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Performance analysis of a pressure swing adsorption unit in removing biogas impurities using zeolite 13X

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Abstract. This study aims to assess the performance of a Pressure Swing Adsorption (PSA) unit in removing the carbon dioxide from biogas by evaluating the breakthrough and adsorption capacity of the adsorption process as well as determining the effects of cyclic regeneration of the adsorbent. The PSA system developed and composed only a main vessel made up of 316 stainless steel components. It was then operated up to 10 bars pressure at ambient temperatures and gas flows at a rate from 0 to 15 L min^{-1}. Use of physical adsorbent (zeolite 13X) will consume the gaseous impurities such as CO_2. Product gas was collected into 1 L Tedlar bags and analyzed using SRI gas chromatograph with TCD and HID detector to validate the CO_2 and CH_4 composition. The results of the pressure swing adsorption (PSA) experiments showed an average increase of 160% in the net heating value over that of a certified gas standard. The amount of methane was also significantly higher although the amount of the other gasses (i.e. nitrogen) remained comparatively the same. The number of other gases was significantly lower and leaving no traces of carbon dioxide was observed in the PSA system product gas indicating that carbon dioxide had been completely adsorbed by the system. This study greatly helps to reduce CO_2 emitted to the atmosphere from the anaerobic co-digestion of biogas to produce high energy content bio-methane fuel.

1 Introduction

Biogas technology has been developed and widely used over the world because it has several advantages – the reduction of the dependence on non-renewable resources, high energy-efficiency, environmental benefits, available and cheap resources to feedstock, relatively easy and cheap technology for production, and additional values of digestate as a fertilizer.

Biogas as one of the sources of renewable energy significantly due to some ecological advantages, mainly being CO_2 as neutral; hence, it reduces greenhouse gas formation. Further, biogas production minimized the waste disposal as agricultural, commercial and municipal waste from anthropogenic sources.

Biogas mainly comprises methane (40-75%) and carbon dioxide (20-55%), and trace components of hydrogen sulfide (H_2S), ammonia (NH_3) and siloxanes. This trace components may destroy the engine, e.g., due to corrosion [1]-[2]. Removing the impurities leads to higher the amount of methane, the higher the output of energy from biogas.

There are technologies commercially available for removal of CO_2 from biogas are typically used for applications such as gas wells, sewage treatment plants, and landfills. Because of the different contaminants, there are processes that can be considered for CO_2 removal from biogas such as pressure swing adsorption, using of amines, vacuum swing adsorption, among others.

A Pressure Swing Adsorption (PSA) processes separate out CO_2, oxygen, and nitrogen by absorption and desorption on activated carbon at different pressures in four stages - adsorption, depressurizing, desorption and pressure build up. The principle of the pressurized process as described by Santos, et. al, 2010 [3] more readily dissolved in activated carbon than methane. Their proposed biogas upgrading plant presented in their research of Santos, et. al, 2010 [3] consists of a scrubber vessel for scrubbing (absorption of CO_2 into adsorbent like activated carbon), a flash tank for methane gas recovery, and a desorption tower for the regeneration.

In Pressure Swing Adsorption (PSA) processes, the absorbent is used as a medium to remove selectively the carbon dioxide gas. The adsorbent is a porous solid, normally with a high surface area.

Among those absorbents, zeolite, activated carbon, carbon molecular sieves (CMS) but also activated carbons, zeolites and other materials (titanosilicates) are used commercially. However, using these Zeolite has encountered difficulty to the adsorption properties to the chemical composition of the surfaces as identified by Siriwardane et.al, (2001) [4]. Moreover, Wang and Levan (2009) [5] measures the adsorption Isotherms for pure water vapor and carbon dioxide on zeolites over a wide of temperatures and the adsorption results to

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confirmed their isotherm model used. Aside from that, Konduru, et. al (2007) [9] studied Zeolite 13X regeneration and recovery efficiency and suggests the determination of the optimum system parameters in order to establish that Zeolite 13X is the best absorbent. Hauchhum and Mahanta (2014) [6], also suggests that extensive study on the regeneration capability on Zeolite 4A and 13X.

