Biomass Conversion and Biorefinery
https://doi.org/10.1007/s13399-021-01945-5

ORIGINAL ARTICLE

Enhancement of thermochemical properties on rice husk under a wide range of torrefaction conditions

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Received: 28 May 2021 / Revised: 2 September 2021 / Accepted: 8 September 2021

Abstract

In the present study, local biomass rick husk (RH) was torrefied by an electronic furnace for improving its thermochemical properties under a wide range of torrefaction temperature (i.e., 240, 280, 320, and 360 °C) and residence time (i.e., 0, 30, 60, and 90 min). In comparison with the thermochemical properties of the starting feedstock, the torrefaction temperature at around 360 °C for residence time of 0 min would be optimal to produce the RH-torrefied product. The calorific value can be raised by 41.2%, increasing from 13.96 to 19.71 MJ/kg. Based on the calorific values of the RH-torrefied products, it was found that torrefaction temperature and residence time are important parameters affecting their fuel properties and applications in solid biofuels. Consistently, their calorific values and carbon-to-hydrogen ratios generally increased at higher torrefaction temperatures for longer residence times. In contrast, the energy yield decreased with an increase in torrefaction temperatures and residence time. These findings also supported the thermal decomposition mechanism of the lignocellulosic biomass by the thermogravimetric analysis (TGA). Using the van Krevelen diagram for all RH-torrefied products as compared to various coals, it showed that several torrefied solids belong to the characteristics of lignite-like coal. However, the RH-torrefied biomass would not be appropriate to be directly reused as an auxiliary fuel in boilers because of the high content of silica (SiO_2).

Keywords Rice husk · Torrefaction · Thermochemical property · Optimization · Lignite-like biofuel

1 Introduction

Biomass is mainly composed of water, lignocellulosic constituents (i.e., cellulose, hemicellulose, and lignin), and small amounts of inorganics and extractives. To improve the thermochemical properties of biomass due to its complex compositions, suitable pretreatment methods are often adopted to aid in further conversion to biofuels. These thermochemical methods are based on the principles of thermal desorption of moisture and light attachments, depolymerization of cellulose, decomposition of hemicellulose, and thermal softening of lignin [1]. Though severe temperature ranges above 300 °C have been performed in the pretreatment of biomass [2–6], typical temperature range for the torrefaction process ranges from 200 to 300 °C for losing its lignocellulosic structure, thus making it grindable [7]. In this regard, torrefaction of biomass is gaining importance for the production of solid biofuels, feedstocks, syngas, heat, steam, or power in the fields of steel-making and chemical industries [8–13]. More noticeably, the combustion of torrefied biomass will emit less amounts of air pollutants such as greenhouse gas carbon dioxide (CO_2), nitrogen oxides (NOx), sulfur oxides (SOx), and toxic metals (e.g., mercury) in comparison with coal [14]. Generally, temperature, residence time, and biomass feedstock are important process parameters in the torrefaction system, which determined the calorific values and energy yields of torrefied products [7, 15, 16]. Li et al. studied the torrefication of sawdust at 240–300 °C and 15–90 min, finding that the higher calorific values increased but the energy yields decreased with the increase in the severity of torrefaction [15]. Simonic et al. performed the torrefication of oak wood, sewage sludge, and mixed wood at 220–400 °C and 30–120 min, also indicating

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the similar results [16]. Furthermore, the authors determined optimal torrefaction conditions based on mass efficiency (yield), enhancement factor, and energy yield.

As a cereal grain, rice may be the most widely consumed food in Asian countries. It is the agricultural commodity with the worldwide production about 500 million metric tons in 2019 according to the statistics of Food and Agriculture Organization (FAO). Considering about 20 wt% of the grain is husk, a total of approximately 100 million metric tons of rice husk was produced annually. A large quantity of the world production of rice husk remains as an available biomass material due to its richness in lignocellulosic constituents and silica. As a result, a large number of possible industrial applications of rice husk have been investigated in a variety of industries [17–19]. Most of rice husks are currently reused as paving materials in fields and poultry houses, animal feeds, composts, crop cultivation covers, and solid fuels. In order to increase the supply of renewable energy and also avoid burning or disposing off in the fields, rice husk has been widely studied as a biomass energy source [17, 20–23]. However, the pretreatment methods (e.g., drying, shredding, densification, torrefaction, pyrolysis) were adopted prior to the thermochemical or biochemical processes (e.g., combustion, pyrolysis, or gasification) for converting rice husk into a diversity of energy forms such as fuels, heat, stream, electricity, or gases with high calorific values [1]. For example, Adamon et al. studied the carbon dioxide and steam gasification of rice husk char, which was prepared by the pyrolysis of rice husk at in a muffle furnace at 450 °C during 45 min [24].

