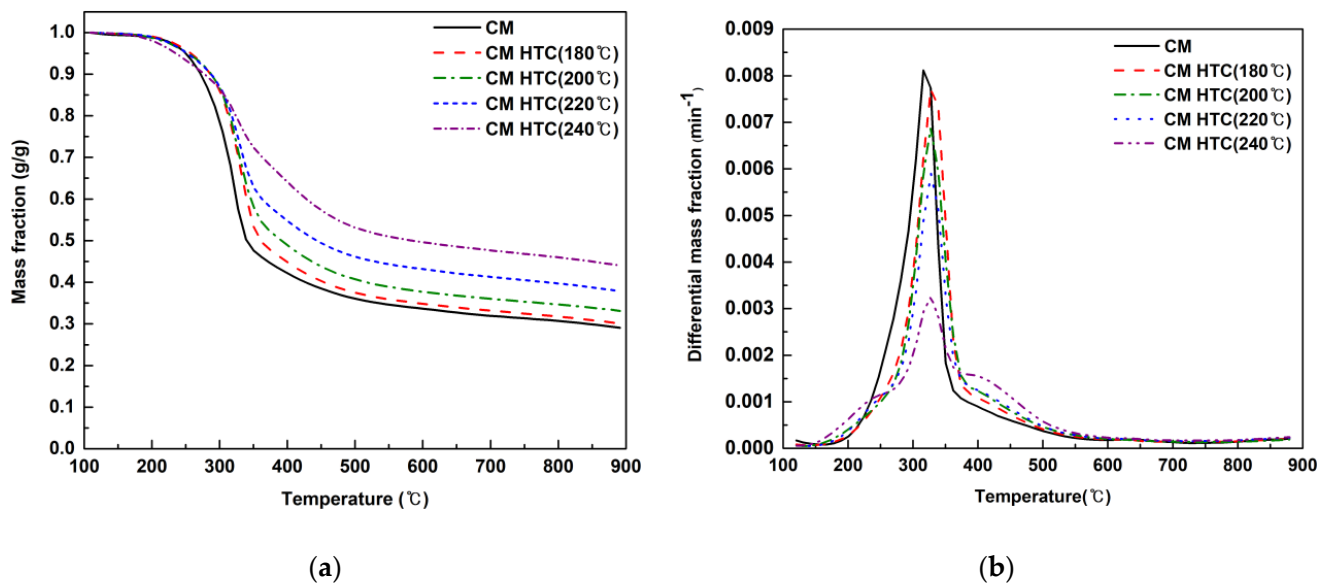


Figure 3. Experimental pyrolytic TG: (a) DTG; (b) curves of cattle manure and the hydrochars with varying temperatures (180, 200, 220, and 240 °C) under the pyrolysis processes.

Table 2. Characteristics of the cattle manure and the HTC hydrochars in the pyrolysis process.

Sample	Regime	T _i (°C)	T _{pk} (°C)	T _f (°C)	R _{pk} (°C)	M _f (g/g)
Cattle manure	1st	201	293	385	3.25×10^{-3}	0.75
	2nd	270	327	362	5.04×10^{-3}	0.81
	3rd	109	373	615	9.14×10^{-4}	0.72
CM hydrochar (180 °C)	1st	201	293	396	1.64×10^{-3}	0.86
	2nd	270	327	396	5.82×10^{-3}	0.74
	3rd	120	385	615	1.05×10^{-3}	0.69
CM hydrochar (200 °C)	1st	201	293	465	1.07×10^{-3}	0.87
	2nd	270	327	396	5.11×10^{-3}	0.76
	3rd	155	385	626	1.07×10^{-3}	0.7
CM hydrochar (220 °C)	1st	132	281	465	1.09×10^{-3}	0.88
	2nd	258	328	396	4.25×10^{-3}	0.81
	3rd	189	385	638	1.19×10^{-3}	0.68
CM hydrochar (240 °C)	1st	135	247	385	7.03×10^{-4}	0.92
	2nd	265	328	396	1.85×10^{-3}	0.91
	3rd	178	385	615	1.50×10^{-3}	0.59

