PREPARATION OF CaO-BASED PELLET USING RICE HUSK ASH VIA GRANULATION METHOD FOR POTENTIAL CO₂ CAPTURE

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ABSTRACT: CO₂ capturing has become very significant option to reduce the emission of CO₂ in the atmosphere and hence, minimizing environmental issues. Among solid CO₂ sorbent, calcium oxide (CaO) is an attractive regenerable sorbent for CO₂ capturing because of their reactivity and high CO₂ absorption capacity. CaO alone suffers from rapid decay of CO₂ adsorption during multiple carbonation/calcination reaction cycles. The stability of CaO sorbents during cyclic runs can be achieved via the incorporation of additive support materials. The silica (SiO₂) from natural sources such as rice husk is the best candidate to be used as an additive in the sorbents. However, the CaO-based sorbent in finely generated powders are prone to severe attrition problems. Therefore, this research focuses on preparation of CaO-based pellets by using rice husk ash (RHA) via granulation method. The result of the raw materials confirmed that Ca(OH)₂ have crystalline structure with finely distributed grains and RHA exhibit amorphous structure with randomly oriented size grains. Based on the XRD, it is confirmed that the insertion of RHA does not alter the phase structure of the pellets. Each ratio yield different intensity value and has formation of new peaks after sintering. Meanwhile, the microstructures of the pellets show that the pores reduced as the calcination temperature increased while the incorporation of RHA caused the pores size increased with randomly oriented shape. These findings indicate that the optimum value for the pellets is with the Ca(OH)₂:RHA ratio of 80:20 and calcination temperature of 750 °C.

KEYWORDS: CO₂ capture; CaO-based pellets; RHA; Granulation method.
1. INTRODUCTION

In Malaysia, the main contribution of CO$_2$ emission is from the energy sectors such as fossil fuels, natural gas, and coal power plants. The energy sectors in Malaysia contributed at about approximately 36% of the total global CO$_2$ emissions in 2004 and among all of the greenhouse gases, CO$_2$ gases responsible for 60% of greenhouse effect that cause the global warming [1]. Moreover, Malaysia plans to reduce the amount of CO$_2$ release by 25% reduction from all sectors and this is according to Green Technology Master Plan 2017-2030 proposed by Malaysia government [2]. Thus, planning and solution must be done in order to control and resolve the problems of CO$_2$ emissions and greenhouse gases effect.

One of the solutions to reduce the CO$_2$ gases emitted to the atmosphere is by introducing the carbon capture and storage (CCS) technology. This technology captures up to 90% of CO$_2$ which led to significant reduction of CO$_2$ level in atmosphere [3]. Among the CO$_2$ capture methods, CO$_2$ capture by adsorption into a sorbent is the most common technique used in the industry due to its better thermal properties and high amount of CO$_2$ adsorption [4]. The adsorbent materials are usually made from ceramic materials such as CaO, MgO, and ZrO$_2$. It is well known that ceramic materials possess better thermal properties, and these materials will be acceptable to be used in the elevated temperature condition.

However, the limitation of the recent CO$_2$ adsorbent materials is that it has low stability and reduction in reactivity in cyclic operation. Recent studies show that other additives such as SiO$_2$, MgO, and Al$_2$O$_3$ reinforced into the sorbents can improve the cycle loop of the CO$_2$ adsorption [4]. Improvement of the CO$_2$ adsorption is done by designing the CO$_2$ capture technologies in the form of pellets rather than sorbents itself and the introduction of biomass resources with the pellets is one of the advantages upon using waste and eco green materials [5]. Thus, this paper aims to study the effect of cycling loops with the pellets design when introducing other additives into the sorbents. Plus, the utilization of waste materials such as rice husk ash introduced into the pellets will be a huge impact on the economic and environmental factor.

There are many methods and techniques have been done on previous study to produce CaO-based sorbents with the addition of SiO$_2$ including, sol-gel, wet impregnation, bio-template via infiltration, mixing and extrusion-spheronization methods. Among all the methods mentioned above, three of the methods utilizing biomass materials, mainly from the rice husks to act as the additives inside the CaO-based sorbents while the other two methods (sol-gel and wet impregnation) used silica sources from synthetic means. Rice husk ash used as the precursor in the CaO-SiO$_2$ sorbent due to the high content of silica. Plus, the sources of rice husk are abundant and easy to obtain as it is being produced as the by-product in paddy field makes it the best candidate to be used in the CaO-based sorbent.