Regarding the torrefaction of rice husk at higher temperatures (> 300 °C), few studies have been reported in the literature [25–33]. Wang et al. used microwave irradiation to induce torrefaction with an increase in its caloric value by 26% under proper processing time [25]. Ahiduzzaman and Sadrul Islam prepared torrefied products at 200–300 °C for 10–30 min [26], showing that the energy yield had a decreasing trend with an increase in temperature and residence time. Chen et al. made two similar experiments at 200–290 °C and 210–300 °C (interval by 30 °C) for 30 min, showing the increases in the calorific values of torrefied products [27, 28]. Manatura et al. produced the torrefied products at 250/350 °C for 60 min, which were used in the fluidized bed gasification for energy analysis [29]. Aslam et al. performed the torrefaction experiments at 200–300 °C for 10–150 min for improving its fuel characteristics [30]. Han et al. studied the production of torrefied products at 270 °C for 30 min for evaluating the emissions of particulate matter during the co-firing of lignite [31]. Qi et al. correlated the thermochemical properties of torrefied products produced at 180–330 °C for 20 min based on the gray-scale analysis [32]. Zhang et al. investigated the effects of torrefaction conditions (i.e., 230–270 °C for 60 min) on the physicochemical properties and reactivities of chars from pyrolysis of torrefied products at 700 °C in a fluidized bed [33].

As mentioned above, the thermochemical conditions of rice husk via torrefaction process were only evaluated at limited ranges and mild conditions in the published literature, thus indicating a lower increase in calorific value. In order to reuse torrefied biomass as an available solid fuel in the combustion or gasification system, this work thus focused on enhancing the fuel properties of rice husk via torrefaction process in a wide range of temperature (240–360 °C) and residence time (0–90 min). According to the findings in the previous study [6], an electronic oven has been proven to be effective for the pretreatment process at lower heating rates (5–10 °C/min) for producing higher yields of torrefied products. Their fuel properties, including calorific value and elemental composition, were determined to evaluate the optimal conditions in the torrefaction process. In the analysis of elemental composition for the torrefied rice husk products, the instruments of elemental analyzer (EA) and energy dispersive X-ray spectroscopy (EDS) were adopted in this work.

2 Materials and methods

2.1 Sample collection and preparation

The biomass rice husk (abbreviated as RH) was obtained from a local agriculture research farm (Pingtung County, Taiwan). In order to convert it into torrefied solid efficiently, the as-received RH was shredded by a milling machine and then sieved to particle sizes ranging from 0.841 mm (opening size in mesh No. 20) to 0.420 mm (opening size in mesh No. 40). Before the determinations of the thermochemical properties, the finely granular RH was dried at about 105 °C for over 12 h to remove the free water and then stored in the desiccator.

2.2 Determinations for thermochemical properties of dried RH

2.2.1 Proximate analysis

The proximate analysis of dried RH refers to the determinations of volatile matter (VM) and ash and the calculation of fixed carbon (FC). In this work, the volatile matter content was determined by placing the dried RH (about 1 g) into the covered crucible in a muffle furnace (pre-heated to 950 °C) quickly and holding for 7 min. The ash content was obtained by using the uncovered crucible where the dried RH (about 1 g) was heated to 750 °C for holding 4 h. By comparing the weight between before and after heating, the values of VM and ash can be calculated. Based on the American Society for Testing and Materials (ASTM) standards (D-3172), the FC was then determined by the difference (i.e., FC = 100 – VM – Ash). In the work, about 1 g of the representative RH sample was tested by the ovens (or furnaces) and the electronic balance.

2.2.2 Ultimate (elemental) analysis

Ultimate analysis, also called as elemental analysis (EA), provides an available method for determining the major organic elements of the dried RH, which include the compositions of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O). In this work, an automatic analyzer (vario EL III; Elementar Co., Germany) was performed by using about 1.5 mg of the representative sample in duplicate.

2.2.3 Calorific analysis

The calorific value of the dried RH in terms of higher heating value was measured by an adiabatic calorimeter (CALORIMETER ASSY 6200; Parr Co., USA) based on the operation mode at 25 °C, which was completely combusted under oxygen atmosphere. About 0.3 g of the representative RH sample was used in the calorific analysis, which was performed in duplicate.

2.2.4 Inorganic element analysis

Due to the possible slagging/fouling in the biomass combustion system [34, 35], the contents of inorganic elements in the RH sample were determined by an inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent 725; Agilent Co., USA). The determined elements included aluminum (Al), calcium (Ca), copper (Cu), iron (Fe), magnesium (Mg), phosphorus (P), potassium (K), silicon (Si), sodium (Na), and titanium (Ti). Prior to the ICP-OES analysis, the concentrated acid solution (i.e., HNO_3/HCl solution) with assistance by microwave digestion was used to dissolve the representative RH sample.

2.2.5 Thermogravimetric analysis (TGA)

In order to observe the thermal decomposition of the dried RH as a function of temperature under the oxygen-deficient environment by purging inert gas (i.e., nitrogen), the thermogravimetric analyzer (TGA-51; Shimadzu Co., Japan) was adopted to give the information about the proper torrefaction conditions. The representative RH sample (about 0.2 g) was placed into a quartz plate and then heated up to 900 °C at two ramping rates (i.e., 5, 10, 15, and 20 °C/min) under nitrogen gas flow of 50 cm^3/min. According to the data on the sample weight at any time (or temperature), the curves of TGA and its derivative thermogravimetry (DTG) can be drawn by the built-in software.