3.3. Effect of HTC Reaction Temperature for the Fuel Quality of Hydrochars

To ascertain the effect of HTC reaction temperatures on the fuel quality of hydrochars, we performed the analysis of apparent kinetic parameters for pyrolysis behaviors using two types of global reaction models, i.e., network and global kinetic models, as mentioned earlier. The apparent kinetic parameters were estimated using a multi-step model, and the optimized pyrolysis characteristics of cattle manure and hydrochars are summarized in Table 3. The comparison of experimental and calculated TG and DTG curves is presented in Figure 4. The estimated data were deduced from the kinetic parameters computed using the multi-step model.

Table 3. The kinetic parameters of cattle manure and the HTC hydrochars in the pyrolysis process at operating temperatures.

Sample	Regime	<i>n</i> (-)	E (kJ/mol)	A (min ⁻¹)	r ² (-)	S (%)	y _i (-)
Cattle manure	1st	1.4	123.72	1.06×10^{11}	0.99	0.014	0.35
	2nd	1.4	332.85	2.08×10^{29}	0.99	0.022	0.26
	3rd	1.6	23.73	3.65	0.99	0.010	0.39
CM hydrochar (180 °C)	1st	1.4	112.87	7.84×10^9	0.99	0.006	0.20
	2nd	1.4	242.552	8.32×10^{20}	0.99	0.013	0.40
	3rd	1.6	25.96	6.09	0.98	0.008	0.43
CM hydrochar (200 °C)	1st	1.4	65.42	2.18×10^5	0.99	0.002	0.20
	2nd	1.6	249.04	4.8×10^{21}	0.99	0.012	0.36
	3rd	1.6	25.87	5.39	0.98	0.012	0.44
CM hydrochar (220 °C)	1st	1.2	63.73	1.66×10^5	0.99	0.004	0.20
	2nd	1.6	282.51	4.30×10^{24}	0.99	0.012	0.30
	3rd	1.8	28.52	10.95	0.97	0.015	0.51
CM hydrochar (240 °C)	1st	1.2	61.69	3.3×10^5	0.99	0.002	0.13
	2nd	1.6	261.45	8.08×10^{22}	0.99	0.005	0.15
	3rd	1.6	30.05	16.31	0.97	0.019	0.72

For the first and second steps, the global activation energies (E_a), pre-exponential factors (A), and the contribution factor of the individual step (y_i) of hydrochars are lower than the raw material. On the other hand, those kinetic parameters for the last step increased via HTC processes compared with raw materials. The thermal decomposition of weak bonds in raw materials occurs in a relatively lower temperature range. For the first and second steps, the initial and maximum weight loss and final temperature decreased as HTC temperatures increased, and such trends corresponded to the trend of E_a , A, and y_i . With the increase in HTC temperatures, the process will lead to a breakdown of macromolecules into smaller molecules. Cattle manure is mostly composed of lignocellulosic components, which have similar pyrolysis characteristics to those of biomasses. The behavior of cattle manure is similar to the findings of previous studies [39]. The pyrolysis temperatures of hemicellulose, cellulose, and lignin correspond to the ranges of 200–315 °C, 315–400 °C, and 100–900 °C, respectively [40]. The first section mainly corresponds to the pyrolysis temperature range of hemicellulose. The activation energies and pre-exponential factor of hydrochar were deduced, ranging from 61.69 to 112.87 kJ/mol and from 3.30×10^5 to 7.84×10^9 min⁻¹, respectively, which are lower than the those of cattle manure, 123.72 kJ/mol and 1.06×10^{11} min⁻¹. As the HTC reaction temperature increased, the initial temperature, maximum reaction temperature, and final temperature shifted to the left, and the pyrolysis gas fraction decreased gradually. In the second section, the maximum pyrolysis temperature and pyrolysis final temperature were somewhat shifted to the right. The result indicated that as HTC reaction temperature increased, the light compounds were decomposed or transformed during polymerization or condensation reactions [39]. The activation energies of hydrochars were estimated from 242.55 to 261.45 kJ/mol, and the pre-exponential factors were calculated to be from 8.32×10^{20} to 8.08×10^{22} min⁻¹. The

