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The Effect of Active Ingredients Impregnated Granular Activated Carbon (GAC) on Carbon Dioxide Adsorption Capacity.

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Abstract

The main objective of this work consist of the biogas purification via the various adsorbents, in order to remove carbon dioxide (CO_2) by Pressure Swing Adsorption (PSA). The comparision of the various adsorbents (Granular Activated Carbon (GAC) and the modified Granular Activated Carbon) on the adsorption capacity performance. The improvement method on activated carbon by using active ingredient impregnated, Lithium Chloride (LiCl), and Polyethyleneimine (PEI) have been investigated in this work by using the synthetic of biogas (45% CO_2, 47.5% CH_4 and 7.5% N_2). The result indicated that the adsorption selectivity of CO_2/CH_4 ratio of PEI/GAC is higher than Li/GAC and GAC, respectively. The PEI/GAC is the suitable material for biogas purification.

Keywords: Adsorption, Activated Carbon, impregnation, Carbon dioxide

1 Introduction

Biogas is a raw gaseous stream produced by anaerobic decomposition of the organic matter and as one of the prominent renewable energy sources. The main composition of biogas is a mixture composed of approximately 50 - 70% CH_4, 30 - 50% CO_2 smaller amounts of NH_3 (80-100ppm), H_2S (500-1,000 ppm) and trace of hydrocarbon (<100 ppm) [1]. The advantage of biogas can be used directly to generate electricity and heat energy. However, the disadvantage of using gas engine is the reduce recovery of the energy content in the biogas. The biogas purification up to natural gas grade for its use as natural gas substitute for car fuel is required especially in the CO_2 removal technique. Many technology was studied for CO_2 capture to reduce CO_2 emision such as liquid absorption, membrane separation and solid adsorbent. Activated carbon was a highly microporous material with the large of surface area. It was used because of their wide availability, low cost and high thermal stability. Plaza et al. [2] studied CO_2 capture using activated carbon and alumina impregnated with various amine such as DETA, pentaethylenehexamine (PEHA) and PEI. The result indicated that DETA – impregnated on alumina have the high CO_2 adsorption capacity. The carbon-base support derived from sewage sludge impregnated with PEI can increase of CO_2 adsorption capacity.

Zhu et al. [3] examined the adsorption on high-surface-area porous carbon systhesized by chemical activation using petroleum coke as precursor and KOH as activation agent. The maximum CO_2 adsorption uptake of 15.1 wt. % together with a CO_2/N_2 selectivity of 9.4 at 0.1 MPa were obtained for a sample activated at 973 K, which indicates its high potential for the CO_2 capture. Plaza et al. [4] investigated the effect of the oxidation upon the CO_2 capture performance with a phenolic resin carbon as the base material. Oxygen surface groups were introduced through liquid and gas phase oxidation treatments, using ammonium persulfate, nitric acid and air, respectively. They observed that the oxidized samples are easily regenerated and reported that the oxidation is a plausible modification technique for developing easy-to-regenerate carbon adsorbents with enhanced CO_2 capture performance. J. Wang et al. [5] developed a sorbent by loading polyethylenimine (PEI) on mesoporous carbons which possessed well-developed mesoporous structures and large pore volumes. The authors reported that the sorbent capture capacity with CO_2 concentration was ranging from 5 wt.% to 80 wt.%. The optimal PEI loading was determined to be 65 wt.% with a CO_2 sorption capacity of 4.82 mmol - CO_2 g-sorbent in 15 wt.% CO_2/N_2 at 348 K. The above presented active carbons are well adapted to the carbon dioxide storage in high pressure and ambient or medium temperature when the heat effect of adsorption is important. It is therefore necessary to eliminate the heat from the bed. But their application for the CO_2 capture from the flue gas of power plants is limited. Rewadee et al. [6] study the preparation of chemical vapor deposition on granular activated carbon (CVD/GAC) from coffee bean and used it in biogas purification. Adsorbent functionalized with the amine are the effective material for CO_2 capture from biogas and flue gas. Wong et al. [7] produced the nanoporous composite sorbent called 'molecular basket' by loading polyethyleneimine (PEI) on molecular sieve such as MCM41 and SBA15. Yang et al [8] produce the strong oxidizing ability, transition metal of Zn

The objective at this work is to prepare the Granular Activated Carbon (GAC) and modified granular activated carbon by imprenated with active ingredients adsorpotion (PEI and LiCl) were studied its CO_2 adsorption performance. The adsorption seclectivity of CO_2/CH_4 have been investigated in this work.

