Int'l Journal of Advances in Chemical Engg., & Biological Sciences (IJACEBS) Vol. 1, Issue 1(2014) ISSN 2349-1507 EISSN 2349-1515

CO_2 Adsorption at Thermophilic Temperature on Alkanolamine Impregnated Activated Carbon

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***Abstract*---**Monoethanolamine (MEA) and diethanolamine (DEA) were impregnated onto activated carbon (AC) by the wet impregnation method to improve its adsorption capacity and selectivity towards CO_2 under thermophilic conditions (40°C and 60°C). The wet impregnation of AC with 3% w/v MEA and DEA gave the mass loading ratio (the impregnating agent:AC) of 0.15 g/g and 0.14 g/g, respectively. FT-IR spectra at frequencies between 3440-3430 cm^{-1} confirmed the deposition of MEA and DEA onto AC. At 40°C, the breakthrough and CO_2 saturation capacities of the native AC and the modified AC were not noticeably different. However, at 60°C, the CO_2 saturation capacity of the AC-DEA was almost doubled. At 60°C, the breakthrough and CO_2 saturation capacities of the native AC were 3.14 mg/g and 4.92 mg/g, the AC-MEA 4.64 mg/g and 7.62 mg/g and the AC-DEA 5.00 mg/g and 8.40 mg/g.

***Keywords*---**Activated carbon, alkanolamines, CO_2 adsorption, thermophilic

I. INTRODUCTION

BIOGAS is an important renewable energy source. Biogas is produced by the anaerobic digestion of biodegradable materials such as agro-industrial waste, farm waste and municipal solid waste. Biogas production can be operated under either mesophilic temperatures (between 25°C and 40°C) [1]-[4] or thermophilic temperatures (between 40°C and 60°C) [3]-[5]. Biogas comprises of methane (CH_4) (55-80%), carbon dioxide (CO_2) (20-45%), trace amounts of hydrogen sulfide (H_2S) (1000-5000 ppm), moisture and other impurities [6]-[8]. The biogas can be utilized for heat production, generation of electrical power and as substitute natural gas. In order to upgrade biogas quality and to reduce risks of machinery and instruments deterioration, the removal of impurities in biogas is a crucial step. The main components that should be removed during biogas upgrading are CO_2, H_2S and moisture. In the presence of moisture in the gas pipeline, CO_2 and H_2S will form carbonic acid (H_2CO_3) and sulfuric acid (H_2SO_4), respectively.

AC has been used for many applications in gas adsorption, separation and purification [9], [10]. Surface characteristics is one of the most important features of AC. The adsorption capacity of AC was determined by the physical properties such as surface area, pore size and pore volume. These features are important for the physical adsorption. However, the physical adsorption capacity of the adsorbent gradually decreased with increasing temperatures. Therefore, the modification of the adsorbent is necessary for the CO_2 adsorption at high temperatures. Amine-based chemicals have been used as the impregnating agent onto AC to improve the adsorption capacity of CO_2 at moderate temperatures [11]. Impregnation process was successfully used as the method to introduce amine-based molecules onto the surface of AC. The modified AC was found to have increased selectivity towards polar molecules.

In this study, the reactive adsorbent was prepared by the wet impregnation of primary alkanolamine (MEA) and secondary alkanolamine (DEA) onto AC for the separation of CO_2 from a gas mixture by adsorption at thermophilic temperatures. Effects of increasing temperatures in the thermophilic range on the breakthrough and CO_2 saturation capacities of the native AC and the modified AC were compared. The potential of the modified AC for uses in biogas upgrading was discussed.

II. EXPERIMENTAL

A. Materials

Commercially available AC (C. Gigantic Carbon Co., Ltd., Thailand) produced from steam activation of palm shell was used as the adsorbent. All chemicals were of analytical grade. MEA and DEA (Carlo Erba, Italy) purity were higher than 99%. Their physical properties are listed in Table I. Methanol (Carlo Erba, Italy) was used as the solvent. CO_2 (HP 99.995%) and N_2 (HP 99.995%) were purchased from Thonburiwattana Ltd., Part (Thailand). Distilled water was used throughout the study.

