Hydrothermal Carbonization of Food Waste for Char Production

Subjects: Environmental Sciences

Contributor: Moonis Ali Khan , Bassim H. Hameed , Masoom Raza Siddiqui , Zeid A. Alothman , Ibrahim H. Alsohaimi

Managing the increasing volume of food waste worldwide has become a major challenge. In addition, the energy crisis in developing nations of the world is increasing at an alarming rate and the need to proffer solutions is not only expedient but must be of high priority. Hydrothermal carbonization (HTC) refers to a conversion of biomass into an energy-densified or carbon-rich char product. It involves hydrolysis, dehydration, polymerization, and carbonization reactions taking place within moderate temperature (between 180 and 260 °C) and pressure (between 35 and 55 bar) ranges.

hydrothermal carbonization   food waste   hydrochar   reactor

1. Introduction

Managing the increasing volume of food waste worldwide has become a major challenge. In addition, the energy crisis in developing nations of the world is currently increasing at an alarming rate and the need to proffer solutions is not only expedient but must be of high priority. On average, developed countries generate 100–170 kg of food waste per capita per year, corresponding to more than twice of that produced in developing countries [1]. Research has shown that liquefaction, microwave heating, pyrolysis, and slow pyrolysis can be used to convert food wastes to valuable solid products. However, unlike hydrothermal conversion and anaerobic digestion processes, there is an additional requirement of pre-drying the wet food wastes [2].

Hydrothermal carbonization (HTC) refers to a conversion of biomass into an energy-densified or carbon-rich char product. It involves hydrolysis, dehydration, polymerization, and carbonization reactions taking place within moderate temperature (between 180 and 260 °C) and pressure (between 35 and 55 bar) ranges [3]. The hydrothermally developed solid product could be used as a fuel, an adsorbent, and a catalyst, while liquid product with high acid and phenol concentrations has very limited applications. Carbon dioxide (CO_2) is the major constituent of hydrothermally developed gaseous product, along with hydrocarbons in trace amount.

2. Effect of Process Parameters

The yield and chemical properties of hydrochars are largely dependent on the process parameters of the hydrothermal process and feedstock type. The important parameters include temperature, pressure, biomass–water ratio, and heating rate. Among them, temperature exerts a greater influence on the product yields of the

HTC. Very high HTC temperatures usually result in low yield of solid hydrochar while favoring higher yields of liquid and gaseous products.

3. Temperature

Temperature affects several characteristics of the final hydrochar produced from food waste. In the literature, the effects of an increase in HTC temperature of food waste on the mass yield of the hydrochar were studied. Microwave-assisted hydrothermal carbonization of food waste digestate was carried out by varying the temperature between 160 and 200 °C. The mass yield decreased with rising temperature from 68.9 to 67.5%. A further rise in temperature up to 260 °C lead to a rapid decline of the mass yield from 67.5 to 58.6% [4]. In another study, HTC of food waste over a wider temperature (between 200 and 300 °C) resulted in a reduced hydrochar mass yield (from 7 to 5.25%) [5]. A similar trend in hydrochar mass yield was also observed for feedstock comprising mainly fruit and vegetable waste, with a small amount of meat waste [6]. The possible cause for a reduced mass yield of the hydrochar in these studies may be the use of subcritical water as the reaction medium. Subcritical water dissociates into H_3O^+ and OH^- ions at 200 °C owing to the weakening of hydrogen bonding, which results in cleavage of the β-(1–4) glycosidic bonds of the hemicelluosic component of the food waste, further leading to the production of sugar monomers. Subsequent decomposition of the sugars to furfurals and other compounds causes a part of carbon in food waste to be transported into the liquid phase, leading to a reduced mass yield of the hydrochar [7] (Ciftci and Saldaña, 2015). Generally, the mass yield reduction with a rise in temperature is expected because the mass loss rate obeys the Arrhenius equation, which implies that an effect of increasing temperature will result in reduction of the hemicellulose component of the waste.

Liu et al. [8] have found that the effect of temperature on mass yield also varies with the type of food waste feedstock. As the HTC temperature varied from 180 to 220 °C, the hydrochars produced from taro, lettuce, and watermelon peel varied in the range 2.8 and 12.7%, 0.7 and 1.0%, and 1.7 and 2.2%, respectively.

