

## **EFFECT OF LOW COMBUSTION TEMPERATURE AND ALKALINE TREATMENT ON BIOCHAR PROPERTIES FROM RICE HUSK**

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### **Abstract**

Biochar is a form of carbon that is produced by heat decomposition of biomass. Pyrolysis under the inert atmosphere is a well-established method to produce biochar with high carbon yield. However, the technology is yet to be fully developed to become viable for commercial applications due to the need of utilisation of inert conditions. In this study, combustion technique was adapted as the novel method to produce biochar from rice husk with low cost. Rice husk is an excellent source for production of biochar due to its high lignin and carbon content. Alkaline treatment of rice husk was carried out with the aim to improve its pore characteristics and physicochemical properties. Hence, rice husk has been subjected to a combination of various treatments, including combustion at different temperatures (200, 300 and 400 °C) and NaOH treatment. Several analytical techniques such proximate analysis, ultimate elemental analysis (CHNS), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) were employed to analyse the characteristics of different biochar samples. Highest carbon content obtained was about 44.25% with NaOH treatment followed by combustion at 200 °C. All the tested samples exhibited amorphous structure. It has been found that specific surface area values between 305 and 467 m<sup>2</sup> g<sup>-1</sup> were obtained when alkaline treatment of the rice husk showing the viability of combustion method for biochar production.

Keywords: Combustion, Alkaline treatment, Rice husk, Biochar.

### **1. Introduction**

Recently, biomass utilisation is receiving great attention as an energy source for providing approximately 14% of the world's energy need. Among all the biomass

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sources, rice husk (RH) offers the most promising option because the annual world RH production is approximately 140 million tonnes per year [1]. RH is an agricultural waste material removed in the first stage of the milling process [2]. The commercial use of RHs has been limited due to their low density, which makes transportation of husks problematic. As a result, RH has been disposed off by open-field burning, creating more environmental issues. Therefore, suitable combustion technology has been developed to convert RH into useful energy since RH has high heating value of 16.3 MJ/kg, indicating that it could be a source of good fuel [3]. Additionally, RH is a great source for biochar production due to its high lignin content (22%) and carbon content (42.2%). There is an increased interest to fuel a direct carbon fuel cell (DCFC) using biochar because they are cheap, abundant and readily available [4]. DCFC is regarded as a highly efficient energy conversion device in which the chemical energy of a carbonaceous fuel is converted directly into electricity [5]. Amorphous structure, high surface area and high carbon content are the desired carbon fuels characteristics to attain high power density in DCFC operation [6,7]. The feasibility of using biochar as carbon fuel for application in DCFC has been discussed in several studies. Kacprzak et al. [8] proved the potential of DCFC to be operated with biochar prepared from biomass including apple, energetic willow, sunflower husks and pine. Dudek et al. [9] showed that there was increased interaction between carbon particles with large surface area and electrolyte, thereby promoting electrochemical reactions in DCFC due to efficient electron transfer [10].

Pyrolysis is the process involving thermal destruction of organic matter for the production of biochar, where the volatiles are released leaving the solid char [11]. However, pyrolysis process is usually carried out at moderate temperature of around 600 °C in inert (nitrogen) atmosphere [12,13]. Therefore, the cost for mass production of biochar using pyrolysis process is high, preventing the widespread application of this method. Combustion, which is another thermochemical process, offers an alternative to produce biochar [14]. Burning of RH at high temperature has resulted in the formation of rice husk ash (RHA), primarily consists of ~90 wt% silica and other metal oxides [15]. To date, an increasing application of RHA is as raw material for production of high quality silica [16]. The study on the production of RH biochar using combustion technique is yet to be reported. Low combustion temperature method appears to be an attractive option to produce biochar, where careful selection of temperature is required to obtain biochar with high carbon content.

To improve the biochar properties of RH, chemical treatment of RH can be carried out. Heating of the NaOH-treated sample for a certain time have been found to cause swelling of the pores, resulting in higher internal surface area and less crystalline structure which are the desired characteristics to achieve high power density in DCFC [17-19]. In addition, Markovska et al. [20] has proven that application of NaOH treatment showed effectiveness in removing ash from RH. However, limited work has been published concerning the influence of NaOH and its application before and after combustion on the RH biochar properties.

In the present research, production of RH biochar using low combustion temperature method and alkaline treatment were proposed to produce carbon fuels without the need of high temperature and inert treatment condition targeted for DCFC application. RH biochar was prepared with combustion temperature at 200,

300 and 400 °C. Changes in the colour of the biochar and the biochar yield were observed, followed by chemical analysis of samples. The effect of the combustion alone or combination of alkaline treatment and combustion on RH biochar was evaluated by X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) to determine the structure and pore characteristics of samples.

