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CHARACTERISTICS OF WOLLASTONITE SYNTHESIZED FROM RICE HUSK AND RICE STRAW

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ABSTRACT

In this work, two types of paddy wastes i.e. rice husk and rice straw have been used as silica (SiO_2) sources to synthesize $CaSiO_3$. Precursor, the husk and the straw were burnt at 950 °C for 1 h to obtain the ash. Some characterization were done to investigate properties of the rice husk ash (RHA) and rice straw ash (RSA) such as XRD, XRF, FTIR and heavy metal element analyses. RHA and RSA contain about 89.50 and 79.0 wt. % of crystalline silica in the cristobalite phase, respectively. The $CaSiO_3$ was synthesized using RHA and RSA mixed with CaO separately with SiO_2:CaO molar ratio of 55:45. The prepared sample was autoclaved, sintered at 950 °C and followed by characterization using XRD and FTIR analyses. For heavy metal elemental study, metal panel that included As, Cd, Hg and Pb were selected and both precursor, RHA and RSA had fulfilled the requirement of ASTM F1538-03 standard specification. XRD results show that a single phase β-$CaSiO_3$ was obtained after 8 h of autoclaving and sintering at 950 °C but different sintering time, which is 2 h for RHA and 3 h for RSA. The different in sintering time was due to the silica content in RHA and RSA. Results obtained from the study show that RHA and RSA can act as a precursor for wollastonite but required different synthesizing parameters.

Keywords: rice husk ash; rice straw ash; β-$CaSiO_3$; heavy metal element;

INTRODUCTION

Wollastonite ($CaSiO_3$) is from the silicate mineral group and taken its name from the English chemist Sir William Hyde Wollaston (1766-1828). It consists of elemental calcium (Ca), silicon (Si) and oxygen (O) with its chemical formula $CaSiO_3$ and theoretically, composition of wollastonite comprises of 48.3% calcium oxide (CaO) and 51.7% silicon dioxide (SiO_2). Most wollastonite is quite pure, it may contain other elements such as iron, magnesium, manganese, aluminum, potassium, sodium, calcium or strontium replacing elements in the structure of the mineral. Wollastonite colour is pure white and change colour to gray, cream, brown, pale-green or red in the present of other element impurities [1]. Nowadays, wollastonite is widely used in ceramic and cement industries due to their excellent properties such as good strength, low shrinkage and lack of volatile constituents [2].

Paddy is the main crop in Malaysia, especially in the northern region of Peninsular Malaysia. Rice husk and rice straw which are an agricultural by-product after the harvest season of paddy. The rice husk is the outermost layer of the paddy grain that is separated from the rice grains during the milling process, while the rice straw is the stem of rice plants, which was cut during the harvesting of paddy. In Malaysia, paddy is planted twice a year, so we can expect the dumping waste of the rice husk and the rice straw after the harvest season. Rice straw will be left in the paddy field after harvest and will be burnt for the next crop. The rice husk was obtained after the milling process of the rice grains and left in a landfill and will also be fired. The major composition of the rice husk and the rice straw are cellulose (32–47%), hemicellulose (19–27%), lignin (5–24%) and ash (13–20%) [3-4].

In this work, we investigate the potential of rice husk ash and rice straw ash as an alternative starting material in the synthesizing of wollastonite. The composition, phase, and heavy metal element of the rice husk ash, rice straw ash and wollastonite has been determined.

EXPERIMENTAL

Rice husks were collected from Ghee Song Hong Rice Mill in Penang, Malaysia and the rice straw was collected from a paddy field in Kodiang, Kedah, Malaysia. Limestone ($CaCO_3$) powder was procured from Holy Mate (M) Sdn. Bhd., Selangor, Malaysia. Rice husk ash (RHA) and rice straw ash (RSA) were obtained via a combustion process at 950 ^{o}C for one hour. Calcined limestone (CaO) powder was obtained through the process of calcining limestone at 1100 °C for 5 h. Chemical elemental, phase, functional group and heavy element analyses of the RHA and RSA were conducted using X-ray Fluorescence (XRF, S8 Tiger, Bruker, Germany), X-ray diffraction (XRD, D8 Advance, Bruker, Germany), Fourier transform infrared spectroscopy (FTIR-ATR, Pelkin Elmer, USA) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). β-wollastonite powders were synthesized using green synthesizing with a simple sol-gel route [5] via autoclaving for 8 h. The sintering time to obtain wollastonite was 1, 2 and 3 h. Phase, functional group and heavy element analyses of the sintered powders were conducted using X-ray Fluorescence (XRF, S8 Tiger, Bruker, Germany), X-ray diffraction (XRD, D8 Advance, Bruker, Germany), Fourier transform infrared spectroscopy (FTIR-ATR, Pelkin Elmer, USA) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of both rice husk ash (RHA) and rice straw ash (RSA). From XRF results of RHA and RSA indicate that it consists mainly of SiO_2 89.5 wt.% and 79.0 wt.% respectively with small amounts of impurities in the form of P_2O_5, K_2O, MgO, Al_2O_3, CaO, and others. The P_2O_5 is high in RHA (3.61 wt. %) whereas