kinetic parameters of hydrochars were lower than those of cattle manure, 332.85 kJ/mol and $2.08 + 29 \text{ min}^{-1}$, respectively. Finally, in the high-temperature region corresponding to the lignin decomposition section, the initial temperature, maximum pyrolysis temperature, and final temperature shifted to the right as the temperature increased. The activation energies and pre-exponential factor for hydrochars were computed from 25.96 to 30.05 kJ/mol and from 6.09 to 16.31 min^{-1} . For the cattle manure, the activation energy and pre-exponential factor were deduced as 23.72 kJ/mol and 3.65 min^{-1} , respectively. Although the maximum speed of pyrolysis decreased, the pyrolysis fraction increased. This was caused by the decomposition of hydrophilic polymer substances by hydrolysis, hydration, and decarboxylation reactions, comprising a series of HTC mechanisms. Subsequently, the hydrophobicity and the degree of carbonization increased by polymerization and condensation reactions [41]. At the reaction temperature of 180 °C, the difference in pyrolysis reaction with the feedstock was insignificant. As the temperature increased to 200–220 °C, the maximum pyrolysis reaction rate decreased, and it significantly decreased at 240 °C. The comprehensive analysis of the pyrolysis reaction rate, fixed carbons, and high heating value confirmed that in terms of the fueling grade of solid fuel, the physical properties satisfied the conditions of transforming peat to lignite at 240 °C or higher temperatures. Furthermore, the distribution of the pre-exponential factors show an interrelationship with the distribution of the activation energies in the first and second sections. The relationship satisfies the compensation effect, i.e., as the activation energy is increased, the pre-exponential factor considerably increases [42]. The result of kinetic parameters is in agreement with the complexities of the chemical characteristics of cattle manure and hydrochars.