From all the technologies presented, the pressure swing adsorption method of CO_2 removal was chosen because of the capability of its material presents stronger surface interactions to CO_2, to adsorb larger loadings as compared to methane [3]. This also supported by the study of Hauchhum & Mahanta, 2014 [6] showing a promising option to separate CO_2 due to its ease of applicability over a wide range of temperature and pressure conditions, also, it's low energy requirements and its low capital investment.

Based on the studies and gaps presented, this study contributes on assessing and determining the optimum system parameters required for zeolite 13X as an adsorbent in removing the carbon dioxide from biogas as a renewable source of fuel. After removal of the carbon dioxide, the methane gas then is used for possible engine testing in a stationary non-road engine. This technology overcomes the problem in increasing the methane recovery from biogas upgrading.

Thus, this study aims to evaluate the performance parameters of a Pressure Swing Adsorption (PSA) unit in removing the carbon dioxide from biogas by evaluating the breakthrough and adsorption capacity of the adsorption process as well as determining the effects of cyclic regeneration of the adsorbent from the anaerobic co-digestion of agricultural biomass waste utilizing dairy manure co-digested with various biomass feedstocks for power generation applications.

2 Materials and methods

2.1. Biogas upgrading experimental conditions

An experimental set-up is created only for the removing carbon dioxide (CO_2) from biogas. Wherein, a representative gas mixture, comprised of 63.18 %vol. CH_4 and 36.82 %vol. CO_2 will be passing through the adsorbent bed in an up-flow motion. After, pure methane in a down-flow motion in order to regenerate the adsorbent [7]. For this study, the researcher aims to compare the effects on the adsorption of using Zeolite 13X (Molecular Sieve) for the removing of carbon dioxide (CO_2) from a representative biogas mixture.

The experiments were conducted using a certified gas mixture standard prepared by Airgas (Airgas Southwest, Woodlands TX). This gas mixture is a good representation of the biogas produced from anaerobic co-digestion processes. For this experiment, the pressure was set at 400 kPa and the product gas outlet flow rate at 0.5-1.0 LPM. The product gas was also analyzed in real time using the Horiba NDIR gas analyzer and simultaneously analyzed using SRI gas chromatograph (SRI Instruments, Torrance, CA) with TCD and HID detector to validate the CO_2 and CH_4 composition.

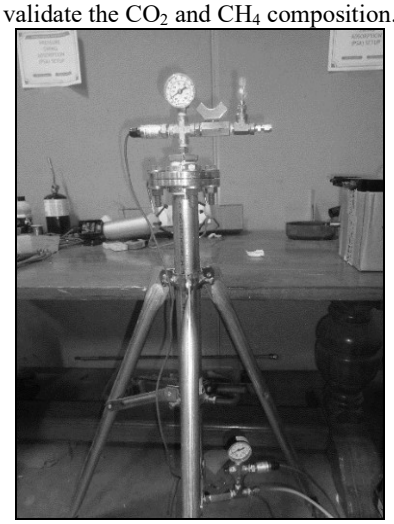

Fig. 1. Pressure Swing Adsorption Unit Schematic Diagram

2.2 CO_2 adsorption studies

Mérel, et.al, 2006 [8] described Pressure Swing Adsorption (PSA), working between high-pressure level during adsorption and a low-pressure level for desorption. Further, the study of Mérel, et.al, 2006 [8] employed the basic sequence of steps, referred to as the skarkstorm cycle, consist of pressurization, followed by adsorption and depressurization (blown down) followed by a purge or evacuation of the highly adsorbed component. On this study, the simple skarkstorm four-step cycle used and selected as the baseline because of the simplicity of the processes.

The removal of carbon dioxide on this study are operated with four steps: pressurization, adsorption, depressurization, and desorption. During the pressurization, gas representing the biogas composition consisting of 63.18% CH_4 and 36.82% CO_2 at ambient temperature is supplied to the bottom of the bed. During the adsorption, carbon dioxide (CO_2) is adsorbed on Zeolite 13X, where methane (CH_4) is obtained as product gas and the high-pressure feed gas enters in the pressurization step.

2.2.1 Breakthrough experiments

The Breakthrough curve will be determined and plotted in Fig. 2. For simplicity, a representative mixture of 63.18% CH_4 and 36.82% CO_2 represented in a typical biogas composition were assumed in this analysis.