Different parameters used in the preparation of the CaO-SiO$_2$ sorbent play a crucial role in determining the performance of the pellet. There are several parameters needed for the investigation and different parameters usually will give different effects on the pellet whether it will improve the performance or becoming unfavourable. One of them is amount of silica sources incorporated with the CaO-based sorbents or the ratio amount between those two materials. Previous studies showed that different ratio or amount of silica added exhibits different cyclic adsorption performance. In one study, ratio of 3:7 RHA/CaO shown better stability over 50 cycles compared to 1:9 RHA/CaO even though 1:9 RHA/CaO has better carbonation conversion in early cycles [6]. Meanwhile, in the other study, 10%, 20%, 30%, 40% and 50% of RHA added into the CaO-based sorbent. Initially, the ratio of 20% RHA express the highest CO$_2$ adsorption compare to other ratios but it reduces significantly started
at the first cycle. Then, it is observed that 40% and 50% RHA into the CaO sorbent maintained the highest CO₂ capture over the nine cycles [7].

The main objective of this paper is to prepare CaO-based pellet with addition of RHA as the sacrificial bio-template through granulation method. The pellets were prepared according to two different ratios and undergo calcination process at 750°C. The effect of RHA addition and calcination at 750°C on the properties of CaO-based pellets were examined through the phase structure and morphological characteristics.

2. EXPERIMENTAL

2.1. Materials

Calcium hydroxide from R&M Chemical Sdn. Bhd. was selected as the calcium precursor. The rice husk ash (RHA) as the biotemplate material was obtained from MARDI Perlis.

2.2. Preparation of the RHA

Initially, RHA is oven-dried at 70°C overnight to eliminate moisture. Then, the fine powder of RHA is obtained by ball milling process at 200 rpm for 1 hour. Finally, the ball milled RHA was sieved at the size range of 50 µm to 90 µm.

2.3. Preparation of the Sorbent Pellets

Next, Ca(OH)₂ and RHA powders were weighed according to two different ratios as shown in Table 1. At first, the weighed materials were vigorously mixed in a granulator machine at 73 rpm speed for 10 minutes. Then, the mixture undergoes granulation process at the speed of 1700 rpm and simultaneously wetted by spraying 300 ml of deionized water. After the granulation process, the Ca(OH)₂-RHA pellet was obtained in spherical shape and randomly in size. Lastly, the CaO-SiO₂ pellets were obtained after calcination process in furnace at 750°C.

Table 1: Two different ratios of Ca(OH)₂ and RHA with different weight of each ratio

| Ratio of Ca(OH)₂ and RHA | Weight of Ca(OH)₂ (g) | Weight of RHA (g) |
|--------------------------|----------------------|------------------|
| 80:20                    | 800                  | 200              |
| 70:30                    | 700                  | 300              |

2.4 Characterization

2.4.1 X-Ray Diffraction (XRD)

The phase structure of Ca(OH)₂, RHA and the prepared CaO-SiO₂ pellets, before and after calcination at 750°C was examined by X-Ray Diffractometer (XRD) model BRUKER D2 PHASER.

2.4.2 Scanning Electron Microscopy (SEM)

The morphological characteristic of raw materials (Ca(OH)₂ and RHA) and the prepared CaO-SiO₂ pellets at different ratio, before and after calcination process was investigated by JSM-IT100 Scanning Electron Microscopy (SEM) machine manufactured by JEOL.
3. RESULTS AND DISCUSSION

3.1. Analysis on the Raw Materials

Fig. 1(a) and 1(b) show the XRD pattern of Ca(OH)$_2$ and RHA at different scale of intensity. Based on the Fig. 1(a), sharp peaks at $\theta = 18.1^\circ$, 29.45$^\circ$, 34.15$^\circ$, 47.25$^\circ$ and 50.85$^\circ$ proved the crystalline structure of Ca(OH)$_2$. Whereas Fig. 1(b) indicated broad peak, centered at about $\theta = 23^\circ$ which confirms the amorphous structure of RHA. It is common that silica contain in RHA has amorphous structure, and its transformation to crytalline structure will occur when temperature is increased beyond 700°C [9].

![XRD Pattern of Ca(OH)$_2$](image1)

Fig. 1. XRD pattern of a) Ca(OH)$_2$ and b) RHA.

Fig. 2 and 3 displayed the SEM micrographs of Ca(OH)$_2$ and RHA. It has been observed for Ca(OH)$_2$ that it consist of finely dispersed, small size particles. Under X5000 magnification (Fig. 2(c)), the morphology of Ca(OH)$_2$ revealed that the microstructure is in granular and agglomerated shape. While for RHA, the SEM images reveals the siliceous nature and with some porosity of the ashes. It was observed that RHA has agglomerated particles in various sizes and irregular structures.
3.2. Characterization of the Sorbent Pellets

3.2.1 Average Size of the Pellets

Fig. 4 (a) and (b) show the different ratio of CaO-SiO$_2$ pellets obtained from the granulation process. As shown in Fig. 4 (a) and (b), the average size of particles for 80:20 and 70:30 pellets are 3.0 mm and 4.5 mm respectively.

