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Submission date: 18-Apr-2020 10:33AM (UTC+0700)
Submission ID: 1300716139
File name: P-15_9-ICGT-2018_paper_53.doc (588K)
Word count: 2554
Character count: 13280

Application of Amine Modified Silica Adsorbenes on CO_2 Adsorption in Biogas

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Abstract- The adsorption process is a technology that is more efficient in CO_2 adsorption. The adsorbent used must have adsorption capacity and high selectivity to CO_2 adsorption. In this study, silica is used because it has sufficient surface area and pore size. In addition, the presence of silanol group on the surface of silica allows silica to be modified with other functional groups for certain applications. One of the interesting points is the modification of silanol groups with amine group, where the amine group is selective towards CO_2. The succes of the adsorbent depends on the succesful modification of the amine group to the surface of the silica through the reaction of the hydroxyl group on the surface of the substrate and silane compounds. Amine compounds used as modifying agents are APTS (aminopropyltriethoxysilane). The method used to modify silca gel is post grafting. Biogas to be purified is made by mixing vegetable waste with cow dung as a starter source of methanogen. The methane gas content can be increased by reducing the amount of CO_2 gas in biogas. Methane gas content in biogas made from vegetable waste is 78.5% while CO_2 gas is 16%. The process of CO_2 gas adsorption is done by passing the biogas on the silica adsorbent which has been modified with amine. This process lasts for 30 minutes. The results of the analysis with TGDTA and FTIR showed that the adsorption has been proceed. CO_2 gas which is successfully adsorpted from biogas is 80% and this increase the level of CO_2 gas which rises from 16% to 12.76%

Keywords—silica-amine; adsorption CO_2; biogas

I. INTRODUCTION

During the current global energy crisis, renewable energy sources such as biogas have enormous potential in meeting energy needs in the future. Biogas is a very important renewable source of methane produced through anaerobic biomass biodegradation. The biogas content in general is 55-70% CH_4, 30-45% CO_2 and the rest is water and hydrogen sulfide (H_2S) [1]. Very large carbon dioxide content can reduce the heating value of the biogas and affect the performance of the engine. In addition H_2S gas is very corrosive and harmful to the environment. Energy conversion from biogas to heat or electricity is possible through combustion. Biogas can be transferred through piping or by compression in a tube. This is possible only if the content of CO_2, H_2S and moisture is removed. Reduction of CO_2 and H_2S content will significantly increase the quality of biogas.

Various techniques have been developed for acid gas separation, including chemical absorption, physical absorption, physical adsorption and membrane separation. Among these techniques, chemical absorption using alkanolamines as monoethanolamine and dietanolamine is the most popular in large-scale industries such as the sweetening of natural gas and the separation of CO_2 from the exhaust gas of power plants. Although the absorption method is a relatively low-cost process, the regeneration of these absorbents requires large costs and energy. In addition this technique provides many problems including high corrosion rates, degradation of absorbents and foam formation in the gas-liquid interface.

The application of this technology is not widely used in small-scale processes such as biogas purification. This is because the use of liquid for the separation of CO_2 gas has many obstacles including the need for large energy for the regeneration process, the stability and selectivity of the chemicals used, the environmental impacts caused by liquid waste, the need for large-sized equipment and the high rate of corrosion of the equipment.

To overcome this problem, an alternative is used through physical adsorption with solid adsorbent. One of them is using nanoporous and mesoporous silica gel which is grafted with amine groups. The development of silica that has been grafted with amine groups has been developed as an absorbent due to its efficiency and selectivity to CO_2. Mesoporous silica is known to have a high amount of silanol groups which can be grafted with organic amine compounds. Therefore, Mesoporous silica is a potential substrate for amines that can be used for the purpose of CO_2 adsorption [2-4].

Based on the studies that have been carried out so far, the raw material used as a source of silica is usually in the form of tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) because of its large silica content. However, TEOS and TMOS are expensive, difficult to obtain and toxic raw materials. Therefore, it is necessary to develop silica which is cheap and non-toxic as ash bagasse.

Bagasse ash which has a high silica content (above 50%) is a very potential raw material due to its low price, abundant amount and amorphous silicic properties which can be easily modified with a relatively cheaper and low energy sol-gel process to obtain desired particle structure. Affandi et al 2009 [5] succeeded in synthesizing high purity mesopore silica (above 99%) from bagasse ash by caustic digestion method.