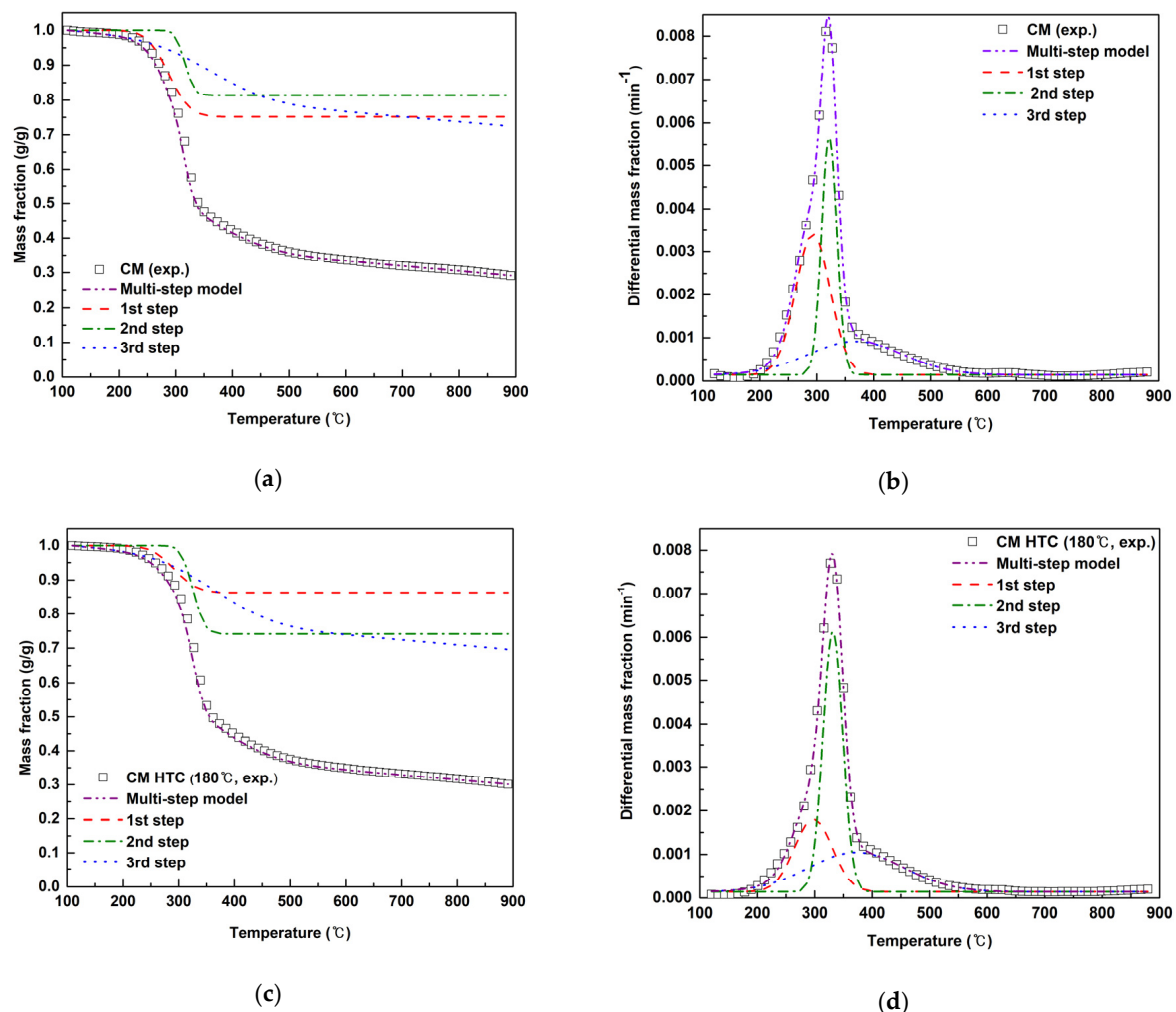
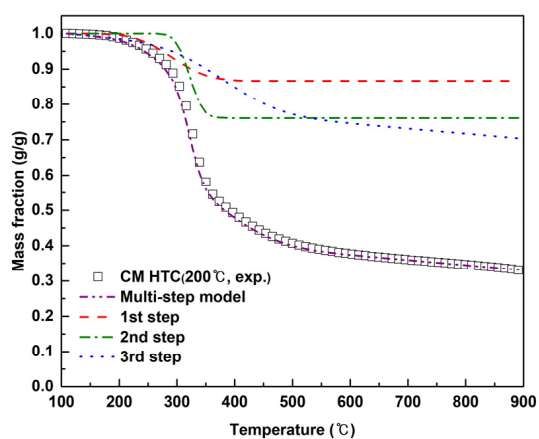
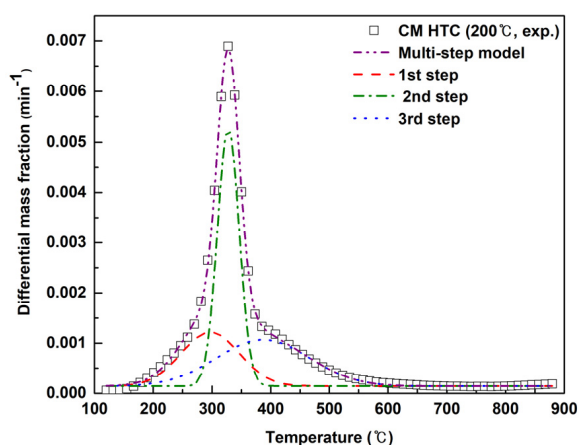


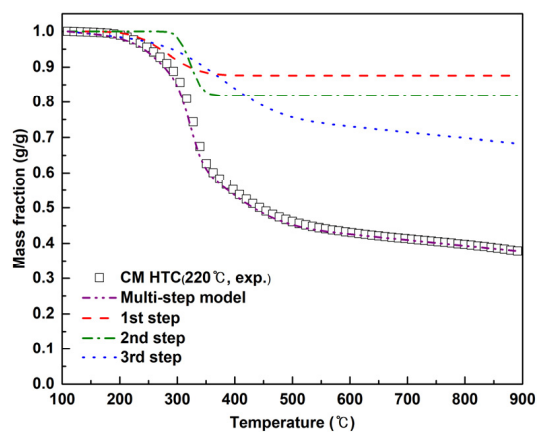
Figure 4. Cont.



