Synthesis and Characterization of Silica Aerogel from Rice Husk with Ambient Pressure Drying Method

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Abstract. Rice husk has become global concern due to the environmental problem since it has been dumped and open burned that contributed to the emissions of carbon dioxide to the atmosphere. Therefore, utilization of rice husk to other useable product such as silica aerogel for adsorption has been studied recently due to the silica content in rice husk is about 60% and this material is sustainable and cost effective. Silica aerogel was prepared from rice husk ash and dried by using ambient pressure drying method with addition of tetraethyl orthosilicate (TEOS) due to its capability to prevent the gel from crack and increase the porosity of gel to increase the capacity of adsorption process. The silica aerogel was further characterized by using Fourier Transform Infrared spectroscopy (FTIR), Elemental Analyzer (EA) and Scanning Electron Microscopic (SEM). The results show that the silica aerogel was successfully synthesized using rice husk ash. The FTIR studies reveal that silica aerogel produced consist of amorphous silica with Si-O-Si bonding and stretching’s. From EA analysis, the carbon in the rice husk decreasing when turned into silica aerogel due to the burning of carbon content in the preparation of silica. The SEM studies confirm that the silica aerogel has a porous structure and has ability to be for the application as adsorption process such as carbon dioxide adsorption, methylene blue adsorption and others application.

1. Introduction
Rice husk has become as a global concern due to the abundantly produced over the year. Rice husk existence cannot be questioned as it acts as natural shield that will cover the paddy grains during their growing process until harvesting period and the farmers will use milling process to collect the rice but discard the husk as it does have commercial value. In Malaysia, a total of 2.7 million tons of rice has been produced in 2016 and all of the agricultural waste is either sent to the landfill or undergoes open burning [1]. Most of the farmers prefer to use the most conventional method which is open burning as it have been used in almost all of the paddy plantation areas not only in Malaysia but also in every country that producing rice in order to reduce the waste easily. 
Open burning will release large amount of carbon dioxide to the atmosphere [2]. However, constant burning of rice husk everyday will cause infinite amount of carbon dioxide is trapped in the stratosphere layer and resulting to depletion of ozone layer and lead to the environmental problem [3].
Based on the study by Matawal & Maton[3], the smog phenomenon will cause a respiratory problems as the air is polluted and people with asthma attack will easily triggered and without fast action, it will increase the possibility of death due to depletion of oxygen besides irritation problems, development of lung disease or skin cancer [4].

Therefore, many research is focus on the utilization of the rice husk into valuable product such as silica due to its high silica content up to 60% [5]. The most economical method that will be proposed is to make silica aerogels from rice husk ash because silica aerogel is categorized as good adsorbent due to its properties in which it has capability to adsorb carbon dioxide in the atmosphere. However, most people are unfamiliar with silica aerogel since it is not widely introduced yet. In fact, silica aerogel has added value in terms of properties. Firstly, due to properties of nano-porous solid which is smaller in size if compared to the wavelength of visible light, thus when the colloidal particles forming a group and then decomposed to form a structure, more than 96% of the liquid component in the silica aerogel been replaced with gas. These properties also resulting to formation of silica aerogel with super low density, low specific area and low thermal conductivity, low refractive index and transparency and better sorption properties [6].

Aerogel with unique frozen-smoke shape somehow is a fragile expanded polystyrene that is sensitive to touch and it is crucial to be extra vigilant when handle it to avoid destruction on the precious shaped-gel. Although there is slightly difference in chemical composition rice husk as it affected by the type of paddy used, climatic and geographical conditions [7] but rice husk still be used as one of the raw material in the production of silica aerogel because it have quality in terms of properties mainly due to its high resistance towards fungal diseases, have anti-corrosion properties of steel, aluminium and copper, low water and moisture permeability, low bulk density which is approximately less than 150 kg/m³, and also low volume of equilibrium moisture content that is below 10% at air relative humidity of 60% [8]. Cellulose, hemicellulose and lignin are the major components information of rice husk and when it is burn at moderate temperature, the ash content is rich in silica which is about 90-98% with the remaining are metallic impurities [9].

