

# Effects Of Calcination Temperature On The Structure And CO<sub>2</sub> Sorption Properties Of Li<sub>4</sub>SiO<sub>4</sub> Sorbents From Rice Husk Ash

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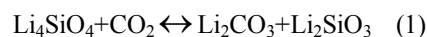
**Abstract**—Highly efficient Li<sub>4</sub>SiO<sub>4</sub>-based sorbents for CO<sub>2</sub> capture at high temperature, were developed using waste rice husk ash (RHA). Two different RHAS resulted from different calcination temperature as raw materials for preparing the Li<sub>4</sub>SiO<sub>4</sub>-based sorbents. These raw ashes and their resulting Li<sub>4</sub>SiO<sub>4</sub>-based sorbents were characterized by X-ray diffraction, thermogravimetry (dynamic and isothermally), and nitrogen adsorption. CO<sub>2</sub> sorption stability was investigated in a dual fixed-bed reactor. The characteristic results showed that high calcination temperature could lead to crystalline silica, which may produce the lower crystalline size, higher porosity and larger surface area as compared with the case of low temperature. This favourable structure appeared to be the main reason for increasing in CO<sub>2</sub> capture performance and kinetic behavior as illustrated by the thermogravimetric analyses. This pretreatment Li<sub>4</sub>SiO<sub>4</sub>-based sorbent also maintained a higher capacity during the multiple cycles. It was concluded that the synthesis of Li<sub>4</sub>SiO<sub>4</sub>-based sorbents obtained from biomass ash is a promising approach for CO<sub>2</sub> capture at high temperature.

**Keywords**-CO<sub>2</sub>; rice husk ash; calcination temperature; Li<sub>4</sub>SiO<sub>4</sub>; sorption

## I. INTRODUCTION

The increasing concentration of CO<sub>2</sub> in the atmosphere, mostly resulting from fossil fuel burning, is a dominant contributor to the greenhouse effect which leads to climate change and global warming [1]. High temperature CO<sub>2</sub> capture technologies based on the direct separation of CO<sub>2</sub> from the high-temperature flue gas were desirable to decrease the concentration of CO<sub>2</sub> in the atmosphere. Various high-temperature absorbents such as hydrotalcites (HTLs) [2], calcium oxides [3], and lithium ceramics [4] have been proposed to capture CO<sub>2</sub>. Among them, lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) received further attention because of excellent performance in absorption rate, sequestration capacity, cyclic stability, wide application temperature

range, and good mechanical strength properties. In this case, several authors reported the CO<sub>2</sub> capture in this material through the following reaction:



The high reactivity of Li<sub>4</sub>SiO<sub>4</sub>-based sorbents is extremely important for their widespread application in CO<sub>2</sub> scrubbing processes. Various synthesis strategies such as solid-state reactions, impregnated suspension, sol-gel method, and precipitation were considered to synthesize Li<sub>4</sub>SiO<sub>4</sub> sorbents. Meanwhile, the sources of Si including quartz, amorphous silica (SiO<sub>2</sub>), tetraethyl orthosilicate (TEOS), and the precursors of Li involving Li<sub>2</sub>CO<sub>3</sub>, LiOH·H<sub>2</sub>O, LiNO<sub>3</sub>, and CH<sub>3</sub>COOLi were also examined. It was also demonstrated that the CO<sub>2</sub> capture performance could be improved by introducing appropriate dopants into the Li<sub>4</sub>SiO<sub>4</sub> crystal structure. On the other hand, more and more researchers attempted to use wasted silicon materials for preparing Li<sub>4</sub>SiO<sub>4</sub>-based sorbents, which could be a cost-effective and eco-friendly route [5]. Olivares-Mari'n et al. [6] synthesized Li<sub>4</sub>SiO<sub>4</sub>-based sorbents from fly ash for CO<sub>2</sub> capture at high temperature. Shan et al. [7] prepared Li<sub>4</sub>SiO<sub>4</sub>-based sorbents from diatomite with fast CO<sub>2</sub> absorption rate. We [8] developed the Li<sub>4</sub>SiO<sub>4</sub>-based sorbents from rice husk ash (RHA), which presented an increased kinetic behaviors compared with pure Li<sub>4</sub>SiO<sub>4</sub>. It was also reported that the calcination temperature had a great effect on the crystallinity of RHA [9], which may in turn determine the performance of Li<sub>4</sub>SiO<sub>4</sub> sorbents. However, the details of the calcination temperature on the sorption behaviors of Li<sub>4</sub>SiO<sub>4</sub> sorbents from RHA were still uncovered.

