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Investigate the Ability of 1000 Micron CaO to Absorb CO_2 Gas through Absorption - Desorption Process for Biomass Producer Gas in Malaysia

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Abstract

Alternative source of energy such as biomass gasification can be used to generate power and electricity. Producer gas produced from biomass gasification consists of carbon monoxide (CO), hydrogen (H_2), methane (CH_4), carbon dioxide (CO_2) and nitrogen (N_2). It has low calorific value (LCV) around 4-6 MJ/Nm^3 because of CO_2 content is about 10-20 % by volume. Calcium oxide, CaO can be used to absorb carbon dioxide (CO_2) of the producer gas to increase its low calorific value. In this paper, an investigation of the 1000-micron CaO ability to absorb CO_2 has been made and studied. The absorption-desorption process of CaO was studied with the thermogravimetric analyzer (TGA) over 1, 4 and a muticycle. Three different temperature (500, 600 and 700°C) were set a variable. The reaction rate of CaO was obtained. Results show that for number 1 cycle the CO_2 absorption reaction rate was fast at first stage and then followed with slower reaction rate. About 0.337 and 0.065 mg/min CO_2 reaction rate were obtained in rapid and slow absorption regime respectively. It is also observed that the CO_2 absorption reaction rates decreases when number of cycle's desorption-absorption process was increased.

Keywords: CO_2 Capture; Calcium Oxide; Producer Gas; Limestone

Introduction

In Malaysia, producer gas which is gas produced from biomass materials can be classified as renewable energy. However, there are several factors why the producer gas cannot be fully utilized. The gas has low calorific value (LCV) around 4-6 MJ/Nm^3 because of CO_2 content is about 10-20 % by volume [1-4]. Removing CO_2 from the producer gas will inadvertently increase its heating value and improve the percentage of all combustible gas contents especially its hydrogen. Limestone or specifically calcium carbonate, $CaCO_3$ can be heated up to form calcium oxide, CaO where is used to absorb carbon dioxide (CO_2) of the producer gas to increase its low calorific value [5-7].

Recently, there are a few methods have been proposed for CO_2 capture. The methods for capturing CO_2 from flue gases are membrane separation, cryogenic fractionation and solvent absorption either physical or chemical sorption on solid surfaces [8-11]. However, these two methods such as membrane separation and cryogenic fractionation have not favored for CO_2 separation. Example membrane separation systems even though are highly efficient and have been employed for the separation of CO_2, but due to their complexity, high energy cost, and limited performance, membrane systems are not entirely well suited. As well as cryogenic fractionation systems, it also required high energy requirements.

Solvent absorption, on the other hand is well recognized. It is using various solvents, for instance, Selexol as a physical solvent or mono-ethanol amine (MEA) as a chemical solvent [12,13]. However, according to Rao et al. [14] severe energy penalties and the high cost of the system are significant disadvantages of the method especially on the use of amine. The low concentration of CO_2 in the flue gases at atmospheric pressure and low temperature (40 - 150°C) required for the absorption and solvent recovery process leading to the high cost of system.

The only one of the most promising method is based on the reversible absorption of CO_2 on specific metal oxides at high temperature. CO_2 capture using sorbents based on the oxides of calcium, potassium, lithium, sodium and magnesium have been reported [15-19]. The most have attention owing among these is calcium oxide (CaO) based sorbents because of their wide availability, low cost, higher absorption capacity and high selectivity for CO_2.

According to Chen et al. [20-23] precursors such limestone (also known as Calcium Carbonate, $CaCO_3$), dolomite, calcium acetate and calcium sulphate hemihydrate can be processed to derive CaO. Among these, the most common CaO precursors are limestone. This is because of the availability and low cost of limestone as mention. According to Zulasmin [24], Malaysia country is blessed with abundant reserve of limestone resources. Extensive limestone resources are located in the states of Perak, Pahang, Kelantan, Kedah and Negeri Sembilan. It was estimated over 10 billion tonnes of limestone resources throughout the country. Example in the state of Perak, there is a 0.0405 km^2 limestone quarry and it estimated limestone reserve of 4 million tones. With current monthly usage of 5000 tonnes per month, the quarry can provide raw limestone for the next 66 years [25]. Talking about the price of raw limestone, it is sold for only RM60 a tonne compared to processed and value-added limestone that can fetch around RM390 a tonne, according to Elan [26].

The reaction of solid CaO with CO_2 can be shown as in Equation 1 called absorption, and this is a spontaneous exothermic process at ambient conditions. At elevated temperatures, the reversed endothermic reaction called desorption (Equation 2) occurs.

$$CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad (1)$$

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad (2)$$
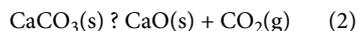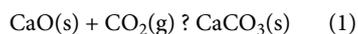
In theory the reactions in Equations 1 and 2 are fully reversible; thus, they can be appropriated to capture CO$_2$ from producer gas and upon desorption, CO$_2$ will be released. The cycle of desorption and absorption is repeated over and over. For such a process, two situations and temperatures are employed. Desorption is performed at higher temperature above 800°C and absorption at temperature below 800°C.

