Effect of Coal Bottom Ash and Binder Addition into CaO-based Sorbent on CO₂ Capture Performance

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CO₂ capture through series of calcination and carbonation cycle using natural solid CaO-based sorbent has been an emerging and promising technologies due to economic and environment advantages. However natural solid sorbent experiences rapid degradation in capture capacity as increasing reaction cycles. This paper described the derivation of CaO-based sorbent from cockle shell (CS) with the addition of coal bottom ash (CBA) and several type of binders as a mean to increase sorbent cyclic-stability. Cockle shell was mixed with coal bottom ash and binders at percentage weight ratio of 85:10:5 while the examined binders were aluminum pillared clay (Montmorillonite), magnesium oxide (MgO) and kaolinite. Series of calcination and carbonation was demonstrated via thermal-gravimetric analyzer (TGA EXSTAR 6300 Series). Calcination was performed at 850 °C in pure N₂ environment (100 mL/min) to synthesize CaO from the cockle shell while carbonation was conducted in pure CO₂ environment (50 mL/min) at 650 °C. The study found that CaO conversion of fresh sorbents was reduced by 15 % once CS was added with CBA and binders. CS with CBA and Montmorillonite displayed the highest CaO conversion during the second regeneration cycle onwards while the lowest conversion was observed from derived-sorbent of CS with CBA and MgO. Fresh sorbent of CS obtained the highest CO₂ capacity which was 0.52 g$_{CO2}$/g$_{sorbent}$ while the capture capacity of other fresh sorbents was within 0.46-0.49 g$_{CO2}$/g$_{sorbent}$. Derived sorbent from CS with CBA and Montmorillonite exhibited the highest capture capacity once it was reused at all reaction cycles. CS-free additive and CS with CBA and MgO illustrated the highest loss in CO₂ capture capacity within all cycles which indicate that suitable binders have increased the performance of the derived natural-sorbents.

1. Introduction

Due to the environmental impact of CO₂, carbon capture and sequestration (CCS) is becoming highly important step to ensure the world sustainability. Carbon dioxide adsorption is considered as an alternative technology for removal high concentration of CO₂ from gas streams due to its generally low energy requirement, ease of operation, and low maintenance (Saiwan et al., 2013). Nowadays, there are numerous porous materials have been used as CO₂ adsorbents with respect to their differences in advantages and drawbacks, such as activated carbon, zeolite, mesoporous silicates, and metal oxides (Kangwanwatana, et al., 2013).

Adsorbents that are made up of calcium oxide, CaO, has become effective substance to trap CO₂ due to high CO₂ capture capacity, abundantly available, low cost raw material, and easy to handle (Kumar and Saxena, 2014). It is environmental-safe towards hassle-free disposal, technology-ready for implementation using fluidized or fixed bed reactors. The spent sorbents of CaO can be reused for cement production and potentially applied for CO₂ removal in flue gases and hydrogen production (Ridha et al., 2013). Solid sorbents have potential to reduce energy demand of capture processes due to potentially higher loading capacities, absence of solvent heating and vaporization during regeneration, lower material heat capacities, and lower heats of sorption (Samanta et al., 2012). The CO₂ separation with solid sorbents has also become a promising technology that can be integrated with existing CO₂ emitting plants (Benedetti et al., 2015).

Waste shells are potential alternative material to capture GHGs such as CO₂, SO₂, NOₓ and other impurities. The shells such as mussel, oyster, clam, and cockle are made up of calcium carbonate (CaCO₃) which can be converted into CaO via calcination process (Castilho et al., 2013). However natural based solid sorbent face several limitation such as rapidly decreasing CO₂ capture capacity with number of repeated cycles (Skoufa et

al., 2016), generally week in structure (Zhang et al., 2015), sintering effect (Wang et al, 2014), filling and blockage of small pores and formation of product layer at outer walls (Broda et al., 2011). Hence numbers of modification studies are conducted to enhance the sorbents performance.