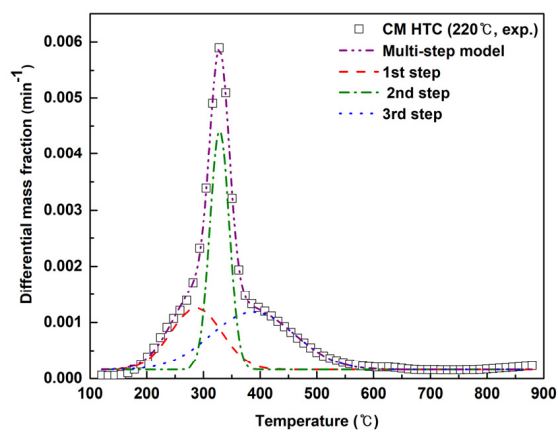
(e)



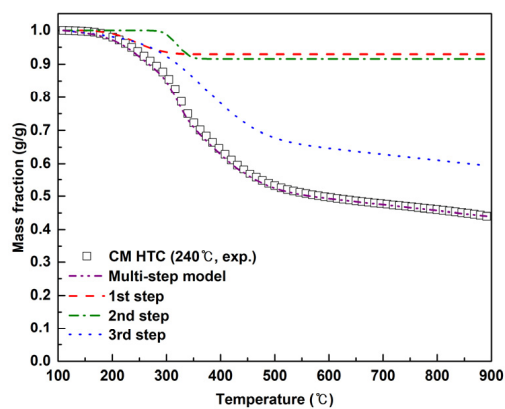
(f)



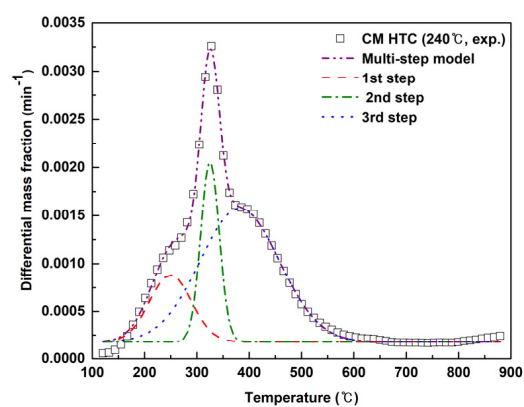
(g)



(h)



(i)



(j)

Figure 4. Experimental and calculated pyrolytic TG (a,c,e,g,i) and DTG (b,d,f,h,j) curves of cattle manure and the hydrochars with varying temperatures (180, 200, 220, and 240 °C) under the pyrolysis process.

4. Conclusions

In this study, the effects of HTC on cattle manure were evaluated in subcritical water at different reaction temperatures (180–240 °C). As the reaction temperature increased, the content of volatile matters decreased from 69.30% to 64.37–48.84%, whereas the content of fixed carbons increased from 19.80% to 24.07–29.05%. The O/C and H/C ratios decreased from 0.57 to 0.52–0.29 and from 1.51 to 1.39–1.15, respectively, but the heating value increased from 4520 kcal/kg to 4810–5770 kcal/kg as the HTC temperature increased.

The application of the multi-step method is demonstrated to be a useful tool for evaluating the pyrolysis kinetic analysis of hydrochars derived from cattle manure. The decomposition process of hydrochars from cattle manure was characterized by three pseudo-components. In the first low-temperature section among the three stages of pyrolysis, the initial pyrolysis temperature decreased from 224 °C to 178–201 °C as the reaction temperature increased. In the second and third high-temperature sections, it increased from 293 °C to 293–305 °C. The pyrolysis end temperature shifted to the right due to the HTC reactions. Furthermore, as the HTC reaction temperature increased, the global activation energy and the pre-exponential factors decreased in the low-temperature section and increased in the high-temperature section. At a reaction temperature of 180 °C, the difference in pyrolysis reactions with the feedstock was insignificant. The maximum pyrolysis reaction rate decreased, and it decreased significantly at 240 °C as the reaction temperature increased to 200–220 °C. A comprehensive analysis of the pyrolysis reaction rate, fixed carbons, and high heating values confirmed that in terms of the fueling grade of solid fuels, the physical properties satisfied the conditions of peat to lignite at 240 °C or higher temperatures.

