

The Effect of Acid Treatment on the Limestone for Calcium Looping Process



N. F. Afandi, M. Amirul Mustaqim, Abreeza Manap, R. Adawiyah Zainuddin, N. F. Kadir

Abstract: Calcium Looping Process (CLP) is one of the carbon capturing technology, in which the sorbent material, CaO is absorbing CO₂ from flue gases in power plant. However, good sorbent material have been facing several drawbacks such as low generability, and low absorption capacity. Acid treatment can improve the physical properties such as surface area of the sorbent material. This study was aim to synthesize and investigate the effect of acid treatment on the limestone as sorbent material using mixing method in order to maximize the CO₂ carrying capacity. The amount of 0 ml, 2 ml, 4 ml, 6 ml, 8 ml and 10 ml of oxalic acid were varied in this study. The result demonstrated that 6 ml of oxalic acid produces highest hardness and high surface area and pore volume size, which favorable to be used as sorbent material in CLP process.

Keywords: Acid treatment, Calcium Looping process, limestone, sorbent material

I. INTRODUCTION

Calcium Looping Process (CLP) is a technological process for carbon capturing that can be utilizes in a power plant to reduce the carbon emissions. The CLP is a post combustion process that use solid CaO based sorbents to absorb CO₂ and remove it from flue gasses at high temperature [1]. The emitted flue gases that contain primarily CO₂ can be easily captured by sorbent material. In CLP, the solid sorbent are cycled in between calciner and carbonator reactor where absorption activity take place in carbonator reactor.

The CO₂ captured by CaO is separated in calciner with the presence of heat. At this phase, addition of limestone is needed in order to compensate the loss of CaO [2]. Therefore, low make up rate is needed in order to reduce the production cost. In CLP, CaO precursor is used from natural limestone due to low cost and abundantly can be found especially country like Malaysia.

Moreover, the effectiveness and the efficiency of sorbent will be degrade after several cycles due to the structure of the sorbent are not stable at high operating temperature especially in calciner [3]. This is mainly due to the continuous cycle in between carbonation and calcination process that occur inside the reactors that convert the CaO to CaCO₃. The carrying capacity tend to decrease after several cycles resulted from sorbent degradation. Therefore, Nicholas et al. [4] stated that the presence of aluminum (Al) in CaO can enhance the durability of capturing and carrying capacity of sorbent due to the properties of Al that can increase the strength of sorbent or CaO material. Moreover, Hamid et al. [5] investigated the usage of inert material such as Al, Zr, Y and Mg with CaO as sorbent material. It was found that the Zr-stabilized and Al-stabilized shows better results in CO₂ uptake compare to other inert material. However, the preparation costs for Zr-stabilized is higher than other material. Therefore, the best inert material that can reduce the operating costs and has good CO₂ carrying capacity is Al-stabilizers.

In addition, acid treatment was used to increase surface area of sorbent material in order to maximize the CO₂ carrying capacity. Juan Miranda-Pizzara et al. [6] was investigating the CaO as sorbent material using acetic acids and found that the energy penalty was able to be reduced by the presence of acetate because acetate can lower the temperature needed in calciner operation. Therefore, the CO₂ capture capacity and reactivity of sorbent can be increase with the presence of acid [7-8]. Moreover, Ridha et al. [9] studied that oxalic acid was found to have good absorption of CO₂ compared to other acids such as formic acid, and vinegar. The oxalic acid prepare the structure of the sorbent to have smaller pore diameter, higher surface area resulted in having more porous structure hence increase the CO₂ absorption than other sorbents material, However, the composition of acid is play an important role in order to produce good sorbent material.

Manuscript published on November 30, 2019.

