

A Study of Calcination and Carbonation of Cockle Shell

N.A. Rashidi, M. Mohamed and S.Yusup

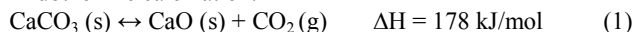
Abstract—Calcium oxide (CaO) as carbon dioxide (CO₂) adsorbent at the elevated temperature has been very well-received thus far. The CaO can be synthesized from natural calcium carbonate (CaCO₃) sources through the reversible calcination-carbonation process. In the study, cockle shell has been selected as CaO precursors. The objectives of the study are to investigate the performance of calcination and carbonation with respect to different temperature, heating rate, particle size and the duration time. Overall, better performance is shown at the calcination temperature of 850°C for 40 minutes, heating rate of 20°C/min, particle size of < 0.125mm and the carbonation temperature is at 650°C. The synthesized materials have been characterized by nitrogen physisorption and surface morphology analysis. The effectiveness of the synthesized cockle shell in capturing CO₂ (0.72 kg CO₂/kg adsorbent) which is comparable to the commercialized adsorbent (0.60 kg CO₂/kg adsorbent) makes them as the most promising materials for CO₂ capture.

Keywords—Calcination, Calcium oxide, Carbonation, Cockle shell

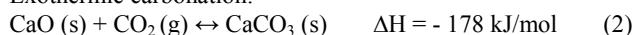
I. INTRODUCTION

RECENTLY rising level of atmospheric carbon dioxide (CO₂) has become the major threat to the society. CO₂ which is currently 385 part per million is the major greenhouse and global warming contributor that causes harms towards the ecological system, living organism and economic sector [1]. By far, there are various kinds of treatment that have been introduced by the researchers in capturing CO₂ in ensuring that only clean gas will be emitted to the air. The current technologies of capturing CO₂ involve membrane separation, cryogenic fractionation, chemical absorption and adsorption [2]. However, the adsorption process is more advantageous compared to the rest since it is easy to handle and they do not contribute to the corrosion problems [3]. By far, alkaline earth oxide (i.e. CaO, MgO) has been the main interest as the CO₂ solid sorbent. It is due to the chemical reaction that takes place between the acidic CO₂ and alkaline earth oxide at the elevated temperature [4]-[5]. In fact, calcium carbonate (CaCO₃) which is abundant in nature is commonly adopted in industrial processes as the solid adsorbent through the reversible calcination-carbonation process as shown below:

Endothermic calcination:



Exothermic carbonation:



Common natural sources of the CaCO₃ that have been applied these days are such as dolomite, limestone and magnesite. However, mining large quantities of raw materials such as limestone result in extensive deforestation and top soil loss [6]. In other words, mining of these carbonate rocks will contribute to the environmental damage and engage with high cost for environmental compliance [7]. Therefore, seashell currently is found to be the alternative as the potential biomass source for CaCO₃. It fits to be the best candidate as the alternative material as they are made up of at least 95% of CaCO₃ [8]-[9]. In addition, Li *et al.* found that composition of calcium oxide (CaO) in seashell is significantly higher than the limestone used in their study [10]. Cockles which are class of bivalve mollusk has retail values estimated to be over 32 million USD dollars and has been regarded as the waste [11]. Further, the shells that have been dumped and left untreated will cause an unpleasant smell and disturbing view to the surrounding. Therefore, the major aim of this study is to determine the influence of operating conditions on the calcination and carbonation process using cockleshells as the natural source of alkaline earth oxide based on thermogravimetric analyses. The study is very significant since there is still lack of literature discussing the potential of cockle shell as CaO sources. Besides, utilizing waste as the adsorbent is beneficial because it will minimize the source of pollution, waste itself can be recovered and lastly, converted to become the value added product [7].

II. MATERIALS AND METHOD

A. Raw materials preparation

Cockle shell was collected from local market in Perak and was thoroughly washed with tap water until they are free from dirt and dust. The clean samples were then sun-dried for two days followed by oven dried at 110°C for two hours. Then, the samples were crushed and grounded to different particle sizes (< 0.125mm-0.4mm) using pestle and mortar and Rocklabs rotation grinder, respectively.