2.2.2 Regeneration and reusability of the zeolite 13X at room temperature

Out of the adsorbent studied, zeolite 13X showed the optimal adsorption capacity of the zeolite 13X adsorbent is at 30^{o}C. Therefore, Zeolite 13X were studied for reusability with free-flowing air desorption at room temperature in the same run followed by vacuum purge.

In the same manner, Jadhav, et.al, 2007 [10] reported that the adsorbent successfully retained adsorption capacity in three consecutive reuse cycles. The slight loss of capacity after the first cycle probably owing to some irreversible adsorption that could have been desorbed at ambient temperature.

2.2.3 Selectivity studies

The selectivity of the zeolite 13X adsorbents on the removal of carbon dioxide was studied using a mixture of 63.18 % vol. of CH_4 and 36.82 %vol. of CO_2 of biogas prepared by setting the flows around 0.63 l/min. prior to the adsorbent study, the adsorbent was pre-weighted and placed in the PSA unit. The mixture then flowed over the Zeolite 13X, and the product gas was gathered using the Horiba NDIR gas analyzer.

3 Results and discussions

3.1 CO_2 upgrading system evaluation

3.1.1 Breakthrough experiments

Hauchhum and Mahanta, 2014 [6] defined Adsorption as "a transient process and the amounts of material adsorbed within a fixed bed will depend on both position and time".

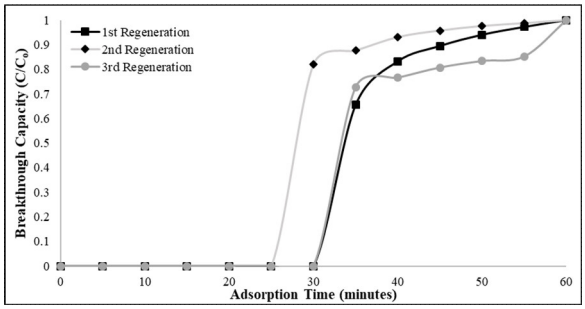

Fig. 2. Breakthrough curve for carbon dioxide (CO_2) removal using zeolite 13X at 400 kPa pressure

The CO_2 breakthrough curves for the zeolite 13X is shown in Fig. 2, and the experimental conditions are a binary gas mixture represented in a typical biogas composition is assumed in this analysis. Further, Hauchhum & Mahanta, 2014 [6] represents breakthrough curves as the ratio of the outlet concentration and the influent concentration against the contact time at an atmospheric pressure, and at some temperatures. For zeolite 13X, the adsorption experiencing breakthrough around 25 – 35 minutes depending on the efficiency of desorption (regeneration) of the adsorbent.

This implies that change in pore diameter of the adsorbent, zeolite 13X (10 Å) plays a vital role in entering the zeolite channels. Also, their cations, which is Na and K also helps in the adsorption of carbon dioxide. Due to its larger pore volume, zeolite 13X saturation is longer. In addition, the difference in chemical composition and nature of the surface and porosity was observed during the adsorption. Since the zeolite 13X has higher surface area can contribute to the higher adsorption capacity of zeolites, as compared with the study of Hauchhum and Mahanta, 2014 [6].

Furthermore, the reported values of carbon dioxide adsorption are in agreement with the published data of Hauchuum and Mahanta, 2014 [6], although the reported values of amount adsorbed are higher than all previous literature. In low-pressure range, the amount adsorbed compares very well with the data reported by [6].

3.1.2 Effects on reusability of adsorbent

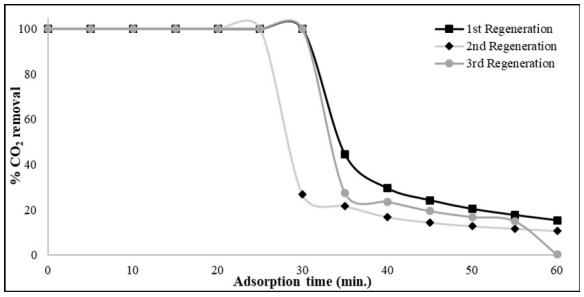

Fig. 3 Percentage removal of CO_2 sorption at different regeneration cycles

The adsorption capacity of the zeolite 13X indicates the reusability (regeneration capacity) of the adsorbent as presented in Fig. 3. Based on the experimental results, a 100% removal of carbon dioxide from the biogas is maintained after some time and the zeolite can be reused by passing through a countercurrent flow of air.

