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Synthesis of CaO-based Sorbent from Biomass for CO₂ Capture in Series of Calcination-carbonation Cycle

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Abstract

This paper described CO₂ capture performance of CaO-based sorbents which were derived from biomass mixture within 9 cycles of calcination-carbonation conducted in TGA. The study utilized commercial sorbent to configure the suitable calcination and carbonation condition as a reference to synthesis biomass-derived sorbent. Calcination was conducted at 850°C in pure N₂ atmosphere for 20 min while carbonation occurred at 800°C in pure CO₂ environment for 30 min. Cockle shells (CS) were utilized as the main precursor to synthesize CaO and its capture performance was enhanced by adding 20 wt.% biomass of rice husk (RH), empty fruit bunch (EFB) and palm kernel shell (PKS). Biomass addition to CS has increased CO₂ capture capacity of the derived sorbents. The highest CO₂ captured was obtained by fresh sorbent of CS with EFB which is 8% higher than non-mixed CS sorbent. However after regeneration, CS with CBA sorbent illustrated the highest capture capacity among all sorbents at every cycle. The derived CS with EFB sorbent also demonstrated the most cyclic-stable material due to minimum loss of CO₂ captured capacity. Overall, application of biomass-derived CaO-sorbent in a series of calcination-carbonation cycle is promising CO₂ capture development.

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Keywords: CaO-based sorbent; CO₂ sorption; cockle shell; rice husk; empty fruit bunch; coal bottom ash

1. Introduction

CaO-based material derived from biomass has been an effective substance in CO₂ sorption and separation activity [1]. The material is technically feasible, costly effective and advantageous to certain extent in capturing CO₂ [2]. CaO-

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based sorbent demonstrates CO₂ sorption and desorption process via carbonation and calcination cycle [3]. Carbonation is a highly exothermic reaction but with proper heat integration, this heat can be channelled for its endothermic sorbent regeneration step which is calcination [4]. Yu et al. [5] mentioned that CO₂ released due to regeneration step is meant to sent for sequestration or storage while Blamey et al. [6] and Ridha et al. [7] stated that the spent sorbent is proven to be suitable for cement industry. Fig. 1 demonstrated the process of CO₂ capture and sorbent generation via calcination-carbonation cycle of CaO-based sorbent. Broda et al. [8] mentioned that Ca-based sorbents through calcination and carbonation reaction has been an emerging CO₂ capture technique due to some limitation of current capture technology such as CO₂ scrubbing using amine-based solvent. Calcium looping system (CaL) is claimed to operate at 38% of the total cost operation using mono-ethanol amine (MEA) solvent to capture CO₂ [9].

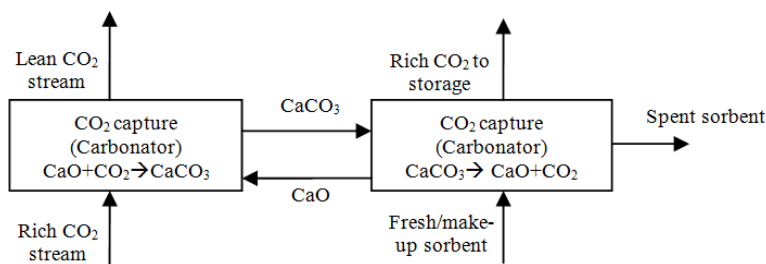


Fig. 1: Schematic diagram of CO₂ capture via calcination-carbonation cycle using CaO-based sorbent

Sorbents that been derived from biomass or natural sources has high initial CO₂ carrying capacity yet it experiences rapid loss in with increasing number of reaction cycles [4,7] and the materials are mechanically fragile which led to excessive sorbent loss [7]. Hence the challenges lie on improving its capture capacity along with reaction cycles. Improve the sorbent synthesis method and synthesized using mixture of oxide has been listed by Wang et al. [10] as the approaches to enhance CO₂ sorbent performance. In addition, wet mixing as synthesis method and thermal pre-treatment such as high calcination temperature (900°C) and hydration at 70°C are also described to improve sorbent cyclic stability [4].