B. Materials Characterization

Two characterization analyses had been performed in this study: Scanning Electron Microscopy (SEM, Leo 1430VP)

N.A. Rashidi is with the Chemical Engineering Department, Universiti Teknologi Petronas, 31750 Tronoh Perak (e-mail: noradilla.88@gmail.com).

M. Mohamed was with Universiti Teknologi Petronas, 31750 Tronoh Malaysia. She is now with The Otomotive College, 46300 Petaling Jaya Selangor (e-mail: MustakimahMohamed@gmail.com).

S. Yusup is with the Chemical Engineering Department, Universiti Teknologi Petronas, 31750 Tronoh Perak (phone: 605-3687642; fax: 605-3688204; e-mail: drsuzana_yusuf@petronas.com.my).

equipped with Energy Dispersive X-ray (EDX, Oxford Inca) and also physisorption analyzer (Micromeritics ASAP 2020 Accelerated Surface Area and Porosimetry). SEM-EDX is useful in visualizing the surface morphology and providing the samples elemental composition meanwhile, specific surface area, pore volume and pore size distribution can be examined from N₂ adsorption-desorption isotherm at 77K using the volumetric adsorption apparatus.

C. Calcination and Carbonation of Cockle Shell

Both calcination and carbonation of cockle shell were analyzed with thermo-gravimetric analyzer, TGA (EXSTAR 6000). Approximately 5- 10 mg of shell powder with size of 0.125- 0.25mm was placed in the ceramic sample holder. It then was heated up to the desired calcination temperature at various heating rate under a nitrogen gas flow of 50 ml/min. After certain time of exposure towards the calcination condition, the sample was cooled or heated to the carbonation temperature. Once the temperature has been reached, nitrogen gas was switched to pure CO₂ for carbonation process to take place. The conditions were held until there are no significant weight changes was observed. Also, the procedures were repeated for different particle size at the same heating rate during the calcination process.

TABLE I
EXPERIMENTAL CONDITION TO STUDY THE EFFECT OF CALCINATION
CONDITION ON CARBONATION

Calcination temperature (°C)	Calcined duration (min)	Particle size (mm)	Heating rate (°C/min)	Carbonation temperature (°C)
750	30	< 0.125	20	650
850	30	< 0.125	20	650
950	30	< 0.125	20	650
850	40	< 0.125	20	650
850	60	< 0.125	20	650
850	30	0.5-1.0	20	650
850	30	2.0-4.0	20	650
850	30	< 0.125	10	650
850	30	< 0.125	50	650

TABLE II
EXPERIMENTAL CONDITION FOR CARBONATION OF SYNTHESIZED CAO

Calcination temperature (°C)	Calcined duration (min)	Particle size (mm)	Heating rate (°C/min)	Carbonation temperature (°C)
850	40	< 0.125	20	500
				650
				850

III. RESULTS AND DISCUSSION

A. Characterization of Cockle Shell

SEM-EDX was conducted to determine the structure and elemental composition of both raw cockle shell and synthesized cockle shell. In addition, the surface morphology of synthesized cockle shell as illustrated in Fig. 2 is quite similar to the calcined limestone, as reported by Sun *et al.*

[12]. Sun *et al.* in his works verify that the grain shapes are almost spherical with some grain-neck growth due to the sintering process [12]. According to the EDX analysis, the cockle shell is found to have 15.77% of carbon, 55.39% of oxygen and the rest is calcium. EDX also has been tested for samples at different calcination conditions, ensuring that the carbon content is fully eliminated and metal oxide is established. It can be summarized that the carbon will completely diminish at the elevated temperature and greater duration time. Besides, N₂ adsorption-desorption isotherm reveal that the samples are elucidated as mesoporous, which is claimed as favourable for the carbonation reactions. Results of the physisorption analysis are as tabulated in Table III. In summary, the performance of BET surface area, pore width and pore volume of calcined cockle shell is significantly higher than commercial Aldrich CaCO₃.

