QUARTERLY PROGRESS
REPORT
March 2019 – May 2019

PROJECT TITLE: CO_2 capture from landfill gas using amine based silica sorbents

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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 second reporting period, we synthesized adsorbents with different loadings and characterized these samples. The adsorbent synthesis was done via grafting method using SBA-15 as the support and immobilizing APTES (primary [3-aminopropyl-triethoxysilane) on it. To achieve different loadings of the amine on silica, different amounts of APTES (0.3 ml, 1 ml, 1.4 ml, and 2.5 ml) were added to SBA-15 (using toluene as solvent) during the synthesis process. The surface areas and pore size distribution of the adsorbent synthesized were found using N2 physisorption (BET and BJH methods). Table 1 shows that the surface areas of the silica decreased once the APTES is added, confirming that the amine functionalization process has occurred inside the pores of the SBA-15.

Table 1: Characterization data of the SBA-15 and different loadings of amine-functionalized SBA-15

Sample	Surface area (m2/g)	Pore Volume (cc/g)	Pore Diameter (nm)
SBA-15	672	0.81	7.8
0.3 ml APTES	354	0.51	6.1
1 ml APTES	349	0.50	5.6
1.4 ml APTES	168	0.26	5.6

Not all APTES added was attached on to the SBA-15, especially as more was added. Some of it was lost during the synthesis process. To have a better understanding of the loading of APTES on the adsorbent, 1 g of the sample was calcined at 800 ^{0}C and the weight loss was measured. At this high temperature, all organic material will be removed and the weight loss can be accounted for the amount of APTES in the sample. Also to confirm the results, temperature programmed oxidation (TPO) was carried to find the weight percent of APTES on silica. The summary is given in Table 2. Figure 1 shows the TPO graph for

Table 2: Actual weight percent study

Sample	**Weight % from calcination of sample**	**Weight % from TPO**
0.3 ml APTES	12	13.5
1 ml APTES	20	18
1.4 ml APTES	26	27.5
2.5 ml APTES	25	24.6

12wt%APTES. The first peak corresponds to CO_2 desorption due to CO_2 adsorption from the air. The peak after 300 ^{0}C corresponds to the CO_2 from the organic compound which was quantified to find the weight percent of the sample. Weight percent obtained from the calcination experiments will be used to name the samples henceforth.

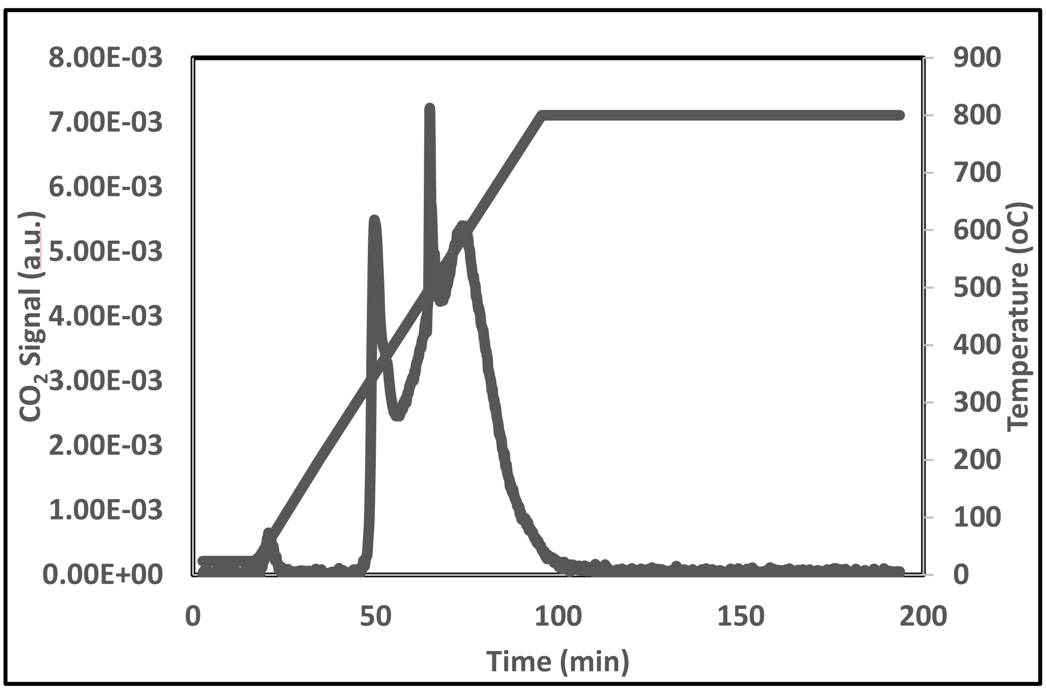

Figure 1: TPO signal for 12wt%APTES

From Table 2, the 26 wt% APTES on SBA-15 sample (calcination experiment data) is the highest possible loading achieved, any further addition of the amine will just be lost during the synthesis process as it will not be bonded to the silica. These samples with various loadings of APTES were then tested to determine the CO_2 removal capacities at room temperature and 1 atm for a dry 50% pure CO_2 in helium feed. Table 3 shows the result for CO_2 adsorption capacities of the sample. With increasing APTES loading, the adsorption capacity of CO_2 increases and the highest adsorption capacity obtained was 0.85 mmol CO_2/ g adsorbent.

Table 3: CO_2 adsorption capacities for various loadings of APTES on SBA-15

Sample	**Moles of CO2 adsorbed (mmol CO2/ g ads)**
SBA-15	0.016
12wt%APTES	0.069
20wt%APTES	0.35
25wt%APTES	0.80
26wt%APTES	0.85

TAG meetings:

Our first TAG meeting was held on March 20, 2019. We had a number of TAG meeting (list here: http://www.eng.usf.edu/~jnkuhn/Hinkley2018.html) attending either in person or remotely. The link to the video is also on the website link above.

Future Tasks:

The future work would be to look at the selectivity of the adsorbent in CH_4/ CO_2 mixture. Cyclic adsorption/desorption studies will be conducted over extended time periods to determine the long term stability and performance of the adsorbents. Also, the performance of the sample in humid conditions will be studied before using the adsorbent to remove CO_2 from real landfill gas.