2.3 Torrefaction experiments

Although residence time is an important parameter influencing the yields and fuel properties of torrefied products, temperature is by far the most remarkable production parameter in the torrefaction process [7]. Therefore, this work focused on maximizing the fuel properties of rice husk in a wide range of torrefaction temperature and residence time. According to the previous reports [6, 36–38], it has been confirmed that a commercial electric furnace capable of high temperature operation (up to 400 °C) is a useful equipment for the production of torrefied products from various biomass feedstocks. In this work, about 1 g of the representative RH sample was placed into a crucible (about 10 cm^3) for each torrefaction experiment, which is equipped with a fitting cover to provide a near oxygen-deficient environment during the experiment. In this work, the torrefaction conditions were set in a wide range of temperature from 240 to 360 °C (interval by 40 °C) at a specific residence time (0 to 90 min by 30-min interval). Herein, the null residence time means that the sample was taken out from the electric furnace immediately when the specified temperature has reached. The yield of the torrefied product was obtained by the ratio of its weight to the weight of RH used. Furthermore, its energy yield was calculated by multiplying the yield (Y_{RH}) and the ratio of calorific value for RHBC (CV_{RHBC}) to calorific value for RH (i.e., CV_{RH} = 13.96 MJ/kg). The calculation of energy yield was as follows:

$$\text{Energy yield} = Y_{RH} \times (CV_{RHBC}/CV_{RH})$$

In addition, the torrefaction experiment at the same conditions was performed in duplicate. In order to write simply and clearly, the torrefied RH products were denoted as RHBC-temperature–time. For example, the torrefied product RHBC-240–30 refers to the production conditions at torrefaction temperature of 240 °C for 30 min.

2.4 Thermochemical analyses of RHBC products

In the thermochemical analyses of RHBC products, we put emphasis on the fuel properties of the RHBC products because the aim of this work was to use them as alterative solid fuels. As a consequence, the calorific value and EA of a series of RHBC products were subsequently determined as mentioned in the Section 2.2.

In order to understand the surface morphology and chemical characterization of RHBC products, they were observed by an energy-dispersive X-ray spectroscopy (Model: Shift ED 3000; Oxford Instrument Co., UK), which was equipped with the scanning electron microscopy (TM3030; Hitachi Co., Japan) with operating at low vacuum and 15 kV accelerating voltage.

3 Results and discussion

3.1 Thermochemical characteristics of RH

The thermochemical properties of the dried RH determined by proximate analysis, ultimate analysis, calorific analysis, and inorganic element analysis are listed in Table 1. It showed that the measured data were slightly different from those by other reports [27, 33, 39–41]. For instance, this dried biomass has a relatively lower ash content (16.46 wt%) than those ranging from 15·30 to 24·60% (dry basis). The calorific value (i.e., 13.96 MJ/kg) was also consistent with its contents (i.e., 39.70 and 5.07 wt%, respectively) of carbon (C) and hydrogen (H). Predictably, the emissions of particulate matter from the combustion of the dried RH may be quite high because the ash content is significantly higher than coal [14] and other biomass fuels [42]. In addition, the contents of nitrogen (N) and sulfur (S) are 0.65 and 0.51 wt%, respectively. It was suggested to pose low emissions of acidic air pollutants when it was combusted directly. However, it should be noted that the sulfur content listed in Table 1 is slightly higher than those reported in the literature.

Table 1 Thermochemical properties of rice husk (RH)

Thermochemical property	Value
Proximate analysis (wt%)[a]	
Volatile matter	66.04
Ash content	16.46
Fixed carbon[b]	17.50
Elemental analysis (wt%)[a]	
Carbon (C)	39.70
Hydrogen (H)	5.07
Oxygen (O)	38.87
Nitrogen (N)	0.64
Sulfur (S)	0.51
Calorific value (MJ/kg)	13.96
Inorganic elements (wt%)[a, c]	
Silicon (Si)	5.521
Potassium (K)	0.110
Magnesium (Mg)	0.068
Calcium (Ca)	0.281
Aluminum (Al)	0.065
Iron (Fe)	0.108
Sodium (Na)	0.015

[a] On a dry basis

[b] By difference

[c] Not detectable for copper (Cu), phosphorus (P), and titanium (Ti) due to the method detection limit

In order to evaluate the potential slagging and fouling problems in the biomass-fired system, the inorganic element contents contained in the ash of the dried RH are also listed in Table 1. The dominant element was silicon (Si) with the elemental contribution to about 89.5 wt%, which should be present in silica. When these inorganic elements were categorized into their corresponding oxides (i.e., SiO_2, K_20, MgO, CaO, Al_2O_3, Fe_2O_3, and Na_2O), the percentage concentration of SiO_2 reached up to 92.7 wt%, which was close to the reported values [41, 42]. A slagging index developed by the coal industry has been used to rate solid fuels for fouling [43]. This index corresponds to the mass of alkali metal oxides (i.e., potassium oxide, sodium oxide) per energy unit in the fuel. In this regard, the dried RH only contains less amounts of potassium (K) and sodium (Na) as listed in Table 1, suggesting that this biomass should pose low slagging risk in the heat exchanger surfaces of boilers during the combustion and/or co-firing.