Wang et al. [10] mentioned that CaO-based sorbent with silica support exhibits stable CaO conversion during reaction cycles. CaO-based sorbent with 10wt% silica reached stable conversion of more than 0.6 which was higher than the untreated sorbent. Increased of alkaline ions such silica and alumina has able to increase CO₂ capture reactivity [11] since it enhances cation–quadrupole interaction with CO₂ [12]. Alkaline earth metal atoms have high polarizabilities and dispersion potentials on the material surface [13].

Lee et al. [14] mentioned that pozzalonic reaction can occur when SiO₂ / Al₂O₃ is mixed with Ca(OH)₂/ CaO using alkaline water producing hydrate compounds which have high surface area and promotes CO₂ sorption. Biomass such as empty fruit bunch (EFB), rice husk (RH) and coal bottom ash (CBA) contained large portion of alumina and silica. Lee et al. [14] found coal ash to contain mainly silica (40-60wt.%) and alumina (15-20wt.%). Jayaranjan et al. [15] and EPRI [16] also recorded that coal ash to contain silica and alumina and yet it also composed of CaO which and lignite coal recorded the highest range of CaO composition which is within 8/6-45.1%.

This paper summarized the effect of calcination dwelling time and addition of biomass that contained SiO₂ and Al₂O₃ into CaO-based sorbent towards the sorbent capture capacity and cyclic stability.

Nomenclature

m_0	initial mass (mg)
m_t	current mass (mg)
m_f	final mass (mg)

2. Methodology

2.1. Material preparation

Cockle shell (CS), empty fruit bunches (EFB), rice husk (RH) and coal bottom ash (CBA) were cleaned by removing the dirt and foreign material. All of the biomass was grind into size of less than 0.125 mm before preparing for mixing. 20 wt.% to 80 wt.% ratio of biomass to CS was used to prepare a total weight of 5 mg raw material. Biomass and CS were mixed in 50 mL of distilled water while stirring for 2 h. Then the slurry was dried in the oven for 4 h at 200 °C. The dried powder was milled again using pestle and mortar to ensure uniform mixing and particle size.

2.2. Influence of calcination dwelling time

The influence of calcination dwelling time on CO₂ capture at various carbonation temperature was conducted as a reference condition to derive biomass sorbent and investigate carbonation temperature. Hence the analysis was performed using commercial CaCO₃ via demonstration in TGA (EXSTAR 6300). Calcination was conducted at 850 °C within two dwelling time which is 20 min and 30 min in pure N₂ environment at flow rate of 200 mL/min and heating rate of 10 °C/min. Derived sorbents were then tested for carbonation in pure CO₂ atmosphere flow rate of 50mL/min at five carbonation temperature within 400-800 °C using similar heating rate. CO₂ capture capacity and carbonation conversion of CaO-based sorbent was calculated using Eq. 1 and Eq. 2 respectively.

$$CO_2 \text{ capture capacity } (g_{CO_2} / g_{sorbent}) = \frac{\text{weight of captured } CO_2}{\text{weight of sorbent}} = \frac{m_f - m_o}{m_o} \quad (1)$$

$$\text{Carbonation conversion } (X) = \frac{\text{mol of reacted CaO}}{\text{mol of sorbent}} = \frac{(m_i - m_o)/44}{m_o/56} \quad (2)$$

2.3. Investigation on calcination-carbonation cycle of derived sorbent

Cycle of calcination-carbonation reaction was demonstrated by TGA using the biomass sorbents at configured calcination dwelling time and carbonation temperature of commercial CaCO₃ sample. The material was initially calcined at 850°C in pure N₂ atmosphere at flow rate of 200mL/min before reducing the temperature for carbonation in pure CO₂ environment at flow rate of 100mL/min for 30 min. Calcination and carbonation reaction was repeated for 9 cycles. The CO₂ capture capacity and carbonation conversion was recorded for all derived sorbents. Fig.2 illustrated the TG curve for calcination and carbonation reaction.