Author Contributions: Conceptualization, E.S.; methodology, E.S. and S.P.; validation, E.S. and E.L.; formal analysis, E.S.; investigation, S.H., H.K. and E.S.; resources, S.P. and E.S.; data curation, S.H. and E.S.; writing and original draft preparation, E.S.; writing, review, and editing, E.S.; supervision, S.H. and H.K.; project administration, H.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry and Energy (MOTIE) of the Republic of Korea (no. 20183010092750).

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest. The funding agencies had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Biogas Research South Korea: Application Study of Biogas Process for Public Treatment of Cattle Dung. 2019. Available online: http://www.me.go.kr/synap/synapView.jsp?sessionId=sTRU0hZmRxLigv11bcrOe3HbXDAbr7Ub5kAafhJwhsSgoZQQU7Dmkf21tYB1DN9k.meweb2vhost_servlet_engine1?fileId=155773&fileSeq=2 (accessed on 2 October 2022).
2. Lee, J.H.; Febrisiantosa, A. Improvement of nitrogen balance (land budget) in South Korea in terms of livestock manure: A review. *IOP Conf. Ser. Earth Environ. Sci.* **2020**, *462*, 012011. [CrossRef]
3. Kim, J.-H.; Nam, J.; Yoo, S.-H. Public acceptance of a large-scale offshore wind power project in South Korea. *Mar. Policy* **2020**, *120*, 104141. [CrossRef]
4. Lee, S.; Yu, B.; Ju, S.; Kang, Y.; Jung, G. Characteristics of solid fuel from cattle manure. *New Renew. Energy* **2016**, *12*, 64–69. [CrossRef]
5. Szymajda, A.; Łaska, G.; Joka, M. Assessment of cow dung pellets as a renewable solid fuel in direct combustion technologies. *Energies* **2021**, *14*, 1192. [CrossRef]
6. Marin-Batista, J.D.; Villamil, J.A.; Qaramaleki, S.V.; Coronella, C.J.; Mohedano, A.F.; de La Rubia, M.A. Energy valorization of cow manure by hydrothermal carbonization and anaerobic digestion. *Renew. Energy* **2020**, *160*, 623–632. [CrossRef]
7. Maj, I.; Kalisz, S.; Ciukaj, S. Properties of Animal-Origin Ash—A Valuable Material for Circular Economy. *Energies* **2022**, *15*, 1274.
8. Kirtania, K. Thermochemical Conversion Processes for Waste Biorefinery. In *Waste Biorefinery*; Elsevier: Amsterdam, The Netherlands, 2018; pp. 129–156.

