

Investigational analysis of torrefied corncob and its application in the production of coal-like fuel

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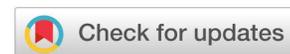
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ABSTRACT

Biochar, a charcoal-like material that is created through the heat treatment of biomass in high-temperature as torrefaction, is an organic carbon-rich and porous material. Currently, in Vietnam, there are several agricultural by-products suitable for biochar production. Therefore, corncob as a popular and potential agricultural product was selected in this study. Through the process, the obtained results on the influence of temperature and time during the torrefaction were investigated. The corncobs will be heated by the torrefaction method at the temperature of 230°C, 260°C, 290°C, and 320°C for 15, 30, and 45 minutes to obtain torrefied biochar. The present work aims to study torrefaction as an environmentally sustainable method for the combined generation of a solid biofuel with better properties compared to the starting material and a combustible vapor phase, which can be immediately burned for energy recovery. The higher heating value of torrefied materials was estimated. The calorific value in this study of biochar from corncob ranges from 22.04 to 32.57 MJ/kg, which is a potential parameter for a renewable energy feedstock. Sample CC320-45 achieved the highest calorific value of 24.29 MJ/kg and the porosity of this sample was 74.94%. The utilization of biomass waste is converted into useful energy, and the high porous nature of biochar allows for a large surface area for the adsorption of contaminants. Especially, compared to raw input feedstocks, average torrefaction operating conditions yielded much superior biofuels.

Key words: Corncob, torrefaction, biochar, fuel, energy

INTRODUCTION

Nowadays, the world is facing the problem of increased CO₂ consumption of fossil fuels, increasing by an average of 2.1% per year and increasing even more in the future¹. Therefore, research is being done to reduce this consumption or replace it with more sustainable fuels, such as biomass or agricultural by-products, which are known to contain high carbon content²⁻⁴. Vietnam is one of the agricultural countries. Annually, Vietnam generates about 50 million tons of crop by-products. Although this is a precious organic resource, it is still mainly burned. That is, for every 1 ton of rice, the amount of rice by-products is equivalent to 1 ton, about 10 - 12 tons of by-products/ha¹. Producing 1 ton of maize, the by-product is 1.2 tons of corn stalks, 1 ha of peanuts emits 11 tons of stems, and 1.0 ha of cassava emits 7 tons of tops and leaves. The results of the studies show that the number of crop by-products has a high nutritional value (45 - 70% of total digestible nutrients) and can provide a large number of calories (1662 - 2549 kcal/kg dry matter)⁵. Therefore, if appropriate technologies are applied, crop by-products will become valuable livestock products, soil nutrients, and environmental protection. However, at present, only

about 10% of crop by-products are used as fuel on-site such as in brick kilns, 5% as industrial fuel, 3% as animal feed, etc. 80% have not been used and discharged directly into the environment or burned, polluting the environment, blocking the flow⁵.

Corn is an important food in the world next to wheat and rice. Corn is also the most important animal feed today with high nutritional content. Besides, it is also a raw material for the food industry and light industry to produce alcohol, starch, oil, and glucose. Therefore, corn production is constantly increasing in terms of area, yield, and output, resulting in a gradual rise in the amount of waste cob. Annual corncob production in Vietnam is roughly 8 to 10 million tons⁶. However, only a small percentage is used for grinding as microbial fertilizer, as a substrate for mushroom cultivation, and as manual fuel, the rest is mostly waste. The post harvest burning of corncob has not only posed a threat to the environment but also to the health of the farmers. Research into the handling of corncob is crucial since it is difficult to manage and produces a significant quantity of trash, unlike other agricultural wastes that may be utilized as feed or compost.

Biochar is a carbonaceous material with a porous structure which are produced from the thermal decomposition of carbon-based feedstock (biomass) in

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an inert environment. The torrefaction of several waste biomass type such as including food waste, agricultural waste, and non-lignocellulosic wastes was studied^{7,8}. Physical and chemical characteristics of biochar products are defined by raw materials and thermal conversion conditions such as temperature, heating time, and gas reagents. Biochar has received increased interest from scientists in recent years because it is a fuel material that may give high-quality fuel in a variety of utilizations such as combustion facilities, entrained flow gasifiers system, and co-firing plants⁹. This could be attributed to the unique and favorable physicochemical properties such as elementary composition, bulk density, particle density, porosity, and calorific value of biochar.

Among different thermal conversion technologies, torrefaction is one technique that operates at a low temperature ranging from 200°C to 300°C in the absence of oxygen conditions¹⁰. Normally, the torrefaction technique is used as thermal pretreatment of biomass to enhance hydrophobicity, grind ability, and energy density. However, at the same time, the carbon content of biomass increases by the affected of torrefaction, providing higher biochar yield and remaining acidic and oxygen functional groups on the biochar surface compared to that of pyrolysis at 400-800°C¹¹. Based on these advantages of the torrefaction technique, the technique is taken into account in this study to produce biochar from corncob feedstock. Corncob waste is a good material as biochar or bio-coal, the application of corncobs to make coal fuel by torrefaction, known as the heating of the input material in a designed reactor that is meant to add heat from the source. Therefore, the objectives of this study were to determine the optimization condition for producing torrefied corncob biochar. The impact of biomass feedstock parameters, manufacturing procedures, reaction circumstances (temperature, retention time, etc.), and heating value on the physical and chemical properties of biochar are compared.