In this paper, an investigation of the CaO ability to absorb CO$_2$ has been made and studied. The absorption-desorption process of CaO was studied with the thermogravimetric analyzer (TGA) over 1, 4 and a multicycle. Three different temperature (500, 600 and 700°C) were set a variable. The reaction rate of CaO was obtained. The purpose of this work is to ensure the successful operation in CO$_2$ bubbling fluidized bed absorption reactor (CO$_2$ BFBAR).

Material and Methods

The operation of CO$_2$ absorption experiment is in the temperature range of 500 to 700°C under simulated gas (SG) conditions while desorption is performed under Nitrogen (N$_2$) gas conditions with temperature of 875°C. The SG used in absorption-desorption experiment contains 16% CO$_2$ and balance is N$_2$. For the first experiment, the system was run for 4 cycles using particle size of 1000 micron (**Figure 1**). Then, followed by 10 absorption-desorption cycles to know the ability of CO$_2$ absorption for multicycle condition using same particle size.

Absorption-desorption experiment was conducted using a Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA), a Perkin Elmer thermal analysis gas station (TAGS), and Pyris v 3.8 software from Perkin Elmer. TGA is performed by determining changes in weight of CaO material in relation to a temperature program in a controlled atmosphere. The effect of SG on the kinetics absorption of the gas-solid reaction between CO$_2$ and CaO is obtained from this experiment. The microbalance of the Pyris 1 TGA operates as a high gain electromechanical servo system which permits detection of weight change versus time as small as 0.1 µg. The TAGS have four gas channels and can automatically switch on either of them to introduce gas over the sample according to the reaction program. The shift between SG and N$_2$ gas with their flows was accurately maintained by the TAGS and the reaction program. **Figure 2** shows the TGA instrumentation used.
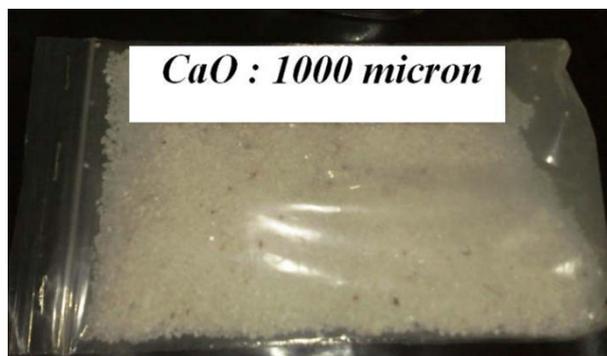

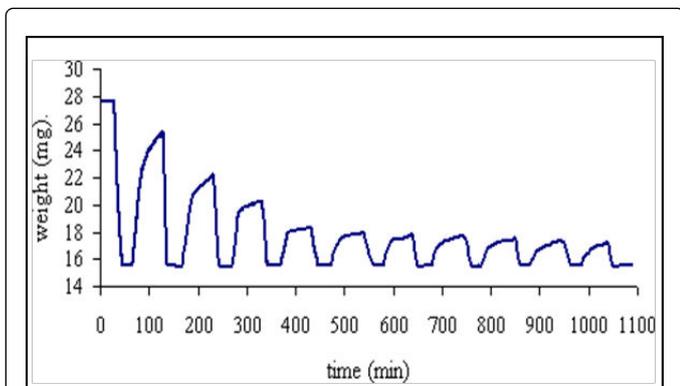**Figure 1:** Photograph of 1000 micron particle sizes of CaO.

Figure 2: TGA instrumentation.

All steps of the absorption and desorption experiments, including heating and cooling the CaO sample, and shifting gases between SG (16% CO2 + balance N2) and 99.9% N2 were programmed. A 29 mg 1000-micron CaCO$_3$ powder was placed in a platinum pan and heated from 100°C to the desorption temperature, 875°C at a heating rate of 25°C/min. Once the sample reached the desorption temperature, the program was automatically switched to isothermal (constant temperature) process for 20 min. Desorption time was set as 20 min to allow CaCO$_3$ to be converted into CaO completely. The time was intentionally kept that short to prevent possible sintering effect of sorbents. The CaO sample then was cooled to the absorption temperature, 500°C at a rate of 25°C/min. For all these processes, N$_2$ gas was used. The program was automatically switched to absorption process for 60 min in order to get relatively high uptake capacity of CO$_2$. After that, immediately the 25 ml/min of SG was automatically switched into the system to react with CaO powder sample. When the absorption process was completed, the temperature was increased at a heating rate of 25°C/min to 875°C and N$_2$ gas was automatically switched back for desorption process.

