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The Kinetic Model of Calcination and Carbonation of Anadara Granosa

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Abstract- Utilization of calcium-based adsorbent in carbon dioxide (CO_2) separation from the gas stream through the calcination and carbonation process is extensively applied in the gas purification process, especially at the elevated reaction temperature. Typically, natural calcium carbonates ($CaCO_3$) such as the limestone, magnesite and dolomite are widely consumed in the process due to their low cost and large abundance of these materials. However, in this research study, the potential of waste cockle shell as the $CaCO_3$ sources were investigated. The main objectives of the work are to examine the influence of the process variables such as heating rate, particle size, temperature and residence time on the calcination rate. Therefore, Arrhenius equation was used to explain the process reactivity. The calcination process were carried out for various particles sizes (<0.125-4.00 mm), calcination temperatures (750-950^{o}C), heating rate (10-50 ^{o}C /min) and also the calcination duration time (30-60 min). Using zero order reaction, the activation energy (Ea) and also the pre-exponential factor (A) were determined. In addition, the effect of temperature (500-850 ^{o}C) on carbonation reaction was also studied. Based on the kinetic analysis, it proves that the resistivity towards the diffusion process is significant in carbonation as compared to chemical reaction at the surface.

Keywords- Arrhenius plots, calcination, cockle shell, kinetic analysis, regression analysis.

1. Introduction

The meat of cockleshells (*Anadara Granosa*) or sometimes known as the mussels are commercially important in Malaysia as the protein sources. These materials are normally cultivated in the tidal mudflats along the coast of Western Malaysia and at major cultivation centers in this country. In Malaysia, the cultivation centers are allocated in Selangor, Penang and Malacca [1]. The suitability of cockle shell as calcium-based adsorbent is confirmed by its high calcium content, as reported by Awang Hazmi et al. [1]. Table 1 shows that percentage of calcium and carbon accounts for more than 98% of total samples composition. In addition, other elements composed of inorganic contents i.e. silica, iron and zinc. Since there are high productions of cockle each year, it indicates that waste generated from this material will also be higher. Furthermore, shells are commonly being thrown away once the mussels are obtained and thus, cause an unpleasant smell and a destructive view of the surrounding [1-2].

Currently, generation of green electricity with in-situ carbon dioxide (CO_2) capture is important. The CO_2emission result in lots of environmental impacts i.e. global warming and at the same time, the desire for electricity is kept on increasing regardless of rapid declining of fossil fuel such as petroleum, natural gas and coal resources. Therefore, new electrical generation with zero or low CO_2 emission should be considered to abate the current issue. The process is highly economical when the feedstock price is low and huge availability, which address the current issue of sustainable development [3]. The use of calcium-based sorbents such as dolomite and calcite offers an opportunity for CO_2 capture and separation due to its applicability in high temperature and pre-combustion process, cheap and vast availability in the country. Chemical reaction during reversible calcination-carbonation process of cockle shell can be represented by Eq. (1) and Eq. (2), respectively [4].

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 178 kJ/mol \tag{1}$$

$$CaO + CO_2 \rightarrow CaCO_3 \quad \Delta H = -178 kJ/mol \tag{2}$$

According to Yan *et al.* [4], calcination is described as a five-step process which involves (i) heat transfer from surrounding to external surface of particle, (ii) heat transfer from exterior surface to interior samples interface, (iii) heat absorption and thermal decomposition at the interface layer, (iv) diffusion of formed CO_2 through porous layer of calcium oxide (CaO) and (v) diffusion of CO_2 towards the surrounding.

Therefore, this paper highlights the kinetic analysis of the calcination and carbonation process of cockle shell. Few process variables were to be studied such as temperature, duration time, heating rate, particle size of cockle shell and carbonation temperature. In a gas-solid reaction, Arrhenius equation is applied for kinetic analysis. Hence, in the kinetic analysis of calcination reaction, the combination of equations is used as shown in Eq. (3) and Eq. (4) below [5].