2 Materials and Methods

2.1 Preparation for adsorbents.

Commercial granular activated carbon (GAC) was purchased from METRA Co.,Ltd. It was sieved to sizes ranging from 20-40 mesh and dried at 120°C for 6 hours before impregnation process. PEI (Molecular weight: MW: 600,000-1,000,000 g/mol) was obtained from Sima-Aldrich. The preparation of PEI solution was dissolution PEI in ethanol solution. After that, the GAC was impregnated with PEI solution in the ratio of 30 wt.% LiCl (Molecular weight: MW: 43.8 g/mol) was obtained from Sima-Aldrich. one mol/dm^3 of LiCl was prepared and impregnated on GAC in the ratio of 30 wt. % The obtained modified products was dried at 105°C overnight and keep in the desiccators. The characterization of the GAC and modified morphology granuular activated carbon (LiCl and PEI impregnated on GAC) were carried out by using JSM-6400. (JEOL, Japan) for Scanning Electron Microscope (SEM) analysis and X-Ray Diffraction (XRD) was performed using Cu-Kα radiation (Rigaku Corp., Japan). The analysis of specific surface area, pore volume, and pore size were determined by nitrogen adsorption-desorption (BET) isotherms at 77 K with discontinuous volumetric apparatus (Quantachrome AUTOSORB 1).

2.2 Adsorption Experiments.

The flow diagram of the experiment set-up is shown as in Figure 1. About 0.2 grams of the prepared adsorbent (GAC, LiCl/GAC and PEI/GAC) were into the tube adsorption using a SS-304 tube with the inner diameter of 4 mm and height of 70 mm which is the single bed column. A synthetic biogas (45% CO_2, 47.5% CH_4 and 7.5% N_2 was passed through the sorbent at the flow rate of 80 ml/min at the room temperature. The outlet of CO_2 and CH_4 concentration was detected by a gas chromatography (Shimadzu)

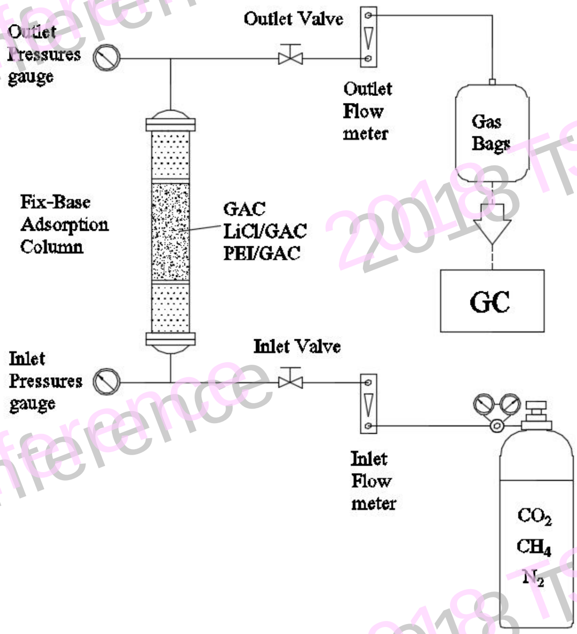

Figure 1 Diagram of the single column system.