Aerogel can be produced by using organic or inorganic precursors with various method and the most suitable method is to synthesis the silica aerogel from tetraethyl orthosilicate (TEOS) and by using ambient pressure drying. Firstly, according to the study by Tadjarodi et al., [10], TEOS can act as a precursor in production of silica aerogel as it produce better result in terms of strength compared to the production of silica aerogel in the presence of water only that will act as the pore fluid since TEOS have the capability to maintain their structural integrity by preventing the gel from crack besides TEOS increasing the porosity for trapping more carbon dioxide. It will also improve the physical property of silica aerogel such as having a better colour which is white-transparent and finally resulting to the lower down of bulk density [10].

Synthesis of silica aerogel use ambient pressure drying (APD) technique is more cost-effective compared to supercritical drying method that is more expensive and carcinogenic as the chemical will disport the superior physiochemical characteristic after surface modification complete. Huge amount of energy is also used for this method and somehow it risky and dangerous since high voltage is required. APD somehow help to increase the strength of gel network, causing surface modification and solvent exchange on the wet gel. APD have the capability to eliminate the capillary stress formed during synthesis of silica aerogel. Due to liquid- vapour interface, the wet gel will become dry due to the liquid evaporation to the surrounding and thus lead to capillary tension. In the meantime, compressive stress on the solid network will balance the tension and cause the shrinkage of gel [11].

Therefore, this study is focus to synthesis and characterize silica aerogel from rice using TEOS as precursor with ambient pressure drying method.

2. Methodology
The materials used for this study are rice husk ash, deionized water, sodium hydroxide in aqueous solution [NaOH], sulphuric acid [H₂SO₄], Tetraethyl Orthosilicate [Si (OC₂H₅)₄] and ethanol [C₂H₅OH].
For sample preparation, the rice husk (RH) were grinded by using grinder and sieved with a siever that have sizing pores of 500 and 250 micrometre. Then, RH was burned in the furnace according to the sequences by using three different temperatures which are 400°C, 600°C and 850°C and each of them will be burn for 5 hours. The same procedure were applied for RHA but with different temperature which are 400°C, 600°C and 750°C to observe the effects for different temperature of burning [12].

For synthesis of silica aerogel, 150 ml of 1.0 mol/L of Sodium hydroxide in aqueous solution [NaOH] was mixed with 5 grams of Rice Husk Ash (RHA) sample. The mixture was heated and continuously stirred by using stirrer at temperature of 90°C for about 2 hour [13]. Then, the mixture was filtered to remove undissolved residues. In order to form silica hydrosol, the filtrate is neutralized with 1 mol/L of H₂SO₄ to pH 7. A small amount of TEOS were added into the hydrosol before the gelation of the hydrosol and the quantity of doped TEOS are taken according to volume ratio (1/10) to hydrosol. The prepared gel was aged for 24 hours at room temperature.

In order to remove sodium sulphate obtained from the neutralization staged, 4 hours were allocating for each gel to be soaked in water before washed by using deionized water and this process need to be repeated three times for complete removal. Then, the water was replaced with ethanol in which the silica gel firstly being soaked into 20% of ethanol solution for 24 hours at 50°C before soaked again for second time by using 70% of ethanol at 70°C for 24 hours [14]. Finally, the silica aerogel could be obtained from the wet gel by drying at ambient temperature for 1hour successively at 120°C and being weighed after the process of drying was completed. Drying and weighing process were repeated for several times until a constant weight was achieved [10].

After the silica aerogel was synthesis, a series of analysis was performed using Fourier Transform Infra-Red Spectroscopy (FTIR), Elemental Analyzer (EA) and Scanning Electron Microscopy (SEM). For FTIR analysis, the samples were analyzed by using FTIR VERTEX 70 from Bruker in the range of temperature from -30°C to 44°C. Heating and cooling rates were varied at different stages of the experiment. The samples were registered in the range from 500 to 4000 cm⁻¹ with a resolution of 1 cm⁻¹ using KBr pellet. Each of the sample was taken as an average of 128 scans in order to increase the signal to noise ratio [15]. The function of this characterization method was to identify the functional group on the silica aerogel and its composite [16].

Elemental analyzer was performed on a Perkin Elmer 2100 Series II CNH/S (carbon, nitrogen, hydrogen and sulphur) analyzer. The temperature of combustion and reduction were set at 925°C and 640°C respectively. In order to analyze the samples, it was prior to keep the samples dried at 100°C under vacuum for 12 hours before being kept under vacuum condition at room temperature. All of the samples yielded negligibly small values of ≤0.12 wt. %. The weight percentages of oxygen were calculated from the difference between the total mass and the mass of carbon and hydrogen. All of the samples were analyzed in triplicate and the average values have been recorded. The instrument accuracy specification is ±0.3 % based upon a triplicate analysis [17]. The ultimate purpose of this characterization was to determine the amount content of Carbon, Nitrogen, Hydrogen and Sulphur in silica aerogel [18].