$$d(\alpha)/d(t) = k\ f(\alpha) \tag{3}$$

$$\ln k = \ln A - E_a/RT \tag{4}$$

Based on Eq. (4), Arrhenius equation is written in a linear form, where k represents specific rate constant, A is pre-exponential factor, Ea is activation energy of the process (J/mol), R is universal gas constant (8.314 J·K-1·mol-1) and T is absolute temperature in Kelvin. Meanwhile, the unit of pre-exponential factor is identical to the specific rate constant and will vary depending on which reaction order is being used. Rearranging Eq. (3) and Eq. (4), a new Arrhenius equation is formed as shown in Eq. (5).

$$\ln[(d\alpha/dt)/f\alpha] = \ln A - E_a/RT \tag{5}$$

Table 1. Percentage of major mineral contents of cockle shells [1]

Sources/Minerals	Ca+C	Mg	Na	P	K	Others
Penang	98.770	0.0476	0.9192	0.0183	0.0398	0.1981
Kuala Selangor	98.8007	0.0477	0.9076	0.0176	0.0392	0.1871
Malacca	98.7834	0.0437	0.9386	0.0178	0.0380	0.1894

According to Samtani et al. [5], value of f (α) is dependent on types of reaction order which can be decided upon the best fit curved. Therefore, the mathematical model proposed for reaction mechanisms is as shown in Table 2.

Table 2. The mathematical model for reaction mechanism

Type of order equation	$f(\alpha)$
Zero order	1
First order	$1-\alpha$
Second order	$(1-\alpha)^2$

Consequently, different Arrhenius plot of ln *k* against 1/T can be plotted, depending on which order equation has been computed. Research work was conducted using zero-order kinetics model and accuracy of the curve was assessed by regression coefficient values (R^2). Besides, the closer value of the coefficient of determination to unity was deemed to provide the best fit. Based on the curve plotted, activation energy is obtained from the slope and meanwhile, y-intercept values indicate the pre-exponential factor.

Meanwhile, in terms of carbonation reactions, method proposed by Lee [6] was being utilized. To obtain value of k in Eq. (4), following Eq. (6) is being followed.

$$\frac{1}{X} = \frac{1}{k}\left(\frac{1}{t}\right) + \frac{1}{kb} \tag{6}$$

Further, by plotting a graph of 1/X versus 1/t, value of k can be calculated from the slope. Besides, he claimed that the parameter k can be assigned as the apparent kinetic rate constant. In consequence, activation energy will be found by applying abovementioned Eq. (4).

2. Experimental

2.1. Material and Methods

The material studied was the cockle shells that were initially washed until all traces of dirt and dust were removed. The clean samples were sun-dried for 2 days followed by oven-dried at 110 ^oC for 2 hours. The samples were crushed and grounded to different particle sizes (< 0.125 mm-4 mm) using pestle and mortar and Rocklabs rotation grinder, respectively. A sieve shaker (CISA Cedaceria Industrial, Spain) was used to separate the particle to corresponding size distributions for 10 minutes of sieving duration. In addition, commercial calcium carbonates ($CaCO_3$) were utilized for the comparison purposes.

2.2. Calcination and Carbonation of Cockle Shell

EXSTAR 6000 thermal gravimetric analyzer (TGA). Approximately10±2 mg of cockle shell with particle size <0.125- 4 mm were placed in the ceramic sample holder. It was then heated up to the desired calcination temperature (750-950 ^oC) at various heating rate (10-50 ^oC /min) under a constant nitrogen (N_2, 99% purity supplied by Linde Sdn. Bhd.) stream flow of 50 ml/min. The experimental design of the work is given in Table 3. Once the system reached an equilibrium state, the sample was cooled down to the carbonation temperature of 650 ^oC and the gas was switched to pure CO_2 (99.8% purity from Linde Sdn. Bhd.). In this study, whilst studying one parameter, all the other parameters were kept constant. In addition, effect of operating temperature on carbonation process was also studied. Temperature studied for the carbonation process is at 500, 650 and 850 °C. Furthermore, the calcination process was fixed at their optimum conditions. The conditions were hold until there were no significant weight change was observed. Basically, all the experimental runs were repeated at least twice to ensure a proper reliability and observation.