The breakthrough concentration of CO_2 outlet was defined as 50% of the initial concentration. The test was stopped when the CO_2 concentration outlet reaches the breakthrough set point. The removal efficiency can be calculated by using the equation (1)

$$CO_2 \text{Adsorption efficency } (\% \; CO_2 \; removal) = \frac{Co - Ce}{Co} x100 \quad (1)$$

$$\text{mol (n)} = \frac{P(V_e)}{RT} \quad (2)$$

$$\text{The Adsorption Selectivity of } \frac{CO_2}{CH_4} = \frac{\text{mol adsorption of of } CO_2}{\text{mol adsorption of of } CH_4} \quad (3)$$

where,

C_0 is the initial of CO_2 concentration
C_e is the outlet of CO_2 concentration.
P is the pressure in operating condition (atm)
V_e is the gas volume (dm^3)
R is the gas constant of 0.082(dm^{3}atm/mol.K)
T is the temperature (K)
n is the mole of gas (mol)

The adsorption selectivity of CO_2/CH_4 can carried out by calculating the mol adsorption of CO_2 and the mol adsorption of CH_4 were convered to mol by using the equation (2) and use it as the adsorption selectivity of CO_2/CH_4 by using and equation (3). The condition was under given 80 ml/min of flow rate, initial concentration and mass of the various sorbent.

3 Results and Discussion

3.1 Characterization of Adsorbent.

The physical characteristics of the adsorbents by using Scanning Electron Microscope (SEM) image of GAC and modified granular activated carbon PEI/GAC and LiCl/GAC are shown in Figure 2, Figure 3 and Figure 4, respectively.

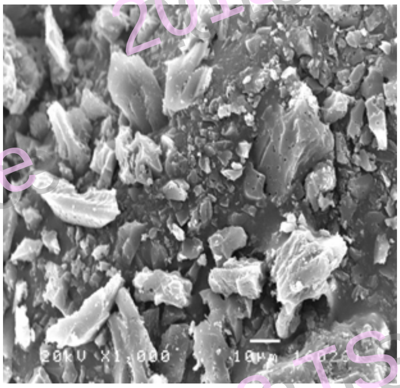

Figure 2 Scanning electron microscope (SEM) images of GAC at magnification scale (x1000 magnification).

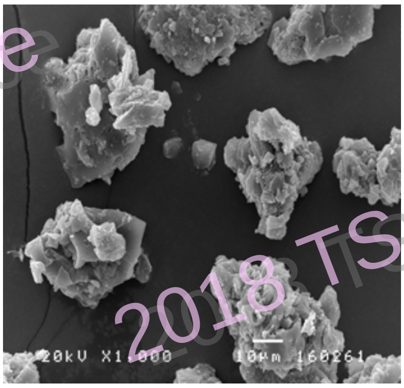

Figure 3 Scanning electron microscope (SEM) images of PEI/GAC at magnification scale (x1,000 magnification).

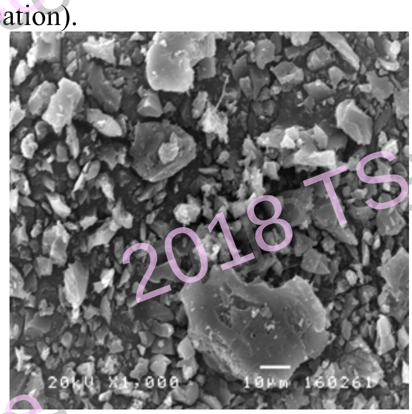

Figure 4 Scanning Electron Microscope (SEM) images of LiCl/GAC at magnification scale (x1000 magnification).

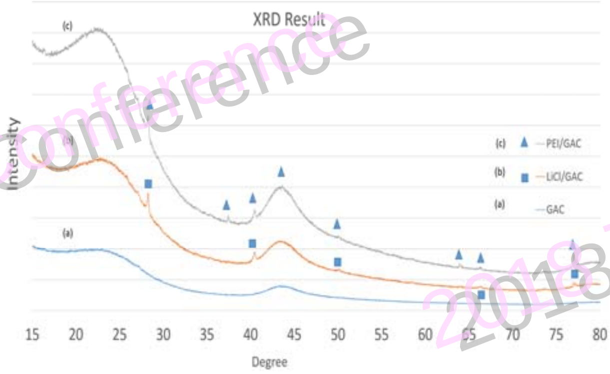

Figure 5 X-Ray Diffraction (XRD) images of (a) GAC, (b) LiCl/GAC and (c) PEI/GAC products

From the figure 5 shown the XRD patten of GAC, LiCl/GAC and PEI/GAC. The peaks of PEI are shown in 2 theta at 37 and 44. Therefore, the peaks of LiCl are shown in 2 theta at 40 and 50.