Coal bottom ash (CBA) is a part of the waste generated from coal fired power plant (CFPP) other than coal fly ash. CBA has lesser application and study found only 21 % of the waste was recycled in the industries (EPRI, 2015). However coal bottom ash is a potential sorbent candidate since it contained various kinds of metal oxides such as SiO_2, Al_2O_3 Fe_2O_3 and CaO (Asokbunyarat et al., 2015). Research on synthesizing activated carbon (Purnomo et al., 2011), silica (Liu et al., 2014), alumina and zeolite (Robledo-Muniz et al., 2010) has been extensively conducted using the coal ash due to various alkaline metals contained. These studies indicated addition of the ash has enhanced the sorbent performance.

A study observed general increased in CO_2 sorption capacity with increasing atomic radii for the alkali metals, such as Li<Na<K<Rb<Cs (Liang et al., 2004). Studies indicated Al_2O_3 as the best support matrix for K_2CO_3 sorbent in capturing CO_2 followed by activated carbon (AC), vermiculite and SiO_2 (Reddy and Smirniotis, 2004). Sub-bituminous and lignite type of coal contain higher calcium concentration compared to bituminous coal (EPRI, 2015). Concentration of CaO in sub-bituminous and lignite coal may reach to 15% and produce alkaline solution (pH 11-12) once reacted with water (EPRI, 2015). Carbonation generally occurs spontaneously once the ash is initially hydrated.

The CaO-based sorbent capture CO_2 via carbonation reaction which is denoted by Eq(1) and sorbent regeneration can be done via calcination which is the reverse of the stated equation. Both reactions are applied in industries as calcium looping (CaL) system which CO_2 rich streamed is fed to storage or sequestration (Antzara et al., 2014). CaL is a type of gas–solid adsorption processes which are promising technologies for carbon capture as an alternative to gas–liquid absorption due to low cost, high CO_2 capacity and fast carbonation/calcination kinetics (Broda et al., 2012). Zhang et al. (2015) mentioned CaL system employed 38 % of the total cost consumed by CO_2 amine-scrubbing system and associated with significantly small energy penalty than amine scrubbing. CO_2 captured via CaL system is applicable due to the established technology of fixed and fluidized bed reactors in the industries (Blamey et al., 2010).

$$CaO\ (s) + CO_2\ (g) \leftrightarrow CaCO_3 \tag{1}$$

Modification which are cost-effective, environmental-friendly and operational convenient are crucial aspects to synthesis a promising CO_2 sorbent. Addition of binder during sorbent development has improved the sorbent performance. Binder affects pore properties, material structure, thermal stability and mechanical strength of the sorbents. Zhang et al. (2015) used MgO as the binder of the sorbent materials and found the binder has enhanced structural ability of the sorbent. MgO acts as an inert dopant that impedes sintering process (Zhang et al., 2015). Wu (2007) also included clay as the binder to synthesize Ca(OH)$_2$-based sorbent and found the derived pallet sorbent has greater mechanical strength. Ridha et al. (2013) used cement as the binder to derive acetified limestone sorbent. Al_2O_3 in the cement reacts with CaO to form mayenite which stabilizes the structure and enhance sintering resistance. Antzara et al. (2014) applied sol-gel auto-combustion method and hydrated lime mixed with kaolin as binder. Kaolin composed of mainly Al_2O_3 and SiO_2 and its addition to CaO lattice leads to formation of mixed phase $Ca_3Al_2Si_2$. Antzara et al. (2014) observed that kaolin decreased the material surface area while MgO acts inversely which might attributed to high surface area of pure MgO. However the sorbent stability has significantly increased in the presence of binders (Antzara et al., 2014).

This paper described one of the approach to synthesize CaO-based sorbent from natural raw material by demonstrating the effect of adding coal bottom ash and binder into CaO-precursors on CO_2 capture capacity and cyclic stability.

2. Methodology

2.1 Material preparation

This study utilizes waste cockle shells (CS) from the type of blood cockle which was obtained from local stall while the coal bottom ash (CBA) was retrieved from nearby power plant TNB Janamanjung, Perak, Malaysia. The examined binders were purchased from Sigma-Aldrich aluminum pillared clay (Montmorillonite), magnesium oxide (MgO) and kaolinite.