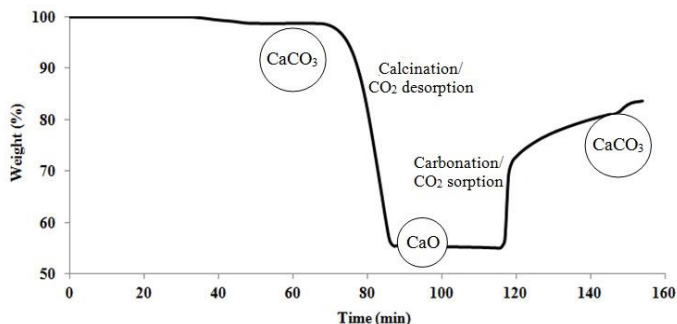


Fig.2: TG curve for calcination and carbonation reaction of metal carbonate material

3. Results and discussion

3.1. Effect of calcination dwelling time with respect to carbonation temperature

The influence of calcination dwelling time to synthesize CaO was determined to study its effect on CO₂ captured capacity. The dwelling time is important to ensure enough interval is provided towards the material to decompose and convert into CaO. However suitable holding temperature needs to determine prior studying its effect on the sorbent capacity. Commercial CaCO₃ was utilized as a reference to experience calcination at typical decompose temperature of metal carbonate which is within 850°C to 1000°C. This research study chose to run the calcination at minimum temperature which is 850°C. Hence Fig. 3 illustrated the decomposition behavior of commercial CaCO₃ at calcination temperature of 850°C in pure N₂ atmosphere. Weight loss signifies the conversion of CaCO₃ compound to CaO which rapidly occurred within temperature of 650 to 830°C. No significant weight loss was observed at temperature higher than 850°C and thus, the stated temperature was chosen as the holding temperature to study the effect of calcination dwelling time. The material experienced 44% weight loss and left with 56wt.% of converted CaO and the conversion was calculated as 0.56g_{CaO}/g_{CaCO₃}.

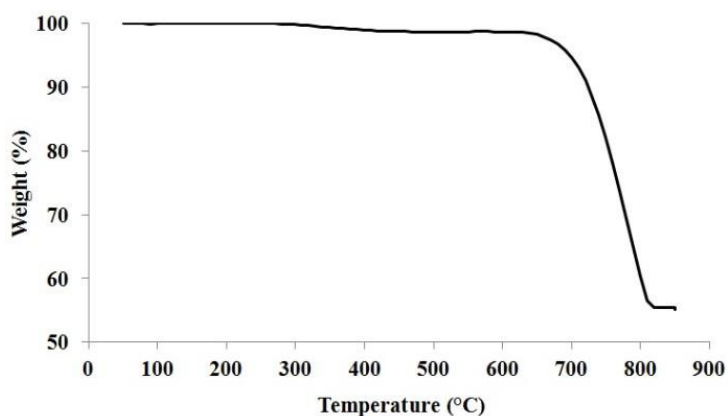


Fig.3: TG curve of commercial CaCO₃ due to calcination at 850°C in pure N₂ atmosphere

Fig. 4 summarized CO₂ capture capacity of CaO sorbent derived from commercial CaCO₃ at two calcination dwelling time. The results indicated sorbent capture capacity increased proportionally to carbonation temperature regardless the difference in calcination dwelling time. Sorbent with calcination dwelling time of 20 min recorded higher capture capacity compared to sorbent with 30 min calcination dwelling time. Longer calcination dwelling time able to promote severe sintering effect and enhance material decay hence reduced sorbent capture capacity and efficiency. Thus calcination dwelling time of 20 min was determined as the suitable condition to synthesis CaO based sorbent. Capture capacity was observed to be equal at both carbonation temperature of 700°C and 800°C which signified that capture capacity of derived sorbent was maximized at 700°C. However the influence of carbonation conversion should be considered to determine the suitable carbonation temperature.