This method does not require large energy and uses environmentally friendly raw materials.

From the description above, in this study the problem is focused on making baggase ash-based silica gel adsorbents that will be grafted with amine as an adsorbent for carbon dioxide (CO_2). The source of silica used is baggase ash and the amine source used is 3-Aminopropyltriethoxysilan (APTS). The purpose of this study are: Develop a method of grafting amine groups on the surface of bagasse ash-based silica gel to capture of carbon dioxide (CO_2) gas in biogas.

II. EXPERIMENT

To obtain mesoporous silica particles which are capable of being grafted with amine groups in large quantities so that they have high acid gas adsorption capacity, it is obtained by regulating the process conditions. To achieve this goal required mesoporous-sized pore silica structure. Particles with this structure, pores with a certain volume and diameter are obtained by controlling pH on gel formation and can also be done by adding a template for more directed pore formation (Rahman, et. al, 2015), and adding organic acids to control gel formation (Rahman, et. al, 2018).

Extraction of silica from bagasse ash.

The extraction process of silica from ash bagasse adopts from a procedure that has been developed by Affandi et al., 2009. The details are carried out in the following way : 10 grams of bagasse ash (PT. Kebon Agung Sugar Factory, Malang) was extracted using 60 ml NaOH 2N (Sigma Aldrich) to produce sodium silicate. Silica from bagasse ash was extracted for 1 hour with constant stirring at its boiling point. The solution is then filtered using ash filter Whatman No. 41 to separate the carbon residue. Filtrates (sodium silicate) are then cooled to room temperature.

Synthesis of silica-amine hybrid

Synthesis silica-amine hybrid with controlled pores using PEG (Polyethylene glycol) adopts procedures that have been developed previously [6]. The complete process is carried out in the following way as shown in Figure. 1. From Figure 1, it can be seen that the amine silica synthesis process from bagasse ash uses the post grafting method. To form pores and network amplifiers, PEG 1000 is used.