Table 3. Experimental design of cockle shell calcination process

Variable studied	Temp. (°C)	Duration time (min)	Size (mm)	Heating rate (°C/min)
Temp. (°C)	750	30	<0.125	20
	850	30	<0.125	20
	950	30	<0.125	20
Duration time (min)	850	30	<0.125	20
	850	40	<0.125	20
	850	60	<0.125	20
Particle size	850	30	<0.125	20
	850	30	0.5-1.0	20
	850	30	2.0-4.0	20
Heating rate (°C/min)	850	30	<0.125	10
	850	30	<0.125	20
	850	30	<0.125	50

3. Results and Discussions

3.1. Effect of Particle Sizes

The particle sizes of the cockle shell influenced the calcination process, and the kinetic analyses are given in Table 4. Theoretically, for the smaller particle size, low activation energy is required and vice versa for large particle size. This phenomenon can be explained by the collision theory in determining rate of reaction. As smaller particle sizes are utilized, rate of reaction increases due to higher surface area available for the collision process to take place. Besides, the highest activation energy required by the particle size of 2-4 mm can be proved by surface area analysis. Based on N2 physisorption analysis, it is shown that the particle size of <0.125 mm and 2-4 mm has specific surface area of 9.63 m^2/g and 4.18 m^2/g, respectively. Borgwardt [7] proposed that the calcination process is under the kinetics reaction control and therefore, the reaction rate is proportional to the BET surface area. In addition, the greatest surface area of the samples will significantly improve the heat distribution within them and thus, accelerates better decomposition process. Consequently, the resistance for the reaction to occur is reduced and thus, results in low activation energy.

According to Yan et al. [4], intermediate particle size will have reaction and mass transfer limitations. Furthermore, he suggests that the calcination rate is also heavily influenced by the pore structure, in which the small particle size has less pore diffusion resistance that influences the mass transfer to the pores [4,8]. Hassibi [9] states that the differences in the particle size do affect the heat penetration towards the samples. At constant residence time and calcination temperature, heat will not completely penetrate core of the larger samples and as a result, only the outer layer is converted to CaO and samples interior will remain as $CaCO_3$. However, based on Table 4, value of activation energy for <0.125 mm particle size is higher as compared to the particle size of 2-4 mm. İt is assumed that the finest particle (<0.125 mm) agglomerated during calcination reaction. Therefore, it may reduce the surface area of the materials and thus limits the heat and mass transfer. Surface morphology of the synthesized CaO at 850 °C is provided in Fig. 1. The surface morphology of calcined cockle shell in this study is similar with the Strassburg limestone studied by Sun et al. [10]. Based on his research work, he claimed that the grain shapes are almost spherical with the initial grain-neck growth during the sintering.

Table 4. Kinetic analysis for samples at various particle sizes using zero order mechanism

Particle sizes (mm)	Kinetic parameters		
	E_a (kJ/mol)	A (mg/min)	R^2
<0.125	297.39	2.44×10^{14}	0.999
0.5-1.0	154.47	1.47×10^{7}	0.960
2-4	142.67	1.58×10^{6}	0.939

