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Torrefaction of Agricultural Wastes: Influence of Lignocellulosic Types and Treatment Temperature on Fuel Properties of Biochar

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Abstract *– In this article, four types of agricultural waste with different amounts of each lignocellulosic type, including rice husk (RH), coconut husk (CH), cassava rhizome (CR), and corncob (CC) were torrefied under inert environment at 200 – 300°C for 30 min. Biochar properties were characterized by various techniques in order to investigate their yield, physicochemical properties, higher heating value (HHV), thermal decomposition behavior, and surface functional group. The experimental results show that yield, HHV, and energy yield (E_y) of biochar were depended significantly on both types of agricultural waste and treatment temperature. The values of those parameters ranged from 81.75 – 35.59%, 19.06 – 28.29 MJ/kg, and 51.34 – 86.22%, respectively. Fuel properties of agricultural waste were greatly enhanced by torrefaction at 300°C. Biochar from torrefied CC provides the highest fuel ratio (2.18) with lowest atomic ratios of O/C and H/C (0.18 and 0.67, respectively) and this is comparative with bituminous coal. The changes of these properties were mainly due to dehydration and deoxygenation reactions. Interestingly, agricultural wastes with high cellulose content (44.41%) could produce biochar with the maximum energy yield (86.22%). These results indicated that torrefaction was a promising technology for conversion of agricultural wastes to biochar as coal substitute material.*

Keywords *– biomass compositions, renewable energy, solid fuel, torrefaction process, torrefied biomass.*

1. INTRODUCTION

Fossil fuels or non-renewable energy use can be the cause of many severe problems such as environmental pollutions and health [1]. To overcome these problems, the utilizations of renewable fuel have been investigated. Biomass is considered as one of the most promising renewable resources [2]. In Thailand, biomass of agricultural wastes is the plentiful where the estimated amount of agricultural wastes generated from major agricultural crops in Thailand is tabulated in Table 1.

Table 1. The estimated amount of major agricultural wastes in Thailand in 2017.

Waste, lignocellulosic biomass	Amount (tons)
Rice husk	6,690,010
Coconut husk	277,901
Cassava rhizome	6,099,038
Corncob	1,053,644

Interestingly, the energy potential from those biomass resources corresponded to 3,290 ktoe or 972 MW [3]-[4]. Thus, those agricultural wastes may substantially contribute to decrease fossil fuel consumptions in Thailand. However, there are several drawbacks associated with the direct use of agricultural wastes as fuels such as:

(1) High moisture content and low heating value
(2) Naturally degraded by biodegradation
(3) High cost during collection and transportation
(4) Uneven and varied compositions

There are many technologies regarded as a pre-treatment technology that have been developed to overcome these drawbacks such as pelletization, torrefaction, pyrolysis, and carbonization. Among them, torrefaction or mild pyrolysis is a promising technology to improve fuel properties of original agricultural waste, resulting biochar product. Torrefaction is a thermal pre-treatment technology conducted under atmospheric pressure in an inert environment at mild treatment temperature (200 – 300°C) [5]-[6]. The biochar product has a higher fuel ratio, and calorific value, accompanied with grindability, and hydrophobicity [7]. Moreover, lower ratio of H/C and O/C atomic are also obtained [8]-[10]. The changes of these properties resulted in biochar with better fuel property than that of original agricultural waste [11]. The use of biochar as fuel can reduce both volatile matter and CO_2 emissions [12]. Furthermore, torrefaction can significantly decrease storage and transportation cost, and enhance the biodegradation resistance [7], [13]-[16]. Therefore, torrefaction has been recommended for production of coal substitute material for industrial applications [17].

Torrefaction does not only remove moisture content but also degrade hemicellulose, cellulose, and lignin as the thermal decomposition temperature of each

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composition are different [18]-[19]. In addition, the characteristics and contents of each composition varied according to biomass types which related to properties of biochar. The properties and structures of biochar also related with process variables such as temperature and time [20]. Recent studies on torrefaction have proven that treatment temperature played a vital key variable on properties and structures of biochar [18], [21]-[22]. Several studies on torrefaction of agricultural wastes such as bamboo [18], textile fibres [21], corn stover [22], oil palm waste [23], [24], sorghum bagasse [9], pine sawdust [25], have already been conducted. They reported that properties of biochar strongly depended on types of agricultural waste and torrefation temperature. However, torrefaction of agricultural wastes with various lignocellulosic type has been limited.

Thus, in this study, the effect of lignocellulosic types on fuel properties and structures of biochar is investigated. The selected biomass is based on different amount of lignocellulosic types as ash, lignin, cellulose, and hemicellulose content. Rice husk (RH), coconut husk (CH), cassava rhizome (CR), and corncob (CC) were selected and torrefied at mild temperatures (200 – 300°C). The properties of the biochar product were further investigated in order to: (1) identify the potential of biochar production by torrefaction of agricultural wastes; (2) explore the properties of biochar from torrefaction of agricultural wastes; (3) investigate the effect of lignocellulosic types and treatment temperature on biochar properties.

2. MATERIALS AND METHODS

2.1 *Feedstock Preparations*

In this study, four types of local agricultural wastes in Thailand including rice husk (RH), coconut husk (CH), cassava rhizome (CR), corncob (CC) were used as feedstocks. RH was collected from Mueang District, Nakhon Pathom Province. CH and CC were collected from Klong Luang District, Pathum Thani Province. CR was collected from Dan Makham Tia District, Kanchanaburi Province. Each feedstock was pulverized to particle size less than 1 mm, dried at 105°C for 24 h and stored in a sealed plastic bag for further experiment.

2.2 *Torrefaction Experiment*

The torrefaction apparatus as schematically shown in Figure 1 composes of quartz tubular reactor (length 100.00 cm; OD 4.6 cm), horizontal furnace (ID 4.6 cm and heated zone 15 cm length), nitrogen gas cylinder, gas rotameter, and gas treatment unit for cleaning the torrefied gas before releasing to the atmosphere.