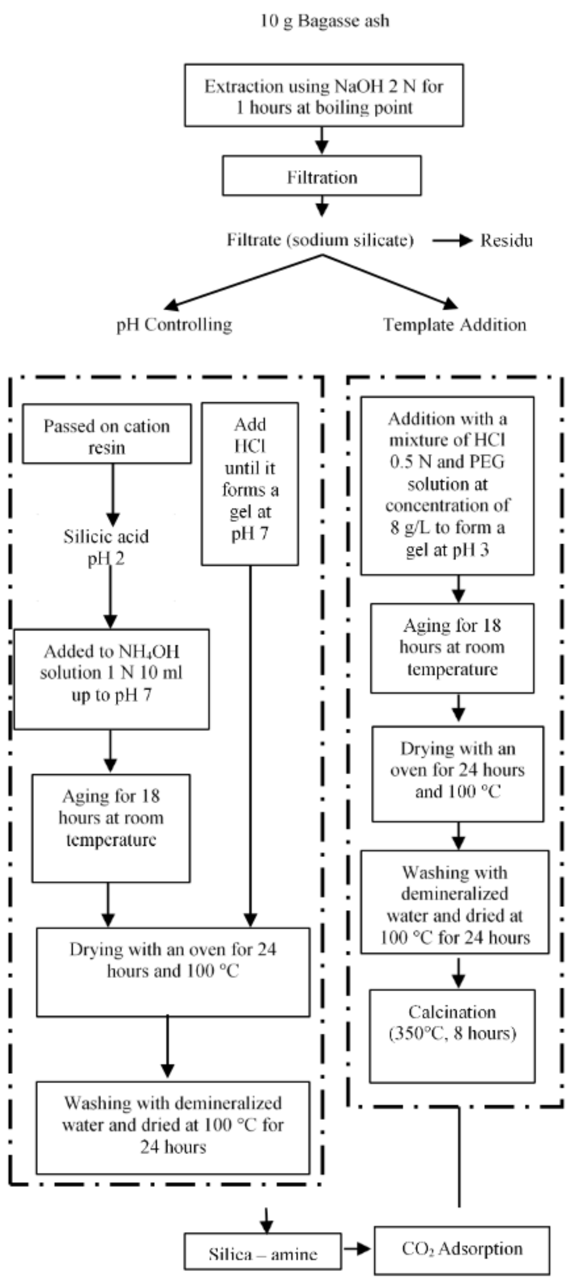

Fig. 1. Flow chart of silica-amine synthesis process

III. Result and Discussion

Silica-amine synthesis that has been produced with the process conditions as in Fig. 1, obtained surface area and pores that fall into the mesopore category. The formation of the characteristics of silica-amine used as an adsorbent of carbon dioxide gas has met the requirements as an adsorbent. Pore size greatly affects the success of the adsorption process, where the appropriate pore size can avoid obstruction of the carbon dioxide gas diffusion process into silica-amine adsorbents. As reported by Rahman [8], where the template used as a pore forming is PEG and the method used to remove templates is the calcination process carried out at 350 ° C for 8 hours. Based on the results of BET (Brunauer-Emmet-Teller) analysis, silica-amines were obtained with a pore volume size of 1.25 cc / g, pore diameter of 7.75 nm and a surface area of 650.2 m^2 / g.

This silica-amine is used to adsorb carbon dioxide gas in biogas. In this study, biogas was obtained from the biogas production process using vegetable waste with cow dung as a starter. Analysis of the biogas produced showed that the content of CH_4, H_2S and CO_2 were 78.5% respectively; 0.2% and 16%, and the rest is a mixture of N_2, H_2 and O_2 gases of 5.3%. Heating value is 11980 kcal / kg. When it will be applied as fuel in the combustion chamber, the presence of large amounts of CO_2 will have a negative impact because it will cause crust and long-term use can cause damage to the combustion chamber. For this reason, it is necessary to reduce CO_2 gas in biogas. In addition, as it is known that the presence of carbon dioxide gas in the atmosphere which is increasing in number each year will have an impact on global warming.

Adsorption of CO_2 gas with silica-amine was chosen as a method to reduce CO_2 levels because this process does not require energy and can be carried out under fairly safe operating conditions. In addition, the desorption process as an adsorbent regeneration is also easier to do. APTS compounds as amine sources provide high reactivity to CO_2 gas so that the CO_2 gas adsorption process can take place quickly.

The advantages of amine compounds as adsorbents of CO_2 gas when compared to other adsorbents such as zeolite or activated carbon are their tolerance to moisture. The results of the study stated that the absorption of CO_2 in the amine solution formed the following reaction: capacity in a humid environment is doubled compared to dry environments

$$2(RNH_2) + CO_2 \rightleftarrows RNHCO_2^- RNH_3^+$$
$$RNH_2 + CO_2 + H_2O \rightleftarrows RNH_3^+ HCO_3^- \rightleftarrows RNH_3^+ CO_3^{2-}$$

The reaction between CO_2 and amine compounds in water-free environmental conditions will produce carbamate compounds where this reaction requires 2 amine molecules to bind one molecule of CO_2. Whereas in a humid environment, CO_2 is adsorbed with bicarbonate formation. capacity in a humid environment is doubled compared to dry environments because it requires one amine molecule to bind one molecule of CO_2. (Guerrero, 2008).

Adsorption is carried out at 40 °C and atmospheric pressure. Biogas is passed through the silica-amine adsorbent in the adsorber column. The adsorbent that has absorbed carbon dioxide gas was analyzed by TGDTA (Thermo Gravimetric and Differential Thermal Analysis), as seen in Fig. 2.