Carbonation conversion for the derived CaO sorbent from commercial CaCO₃ was demonstrated in Fig. 5. Carbonation conversion behaviour indicated two significant regions of weight gain which signified CO₂ uptake by the sorbent. Lu et al. [1] described carbonation to experience two step reactions which are initial fast stage followed by slow stage. Fast stage is controlled by chemical reaction while the second stage is controlled by CO₂ diffusion within product layer. Thick product layer that build up on the free CaO surface introduce the limitation for rapid carbonation reaction [8].

Carbonation behaviour of derived sorbent in Fig. 5 signified that gas diffusion took major control during carbonation in pure CO₂ environment. Chemical reaction region able to sustain only 1 min for carbonation temperature of 400-600°C while 3 and 4 min for respective carbonation temperature of 700°C and 800°C. Derived sorbents

obtained equally high carbonation conversion at carbonation temperature of 700°C and 800°C. However CaO sorbent recorded higher carbonation conversion in chemical reaction control region at carbonation temperature of 800°C which was 0.77 compared in the same region for carbonation temperature of 700°C which was 0.63. Thus carbonation temperature of 800°C was determined as the referral carbonation temperature. In addition carbonation dwelling time of 30 minutes was observed to be enough intervals for complete carbonation conversion to occur at the selected carbonation temperature.

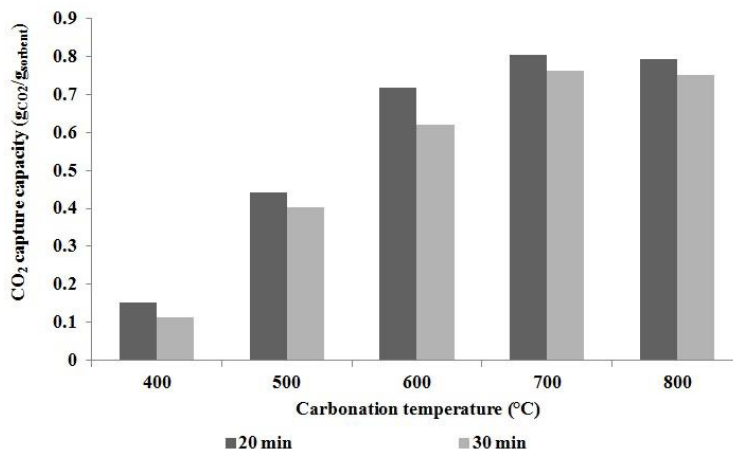


Fig. 4: Effect of calcination dwelling time towards CO₂ capture capacity at different carbonation temperature

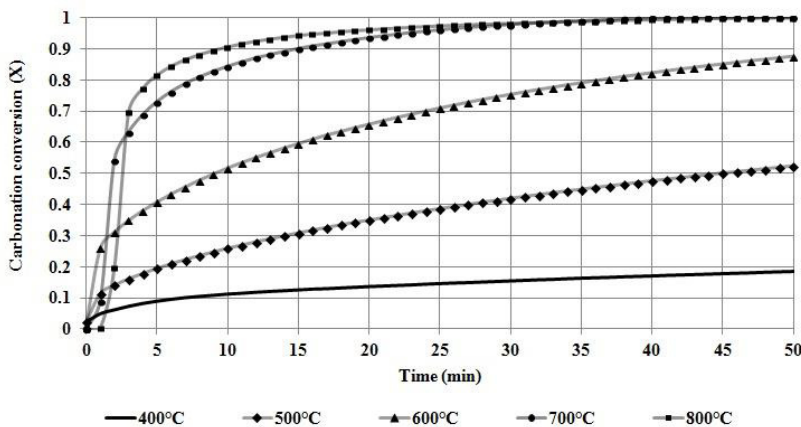


Fig. 5: Carbonation conversion of derived sorbent at dwelling time of 20 min for different carbonation temperature