The effect of temperature on hydrochar's surface area has also been reported in some studies. As the temperature varied from 200–300 °C, the BET surface area of hydrochar produced from food waste (comprising a mixture of vegetables, fruits, staple foods, and meat waste) varied between 5.23 and 7.14 m^2/g [5]. Generally, hydrochars produced from food waste were found to have a low surface area (1.76 to 30.59 m^2/g) and were not suitable for use as supercapacitors, electrocatalysts, and adsorbents without chemical modification of their structure. However, the surface area of food waste-derived hydrochars may be too low to be considered for adsorptive application; this may be compensated by the presence of functional groups. Just like the mass yield, the effect of temperature on surface area has been found to depend on the type of feedstock used. Liu et al. [8] found that as the HTC temperature varied from 180 to 240 °C, the specific surface area of hydrochar produced from lettuce, taro, and watermelon peel varied in the range between 3.67 and 6.90, 0.68 and 9.23, and 3.29 and 8.45 m^2/g, respectively. Furthermore, an increase from 180 to 220 °C for lettuce waste hydrochars did not significantly affect their specific surface up to 220 °C, beyond which a rapid decrease was observed at HTC temperature of 240 °C. At 220 °C, watermelon peel-derived hydrochar had the highest specific surface area at 8.45 m^2/g, with stable mesoporous carbon among the three hydrochars produced.

The effect of temperature in most studies on HTC of food waste is also seen on the amount of volatile matter. During the HTC of kitchen waste, it was observed that a rise in temperature led to a decrease in volatile matter accompanied by a corresponding increase in fixed carbon and ash [9]. It is hypothesized that the extent of changes in volatile content of hydochar with increasing temperature is also a function of the type of feedstock [6].

In most studies, increasing temperature generally resulted in a higher carbon content of hydrochar at a given reaction time. A study was carried out for the HTC of food waste at different temperatures (195, 225, and 255 °C) for 12 h. The carbon content of hydrochar increased from 67.72 to 72.99% with increases in the temperature [10]. In another study involving HTC of real cooked FW (without addition of water) at a fixed reaction time (5 h), approximately 10% rise in the carbon content was observed for every 20 °C rise in reaction temperature [11]. In a similar study, as the temperature increased from 200 to 250 °C, the fixed carbon content of food waste increased from 30.34 to 45.41% and subsequently to 47.43% as the temperature was further raised to 300 °C [5]. A similar trend was also observed elsewhere [6].

The effect of temperature on both carbon and oxygen contents was also found to be dependent on the type of food waste. This is because different food wastes possess dissimilar chemical compositions, rates of dissolution, and thermal stability. According to Zhang et al. [12], HTC of lignin-rich food waste results in hydrochar with high carbon content as most of the carbon is retained in it. Thus, appropriate temperatures for particular food waste feedstock should be selected based on the specific application.

The effect of temperature on hydrochar's oxygen content was also investigated. A study varied the HTC temperature of a complex food waste mixture between 200 and 260 °C at a fixed time of 1 h and observed that the oxygen content of the produced hydrochars reduced from 12.76 to 9.87% with increasing temperature [13]. Liu et al. [8] investigated the impact of temperature parameters on both carbon and oxygen contents of hydrochar produced from lettuce, watermelon peel, and taro waste. It was found that the carbon content of the food waste hydrochar increased while the oxygen content declined with the rising HTC temperature from 180 to 240 °C. An obvious change of the carbon and oxygen contents in the lettuce and watermelon peel hydrochars was observed when the HTC temperature was raised to 240 °C, while this change appeared at a lower HTC temperature (200 °C) for taro waste hydrochar.

Some studies on HTC of food waste have revealed that an increase in temperature has affected the nitrogen and hydrogen contents to a certain extent, depending on the feed. A study on HTC of food waste with the temperature range between 180 and 220 °C led to a significant reduction in percentage nitrogen content (from 52.76 to 40.97%) [14]. As regards hydrogen, some of the studies revealed that its content in the hydrochar is not affect by temperature [6]. In studies where a noticeable change was observed, no specific trend was noted. However in all the studies, the hydrogen content of the hydrochar improved relatively to the raw food waste feedstock [15].