MATERIALS AND METHODS

Corncob biochar preparation

The raw material in the study is corncob, which is collected from retail corn stalls in Ho Chi Minh City, Vietnam. Pre-treatment corncob was cut into pieces of 1-2 cm. Then placed in the oven at 105°C for 2 days to measure the moisture content of the core. After drying, corn will be milled into 1-2 mm pieces, and then transferred to the firing stage in porcelain crucibles under limited O₂ conditions. To begin, 2g of material with particle sizes ranging from 0.5 to 1 mm

was weighed and placed in the bottoms of three crucibles to guarantee consistent heating. The kiln used is a laboratory-equipped Nabertherm Furnace. The heating furnace was then opened, and the sample was rapidly heated at a rate of 50°C/min up to the torrefaction temperature (230°C, 260°C, 290°C, or 320°C), which was maintained for three-time conditions of 15 minutes, 30 minutes, and 45 minutes. The sample was chilled in a desiccator and weighted at the end of the experiment. The performed biochars were produced at temperatures between 260 to 320 °C in 15 to 45 minutes as CC260-45; CC290-30; CC290-45; CC320-15; CC320-30; CC320-45.

Characteristics of materials

Ultimate fresh corncob and produced biochar analysis after drying were characterized using an elemental analyzer (Elementar Analyzer Vario MICRO cube, Thermo Fisher Scientific, Germany) to quantify the value of carbon, hydrogen, nitrogen, and sulfur content, and the oxygen content was calculated by different. Proximate analysis parameters including moisture, ash content, volatile matter, and fixed carbon, which were decided in triplicate by utilizing controlled testing procedures of the prescribed standard methodologies ASTM D3172-07a (American Society for Testing and Materials). The calorific value (HHV) of the raw and torrefied samples was analyzed by a Parr Model 1108 - Bomb calorimeter (ASTM: E711-87). Before and after torrefaction, the samples were weighed, and Eqs. 1; 2; and 3 were used to compute the mass yield, energy density, and energy yield, respectively^{12,13}. The derived properties of biochars were determined by bulk density, particle density, and porosity (ASTM: D2638 – 10).

$$\text{Mass yield (\%)} = \frac{\text{Torrefied sample weight (g)}}{\text{Sample weight (g)}} \times 100 \quad (1)$$

$$\text{Energy density} = \frac{\text{HHV of torrefied sample} \left(\frac{\text{MJ}}{\text{kg}} \right)}{\text{HHV of sample} \left(\frac{\text{MJ}}{\text{kg}} \right)} \quad (2)$$

$$\text{Energy yield (\%)} = \text{Mass yield(\%)} \times \text{Energy density} \quad (3)$$

Table 1: Corncob properties

Item	This study	14	15	16
Proximate analysis (%)				
Moisture content	9.55 ± 0.76	11.7	7.14	7.36
Volatile matter	80.25 ± 0.30	69.5	87.76	79.58
Fixed carbon	8.77	15.9	11.19	11.57
Ash	1.43 ± 0.16	2.9	1.05	1.49
Ultimate analysis (%)				
C	41.45	48.12	43.81	49.0
H	6.40	6.48	6.54	5.6
	0.44	1.89	0.77	0.5
	-	-	0.69	-
O	40.74	43.51	48.19	43.8
Energy content (MJ/kg)				
Higher heating value	15.93	-	16.46	16.38

Table 2: Characteristic of orrefied corncob biochar

Proximate analysis (%)	CC260-45	CC290-30	CC290-45	CC320-15	CC320-30	CC320-45
Moisture	6.41	6.59	6.67	6.31	6.60	6.97
Ash	5.14	5.57	5.50	8.73	8.83	9.15
Volatile matter	51.14	49.98	53.77	48.78	46.73	46.57
Fixed carbon	37.31	37.86	34.06	36.19	37.84	37.30
Ultimate analysis (%)						
C	60.96	62.83	59.7	62.23	63.29	62.23
H	3.178	3.824	3.427	3.245	3.569	3.245
N	1.2	1.21	1.2	1.01	1.34	1.01
S	-	-	-	-	-	-
O	23.12	19.97	23.50	18.48	16.37	15.94
O/C ratio	0.38	0.32	0.40	0.30	0.26	0.25
H/C ratio	0.052	0.061	0.057	0.052	0.056	0.06
Energy content						
HHV(MJ/kg)	21.09	23.21	21.17	22.45	23.65	24.29
Mass yield (%)	1.32	1.45	1.33	1.41	1.48	1.52
Energy density (%)	34.72	47.48	29.30	43.23	38.65	23.03
Energy yield (%)	26.22	32.57	22.04	30.67	26.03	15.10
Bulk density (g/cm ³)	0.31	0.30	0.33	0.28	0.29	0.23
Particle density (g/cm ³)	0.61	0.85	0.78	0.33	0.58	0.90
Porosity (%)	48.82	64.55	58.15	16.21	50.02	74.94