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http://dx.doi.org/10.15242/IJACEBS.C0114030

TABLE I
PHYSICAL PROPERTIES OF ALKANOLAMINES.

Properties	MEA	DEA
Molecular formula	C_2H_7NO	$C_4H_{11}NO_2$
Molar mass (g/mol)	61.08	105.14
Density (g/cm^3)	1.012	1.097
Melting point (°C)	10.3	28
Boiling point (°C)	170	271
Solubility in water	Miscible	Miscible
Vapor pressure (Pa)	64 (20°C)	<1 (20°C)

B. Wet impregnation

The procedure was followed those of [12]-[15]. The AC sample was washed with distilled water to remove fines and dirt and then dried at 110°C for 24 h. One g of AC was immersed in 5 mL of 3% w/v MEA in methanol and in 5 mL of 3% w/v DEA in methanol. The samples were agitated at an ambient temperature for a period of 15 min and were placed in a water bath at 70˚C to allow slow evaporation of the solvent. Finally, the modified AC with MEA (AC-MEA) and the modified AC with DEA (AC-DEA) were dried in a vacuum oven (Model VO 500, Memmert, Germany) overnight.

The quantity of impregnating agents deposited onto the adsorbent was calculated from the difference between the initial dry weight and the final dry weight of the same sample after the modification procedure. The mass loading ratio of impregnating agents was the quantity of the impregnating agents normalized by the original adsorbent weight.

C. Characterization of the Modified Adsorbent

BET surface area, pore volume and pore size of the native and the modified adsorbent were determined by an nitrogen adsorption method at -196°C (Autosorb-1C, Quantachrome, USA). The BET surface area was evaluated based on the Brunauer, Emmett and Teller (BET) method. Pore volume and pore size from the desorption isotherm were calculated by the Barrett, Joyner and Halenda (BJH) method. Morphology of the native and the modified adsorbent were investigated from the magnified images taken by a scanning electron microscope (SEM) (Model JSM-5800LV, JEOL, Japan). The IR spectra of the native and the modified adsorbent were investigated by Fourier Transform Infrared (FT-IR) spectrometer (Model EQUINOX 55, Bruker, Germany) using the KBr technique. The sample peaks in the wavelength range of 4000-400 cm^{-1} were analyzed.

D. Equipment and Dynamic Adsorption Test

Schematic diagram of the dynamic CO_2 adsorption system are shown in Fig. 1. The main equipment of the adsorption system consisted of a gas supply unit, a gas mixing chamber, solenoid valves, cartridge heaters, an adsorption column, a vacuum pump and a gas monitoring system. The flow rates of CO_2 and N_2 streams to the gas mixing chamber were controlled by two rotameters (Dwyer Instruments Inc., USA). The gas mixture composition was 40%/60% CO_2/N_2 (v/v), corresponding to the CO_2 concentration in the gas mixture of 4974 ppm. The column pipelines were made of polyurethane and stainless steel with an inside diameter of 0.65 cm. The adsorption column was equipped with four automatic solenoid valves (Swagelok Model 133-SR, 1.379 MPa maximum, pneumatic spring return actuator with SS-43GS6-33CB valve). The adsorption column made of stainless steel (2 cm internal diameter and 84 cm length) was packed with about 148 g of the native AC, 165 g of AC-MEA and 170 g of AC-DEA. Temperature of the gas stream was controlled by two cartridge heaters (Model CH-02, AC 220 V, 500 W, Primus Co., Ltd, Thailand) coupled with the digital temperature controller (Model 600-R-D-R-R-0, GEFRAN, Italy). The adsorption temperature within the column was maintained using heating tape (AC 220 V, 100 W, SL Heater Co., Ltd, Thailand) covered with insulator. Two thermocouples (Type K, Model TSK-03, Primus Co., Ltd, Thailand) were positioned at the column inlet and outlet for measuring the gas stream temperatures. A vacuum pump (30 kPa, AC 220 V, 0.75 kW, GAST Manufacturing Corp., USA) was employed to evacuate gas before and after each experiment. A gas chromatograph (GC-TCD, GC-2014, SHIMADZU, Japan) was used to measure the concentration of CO_2 from the outlet of the adsorption column.

