Characterization of carbonized waste materials: Rice husk and saw dust

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Abstract. Waste materials can be categorized into household, commercial, agricultural, synthetic wastes, and so on. Agricultural wastes play a great role as an alternative material to be derived into valuable carbon materials, due to their low cost and abundancy, in contrast to conventional carbon material sources. Feasible carbonization process of agricultural wastes can be conducted by using heat treatment. The focused agricultural wastes in this study are rice husks (RH) and saw dusts (SD). They are converted into carbon materials through heat treatment under the presence of inert gas at 500°C and 800°C for 2 hours. Then, their characteristics such as structure, morphology, elemental composition, and crystallinity are investigated by utilizing scanning electron microscopy (SEM), Energy Dispersive X-ray (EDX) spectroscopy, and X-ray Diffraction (XRD). Similarly, the carbonized RHs and SDs can be classified as amorphous carbon and possess porous structure. The characteristics of carbonized RHs and SDs indicate that they could be a promising material to be utilized in particular or various applications.

1. Introduction
Rice husk (RH) is an agro-based lignocellulosic waste material that is abundant in various countries, majorly produced from by-product of rice milling industries [1, 2]. Based on the report from Food and Agriculture Organization of the United Nations (FAO), in year 2016, world rice production is approximately 741 million tonnes, and approximately 2.3 million tonnes was contributed by Malaysia. RH is accountable for around 20% from the rice production, which is ready to be utilized [3]. Generally, RH is manipulated as low value energy resource, discarded, or simply burnt at the field, which will influence the air quality and threaten the environment [4].

On the other hand, saw dust (SD) is an ample lignocellulosic waste material obtained from the processing of wood including cutting, grinding, drilling, scraping, or pummeling wood with saw or any other cutting tool used in sawmills, factories, or in the household activities [5-7]. Based on the report from FAO, in year 2017, world wood residue production is approximately 225 million m³, and approximately 1.7 million m³ was produced in Malaysia. SD, together with wood offcuts and chips, is accountable for around 20% of the total input mass [6]. Commonly, SD is accumulated or combusted in factories or mills, which hinder its effective utilization and unfavorable to the environment [5, 6].

Therefore, it is essential to conduct research on RH and SD in order to fully utilize and unlock their potential for broad applications. Both RH and SD are lignocellulosic materials, which is in favor to
convert them into raw carbon materials [8]. The conversion simply can be accomplished through carbonization process using heat treatment [9]. Due to the low cost and abundancy of RH and SD, in contrast with other carbon materials such as carbon nanotubes, carbon black, graphene, and so on, they can be expected to play a significant role to be fully utilized as the source of carbon materials. In this study, the RH and SD were carbonized and then their structure, morphology, elemental composition and crystallinity were characterized and compared.

2. Experimental
Dried RHs and SDs without further modification were used as the source to be carbonized. They were carbonized at different temperatures of 500°C and 800°C. The raw RHs and SDs were carbonized at 500°C, 2 h using furnace, under the presence of argon gas. Similar step was repeated for carbonization at 800°C. All samples were cooled down naturally and then grounded into powder before further characterization. RHs and SDs carbonized at 500°C will be denoted as RH500 and SD500; RHs and SDs carbonized at 800°C will be denoted as RH800 and SD800, hereafter.

The samples were observed using scanning electron microscopy (SEM; Hitachi S-3400N) equipped with energy dispersive X-ray (EDX), in order to investigate the structure and morphology. EDX was utilized to characterize the elemental composition. X-ray diffraction (XRD; Philips X'Pert) measurement was performed in order to determine the crystallinity of produced carbon materials.

3. Results and discussions
The mass difference of the samples before and after carbonization at different temperatures is tabulated in table 1. As the carbonization temperature increased, the mass difference also increased. The decomposition of volatile materials during carbonization process leads to the mass loss. Overall, SD showed higher mass loss when compared to RH, for both temperatures. The highest mass difference was marked by SD800, which is 77%.