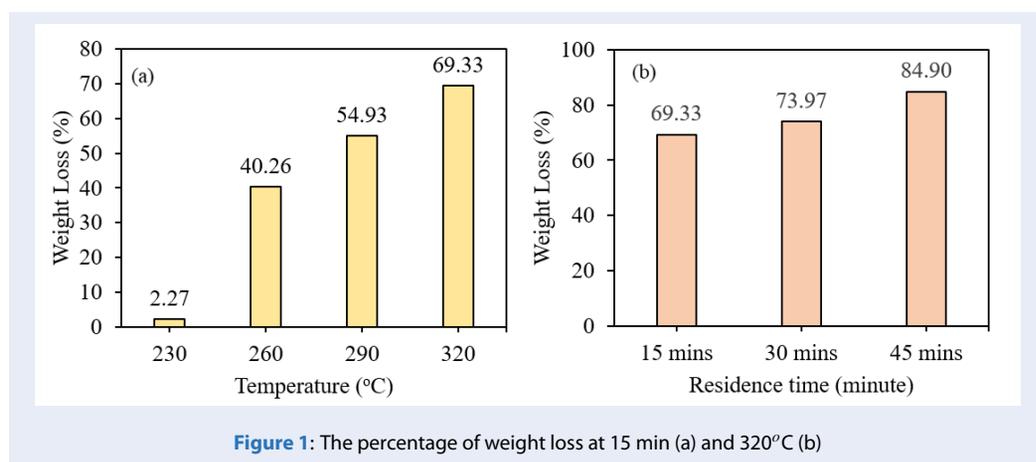


Figure 1: The percentage of weight loss at 15 min (a) and 320°C (b)

RESULTS AND DISCUSSION

Properties of corncob

Table 1 illustrates the physicochemical properties of the corncob. Regarding the proximate analysis, the raw corncob waste contains moisture, volatile matter, and fixed carbon at 9.55 ± 0.76 (%), 80.25 ± 0.30 (%), and 8.77 (%) respectively. Due to the corncob high volatile content, it is proposed that corncob is a suitable feedstock for the method of thermochemical conversion. A large amount of volatile matter of corncob also makes it a highly reactive fuel with a faster devolatilisation phase combustion rate than other fuels such as coal. The relatively low overall ash content was 1.43 ± 0.16 (%), which could be explained by the low mineral and metallic concentrations in the corncob before torrefaction. Table 1 compares the findings of this investigation with those from other documents. It can be seen that the analytical parameters of the physicochemical properties of the corncob are relatively similar^{14–16}. The corncob feedstock comprises 41.45 % C, 6.40 % H, 0.44 % N, 40.74 % O, and without sulfur, as determined by elemental analysis. As a result of their low nitrogen and sulfur content, maize cobs are an environmentally benign feedstock for the torrefaction process, as determined by their elemental composition. During biochar manufacturing, the maize cobs feedstock will emit minor levels of nitrogen oxide and sulfur oxide. In addition, the net calorific value of corncob was determined to be approximately 15.93 MJ/kg, indicating that corncob is a suitable material for energy applications.

Effects of torrefaction temperature and reaction time on corncob

Figure 1a shows the weight loss by heating the corncob under four different temperature conditions with

a retention time of 15 min. The weight loss is quite large, compared to 230°C and 260°C. For the 230°C, only 2.27 % is lost but at 260°C, the significant weight loss is 40.26 %. This proves that, at higher temperatures, the corncob is burned, and the color change is shown in Figure 2. After increasing the temperature to 290°C and 320°C, can be seen that the higher the temperature, the higher the percentage of weight loss. For the temperature of 320°C in Figure 1b, the percentage weight loss rises steadily with increasing time. It can be said that the higher the temperature and the longer the retention time, the greater the percentage of weight loss.

To determine the optimal conditions for derived biochar, the adjustable parameters such as temperature and retention time were investigated. Figure 2 showed that the amount of corncob at a temperature of 230°C and in 15 minutes (CC230-15) lost quite a bit, and the color compared to the original material did not change much. To increase the retention time by 30 min and 45 min, a significant color change but not enough to convert the corncob into biochar. For the temperature of 260°C in the first two retention times, although there was some conversion to biochar, there were still many fragments that did not reach, by the third retention time of 45 minutes, the corncobs were completely converted to biochar. Torrefaction between 260 and 320 °C for 15 to 45 minutes was found to be the ideal situation. Therefore, the biochar from corncob was synthesized in these conditions for further discussion.