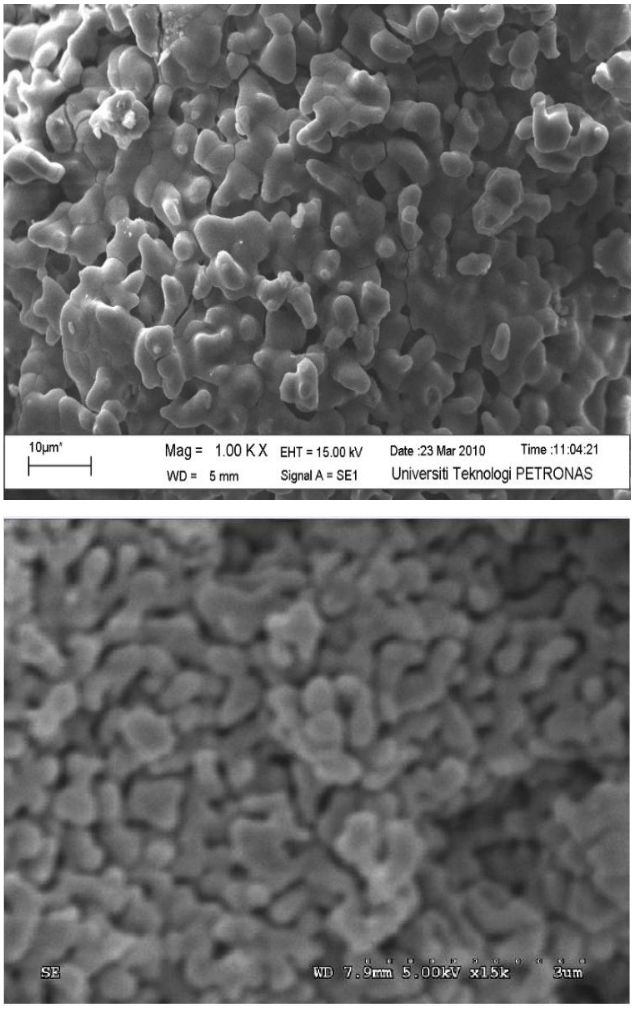

Fig. 1. (a) SEM image of synthesized CaO under inert condition (100%N_2) at 850°C obtained in the study (b) SEM images of calcined limestone under inert condition at 850°C [10]

3.2. Effect of Calcination Temperature

Based on the kinetic analysis in Table 5, the influence of temperature on the calcination process is best fitted with zero order reaction mechanism. This is proven by the highest regression values that lie within the range of 0.990 to 0.999. Lower activation energy values at higher calcination temperature are attributed to the kinetic motion of the samples itself. At higher temperatures, the samples have more energy that hastens their kinetic motion and the calcination process. Therefore, the easiness of the process results in a fast reaction and lower activation energy values. Likewise, Kim [11] found similar findings in which the calcination reaction proceeds slowly at temperature below 850 °C compared to temperature at and beyond 850 °C. The trend of increase in activation energy with respect to temperature is also found in other works [12-15].

Table 5. Kinetic analysis for samples at different calcination temperature using zero order mechanism

Calcination temperature (°C)	Kinetic parameters		
	E_a (kJ/mol)	A (mg/min)	R^2
750	399.83	4.14×10^{19}	0.992
850	297.39	2.44×10^{14}	0.999
950	222.40	4.28×10^{10}	0.997

3.3. Effect of Heating Rate

Heating rate is another factor that contributes to the reactivity and kinetic analysis of the calcination process. When Arrhenius curve (ln k vs. 1/T) was plotted, a straight line is produced. Findings of kinetic analysis for different heating rate at zero order reaction was tabulated in Table 6.

Table 6. Kinetic analysis for calcination process at different heating rate

Heating rate (°C/min)	Kinetic parameters		
	E_a (kJ/mol)	A (mg/min)	R^2
10	299.22	1.29×10^{15}	0.999
20	297.39	2.44×10^{14}	0.999
50	272.03	5.45×10^{13}	0.900

According to the findings shown in Table 4, it proves that the activation energy is kept on decreasing with the increment of heating rate. This is attributed to the fact that higher heating rate do assist the calcination process by supplying the heat for the process to occur. In addition, the concept of low apparent activation energy at higher heating rate is well-agreed by other researchers [16-17]. This phenomenon might be due to the greater rates of heat transfer that occurred and further assisted the decomposition process. Nevertheless, excess heating rate may results in non-uniformity of the heat distribution and does not bring any positive affects towards calcination reaction. Similar finding was observed by Samtani et al. [5] in his recent work. According to Table 7, as heating rate increases from 5 to 10°C /min, the activation energy is reduced, suggesting that further heat supply aid the calcination process up to certain point only.

Table 7. Kinetic analysis for limestone calcination at different heating rate using zero order mechanism

Heating rate (°C/min)	Kinetic parameters		
	E_a (kJ/mol)	ln A (mg/min)	R^2
5	182.66	19.36	0.9939
10	173.21	18.45	0.9959
20	183.41	19.55	0.9981
25	185.42	19.77	0.9980