The equilibrium partial pressure of CO$_2$ increases with increasing temperature. Since the feed simulated gas composition has been set, the equilibrium absorption temperature is purely a function of the CO$_2$ partial pressure. Here, the equilibrium temperature for a CO$_2$ partial pressure 0.16 atm is approximately 790°C. Thus, the maximum absorption temperature was set at 700°C in order to have an appropriate CO$_2$ concentration gradient for the reaction to proceed. The minimum absorption temperature was set at 500°C, as temperatures lower than this value result in extremely slow rates of absorption. Based on the minimum and maximum temperatures, the process of absorption-desorption has been repeated until 4 cycles. Three temperatures were chosen for absorption process. The temperatures were 500, 600 and 700°C to provide adequate kinetic data needed for comparison purpose. For multiple cycle experiment, 10 cycles of absorption and desorption process were conducted. During the entire process, the sorbent weight together with the temperature were continuously recorded and stored in a Microsoft Excel file automatically.

Results and discussion

Figure 3 illustrates the comparison in the CO_2 capture capacity of the first cycle CaO sorbent for three different absorption temperatures (500, 600 and 700°C). The CO_2 capture capacity has been defined by the weight CO_2 absorbed into the CaO sorbent.

Figure 3: (a) Data recorded **(b)** CO_2 capture capacity for number 1 cycle of absorption/desorption process at 500, 600 and 700°C. Size: 1000 micron, $T_{desorption}$ 875°C for 20 min.

It was found that the absorption reaction of CaO proceeds through two reaction stages, a very rapid absorption followed by a slower absorption stage. In the first stage, the slope of the linear line for 3 different temperatures (isothermal 500, 600 and 700°C) are very similar where 0.302, 0.336 and 0.337 mg/min were obtained using Equation 3 and 4 [27-28].

$$Weight\ capture(\%): C = \frac{W_t - W_o}{W_o} \times 100 \qquad (3)$$

$$Absorption\ reaction\ (\%/min) = \frac{dc}{dt} \qquad (4)$$

Where, W_t and W_o are the weight of the $CaCO_3$ desorption at a given time, t and at the beginning of the absorption reaction respectively, dt is the absorption time.

These rapid absorptions occurred approximately for 20 minutes duration time. Compared to the second stage where 0.056, 0.065 and 0.064 mg/min were found; these values were less than the first stage. The values of the slope obtained were from the line graph that was describing the CO_2 absorption reaction rate. It shows that the rates of absorption increase with temperature, peak at 700°C and decrease above 700°C as a result of the thermodynamically favored reverse $CaCO_3$ decomposition reaction. This situation can be seen in **Figure 4** for 1st and 2nd reaction stages.

Figure 4: CO_2 absorption rate for 1st and 2nd reaction stages in number 1 cycle of absorption/desorption process.

At the first linear stage, absorption reaction is rapid because the rate is typically kinetically-controlled for a chemically rate-controlling mechanism at the surface of CaO. The rapid surface reaction between CaO and CO_2 leads to the formation of a $CaCO_3$ product layer which shields the sorbent surface and slows the flow of CO_2 to the unreacted CaO core in the second stage. The formation of the $CaCO_3$ layer also block small pores which prevent the CO_2 diffusion through the solid $CaCO_3$ layer. The kinetically-controlled regime then changes to the diffusion-controlled regime process. The result found for number 1 cycle of absorption- desorption process as shown in **Figure 3** is in agreement with the result obtained by Ozcan et al. [29].

The number 4 cycles of the absorption and desorption reaction process is represented in **Figure 5**. As can be seen in the figure, there is a different in CO_2 absorption capacity in weight (mg) when compared to a number 1 cycle. As expected, the weight of $CaCO_3$ desorption at a given time is lower which is around 18 mg for 3 different temperatures compared to 24-26 mg in cycle number 1.

Figure 5: CO_2 capture capacity for number 4 cycle of absorption/desorption process at 500, 600 and 700°C. Size: 1000 micron, $T_{desorption}$ 875°C for 20 min.

The CO_2 absorption reaction rate obtained in the kinetically-controlled regime are 0.126, 0.144 and 0.143 mg/min for temperatures 500, 600 and 700°C, respectively which is small compared to number 1 cycle. For the diffusion-controlled regime process, the slopes obtained are 0.005 to 0.008 mg/min CO_2 absorption reaction rate. The trend of results is similar to the research done by Bhatia et al. [30,31]

To determine the recyclability of the sorbent, a multicyclic absorption-desorption test was conducted and the results are shown in

Figure 6. Ten cycles have been conducted and the operation time is around 1090 minutes. As seen in the figure, it was found that CaO (in weight mg) experienced a decline during the absorption process in each cycle.