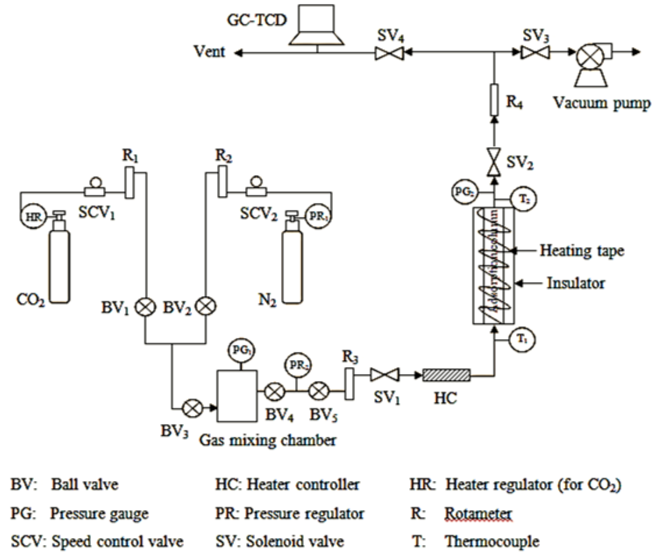


Fig. 1 Schematic diagram of the dynamic CO_2 adsorption system.

The CO_2 uptake capacity of the adsorbent was determined from breakthrough curves. The dynamic CO_2 adsorption was investigated at the thermophilic temperature ranges (40°C and 60°C). Before each experiment, the system was evacuated to 30 kPa by the vacuum pump. Three steps adsorption cycle were operated: (I) pressurization, (II) adsorption and (III) depressurization, via four automatic solenoid valves. The flow rate of inlet gas mixture during the pressurization, adsorption and depressurization steps was 2000 cm^3 STP/min. The pressure during the pressurization and the adsorption steps was 300 kPa. The adsorption step was operated until the breakthrough and the saturation of CO_2 were reached. The breakthrough capacity (BC) and the saturation capacity (SC) of CO_2 were calculated according to (1) and (2), respectively, [15], [16].

$$BC_{CO_2} = \frac{44QC_a}{22.4\times10^6 m_i}\left(t_b - \int_{t_0}^{t_b}\frac{C_{(t)}}{C_a}dt\right) \quad \text{(mg/g)} \quad (1)$$

$$SC_{CO_2} = \frac{44QC_a}{22.4\times10^6 m_i}\left(t_a - \int_{t_0}^{t_a}\frac{C_{(t)}}{C_a}dt\right) \quad \text{(mg/g)} \quad (2)$$

where C_a is the CO_2 concentration in the gas mixture at the bed entrance (ppm), $C_{(t)}$ is the CO_2 concentration in the gas mixture at time t (ppm), m_i is the initial dry weight of the adsorbent (g), Q is the volumetric flow rate of the gas mixture at the bed entrance (cm^3/min) and t_0, t_b and t_a are the time when the content of CO_2 in the gas mixture becomes higher than zero, a breakthrough point (194 ppm) and C_a, respectively (s).

III. RESULTS AND DISCUSSION

From a preliminary experiment, we found that the wet impregnation with high concentrations of MEA and DEA reduced the surface area and the adsorption capacity of the adsorbent dramatically. Therefore, the concentration of 3% w/v was used for the modification, which gave the loading of MEA and DEA onto AC of 0.15 g/g and 0.14 g/g, respectively. The corresponding molar amounts of the impregnating agents loading onto AC were 2.41 mmol/g and 1.39 mmol/g, respectively. It was noted that the numbers of the MEA molecules which can be loaded on the AC was almost double those of the DEA molecules.

A. Characterization

Table II shows the surface properties of the native and the modified AC. The total surface area of the native AC dropped by 51% and 18% after the impregnation with MEA and DEA, respectively. Pore volume of the modified AC was also decreased substantially indicating that the alkanolamines filled in the inner pores of the AC. The reductions in the surface area and the pore volume of the AC-MEA were more pronounced than those of the AC-DEA. The results suggested that higher numbers of MEA molecules may reach the inner pores of the AC due to its smaller molecular structure.