## 2. Materials and Method

### 2.1. Materials and sample preparation

Rice husk was collected from the Oblique Titi Rice Mill Co., Inc., Perak, Malaysia, followed by washing with distilled water few times and drying at 105 °C for 24 h using laboratory oven. The dried RH was grind, and then sieved to obtain particles within the indicated size range (2 mm to 500 µm). Laboratory grade (FriendemannChmidt) NaOH was used for treatment of samples.

The process of preparing biochar from RH can be divided into three sets, which are illustrated as follows. In first set, about 30 g of dried RH was placed in a crucible and combusted at 200, 300 and 400 °C for 2 h in a Carbolite 1200 °C muffle furnace of ambient atmosphere without any external gas supply. In the second set, about 30 g of dried RH was stirred with 0.1 M NaOH for 12 h in conical flask. After treatment, RH was washed with distilled water few times until constant pH was achieved, and then dried for 24 h at 105 °C. The NaOH-treated RH was combusted at temperature following the same procedure as above. In the last set, the procedures were similar to the first and second sets, except combustion was carried out prior to alkaline treatment. All the samples were assigned with sample codes as presented in Table 1.

**Table 1. Samples label.**

Treatment Condition	Combustion temperature (°C)		
	200	300	400
Untreated	A1	A2	A3
Pre-treatment	B1	B2	B3
Post-treatment	C1	C2	C3

### 2.2. Characterisation of biochar

The biochar yield from RH was calculated by measuring the weight of the samples before and after combustion. The weight percent of biochar as the product formed was calculated using Eq. (1)

$$\text{Biochar yield (\%)} = \frac{\text{Mass of biochar}}{\text{Initial mass of biomass}} \times 100\% \quad (1)$$

The amount of main constituent of biochar was determined by proximate analysis through a thermogravimetric analyser, TGA/DSC Stare System (Mettler Toledo Inc.). Samples were heated in nitrogen atmosphere from room temperature to 110 °C at a heating rate of 10°C min<sup>-1</sup>, followed by holding them for 10 min at the same temperature until constant weight was reached. The amount of the moisture content was observed from the first weight loss. Under the same flowing gas, the samples

were heated from 110 to 950 °C where the amount of volatile matter was estimated by observing the second weight loss. The atmosphere was then switched to air and the temperature was maintained at 950 °C. Ash content was determined from the amount of residue remained. Gas flow rates of 20 ml min<sup>-1</sup> were used in all cases. Elemental analysis of RH biochar was performed using a CHNS elemental analyser (Elementar vario MACRO Cube) to obtain the weight percent of carbon, hydrogen, nitrogen and sulphur elements.

XRD characterisation was carried out with a diffractometer (D8 Bruker Discover) for crystal structure identification of RH biochar at 40 kV and 40 mA. The analysis was performed with Cu-K $\alpha$  radiation at a scan speed of 2 ° min<sup>-1</sup> within the 2 $\theta$  range from 10 to 90°.

Nitrogen adsorption isotherms were investigated using a surface area and porosity analyser (Micromeritics ASAP 2020) at -196 °C. The specific surface area was calculated using BET model at relative pressure ( $P/P_0$ ) ranging from 0.01 to 0.99. Barrett-Joyner-Halenda (BJH) model was applied to determine the diameter of the pore ( $D_{pore}$ ), while the total pore volume ( $V_{total}$ ) was estimated based on the amount of the nitrogen gas adsorbed on the sample surface.