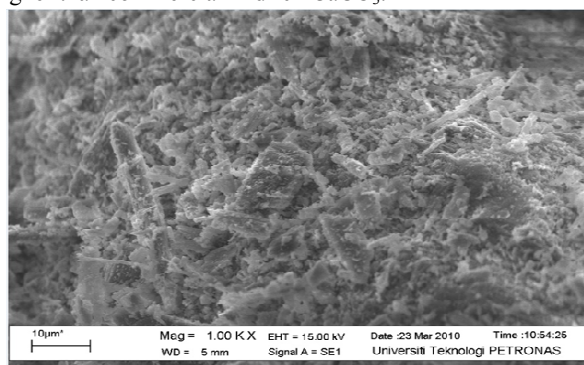


Fig. 1 SEM image of aragonite in raw cockle shell

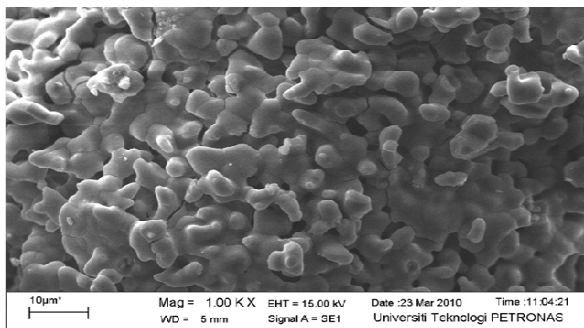


Fig. 2 SEM image of calcined cockle shell under inert atmosphere at 850°C

TABLE III
SUMMARY OF NITROGEN PHYSISORPTION ANALYSIS

Sample	BET surface area (m ² /g)	Pore volume (m ³ /g)	Adsorption average pore width (4V/A by BET) (m)
Aldrich CaCO ₃	3.44	1.28 x 10 ⁻⁹	1.5 x 10 ⁻⁹
Aldrich CaO	2.18	6.17 x 10 ⁻⁹	1.1 x 10 ⁻⁸
Cockle shell	1.56	4.92 x 10 ⁻⁹	1.3 x 10 ⁻⁸
Synthesized CaO	9.63	2.34 x 10 ⁻⁸	9.7 x 10 ⁻⁹

B. Effect of Calcination Condition towards Carbonation of Cockle Shell

1. Calcination temperature and Residence Time

Both of reaction temperature and residence time are crucial since they are directly related to the surface area and pore distribution of the samples. It has been reported in the literature that the threshold point in which the solids may begin sintering is 1154°C for CaO and 533°C for CaCO₃ [13]. Therefore, the selection of reaction temperature is significantly essential before running the experimental works. Also, at particular temperature in which the surface area is at the highest, the decomposition rate of CaCO₃ is at the peak and thus will accelerate the calcination temperature. The scenario can be illustrated from both TG and dTG curve as shown in the Fig. 3 and Fig. 4 below.

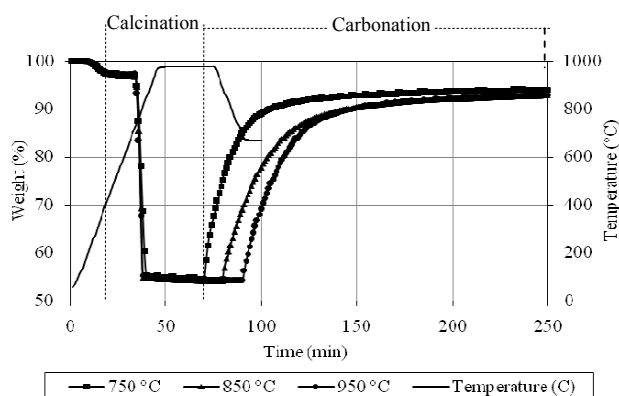


Fig. 3 TG curves during calcination and carbonation of cockle shell at different calcination temperatures

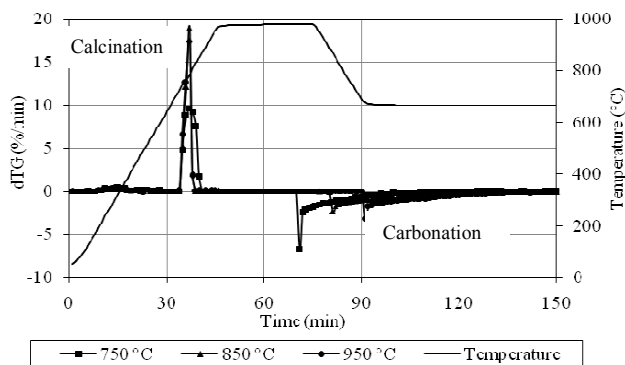


Fig. 4 dTG curves during calcination and carbonation of cockle shell at different calcination temperatures