In order to understand the thermal decomposition behaviors of the dried RH biomass, the TGA experiments were conducted at two heating rates (i.e., 5 and 10 °C/min) in the temperature range of about 25–900 °C under the non-isothermal condition. The heating rates adopted in this work were in accordance with the thermal conditions in the torrefaction experiments. Figure 1 shows the mass loss by percentage vs. temperature in the TGA curves and their corresponding DTG curves at heating rates of 5 and 10 °C/min. Obviously, these curves revealed similar thermal decomposition behaviors as reported by other studies [40, 44]. There are three stages in the thermal decomposition behaviors of the dried RH presented in Fig. 1. In addition, there was a gradual shift to the right in the residual mass of sample with

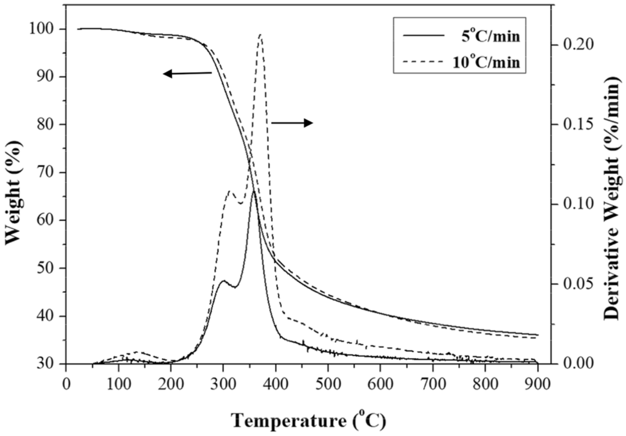

Fig. 1 TGA curves at heating rates of 5 and 10 °C/min for rice husk (RH)

temperature as the heating rate increased. The initial mass loss started from temperature of 50 to 200 °C should be due to the thermal evaporation of water and adsorbed matters. In the second stage, the biomass undergoes the devolatilization mechanism where carbon, hydrogen, and other volatiles were released from the lignocellulosic compositions of RH in the temperature range of 200–420 °C. During the progressive heating between the temperature of 420 and 900 °C, the remaining mass loss occurs as a result from the decomposition of the remaining lignin and inorganic compositions with low melting points. For most lignocellulosic biomass, it is interesting that there are two peaks in the second stage. In the first peak, it should correspond to the decomposition of hemicellulose, which occurred at the temperature range of 300 to 310 °C [45]. Subsequently, the RH sample began to lose its mass due to the decomposition of cellulose, showing the peaks in the range of 360 to 370 °C. Based on the data on the TGA/DTG curves (Fig. 1), the torrefaction of dried RH for producing char-like products should range from 200 to 400 °C. In this work, more serious conditions in the torrefaction experiments were adopted in the range of 240–360 °C for different residence times (i.e., 0, 30, 60, and 90 min), which were higher than traditional torrefaction conditions at 200–300 °C for residence time within 60 min [7].

3.2 Yields of RH-torrefied products

Due to more serious decomposition reactions of lignocellulosic constituents occurred at higher temperatures for longer residence times, the yields of RH-torrefied products indicate a decreasing trend as listed in Table 2. In this work, there were 16 experiments as a function of torrefaction temperature (i.e., 240–360 °C with an interval of 40 °C) and residence time (i.e., 0–90 min with an interval of 30 min) performed in duplicate. More significantly, the maximal variations on the yields of RH-torrefied products seem to occur at 280–320 °C, which was consistent with the data depicted in Fig. 1. As mentioned above, hemicellulose is the first thermal decomposition, occurred in the range of 220–320 °C [45]. However, this change was not obvious at longer residence time. For example, the yields of RHBC-temperature-0 products decreased from 83.17 wt% (280 °C) to 65.00 wt% (320 °C), but the yields of RHBC-temperature-60 only decreased from 59.10 wt% (280 °C) to 51.88 wt% (320 °C). Although the yields of RHBC products occurred at lower torrefaction temperatures for shorter residence times, their thermochemical properties may be not suitable for its use as solid fuels.