Therefore, in this work, two kinds of original RHAs based on different calcination temperature were selected as raw materials to prepare higher performance of Li<sub>4</sub>SiO<sub>4</sub> for CO<sub>2</sub> capture at high temperatures. Specifically, the

crystallinity of characteristics of raw materials and their performance in CO<sub>2</sub> capture were investigated comparatively.

## II. EXPERIMENTAL

Rice husk was burnt at a temperature of 600 °C or 1000 °C for over 1 h in a muffle furnace, which were designed as 600RHA and 1000RHA, respectively. Then Li<sub>4</sub>SiO<sub>4</sub>-based sorbents from RHAs were prepared by using the solid-state reaction of Li<sub>2</sub>CO<sub>3</sub> (99.5%) with RHAs in a Li:Si mixture with molar ratio of 4.1:1. The powders were all calcined at 800 °C for 4 h. Powders derived from 600RHA and 1000RHA were denoted as Li-600RHA and Li-1000RHA, respectively. A fraction of all synthesized sorbents with particle size less than 100 μm was collected for characterization.

The X-ray diffraction patterns (Panalytical B.V., Almelo, the Netherlands) using Cu-Kα radiation were collected to characterize the crystal structure of the sorbent. The scans were recorded in the 2θ range between 10 and 90°. CO<sub>2</sub> absorption was resolved by a thermogravimetric analyzer (TGA, TA Q600). About 10 mg of the sorbent was placed into the crucible, and then heated from room temperature to 1000 °C at a heating rate of 5 °C/min with 50 ml/min of the 100 vol. % CO<sub>2</sub> flow. Furthermore, CO<sub>2</sub> absorption isotherms of the sorbents were tested in 100 vol. % CO<sub>2</sub> at 650 °C for 2.0 h to observe sorption/desorption properties of the sorbents dynamically. The surface area and pore size distribution of the sorbents was quantified by N<sub>2</sub> adsorption/ desorption isotherms using a TriStar 3020 volumetric adsorption analyzer.

The twin fixed bed reactor system was designed to examine the working cyclic capacity of these sorbents through 15 CO<sub>2</sub> sorption/desorption cycles. This particular reactor system was composed of an adsorption reactor and a desorption reactor designed at atmospheric pressure. An inert sample boat could be shifted between the two reactors, meanwhile, the flow of the reacting gas was also adjusted using a mass flow-meter. The temperature was remained at 680 °C in 100% CO<sub>2</sub> for absorption within 15 min and maintained at 800 °C in 100% N<sub>2</sub> for desorption within 10 min. In addition, during the multiple cycles, the variation in sample mass was monitored using a delicate electronic balance with a weight range.

## III. RESULTS AND DISCUSSION

### A. XRD Characterization of starting materials

The chemical composition and XRD profiles of three kinds of biomass ashes are given in TABLE 1 and Fig .1, respectively. It was shown that major component of SiO<sub>2</sub> with small amounts of trace elements, such as potassium, sodium, calcium, magnesium and aluminum were present in both materials. Some metal impurities of Na and K elements were reported to have a eutectic reaction with SiO<sub>2</sub> during combustion of rice husks, which changed amorphous silica to a crystalline structure. [10]. These metal impurities were also sublimated at high temperature (>700 °C). Due to calcination at a lower temperature, as shown in Fig .1, 600RHA only presented a broad peak appearing around (2θ=22°), which clearly composing mainly of an amorphous silica. Conversely, subjected to a higher temperature, alkali metals (K<sub>2</sub>O and Na<sub>2</sub>O) were

decreased some because alkali metals were lost during thermal treatments (1000 °C), while the amount of SiO<sub>2</sub> was increased in 1000RHA (Table 1). XRD results further suggested that this ash not only consisted of amorphous silica but also presented the peaks of quartz.

TABLE I. CHEMICAL COMPONENTS (WT. %).

Sample	K <sub>2</sub> O	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>	other
600RHA	2.997	0.099	0.419	1.243	0.612	91.40	1.555
1000RHA	1.656	0.085	0.349	1.130	0.447	92.50	1.007

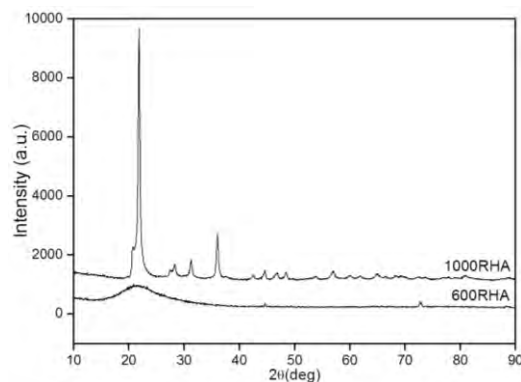


Figure 1. XRD patterns of two kinds of rice husk ashes.