Despite of different saturation time and calcination rate shown by these samples at different reaction temperature, the percentage of weight gain (92-95%) and carbonation conversion (≈ 0.91) after the carbonation process is quite similar to each other. Thus, it can be concluded that the CO₂ adsorption capacity is similar at different calcination temperatures. Considering that the duration of calcination process is crucial in ensuring the heat fully penetrates the particles and desorb CO₂ away, performance comparison of

different reaction time (30-60 minutes) has been investigated. Based on the results, it is shown that the duration time for the calcination process to take place is inversely proportional to the time taken for CO₂ saturation point, as shown in Fig. 5 below. Besides, referring to Fig. 6, duration time of 40 minutes is taken as the optimal point due to highest carbonation conversion exhibits by the samples.

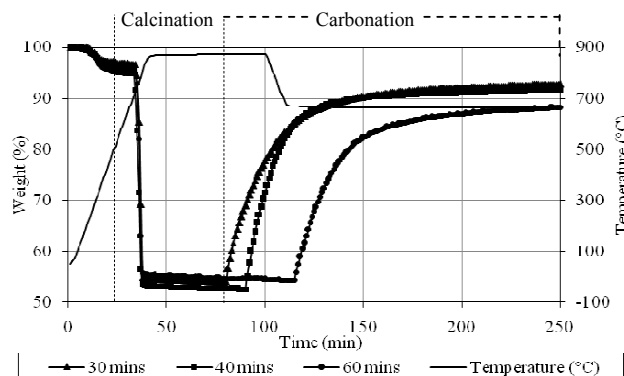


Fig. 5 TG curves during calcination and carbonation of cockle shell at different calcination duration

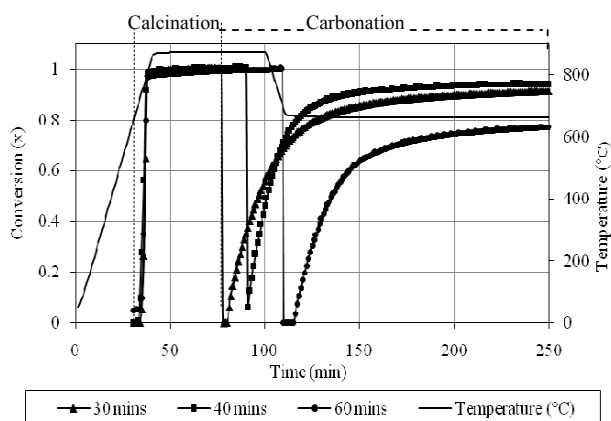


Fig. 6 Conversion plot of cockle shell during calcination and carbonation reaction

2. Heating rate

Heating rate is basically important since it influences the samples decomposition during the calcination process. Larger heating rate commonly has maximum calcination rate, shorter operating time to reach the desired calcination temperature, yet the longest time for CO₂ saturation point during the carbonation process. This phenomenon can be shown in TG curve as shown in Fig. 7. Basically, when higher heating rate is applied, the process itself will rapidly take place and thus, consume shorter operating time to reach the desired temperature. Further, with respect to the carbonation conversion and CO₂ capture capacity, the performance at various heating rate can be concluded as 20°C/min > 10°C/min > 50°C/min. In addition, the findings from the dTG curves, especially at 50°C is aligned with the previous works as reported by Hatakeyama and Liu, whom states that the elevated heating rate results of narrower and sharper reaction profiles [14].

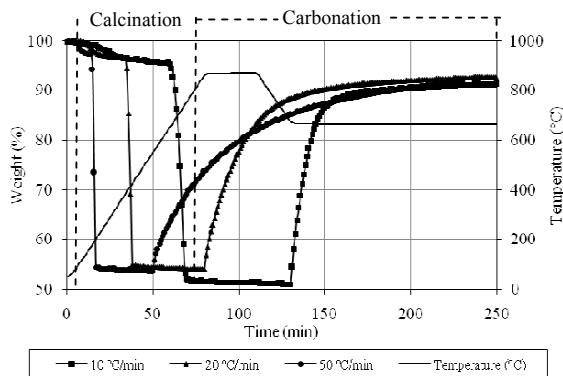


Fig. 7 TG curves for calcination and carbonation for cockle shell at different heating rate