Characteristics of biochar

The proximate and ultimate analyzed results are given in Table 2. That can be seen in the trends of each parameter, as the temperature and time conditions increase, the percentage of moisture, the fixed ash, and

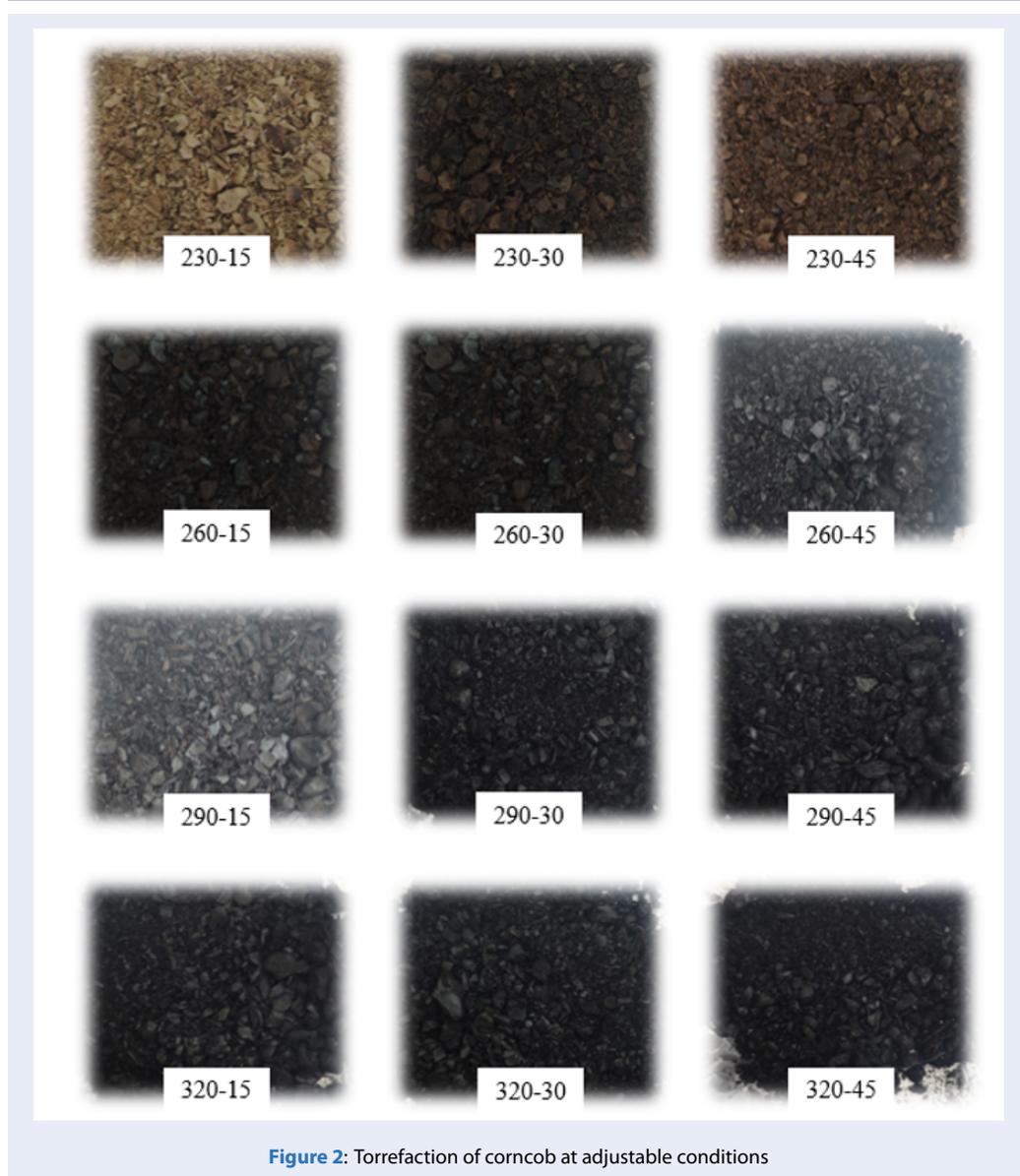


Figure 2: Torrefaction of corncob at adjustable conditions

carbon content also increase, conversely, the volatile matter tends in the downward direction. According to the study of Gómez et al., 2014 on four different types of biomass, the higher the process temperature, the lower the volatile matter content will be generated due to the increase in pyrolysis of lignocellulosic components and the decomposition of biochar destruction of organic materials¹⁷. Volatile content decreased from 80.25 % in the base material to 51.14% and for optimal treatment to 46.57 % for the most severe fused samples. On the other hand, fixed carbon is improved from 18.77 % to 37.3 % in that respect (Figure 3). These findings propose that the combustion of biochar decreased the gen-

eration of volatile gaseous byproducts (such as CO₂ and CO) and successfully decreased greenhouse gas emissions^{18,19}. Therefore, the substantial increases in fixed carbon and ash concentrations of corncob biochar samples enhanced biochar production efficiency²⁰. Similar results were found in a research of the peanut shells and grape pomace torrefaction²¹. Figure 4 describes the ultimate analysis of the corncob samples, whereas Figure 5 indicates the atomic ratios of hydrogen/carbon (H/C) and oxygen/carbon (O/C) of the char samples. The proximate and ultimate analytical results indicate that the carbon content tends to grow by 60.96 % and 62.23 %, respectively, under the fusion conditions necessary to achieve the highest