### 3. Results and Discussion

#### 3.1. Visual analysis

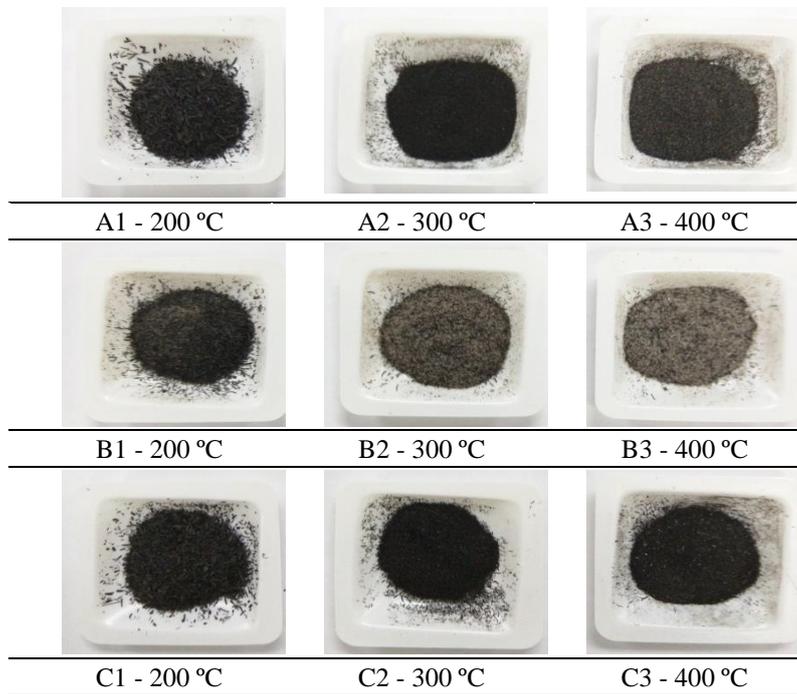
The colour changes of the samples were observed when RH was prepared under different combustion temperatures and treatment of NaOH, as shown in Fig. 1. The colour for three sets of samples became more greyish as the combustion temperature increased from 200 to 400 °C. Burning of RH in air up to 200 °C produced powder almost black in colour, indicating that the presence of carbon in RH which had not been oxidised completely yet. With the temperature increasing to 300-400 °C, the non-oxidised carbon started to decompose, transforming the black powder into grey-white ash. The effect of alkaline treatment on biochar was analysed in the subsequent analyses.

#### 3.2. Biochar yield

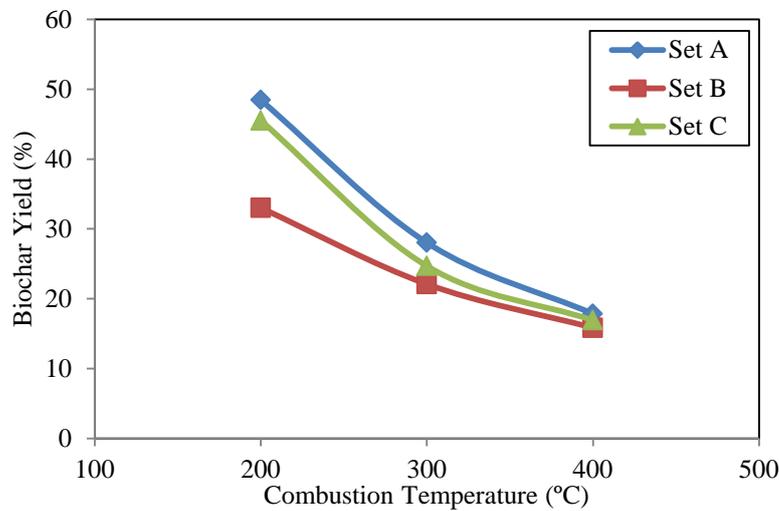
The yield of RH biochar is important to determine the possibility to be applied as carbon fuel in DCFC. Increasing combustion temperature significantly decreased the biochar yield, as shown in Fig. 2.

The decrease for the untreated RH was 30.6% (from 48.44 to 17.84%) when temperature was increasing from 200 to 400 °C. Similarly, the decrease for the pre-treated RH was 17.16% (from 33 to 15.84%) under the same condition, while reduction for post-treated RH was 28.58% (from 45.5 to 16.92%). The yield reduction was caused by the transformation of carbon component of biomass to biochar and simultaneously combustion of volatile matter occurred during the burning process [21]. Lee et al. [22] reported that thermal degradation of hemicellulose and cellulose of RH occurred in the temperature range of 210 to 360 °C. As a result, more volatiles evolved within the temperature range, reducing the biochar yield. Compared to biochar from other carbonaceous material which yielded lesser than 35 wt% [23], RH combusted at

200 °C seems to be an attractive resource as carbon fuel because the biochar yield was about 48%, 33% and 45.5% for untreated, pre-treated RH and post-treated RH respectively.



**Fig. 1.** Visual images of RH biochar.



**Fig. 2.** Biochar yield for untreated (Set A) and NaOH-treated (Set B and C) sample.

### 3.3. Characterisation of biochar

#### 3.3.1. Chemical analysis

Table 2 compares the four main components of each of the biochar sample, including moisture, volatile matter, fixed carbon and ash content.

From Table 2, it was shown that RH biochars consist of volatile matter contents of about 21.11 to 23.01%, which was slightly higher than volatile content of coal (less than 20%) [24]. Generally, raw biomass has high volatile matter content where 80-90% of biomass is combusted in the form of volatiles. Since most of the energy is stored in the volatiles, volatile matters are highly reactive, which makes the combustion process more difficult to be controlled [25]. Hence, lower content of volatile matter is desirable because it is an indication that the combustion process is easier to be controlled.