The internal microstructure of the silica aerogel micro particles was studied by scanning electron microscopy (SEM, JEOL). Before the micrographs were taken, the dried silica powders were sputtered with a gold layer.

3. Results and Discussion

From FTIR analysis, cellulose, hemicellulose and lignin are main components that contained in RH that are rich in OH bonds besides C-H stretching vibrations, hemicellullosic sub-fractions and C-O-C stretching for glucose rings that can be determined at FTIR bands less than 3000cm⁻¹ which starts at range of 1700-1740 cm⁻¹ and 900-1100 cm⁻¹. Figure 1 shows there is a broad absorption bands at the peak of 3348.27 cm⁻¹ which indicates presence of cellulose that contain OH stretching vibration bonds while peak at 1633.63 cm⁻¹ represents C=O symmetric stretching of alkene group shows existence of lignin structure in the rice husk. The strong absorption peak at 1031.87 cm⁻¹ indicates formation of Si-
O-Si as an asymmetric and symmetric stretching band which is one of the obligatory compound that contain in rice husk [19].

The carbonization of rice husk at 400°C and 600°C shares the same value at the first peak at 2925.88 cm\(^{-1}\) but different value at second peak which is at 2852.59 cm\(^{-1}\) for 400°C and 2854.52 cm\(^{-1}\) for 600°C. These peaks attest that there are strong H-C-H asymmetric and symmetric stretching vibrations. An asymmetric and symmetric stretching of N=O occur in between 1602.77 cm\(^{-1}\) and 1373.25 cm\(^{-1}\) during burning rice husk at 400°C and future burning lead to formation of new absorption peak at 1463.90 cm\(^{-1}\) indicates more formation of silica during burning of rice husk ash at 600°C. Increases of temperature has increases the asymmetric and symmetric stretching band and cause the band to shift slightly resulting in decrease on absorption peak value from 1083.94 cm\(^{-1}\) to 1068.5 cm\(^{-1}\) and due to the tighten of bond because most of the SiO\(_2\) compound has turned to Si-O-Si functional group respectively via condensation of Si-OH. The absorption peaks formed at 784.99 cm\(^{-1}\) and 804.28 cm\(^{-1}\) during carbonization of 400°C and 600°C rice husk ash shows the remaining of SiO\(_2\) compound present.

![Figure 1. FTIR Spectra of SiO\(_2\) obtained from Raw Rice Husk and via burning at 400°C and 600°C.](image)

The FTIR Spectrum of TEOS-based silica aerogel was shown in Figure 2. The symmetric stretching vibration of Si-O-Si is higher at 750°C compared to the temperature of 850°C. However, it has the opposite result in terms of peak as silica aerogel at 850°C have higher peak than 750°C at 1078.16 cm\(^{-1}\). This indicates silica aerogel at 850°C is better than silica aerogel at 750°C in terms of silica network that uses oxygen as bridges between two silicon sites. Low energy band is further shown by silica aerogel at peak of 775.35 cm\(^{-1}\) compared to peak of 813.92 cm\(^{-1}\) regarding bending of Si-O-Si bonds. Overall, the pattern of the graph for silica aerogel at 750°C and 850°C is almost the same and only the stretching vibration of Si-O-Si is quite different. However, the potential of silica aerogel at 750°C and 850°C to adsorb pollutant such as carbon dioxide gases cannot be determined through this study because it is done only to observe the character of each silica aerogel. Therefore, further study need to be done in order to determine which silica aerogel have better adsorption capacity to be the best adsorbent.

Elemental analyser was performed on raw rice husk as shown in Table 1. This analysis used to identify the compound present in the sample [20]. The function of elemental analyser is to detect the presence of Carbon, Hydrogen, Nitrogen, and Sulphur. Based on Table 1, the elemental analysis in raw rice husk are 37.93% C, 6.19% H, 1.27% N, compared to the previous study in [21], the elemental analysis of the rice husk showed 34.33% C, 4.98% H, 0.38% N. Based on the comparison, there is
only slight difference between elements Table 1 and the previous study since the results obtained were within the ranges.