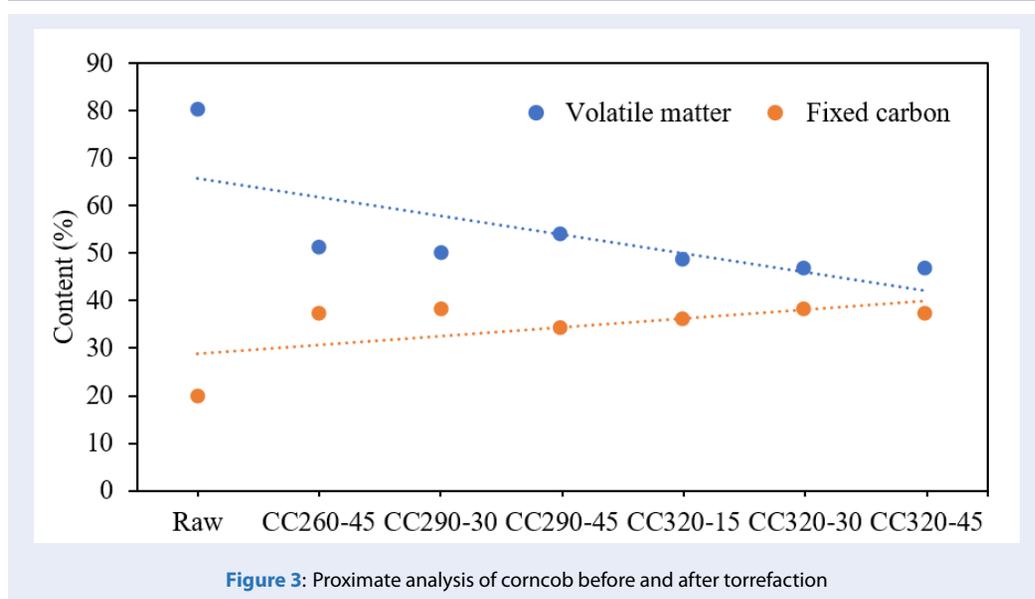


Figure 3: Proximate analysis of corncob before and after torrefaction

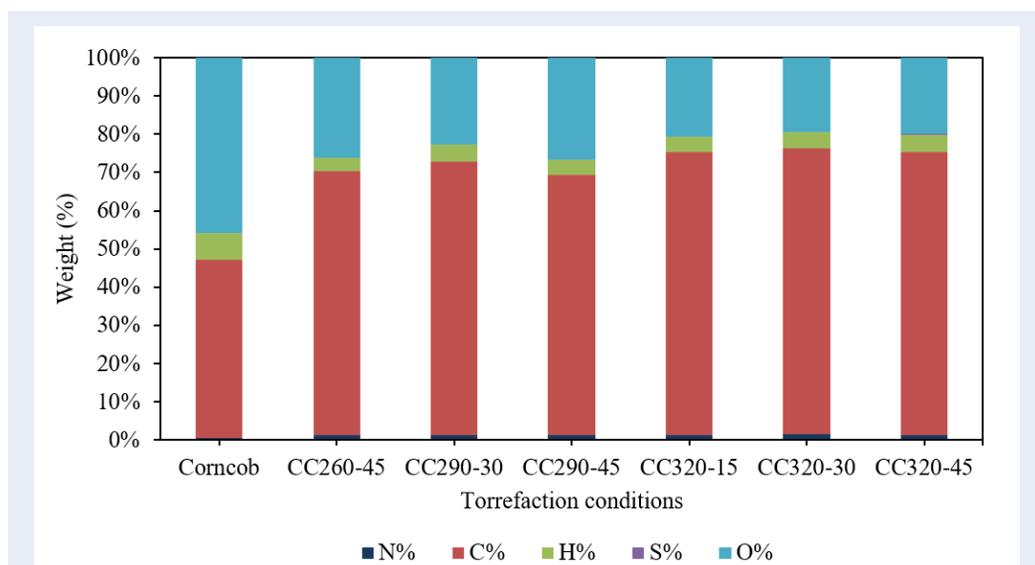


Figure 4: Ultimate analysis of the raw and torrefied corncob at different torrefaction temperatures and reaction time

HHV of biochar from the cob; the carbon content of the raw cob sample was 41.45 %. At various temperatures, nitrogen and sulfur levels in the biochar samples varied considerably but remained low, sulfur was nearly nonexistent. In addition, the oxygen and hydrogen content of the biochar sample reduced dramatically from 40.74 % and 6.39 % in the raw materials to 17.39 % and 3.245 % at the highest temperature of 320°C for the maximum retention time of 45 minutes. These outcomes can be attributable to sample dehydration and deoxygenation during fusing²².

Figure 5 demonstrates that as torrefaction temperatures increased, both the H/C and O/C ratios often dropped. The O/C ratio reduced dramatically from 0.38 to 0.25 when the torrefaction temperature was 320°C because, when the temperature was increased, the corncob-derived biochar underwent dehydration processes, decarboxylation reactions, and a significant loss of volatiles. The lowering of hydroxyl substituents has a comparable effect on the H/C ratio, which similarly tends to decrease²³. A Low O/C ratio in biochar generated at higher temperatures in-