3.4. Effect of Duration Time

Duration time plays a key role in determining the effective calcination process to occur. In the calcination process, balancing between the reaction temperature and residence time is desirable. It is often that the calcination process is carried out at high temperature and low residence time, or longer residence time but with much lower calcination temperature [8,18]. Hassibi [11] explained the importance of residence time of $CaCO_3$ during the calcination process. Short residence time has a probability to not fully convert the $CaCO_3$ to become CaO and on the other hand, long residence times will result in shrinkage of samples volume that results in closing of the pores and disallow the release of CO_2. Similarly, comparable findings were also found by Wang et al. [20] through their research study. As the residence time increases from 40 min to 100 min, the fraction conversion of below than 10% of the limestone decreases from 7% to 1%. Therefore, it is concluded that rise of residence time increase the limestone conversion. Nevertheless, too long residence time will result in smaller porosity and surface area of the samples and thus, limit the reactivity of the process. Also, Chen et al. [21] proved that at low reaction temperature, longer calcination times are required to achieve the highest conversion i.e. ≈1. For the kinetic study, Arrhenius curves were plotted at 3 different holding times to establish the value of activation energy and pre-exponential factor from the slope and y-intercept, respectively.

Table 8. Kinetic analysis for samples at different calcination holding time using the zero order reaction

Calcination duration (min)	Kinetic parameters		
	E_a (kJ/mol)	A (mg/min)	R^2
30	297.39	2.44×10^{14}	0.999
40	366.48	3.41×10^{21}	0.966
60	305.87	6.26×10^{14}	0.948

Besides, most of the research work conducts the calcination process for > 20 min to make sure the sample is fully calcined. However, according to the findings, there was no direct relationship was found between the variation in residence time and the activation energy. Recent work proved that the holding time has a negligible influence on the performance provided that it was long enough to achieve complete calcination and also, it was found that the variation in duration time do not change the sorbent reversibility [22-23].

3.5. Effect of Carbonate Sources

Apart from the operating condition, the kinetic data is also dependent on type of materials. Three sources of feedstock were utilized to compare the conversion of feedstock to CaO. These include commercial $CaCO_3$, pure cockle shell and mixture of synthesized and commercial $CaCO_3$. In this research work, optimal operating conditions at temperature of 850 °C; heating rate of 20 °C /min; holding time of 40 min and particle size of < 0.125 mm were applied. Results of the activation energy for each carbonate sources are summarized in Table 9. Difference in the value of activation energy proves that each sample has distinct reactivity in calcination process but the conversion values for these samples is similar as shown in Fig. 2.

Table 9. Kinetic analysis using each order of reaction for samples with different carbonate source

Materials	Kinetic parameters		
	E_a (kJ/mol)	ln A (mg/min)	R^2
Cockle shell	297.39	33.13	0.999
Commercial $CaCO_3$	165.37	18.09	0.981
Cockle shell + commercial $CaCO_3$	180.75	19.91	0.981

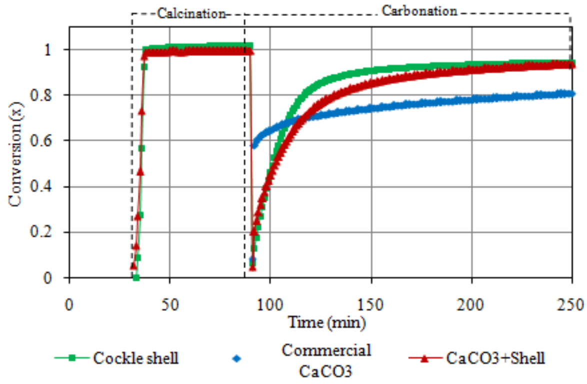

Fig. 2. Conversion values for types of carbonate sources.

Blending ratio of 1:1 based on weight % was applied in the process. The amount of energy needed to convert the cockle shell is reduced by blending with commercial $CaCO_3$ as shown in Table 7. According to Long and Wang [24], this synergistic effect is due to combination of two or more factors that amplified the results compared to total sum of its individual part. Besides, in recent work of Aghalayam et al. [25] on coal/biomass blend proves to also show a synergetic effect in terms of reaction rate at various heating rate. Based on his findings, it shows that activation energy of binary mixture at heating rate of 100 K/min is 55 kJ/mol, whereas the activation energy for biomass and coal is 70.1 and 76.6 kJ/mol respectively. In other words, co-gasification of the binary mixtures results in faster reaction time and less amount of gasification agent is needed for complete reaction.