### B. XRD Characterization of sorbents

After the Li<sub>4</sub>SiO<sub>4</sub> sorbents synthesis, both samples were characterized XRD. In both cases, the XRD patterns (Fig .2) showed only the characteristic XRD peaks of Li<sub>4</sub>SiO<sub>4</sub> (JCPDS 37-1472) while the peaks of the starting materials were not visible indicating that both compounds reacted completely, at least at the XRD detection limits. Previous studies suggested that lithium has a very small dispersion diffraction coefficient in comparison to the doping elements and the closed packed structure of the silicate. Therefore, the doping elements did not expect to diffuse so much into the Li<sub>4</sub>SiO<sub>4</sub> network. Similar to Li<sub>4-x</sub>Na<sub>x</sub>SiO<sub>4</sub>, the unchanged of the peaks observed here seemed to indicate that most of metal impurities were mainly located over the surface of Li<sub>4</sub>SiO<sub>4</sub>. Moreover, according to the intensities obtained in both case, the sample prepared from 1000RHA presented smaller crystalline size than that derived from the 600RHA. This result is similar to Seggiani's findings [11], who demonstrated that the used silica source had an important impact on the structure of the resulting Li<sub>4</sub>SiO<sub>4</sub> sorbents.

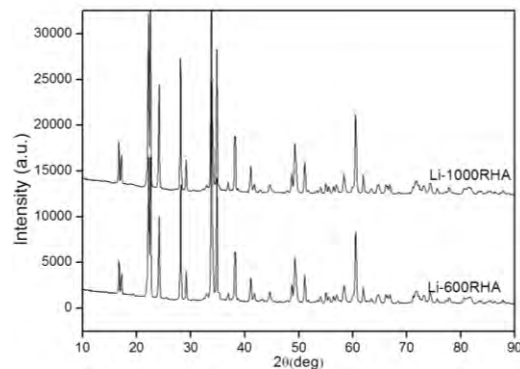


Figure 2. XRD patterns of two kinds of Li<sub>4</sub>SiO<sub>4</sub> sorbents.

### C. N<sub>2</sub> absorption Characterization

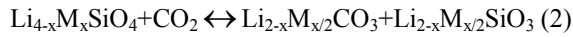
The surface area analysis (Fig. 3) performed on the sorbents confirmed the characteristic differences observed by XRD. According to the IUPAC classification, both samples exhibited isotherms of type III with a very narrow H3 type hysteresis loop. This observation suggested that both samples were composed of aggregates of nonporous materials or macroporous materials. Meanwhile, the surface areas measured for Li-600RHA was small, indicating the presence of large particles with nonporous dense morphology. Comparatively, Li-1000RHA displayed higher surface areas than those of Li-600RHA. Moreover, Li-1000RHA presented a higher porosity structure. This larger surface areas as well as higher pore volume correspond to the presence of porous agglomerates. These results mentioned above indicated that the high calcination temperature may be more suitable for preparing lithium based ceramics.

TABLE II. PROPERTIES OBTAINED FROM Li<sub>4</sub>SiO<sub>4</sub> SORBENTS.

Sample	Surface Area(m <sup>2</sup> /g)	Pore Volume(cm <sup>3</sup> /g)	k <sub>1</sub>	k <sub>2</sub>	R <sup>2</sup>
Li-600RHA	5.53	0.0031	0.58	0.05	0.98
Li-1000RHA	6.81	0.0042	0.63	0.09	0.96

### D. TG Characterization

As was previously mentioned, Li<sub>4</sub>SiO<sub>4</sub> is a promising CO<sub>2</sub> absorbent material. Moreover, enhancing CO<sub>2</sub> absorption on lithium ceramics by addition of potassium or sodium has been reported for other ceramics. If Li<sub>4</sub>SiO<sub>4</sub>-based RHA sorbents present a synergetic effect, these sorbents should capture CO<sub>2</sub> more efficiently than pure Li<sub>4</sub>SiO<sub>4</sub> with a reaction represented as follows:



where M denotes potassium and sodium, Li<sub>2-x</sub>M<sub>x/2</sub>CO<sub>3</sub> represents only a mixture of Li<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>.