* Correspondence Author

N. F. Afandi*, College of Engineering, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia; Institute of Sustainable Energy (ISE), Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia

M. Amirul Mustaqim, College of Engineering, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia.

Abreeza Manap, College of Engineering, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia; Institute of Sustainable Energy (ISE), Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia

R. Adawiyah Zainuddin, Uniten R&D Sdn Bhd, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia

N. F. Kadir, Uniten R&D Sdn Bhd, Universiti Tenaga Nasional, Jalan IKRAM-UNITEN, 43000 Kajang, Selangor, Malaysia

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an [open access](http://creativecommons.org/licenses/by-nc-nd/4.0/) article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

There were many methods were used to synthesize the sorbent with inert material such as sol-gel combustion, milling, and hydration. However, sol-gel combustion produces sorbent with small carrying capacity due to the insufficient time during chelating process [10]. Meanwhile, hydration method can reduce the durability of sorbent material after several cycles in CLP process [3]. Moreover, Wei et al. [11] stated that the mixing method can perform better than dry powder processing systems to generate homogenous mixture. Therefore, this research focuses on synthesizing and investigating the effect of oxalic acid using Malaysia limestone as a sorbent material in CLP process using mixing method. In this research, various volume such as 0 ml, 2 ml, 4 ml, 6 ml, 8ml and 10 ml of oxalic acid were varied in order to determine the best composition of limestone with Al₂O₃ since no extensive studies were found on synthesizing Malaysia limestone with Al₂O₃ as sorbent material for CLP application.

II. METHODOLOGY

In this research, limestone from GCCP Resources was used as a sorbent material and was mixed with aluminum oxide from Sigma Aldrich. Firstly, the limestone was crushed using pestle and mortar. Then, the small particles was further crushed and sieved to get the fine powder form using the laboratory grinder for particle size less than 1mm. The limestone was dissolved with distilled water and stirred thoroughly using ultrasonic bath. Then aluminum oxide was added into the dissolved limestone in beaker. After that, oxalic acid was added at different volume in order to characterize and analyze the properties such as nano-hardness, particle size, surface area and pore volume size of the limestone as carbon capture. The volume of 0 ml, 2ml, 4ml, 6ml, 8ml and 10 ml were used to identify which amount of acid can produce a good sorbent. Later, the sorbent solution was heated inside the furnace (TDW KSW-6-16) at 300°C for 1 hour to become a powder form. Next, it was cooled down at room temperature for 24 hours.

Morphology analysis and elemental analysis of the samples were characterized using Scanning Electron Microscopy (SEM, JEL JSM-6010PLUS/LV). Powder composition was analyzed using X-ray Diffraction (XRD, SHIMADZU 6000) at the scan range of 10° to 90° at 30kV and 20mA of voltage and current, respectively. The crystallite size was obtained using the Scherer's equation by using [12];

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where, L is the crystallite size, k is crystallite shape constant, 0.9, λ is X-ray wavelength, β is the line broadening which is Full Width at Half maximum (FWHM) and θ is the angle of diffraction peak. Moreover, particle size distribution and nano hardness was measured using ImageJ analysis and Nano indentation, respectively.

Surface area and pore volume size was analyzed using Brunauer–Emmett–Teller (BET) analysis.

III. RESULTS AND DISCUSSIONS

Results



Fig. 1 Morphology of limestone – Al₂O₃ with (a) No Acid (b) 2 ml Oxalic acid

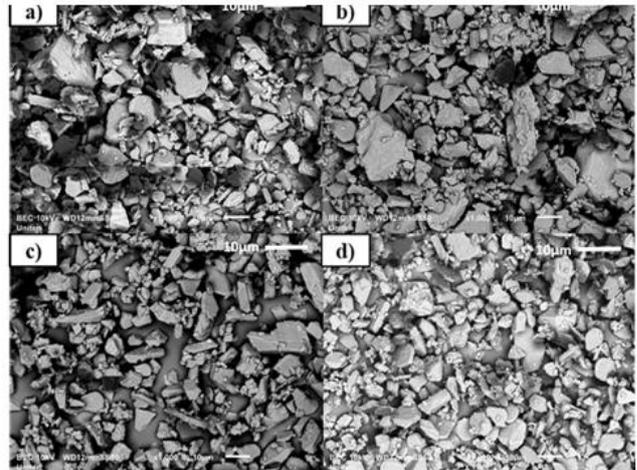


Fig. 2 Morphology of limestone-Al₂O₃ at volume (a) 0 ml (b) 2 ml (c) 4 ml (d) 6 ml of oxalic acid