3.6. Effect of Carbonation Temperature

Generally, carbonation process is relied on the operating temperature. So, three different temperatures within the range of 500 to 850 °C is explored in terms of their activation energy. Moreover, temperature has pronounced effect on the diffusivity since diffusivity of CO_2 is dependent on the temperature. Literally, CO_2-CaO reaction proceeds under two controlling reactions regimes, namely as chemical reaction control regime and diffusion control regime [6]. At first, reaction rapidly occurs by heterogeneous surface chemical reaction kinetics. Then, compact layers of $CaCO_3$ begin to develop at outer surface of CaO particles. Thus, reaction rate will decrease due to diffusion limitations of reactants through the layers.

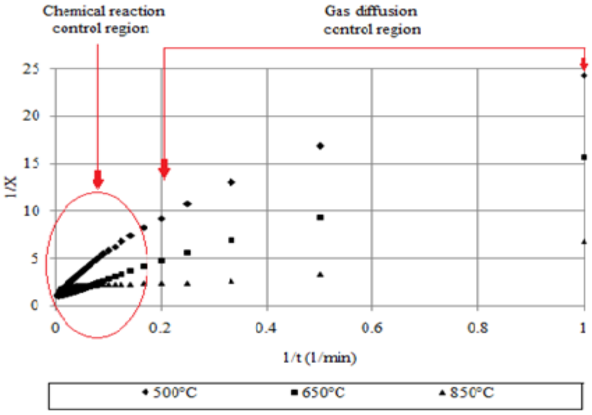

Fig. 3. Plot of 1/X against 1/T

Fig. 3 shows plotted graph of 1/X versus 1/t for each temperature. Based on Fig. 3, carbonation reaction rapidly takes place at elevated temperature by chemical reaction with less effect on diffusion limitation. On the contrary, diffusion control regime is pronounced at lower temperature. Besides, chemical reaction kinetics and diffusivity effect can be further observed in Fig. 4. Based on carbonation part in Fig. 4, it can be observed that there were rapid weight changes for the first few minutes. Moreover, Gupta and Fan [26] reported that the CaO conversion to $CaCO_3$ obtained in this region was governed by chemical reaction control. Subsequently, as reaction times proceeded, slower conversion was observed.

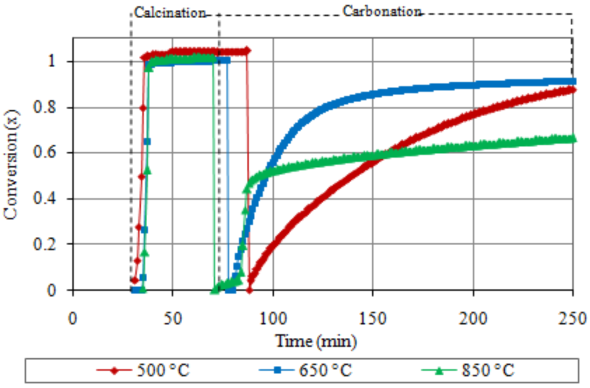

Fig. 4. Conversion plot for calcination and carbonation of cockle shell

Then, separate graph of 1/X versus 1/t for both controlling regimes was plotted. Based on Fig. 5 and Fig. 6, value of k was calculated from the slope and will be further used for kinetic analysis, as in Eq. (4). Fig. 5 and Fig. 6, shows the best fit curve for each region.