Torrefaction process of each biomass feedstock was carried out in a quartz tubular reactor, being heated by horizontal furnace under inert environment of nitrogen (N_2) gas (>99.99 vol%). Prior to the experiment, 3 grams of dried feedstock was loaded into the quartz boat (length 10.00 cm, width 0.38 cm, and height 2.00 cm) before placing into a quartz tubular reactor. Then N_2 gas was introduced through the tube reactor with a flow rate of 100 mL/min for 30 min before heating. The torrefaction process was then started with increasing temperature from 30°C to the desired temperature (200, 250, and 300°C) with a constant ramping rate of 10°C/min. The residence time was set to 30 min for each sample. After the completion of the reaction, the temperature was naturally dropped to 90 °C under carrier gas flow. Then, the biochar was collected and stored in a sealed plastic bags for further analysis. All experiments were performed in duplication while the third was also conducted in case of the results were inconsistent. In this article, the biochar samples were labeled as “BM – T” where BM represents the biomass types (cassava rhizome (CR), coconut husk (CH), corncob (CC), and rice husk (RH)), and T represents the reaction temperature. For example, CR-200 stands for the biochar sample obtained from torrefaction of cassava rhizome at 200°C.

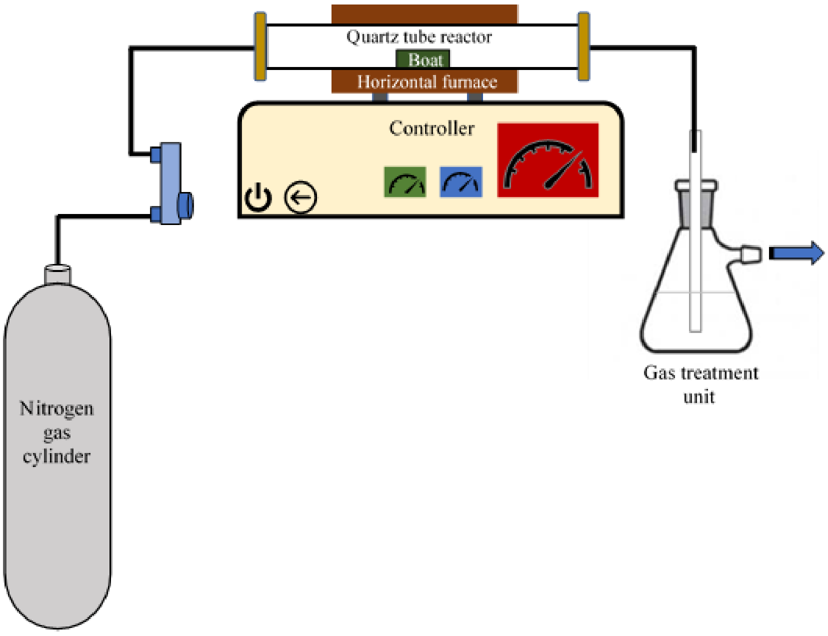

Fig. 1. Schematic of torrefaction apparatus.

2.3 Biochar Characterization

To observe the biochar properties, the analysis of biochar yield, proximate, ultimate, higher heating value (HHV), thermal decomposition behavior, and surface functional group of feedstock and biochar were conducted. For proximate analysis, ash and volatile matter (VM) were determined according to the standard method of NREL/TP-510-42622 [26] and ASTM D 7582 [27], respectively. Fixed carbon (FC) content was determined by subtracting ash and VM contents from 100%. Ultimate analysis (CHNS) was performed by using an elemental analyzer (LECO CHNS628, LECO, USA). Oxygen content was determined by subtracting the contents of C, H, N, S and ash from 100%. Higher heating value (HHV) was analyzed by using a bomb calorimeter (LECO AC600, LECO, USA). Surface functional groups were observed using a Fourier transform infrared (FTIR) spectrophotometer (Thermo Scientific Nicolet 6700, Thermo Scientific, USA) equipped with a diamond attenuated total reflectance (ATR) attachment by using 64 scans at a resolution of 4 cm^{-1}. Before FTIR analysis, the samples were pulverized to fine powder and dried at 105°C for overnight. Thermal decomposition behavior of samples was analyzed by thermogravimetric analyzer (TGA/SDTA851e METTLER TOLEDO, USA). The samples (5-10 mg.) were loaded in alumina pan and heated from 30°C to 750°C with the heating rate of 10°C/min under nitrogen flow rate 25 mL/min. Carbohydrate and lignin contents in original agricultural wastes were determined according to the online standard analysis method of NREL/TP-510-42618 [28].

2.4 Calculations

Biochar yield, FC densification (FC_d), FC recovery efficiency (FC_{re}), carbon densification (C_d), carbon recovery efficiency (C_{re}), fuel ratio (Fr), energy density (E_d), energy yield (E_y), and HHV improvement (HHV_i) of biochar were calculated according to Equations (A1) – (A12) as shown in the supplementary data [29].

Decarboxylation (DC) was calculated according to Equations 1 to 3 [30]:

$$O_c\ (g) = M_0 \text{ x } (100 - W_0 - A_0) \text{ x } 10^{-2} \text{ x } Y_{c,0} \quad (1)$$

$$R_c\ (g) = M_0 \text{ x } SY \text{ x } (100 - W_t - A_T) \text{ x } 10^{-2} \text{ x } Y_{c,T} \quad (2)$$

$$DC\ (\%) = 1 - (R_c/O_c) \text{ x } 100 \quad (3)$$

where O_c and R_c are amounts of carbon in original agricultural waste and residual carbon in biochar, respectively. M, W, A, and Y stand for the sample weight (g), moisture content (%), ash content (%), and mass fraction of carbon, respectively. The subscripts 0 and t represent the original agricultural waste and torrefaction temperature of biochar, respectively. Dehydration (DH), and deoxygenation (DO) were also computed according to the same procedure.