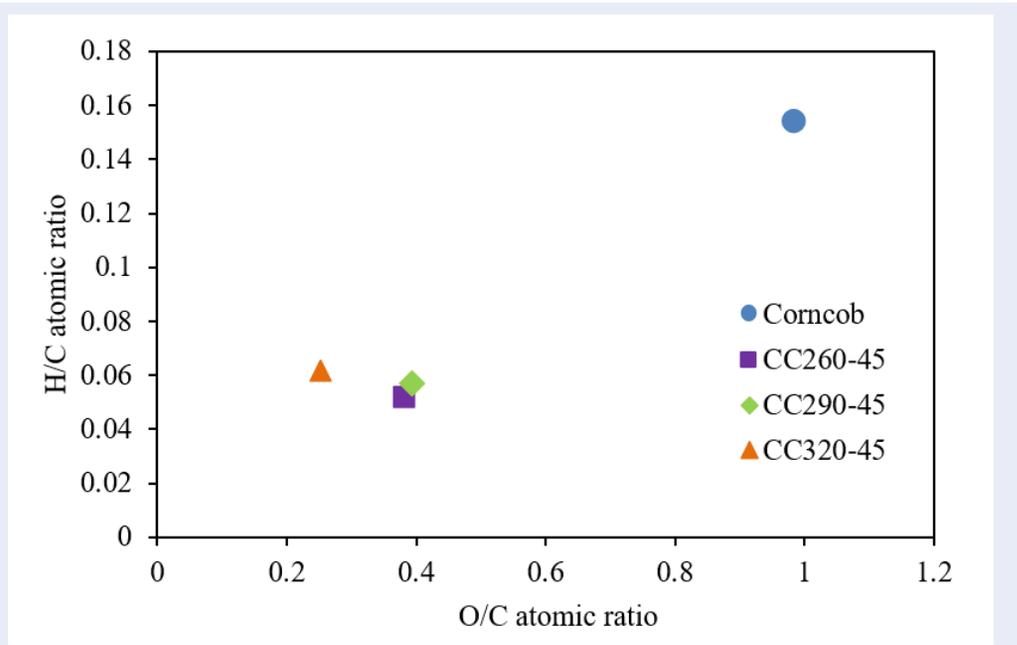


Figure 5: O/C and H/C ratio for torrefied corncob

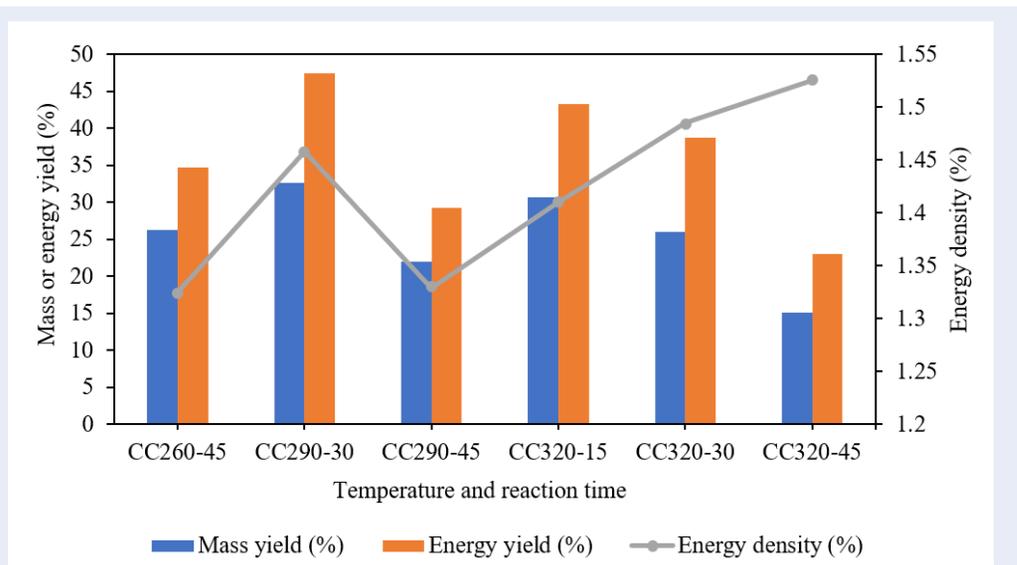
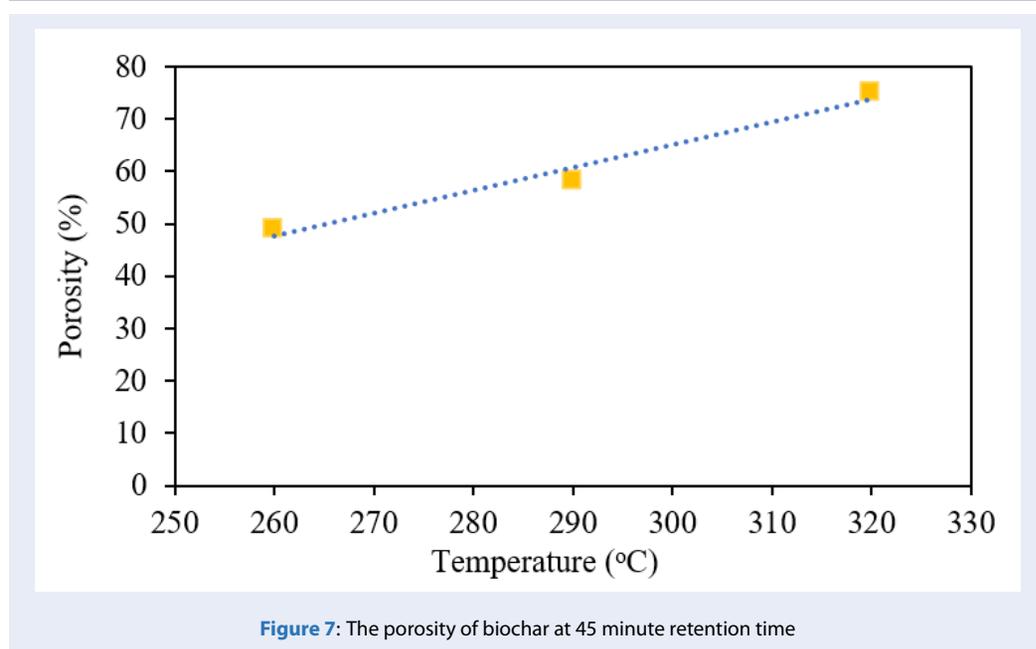