Initially, CS and CBA were cleaned by removing the leftover foreign particles and later ground into fine powder (particle size less than 0.125 mm). CS was mixed with CBA and binders at percentage weight ratio of 85:10:5 in the deionized water at temperature of 70 °C while stirring for 4 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 and ready for calcination and carbonation analysis.

2.2 Investigation on calcination-carbonation cycle of derived sorbent

Cycle of calcination-carbonation reaction was demonstrated by TGA (EXSTAR 6300) using the biomass sorbents at configured calcination residence time and carbonation temperature of commercial $CaCO_3$ sample. The material was initially calcined at 850 °C in pure N_2 atmosphere at flow rate of 200 mL/min. Then the temperature was reduced to 650 °C and gas stream was switched to pure CO_2 flow at 50 mL/min for carbonation within 30 min. Calcination and carbonation reaction was repeated for 9 cycles. The CaO conversion, CO_2 capture capacity and average sorption decay of derived CaO-based sorbent was determined using Eq(2), Eq(3) and Eq(4).

$$CaO\ conversion, X_{CaO} = \frac{mol\ of\ decomposed\ sorbent}{mol\ of\ sorbent} = \frac{(m_i-m_f)/44}{m_i/100} \tag{2}$$

$$CO_2\ capture\ capacity \left(\frac{g_{CO2}}{g_{sorbent}}\right), CC = \frac{weight\ of\ captured\ CO_2}{weight\ of\ sorbent} = \frac{m_i-m_f}{m_i} \tag{3}$$

$$Average\ sorption\ decay \left(\frac{g_{CO2}}{cycle}\right) = \frac{total\ difference\ of\ capture\ capacity}{total\ cycle\ number} = \frac{CC_9-CC_0}{9} \tag{4}$$

3. Results and Discussion

CaO conversion of the raw material and CO_2 capture performance of derived sorbents is obtained based on TG analysis during calcination process and carbonation reaction respectively. Material decomposition during calcination is indicated by the sample weight loss which also signifies the CaO conversion. Figure 1 demonstrated TG curves for all of the fresh samples during calcination. No rapid weight loss was observed earlier than 600 °C indicated the samples are stable and contained insignificant volatile materials. Rapid decomposition occurred once temperature was nearing to 700 °C and reached plateau at temperature lower than 850 °C. Addition of CBA and binders into CS appeared to reduce the decomposed fraction by ~7wt. % although it maintained the calcination temperature regime of CS. This behavior signified CBA and binders have hindered CS decomposition and CBA and binders are thermally-stable materials. According to MSDS of OSHA (HHS, 1995) $CaCO_3$ is known to decompose and convert to CaO at temperature of 825 °C. Hence calcination temperature of 850 °C is a substantiate temperature for complete conversion of CaO contained in the samples. Figure 2 illustrates the overall TG curves obtained for calcination-carbonation cycles. Weight gained occurred during carbonation and the amount constantly decreasing with increasing number of cycles. The behavior indicated the sorbents managed to capture CO_2 once regenerated during calcination but capture performance of the derived sorbent was declined. Severe difference of weight change during carbonation was observed during once the fresh sorbent was recycled (0-1st cycle) and this behavior was similar for all samples. Castilho et al. (2013) mentioned that particle-swelling occurred during carbonation and promotes grain boundary migration. This occurrence initiated the sintering effect which aggravated once high temperature is introduced.
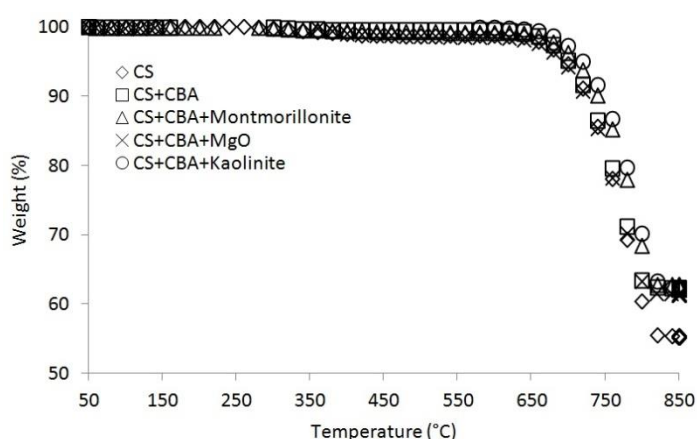