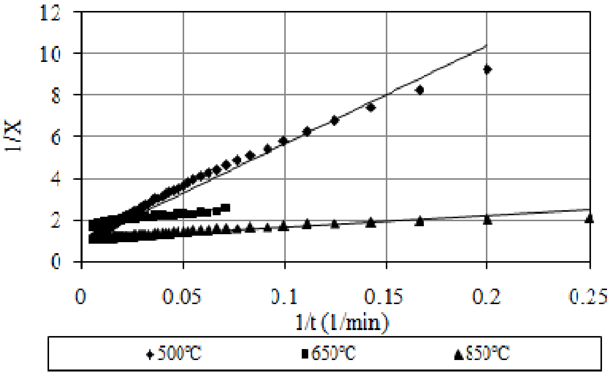

Fig. 5. Plot of 1/X against 1/t for chemical reaction kinetic control

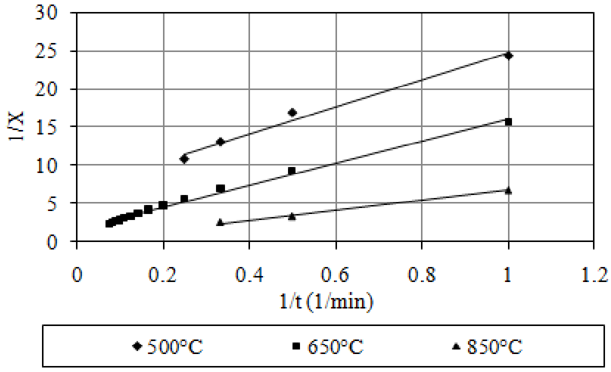

Fig. 6. Plot of 1/X against 1/t for product layer diffusion control

Table 10 summarizes the kinetic analysis of the carbonation process from synthesized cockle shell. Based on these findings, it shows that activation energy for product layer diffusion control is much greater compared to chemical reaction control. In general, it may be due to high resistance caused by product layers of outer CaO particles. As a result, higher kinetic energy is required for the process to take place due to resistance for the CO_2 to diffuse through CaO pores and initiate the carbonation reaction.

Table 10. Kinetics analysis for carbonation reaction

Region	Kinetic parameters	
	E_a (kJ/mol)	In A (1/min)
Product layer diffusion control	40.86	1.16
Chemical reaction control	31.78	4.44

4. Conclusion

Calcination and carbonation of waste cockle shell using the TGA was studied to verify the effects of particle sizes (<0.125-4.00 mm), calcination temperature (750-950 °C), residence time (0.5-1.0 hr), heating rate (10-50 °C /min) and carbonation temperature (500-850 °C) on the reactivity of calcinations and carbonation process. From the economical point of view, utilization of waste cockle shell is attractive due to the low cost and good potential to convert the waste to value-added products. Based on kinetic analyses, it proves that the calcination process is dependent on few variables; reaction temperature, heating rate and particle size. The kinetic analysis on carbonation proves the theoretical framework that gas-solid reaction is controlled by two mechanisms which are surface chemical reaction and diffusion control kinetics and in this case the diffusion control kinetics offer the greater obstacles to the carbonation process studied.

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References

[1] A.J. Awang-Hazmi, A.B.Z. Zuki, M.M. Noordin, A. Jalila, and Y. Norimah, “Mineral composition of the cockle (Anadara granosa) shells of West Coast of Peninsular Malaysia and its potential as biomaterials for use in bone repair”, J. Anim. Vet. Adv, vol. 6 , pp. 591-594, 2007.

[2] M. Mustakimah, and S. Yusup , “Decomposition study of calcium carbonate in cockle shell”, World Engineering Congress 2010, Sarawak, pp. 16-22, 2 -5 August 2010.

[3] R.W. Hughes, D. Lu, E.J. Anthony, and Y. Wu, “Improved long-term conversion of limestone-derived sorbents for in situ capture of CO_2 in a fluidized bed combustor”, Ind. Eng. Chem. Res., vol. 43, pp. 5529-5539, August 2004.

[4] C. Yan, J.R. Grace, and C.J. Lim, “Effects of rapid calcination on properties of calcium-based sorbents”, Fuel Process. Technol., vol. 91, pp. 1678-1686, November 2010.

[5] M. Samtani, D. Dollimore, and K.S. Alexander, “Comparison of dolomite decomposition kinetics with related carbonates and the effect of procedural variables on its kinetic parameters”, Thermochimic. Acta., vol. 392-393, pp. 135-145, September 2002.

[6] D.K. Lee, "An apparent kinetic model for the carbonation of calcium oxide by carbon dioxide", Chem. Eng. J., vol. 100, pp. 71-77, July 2004.

[7] R.H. Borgwardt, “Calcination kinetics and surface area of dispersed limestone particles”, AIChE J., vol. 31, pp. 103-111, January 1985.

[8] Z. Ye, W. Wang, Q. Zhong, and I. Bjerle, “High temperature desulfurization using fine sorbent particles

under boiler injection conditions", Fuel, vol. 74, pp. 743-750, May 1995.

[9] M. Hassibi, "An overview of lime slaking and factors that affect the process", 3rd International Sorbalit Symposium, New Orleans, pp. 1-20, 3-5 November 1999.