3.2. CO₂ sorption of biomass-derived sorbent in calcination-carbonation cycle

CO₂ capture capacity for biomass-derived sorbents during calcination-carbonation cyclic reaction was summarized in Fig. 6. Fresh sorbent synthesized from CS with EFB demonstrated the highest CO₂ captured capacity which was 0.59 gCO₂/g_{sorbent} followed by CS with RH at 0.58 gCO₂/g_{sorbent}. Capture capacity of fresh sorbent derived from CS with

CBA was 23% lower than non-added CS. Fresh sorbent synthesized using CS with CBA recorded the lowest capture capacity among all CS-synthesized sorbent samples. The observation implied that addition of CBA into CS can reduce initial sorbent capture capacity of the fresh sorbent. However CS-with-CBA sorbent maintained the highest capture capacity among all of the sorbents during the third carbonation cycles onwards. All of the synthesized sorbents demonstrated almost equal capture capacity (0.60-0.65 $\text{g}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$) once the sorbents were regenerated for the second time.

Loss of CO_2 capture capacity was defined as the percentage difference in CO_2 capture capacity of current cycle with respect to previous cycle. The observation was summarized in Fig. 7 which indicated fresh sorbents experienced the biggest lost in capture capacity after sorbent regeneration. Sorbent synthesized using CS, CS with RH and CS with EFB loss their capture capacity within 28-33% during the first carbonation cycle. Sorbent derived from CS with CBA obtained the minimum loss of CO_2 capture throughout the cycles. This behavior indicates CBA addition into CS has able to increase the cyclic-stability of synthesized sorbent. Sorbent synthesized using CS, CS with RH and CS with EFB recorded loss in CO_2 capture capacity lower than 10% once reaching the fourth cycle onwards.

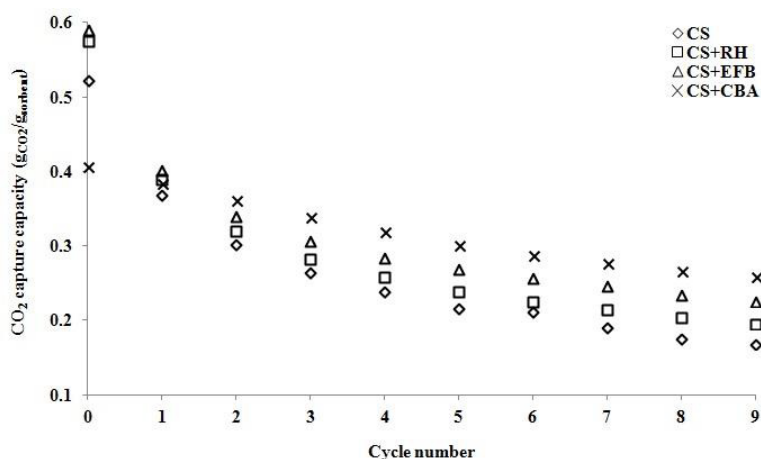


Fig. 6: CO_2 capture capacity of biomass-derived sorbent at carbonation temperature of 800°C in pure CO_2 atmosphere (50mL/min)

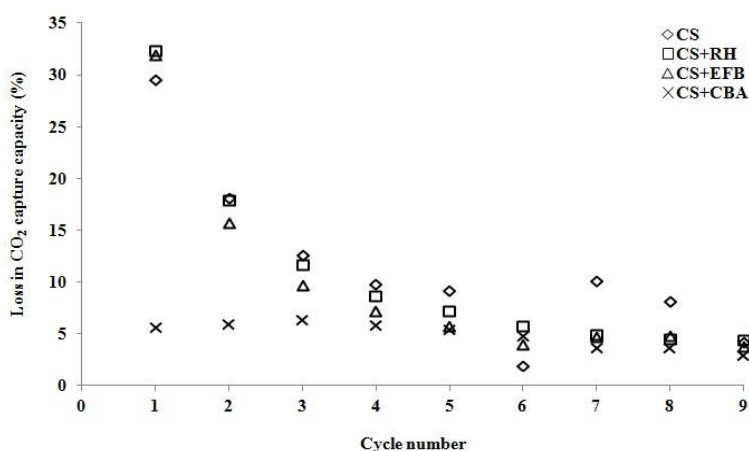


Fig. 7: Loss of CO_2 captures capacity of biomass-derived sorbent within 9 cycles of calcination-carbonation reaction in pure N_2 and pure CO_2 environment respectively