A positive effect of temperature on heating value of the hydrochar has been observed in many studies. At a fixed reaction time of 5 h, the hydrochars produced at 160 °C had a HHV value of 23 MJ/kg, which increased to 29.5 MJ/kg with a rise in temperature to 180 °C. A further increase in temperature to 200 °C did not show an appreciable

increase in HHV [11]. Another study on food waste, carried out at a reaction temperature between 200 and 300 °C, revealed an increase in HHV from 20.81 to 28.98 MJ/kg when the temperature varied from 200 to 250 °C, and a further rise to 31 MJ/kg at 300 °C [5]. A similar finding was observed in another study where there was a consistent increase in HHV with increasing temperature [13].

Research has also shown that temperature also affects the energy density of the food waste-derived hydrochar. The energy density of hydrochar is usually a function of the relative amount of lignin in the corresponding food waste. The HTC of food waste were studied between 200 and 300 °C. It was revealed that the energy density ranged from 20.81 to 31 MJ/kg [5]. Similar findings were observed in other studies [2][11]. It was generally observed that higher HTC temperature caused no significant improvement on the energy densification though an improvement in the carbon densification. Moreover, the effect of varying the HTC temperature for coffee silver skins between 180 and 260 °C significantly led to an increase in the energy density from 1.3 to 1.62 MJ/cm^3 [16].

Some studies have investigated the effect of temperature on energy yield of the hydrochar. The energy yield of a hydrochar is the product of the mass yield and the energy densification ratio (ratio of the lower heating values (LHV) of the char and feedstock) [17]. A study observed that varying the temperature in a range between 175 and 250 °C gave a maximum energy yield of 63.5% on dry basis at 250 °C [18], consistent with another study where an increase in temperature from 200 to 300 °C led to a corresponding drop in the energy yield from 12.81 to 10.92% on dry basis [5]. However in another study, varying HTC temperature of food waste comprising cellulose (3.12%), hemicelluloses (22.76%), carbohydrates (34.21%), lignin (2.68%), protein (23.28%), and lipids (25.79%) in a range between 210 and 270 °C was found to result in a decrease in energy yield from 56.31 to 20.48% [19]. This was due to higher hydrochar yield and lower energy densification at 210 °C.

Some works reported the effect of temperature on the ease of combustibility of hydrochars. Although increasing the temperature of food waste HTC in some studies did not affect the number of degradation stages, the activation energies were affected. The activation energies for the first and second degradation stages were 56.78 and 47.38 kJ/mol, respectively, for hydrochar produced at 200 °C, while the activation energies of 33.60 and 29.80 kJ/mol were respectively observed at 300 °C [5]. From these results it could be concluded that the activation energy during both stages (first and second) decreased with an increase in temperature from 200 to 300 °C. However, during the HTC of sweet potato waste, an increase in reaction temperature from 180 to 300 °C at 1 h resulted in an increase in activation energy from 197.69 to 264.28 kJ/mol during the first stage and an increase in activation energy from 150.57 to 190.52 kJ/mol during the second stage [20]. The decrease in activation energy during the first stage (which commenced within the temperature range: 315–390 °C) could be explained by the fact that unstable volatile components were released, thereby reducing the specific surface area and porosity of the hydrochar. On the other hand, the decrease in activation energy during the second stage (which commenced within the temperature range: 400–540 °C) could be explained by the occurrence of an aromatization reaction which leads to an increase in aromatic compounds generation.

4. Contact Time

Contact time also affects the physicochemical properties such as carbon and hydrogen contents, energy density, and mass yield of a hydrochar. Generally, increased contact time of HTC usually led to an enhanced carbon content and reduced mass yield of the produced hydrochars. Several experiments have studied the effect of contact time on HTC of food waste using a time that ranged between 0.5 and 12 h. At very high temperatures, contact time may not have a significant impact on the mass yield except that higher contact time could lead to a complete decomposition of the food waste. Moreover, increasing the contact time may affect the chemical composition of the resulting hydrochar. A study was carried out which revealed that during longer contact time durations, the carbonization of household waste increased the intensity of polymerization and formation of phenolic compounds while decreasing carbonyl compounds formation [21]. The effect of contact time on mass yield was studied for HTC of food waste by changing contact time from 20 to 120 min, where a gradual decrease in hydrochar mass yield from 68.5 to 65.3% was observed [4]. Another effect of contact time on mass yield was found in the HTC of food waste under varying contact time between 5 and 120 min, where a 13% increase in the mass yield was recorded after 60 min [18].