9. Funke, A.; Ziegler, F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels Bioprod. Biorefining* **2010**, *4*, 160–177. [\[CrossRef\]](#)
10. Escala, M.; Zumbuhl, T.; Koller, C.; Junge, R.; Krebs, R. Hydrothermal carbonization as an energy-efficient alternative to established drying technologies for sewage sludge: A feasibility study on a laboratory scale. *Energy Fuels* **2013**, *27*, 454–460. [\[CrossRef\]](#)
11. Sevilla, M.; Fuertes, A.B. The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon* **2009**, *47*, 2281–2289. [\[CrossRef\]](#)
12. Ferreira, A.I.; Giudicianni, P.; Grottola, C.M.; Rabaçal, M.; Costa, M.; Ragucci, R. Unresolved issues on the kinetic modeling of pyrolysis of woody and nonwoody biomass fuels. *Energy Fuels* **2017**, *31*, 4035–4044. [\[CrossRef\]](#)
13. Rabaçal, M.; Costa, M.; Vascellari, M.; Hasseb, C. Kinetic modelling of sawdust and beech wood pyrolysis in drop tube reactors using advanced predictive models. *Chem. Eng.* **2014**, *37*, 79–84.
14. Varhegyi, G.; Antal, M.J., Jr.; Jakab, E.; Szabó, P. Kinetic modeling of biomass pyrolysis. *J. Anal. Appl. Pyrolysis* **1997**, *42*, 73–87.
15. Wu, K.; Gao, Y.; Zhu, G.; Zhu, J.; Yuan, Q.; Chen, Y.; Cai, M.; Feng, L. Characterization of dairy manure hydrochar and aqueous phase products generated by hydrothermal carbonization at different temperatures. *J. Anal. Appl. Pyrolysis* **2017**, *127*, 335–342. [\[CrossRef\]](#)
16. Ghanim, B.M.; Pandey, D.S.; Kwapinski, W.; Leahy, J.J. Hydrothermal carbonisation of poultry litter: Effects of treatment temperature and residence time on yields and chemical properties of hydrochars. *Bioresour. Technol.* **2016**, *216*, 373–380.
17. Hendriks, A.T.W.M.; Zeeman, G. Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresour. Technol.* **2009**, *100*, 10–18.
18. Reza, M.T.; Andert, J.; Wirth, B.; Busch, D.; Pielert, J.; Lynam, J.G.; Mumme, J. Hydrothermal carbonization of biomass for energy and crop production. *Appl. Bioenergy* **2014**, *1*, 11–29.
19. Titirici, M.-M.; Antonietti, M. Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization. *Chem. Soc. Rev.* **2010**, *39*, 103–116. [\[CrossRef\]](#)
20. Rillig, M.C.; Wagner, M.; Salem, M.; Antunes, P.M.; George, C.; Ramke, H.G.; Titirici, M.M.; Antonietti, M. Material derived from hydrothermal carbonization: Effects on plant growth and arbuscular mycorrhiza. *Appl. Soil Ecol.* **2010**, *45*, 238–242. [\[CrossRef\]](#)
21. Reza, M.T.; Wirth, B.; Lüder, U.; Werner, M. Behavior of selected hydrolyzed and dehydrated products during hydrothermal carbonization of biomass. *Bioresour. Technol.* **2014**, *169*, 352–361.
22. Reza, M.T.; Uddin, M.H.; Lynam, J.G.; Hoekman, S.K.; Coronella, C.J. Hydrothermal carbonization of loblolly pine: Reaction chemistry and water balance. *Biomass Convers. Biorefinery* **2014**, *4*, 311–321. [\[CrossRef\]](#)
23. Fakkaew, K. *Evaluation of Hydrothermal Carbonization Reactions for Faecal Sludge Treatment and Hydrochar Production*; Asian Institute of Technology School of Environment, Resources and Development Thailand: Bangkok, Thailand, 2016.
24. Brown, A.E.; Adams, J.M.; Grasham, O.R.; Camargo-Valero, M.A.; Ross, A.B. An Assessment of Different Integration Strategies of Hydrothermal Carbonisation and Anaerobic Digestion of Water Hyacinth. *Energies* **2020**, *13*, 5983.
25. Chen, C.; Liang, W.; Fan, F.; Wang, C. The Effect of Temperature on the Properties of Hydrochars Obtained by Hydrothermal Carbonization of Waste Camellia oleifera Shells. *ACS Omega* **2021**, *6*, 16546–16552. [\[CrossRef\]](#)