TABLE II
SURFACE PROPERTIES OF THE NATIVE AND THE MODIFIED AC WITH ALKANOLAMINES.

Parameters	Native AC	AC-MEA	AC-DEA
BET surface area (m^2/g)	797.5	393.4	652.6
Pore size (Å)	23.73	23.15	23.38
Pore volume (cm^3/g)	0.43	0.24	0.38

Fig. 2 shows the SEM micrographs of (a) the native AC, (b) AC-MEA and (c) AC-DEA at a 5000x magnification. Pore mounts can be seen on all samples and the coverage of pore mounts by the impregnating agents were not obvious.

The FT-IR spectra of the samples are summarized in Table III. FT-IR spectra of the native AC at frequencies of 3434 cm^{-1} and 2919 cm^{-1} indicated the presence of hydroxyl group (-OH) of phenol and methylene group ($-CH_2-$), respectively. The aldehyde group (-CHO) was also detected at 2851 cm^{-1}. The spectrums at 1580-1540 cm^{-1} were assigned to ring vibration in a large aromatic skeleton. The spectrums at a frequency around 1465 cm^{-1} and 1370 cm^{-1} were an indication of the presence of pyrones and aromatic groups, respectively. The strong spectrum at a frequency of 1024 cm^{-1} was attributed to the asymmetric stretching of Si-O band. These FT-IR spectrums have been shown to indicate the common chemical functional groups of AC [17]. However, the presences of spectrums at frequencies of 3440-3430 cm^{-1}, which were attributed to the N-H stretching vibration [13], were special for the modified AC.

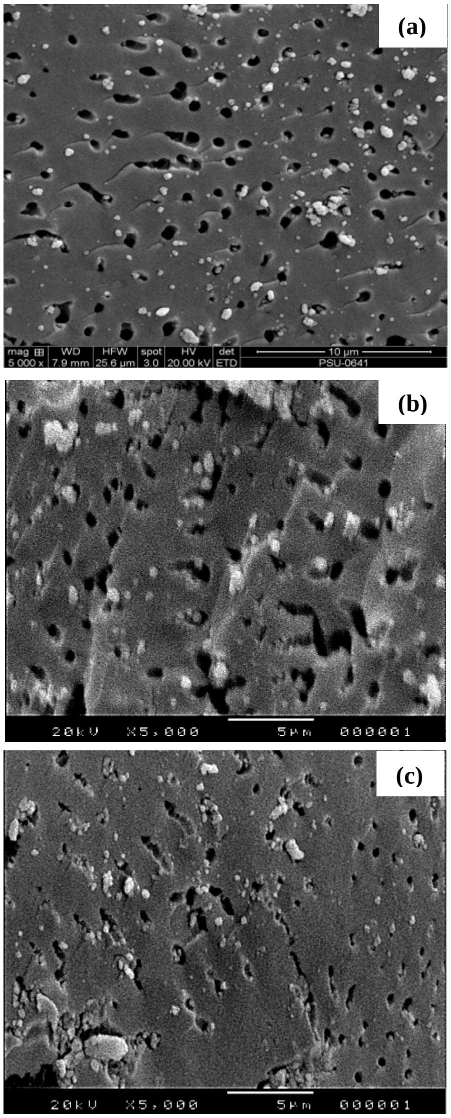
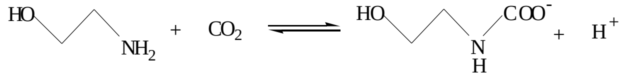


Fig. 2 SEM micrographs of (a) native AC, (b) AC-MEA and (c) AC-DEA at a 5000x magnification.

TABLE III
VIBRATIONAL FREQUENCIES OF FT-IR SPECTRA OF THE MODIFIED AC WITH MEA AND DEA.