3. RESULTS AND DISCUSSION

3.1. Compositions of Original Agricultural Wastes

Table 2 summarizes the amount of lignocellulosic types of original agricultural waste feedstocks including rice husk (RH), coconut husk (CH), cassava rhizome (CR), and corncob (CC). As can be seen, the amounts of cellulose, hemicellulose, and lignin in these agricultural wastes are significantly different which agree well with literatures [31]-[34]. CH composes mainly of lignin, consisting three hydroxycinnamyl alcohol monomers accompanied with differences in their degree of methoxylation: p-coumaryl, coniferyl, and synapyl alcohol. In addition, lignin is the most resistant component of lignocellulose [5]. CR composes mainly of cellulose which is the homopolymer of glucose units joined by β-1-4-glycoside bonds with crystalline ribbon like structure. On the other hands, CC composes mainly of hemicellulose with heteropolymer (50 - 200 units) of D-xylose, D-glucose, D-galactose, L-arabinose, D-glucuronic acid, and D-mannose which these sorts in a mess and easily to be decomposed [35].

Table 2. The amount of lignocellulosic types of agricultural wastes.

Lignocellulosic compositions	RH	CH	CR	CC
Cellulose	28.50	26.27	44.41	37.27
Hemicellulose	25.49	26.00	25.18	36.32
Lignin	25.68	43.34	25.26	23.35

3.2. Biochar Yield

Biochar yield is a key property which was used to observe the influence of lignocellulosic types and treatment temperature on biochar from torrefaction process. As indicated in Figure 2, biochar yield from torrefaction of RH, CH, CR, and CC significantly varioed with types of agricultural waste and treatment temperature. The maximum biochar yield was obtained from torrefied RH 200°C (81.75%). Whereas the treatment temperature at 250 and 300°C could be remarked for torrefied CH, yielding biochar as 60.60 and 52.15%, respectively. The reason of this phenomenon was due to the difference of lignocellulosic compositions in original agricultural wastes. Original RH has a higher ash (inorganic) content, but lower organic content than those of other agricultural waste feedstocks (Table 3). High content of ash in agricultural waste feedstocks could decrease the devolatilization rate during mild torrefaction [36]. The mass loss at treatment temperature of 200 °C was significantly caused by the low degree of organic content decomposition [8]. On the other hand, original CH composes mainly of organic content particularly lignin which is the most resistant organic component. This affected biochar yield of torrefied CH at 250 and 300°C was higher than that of torrefied CR, CC, and RH. In contrast, the minimum biochar yield at treatment temperature of 200, 250, and 300°C could be obtained from torrefied CC. This was due to CC composes mainly of hemicellulose which is easily to be degraded. In addition, biochar yield from torrefaction of CH, RH, CR, and CC decreased continuously from 75.68 – 52.15%, 81.75 – 41.26%, 74.30 – 36.37%, and 65.58 – 35.59%, respectively with increasing treatment temperature from 200 – 300°C. The reason for this result was mainly due to the vaporization of volatile content and thermal degradation of hemicellulose [23], [37]. Similar results were revealed for torrefaction of de-oiled Jatropha seed kernel [8], woody biomass [38], and peat [39].

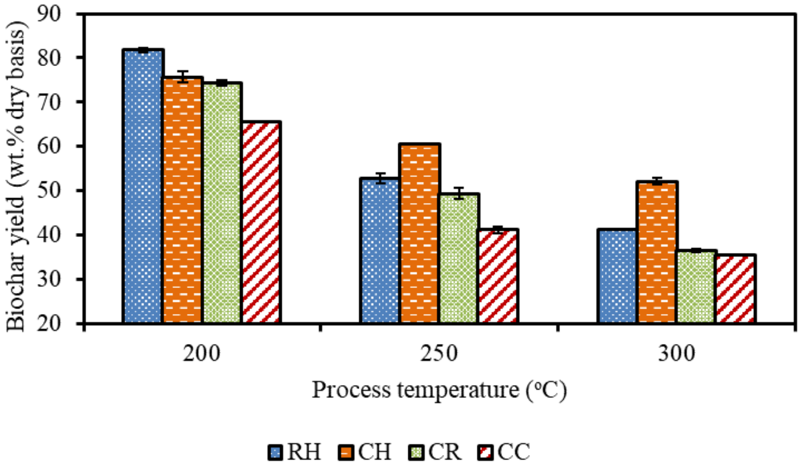

Fig. 2. Biochar yield from torrefaction of RH, CH, CR, and CC at 200 to 300°C.

Table 3. Proximate and ultimate analysis of original and torrefied agricultural wastes at different treatment temperatures.

Sample name	Proximate analysis (wt.%, dry basis)			Ultimate analysis (wt.%, dry basis)					HHV (MJ/kg)
	Ash	VM	FC	C	H	N	S	O	
RH	9.57	62.83	27.60	45.87	5.87	0.56	0.14	38.00	18.78
RH-200	9.69	60.33	29.98	47.86	5.36	0.61	0.12	36.35	19.06
RH-250	14.30	42.43	43.28	57.16	4.52	0.93	0.14	22.95	22.59
RH-300	18.58	26.64	54.78	60.74	3.55	0.99	0.13	16.01	23.33
CH	6.70	61.78	31.52	49.03	5.37	0.41	0.13	38.36	19.33
CH-200	7.70	52.18	40.13	53.01	4.78	0.55	0.10	33.86	20.47
CH-250	9.64	40.40	49.96	58.61	4.19	0.59	0.10	26.88	22.40
CH-300	11.52	32.32	56.16	62.53	3.70	0.57	0.10	21.58	23.70
CR	4.95	71.92	23.13	45.14	5.82	0.84	0.13	43.12	18.04
CR-200	6.71	67.00	26.29	52.27	5.40	1.27	0.23	34.12	20.92
CR-250	9.03	40.45	50.53	58.72	4.98	1.38	0.11	25.78	23.49
CR-300	10.83	30.80	58.37	64.24	4.27	1.43	0.11	19.13	25.22
CC	2.01	76.04	21.95	46.74	6.04	0.84	0.15	44.23	18.80
CC-200	9.10	61.65	29.25	55.52	5.46	1.26	0.13	28.53	22.65
CC-250	3.97	38.99	57.04	62.20	5.14	1.47	0.15	27.08	24.86
CC-300	3.35	30.39	66.26	72.94	4.05	1.63	0.14	17.88	28.29