Table 2 Yields and calorific values of RH-torrefied products (RHBC) produced from rice husk (RH) at different torrefaction temperatures (200–360 °C) and residence times (0–90 min)

RH-torrefied product[a]	Yield[b] (wt%)	Calorific value[b] (MJ/kg)	Enhancement factor[c] (-)	Energy yield[d] (%)
RHBC-240-0[e]	95.26 ± 0.41	16.81 ± 0.19	1.20	114.71
RHBC-240–30	83.84 ± 0.25	17.22 ± 0.13	1.23	103.42
RHBC-240–60	76.03 ± 0.24	17.52 ± 0.05	1.26	95.42
RHBC-240–90	71.95 ± 1.38	16.92 ± 0.06	1.21	87.21
RHBC-280–0	83.17 ± 0.39	17.60 ± 0.16	1.26	104.86
RHBC-280–30	70.45 ± 1.99	18.18 ± 0.20	1.30	91.75
RHBC-280–60	59.10 ± 0.89	18.31 ± 0.11	1.31	77.52
RHBC-280–90	55.34 ± 0.26	17.04 ± 0.12	1.22	67.55
RHBC-320–0	65.00 ± 0.51	19.41 ± 0.09	1.39	90.38
RHBC-320–30	55.29 ± 0.34	18.45 ± 0.51	1.32	73.07
RHBC-320–60	51.88 ± 1.47	17.29 ± 0.13	1.24	64.26
RHBC-320–90	48.07 ± 1.26	16.05 ± 0.46	1.15	55.27
RHBC-360–0	56.31 ± 1.27	19.71 ± 0.01	1.41	79.50
RHBC-360–30	50.83 ± 0.09	18.60 ± 0.32	1.33	67.72
RHBC-360–60	42.92 ± 1.44	16.87 ± 0.19	1.21	51.87
RHBC-360–90	40.32 ± 1.15	15.02 ± 0.04	1.08	43.38

[a] Dry basis (moisture free)

[b] Means with standard deviations for two–three replications

[c] The data on enhancement factor were obtained by ratio of calorific value for RHBC to calorific value for RH (i.e., 13.96 MJ/kg)

[d] The data on energy yield were obtained by multiplication of yield and ratio of calorific value for RHBC to calorific value for RH (i.e., 13.96 MJ/kg)

[e] RH-torrefied product (RHBC-200–0) produced at torrefaction temperature of 200 °C for residence time of 0 min

3.3 Calorific values of RH-torrefied products

In this work, the calorific value should be the most important property when the RH-torrefied product was used as a solid fuel in the combustion and/or co-firing system. Table 2 also lists the calorific values of these RH-torrefied products. Based on the data in Table 2, Fig. 2 shows the variations on calorific values of RHBC products produced at different residence times and torrefaction temperatures. Obviously, the calorific values of RHBC products indicated an increasing trend as temperature increased from 240 to 360 °C at residence time of 0 min. On the other hand, the data in Table 2 also show that the enhancement factors of RHBC products increased with temperature up to 1.41 at 360 °C for residence times of 0 and 30 min. This result was reasonable because the densification of carbon will be enhanced in the RH-torrefied product produced at higher temperature. As seen in the TGA curves (Fig. 1), the maximal mass loss at about 360 °C could be attributable to the thermal decomposition of cellulosic constituent, thus resulting in more releases of organic volatiles and product water. However, the calorific values slightly decreased at higher temperature (˃ 280 °C) for longer residence time (>30 min). On the other hand, the higher contents of ash remained in the RH-torrefied products will be more significant at the conditions, thus causing lower calorific values. In this work, the torrefaction temperature at around 360 °C for residence time of 0 min will be preferable to produce the RH-torrefied product with a maximal calorific value (i.e., 19.71 MJ/kg), giving a significant increase by 41.2% or a maximal enhancement factor (i.e., 141.2%) in comparison with 13.96 MJ/kg. Furthermore, the energy yield of optimal RH-torrefied product (i.e., RHBC-360–0) can be further obtained by its yield (i.e., 56.31 wt%) and calorific value as compared to the calorific value of the starting biomass (i.e., 13.96 MJ/kg, listed in Table 1) [6, 30, 46, 47]. According to the data on the yields, calorific values (or enhancement factor), and energy yields of RH-torrefied products (Table 2), the torrefaction conditions at 320 °C (residence time of 0 min) may be optimal for the production of RH-torrefied product (i.e., RHBC-320–0) [16]. It showed that the energy yield or net usable energy percentage (i.e., about 80%) was retained in the torrefied product after the optimal torrefaction, which was similar to other studies [26, 27]. In the study by Ahiduzzaman and Sadrul Islam [26], the energy yields were found in the range of 55 to 105%, also showing a decreasing trend with temperature and residence time. As compared to the previous reports [6, 36, 38], the energy yields obtained in this work were higher than those of the torrefied products produced from water caltrop husk (WCH), cocoa pod husk (CPH), and coffee residue (CR) at the same conditions. For example, the energy yields of RHBC at 240–360 °C (residence time of 0 min) ranged from 114.7 to 79.5%, which were higher than those (93.0–66.2%) of torrefied products from WCH [6]. The energy yield (i.e., 91.8%) of RHBC at 280 °C for 30 min was also higher than (i.e., 74.3%) that of torrefied produced from CPH at the same conditions [38].