**Table 2. Constituents in biochar produced from combustion at 200 °C.**

Bioc har	Moisture (% wt.)	Volatile matter (% wt.)	Fixed carbon (% wt.)	Ash (% wt.)
A1	2.79	22.28	34.10	40.83
B1	2.96	23.01	37.12	36.94
C1	2.15	21.11	33.26	43.48

The fixed carbon content obtained in this work ranged from 33.26 to 37.12%. The result suggested that the fixed carbon content was affected by the higher ash content of RH, which inhibited the formation of aromatic carbon during the thermochemical conversion process [26].

Among all the three samples, the ash content of sample B1 was the lowest (36.94%). Biomass treatment using diluted acid or alkali has been regarded as one of the effective ways in removing inorganic elements under influence of mineral dissolution and desorption [27]. The ability to reduce ash content in biochar with NaOH pretreatment prior to combustion was attributed to the reaction of silica in RH with NaOH, in which silica was extracted in a form of  $\text{Na}_2\text{SiO}_3$  [20]. This study also showed that post-treatment of RH biochar with NaOH was inefficient in leaching out ash-forming elements, given that the sample C1 consisted of the highest ash content. It is a common consensus that high ash content is likely to cause fouling at the current collector in DCFC [28]. Hence, further study is required to further reduce the ash content despite the success of this study using low temperature combustion method to produce biochar.

Next, compositions of the selected samples were examined by analysing the main elements (carbon, hydrogen, nitrogen, sulphur) as illustrated in Table 3. At the same combustion temperature, only slight composition difference was observed in samples A1, B1, and C1. Sample B1 has the carbon content of about 44.254%, which was the highest among all the tested biochar samples. The increase in carbon content after the alkaline treatment was probably due to the extraction of impurities by NaOH. The results also showed that the nitrogen and sulphur content in the biochar prepared were considerably lower, which was an

indication that deposit formation was unlikely to occur in the operation of the DCFC [25].

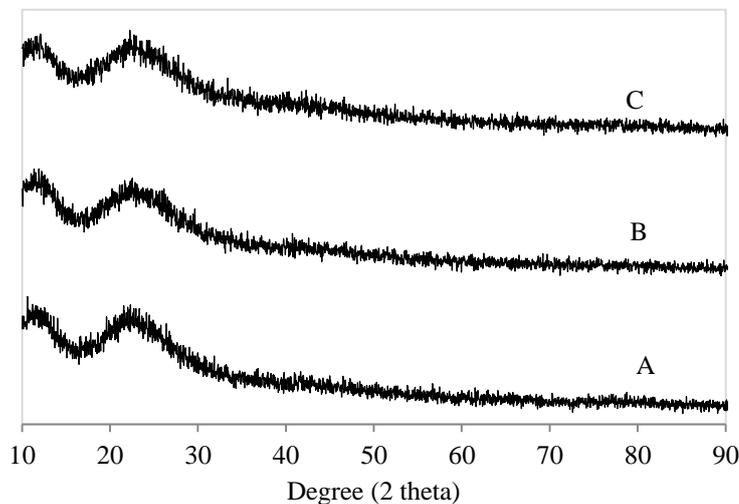
For comparison, the carbon content of RH combusted at 300 °C was 34.03%, indicating that combustion temperature had significant effect on the contents of organic component. It was found that treatment of RH before combustion at 200 °C appeared to have positive effect on the carbon content, where high carbon content was one of the desired characteristics to be used as carbon fuel in DCFC [7].

**Table 3. Elemental composition of A1, B1, C1 and C2.**

Sample	C (%)	H (%)	N (%)	S (%)
A1	43.709	2.946	7.529	0.109
B1	44.254	2.798	6.615	0.079
C1	42.812	3.324	5.986	0.064
C2	34.030	2.146	5.538	0.034

### 3.3.2. Phase structure of biochar samples

Figure 3 shows the XRD patterns of untreated, pre-treated and post-treated biochar prepared at combustion temperature of 200 °C. All the samples exhibited the same diffraction patterns, where broad peaks were observed between 15 and 35° 2  $\theta$ . According to Krishnarao et al. [29], the range corresponded to the presence of amorphous silica. Also, the XRD patterns revealed the absence of any ordered crystalline structure [30]. It was reported that the broad peak at 22° corresponded to the contribution from both amorphous carbon and silica [31]. Therefore, it could be concluded that the amorphous structure of untreated and treated RH were retained after combustion. It is desirable to have amorphous carbon as the carbon fuel for DCFC [32]; nonetheless, we are unable to tell the percentage of amorphous carbon and silica in the biochar.