3.3. Proximate and Ultimate Analysis

Proximate and ultimate analysis results of the original and torrefied agricultural wastes (rice husk (RH), coconut husk (CH), cassava rhizome (CR), and corncob (CC) with higher heating value (HHV) are tabulated in Table 3. The results illustrated that both lignocellulosic types and treatment temperature affected significantly proximate and ultimate analysis results of biochar. Proximate analysis results determined that the biochar with high and low ash content could be obtained from torrefied RH and CC, respectively which was associated to the difference of the amount of each composition in original agricultural waste. Ash content of biochar was higher than that of original agricultural wastes, and it also increased with an increase in treatment temperature. This was mainly caused by the degradation rate of organic matter was increase by severe torrefaction [40]. The maximum volatile matter (VM) content after terrifying at 300°C was obtained from CH, while RH provided a minimum VM content. This is due to some inorganic materials in RH encouraged devolatilization rate during severe torrefaction. In addition, VM content of biochar was lower than primal agricultural wastes, and it also decreased with an increasing temperature during the process. The reason of this result was substantially due to devolatilization rate which was enhanced by severe torrefaction [5]. With the same condition, the maximum fixed carbon (FC) content was obtained from CC sample, while RH sample provided a minimum FC content. This was due to the fact that CC sample mainly composed of hemicellulose which was easily degraded through devolatilization reactions. On the other hand, RH mainly composed of ash which was difficult to degrade through this reaction. FC contents of all biochars were higher than the primal agricultural wastes, and it also increased significantly with an increase in treatment temperature. This phenomenon was mainly related to the reaction of thermal cross-linking and the formation of carbonized materials [41]. Similar results were reported in the torrefaction of de-oiled Jatropha seed kernel [8], palm kernel shell [42], and bamboo [43].

The ultimate analysis result shows that carbon content of original RH, CH, CR, and CC increased significantly after torrefaction, and it increased continuously with an increase in treatment temperature. The carbon content of biochar with maximum and minimum values were the torrefied CC and torrefied RH, respectively. Normally, the major lignocellulosic type of CC is hemicellulose which has low thermal decomposition temperature and is easily degraded through dehydration and deoxygenation reactions. On the other hand, the major component of RH is ash. In addition, an increase in treatment temperature from 200 – 300°C resulted in an increase of carbon content of torrefied RH, CH, CR, and CC from 47.86 – 60.74%, 53.01 – 62.53%, 52.27 – 64.24%, and 55.52 – 72.94%, respectively. Simultaneously, oxygen and hydrogen contents of torrefied agricultural wastes decreased substantially because of the decrease of hydroxyl (-OH) functional group by dehydration and deoxygenation reaction during torrefaction [44]-[46]. The changes in these elemental contents after torrefaction could enhance the HHV of agricultural wastes, and the biochar with maximum and minimum HHV could be obtained from torrefied CC and RH, respectively. This indicated that the difference in HHV of biochar was related with the amount of each lignocellulosic type in original agricultural waste.

The O/C and H/C atomic ratios of biomass and biochar were plotted on Van-revelen diagram as illustrated in Figure 3. Van-Krevelen diagram is a useful way to elucidate the fuel properties of solid fuel. A better fuel property is located close to the origin [20]. As can be seen, O/C and H/C of biochar from each type of original agricultural waste and treatment temperature were located in different area. O/C and H/C of biochar obtained from torrefied CC at 300°C was lower than that from other agricultural wastes and sub-bituminous. This implied that torrefied CC at 300°C could produce a promising biochar for being used as bituminous coal. An increase in treatment temperature from 200 to 300°C continuously reduced O/C and H/C of biochar. Biochar with low H/C and O/C is generally accepted as fuel replacement because of its low energy loss and smoke emission during its combustion process [47]. This finding on O/C and H/C atomic ratio of biochar from torrefied CR, CH, CC, and RH at different treatment temperature agreed with other studies on other types of biomass, *e.g.* de-oiled Jatropha seed kernel [8], sorghum bagasse [9], and municipal solid waste [49].

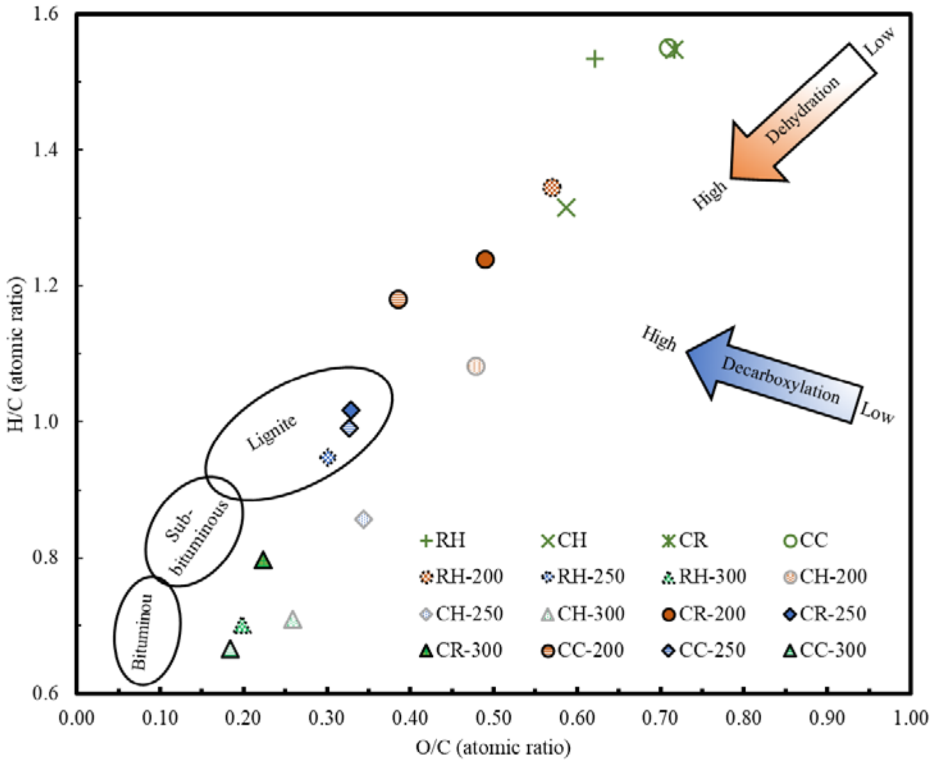

Fig. 3. Van-Krevelen diagram of RH, CH, CR, CC and their biochar from torrefaction at 200 - 300°C, and fossil coal including lignite [47], sub-bituminous, and bituminous [48].