![Figure 2. FTIR Spectra of Silica Aerogel.](image)

Based on Table 1 and 2, the percentage of Carbon in the rice husk is decreasing. This is because the Carbon has turned into silica due to combustion. In Table 2, the Carbon percentage of rice husk ash at 400°C is 33.8% while in the rice husk ash at 600°C was only 0.2%. This significant reduction of carbon content was due to the temperature effect of burning processes. Then, the hydrogen and nitrogen percentage of rice husk ash at 400°C is higher than 600°C as shown in Table 2 where the hydrogen percentage of rice husk ash at 400°C is 1.38% while hydrogen percentage of rice husk ash at 600°C is only 0.36%. The nitrogen percentage of rice husk ash at 400 °C is 1.34% while at 600 °C only 0.03%.

Based on Table 3, the elemental analysis in silica aerogel at 750 °C is 0.29% C and 1.7% H while the elemental analysis in silica aerogel at 800 °C is 0.33% C and 0.95% H. Compared to the previous study in [22], the elemental analysis of the silica aerogel A and B are 12.91% C with 2.97% H and 0.89% C with 0.23% H respectively. Based on this comparison, only the amount of Carbon has a big difference between silica aerogel A and others three aerogels. This may due to different range of temperature of rice husk used for combustion process of rice husk ash to form a silica aerogel. For hydrogen, the amount for four aerogels is on their range and do not have a very large differences.

| Sample                      | Results Carbon (%) | Hydrogen (%) | Nitrogen (%) |
|-----------------------------|--------------------|--------------|--------------|
| Raw Rice Husk               | 37.93              | 6.19         | 1.27         |

| Sample                        | Results Carbon (%) | Hydrogen (%) | Nitrogen (%) |
|-------------------------------|--------------------|--------------|--------------|
| Rice Husk Ash (400 °C)       | 33.8               | 1.38         | 1.34         |
| Rice Husk Ash (600 °C)       | 0.2                | 0.36         | 0.03         |

Table 1. EA of Raw Rice Husk.

Table 2. The EA of Rice Husk Ash at Two Different Temperatures.
Table 3. The EA of Silica Aerogel at Two Different Temperatures.

| Sample               | Results |                |                |
|----------------------|---------|----------------|----------------|
|                     | Carbon (%) | Hydrogen (%)   |                |
| Silica Aerogel (750 °C) | 0.29    | 1.7            |                |
| Silica Aerogel (800 °C) | 0.33    | 0.95           |                |

Figure 3 shows the morphology of raw rice husk and silica aerogel form at temperature 750°C and 850°C. Figure 3 (a) shows that the surface of raw rice husk possesses bulgy tissue in the shape of rectangle [23]. Figure 3 (b) shows the silica aerogel has been formed with irregular-shaped morphology with nanosize particles. These particle is homogenous and agglomerate indicate that parts of micropores exist between silica grains [24]. Figure 3(b) shows the silica aerogel consist of large pores indicate that the silica forms have increase the sample’s porosity [25]. According to the above observation, the silica aerogel forms has increase the porosity when increasing the temperature of burning of silica aerogel.

Figure 3. SEM micrographs of a) raw rice husk b) silica aerogel at temperature 750°C c) silica aerogel at temperature 850°C.

4. Conclusion
Silica aerogel formed from rice husk ash with addition of TEOS and dried by using ambient pressure drying method were characterized using FTIR, EA and SEM. The overall result of FTIR spectrum shows that the intensity of the absorption bands and the wavelength of rice husk was altered as the
temperature increases. These alterations can be clearly identified at the peak of 1031.87 cm\(^{-1}\), 1083.94 cm\(^{-1}\), 1068.51 cm\(^{-1}\), 1066.59 cm\(^{-1}\) and 1078.16 cm\(^{-1}\). The silica aerogel obtained which is light white solid will be better than rice husk ash only since there is no presence of water in both silica aerogels at temperature 750°C and 850°C and it may have the possibility to have greater surface area for absorption of carbon dioxide. For EA characterization, the results prove that silica aerogel can be synthesized by using rice husk ash by drying at ambient pressure. This is due to the reading of percentage of elemental analysis such as Carbon, Hydrogen and Nitrogen obtained are on their ranged which was 37.93% C, 6.19% H, 1.27% N when compared with other silica aerogel obtained from other research findings. For SEM characterization, the silica aerogel porosity has increase with increasing temperature of burning in preparation of the aerogel. The SEM image shows that silica aerogel is porous silica and have uneven distribution of pore in the structure.

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