Fig. 8 demonstrated carbonation conversion of the biomass-derived CaO sorbent and found that CS-derived sorbent displayed the lowest carbonation conversion compared to sorbent synthesized from biomass mixture. Fresh sorbent synthesized from CS with EFB and RH displayed the highest carbonation conversion which is within 0.73-0.75. However its conversion dropped dramatically after regeneration to 0.50. Derived sorbent from all samples demonstrated almost similar carbonation conversion after fresh sorbents were regenerated which was within 0.45-0.50. However sorbent derived from mixture of CS with CBA recorded the highest carbonation conversion during second carbonation cycle onwards. CO₂ capture capacity and carbonation conversion for all sorbents, excluding CS-with-CBA sorbent, dropped to more than 60% during the eight cycles onwards. The performance of sorbent was inefficient and illustrated exhaustive behavior of the sorbents. It is economically-unfavorable to use the sorbent at this stage since large amount of energy required for sorbent regeneration yet the capture is low. Thus this study would like to suggest for the cyclic reaction using biomass-derived sorbent to run at maximum of eight cycles.

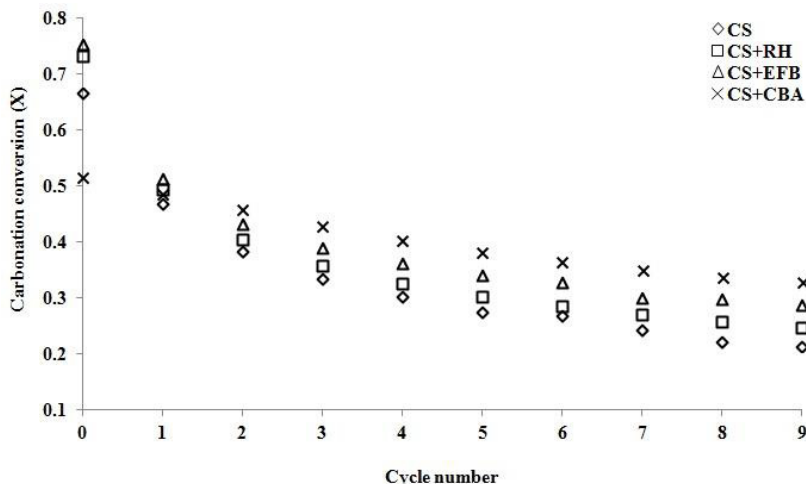


Fig. 8: Carbonation conversion of biomass-derived CaO-based sorbent for CO₂ sorption at 650°C in pure CO₂ environment for 9 cycles

4. Conclusion

Commercial-derived CaO sorbent it is confirmed that calcination at minimum temperature of 850°C is able to decompose CaCO₃ into CaO. Calcination dwelling time of 20 min yielded sorbent with higher capture capacity compared to sorbent that was synthesized for 30 min. Commercial-derived sorbent demonstrated higher capture capacity within chemical reaction control region at carbonation temperature of 800°C. Applying configured conditions of commercial-derived sorbent, CaO-based sorbent from biomass mixture was synthesized (calcined) at 850°C for 20 min and carbonation was conducted at 800°C. Mixing biomass which consists of silica and alumina into cockle shell increased the capture capacity and cyclic stability of CaO-derived sorbent. Fresh sorbent derived from mixture of CS and EFB recorded the highest capture capacity which is 8% higher than non-mixed CS and demonstrated as the most cyclic-stable sorbent. Mixture of CS and CBA has derived CaO-based sorbent that able to maintain the highest cyclic carbonation stability. Overall synthesis of CaO-based sorbent from biomass that is rich with carbonate, silica and alumina has demonstrated great potential in CO₂ capture and further studies on the influence of carbonation atmosphere is highly recommended.

Acknowledgements

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