3.4 Organic elemental values of RH-torrefied products

Regarding the organic elemental values of the RH-torrefied products, the results are presented in Table 3. The carbon contents ranged from 38.47 to 52.95 wt%, depending on both the conditions of torrefaction temperature and residence time. In general, the values were continuously increased as torrefaction temperature increased from 240 to 280 °C, but subsequently decreased in the range of 280–360 °C for longer residence time (˃ 30 min). The maximal carbon content (i.e., 52.95 wt%) occurred at the torrefaction temperature of 280 °C for residence time of 60 min. Due to the lignocellulosic precursor (i.e., RH), the hydrogen contents

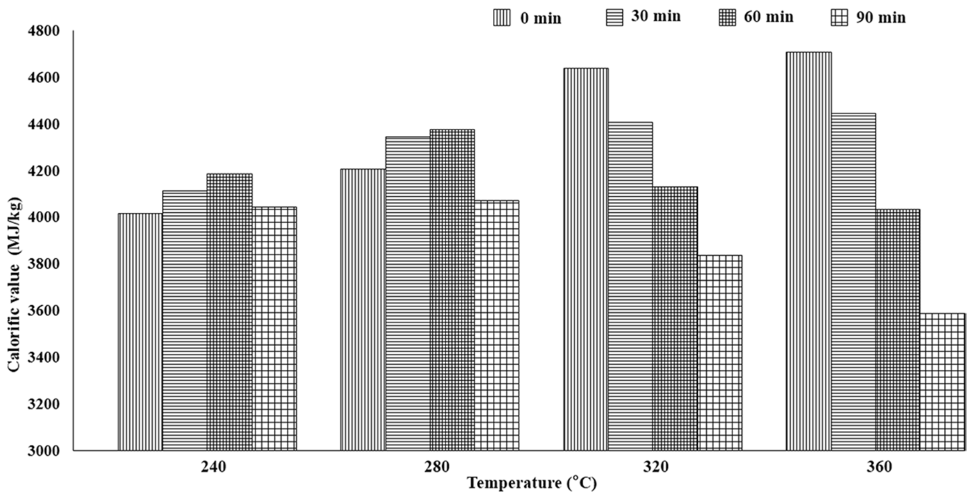

Fig. 2 Variations on calorific values of RH-torrefied products (RHBC) produced at different residence times

Table 3 Elemental analysis of rice husk (RH) and its torrefied products (RHBC) at different torrefaction temperatures (200–360 °C) and residence times (0–90 min)

Rice husk (RH) and its bio-char products (RHBC)	Elemental analysis (wt%)					H/C[a]	O/C[a]
	C	H	N	O	S		
RH	39.70	5.07	0.64	38.87	0.51	1.53	0.75
RHBC-240–0	44.61	5.46	0.71	36.27	0.24	1.47	0.61
RHBC-240–30	48.28	5.16	0.76	35.03	0.14	1.28	0.54
RHBC-240–60	47.44	4.49	0.96	33.41	0.14	1.14	0.53
RHBC-240–90	46.99	3.99	0.93	30.94	0.17	1.02	0.49
RHBC-280–0	47.58	5.19	0.87	33.64	0.13	1.31	0.53
RHBC-280–30	50.34	4.32	1.02	28.68	0.12	1.03	0.43
RHBC-280–60	52.95	3.37	1.22	25.27	0.15	0.76	0.36
RHBC-280–90	47.77	2.85	0.99	26.03	0.12	0.72	0.41
RHBC-320–0	50.61	4.06	1.01	23.54	0.20	0.96	0.35
RHBC-320–30	49.92	3.12	1.05	22.73	0.17	0.75	0.34
RHBC-320–60	48.64	2.82	1.20	24.04	0.15	0.70	0.37
RHBC-320–90	46.95	2.77	1.22	24.34	0.16	0.71	0.39
RHBC-360–0	49.53	3.44	1.16	22.73	0.26	0.83	0.34
RHBC-360–30	46.63	2.76	1.22	22.63	0.19	0.71	0.36
RHBC-360–60	42.00	2.45	1.21	23.08	0.18	0.70	0.41
RHBC-360–90	38.47	2.35	1.24	24.71	0.17	0.73	0.48

[a] Molecular ratio

of the RH-torrefied products were generally low, ranging from 2.35 to 5.54 wt%. Obviously, an increase in the torrefaction temperature or holding time resulted in a decreasing trend in the hydrogen contents. This result can be attributed to the decreasing trend in the yields and calorific values of RH-torrefied products produced at longer residence time because of more releases of carbon and hydrogen by the intense devolatilization at the strict torrefaction conditions. Similar trends were obtained for the torrefaction of RH at 300 °C by increasing residence time from 30 to 60 min [48]. As explained above, more amounts of volatile products and process water were released under the severe torrefaction conditions due to the intense reactions like depolymerization, polymerization, and dehydration [49]. In this regard, the oxygen contents, ranging from 22.63 to 39.36 wt%, also indicated a decreasing trend under the severe torrefaction conditions. In fact, the increase in the carbon content with increasing the torrefaction conditions are often associated with the releases of hydrogen and oxygen from the torrefied or charred products [50]. By contrast, the RH-torrefied products contained lower contents of nitrogen and sulfur because of the chemical characteristics of lignocellulosic precursor. In addition, there was substantially more variability in the reported values of these acidic elements compared to those of carbon, hydrogen, and oxygen. As mentioned in the Section 3.1, the emissions of acidic air pollutants, especially in nitrogen oxides (NO/NO_2), could be significant when reusing the RH-torrefied product as an auxiliary fuel in the combustion or co-firing system. Based on the organic elemental values, the calorific values of the RH-torrefied products can be also estimated by the correlation equations like Dulong's formula [51]. When citing the organic elemental values in Table 3, it shows that the estimated values were close to the calorific values (Table 2).