RSA consists only 0.47 wt.%. However RSA has higher composition of K_2O (9.7 wt.%) and CaO (2.02 wt. %). Other researchers also reported that SiO_2 is the main element in the RHA (91.42 wt. %) after firing the husk at 600 °C for 4 h [6] and RSA is 75.38 wt. % after firing the straw at 525 °C for 4 h [7]. The ash elements either in RHA or RSA are being influenced by the rice type, climate and geographic location [8]. RHA and RSA was selected as alternative precursor for substitution of commercially SiO_2 because of its silica content, is the highest compared to other agricultural wastes [6], [7]. In addition, rice husk and rice straw are easily obtainable in large quantities from the rice mill factory and paddy field.

Table 1: Composition of the rice husk ash (RHA) and rice straw ash (RSA)

Composition	Rice husk ash (wt %)	Rice straw ash (wt %)
SiO_2	89.50	79.0
P_2O_5	3.61	0.47
K_2O	3.36	9.70
MgO	1.24	1.21
Al_2O_3	0.58	0.23
CaO	0.57	2.02
Others	1.14	7.37

The XRD patterns of the RHA and RSA are shown in Figure 1 with a single phase of cristobalite as the main peak for both RHA (Figure 1a) and RSA (Figure 1b) after combustion at 950 °C for 1 h. The overall peak pattern are similar for RHA and RSA with reference peak of cristobalite used is 00-082-0512. The XRD patterns obtained for RHA and RSA are akin to those described by Liou [9] and Umamaheswaran and Batra [10].

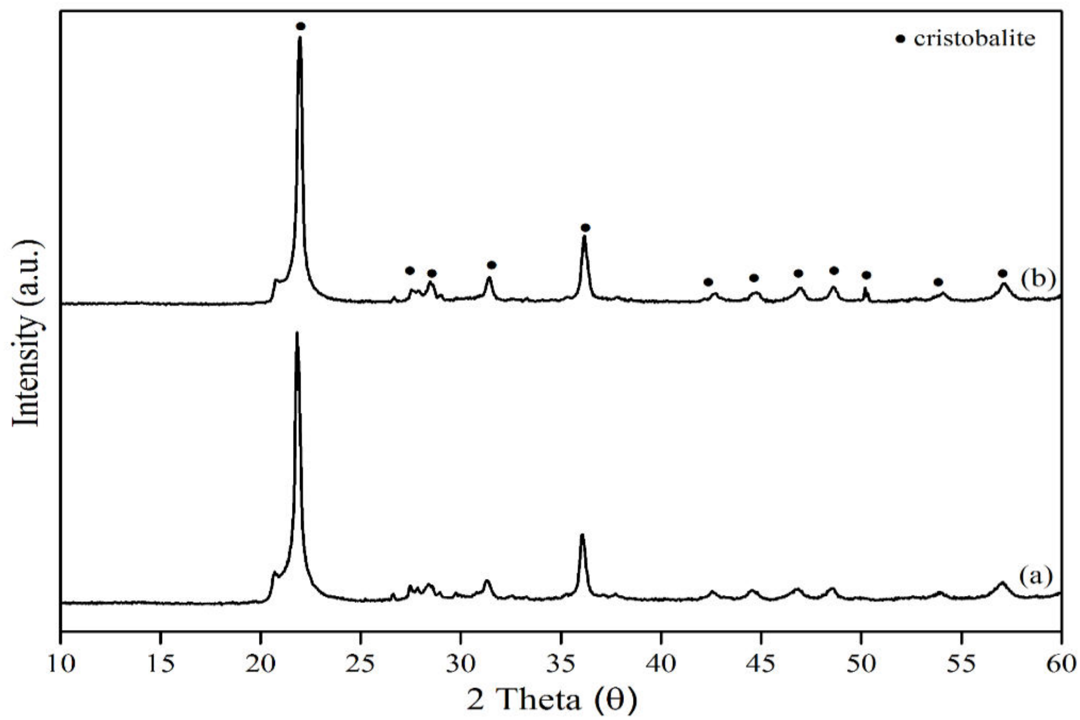

Figure 1 XRD patterns of the (a) rice husk ash (RHA) and (b) rice straw ash (RSA).