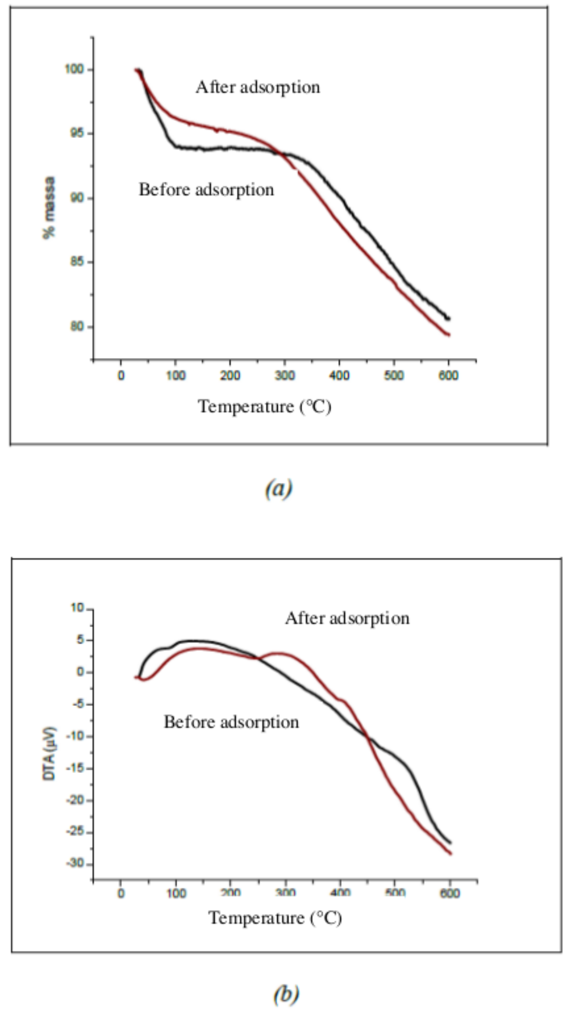

Fig. 2 TGDTA Analysis (a) thermal gravimetry analysis and (b) differential thermal analysis

Thermal gravimetry-differential thermal analysis analysis is used to estimate the amount of CO_2 adsorbed by silica particles (Fig. 2). The results of the analysis can be divided into 2 regions with a temperature limit of 280 ° C which is where there is an energy release which is indicated by an increase in the DTA curve (Fig. 2b) which indicates the occurrence of a chemical reaction.

At temperatures less than 280 ° C the evaporated component is the solvent used, in this case water is at 100 ° C and physically adsorbed CO2 gas and other volatile components. Whereas at temperatures above 280 ° C there is a release of carbamate bonds which are chemically bound CO_2 with amines which are grafted on the surface of silica. The amount of chemically bound CO_2 is estimated to be 0.07 g / g silica or 1.61 mmol / g silica.

The amount of amine successfully grafted onto the silica surface is 2.37 mmol / g silica, in this number silica-amine is able to adsorb carbon dioxide gas as much as 1,185 mmol CO_2 / g silica.The amount of CO_2 absorbed also provides CO_2 concentration information that has been successfully removed from biogas. Analysis with GC-MS showed that there was a decrease in CO2 levels in biogas. In the initial conditions, before the adsorption process occurred, CO2 levels in biogas were 16%. After the adsorption process, the CO_2 content in the biogas becomes 12.76%. GC-MS analysis shows the amount of methane gas in biogas after the adsorption process is 98%. This also means that methane gas was successfully purified 80% of the initial methane rate (78.5%).

III. CONCLUSIONS

Biogas as a renewable alternative fuel has been widely applied, both as fuel for household needs such as stoves, lighting, currently biogas is also applied to meet energy needs in energy installations in industry. To meet the needs as fuel, the presence of carbon dioxide gas in biogas must be minimized. Carbon dioxide gas which is included in the category of acid gas will cause problems if the acid gas is in sufficient quantities. Carbon dioxide gas is also known as the biggest contributor to the cause of global warming. Adsorption by adsorbent silica-amine provides a solution for handling carbon dioxide gas. In addition to the easy process, the energy consumption needed to reduce the amount of carbon dioxide gas by the adsorption process is much cheaper because it is operated at room temperature and atmospheric pressure.

Silica-based carbon dioxide gas adsorbent from bagasse ash, provides an alternative choice of adsorbent that is cheap, easy to produce and most importantly environmentally friendly and can solve the problem of solid waste generated from the sugar production process.

From the results of the analysis, both with TGDTA and GC-MC, it can be concluded that biogas produced from vegetable waste can be used to meet energy needs, both for combustion chambers in motorized vehicles and energy installations in industries and households. CO_2 levels were reduced by 80%, and methane gas content was increased from 78.5% to 98%.

ACKNOWLEDGMENT

Nanik Astuti Rahman (NAR) thanked the Ministry of Research, Technology and Higher Education through the Post-Doctoral Research grant for the 2018/2019 Fiscal Year. This grant is a second year research grant for post-doctoral research

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