In order to evaluate the classification of RH-torrefied products related to the similarity with fossil fuels like coal, the van Krevelen diagram is made on a plot of atomic O/C versus atomic H/C from the organic elemental values in Table 3. Figure 3 shows the van Krevelen diagram for all RH-torrefied products. As expected, the lower values of molar H/C and O/C often occurred at higher torrefaction temperatures and longer residence time. For example, the values of molar H/C vs. O/C decreased from 1.47 vs. 0.61 for the RHBC-240–0 to 0.83 vs. 0.34 for the optimal RH-torrefied product (RHBC-360–0). Obviously, the ratios for the optimal RH-torrefied product should possess thermochemical feature like lignite [7]. The results were consistent with those by the previous reports [6, 38] and recent reviews [10, 12, 13].

In order to observe the morphological features of the RH-torrefied products, the SEM images of the torrefied products with high calorific values (i.e., RHBC-360–0 and RHBC-320–0) are shown in Fig. 4 (left side). Obviously, rice husk features the aligned and symmetrical bumps which are mainly composed of silica (SiO_2) and lignocellulosic constituents [30]. Although the lamina structure was maintained in the RH-torrefied product, some conoids and swollen bumps can be seen in the biochar surface. In addition, the elemental compositions of the torrefied product on its surface were further analyzed by