The utilization of high speed of granulator and optimum amount of deionized water added during the granulation process resulted in small size of pellets. A small size of pellets was desired as the smaller the pellets, the higher the surface area of the pellets to covered for potential CO$_2$ adsorption application. However, the significant difference in the average particles size among the two ratios is presumed to occur due to the different amount of RHA, as the SiO$_2$ source added in CaO-SiO$_2$ pellets. The smaller size of pellets is obtained when lower amount of RHA added. Table 2 summarized the details of granulation process and the resulted average particles size for each ratio before undergo calcination process at 750°C.
Table 2: Summary of the pellets obtained from two different ratios.

| Ratio of Ca(OH)$_2$ and RHA | Impeller and Chopper Speed (rpm) | Amount of Deionized Water (ml) | Average Size (mm) |
|-----------------------------|---------------------------------|-------------------------------|-------------------|
| 80:20                       | 73, 1700-1800                   | 300                           | 3.0               |
| 70:30                       | 73, 1700-1800                   | 300                           | 4.5               |

Fig. 5 shows that CaO-SiO$_2$ pellets after the calcination process at 750°C. As can be observed in Fig. 5, all pellets have significant reduction in the size of pellet which is much smaller compared to the one before the calcination. This is probably due to the elimination of moisture from the pellets and significant reduction/shrinkage in pellets size after the calcination indicates huge amount of moisture content in each pellets.

Fig. 5. Pellets after calcination of different ratio ;(a) 80:20 and (b) 70:30.

3.2.2 Different Ratio of CaO-SiO$_2$ Pellets Before Calcination

The phase structure of CaO-SiO$_2$ pellets for each ratio before the calcination process was characterized by XRD analysis, as displayed in Fig. 6 (a) and (b). The peak characteristics of Ca(OH)$_2$ and SiO$_2$ are detected in XRD pattern of all CaO-SiO$_2$ pellets. According to Fig. 6, it is evident that the main crystalline peaks of Ca(OH)$_2$ were detected at about $2\theta = 28.76^\circ$,
34.17°, 47.21° and 62.78°. However, the intensity for each peak was decreased with increasing amount of RHA added. Besides, the characteristics peak of silica also could be observed from the XRD pattern, however, the intensity of the peaks was very low due to its amorphous nature. The silica peak centered about 2θ = 23° was observed in both XRD spectras of pellets prepared.

![XRD spectras for different ratio of CaO-SiO\textsubscript{2} before calcination, (a) 80: 20 and (b) 70:30](image)

Fig. 6. XRD spectra for different ratio of CaO-SiO\textsubscript{2} before calcination, (a) 80: 20 and (b) 70:30

Different ratio of RHA addition in the CaO-SiO\textsubscript{2} pellets as the biomass sacrificial template did not disrupted the crystalline structure of the calcium precursor. This is proved by the almost similar XRD pattern obtained from the CaO-SiO\textsubscript{2} pellets with the XRD pattern of the raw Ca(OH)\textsubscript{2}. Besides, the detection of similar major diffraction peaks from XRD pattern of all pellets evidenced the incorporation of sacrificial biomass template materials did not modify the crystallinity of the pellets produced [8].

The SEM micrograph of the prepared CaO-SiO\textsubscript{2} pellets at different ratios were shown in Fig. 7 and 8. All the micrographs illustrated that addition of RHA had significantly altered the morphology of CaO-SiO\textsubscript{2} pellets prepared, according to the ratio. Based on Fig. 8, 80:20 pellet shows large and irregular grains size with random distribution. Meanwhile, 70:30 pellet exhibits randomly distributed, irregular, and smaller shape of microstructures. Some small needle-like or flake structure could be observed which indicates the presence of ash or biomass material inside the pellets that have been prepared. According to the micrographs obtained, increasing amount of RHA added caused the grains size to decrease significantly which lead to the development of irregular microstructures.
3.2.3 Effect of Different Ratio after 750 °C Calcination

The effect of calcination at 750°C on the phase structure of CaO-SiO₂ pellets prepared is shown in Fig. 9. Sharp peaks were detected from all of the XRD pattern obtained which confirmed the existance of crystalline phase. This is due to the formation of CaO after sintering at 750°C. The CaO peaks can be observed at $2\theta = 29.76^\circ, 33.02^\circ, 39.49^\circ, 47.56^\circ, 51.91^\circ$ and $54.58^\circ$.