The effect of contact time (1.5–12 h) on the carbon content was studied during HTC of kitchen waste at 225 °C. As the contact time varied from 1.5 to 9.0 h, the carbon content of hydrochar slightly increased from 69.31 to 70.91% [10]. Atallah et al. [22] studied the effect of contact time on HTC of spent mushroom compost waste at 250 °C. A 23.45% increase in carbon content was recorded within 2–4 h time range. In another study, contact time of less than 1 h did not show a significant increase in carbon content of the hydrochar at a fixed temperature of 200 °C. However, after 30 min of contact time, a decreasing trend was first observed. Thereafter, from 1 to 5 h, the carbon content of hydrochar increased in range: 16–20% [11]. Some studies have found that the effect of content on hydrogen and fuel ratio of the hydrochar were not very significant, possibly due to reduced mass yield [9][11], even though Gupta et al. [11] found that increasing contact time from 0.5 to 1 h led to a significant increase in H/C ratio.

5. Water–Biomass Ratio

Water–biomass ratio is an important process parameter for HTC of food wastes because it determines the extent of hydrolysis reaction or the extent of solubilization of the food waste. Thus, appropriate water–biomass ratio is necessary so as not to cause excessive hydrolysis of the food waste which would result in low mass yield. In addition, the study of the effect of the water–biomass ratio is critical in ensuring an appropriate food waste biomass dispersion in the HTC reactor. According to Guo et al. [23], a low water–biomass ratio will reduce the contact time required for the HTC of the food, which will in turn causes an early onset of the polymerization reaction, thereby leading to higher hydrochar yield.

Limited works have reported effect of water–biomass ratio on the mass yield of hydrochar produced from real food waste. The effect of water–biomass ratio on mass yield of HC produced from sewage was investigated by Xie et al. [4]. It was found that an increase in the water–biomass ratio from 2 to 25 wt.% led to an increase in mass yield from 62.9 to 66.1%. In the HTC of starch and glucose, the water–biomass ratio of the reaction was studied between the ratios of 5 and 10. An increase in the water–biomass ratio from 5 up to 8 led to an increase in the mass yield of hydrochar, whereas decreased mass yield was found at a water–biomass ratio below 5 [24]. In stirred HTC reactors,

it is pertinent to regulate the water–biomass ratio in such a way that the efficiency of the stirrer is not retarded. However, some operational challenges were encountered when a water–biomass ratio of 5 and 8 was used during the HTC of acacia wood in a stirred HTC reactor at 200 °C [25]. It was concluded in the study that a water–biomass ratio of 10 led to stirring the solution with ease. Optimization studies need to focus optimization methods in order to ascertain the effect of water–biomass ratio for real and multicomponent food waste as only few studies are available. For example, in the HTC optimization of oat husk using a response surface methodology, the optimal water–biomass ratio of 12.5 was necessary if a hydrochar was to be produced with mass yield of 53.8% with a heating value of 21.5 MJ/kg [26].

6. Pressure

Few works have analyzed the effect of HTC pressure on the properties of food waste-derived hydrochar. This may be due to the fact that the pressure of an HTC reactor in most studies [27][28] were measured or monitored after few minutes into the duration of dwelling time. According to Das et al. [29], HTC process normally records a final pressure of about 2 MPa at 200 °C within 1 h of dwelling time. Lachos-perez et al. [30] opined that pressure may not be a key parameter in HTC of food waste, especially in batch reactors. In continuous reactors, a pressure of 300 bar was reported to show significant intense graphitization of hydrochar leading to improved heating values, however, very high pressure can lead to high operating costs. However, increased pressure is important because it increases the hydrolysis and decomposition rate of the food waste. In addition, pressure is required to keep the aqueous reaction media in a subcritical state and expedite the exchange of hydrogen ions.

7. Heating Rate

The effect of heating rate on the properties of hydrochar is sparse in the literature. Most studies were carried out at heating rates ranging between 2 and 15 °C/min. The heating rate is critical when controlling the distribution of the solid, liquid, and gaseous products of the HTC of food waste. Higher heating rate is known to result in very low hydrochar yield. However, higher heating rate may reduce heat transfer restrictions and prevent a secondary reaction that may lead to stable products [20]. Lower heating rate increases the carbon content of the char with reasonably low calorific value.

8. Properties of the Produced Hydrochars

Hydrochars have specific properties which qualify them for different applications. Many studies have shown that the chemical and energy properties of a hydrochar are largely dependent on both the process parameters and the type of food waste used. The use of hydrochar for different applications is dependent upon its elemental composition, ultimate composition, and energy properties.