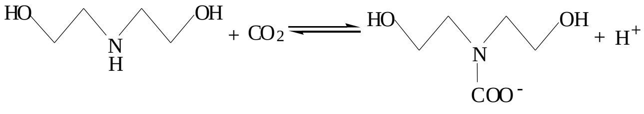
Adsorbent	Wavelength (cm^{-1})		
AC-MEA	3430 (N-H stretching)	1655 (N-H bending)	1393 (C-N stretching)
AC-DEA	3440 (N-H stretching)	1641 (N-H bending)	1368 (C-N stretching)

Based on the presence of the amine groups on the surfaces of the AC-MEA and AC-DEA, it was expected that the CO_2 adsorption on the AC-MEA and the AC-DEA are based on the reactions between alkanolamines and CO_2 [18]. The reaction yielded carbamate ions ($RNHCOO^-$) as the product. The reaction mechanism (3) shows the formation of the carbamate ion from the reactive between a primary amine and CO_2 [13], [18], [19]. A similar reaction between a secondary amine and CO_2 is shown in reaction (4).



(3)

(MEA) (MEA carbamate ion)



(4)

(DEA) (DEA carbamate ion)

B. Comparative CO2 Adsorption Capacities of the Native and the Modified AC

The representative breakthrough curves of CO_2 on the native and the modified AC with MEA and DEA at 40°C are shown in Figs. 3(a) and 60°C in Fig. 3(b). C_0 and C are the concentration of CO_2 in the feed and the exit stream, respectively. The breakthrough capacity and the saturation capacity of the three adsorbents at 40°C and 60°C are summarized in Table IV.

At 40°C, the breakthrough capacities of the three adsorbents were more or less the same, while the saturation capacity of the native AC was higher than the modified AC.

At 60°C, the breakthrough capacities of the modified AC were greater than those of the native AC. Especially for the AC-DEA, the breakthrough capacity and the saturation capacity of the modified AC was 1.6-1.7 times that of the native AC.

The effects of the increasing temperatures on the CO_2 adsorption capacities were found to be different for the native AC and the modified AC. For the native AC, the increase in the adsorption temperature decreased the CO_2 adsorption capacities. The CO_2 breakthrough and saturation capacities of the native AC at 60°C were decreased by 18% and 26%, respectively. The results may be explained by the underlying adsorption mechanism. For the native AC, the adsorption mechanism is only a physical adsorption [13]. In physical adsorption, the attraction forces between CO_2 molecules and the adsorbent surface are due to dipole-dipole interactions (also known as the van der Waals force), which are relatively weak. Typically the heat of physisorption is usually in the range of 20-40 kJ/mol. Due to the nature of this force, the adsorbate molecule will desorb from the adsorbent surface when the temperature is raised.

For the modified AC, the increase in the adsorption temperature increased the CO_2 adsorption capacities. The CO_2 breakthrough and saturation capacities of the AC-MEA and the AC-DEA were increased by 18-22% and 28-30%, respectively. The results suggested that the main underlying mechanism was the chemical adsorption. For the chemical adsorption or reactive adsorption, a chemical bond is formed between the CO_2 molecule and the active adsorbent surface. Chemisorption is typically characterized by the formation of a monolayer, which involves the exchange or sharing of electrons between the CO_2 molecule and the alkanolamines. Chemisorption is known to be much stronger than physisorption. The mechanism gives an average adsorption energy of -69.13 kJ/mol [20], [21]. Amine-CO_2 reactions in aqueous solution usually occur with a stoichiometry of 1:2 CO_2:amine.

The greater CO_2 adsorption capacity of the native AC at 40°C suggested that the physical adsorption is dominant over the chemical adsorption and that the modification of the adsorbent was not necessary for the CO_2 separation at this temperature. In contrast, at 60°C, the results suggested that chemical adsorption is dominant. Even though the surface area and the pore volume of the AC were reduced by the wet impregnation, the CO_2 adsorption capacities of the modified AC were greater than those of the native AC at this elevated temperature.

When comparing the adsorption capacities of the AC-MEA and the AC-DEA, both the breakthrough capacity and the saturation capacity of the AC-DEA were significantly higher than those of the AC-MEA ($P<0.05$). The results suggested that the available surface area was still important for the chemical adsorption. It was also noted that the uptake rate of CO_2 on the AC-DEA to its saturation point was longer time than that on the AC-MEA. The results suggested that the impregnated DEA caused more steric hindrance on the transport of CO_2 in the pores [11], [13] than the impregnated MEA.