Figure 1(a) and 1(b) shows the morphology of limestone-Al₂O₃ with no acid and 2ml oxalic acid, respectively. The limestone-Al₂O₃ treated with oxalic acid are having similar morphology with without acid treatment. The presence of Al₂O₃ in the limestone reduce the dissolution of limestone since Al₂O₃ acts as a binder for the limestone in order to strengthen the sorbent [4]. Therefore, small amount of acid are not significantly affect the particle size. Hence, addition of more amount of oxalic acid is needed to reduce the particle size since the presence of oxalic acid can decrease the particle size, and increase the surface area. R. Sun et al. [7,8] stated that acid treatment can increase the reactivity of sorbent since it increases the surface area due to the decreases of particle size hence can increase the CO₂ capture capacity. Figure 2 shows the morphology of limestone-Al₂O₃ at 0 ml, 2 ml, 4 ml and 6 ml of oxalic acid.

The result shows that the morphology of limestone- Al_2O_3 is in irregular shape for 0 ml, 2 ml, 4 ml and 6 ml of oxalic acid. This is possibly due to the oxalic acid only acts at the surface of the sorbent material in order to create porous structure. This result clearly can be seen in Table 2 that the presence of acid at 6 ml oxalic acid can increase surface area from $0.302 \text{ m}^2/\text{g}$ at 0 ml oxalic acid to $0.4904 \text{ m}^2/\text{g}$.

Figure 3 shows XRD result at different volume of oxalic acid which were 0 ml, 2ml, 4 ml and 6 ml. Presence of limestone and Al_2O_3 can be seen corresponding to the JCPDS 47-1743 [13] and JCPDS 46-125 [14], respectively, where the limestone matched with rhombohedra-cubic phase and Al_2O_3 was crystallized in a orthorhombic crystal structure. The XRD shows some increasing of peaks when adding oxalic acid from 0 ml to 2 ml at 31.12° . This result indicate the increases of the Al_2O_3 in the samples occurs due to the dissolution of limestone with the presence of oxalic acid. However, the formation of Al_2O_3 becomes more stable with the presence of 6 ml oxalic acid that may block the further reaction between limestone and oxalic acid and causes inhibition of limestone degradation.

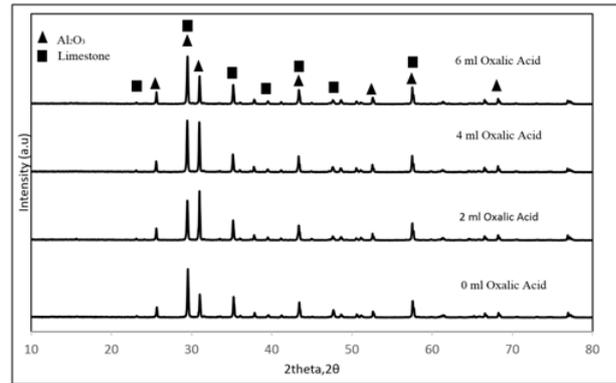


Fig. 3 XRD analysis of limestone- Al_2O_3 at different volume of oxalic acid

Table. 1 The crystallite size of all samples

Samples	Crystallite size (nm)
0 ml acid	65
2 ml acid	64
4 ml acid	63
6 ml acid	61

Table. 2 Properties of limestone- Al_2O_3 with oxalic acid at different volume of acid