The volatile matter of food waste ranged between 50 and 65.4%, except for chicken and household wastes where it is greater than 90%. The fixed carbon content of food waste that hydrochar produced was in the range of 31.1 to

49.3%, except for corn fiber, household waste, and chicken, which were less than 10%. Cooked food and protein-rich food waste was found to contain less ash than fruit peels, which in turn was also less that cereal waste. The ash content was also less than the value of 20 to 40% that is normally contained in lignite coal. The ash content present in the hydrochar comes from the alkali metals (Na and K) in corresponding food waste, and the amount present in the hydrochar determines its application as a biofuel. The alkali metals (Na and K) resulted in fouling of the heating surfaces of the boilers, thereby reducing their thermal efficiency.

Elemental composition of hydrochars produced from different food wastes shows that the carbon contents ranged between 45 and 71%, while the hydrogen contents are less than 10%. The relatively higher elemental carbon content in food waste compared to a carbon content range of 45–51% in coal may be due to the higher carbohydrate content of food waste. Except for simulated waste, chicken, and brewers spent grain hydrochar, which had nitrogen content above 5.0%, most of the food wastes ranged between 1.5 and 3.74%. It is worth noting that hydrochar developed from pomegranate residue grape marc had a nitrogen content less than the value of 1.82% contained in lignite [31]. This signifies that these fruit waste-derived hydrochars may be a more appealing source of clean energy. The sulphur contents of most of the food wastes were less than 0.6% (found in Canadian coal). Except for grape marc hydrochar, which had an oxygen content of about 40%, most food waste had an oxygen content of less than 37%, which is found in Thailand coal. These results show that food waste hydrochars could be a potential co-feed with coal in combustion plants for energy generation.

In terms of energy properties, most studies showed that the heating values of food waste hydrochars are greater than 20 MJ/kg. This suggests that food waste hydrochars are commercially feasible for use as biofuels [2]. The high heating content of the hydrochar developed from food waste is comparable with coal (15 to 35 MJ/kg) [32]. This might be due to their high lignocellulosic content. Usually, according to ISO/TS 17225–8, a hydrochar with heating value between 18.6 and 26.2 MJ/kg would be allowed for its application as a biofuel in industry [6]. The fuel ratio of most food wastes is ranged between 0.62 and 0.98 except for chicken, household waste, and corn fiber, which have a fuel ratio less than 0.2. A hydrochar with a fuel ratio of less than 2.5 meets the standard for use as solid fuel in pulverized combustion systems [2][18]. Some studies have investigated the energy yield of food waste hydrochars from fruit peels, and the values ranged between 60 and 70%. The energy yield for corn fiber is found to be much lower (27.26%).

9. Combustion Kinetics of the Produced Char from HTC

Combustion of hydrochars is carried out by heating the samples from room temperature to a high temperature (>1000 °C) under air flow at a particular heating rate. Using a DTG curve, the combustion process may be divided into three stages depicting the devolatilization, combustion phase, and the burnout phase. A thermogravimetric analyzer is usually used to study the combustion kinetics of hydrochar, after which activation energy is determined to evaluate the process since it essentially affects the temperature sensitivity of the combustion rate. The thermogravimetric analysis (TGA) parameters reported for combustion kinetics studies of hydrochar produced from different food wastes are presented [19][20][21][33][34][35][36][37]. The combustion kinetics experiments were conducted using a thermogravimetric analyzer in order to determine the characteristic of the hydrochars. Combustion kinetics

analysis of the hydrochar mass loss at different time and temperature intervals usually provides insight into its combustion behavior as well as the necessary data required to design large-scale combustion plants. The combustion kinetics analysis of the food wastes is carried out in the temperature range between 25 and 1000 °C under air flow at the volumetric flow rate ranging between 16 and 100 mL/min. The heating rate in most of the studies is maintained between 5 and 40 °C/min. Generally, most of the studies used a sample weight in the range between 5 and 15 mg to improve the flow of heat between the wall of the crucible and sample.

Table 1. Kinetic parameters of combustion of hydrochar from food waste.