Figure 6: Cyclic desorption/absorption for 1000-micron CaO, desorption at 875°C with N$_2$ and absorbed at 600°C with 16% CO$_2$, and balance N$_2$.

The decreasing phenomenon is caused by the loss of small pores and surface area of CO$_2$ absorbing material during the sintering process at high temperature according to Manovic et al. [15]. The similar trend of the multicyclic absorption-desorption process is also obtained by researchers [32-34].

Figure 7 shows the CO$_2$ absorption reaction rate versus number of cycles absorbed at 600°C with 16% CO$_2$ and balance N$_2$. It was found that the CO$_2$ absorption reaction rates decreases when number of cycle desorption/absorption process increases. The curve line obtained is similar to Abanades et al. [35] as shown in **Figure 8**.
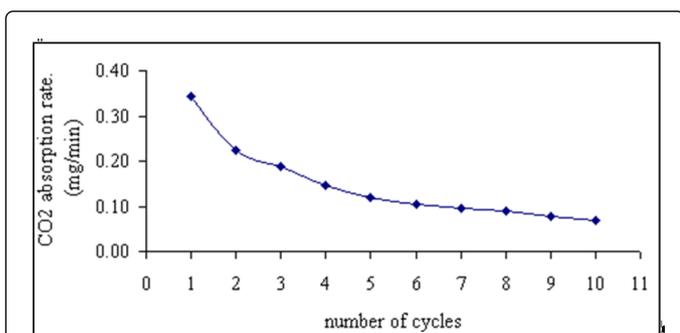
Figure 7: CO$_2$ absorption rate versus cycles of the desorption / absorption test.
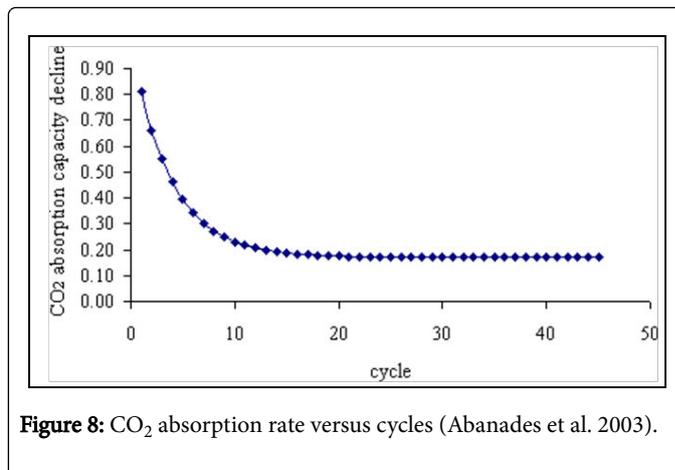
Figure 8: CO$_2$ absorption rate versus cycles (Abanades et al. 2003).

As mention earlier, the decreasing of CaO weight (mg) is caused by the loss of small pores and surface area of CO$_2$ absorbing material during the sintering process at high temperature. This sintering causes a reduction in the reactive surface affecting in the drop-off in reactivity. Sintering is the bonding together of compacted powder particles at temperatures below the melting point. Sintering is resulted in the pore closure, particle aggregation or decreasing in surface area and pore volume Zhen et al. [36]. When this happens, the micropores closure occurs when CaO is converted to CaCO$_3$. Therefore, the closed pores lead to defective CO$_2$ absorption reaction rate in each subsequent cycle.

Sintering of CaO increases at higher temperatures, durations of calcinations, and also with impurities. This condition is also agreed by researchers [37-40]. Others factors that reduce the activity of sorbents are the loss of bed material through attrition of sorbent grains during the process causing elutriation of fines, and chemical inactivation and ash fouling.

Conclusion

This research has achieved its objectives, where the CO$_2$ absorption-desorption using TGA have been conducted and presented. The ability to absorb has been successful and can be verified by referring to the absorption techniques described in the literature. The absorption-desorption process of CO$_2$ was conducted using Thermogravimetric analysis (TGA). Using a small amount of CaCO$_3$ approximately 29 mg then produced 16 mg CaO, the CO$_2$ absorption occurred in 2 stages, a very rapid absorption followed by a slower absorption stage when 16% CO$_2$ and 84% N$_2$ was used. From the graphs plotted show that at rapid absorption, 0.302, 0.336 and 0.337 mg/min CO$_2$ reaction rate were obtained at 3 different temperatures. While, only 0.056, 0.065 and 0.064 mg/min of CO$_2$ reaction rate were found at slower absorption stage. Apart from that, it is also observed the CO$_2$ absorption reaction rates decreasing when number of cycle desorption-absorption process was increased.

Acknowledgments

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