Samples	Particle size (μm)	Surface area (m^2/g)	Pore volume (cm^3/g)
0 ml Acid	24.89	0.3020	0.00151
2 ml Acid	19.53	-	-
4 ml Acid	15.72	-	-
6 ml Acid	11.96	0.4904	0.03654

Table 1 shows the crystallite size of the samples when varying the amount of oxalic acid. This result indicates that increases of amount of oxalic acid cause slightly decreases of crystallite size. This result is in agreement with Tsega et al. [12] that the crystallite size decreases when the acid content increased. However, the decreases in the crystallite size does not show significant change when varying the amount of oxalic acid. This is probably due to the less change in lattice parameters as shown in Fig 3 due to the presence of Al_2O_3 [16]. Meanwhile, Table 2 shows the properties of limestone- Al_2O_3 at 0 ml, 2 ml, 4 ml, and 6 ml oxalic acid. The mean particle size was calculated based on particle size distribution shown in Fig. 4. The particle size slightly decreases when volume of acid is added to the limestone- Al_2O_3 . This is due to the decomposition of limestone caused by oxalic acid that reduces the mass and weight of the particles resulting the decrement of particle size [6]. Smaller particle size can increase the surface area hence increase the pore volume of the structure [7,8]. Moreover, the surface area of samples increase from $0.302 \text{ m}^2/\text{g}$ to $0.4904 \text{ m}^2/\text{g}$ for 0 ml oxalic acid to 6 ml oxalic acid, respectively. Then, the pore volume size at 0 ml is $0.001510 \text{ cm}^3/\text{g}$ and 6 ml is $0.03654 \text{ cm}^3/\text{g}$. This result shows decreases in particle size can increase the surface area and pore volume size of the samples. Moreover, addition of Al_2O_3 can limit the

dissolution of limestone and surface area. However, increases the amount of acid at 6 ml of oxalic acid can increase the surface area and pore volume size of the sorbent material.

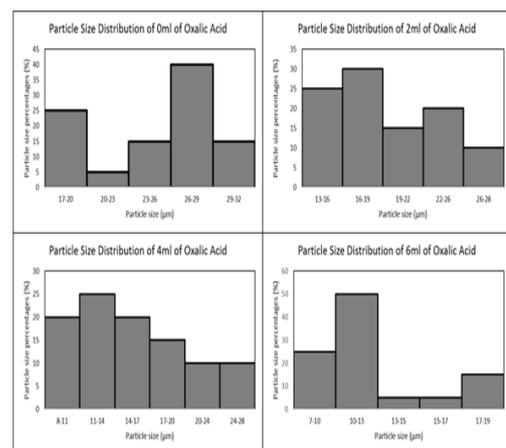


Fig. 4 Particle size distribution of limestone- Al_2O_3 at different volume of oxalic acid

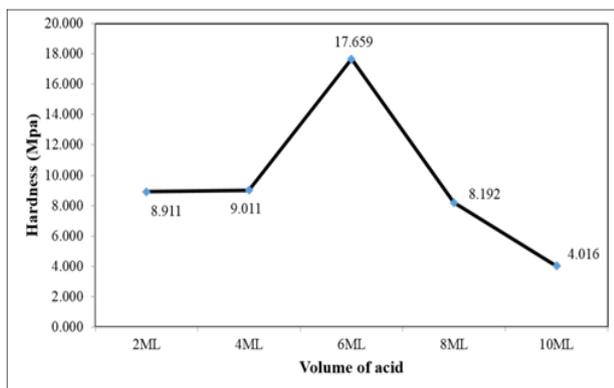


Fig. 5 Nano hardness of limestone- Al_2O_3 at different volume of oxalic acid

Figure 5 shows Nano-hardness of limestone- Al_2O_3 at different volume of oxalic acid. The 8 ml and 10 ml of oxalic acid were synthesized in order to find optimum amount of oxalic acid used. The result indicates the 6ml of oxalic acid has the highest hardness, which is 17.66 MPa. From 0ml to 6ml, the hardness increase probably due to the low concentration of acidic solution. Deepthi et al. [15] stated that acidic environment can lowers the hardness and clearly can be seen when using 8ml and 10ml. In CLP, the cyclic process of calcination-carbonation of limestone require the long-term sustainability of sorbent material in order to reduce the make-up rate, hence reduce the production cost. Therefore, 6 ml is an optimum used of oxalic acid volume for this limestone since it produces the small particle size, high surface area and has the highest hardness.