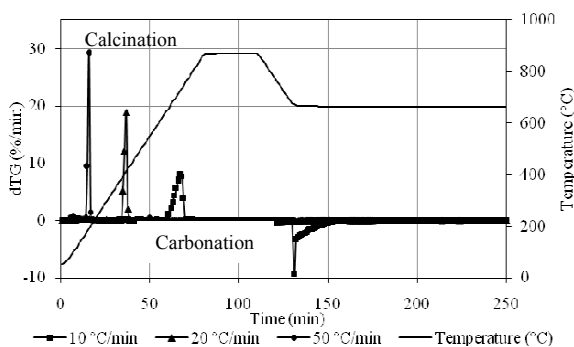


Fig. 8 dTG curves for calcination and carbonation for cockle shell at different heating rate

3. Particle sizes

Particle sizes are basically one of the critical variables in the calcination process since they directly influence the reaction rate. Therefore, since the selection of particle sizes are significantly important, three different particles have been investigated in the study; < 1.25 mm, 0.5-1.0mm and 2.0-4.0mm. Similar to the other variables, the performance is based on TG and dTG curve analysis as well as the carbonation conversion. According to Fig. 9 and 10 below, despite of fastest time taken for the saturation process to occur, still the CO₂ capture capacity is comparable to particle sizes of 2-4mm. On the other hand, the smallest size of the samples give better results in percentage of weight gain and also exhibits the utmost calcination rate compared to the rest. In addition, small particles commonly have the largest surface area, which lead towards better CO₂ capture capacity during the carbonation stage. Thus, physisorption analysis through the N₂ adsorption-desorption isotherm has been tested for materials with size of < 1.25mm and 2-4mm. Based on the findings, the surface area of particle size 2-4mm is significantly lower (4.18m²/g) compared to the other one (9.63m²/g). As reported in the literature, too small of particle size (<5µm) is unfavorable since it cause destruction of pore, increase the grinding cost as well possibility of clogging in the reactor [15]. However, the main advantageous associated with small particle size is due to less pore diffusion resistance in which will influence the mass transfer of CO₂ through the pore structure [15].

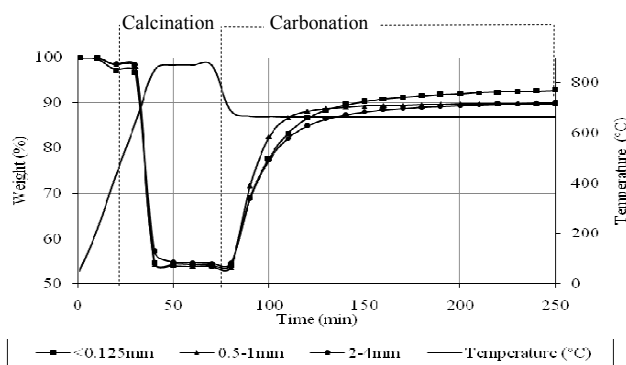


Fig. 9 TG curves for calcination and carbonation reaction using samples with different particle sizes.

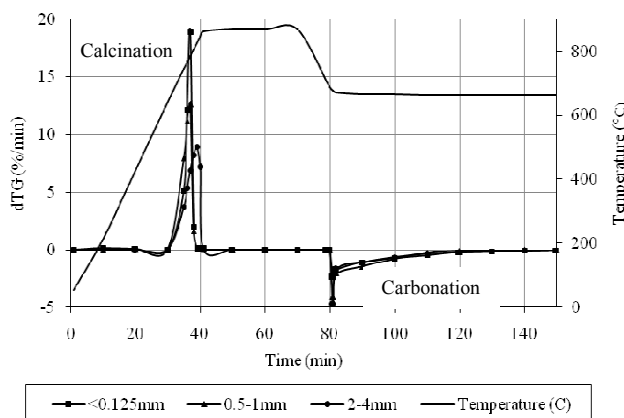


Fig. 10 dTG curves for calcination and carbonation reaction using samples with different particle sizes

C. Performance of Synthesized Cockle Shell at Different Carbonation Temperature

The competency of calcined cockle shells in adsorbing pure calcium dioxide at different reaction temperature (i.e. 500-850°C) has been investigated. Referring to Fig.11 and 12, it is shown that the calcined cockle shell has the utmost weight percentage of approximately 93% and the highest conversion when the carbonation temperature is at 650°C.