Carbon and energy-related properties of biochar obtained from torrefaction of RH, CH, CR, and CC at 200 – 300°C is summarized in Table 4. FC densification (FC_d), FC recovery efficiency (FC_{re}), fuel ratio (Fr), Carbon densification (C_d), carbon recovery efficiency (C_{re}), energy density (E_d), energy yield (E_y), and HHV improvement (HHV_i) were calculated to identify the influence of lignocellulosic types of original agricultural wastes and treatment temperature on biochar properties. FC_d, C_d, and E_d determine the densification of fixed carbon, carbon, and energy in the biochar (based on dry basis), respectively [50]. As depicted in Table 4, FC_d, C_d, and E_d of biochar changed with agricultural waste types and treatment temperature. The maximum FC_d, C_d, and E_d of biochar could be obtained from torrefied CC at 300°C. This was due to CC possess a high hemicellulose content than others. In general, hemicellulose is easily degraded via dehydration and deoxygenation reactions. These reactions affected an increase in carbon proportion of biochar which corresponded to FC_d, C_d, and E_d values. An increase in treatment temperature could enhance FC_d, C_d, and E_d substantially. FC_{re}, C_{re}, and E_y determine the amount of fixed carbon, carbon, and energy in the feedstock contained in the resulting biochar after torrefaction, respectively. As can be seen, FC_{re}, C_{re}, and E_y of biochar also depend significantly on agricultural waste types and treatment temperature. The maximum FC_{re} could be obtained from torrefied CC at 250 °C while maximum C_{re}, and E_y of biochar could be obtained from torrefied CR at 200°C which maximum E_y could be used to determine optimum condition for alternative fuel production [51].

Fr could be defined as the relationship between FC and VM. The higher Fr represents a high fixed carbon of the solid fuel compared to the volatile components, which generally means a fuel with higher heating content. This value is depended on the type of agricultural waste and treatment temperature. High treatment temperature can increase the Fr value of biochar. The maximum Fr of 2.18 was found in biochar obtained from torrefied CC at 300°C, which implies that the biochar of CC could have a higher combustibility than that of CH, RH, and CR. Similar results were reported for de-oiled Jatropha seed kernel [8], sorghum bagasse [9], and olive tree pruning [52].

HHV_i is determined as the ratio of the increased HHV to feedstock HHV [51]. HHV_i of biochar upon on types of agricultural waste, and it increased continuously with an increase in treatment temperature. The maximum HHV_i could be obtained from torrefied CC at 300°C, probably due to CC composes mainly of hemicellulose which was easily decomposed through dehydration and deoxygenation reaction during torrefaction process.

Table 4. Carbon and energy-related properties of biochar obtained from torrefaction of various agricultural wastes and treatment temperatures.

Sample name	FC densification	FC recovery efficiency	Fuel ratio	Carbon densification	Carbon recovery efficiency	Energy density	Energy recovery efficiency	HHV improvement
RH			0.50					
RH-200	0.91	74.47	0.44	1.04	85.14	1.01	82.78	0.01
RH-250	1.44	76.38	1.02	1.25	66.23	1.20	63.91	0.20
RH-300	1.82	75.21	2.06	1.32	54.74	1.24	51.34	0.24
CH			0.51					
CH-200	1.27	96.89	0.77	1.08	82.29	1.06	80.57	0.06
CH-250	1.59	96.15	1.24	1.20	72.51	1.16	70.28	0.16
CH-300	1.78	92.83	1.74	1.28	66.45	1.23	63.88	0.23
CR			0.32					
CR-200	1.14	84.54	0.39	1.16	86.12	1.16	86.22	0.16
CR-250	2.18	107.81	1.25	1.30	64.23	1.30	64.27	0.30
CR-300	2.52	92.73	1.90	1.42	52.30	1.40	51.38	0.40
CC			0.29					
CC-200	1.33	87.22	0.47	1.19	77.77	1.20	78.88	0.20
CC-250	2.60	107.93	1.46	1.33	55.28	1.32	54.92	0.32
CC-300	3.02	107.36	2.18	1.56	55.52	1.50	53.53	0.50

Dehydration (DH), deoxygenation (DO), and decarboxylation (DC) are the indexes used to determine the amount of weight loss of hydrogen, oxygen, and carbon in original agricultural waste from torrefaction [52]. DH, DO, and DC of biochar from torrefaction of RH, CH, CR, and CC at 200 – 300°C is illustrated in Figure 4. As can be seen, DH, DO, and DC changed significantly with types of original agricultural waste and treatment temperature. The maximum DH, DO, and DC at 200°C (45.07, 60.82, and 27.86%, respectively) and 250°C (65.37, 75.07, and 45.83%, respectively) could be found in torrefaction of CC, while at 300°C could be found in torrefaction of RH (77.46%), CC (85.81%), and CR (50.93%), respectively. An increase in treatment temperature affected DH, DO, and DC increased remarkably. In addition, the changes in DH, DO, and DC of individual original agricultural waste after torrefaction presented that the removal element during torrefaction could order as DO > DH > DC. This implied that torrefaction had much larger effect on oxygen and hydrogen than that on carbon, and it also corresponded to a decrease of O/C and H/C atomic ratio, and an increase in HHV_i.

