QUARTERLY PROGRESSREPORT

June 2019 – August 2019

PROJECT TITLE: CO₂ capture from landfill gas using amine based silica sorbents

PRINCIPAL INVESTIGATOR(S):

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PROJECT WEBSITE: http://www.eng.usf.edu/~jnkuhn/Hinkley2018.html

Research Description:

Biogas is a renewable energy source of methane that can be used directly as fuel for combustion engines, gas turbines, and fuel cells as an energy source after its purification. CO_2 being the major contaminant (30–50%), its removal from methane becomes one of the critical steps in upgrading to increase the energy content of the biogas. The goal of the project is to identify a low cost adsorbent for CO_2 separation from biogas. Mesoporous silica functionalized with amine groups have been proven to be good adsorbents of CO_2 with high selectivity, low energy utilization and low regeneration costs. This study will benefit WTE processes through improved economics.

Work accomplished during this reporting period:

For this reporting period, we performed adsorption of CO_2/CH_4 mixture in dry and humid conditions using the 26 wt% APTES-SBA 15 adsorbent material. This adsorbent was used because it gave the highest adsorption capacity of CO_2 (0.85 mmol CO_2/g adsorbent) from the CO_2 adsorption study.

Adsorption of CO₂/CH₄ mixture (Dry condition)

The adsorption study of the CO_2/CH_4 mixture was performed to evaluate/ ascertain the affinity of the adsorbent material towards CO_2 in a gas mixture with similar concentration to that present in landfill gas (LFG). The dry condition adsorption study was performed by flowing gas feed mixture (40 sccm) containing 50 % He and dry $CO_2/CH_4(1: 1)$ through the 26 wt% APTES-SBA 15 adsorbent material for 30 min. A desorption test was carried out after the adsorption test. In addition, an adsorbent regeneration experiment was performed at a regeneration temperature of 100 °C and 5 cycles of adsorption-desorption. The obtained adsorption capacity of the 26 wt% APTES-SBA 15 in the CH_4/CO_2 mixture (dry condition) was 0.83 mmol/g of adsorbent material. This adsorption capacity is lower than the adsorption

capacity in pure CO_2 (0.85 mmol/g). The difference in adsorption capacity indicated that the 26 wt% APTES-SBA 15 material has high affinity of CO_2 .

Adsorption of CO₂/CH₄ mixture (Humid condition)

Due to the presence of moisture in real LFG, the adsorption study of CO_2/CH_4 mixture in humid conditions was performed to evaluate the effect of moisture on the CO_2 adsorption capacity of the adsorbent material. For this study, different amount of water vapor was flown through the 26wt%APTES adsorbent bed along with CO_2/CH_4 . A feed gas mixture consisting of 10 sccm He and 30 sccm dry CO_2/CH_4 feed in the ratio 1:1 was used. He was flowed through a bubbler system (Figure 1) set at a calculated temperature such that the total flow rate of He remained 10 sccm always. The feed gas mixture was flown through the sample for 30 min followed by a desorption test. The CO_2 and H_2O adsorption capacities obtained are presented in Table 1 below.

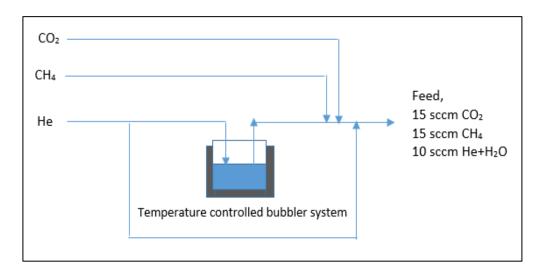


Figure 1. Bubbler set-up for CO_2 adsorption in humid conditions.

Prior to the introduction of H_2O in the feed (i.e. dry condition), the CO_2 and H_2O adsorption capacities were 0.79 mmol/g and 0.0090 mmol/g respectively. The H_2O adsorption capacity (0.0090 mmol/g) obtained without including water in the feed mixture is from H_2O present in the CO_2 cylinder (99.99 % purity) used for the study. Upon introducing 0.20 sccm of H_2O into the feed mixture, the CO_2 adsorption capacity decreased from 0.79 to 0.72 mmol/g while the H_2O adsorption capacity increased from 0.0090 to 0.24 mmol/g. The reduction in CO_2 adsorption capacity in the presence of H_2O may be due to the blockage of some of the CO_2 adsorption sites by H_2O . An increase in H_2O flowrate from 0.20 to 0.67 sccm resulted in an increase in CO_2 adsorption capacity from 0.71 to 0.72 mmol/g while the H_2O adsorption capacity with increasing H_2O flow rate in the feed was also observed at 1.7 sccm of H_2O in the feed. An explanation for the observed trend is SBA's affinity for water and this does not affect CO_2 adsorption. Table 1. CO₂ adsorption in the presence of water in a total feed flow rate of 40 sccm (10 sccm He+H₂O, 15 sccm CH₄ and 15 sccm CO₂)

Water vapor flow rate (sccm)	CO₂ adsorption (mmol/g)	H ₂ O adsorption (mmol/g)
Dry	0.79	0.0090
0.20	0.71	0.24
0.67	0.72	0.30
1.7	0.72	0.41

In addition, a regeneration study was carried out for 5 cycles of adsorption-desorption. The regeneration study is important because it helps to evaluate the degree of reusability of the adsorbent after several cycles of adsorption and desorption. The regeneration study of the adsorbent material was performed using a total feed flow of 40 sccm ($1.7 \text{ sccm } H_2O$ and $1:1 \text{ CO}_2/\text{CH}_4$). Figure 2 shows the adsorption capacities of CO₂ and H₂O for the 5 cycles. The CO₂ adsorption capacity remained constant at 0.72 mmol/g for the 5 cycles the study was conducted and the water adsorption capacity for the first cycle was 0.40 mmol/g.

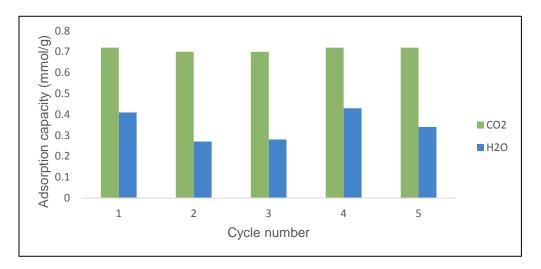


Figure 2. Cyclic regeneration of 26wt%APTES-SBA15. Adsorption of model biogas at T = 26 °C and desorption in He at T = 100 °C

TAG meetings:

The next TAG meeting for this project is anticipated to be held on October 15, 2019. Details will be announced in the near future.

Future Tasks:

The future work would be to evaluate the adsorption capacity of 26 wt% APTES-SBA 15 for real landfill gas. We will investigate how the presence of impurities such as H_2S , N_2 , siloxanes present alongside with H_2O in LFG affect the CO₂ adsorption capacity of the material.

We will also look at the economics of using amine functionalized materials for CO2 adsorption. Impact of various factors such as adsorption capacity and degradation rate on separation costs will be examined.