Figure 2 presents the FTIR spectra of rice husk ash (RHA) and rice straw ash (RSA) powders. Si-O-Si band was observed at the wavenumber of ~1067 cm^{-1} for RHA (Figure 2a) and ~1056 cm^{-1} for RSA (Figure 2b). Peaks at the wavenumber of ~785 cm^{-1} and ~781 cm^{-1} were referring to the vibration stretching modes of Si-O in the RHA and RSA, respectively. Previous studies showed that RHA and RSA had the same wavenumber at 1095 cm^{-1} and 1090 cm^{-1} which is due to the vibration stretching mode of Si-O-Si [11], [12]. Prasetyoko et al.[13] reported that the wavenumber at 1099 cm^{-1} and 791 cm^{-1} for RHA and RSA, respectively belong to the stretching vibration of tetrahedra SiO_4. All the detection peaks in this study exhibited the presence of silicate in the RHA and RSA samples.

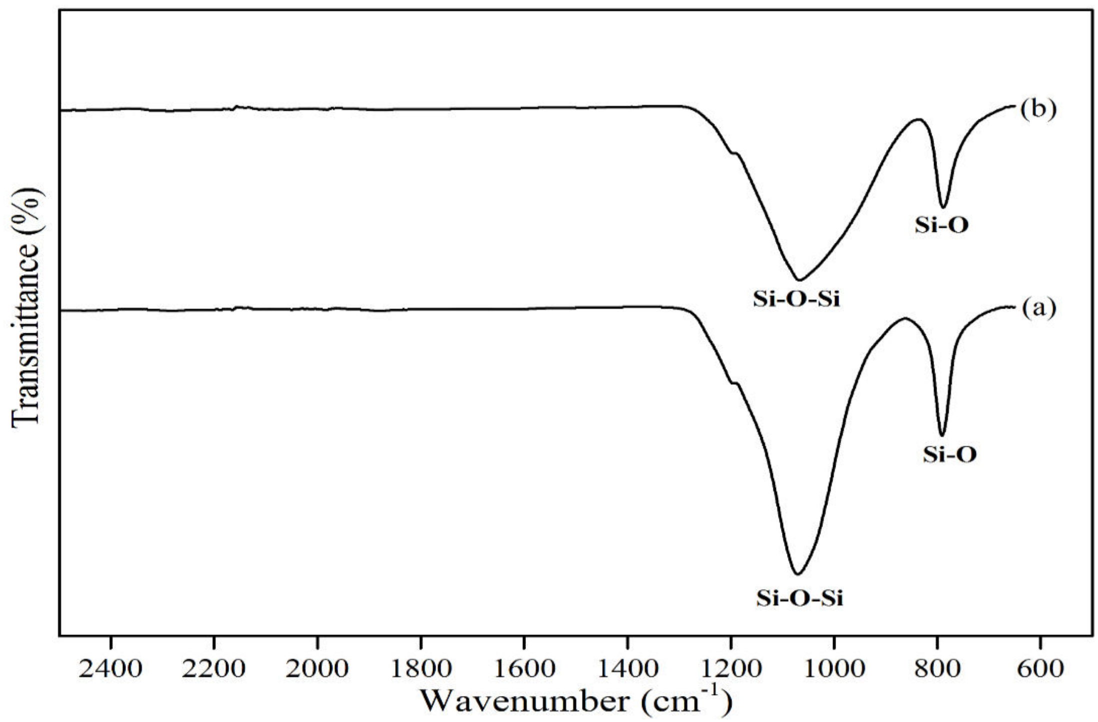

Figure 2: FTIR spectra of (a) rice husk ash (RHA) and (b) rice straw ash (RSA)

The results of X-ray analysis of the sintered powders from both RHA and RSA at 950 °C for various soaking time was shown in Figure 3. Single phase β-wollastonite from RHA was obtained after 2 h sintering (Figure 3b) meanwhile for RSA after 3 h sintering (Figure 3e). RSA needs longer sintering to produce single phase β-wollastonite compare to RHA because RSA contains less silica and needs a lot of rice straw ash compare to RHA. The reference peak of β-wollastonite used is 00-043-1460.