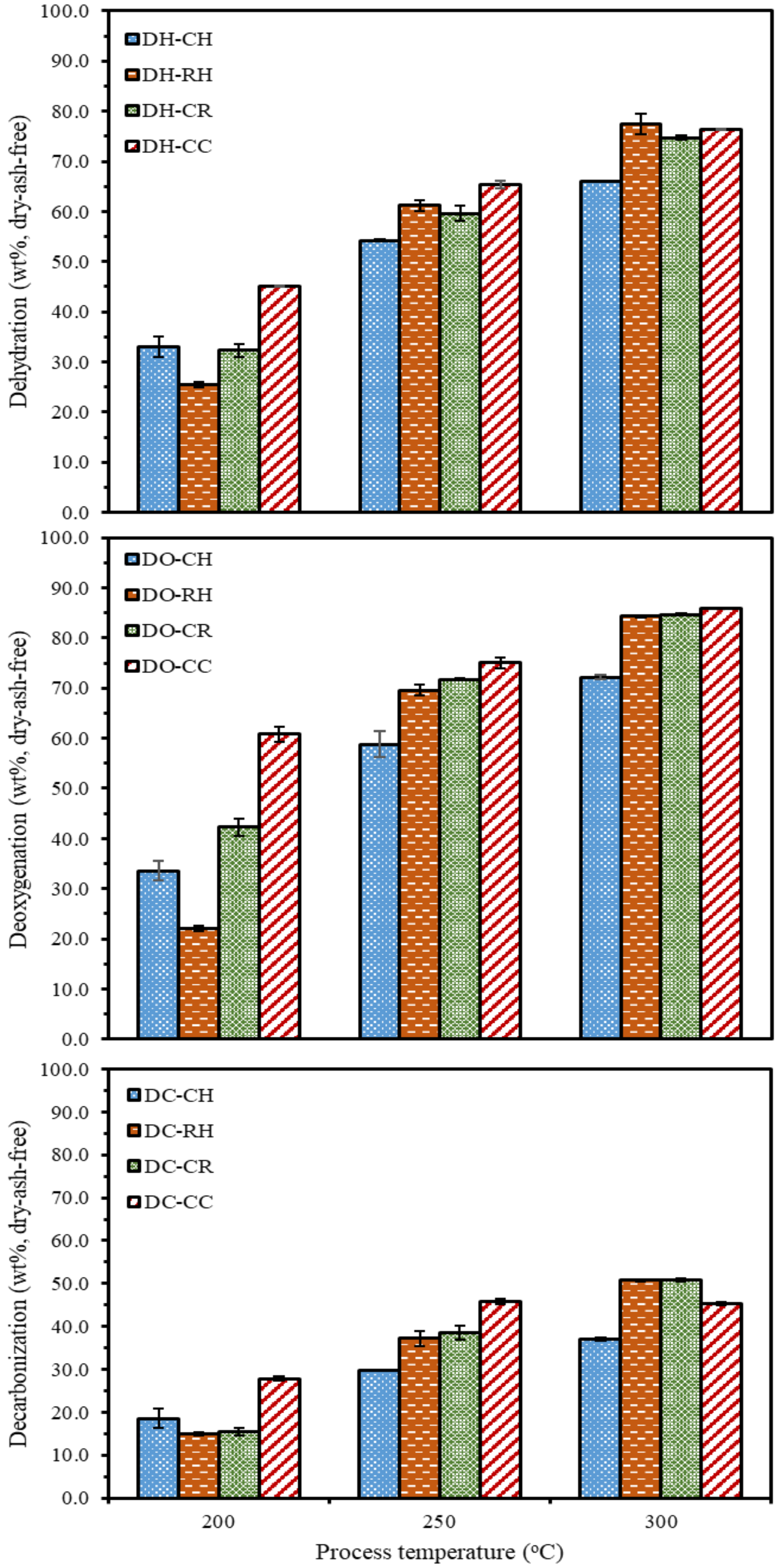

Fig. 4. Dehydration (DH) (A), deoxygenation (DO) (B), and decarbonization (DC) (C) of biochar from torrefaction of CH, RH, CR, and CC at 200 – 300°C.

3.4 Thermal Decomposition Behavior

Thermal decomposition behavior of original RH, CH, CR, and CC, biochar from torrefaction of CR at different treatment temperatures (200, 250, and 300°C), and biochar from torrefaction of RH, CH, CR, and CC at 300°C is illustrated in Figure 5 (A1 and A2), (B1 and B2), and (C1 and C2), respectively. Figures 5 (A1 and A2) depict that thermal decomposition behaviors of original RH, CH, CR, and CC were marginally different, it can be divided into three major stages. The first stage occurred between ambient temperature and 150°C with the maximum weight loss occurred at 95 to 100°C. The present of this stage was due to the vaporization of moisture content. In the temperature range 150 to 370°C, the second stage of biomass thermal decomposition took place which was related to the decomposition of holocellulose. This stage could be sub-divided into two minor stages; 150 to 320°C and 320 to 370°C; where the weight loss at the first stage was related to hemicellulose decomposition and the second was cellulose decomposition. The third stage was observed at the temperature between 375 and 700°C which was due to lignin decomposition. The results on thermal decompositions of hemicellulose, cellulose, and lignin were similar to the previous reports [8], [53] which reveal similar decomposition behavior of various original agricultural wastes. In addition, Table 5 demonstrated that, due to the different compositions, the weight loss behavior of each original agricultural waste was also different.

Table 5. Thermal decomposition parameters of RH, CH, CR, CC, and their biochar from torrefaction at 200 – 300°C.

Samples	T_i^a (°C)	DTG_{max}^b (%/min)	T_{max}^c (°C)	M_f^d (%)
Original agricultural wastes				
RH	201.53	0.864	338.05	24.97
CH	187.31	0.410	309.34	33.90
CR	194.08	0.625	298.48	22.09
CC	164.14	0.818	339.26	19.41
Biochar from torrefaction of CR at different treatment temperature				
CR	194.08	0.625	298.48	22.09
CR-200	236.08	0.552	338.03	38.89
CR-250	273.40	0.220	343.48	47.28
CR-300	374.70	0.141	482.05	61.32
Biochar from torrefaction of CH, RH, CR, and CC at 300°C				
RH -300	332.30	0.087	463.34	68.16
CH-300	383.20	0.086	475.24	67.07
CR-300	374.70	0.141	482.05	61.32
CC-300	284.56	0.100	468.38	65.15

[a] T_i, the initial temperature of thermal decomposition.
[b] DTG_{max}, the maximum mass loss rate according to the peak.
[c] T_{max}, the temperature at maximum mass loss rate.
[d] M_f, the residual mass.

Torrefied CR at different treatment temperature was selected as representative samples to determine the influence of treatment temperature on thermal decomposition behavior of biochar. As can be seen in Figure 5(B1 and B2), mass loss rate of biochar produced at high treatment temperature (300°C) was lower than that at low temperature (200°C) which corresponded to the results of [8] and [43]. In addition, the temperature of maximum mass loss rate and the solid residue after TGA increased with an increase in treatment temperature. The increase of that temperature and residue content implied that more volatile matters degraded and thermal stability of torrefied biomass increased with increasing torrefaction temperature [7].