Figure 6: Mass yield, energy yield, and energy density of the corncob as a function of torrefaction temperature and reaction time



increases its environmental stability, as it contains fewer O-based functional groups. Moreover, according to Deenik and Cooney (2016), a low O/C and H/C ratio indicates a higher degree of thermal modification and aromaticity²⁴. Hassan et al. (2020) discovered that the O/C and H/C ratios reveal the polarity and aromaticity of biochar, which are essential features for biochar usage as adsorbents²⁵. The O/C molar ratio can be utilized to demonstrate the hydrophilic character of biochars, which varies with biomass type and torrefaction temperatures²⁶. Changes in the H/C and O/C ratios could be used to illustrate potential chemical reaction pathways during biochar synthesis. These findings the atomic ratio of H; C; and O including H/C and O/C were quite low, indicating that deoxygenation, decarboxylation, and dehydration took place during torrefaction, which might reduce CO₂, CO, and H₂O emissions at a power plant (22).

The mass yields and energy density of torrefied corn-cob samples at 260°C were 1.32 % and 34.72 %, respectively (Table 2). In addition, the energy density of these samples gradually increases from 1.32 (torrefaction at 260°C for 45 minutes) to 1.52 (torrefaction at 320°C for 45 minutes). These results suggest that the biochar underwent substantial carbonization during torrefaction, which the intense torrefaction conditions may explain²⁷. Remarkably, the energy yields were greater than the mass yields, which can be attributable to the augmentative energy densities during torrefaction²⁰. In practical applications, samples with high energy densities are preferred. Conse-

quently, our findings demonstrate that torrefied corn-cob has a considerable amount of promise as a renewable energy source. Figure 6 shows the mass yields, energy yields, and energy densities of the corn-cob samples as a function of the reaction time and torrefaction. As reaction time and temperature increase, the biochar yield steadily decreases. The fusing temperature increased from 260°C to 320°C, whereas the bulk output of cob biochar reduced from 26.22 % to 15.10 %. These findings might be explained by moisture loss and thermal degradation of various low-molecular-weight volatile compounds (such as cellulose and hemicelluloses) in biomass²⁰.

During torrefaction, mass loss in the form of solids, liquids, and gases causes the biomass to become more porous. While the porosity of biochar increases as the temperature of treatment rises, bulk density exhibits the reverse tendency, as seen in Table 2. It can be seen that bulk density at the lowest temperature of 260°C for 45 minutes is 0.31 g/cm³, while at the highest temperature of 320°C for 45 minutes is 0.23 g/cm³. In contrast, the porosity of biochar tends to increase gradually, as shown in Figure 7. In the same retention time, at three different temperatures, the porosity gradually increases from 48.82 %, 58.15%, and 74.94 % respectively. The porosity varies due to the volatile gases released during carbonization and the total surface area of the biomass²⁸. While for application as an energy source, less porous biochar pellets are more suitable because they have a higher tendency to catch

fire²⁹. This is a favorable condition for biochar production, especially in the condition that the highest temperature is 320°C and the highest retention time is 45 minutes so the efficiency that gives the pellets the highest efficiency. Significant alterations in the internal porosity and surface functionality of biochar were caused by the temperature and air oxidation differences³⁰.

Using char as charcoal or biochar is contingent on the char high heating value (HHV); the higher its HHV, the greater its utility as a fuel. As shown in Table 2, the HHV of char products increases as the torrefaction temperature rises, with CC260-45 having an HHV of 22.04 (MJ/kg) and CC320-45 having an HHV of 24.10 (MJ/kg). This is related to the breakdown of low-energy chemical components and the creation of high-energy chemical components in biomass. HHV represents the energy released from the combustion of volatile and stable carbon and is dependent on the carbon content. The heating value is also proportional to the cellulose and lignin concentration. Due to its greater degree of oxidation, lignin has a higher heating value than cellulose (26.70 MJ/kg vs. 17.30 MJ/kg)³¹. Additionally, the resident time has a minor effect on the HHVs of biochar products. The higher heating values of biochars left for 15 minutes are lower than those left for 45 minutes at all three torrefied temperatures. However, when the time increased from 30 to 45 minutes at 290°C, HHV decreased slightly from 23.11 MJ/kg to 21.17 MJ/kg, then continued to increase at a higher temperature than 320°C. This can be explained by the error in the experimental performance, although the final HHV tends to increase gradually. It is typically true that coals have a higher heating value than biomass because of their lesser oxidation.