[10] P. Sun, J.R. Grace, C.J. Lim, and E.J. Anthony, "Determination of intrinsic rate constant of the CaO- CO_2 reaction", Chem. Eng. Science, vol. 63, pp. 47-56, January 2008.

[11] H.T. Kim, and H.B. Kwon, "Kinetic study of limestone calcination and sulfation reaction under AFBC environment", Environ. Eng. Res. , vol. 3, pp. 105-113, May 1998.

[12] B. Li, X. Wang, M. Yan, and L. Li, "Preparation and characterization of nano-TiO2 powder," Mater. Chem. Phys., vol. 78, pp. 184-188, February 2003.

[13] Telfer M, Zhong Z, Xu Y, Li D, Zhang M, and Zhang D.K, "An experimental study of calcination of South Australian Caroline limestone", Dev. Chem. Eng. Mineral Process., vol. 8, pp. 245-267, 2000.

[14] B.B. Sakadjian, M.V. Iyer, H. Gupta, and L. Fan, "Kinetics and structural characterization of calcium-based sorbents calcined under subatmospheric conditions for the high-temperature CO_2 capture process", Ind. Eng. Chem. Res., vol. 46, pp. 35-42, 2007.

[15] A. van de Runstraat, J. van Grondelle, and R.A. van Santen, "On the temperature dependence of the Arrhenius activation energy for hydroisomerization catalyzed by Pt/Mordenite", J.Catal., vol. 167, pp. 460-463, April 1997.

[16] J.O. Jaber, and S.D. Probert, "Non-isothermal thermogravimetry and decomposition kinetics of two Jordanian oil shales under different processing conditions", Fuel Process. Technol., vol. 63, pp. 57-70, March 2000.

[17] N. Wang, and Q. Qi, "Study on thermal decomposition mechanism and influencing factors of calcium-base desulfurizer," 2011 5th International Conference on Bioinformatics and Biomedical Engineering, (iCBBE), Fuxin, pp. 4142-4145, 10-12 May 2011.

[18] H. Haykiri-Acma, S. Yaman, and S. Kucukbayrak, "Effect of heating rate on the pyrolysis yields of rapeseed", Renew Energ., vol. 31, pp. 803-810, May 2006.

[19] C. Marsh, "CFD modelling of alumina calciner furnaces", Seventh International Conference on CFD in the Minerals and Process Industries, Melbourne, pp. 1-4, 9-11 Dec 2009.

[20] Y. Wang, S. Lin, and Y. Suzuki, "Study of limestone calcination with CO_2 capture: Decomposition behavior in a CO_2 atmosphere", Energy Fuels, vol. 21, pp. 3317-3321, November 2007.

[21] Z. Chen, H.S. Song, M. Portillo, C.J. Lim, J.R. Grace, and E.J. Anthony, "Long-term calcination/carbonation cycling and thermal pretreatment for CO_2 capture by limestone and dolomite", Energy Fuels, vol. 23, pp. 1437-1444, January 2009.

[22] P. Sun, C.J. Lim, and J.R. Grace, "Cyclic CO_2 capture by limestone-derived sorbent during prolonged calcination/carbonation cycling", AIChE J., vol. 54, pp. 1668-1677, June 2008.

[23] P. Sun, J.R. Grace, C.J. Lim, and E.J. Anthony, "The effect of CaO sintering on cyclic CO_2 capture in energy systems," AIChE J., vol. 53, pp. 2432-2442, September 2007.

[24] H.A. Long, and T. Wang, "Case studies for Biomass/coal co-gasification in IGCC applications", ASME Turbo Expo 2011, Vancouver, pp. 1-15, 6-10 June 2011.

[25] P. Aghalayam, J. Baretto, A. Ganesh, and S. Kauchali, "Pyrolysis of sawdust-lignite blends", 25th International Pittsburgh Coal Conference, Pittsburg, 29 September - 2 October 2008.

[26] H. Gupta, and L. Fan, Carbonation-calcination cycle using high reactivity calcium oxide for carbon dioxide separation from flue gas. Ind. Eng. Chem. Res., vol. 41, pp. 4035-4042, July 2002.