In addition, torrefied RH, CH, CR, and CC at 300°C were selected as model samples to observe the influence of lignocellulosic types of original agricultural wastes on thermal decomposition behavior of biochar. As can be seen, the weight loss characteristics of each biochar were slightly different, particularly biochar from torrefied CR. The main thermal decomposition of biochar occurred in one stage. Biochar from torrefied CR had a higher mass loss rate and lower solid residue after TGA than those from other agricultural wastes. Indicating that, biochar from torrefied CR had the lowest thermal stability while biochar from torrefied RH had the highest thermal stability.

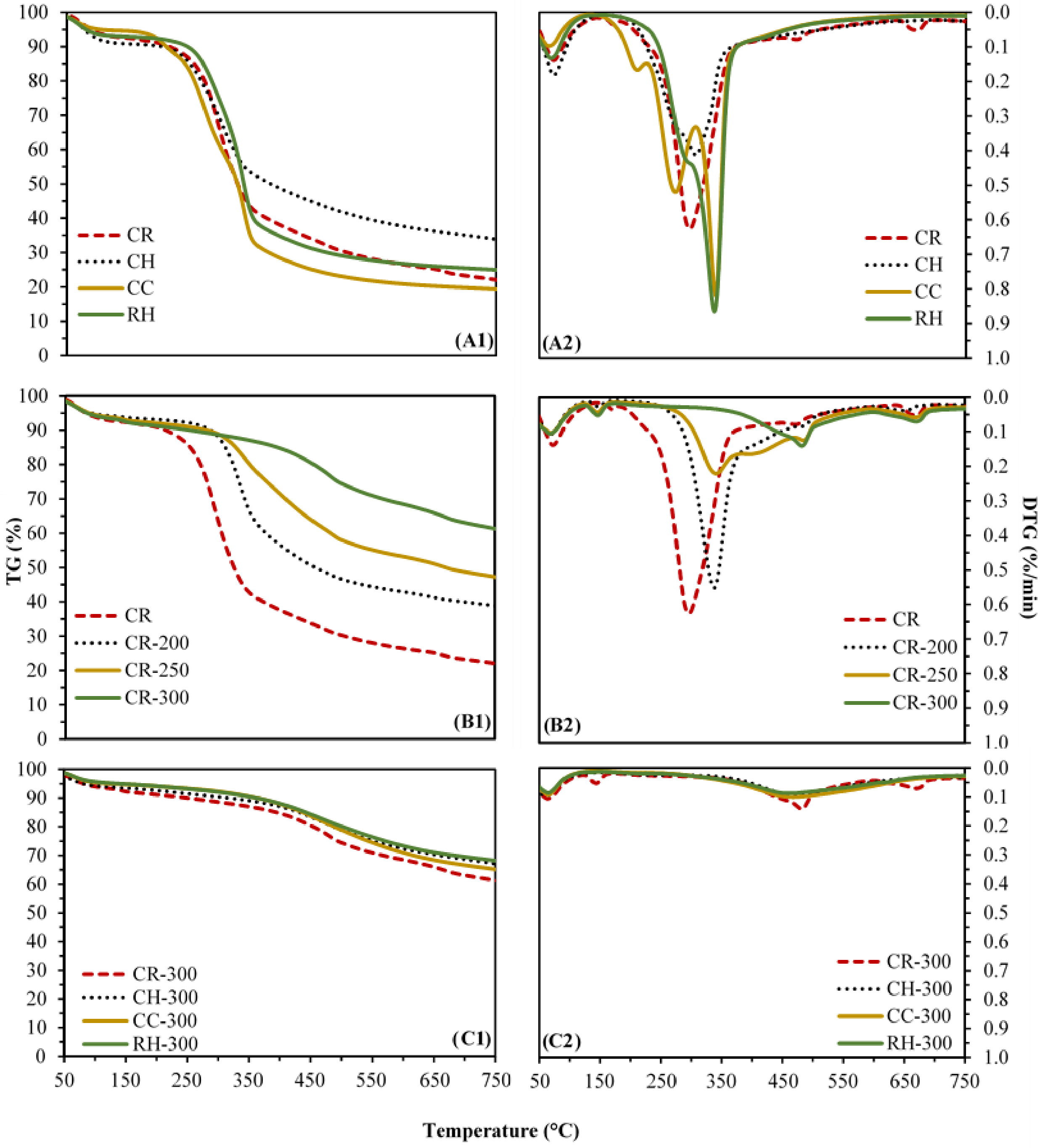

Fig. 5. Thermal decomposition behavior of original RH, CH, CR, CC (A1 and A2), biochar from different treatment temperature (200 – 300°C) of CR (B1 and B2), and biochar from torrefaction if RH, CH, CR, and CC at 300°C (C1 and C2).