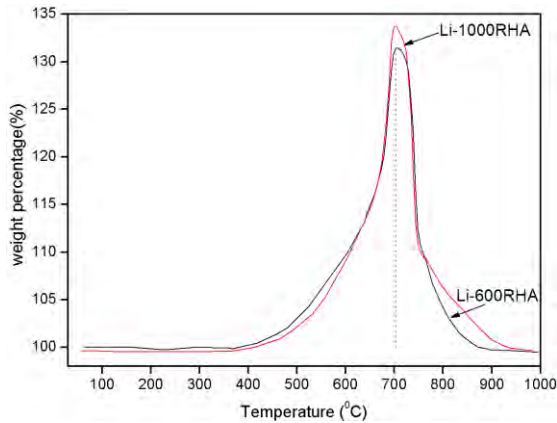


Figure 3. Thermogravimetric analyses of Li<sub>4</sub>SiO<sub>4</sub> sorbents.

The TG curves of both Li<sub>4</sub>SiO<sub>4</sub> sorbents are illustrated in Fig. 3. The curves appeared to display similar absorption behavior. They all began to absorb CO<sub>2</sub> at around 450 °C and finish this process at 700 °C. Later, at temperature higher than 700 °C, the sample presented a desorption process. The maximum CO<sub>2</sub> absorption was for Li-600RHA was equal to 30.3 wt % owing to its high

amounts of Li<sub>4</sub>SiO<sub>4</sub>. Especially Li-1000RHA even obtained with 33.6 wt % maximum absorption, which corresponded to 91.6% efficiency. This higher capacity of Li<sub>4</sub>SiO<sub>4</sub> sorbents were also observed using sodium orthosilicates [12] and RHA-Li<sub>4</sub>SiO<sub>4</sub> sorbent [8].

The isothermal studies were investigated at 650 °C to further confirm their sorption behaviors. As shown in Fig. 4, there are two different processes taking place: First, CO<sub>2</sub> reacts with the lithium present on the surface of the Li<sub>4</sub>SiO<sub>4</sub> particles producing a Li<sub>2</sub>CO<sub>3</sub> external shield; Later, once the external layer of lithium carbonate is totally produced, a diffusion process begins, where lithium has to diffuse throughout the carbonate layer in order to reach the surface and react with the CO<sub>2</sub>. These results revealed that the lithium diffusion is the limiting step in the absorption process. Moreover, compared with Li-600RHA, the absorption seemed to be and higher and faster in Li-1000RHA due to the higher peak and higher slope observed on the sorption temperature range. This increased behavior in the kinetic reaction could be attributed to the decreased crystalline size of sorbents resulted from the quartz component. These distinct results highlighted that the different calcination temperature resulted in different crystalline size of RHAs and Li<sub>4</sub>SiO<sub>4</sub> sorbents, which led to different sorption behaviors.

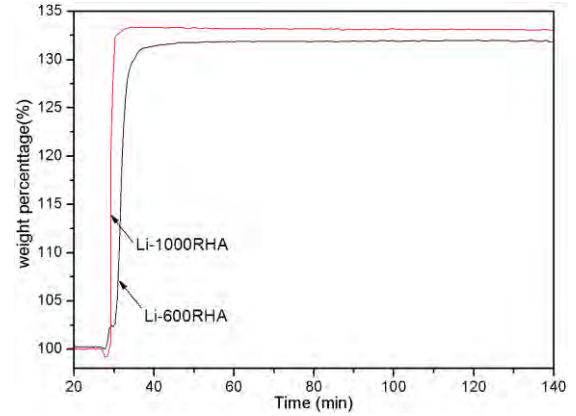


Figure 4. Isotherms of the CO<sub>2</sub> sorption on Li<sub>4</sub>SiO<sub>4</sub> sorbents.

A double exponential model was successfully used to simulate the CO<sub>2</sub> absorption on lithium-based sorbents such as Li<sub>4</sub>SiO<sub>4</sub> [18], Li<sub>4-x</sub>Na<sub>x</sub>SiO<sub>4</sub> [21], and Li<sub>5</sub>AlO<sub>4</sub> [14]. This model can be represented as:

$$y = A \exp(-k_1 t) + B \exp(-k_2 t) + C \quad (3)$$

where  $y$  represents the weight change of CO<sub>2</sub> absorbent,  $t$  is the time,  $k_1$  and  $k_2$  are the rate constants for the CO<sub>2</sub> chemisorption produced directly over the Li<sub>4</sub>SiO<sub>4</sub> particles and CO<sub>2</sub> chemisorption kinetically controlled by lithium diffusion, respectively. In addition, the pre-exponential factors  $A$  and  $B$  indicate the intervals at which each process controls the whole CO<sub>2</sub> capture process, and the  $C$  constant indicates the  $y$ -intercept.