26. Wang, G.; Zhang, J.; Lee, J.-Y.; Mao, X.; Ye, L.; Xu, W.; Ning, X.; Zhang, N.; Teng, H.; Wang, C. Hydrothermal carbonization of maize straw for hydrochar production and its injection for blast furnace. *Appl. Energy* **2020**, *266*, 114818.
27. Krysanova, K.; Krylova, A.; Zaichenko, V. Properties of biochar obtained by hydrothermal carbonization and torrefaction of peat. *Fuel* **2019**, *256*, 115929. [\[CrossRef\]](#)
28. Gao, P.; Zhou, Y.; Meng, F.; Zhang, Y.; Liu, Z.; Zhang, W.; Xue, G. Preparation and characterization of hydrochar from waste eucalyptus bark by hydrothermal carbonization. *Energy* **2016**, *97*, 238–245. [\[CrossRef\]](#)
29. Fan, F.; Zheng, Y.; Huang, Y.; Lu, Y.; Wang, Z.; Chen, B.; Zheng, Z. Preparation and characterization of biochars from waste Camellia oleifera shells by different thermochemical processes. *Energy Fuels* **2017**, *31*, 8146–8151. [\[CrossRef\]](#)
30. Zhao, Y.; Su, R.; Zhang, W.; Yao, G.L.; Chen, J. Antibacterial activity of tea saponin from Camellia oleifera shell by novel extraction method. *Ind. Crops Prod.* **2020**, *153*, 112604. [\[CrossRef\]](#)
31. Sharma, R.; Jasrotia, K.; Singh, N.; Ghosh, P.; Srivastava, S.; Sharma, N.R.; Singh, J.; Kanwar, R.; Kumar, A. A comprehensive review on hydrothermal carbonization of biomass and its applications. *Chem. Afr.* **2020**, *3*, 1–19. [\[CrossRef\]](#)
32. Sheng, C.; Azevedo, J.L.T. Estimating the higher heating value of biomass fuels from basic analysis data. *Biomass Bioenergy* **2005**, *28*, 499–507.
33. Yuan, X.; He, T.; Cao, H.; Yuan, Q. Cattle manure pyrolysis process: Kinetic and thermodynamic analysis with isoconversional methods. *Renew. Energy* **2017**, *107*, 489–496.
34. Chen, S.; Wen, Z.; Liao, W.; Liu, C.; Kincaid, R.L.; Harrison, J.H.; Elliott, D.C.; Brown, M.D.; Stevens, D.J. Studies into using manure in a biorefinery concept. *Appl. Biochem. Biotechnol.* **2005**, *124*, 999–1015.
35. Langone, M.; Soldano, M.; Fabbri, C.; Pirozzi, F.; Andreottola, G. Anaerobic digestion of cattle manure influenced by swirling jet induced hydrodynamic cavitation. *Appl. Biochem. Biotechnol.* **2018**, *184*, 1200–1218.
36. Keiller, B.G.; Muhlack, R.; Burton, R.A.; van Eyk, P.J. Biochemical Compositional Analysis and Kinetic Modeling of Hydrothermal Carbonization of Australian Saltbush. *Energy Fuels* **2019**, *33*, 12469–12479.
37. Kruse, A.; Funke, A.; Titirici, M.M. Hydrothermal conversion of biomass to fuels and energetic materials. *Curr. Opin. Chem. Biol.* **2013**, *17*, 515–521. [\[CrossRef\]](#)

-
38. Lucian, M.; Volpe, M.; Fiori, L. Hydrothermal carbonization kinetics of lignocellulosic agro-wastes: Experimental data and modeling. *Energies* **2019**, *12*, 516. [[CrossRef](#)]
 39. Cao, H.; Xin, Y.; Wang, D.; Yuan, Q. Pyrolysis characteristics of cattle manures using a discrete distributed activation energy model. *Bioresour. Technol.* **2014**, *172*, 219–225.
 40. Yang, H.; Yan, R.; Chen, H.; Lee, D.H.; Zheng, C. Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel* **2007**, *86*, 1781–1788.
 41. Wang, T.; Zhai, Y.; Zhu, Y.; Li, C.; Zeng, G. A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. *Renew. Sustain. Energy Rev.* **2018**, *90*, 223–247. [[CrossRef](#)]
 42. Hayhurst, A.N. The kinetics of the pyrolysis or devolatilisation of sewage sludge and other solid fuels. *Combust. Flame* **2013**, *160*, 138–144. [[CrossRef](#)]