Feedstock	Hydrochar Code	Kinetic Modelling Approach	Stages	Activation Energy, E (kJ/mol)	Reaction Order, n	Frequency Factor, A (1/s)	Reference
Mixed food waste	HTC220	Arrhenius	2	Stage 1: 25.47 Stage 2: 16.52	3.0 0.9	11.36×10^{-2} 7.37×10^{-2}	[37]
PVC_R was co-treated with bagasse	HC-P-S	-	2	Stage 1: 86.07 Stage 2: 47.62	-	-	[36]
Spent mushroom substrate	SMS-180/260	Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS)	3	81.76 (FWO) and 75.22 (KAS) for SMS180 and 91.99 (FWO) and 85.71 (KAS) for SMS260	-	-	[34]
Sweet potato	220–60	Coats–Redfern integral	2	Stage 1: 211.94 Stage 2: 181.65		7.58×10^{17} 2.40×10^{9}	[20]

Most of the combustion kinetics studies presented limited their studies to only the combustion behavior of food waste [19][35] (Sharma et al., 2022; Su et al., 2021) and did not study the kinetics. For example, Su et al. [19] carried out a TGA of hydrochar. Results showed that compared to oil extracted food waste, the hydrochar had a more stable and longer combustion process with the higher ignition temperature and burnout temperature. Likewise, Sharma et al. [35], found that hydrochar produced from a mixture of food and yard wastes exhibited a smoother combustion profile with a single combustion zone which depicts its improved combustion stability. A further kinetics analysis of the combustion of the hydrochar produced in these studies under reference would deepen an understanding of complex reaction in addition to providing a basis for cost-effective and eco-friendly conversions of these hydrochars in the future. **Table 1** displayed the combustion kinetics parameters (activation energy, pre-exponential factor, and reaction order) obtained for some hydrochars using two common model-free kinetic approaches of Kissenger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO). These approaches requires the determination of kinetics parameters from the TGA data obtained at different heating rates for a given sample [33] [34][38]. These methods were usually reported in most of the studies probably because of their simplicity or for the need to avoid mistakes that are commonly associated with choosing a particular reaction model. Noteworthy in

Table 1 [20][34][36][37] is the decreasing trend of the activation energy kinetics parameter of the hydrochars across the different stages (2 to 4) in the combustion. Islam et al. [38] investigated the combustion kinetics of hydrochar produced from Karanj fruit hulls using the TGA data obtained at three different heating rates between 5 and 20 °C/min using the KAS. During the study, the activation energy varied from 114 to 67 kJ/mol as the conversion varied from 0.1 to 0.8. Kojić et al. [34] investigated the combustion kinetics analysis of hydrochar produced from spent mushroom substrate at 180 °C and found that E_a decreased from 158.83 to 38.25 kJ/mol (FWO) and from 157.64 to 27.89 kJ/mol (KAS). Combustion kinetics analysis of the hydrochar produced from the same substrate at 260 °C also showed a decrease in E_a from 133.06–64.25 kJ/mol (FWO) and from 130.18–55.35 kJ/mol (KAS). A similar decreasing trend was also observed during the combustion kinetics analysis of mixed food waste [37] using the classical Arrhenius equation where respective activation energies calculated for the first and second peaks were 25.47 and 16.52 kJ/mol. The decrease in activation energy as the combustion reaction progressed was expected given that the cellulose and hemicellulose structure of the hydrochar would be destroyed at higher temperatures. Apart from this factor, the observed decrease in activation energy may be attributed to the improved surface area and porosity of the hydrochar.

References

1. Ingrao, C.; Faccilongo, N.; Di Gioia, L.; Messineo, A. Food waste recovery into energy in a circular economy perspective: A comprehensive review of aspects related to plant operation and environmental assessment. J. Clean. Prod. 2018, 184, 869–892.

2. Mannarino, G.; Sarrion, A.; Diaz, E.; Gori, R.; De, M.A.; Mohedano, A.F. Improved energy recovery from food waste through hydrothermal carbonization and anaerobic digestion. Waste Manag. 2022, 142, 9–18.

3. Mendoza Martinez, C.L.; Sermyagina, E.; Saari, J.; Silva de Jesus, M.; Cardoso, M.; Matheus de Almeida, G.; Vakkilainen, E. Hydrothermal carbonization of lignocellulosic agro-forest based biomass residues. Biomass Bioenergy 2021, 147, 106004.

4. Xie, X.; Peng, C.; Song, X.; Peng, N.; Gai, C. Pyrolysis kinetics of the hydrothermal carbons derived from microwave-assisted hydrothermal carbonization of food waste digestate. Energy 2022, 245, 123269.