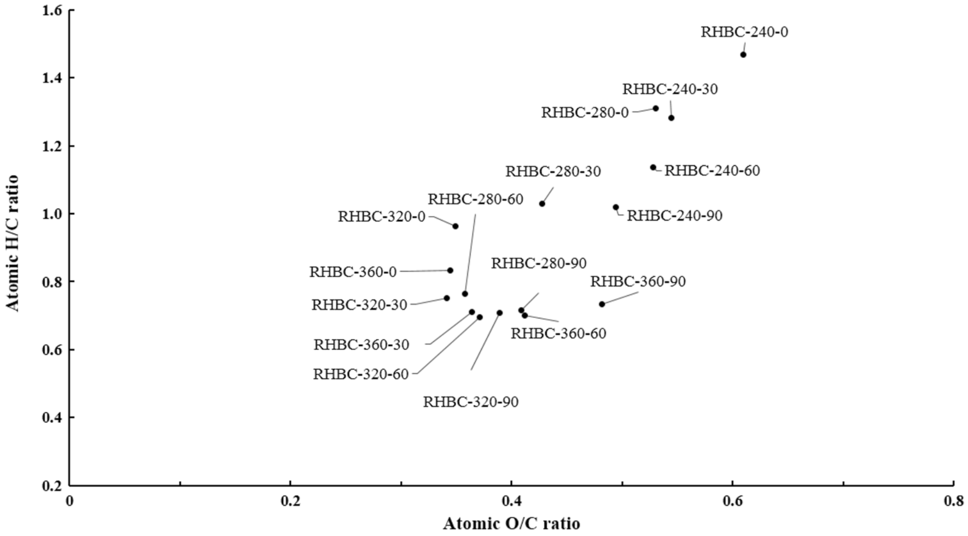

Fig. 3 The van Krevelen diagram of RHBC products

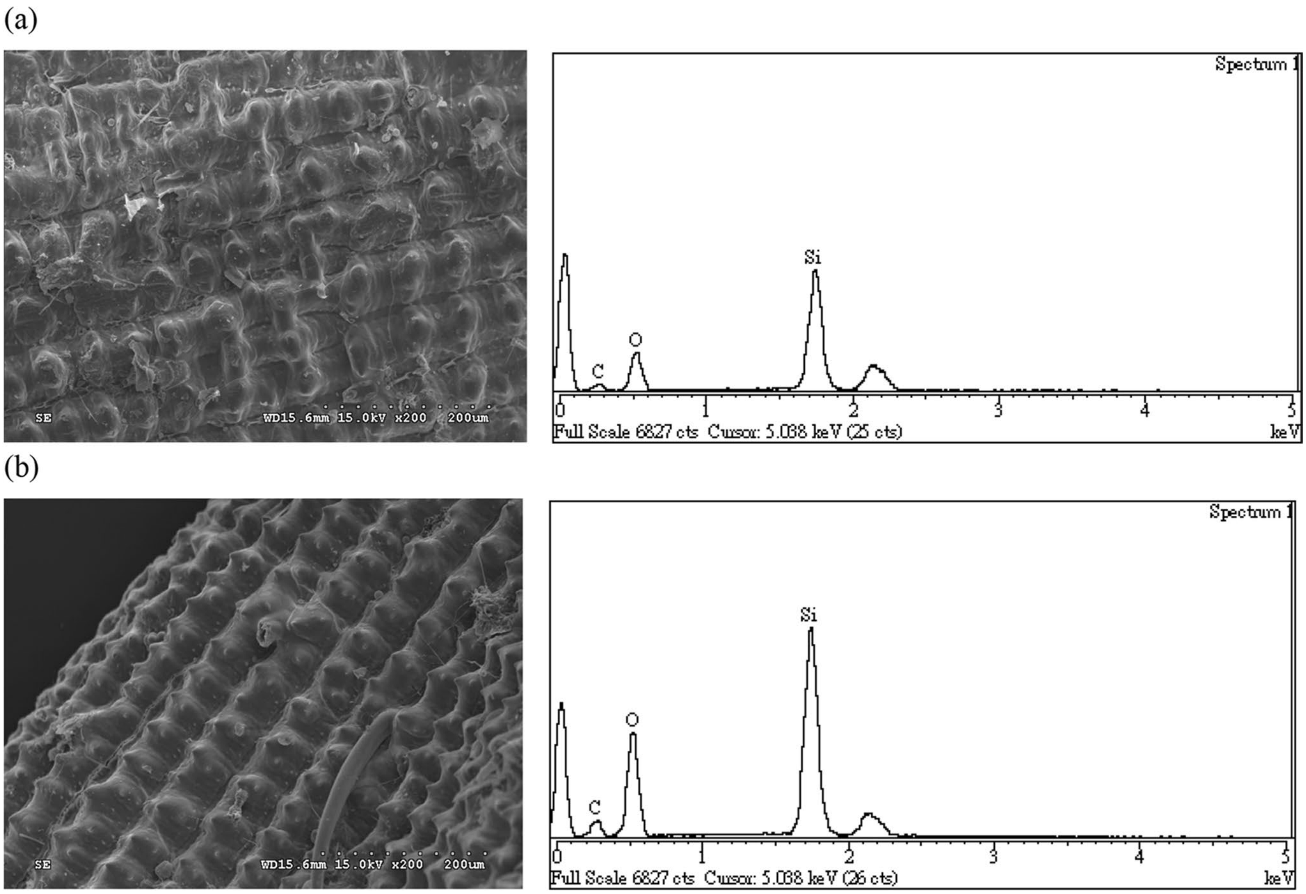

Fig. 4 SEM/EDS analyses of typical RHBC products with high calorific values for (**a**) RHBC-360–0 and (**b**) RHBC-320–0

the EDS (Fig. 4 (right side)), revealing the major elements of carbon (C), oxygen (O), and silicon (Si). This result is consistent in comparison with the data in Table 1. In order to reduce emissions of CO_2 and SOx due to the low sulfur content and neutral carbon in the RH-torrefied products, their applications for co-firing with pulverized coal exist in boilers [31]. Furthermore, co-firing Si-rich torrefied RH with low-rank (high Na/Ca/Cl) coal can lead to lower emissions of particulate matter (PM) and released elements such as Cl and Na [52]. Sometimes, the gasification of RH or its torrefied products is another energy utilization option where the biomass feedstocks are converted into gaseous products (i.e., CO and H_2) with high calorific values [53]. These so-called syngas products can be further used for the production of petroleum-like chemicals and electricity power.

4 Conclusions

Rice husk (RH), a large local agricultural biomass, was converted into torrefied solid for improving fuel properties in this work. In order to obtain the optimal torrefaction conditions, the dried RH was processed by the thermal treatment in the range of temperatures (240–360 °C) and residence times (i.e., 0–90 min). In comparison with the thermochemical properties of the starting feedstock, including thermogravimetric analysis (TGA), the primary changes in the fuel properties of the RH-torrefied products were analytically carried out in this work.

Based on the calorific values of the RH-torrefied products as a function of temperature and holding (or residence) time, it was suggested that they are important parameters affecting their fuel properties and applications in solid biofuels. In this regard, the torrefaction temperature at around 360 °C for residence time of 0 min would be optimal to produce the RH-torrefied product with a maximal calorific value (i.e., 19.71 MJ/kg), giving a significant increase by 41.2% in comparison with its starting feedstock (i.e., 13.96 MJ/kg). The yield and carbon content of the optimal RH-torrefied product reached up to 56.31 and 49.53 wt%, respectively. In addition, the values of molar H/C and O/C of the RH-torrefied products and their corresponding energy yields indicated a decreasing trend as torrefaction temperature and/or residence time increased. According to the van Krevelen diagram for all RH-torrefied products as compared to various coals, several RH-torrefied products belong to the characteristics of lignite coal. However, the RH-torrefied biomass would not be appropriate to be directly reused as an auxiliary fuel in boilers because of its richness in ash mineral, especially in silica (SiO_2). By contrast, it can be adopted for co-firing with coal in existing large-scale coal-fired power plants.

Acknowledgements The authors acknowledge the Instrument Centers of National Pingtung University of Science and Technology and National Ching-Hwa University for the scanning electron microscopy – energy-dispersive X-ray spectroscopy (SEM-EDS) and the inductively coupled plasma – optical emission spectrometry (ICP-OES), respectively.

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