In this study, the calorific value of biochar produced from corncob torrefaction was up to 24.29 MJ/kg (Table 3), which is an ideal parameter for biochar production as a combustion energy source to biochar of the cob, the three with the highest temperature have the highest calorific value. The comparison to previous studies focused on different types of waste materials, which contributed to different calorific values, and corncob is also a potential material for this process^{19,32–34}. According to Hamzah et al., 2017, the HHV value of coal is up to 32 MJ/kg, while the HHV value of current torrefied corncob pellets also has an ideal figure of 24.24 MJ/kg³⁵. The fixed carbon content of bio pellets from the cob is lower, so it is more environmentally friendly, but the efficiency can still be enough to meet energy production.

CONCLUSION

This study investigated the feasibility of biochar produced from corncob feedstock at torrefaction temperatures. The cob is a potential material for biochar production, which takes full advantage of its uses. After investigating many processes for biomass production, torrefaction is one of the low-temperature calcination methods (200 – 350°C) that has been selected successfully to produce biochar from corn cobs namely CC260-45, CC290-30, CC290-45, CC320-15, CC320-30 and CC320-45. The optimization condition for producing torrefied corncob biochar at 320°C in 45 minutes achieves the highest calorific value of up to 24.29 MJ/kg and the largest porosity is 74.94%. From the perspective of the yield of mass and energy, the torrefied condition of 290°C and 30 min. remaining time should be a prospective candidate. In conclusion, applying torrefied corncob biochar in the production of coal-like fuel is an environmentally friendly material and can reduce greenhouse gas emissions.

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COMPETING INTERESTS

There are no conflicts of interest to declare.

AUTHOR CONTRIBUTION

Nhu Thuyen Nguyen Huu: conceptualization; writing original draft; writing review and editing. Thi Ngoc Lan Thao Ngo: reviewing; revising; supervising. All authors are read and approved the final manuscript.

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Table 3: The characteristics of various types of biomass before and after torrefaction

Biomass	Torrefaction parameter	HHV (MJ/kg)	Reference
Corncob	Raw	16	This study
	260 - 320°C, 15 - 45 min	21 - 24	
Grape pomace	Raw	20	19
	250 - 300°C, 30 min	23 - 25	
Rice husk	Raw	17	32
	250 - 300°C, 60 min	17-22	
Bagasse	Raw	18	32
	250 - 300°C, 60 min	20 - 23	
Eucalyptus	Raw	18	33
	250 - 300°C, 60 min	20 - 23	
Ananas comosus peel	Raw	17	34
	210 - 300°C, 30 - 60 min	20 - 28	
Annona squamosa peel	Raw	17	34
	250 - 300°C, 30 - 60 min	19 - 23	

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Nghiên cứu tiềm năng chế tạo than sinh học từ sinh khối nhằm ứng dụng nguyên liệu đốt than thay thế than thương mại

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TÓM TẮT

Than sinh học (TSH) là một loại vật liệu được tạo ra thông qua quá trình xử lý nhiệt sinh khối ở nhiệt độ cao như nhiệt nung chảy. TSH là một loại vật liệu xốp và giàu carbon hữu cơ. Hiện nay, Việt Nam cũng có nhiều nghiên cứu về ứng dụng than sinh học. Trong nghiên cứu này, lõi ngô là phụ phẩm nông nghiệp phổ biến và có tiềm năng. Lõi ngô sẽ được nung bằng phương pháp nhiệt nung chảy ở nhiệt độ 230 °C, 260 °C, 290 °C và 320 °C trong thời gian lưu 15, 30 và 45 phút để nghiên cứu ảnh hưởng của các yếu tố nhiệt độ và thời gian lưu đến chất lượng TSH thu được. Nghiên cứu nhằm giới thiệu phương pháp hiệu quả trong việc tận dụng nguồn sinh khối có khả năng cháy cao nhằm thay thế nguồn than hoá thạch. Kết quả ghi nhận giá trị gia nhiệt lượng của TSH từ lõi ngô dao động từ 22,04 đến 32,57 MJ/kg, nhiệt lượng cao thể hiện tiềm năng thay thế cho nguyên liệu năng lượng tái tạo. Mẫu CC320-45 đạt nhiệt trị cao nhất là 24,29 MJ/kg và độ xốp của mẫu này là 74,94%. Việc tận dụng lượng phế phẩm sinh khối chuyển hóa thành năng lượng hữu ích và độ xốp cao của TSH cho phép ứng dụng TSH về xử lý ô nhiễm và cải tạo đất trong nông nghiệp. Đặc biệt, so sánh hiệu quả từ nguồn nguyên liệu thô, TSH từ công nghệ nhiệt nung chảy tạo đạt sản phẩm than vượt trội về khả năng tạo nhiệt so với các phương pháp khác.

Từ khoá: Lõi ngô, nhiệt nung chảy, than sinh học, nhiên liệu, năng lượng

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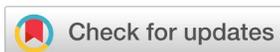
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