5. Saqib, N.U.; Baroutian, S.; Sarmah, A.K. Physicochemical, structural and combustion characterization of food waste hydrochar obtained by hydrothermal carbonization. Bioresour. Technol. 2018, 266, 357–363.

6. Sarrion, A.; Diaz, E.; Rubia, M.A.; De Mohedano, A.F. Fate of nutrients during hydrothermal treatment of food waste. Bioresour. Technol. 2021, 342, 125954.

7. Ciftci, D.; Saldaña, M.D.A. Hydrolysis of sweet blue lupin hull using subcritical water technology. Bioresour. Technol. 2015, 194, 75–82.

8. Liu, Y.; Sun, Y.; Wan, Z.; Jing, F.; Li, Z.; Chen, J.; Tsang, D.C.W. Tailored design of food waste hydrochar for efficient adsorption and catalytic degradation of refractory organic contaminant. J. Clean. Prod. 2021, 310, 127482.

9. Yan, M.; Liu, Y.; Song, Y.; Xu, A.; Zhu, G.; Jiang, J.; Hantoko, D. Comprehensive experimental study on energy conversion of household kitchen waste via integrated hydrothermal carbonization and supercritical water gasification. Energy 2022, 242, 123054.

10. Zhou, Y.; Engler, N.; Li, Y.; Nelles, M. The influence of hydrothermal operation on the surface properties of kitchen waste-derived hydrochar: Biogas upgrading. J. Clean. Prod. 2020, 259, 121020.

11. Gupta, D.; Mahajani, S.M.; Garg, A. Investigation on hydrochar and macromolecules recovery opportunities from food waste after hydrothermal carbonization. Sci. Total Environ. 2020, 749, 142294.

12. Zhang, Z.; Yang, J.; Qian, J.; Zhao, Y.; Wang, T.; Zhai, Y. Biowaste hydrothermal carbonization for hydrochar valorization: Skeleton structure, conversion pathways and clean biofuel applications. Bioresour. Technol. 2021, 324, 124686.

13. Zhai, Y.; Wang, T.; Zhu, Y.; Peng, C.; Wang, B.; Li, X.; Li, C.; Zeng, G. Production of fuel pellets via hydrothermal carbonization of food waste using molasses as a binder. Waste Manag. 2018, 77, 185–194.

14. Wang, T.; Zhai, Y.; Zhu, Y.; Peng, C.; Xu, B.; Wang, T. Influence of temperature on nitrogen fate during hydrothermal carbonization of food waste. Bioresour. Technol. 2018, 247, 182–189.

15. Motavaf, B.; Dean, R.A.; Nicolas, J.; Savage, P.E. Hydrothermal carbonization of simulated food waste for recovery of fatty acids and nutrients. Bioresour. Technol. 2021, 341, 125872.

16. Kumar, N.; Weldon, R.; Lynam, J.G. Hydrothermal carbonization of coffee silverskins. Biocatal. Agric. Biotechnol. 2021, 36, 102145.

17. Al Afif, R.; Anayah, S.S.; Pfeifer, C. Batch pyrolysis of cotton stalks for evaluation of biochar energy potential. Renew. Energy 2020, 147, 2250–2258.

18. Akarsu, K.; Duman, G.; Yilmazer, A.; Keskin, T.; Azbar, N.; Yanik, J. Sustainable valorization of food wastes into solid fuel by hydrothermal carbonization. Bioresour. Technol. 2019, 292, 121959.

19. Su, H.; Zhou, X.; Zheng, R.; Zhou, Z.; Zhang, Y.; Zhu, G.; Yu, C.; Hantoko, D.; Yan, M. Hydrothermal carbonization of food waste after oil extraction pre-treatment: Study on hydrochar fuel characteristics, combustion behavior, and removal behavior of sodium and potassium. Sci. Total Environ. 2021, 754, 142192.

20. Chen, X.; Ma, X.; Peng, X.; Lin, Y.; Yao, Z. Conversion of sweet potato waste to solid fuel via hydrothermal carbonization. Bioresour. Technol. 2018, 249, 900–907.

21. Gupta, D.; Mahajani, S.M.; Garg, A. Hydrothermal carbonization of household wet waste—Characterization of hydrochar and process wastewater stream. Bioresour. Technol. 2021, 342, 125972.