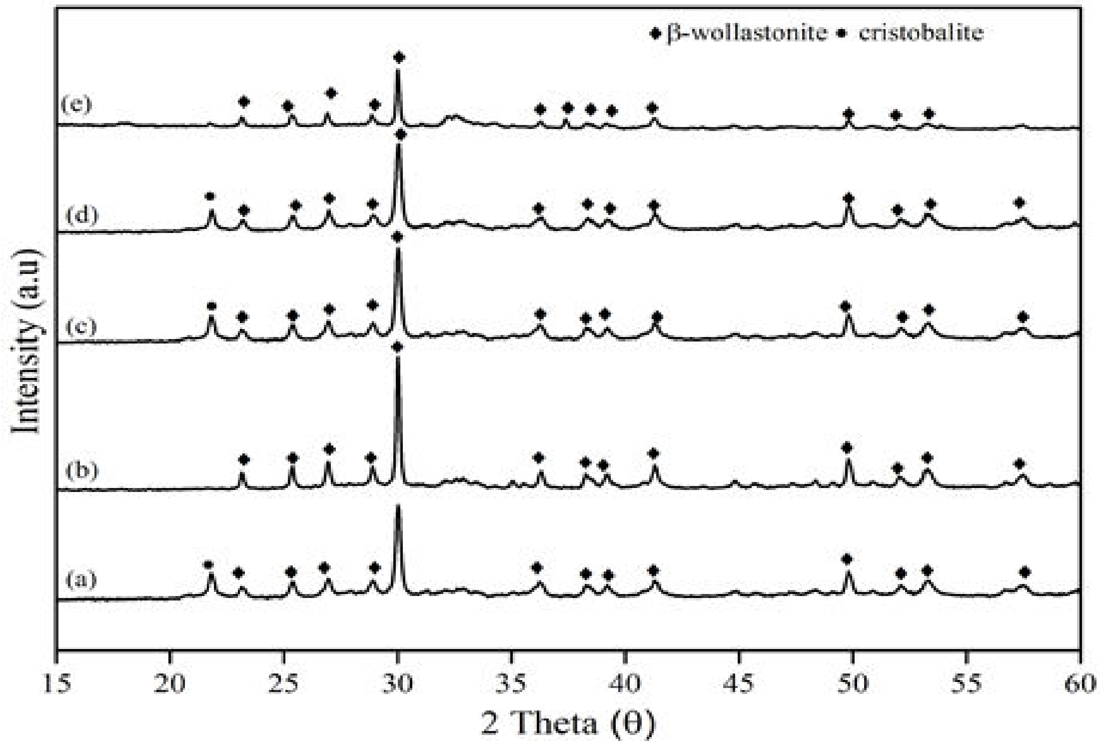

Figure 3: X-ray diffraction spectra of the sintered wollastonite at 950 °C from the RHA and RSA for various sintering period; (a) RHA 1 h, (b) RHA 2 h, (c) RSA 1 h, (d) RSA 2 h and (e) RSA 3 h

The vibrational spectra of wollastonite from RHA and RSA samples are shown in Figure 4. Absorption band of Si-O vibration for RHA wollastonite occurs at 1060 and 1010 cm^{-1} and for RSA wollastonite is detected at 1060 and 1012 cm^{-1}, which is comparable to the results obtained by Kolhe and Kannan [14], Paluszkiewicz et al. [15] and Rashita et al. [16]. Wavenumbers appear at 931, 897 and 681cm^{-1} refers to a stretching of silicon ions Si-O-Si in the RHA wollastonite and wavenumbers at 936, 899 and 697 cm^{-1} belong to RSA wollastonite. These results are similar to those reported by Sreekanth et al. [17] for β-$CaSiO_3$ sintered at 950 °C for 3 h. The existence of asymmetric stretching band carbonate, CO_3^{2-} in RHA and RSA wollastonite was detected at the wavenumber of 1432 and 1430 cm^{-1}, respectively. Shallow peaks at 1700 cm^{-1} (RHA wollastonite) and 1662 cm^{-1} (RSA wollastonite) are also referring to the CO_3^{2-} band. Zaki et al. [18] obtained the carbonate group at the wavenumber of 1444 cm^{-1}. CO_3^{2-} intensity in RSA wollastonite is reduced when the sintering time became longer compared to the RHA wollastonite. This result was also supported by Sreekanth et al. [17] that noted the peak of carbonates decreases with sintering time.