Table 1. Struture properties of granular activated carbon (GAC) before and after impregnation with LiCl and PEI.

Sample	$S_{BET}(m^2/g)$	$V_t(cm^3/g)$
GAC	$9.67x10^2$	275
LiCl/GAC	$8.46x10^2$ (-12.5%)	240
PEI/GAC	$20.2x10^2$ (-79.11%)	42

Table 1 shown that PEI impregnated of GAC was expected to lower the BET surface area and the pore volume of the adsorption. At the loading of 30 wt.% of LiCl, the BET surface area of LiCl/GAC was $8.46x10^2$ m^2/g, about 12.5%. For a loading of 30 wt.% of PEI, the BET surface area of PEI/GAC was $20.2x10^2$ m^2/g, about 79.11%. BET content to 30 wt.% significent decreased in BET surface area because of the filled PEI impregnation.

3.2 Adsorption performance.

The breakthrough capacity cuvrve of the various products (GAC, PEI/GAC and LiCl/GAC) are shown in Figure 6. The adsorption selectivity CO_2/CH_4 versus various adsorbent plotted base on the average value of the CO_2 adsorption for various adsorbents.

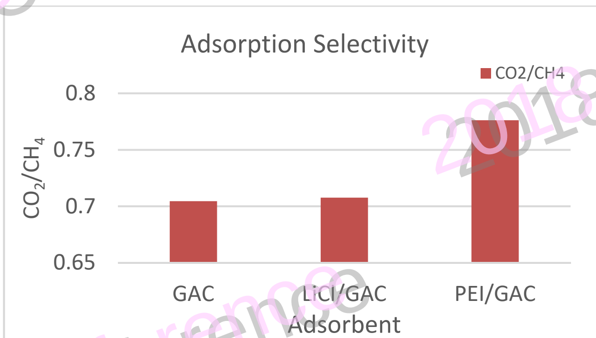

Fig. 6 Adsorption seclectivity performance of various adsorbent for CH_4 and CO_2 (GAC, PEI/GAC, LiCl/GAC)

The breakthrough capacity of all adsorbents show that the PEI/GAC has high capacity of CO_2 adsorption and not good adsorption performance for CH_4. It is concluded that PEI/GAC can be as good adsorbents for biogas purification.

Table 2 Adsorption capacity of GAC, PEI/GAC and LiCl/GAC in biogas composition.

Adsorbent	CO_2 adsorption capacity (mmol/g)
GAC	7.3628
LiCl/GAC	6.4062
PEI /GAC	8.3784

The table 2 indicated that chemical adsorption for CO_2 on LiCl/GAC and PEI /GAC at the room temperature (30°C) under 1 atm. The modified activated carbon after impregnation (LiCl/GAC and PEI /GAC) will increase the high adsorption capacity than GAC. From the CO_2 adsorption performance of PEI/GAC. PEI is the polymer which the large molecular wight. There are lewis acid and base electron-pairing in PET structure effects and CO_2 adsorption moleculas which can give long pairs of electron. It can be concluded as the chemisorption. LiCl/GAC is the similarly chemisorption mechanism. It can concluded that active ingredients impregranated on GAC can improve the CO_2 adsorption capacity performance.

4 Conclusions

In summary, the modified activated carbon (LiCl/GAC and PEI /GAC) can improve the CO_2 adsorption capacity. The PEI/GAC is the good material in biogas pulification at the room temperature under 1 atm. It is concluded that the impregnation method can give alone pairs electron and improve the force in CO_2 adsorption performance via chemisorption mechanism.

5 Acknowledgements

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