Figure 1: TG curves for fresh samples during calcination process in pure N_2 environment at 850 °C
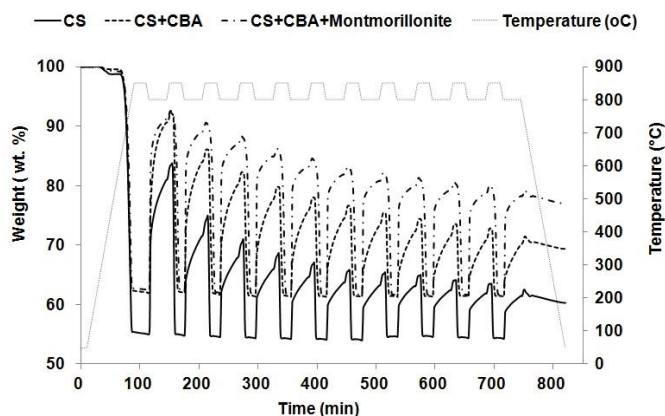
Figure 2: TG curves for three type of sample in series of calcination and carbonation cycles
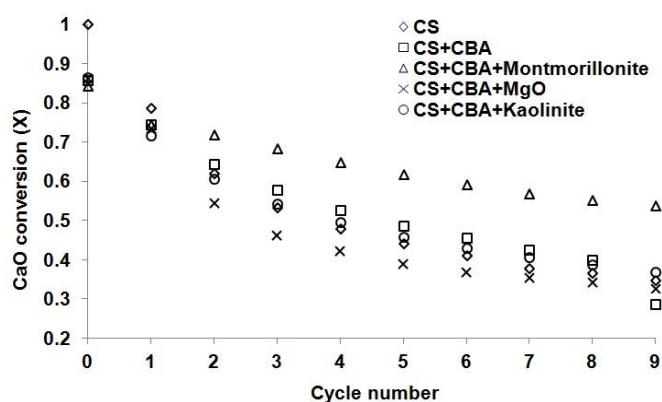

Figure 3: CaO conversion of derived sorbents due to calcination in pure N_2 environment at 850 °C

CaO conversion which is denoted as mol fraction of decomposed sample to sorbent is illustrated in Figure 3. Fresh CS sorbent experienced the highest conversion while the CBA-added fresh sorbents obtained 0.15-0.11 lesser conversion. CS maintained highest CaO conversion during first sorbent regeneration yet the conversion gap with other CBA-added sorbents had reduced by 0.1-0.4. CS with CBA and Montmorillonite recorded the highest CaO conversion at second regeneration cycle and maintained the highest conversion until the tenth cycle. Hence it indicated Montmorillonite as a favorable sorbent for the mixture. Inversely, adding MgO as the binder into the mixture was unable to improve CaO conversion of CS during repeated cycles of calcination-carbonation. The derived sorbents recorded the lowest CaO conversion as early as second cycle and continued towards the end. This observation suggested MgO could exaggerate pore blockage or alter the crystalline properties of synthesized CaO which lead to sorbent decay.

Figure 4 summarized the CO_2 capture capacity of the derived sorbents. Fresh sorbent of CS obtained the highest capture capacity which was 0.52 $g_{CO2}/g_{sorbent}$ compared to other sorbents that fall within 0.46-0.50 $g_{CO2}/g_{sorbent}$. However the sorbent capacity dropped by 30 % after being regenerated for the first time and as depicted in Figure 5 where additive-free sorbent (CS) experienced the largest loss among all sorbents for overall carbonation cycle. It verified that natural sorbent without additive in cyclic-capture system has low cyclic-stability and capture capacity.

Derived sorbent with Montmorillonite binder illustrated the highest capture capacity once the sorbent was regenerated for each cycle. The sorbent managed to maintain high capture capacity compared to other derived sorbents at each carbonation cycle. CS with CBA and Montmorillonite binder recorded the lowest CO_2 sorption decayed which was at average of 0.02 $g_{CO2}/g_{sorbent}$ within 9 cycles. Hence the sorbent demonstrated high cyclic-stability since it loss the capture capacity with respect to each cycles and was relatively low (<10 %) as recorded in Figure 5.