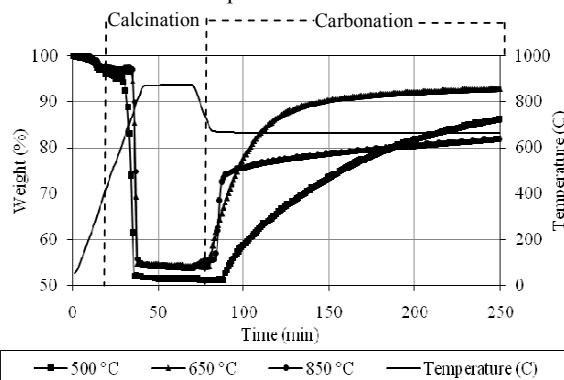


Fig. 11 TG curves during calcination and carbonation if cockle shell at different carbonation temperatures

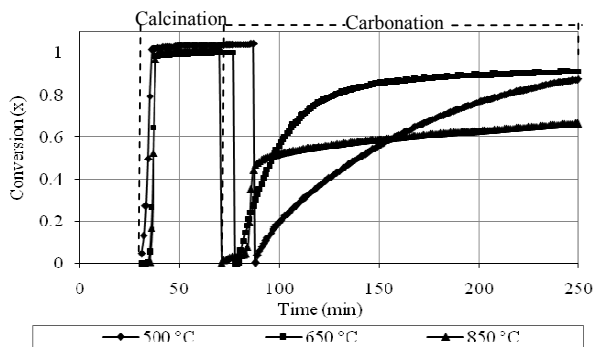


Fig. 12 Conversion plot for calcination and carbonation of cockle shell at different carbonation temperature

In addition, same scenario is reported by Gupta and Fan which found that the carbonation is performed best at temperature above 600°C [16]. This is due to its moderate carbonation reaction and faster saturation time. However, when the temperature is too high, it will cause shrinkage, pore closure and volume reduction of the particles and thus, unsuitable for the carbonation process to take place [17]. On the other hand, too low carbonation temperature (<500°C) does not favour the carbonation process. The scenario is due insufficient reaction temperature to trigger the reaction and later cause high pressure to build up during the reaction. Therefore, it can be concluded that the carbonation process is well-dependent on the reaction temperature.

D. Comparison of Carbonation Capacity between Synthesized CaO and Commercial Adsorbent

In addition, the performance of cockle shell in capturing CO₂ has been compared with commercial CaCO₃ (i.e. Aldrich CaCO₃) and mixture of cockle shell and Aldrich CaCO₃ with ratio of 1:1. The experimental works has been fixed at the optimal condition of both calcination and carbonation. According to Fig. 13, the performance for both CO₂ capture and conversion processes can be concluded as cockle shell > mixture of cockle shell and commercial adsorbent > commercial adsorbent. Therefore, cockle shell can be said as one of the economical and promising adsorbent for CO₂ removal.

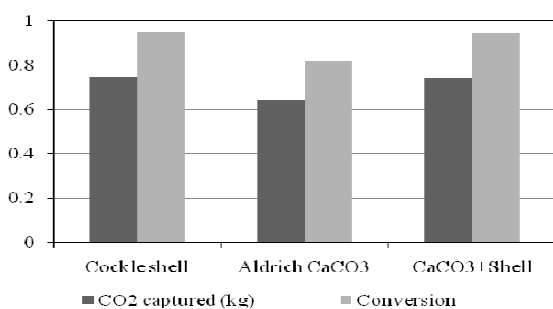


Fig. 13 Amount of CO₂ captured and carbonation conversion by each adsorbents

IV. CONCLUSION

Based on the findings, it can be concluded that samples performance in the calcination stage is strongly dependent on few variables such as reaction temperature, duration of the process to take place, heating rate as well as the particles size. Overall, these operating parameters will directly influence the sample decomposition, sintering effect, surface area, pore volume and distribution plus the reaction rate. Thus, from sets of experimental works done, the optimal point is basically at 850°C, duration time of 40 minutes, heating rate of 20°C/min and the size of <1.25mm. Similar to the calcination, carbonation process also depends on the reaction temperature, that will determine the qualities of the sorbent, whether they are in a good quality or otherwise.