Table 1. Mass difference after carbonization process

| Material | Mass Before (g) | Mass After (g) | Mass Difference (%) |
|----------|-----------------|----------------|---------------------|
| RH500    | 30.0            | 12.7           | 58                  |
| RH800    | 30.0            | 11.4           | 62                  |
| SD500    | 30.0            | 8.3            | 72                  |
| SD800    | 30.0            | 6.8            | 77                  |

SEM images of carbonized RH at different temperatures are depicted in figure 1. Porous structure is obvious, and can be clearly seen from RH500 and RH800. The pores can be considered as macroporous, in μm range. No drastic structure changes are observed at this temperature range, dissimilar to Ref. [9]. From figure 1(b), sand-like particles (red circled) can be observed. Relatively, higher silicon is traced via EDX at these particles, which indicated they are rich in silica. SEM images of carbonized SD at different temperatures are depicted in figure 2. Similarly, porous structures can be observed from SD500 and SD800. From figure 2(b), smaller pores, around nm range, can be observed. However, they are not evident for SD800. The porous structure of carbonized RH and SD can provide good adhesion with matrix materials such as polymer matrix, which can acts as reinforcement.
EDX spectroscopy measurement was conducted to determine the elemental composition of carbonized RH and SD, and summarized in table 2. The main component obtained after carbonization process is carbon. In contrast with carbonized SD samples, silicon element was only observed in carbonized RH samples. The silica absorption of rice plants in the form of silicic acid from the soil is thinkable [10]. Furthermore, oxygen also can be traced, and this can be linked with certain amounts of functional groups such as hydroxyl and carboxyl [11, 12]. Other elements can be referred to impurities, mineral absorbed by paddy or wood, fertilizers, and so on. Overall, carbonized SD produced higher carbon purity, around 85%, in contrast to carbonized RH. This is in accordance to the higher mass
difference (table 1) of SD. It is also worth to notice that the increment of carbonization temperature from 500°C to 800°C for SD did not result in higher carbon contents.

Table 2. Elemental composition of carbonized RH and SD.

| Material | Carbon (wt.%) | Oxygen (wt.%) | Silicon (wt.%) | Others (wt.%) |
|----------|--------------|--------------|---------------|--------------|
| RH500    | 73.42        | 9.95         | 4.05          | 12.58        |
| RH800    | 78.74        | 11.50        | 1.62          | 8.15         |
| SD500    | 85.38        | 7.34         | -             | 7.28         |
| SD800    | 85.43        | 5.52         | -             | 9.05         |

XRD result of RH500 is illustrated in figure 3. Generally, all carbonized RH and SD showed similar XRD patterns with RH500. This further revealed that both carbonized RH and SD possess typical amorphous carbon broad peak (002), at around $2\theta = 22^\circ$~$23^\circ$. In order to further characterize the results, fitting line is fixed to the main peak. The results obtained from fitting line are tabulated in table 3. Based on the fitting line of carbon peak for carbonized RH and SD, the full width at half maximum (FWHM) is around 8~9°. This further confirms that the carbonized RH and SD are similar, regardless the carbonization temperature, which they can be classified as low crystallinity carbon materials.

![XRD of RH500](image)

Table 3. XRD results based on fitting line

| Material | Peak Position (°) | FWHM (°) |
|----------|------------------|----------|
| RH500    | 22.662           | 8.532    |
| RH800    | 23.388           | 8.138    |
| SD500    | 22.533           | 9.386    |
| SD800    | 23.545           | 8.930    |
Notably, this type of carbon materials usually further developed as the activated carbon through physical or chemical activation for applications such as absorbent, energy storage devices, and so on [3, 4, 6, 13]. Furthermore, they also exhibited high potential to be developed as the multifunctional composite materials for various applications such as hybrid nanomaterials, electromagnetic wave absorber, and so on [14-16]. They can be exploited as an abundant and cost effective material for various applications.

4. Conclusions
Carbon materials derived from RHs and SDs were prepared by carbonizing them at 500°C and 800°C. Their structure, morphology, elemental composition and crystallinity were evaluated through SEM observation, EDX evaluation, and XRD measurement. Both carbonized RHs and SDs showed porous structure and significantly high content of carbon element. Furthermore, they can be categorized as low crystallinity material which is amorphous carbon. It is undeniable that their performance might be limited in comparison to the high grade or high crystallinity carbon materials. However, since they are available in large scale, greener technology to produce bulk quantity of valuable carbon materials from agricultural wastes can be promoted.

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