22. Atallah, E.; Zeaiter, J.; Ahmad, M.N.; Kwapinska, M.; Leahy, J.J.; Kwapinski, W. The effect of temperature, residence time, and water-sludge ratio on hydrothermal carbonization of DAF dairy sludge. J. Environ. Chem. Eng. 2020, 8, 103599.

23. Guo, S.; Dong, X.; Wu, T.; Zhu, C. Influence of reaction conditions and feedstock on hydrochar properties. Energy Convers. Manag. 2016, 123, 95–103.

24. Sevilla, M.; Fuertes, A.B. Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides. Chem. Eur. 2009, 15, 4195–4203.

25. Wilk, M.; Magdziarz, A.; Kalemba-rec, I.; Szymańska-Chargot, M.; Szyma, M. Upgrading of green waste into carbon-rich solid biofuel by hydrothermal carbonization: The effect of process parameters on hydrochar derived from acacia. Energy 2020, 202, 117717.

26. Murillo, H.A. Bioresource Technology Valorization of oat husk by hydrothermal carbonization: Optimization of process parameters and anaerobic digestion of spent liquors. Bioresour. Technol. 2022, 343, 126112.

27. Ischia, G.; Fiori, L.; Gao, L.; Goldfarb, J.L. Valorizing municipal solid waste via integrating hydrothermal carbonization and downstream extraction for biofuel production. J. Clean. Prod. 2021, 289, 125781.

28. Sobek, S.; Tran, Q.K.; Junga, R.; Werle, S. Hydrothermal carbonization of the waste straw: A study of the biomass transient heating behavior and solid products combustion kinetics. Fuel 2022, 314, 122725.

29. Das, P.; Chandramohan, V.P.; Mathimani, T.; Pugazhendhi, A. A comprehensive review on the factors affecting thermochemical conversion efficiency of algal biomass to energy. Sci. Total Environ. 2021, 766, 144213.

30. Lachos-perez, D.; Paulo, C.; Abaide, E.R.; Zabot, G.L.; De Castilhos, F. Hydrothermal carbonization and Liquefaction: Differences, progress, challenges, and opportunities. Bioresour. Technol. 2022, 343, 126084.

31. Qi, J.; Fan, C.; Wu, H.; Li, S. Structure evolution of lignite char in step pyrolysis and its combustion reactivity. Fuel 2022, 315, 123256.

32. Richards, A.P.; Haycock, D.; Frandsen, J.; Fletcher, T.H. A review of coal heating value correlations with application to coal char, tar, and other fuels. Fuel 2021, 283, 118942.

33. Wilk, M.; Śliz, M.; Gajek, M. The effects of hydrothermal carbonization operating parameters on high-value hydrochar derived from beet pulp. Renew. Energy 2021, 177, 216–228.

34. Kojić, M.M.; Petrović, J.T.; Petrović, M.S.; Stanković, S.M.; Porobić, S.J.; Marinović-Cincović, M.T.; Mihajlović, M.L. Hydrothermal carbonization of spent mushroom substrate: Physicochemical characterization, combustion behavior, kinetic and thermodynamic study. J. Anal. Appl. Pyrolysis 2021, 155, 105028.

35. Sharma, H.B.; Panigrahi, S.; Vanapalli, K.R.; Cheela, V.R.S.; Venna, S.; Dubey, B. Study on the process wastewater reuse and valorisation during hydrothermal co-carbonization of food and yard waste. Sci. Total Environ. 2022, 806, 150748.

36. Liu, Z.; Ma, D.; Liang, L.; Hu, X.; Ling, M.; Zhou, Z.; Fu, L.; Liu, Z.; Feng, Q. Co-hydrothermal dechlorination of PVC plastic and bagasse: Hydrochar combustion characteristics and gas emission behavior. Process Saf. Environ. Prot. 2022, 161, 88–99.

37. Khan, M.A.; Hameed, B.H.; Raza Siddiqui, M.; Alothman, Z.A.; Alsohaimi, I.H. Physicochemical properties and combustion kinetics of food waste derived hydrochars. J. King Saud Univ. Sci. 2022, 34, 101941.

38. Islam, M.A.; Kabir, G.; Asif, M.; Hameed, B.H. Combustion kinetics of hydrochar produced from hydrothermal carbonisation of Karanj (Pongamia pinnata) fruit hulls via thermogravimetric analysis. Bioresour. Technol. 2015, 194, 14–20.