ACKNOWLEDGMENT

The author gratefully acknowledges the financial support from Petroleum Research Fund of PETRONAS and Universiti Teknologi PETRONAS to conduct the current research work.

REFERENCES

- [1] J. Butler, "NOAA annual greenhouse gas index," <http://www.esrl.noaa.gov/gmd/aggi>, August 12, 2011.
- [2] Herzog, H.; Drake, E.; and E. Adams, "CO₂ capture, reuse, and storage technologies for mitigating global climate change," Final Report DOE Contract No. DE-AF22-96PC01257, January 1997.
- [3] M. G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, and J. Pis, "CO₂ capture by adsorption with nitrogen enriched carbons," *Fuel*, vol. 86, no. 14, pp. 2204-2212, 2007.
- [4] Z. Yong, V. Mata, and A. E. Rodrigues, "Adsorption of carbon dioxide at high temperature—A review," *Sep. Purif. Technol.*, vol. 26, no. 2-3, pp. 195-205, 2002.
- [5] A. Auroux, and A. Gervasini, "Microcalorimetric study of the acidity and basicity of metal oxide surfaces," *J. Phys. Chem.*, vol. 94, no. 16, 6371-6379, 1990.
- [6] P. K. Mehta, "Reducing the environmental impact of concrete," *Concrete International*, vol. 23, no. 10, pp. 61-66, 2001.
- [7] W.H. Langer, Potential environmental impacts of quarrying stone in karst—A literature review. USGS Open-File Report of-01-0484. <http://pubs.usgs.gov/of/2001/ofr-01-0484/ofr-01-0484so.pdf>, August 12, 2011.
- [8] N. Nakatani, H. Takamori, K. Takeda, and H. Sakugawa, "Transesterification of soybean oil using combusted oyster shell waste as a catalyst", *Bioresource Technol.*, vol. 100, no. 3, pp. 1510-1513, 2009.
- [9] M. C. Barros, P. M. Bello, M. Bao, and J. J. Torrado, "From waste to commodity: transforming shells into high purity calcium carbonate", *J Clean Prod.*, vol. 17, no. 3, pp. 400-407, 2009.
- [10] Y. Li, C. Zhou, H. Chen, L. Duan, and X. Chen, "CO₂ capture behaviour of shell during calcination/ carbonation cycles", *Chem Eng Technol.*, vol. 32, no. 8, pp. 1176-1182, 2009.
- [11] Boey, P., Maniam, G. P., Hamid, S. A., & Ali, D. M. H. "Utilization of waste cockle shell (anadara granosa) in biodiesel production from palm olein: Optimization using response surface methodology," *Fuel*, vol. 90, no. 7, pp. 2353-2358, 2011.
- [12] P. Sun, J. R. Grace, C. J. Lim, and E. J. Anthony, "Determination of intrinsic rate constant of the CaO-CO₂ reaction," *Chem. Eng. Sci.*, vol. 63, no.1, pp. 47-56, 2008.
- [13] R. Barker, "The reversibility of the reaction CaCO₃ ↔ CaO+CO₂," *Journal of Applied Chemistry and Biotechnology*, vol. 23, pp. 733-742, 1973.
- [14] T. Hatakeyama and Z. Liu, *Handbook of thermal analysis*, John Wiley and Sons, England, 1998.

- [15] Z. Ye, W. Wang, Q. Zhong, and I. Bjerle, "High temperature desulfurization using fine sorbent particles under boiler injection conditions", *Fuel*, vol. 74, no. 5, pp. 743-750, 1995.
- [16] H. Gupta and L.S. Fan, "Carbonation-calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas," *Ind. Eng. Chem. Res.*, vol. 41, no. 16, pp. 4035-4042, 2002.
- [17] B. R. Stanmore and P. Gilot, "Review—calcination and carbonation of limestone during thermal cycling for CO₂ sequestration," *Fuel Process Technol.*, vol. 86, no. 16, pp. 1707-1743, 2005.