Inversely, MgO binder is unable to increase the capture capacity of derived sorbents at stated calcination and carbonation conditions. The derived sorbent of CS with CBA and MgO demonstrated capture capacity that was lower than CS-free additive once the sorbent was recycled. The stated sorbent also has high average decay in sorption capacity as illustrated in Figure 5. CBA and MgO are both materials with high thermal stability properties. Mixing both materials together might not be the best formulation for sorbent derivation in this study.
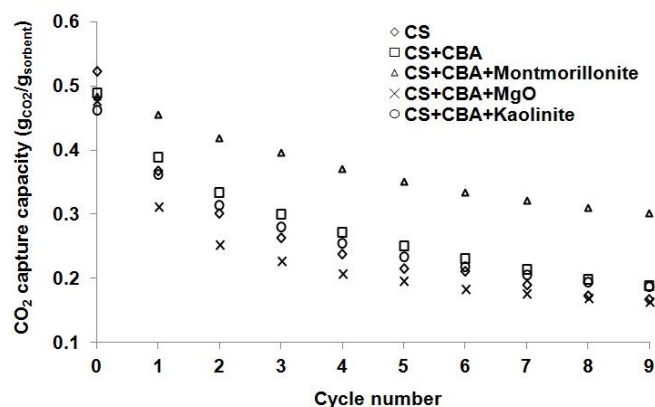

Figure 4: CO_2 capture capacity of derived sorbents during carbonation in pure CO_2 environment at 650 °C
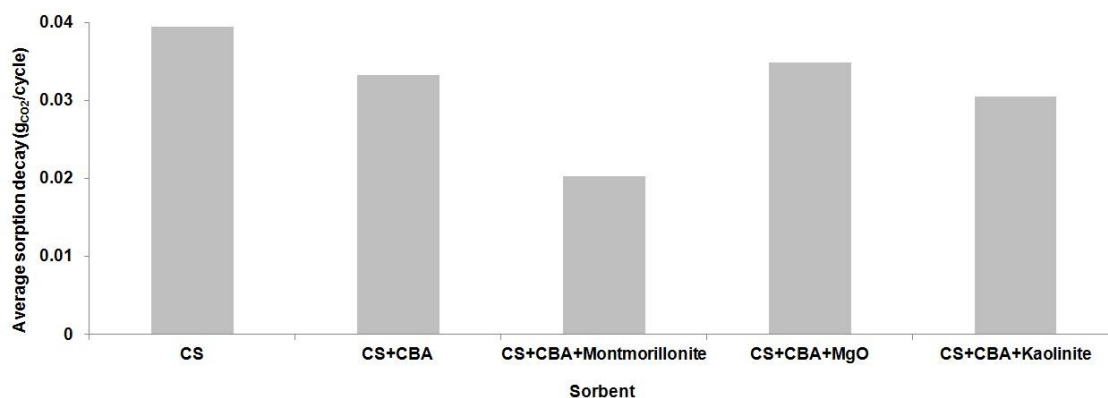

Figure 5: Loss in CO_2 capture capacity of derived sorbents during carbonation in pure CO_2 environment at 650 °C

4. Conclusions

All of the derived sorbents are thermally stable materials and able to capture CO_2 for several reaction cycles. Fresh sorbent of CS-free additive displayed the highest CaO conversion and CO_2 capture capacity but the performance decreased rapidly once it was regenerated for carbonation. Hence the fresh sorbent without any additive signified largest loss of its reactivity and cyclic stability. Adding CBA into the CaO precursor has increased the CaO conversion and CO_2 capture capacity of the derived sorbents. However, addition of binder is able to further increase the performance of derived sorbents during multiple cycles of calcination and carbonation reaction. Montmorillonite binder is the most favorable binder for CS with CBA while magnesia (MgO) binder is unable to improve the performance of the derived sorbents.

Acknowledgments

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