IV. CONCLUSIONS

In this research, effect of acid treatment on the limestone- Al_2O_3 as sorbent material were investigated. The characterization data showed that limestone from Malaysia with Al_2O_3 were successfully synthesized in this process and acid treatment did affect several properties such as hardness, surface area and pore volume size of this sorbent material. This research succeeded in producing limestone- Al_2O_3 using 6 ml oxalic acid with nano-hardness at 17.659 MPa, surface area at $0.4904 \text{ m}^2/\text{g}$ and pore volume size at $0.0364 \text{ cm}^3/\text{g}$, which favorable to be used as sorbent material in CLP process.

ACKNOWLEDGMENTS

The authors acknowledge Universiti Tenaga Nasional, UNITEN R&D Sdn Bhd and Institute of Sustainable Energy (ISE) of UNITEN for the lab facilities and the financial supports from the TNB Seed Fund (U-TG-RD-18-28), and UNITEN UNIIG grant (J510050867).

REFERENCES

1. A. Rolfe, Y. Huang, M. Haaf, S. Rezvani, A. Dave and N.J.Hewitt, *Energ Proc.* 142, 3447-3453 (2017).
2. M. Evans, V. Manovic, E.J. Anthony, *Appl Energ.* 180, 722-742 (2016).
3. K. Wang, P.F. Zhao, X.Guo, D. Han, Y. Chao, *Energy Convers Manag.* 86, 1147-1153 (2014).

4. N. Florin, P. Fennell, *Energy Procedia.* 4, 830-838 (2011).
5. Hamid R, R. Maria, C. Iliuta, *Chem. Eng. J.* 232, 280-289 (2013).
6. J. M. Pizarro, A. Perejón, J. M. Valverde, L. A. Pérez-Maqueda, P. E.Sánchez-Jiménez, *Fuel.* 196, 497-507 (2017).
7. R. Sun, Y.J. Li, J. L. Zhao, C. Liu, C. Lu, *Int. J. Hydrog. Energy.* 38, 13655-13663 (2013).
8. R. Sun, Y.J Li, S. Wu, C. Liu, H. Liu, C. Lu, *Powder Technol.* 233, 8-14 (2013).
9. F.N. Ridha, V. Manovic, A. Macchi, M.A. Anthony, E.J. Anthony, *Fuel Process Technol.* 116, 284-291 (2013).
10. C. Luo, Y. Zheng, C. Zheng, J. Yin, C. Qin, B. Feng, *Int. J. Greenh. Gas Con.* 12, 193-199 (2013).
11. D Wei, R Dave, R Pfeffer, *J. Nanopart Res.* 4, 21-41 (2002).
12. M. Tsega, F.B. Dejene, *Heliyon.* 3, e00246 (2017).
13. QW. Zhan, C.X. Qian, "Synthesis of calcium carbonate and calcium sulfate by bio-activated method and application in stabilization of sand particles" (International Conference on Energy, Power and Environmental Engineering, 2017), pp. 488-494.
14. Z. Khoshkhan, M. Salehi, *Journal of Nanostructures.* 4, 443-448 (2014).
15. V. Deepthi, E. Mallikarjun, B. Nagesh, P. Mandava, *J Conserv Dent.* 21, 408-412 (2018).
16. D. Guzman, C. Garcia, A. Soliz, R. Sepulveda, C. Aguilar, P. Rojas, I. Iturriza, C. Luno-Bilbao, *Metals.* 8, 417 (2018).