However, removal (desorption) efficiency of zeolite decreases every time it regenerates and it implied that the zeolite is not completely regenerated by air. This issue will be addressed by introducing hot air during the regeneration process.

3.1.3 Adsorption kinetics and contact time studies

The effluent concentration of the CH_4-CO_2 gas mixtures dropped to zero ppm_v for approximately 26 - 33 minutes at initial capacity is 22.5 g_{CO2} /$kg_{Zeolite13X}$. These results are slightly lower than the reported values of by Konduru, et. al, 2007 [9], for a gas mixture containing N_2 (75%) and CO_2 (25%).

The experimental results were expected as dismal since the gas mixture is different (63.18% CH_4 and 36.82% CO_2) from related studies. Also, adsorption was terminated prior to the complete saturation due to instrumentation limitations. Moreover, Figure 4 shows the time required in reaching the saturation capacity decreases with each regeneration cycle. These results attributed to the residual (remaining) CH_4-CO_2 mixture were not removed during the regeneration cycle.

The adsorption isotherms of breakthrough and carbon dioxide adsorption were shown in Fig. 4. Based on the results, indicated in Figure 4 the adsorption of zeolite 13X is fully reversible and complete regeneration

can have done and obtainable by evacuation of the adsorbent after adsorption process.

In addition, final adsorption curve shown with CO_2 was similar with Mérel, et. al, 2006 [8] and it indicates adsorbent was not affected by the adsorption of methane (CH_4) even after third regeneration. These results suggest that separation of carbon dioxide of carbon dioxide from a CH_4-CO_2 mixture is possible with Zeolite-13X adsorbents.

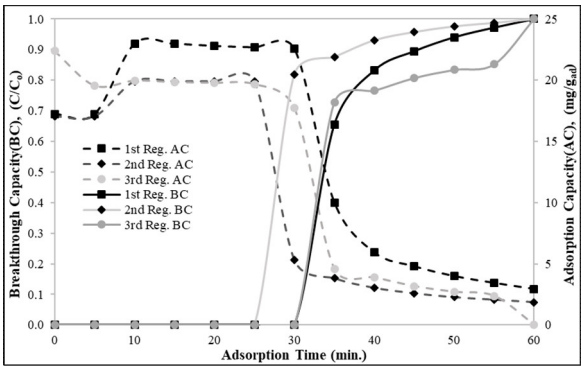

Fig. 4 CO_2 sorption isotherms of Breakthrough and Adsorption Capacity at different regeneration cycles

3.1.4 Selectivity studies

As shown in Figure 4, CO_2 adsorption breakthrough occurred around 25-30 minutes of adsorption, until the maximum adsorption capacity of the zeolite 13X was spent.

As reported by Jadhav, et.al (2007) [10], that the adsorption capacity of the zeolite 13X is found to be higher for CO_2 than for CH_4 [8]. As compared with the saturation adsorption capacities of Zeolite 13X for CO_2 and CH_4 are for this experiment are (22.50, 19.92 and 17.74 mg/g_{ads}) respectively.

Thus, CH_4 breakthrough shows a bulge or hump of (C/Co > 1) as reported by Jadhav, et. al, 2007 [10]. This implies that competitive adsorption of carbon dioxide from biogas was taking place [10]. Since CH_4 being in higher concentration occupies more sites and kinetic selectivity for CO_2 plays a vital role that the adsorbed CH_4 is displaced making space for CO_2. Thus, the product gas values of CH_4 shows an increase of values over than in the inlet.

4 Conclusion

The results of the PSA experiments showed an average increase of 160% in the net heating value over that of the certified gas standard. The amount of methane was also significantly higher although the amount of the other gasses (i.e. nitrogen) remained comparatively the same. The quantity of carbon monoxide (CO_2) in the product gas was significantly lower and no traces of carbon dioxide was observed in the PSA product gas indicating that carbon dioxide had been completely adsorbed by the system. The raw gas inlet flow rate started at 0.71 LPM and ended at around 0.80 LPM until the vessel was regenerated in a countercurrent of air. Based on the product gas composition during the adsorption and desorption cycles, the desired concentration of the product gas was achieved in a short span of 1 minute during adsorption. A longer stable gas concentration may be achieved by using more adsorbent.

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