The exponential constant values obtained from both sorbents are presented in TABLE II.  $k_1$  values are at least 1 order of magnitude higher than those of  $k_2$ , revealing that the lithium diffusion is the limiting step in the absorption process. These results are in agreement with previous reports. The kinetic constant values of Li-1000RHA were higher than those obtained for the Li-600RHA sample.

Both chemisorption and diffusion constant values were enhanced, which is in agreement with previous reports on pure  $\text{Li}_4\text{SiO}_4$  and sodium orthosilicates. This increased behavior in the kinetic reaction could be attributed to the special morphology of the Li-1000RHA: the decreased crystalline size, higher porosity and larger surface area. The larger specific surface area formed was associated with the presence of more lithium atoms over the surface of the particle formed. On the other hand, the presence of smaller crystalline size was allowed to reduce  $\text{CO}_2$  diffusion resistance to the solid shell. Thus, Li-1000RHA improved the kinetics of  $\text{CO}_2$  adsorption.

#### E. Multicycle properties

The stability of a sorbent is crucial when applied to the separation of  $\text{CO}_2$  from fuel fired power stations at high temperatures. The working cyclic capacity, stability, and lifetime of the sorbents can be determined and the results are presented in Fig. 5. The flow was switched to 100 vol. %  $\text{CO}_2$  and the temperature was maintained at 680 °C for 15 min (absorption step). After that, the flow was switched to 100%  $\text{N}_2$  and the temperature was raised to 800 °C with heating rate of 10 °C /min and maintained at 800 °C for 10 min (desorption step). At the end of the first regeneration, no weight loss was observed for both samples. Then, after the first cycle, their  $\text{CO}_2$  absorption capacity and capture-regeneration behavior remained essentially constant during the subsequent cycles, implying an excellent stability. Moreover, the cyclic results displayed higher  $\text{CO}_2$  multicycle properties of 1000RHA. These results suggested that the used samples still exhibited loose and porous. Therefore,  $\text{CO}_2$  can diffuse easily into the interior of the sorbent during the sorption process.

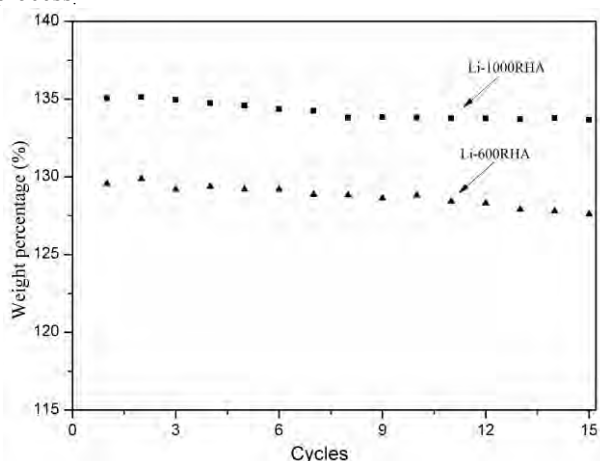


Figure 5. Multiple cycles of  $\text{CO}_2$  sorption (15 min) and desorption (10 min) on  $\text{Li}_4\text{SiO}_4$  sorbents.

#### IV. CONCLUSION

The effects of calcination temperature on the sorption behaviors of  $\text{Li}_4\text{SiO}_4$  sorbents from RHA were examined. XRF, XRD results indicated that the different calcination temperature could lead to different crystalline size of RHAs. This morphological difference of raw material had a significant effect on the phase composition its resulting sorbent. The sorption analysis conformed the characterization data and revealed that Li-1000RHA with the decreased crystalline size, higher porosity and larger

surface area experienced a more rapid absorption-desorption process with higher absorption efficiency. Isothermal analyses also indicated that the sorbents adjust to the same  $\text{CO}_2$  sorption mechanism: a chemical sorption process followed by a lithium diffusion process. Kinetic analyses further implied that the kinetics values of Li-1000RHA obtained for the chemisorption process and diffusion process was larger than that of Li-600RHA. Moreover, Li-1000RHA could maintain higher absorption capacities during multiple adsorption/desorption cycles, showing that this sorbent may be a new option for  $\text{CO}_2$  absorption at high temperature.

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