However, there is significant difference in intensity of peak at $2\theta = 29.76^\circ$. The highest peak intensity was observed in 70:30 pellet followed by 80:20 pellet. Supposedly, if the amount of CaO is higher compared to the silicate, the significant increment in peak intensity of CaO should be obtained whereas the silicate peaks should remain unchanged [10]. But from the XRD pattern obtained, pellet with low amount of CaO (70:30 pellet specifically) possessed the highest peak of CaO. This is presumed to occur due to the calcination process at 750°C might have altered the phase structure of silica in RHA and thus modified the XRD pattern of all pellets.
Morphology of the calcined CaO-SiO$_2$ pellets for each ratio are shown in Fig. 10 and 11. After calcination at 750°C, the formation of pores was observed in micrographs acquired. For 80:20 pellet, grains with random sized have been developed after sintering at 750°C with the presence of needle-like structure. The presence of needle-like structure suggests formation of a new compound resulted from the calcination of CaO-RHA which mainly composed of Ca, Si and O elements [11]. As for 70:30 pellet, the morphology consists of randomly scattered grains which is small in size as shown in Fig. 11. 70:30 pellet has irregular pores structure but not as large as compared to the pore structure in 80:20 pellet. However, 80:20 pellet shows better porosity as the pores size were larger which caused an increased in porosity. Higher amount of well-structured pores were more preferred for CO$_2$ capture application; in which it would contribute to an excellent performance of CO$_2$ adsorption.
4. CONCLUSION

This study presented the CaO-based pellets with addition of RHA as the sacrificial bio-template had been successfully prepared via granulation method. The calcium precursor, Ca(OH)$_2$ has agglomerates and granular microstructures and RHA has an irregular and in definitive shape of microstructures. Based on the XRD analysis, the Ca(OH)$_2$ has crystalline structure, while RHA has amorphous structure. XRD analysis proved that the inclusion of RHA in the Ca(OH)$_2$ did not disrupted the crystalline structure of the samples and intensity of the peaks were reduced with increasing amount of RHA added. However, the calcination at 750°C has significantly modified the XRD pattern of all CaO-SiO$_2$ pellets. The sharp peaks indicated the development of crystalline CaO and different ratio has different peak intensity. The pellets with low amount of RHA has finer grain structure observed as for increased the amount of RHA caused the pores became agglomerate, increase in size and randomly distributed. To conclude, based from the characterization result it indicates that ratio 80:20 and calcination temperature of 750 °C were the optimum parameters to be used for the pellets production.

REFERENCES

[1] Rawshan AB, Kazi S, Sharifah Mastura SA, Mokhtar J. (2015) CO$_2$ emissions, energy consumption, economic and population growth in Malaysia. Renew. Sust. Energ. Rev., 41:594–601.
[2] Alifah Z. (2017). Malaysia to slash another 25% of CO$_2$ emission by 2030. Retrieved from: https://themalaysianreserve.com/2017/06/21/malaysia-slash-another-25-co2-emission-2030/
[3] Naeem MA, Armutlulu A, Kierzkowska A & Müller CR. (2017) Development of High-performance CaO-based CO$_2$ Sorbents Stabilized with Al$_2$O$_3$ or MgO. Energy Procedia, 114: 158–166.
[4] Zhang Z, Tohid NGB, Muftah HEN. (2018) Carbon Capture. Chapter 4.5, Exergetic, Energetic Environ. Dimensions, 997-1016.
[5] Wang J, Huang L, Yang R, Zhang Z, Wu J, Gao Y, Wang Q, O’Hare D, Zhong Z. (2014) Recent advances in solid sorbents for CO$_2$ capture and new development trends. Energy. Environ. Sci., 7:3478–3518.
[6] Monica BG, Jose, MV, Antonio P, Pedro ESJ, Luis APM. (2018) Low-cost Ca-based composites synthesized by biotemplate method for thermochemical energy storage of concentrated solar power. Appl. Energy, 210:108–116.

[7] Mustakimah M, Suzana Y, Armando TQ, Tetsuya K. (2018) Utilization of rice husk to enhance calcium oxide-based sorbent prepared from waste cockle shells for cyclic CO₂ capture in high-temperature condition. Environ. Sci. Pollut. Res., 26:33882-33896.

[8] Liu, W., An, H., Qin, C., Yin, J., Wang, G., Feng, B., Xu, M. (2012) Performance Enhancement of Calcium Oxide Sorbents for Cyclic CO₂ Capture: A Review. Energ. Fuels, 26:275-2767.

[9] María E, Vasilije M, Edward JA. (2016) Calcium looping sorbents for CO₂ capture. Appl. Energy, 180:722–742.

[10] Sanchez-Jimenez PE, Perez-Maqueda LA, & Valverde JM. (2014) Nanosilica supported CaO: a regenerable and mechanically hard CO₂ sorbent at Ca-looping conditions. Appl. Energy, 118:92-99.

[11] Li Y, Zhao C, Ren Q, Duan L, Chen H, Chen X. (2009) Effect of rice husk ash addition on CO₂ capture behavior of calcium-based sorbent during calcium looping cycle. Full Processing Technology, 90: 825-834.