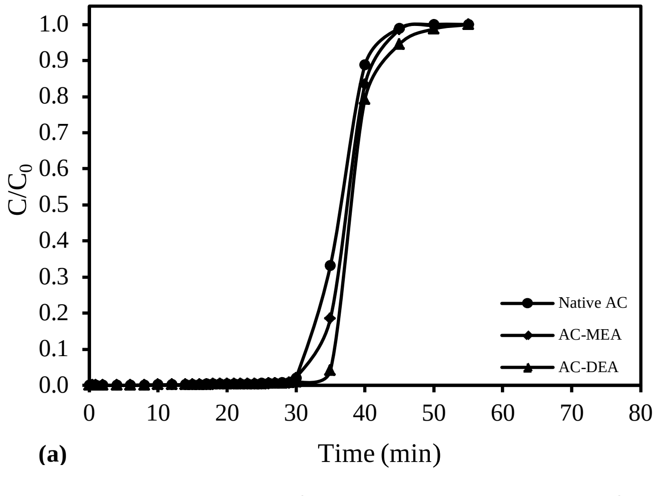


Fig. 3 Breakthrough curves of CO_2 on the native and the modified AC with MEA and DEA at (a) 40°C and (b) 60°C.

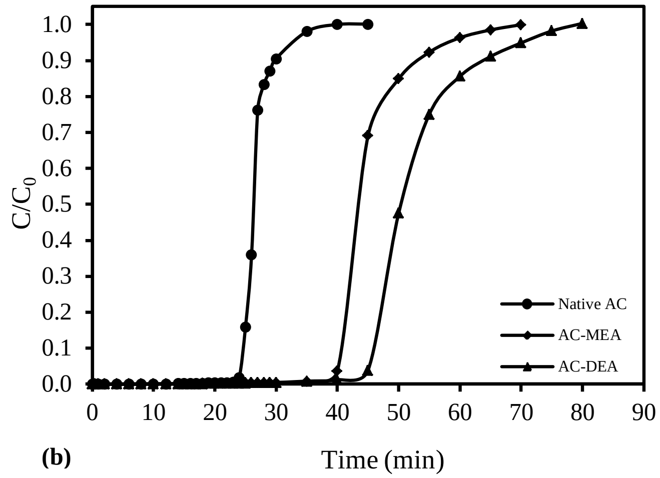


Fig. 3 Breakthrough curves of CO_2 on the native and the modified AC with MEA and DEA at (a) 40°C and (b) 60°C (Cont').

TABLE IV

BREAKTHROUGH AND SATURATION CAPACITIES OF CO_2 ON THE NATIVE AND THE MODIFIED AC WITH MEA AND MEA AT 40°C AND 60°C.

Adsorbent	BC (mg/g)		SC (mg/g)	
	40°C	60°C	40°C	60°C
Native AC	3.85	3.14	6.62	4.92
AC-MEA	3.81	4.64	5.50	7.62
AC-DEA	3.91	5.00	5.84	8.40

IV. CONCLUSION

AC-MEA and AC-DEA were successfully prepared by the wet impregnation method. The presence of IR spectra of amine functional groups indicated the deposit of the alkanolamines on the AC surface. The separation of CO_2 from CO_2/N_2 mixtures was successfully illustrated. The alkanolamines modified AC had superior performances to the native AC at 60°C. Especially for the AC-DEA, the breakthrough capacity and the saturation capacity of the modified AC was 1.6-1.7 times that of the native AC. Hence, the AC modified with DEA had a potential for use in an upgrading process of biogas produced under thermophilic conditions.

ACKNOWLEDGMENT

The authors would like to acknowledge the National Research Council of Thailand for the research funding (2554A11902006). The authors appreciate the scholarship from The Joint Graduate School of Energy and Environment to A. Kongnoo. Special thanks to Thai Master Hitech Co., Ltd. (Thailand) for the support of equipment.

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