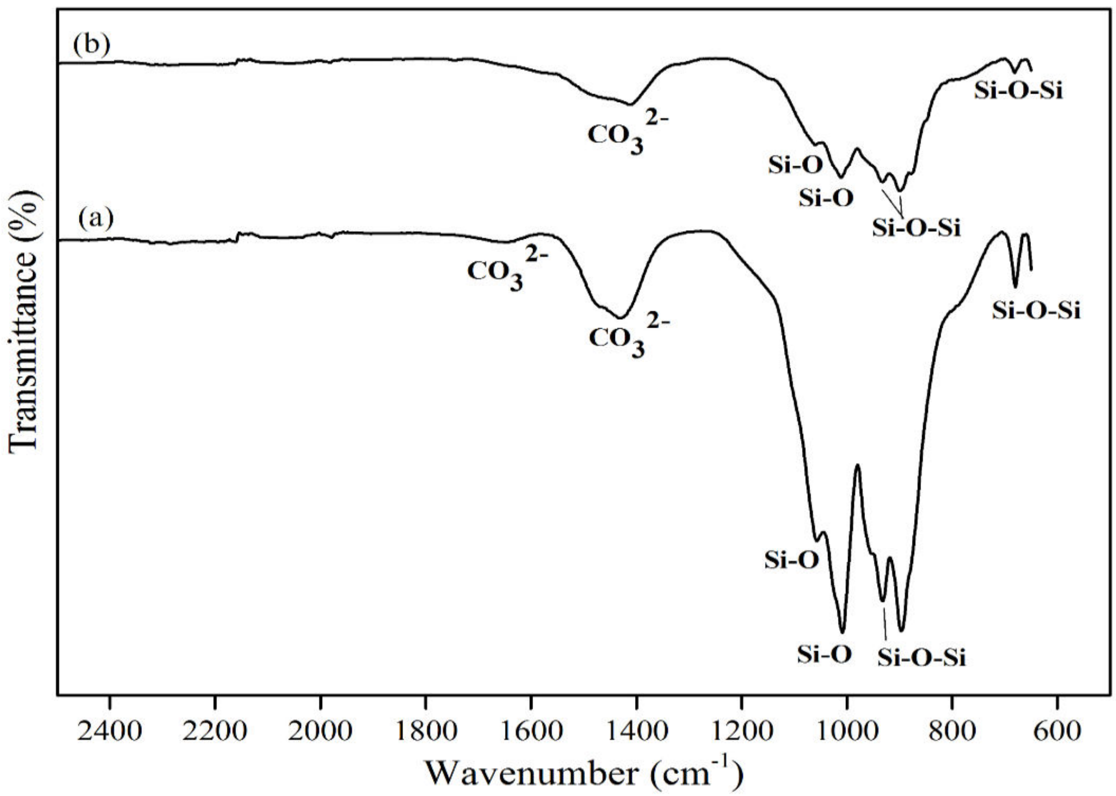

Figure 4: FTIR spectra of of the wollastonite from (a) rice husk ash and (b) rice straw ash.

Table 2 summarized the heavy element results obtained for the RHA, RSA, wollastonite (both RHA and RSA). The results of ICP-AES analysis showed that the concentrations of heavy elements for RHA, RSA, wollastonite (RHA and RSA) are below the maximum accepted limits using the ASTM F1538-03. Hence the obtained RHA and RSA are safe, non-toxic and suitable to be used as starting materials in synthesizing the wollastonite.

Table 2: Trace heavy element of RHA, RSA, β-WRH and β-WRS

Sample	Heavy element content (ppm)			
	Arsenic (As) ($x10^{-3}$)	Cadmium (Cd) ($x10^{-4}$)	Plumbum (Pb) ($x10^{-3}$)	Mercury (Hg) ($x10^{-3}$)
RHA	22.0	30.0	7.0	0.0
RSA	1.5	1.0	13.0	0.0
β-WRH	23.0	30.0	2.0	0.0
β-WRS	45.0	30.0	14.0	0.0
ASTM F 1538-03	3000	50000	30000	5000

CONCLUSION

Wollastonite has been successfully synthesized from rice husk ash (RHA) and rice straw ash (RSA) using autoclaving via sol gel method. Single phase of β-wollastonite was obtained after 2 h of sintering for RHA and 3 h for RSA. The difference in sintering time between RHA and RSA was due to the silica content in them. Since RHA and RSA possess non-toxic property therefore, both of them can be used as alternative silica sources for synthesizing wollastonite.

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