**Fig. 3. X-ray diffraction patterns for samples A1, B1 and C1.**

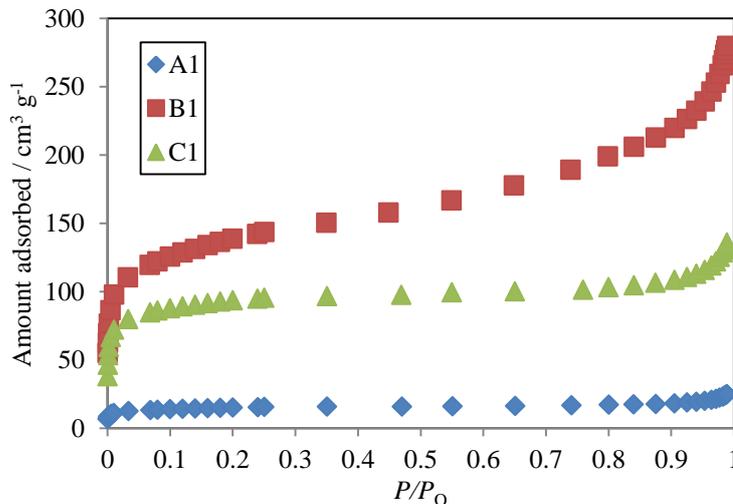
### 3.3.3. Textural properties of biochar samples

The pore structures of the biochars obtained by BET analysis are summarised in Table 4. Specific surface area, total volume and pore size of biochars treated with alkali were generally higher than the untreated biochar. The pore structure of sample A1 was insufficiently developed, with surface area and total volume of  $50 \text{ m}^2\text{g}^{-1}$  and  $0.037 \text{ cm}^3\text{g}^{-1}$ , respectively. Combustion process alone seemed to be insufficient to enhance the pore structures. On the other hand, sample B1 exhibited the highest specific surface area of about  $467 \text{ m}^2\text{g}^{-1}$  with pore volume of  $0.414 \text{ cm}^3\text{g}^{-1}$ . Alkaline treatment is usually conducted to remove the inorganic matters in the biomass, allowing the generation of more developed pore network [33]. In this study, NaOH pretreatment was found to decrease the ash content, as demonstrated in section 3.3.1. Therefore, the combined effect of combustion and alkaline treatment improved the pore structures significantly.

Additionally, the sequence of alkaline treatment on RH greatly influences the pore characteristics developed. It can be seen that specific surface area and pore volume of biochar was higher for pre-treated sample than post-treated sample. When alkaline treatment was conducted after combustion, the post-treated biochar experienced porosity shrinkage where the pore shrank to narrower size, leading to pore size reduction [34]. The shrinkage effect was not obvious in pre-combustion-treatment sample, since combustion process helps to generate pores.

**Table 4. Pore characteristic of the untreated and treated biochars.**

Biochar	$S_{\text{BET}} (\text{m}^2 \text{g}^{-1})$	$V_{\text{total}} (\text{cm}^3 \text{g}^{-1})$	$D_{\text{pore}} (\text{nm})$
A1	50	0.037	2.91
B1	467	0.414	3.57
C1	305	0.202	2.65



**Fig. 4. Nitrogen adsorption isotherms of A1, B1 and C1.**

The nitrogen adsorption isotherms of A1, B1 and C1 are shown in Fig. 4. The adsorption curves of samples B1 and C1 showed a better adsorption performance than sample A1. At low relative pressure, steep adsorption in B1 and C1

isotherms confirmed the existence of micropores as a result of alkaline treatment [35]. Both the samples showed a gradual increase in isotherms after the initial micropores filling. At high relative pressure, large adsorption capacity took place which indicated that the presence of mesopores with wider porosity. However, the small adsorption capacity of the sample A1 proved an obvious decrease in the mesoporosity. The results suggested that combustion process alone was insufficient to produce microporous and mesoporous biochar.

#### 4. Conclusions

Biochar samples were successfully produced from RH using low combustion temperature method and alkaline treatment. Combustion method is a viable method to produce biochar with high carbon content, large surface area and amorphous structure comparable to pyrolysis process despite of its high ash content. Especially with NaOH treatment followed by combustion at 200 °C, the treated biochar (sample B1) shows the highest carbon content (44.25%) and specific surface area ( $467 \text{ m}^2\text{g}^{-1}$ ) compared to all of the tested samples. In the future work, the cost effective method can be further modified to reduce the ash content in order to meet the specification for DCFC fuel.

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