3.5 Surface Functional Group

Surface functional groups of original agricultural wastes, biochar from torrefaction of CR at various treatment temperature (200, 250, 300°C), and biochar from torrefaction of CH, RH, CR, and CC at 300°C are illustrated through FTIR spectra in Figure. 6(A), 6(B), and 6(C), respectively. It was found that each original agricultural feedstock provided the same FTIR finger print while biochar from different treatment temperature provided a substantial different spectrum. Moreover, individual spectrum of each biochar from different agricultural feedstock was similar. The signal peak present at 3500-3300 cm^{-1} (1) was attributed to O-H stretching vibration of hydroxyl and carbonyl groups [8]. The intensity of this peak decreased with increasing treatment temperature indicating that hydrogen bond and water loss occurred during torrefaction. This phenomenon was related with the degradation of hemicellulose and cellulose, and an increase in hydrophobicity of feedstock after torrefaction [7]. The transmittance peak at 3000-2800 cm^{-1} (2) was attributed to C-H stretching vibration in aliphatic structures of cellulose. This peak became weak with increasing treatmennt temperature, implying that an increase in treatmennt temperature intensified the dehydration reaction [7]. The bands at around 1670 cm^{-1} (3) was ascribed to C=O stretching vibration of carboxylic groups in hemicelluloses. After torrefaction, the intensity of this peak diminished indicating that the degradation of hemicellulose was appeared. The signals at 1604 and 1510 cm^{-1} (4, 5) were assigned to C=C stretching vibration of aromatic rings presented in lignin [18]. The existence of these signals after torrefaction indicated that the core structure of lignin was preserved. The transmittance peak at 1230 cm^{-1} (6) was attributed to syringyl ring and C-O stretch in lignin and hemicellulose, which could be clearly seen in original corncob. This peak disappeared after torrefaction, which was due to the degradation of hemicellulose. The peak of C-O stretching bond of cellulose and hemicellulose was ascribed at 1060-1030 cm^{-1} (7) [54]. It became less intense after torrefaction at 200 and 250°C, and disappeared after torrefaction at 300°C. This was mainly reflected by dehydration and decarboxylation reaction of carbohydrates [18]. In addition, there was the additional band at 450 cm^{-1} (8) which is present only in torrefied RH. It is the band of Si-O out-of-plane deformation [34].

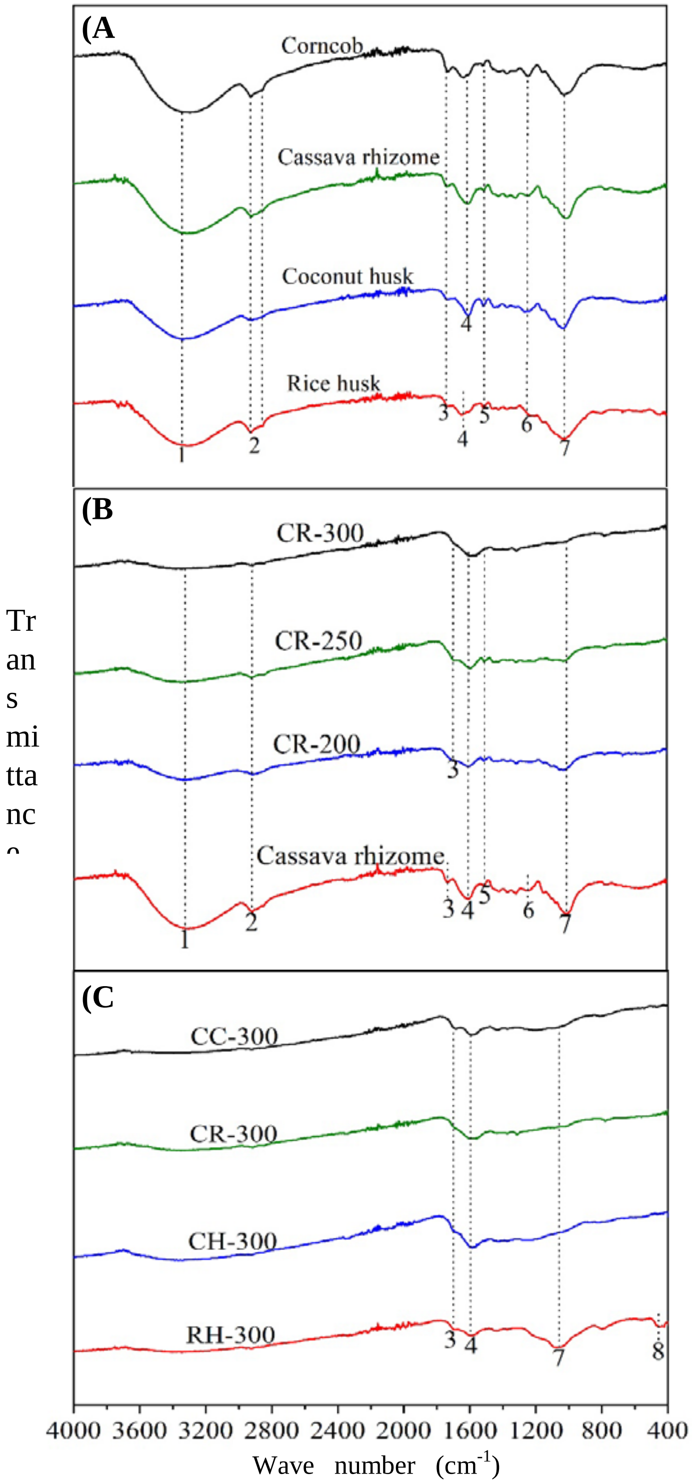

Fig. 6. FTIR spectra of RH, CH, CR, CC (A), biochar from different treatment temperature (200 – 300°C) of CR (B), and biochar from RH, CH, CR, and CC (C).

4. CONCLUSIONS

Torrefaction of agricultural wastes with different amount of lignocellulosic types, including ash, lignin, cellulose, and hemicellulose, were successfully performed over temperature of 200 to 300°C under inert atmosphere. Torrefaction enhances thermal stability of agricultural waste. Properties of biochar are not only depending on types of agricultural waste but also treatment temperatures. Severe torrefaction can yield biochar with fuel properties similar to bituminous coal, particularly biochar from high hemicellulose feedstock (CC). The feedstock with high cellulose content (CR) could provide biochar with high energy yield.

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APPENDIX

The biochar yield, FC densification (FC_d), FC recovery efficiency (FC_{re}), Carbon densification (C_d), Carbon recovery efficiency (C_{re}), Fuel ratio (Fr), Energy density (E_d), Energy yield (E_y), and HHV improvement (HHV_i) of biochar were calculated according to Equations A1 – A9:

Biochar yield (%) = (mass of biochar / mass of dried feedstock) x 100% (A1)

FC_d = FC content of dried biochar / FC content of dried feedstock (A2)

FC_{re} (%) = Biochar yield x FCd (A3)

C_d = Carbon content of dried biochar / Carbon content of dried feedstock (A4)

C_{re} (%) = Biochar yield x Cd (A5)

Fr = FC/VM (A6)

E_d = HHV of dried biochar / HHV of dried feedstock (A7)

E_y (%) = Biochar yield × Ed (A8)

HHV_i = (HHV of biochar - HHV of feedstock) / HHV of feedstock (A9)