QUARTERLY PROGRESS
REPORT

September 2020 – November 2020

PROJECT TITLE: ASSESSMENT OF LOW-COST ADSORBENTS FOR SILOXANES REMOVAL FROM LANDFILL GAS

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PROJECT WEBSITE: **http://www.eng.usf.edu/~jnkuhn/Hinkley2019.html**

Research Description:

Landfill gas (LFG) is increasingly used and researched as a feedstock for a variety of traditional and proposed Waste-to-Energy (WTE) technologies, which includes electricity generation, compressed natural gas, or liquid hydrocarbon fuels. In these various scenarios, contaminants in the LFG can have substantial economic and environmental consequences in the WTE processes.

Siloxanes are increasing contaminants of LFG as many consumer products being land-filled contain this compound. Siloxanes in biogas cause damage to machines if not removed because it thermally decomposes to silica. This leads to high maintenance cost of WTE technologies thereby serving as a disadvantage to the economics of the entire process. Current purification techniques available for siloxanes removal are expensive; it costs less to repair damaged engine parts than to adopt current siloxane purification techniques. In order to accelerate adoption of WTE processes, a need for more economical methods for removing siloxanes from LFG exists. The goal of this research project is to develop low cost strategies for siloxane removal from LFG. The study will be evaluating the economic potential and environmental impact of selected scrubbing technologies using low cost adsorbents.

Work accomplished during this reporting period:

For the period outlined in this report, biochar samples were obtained from the Department of Civil and Environmental Engineering at the University of South Florida. The biochar samples obtained are displayed in Figure 1 below. N_2 physisorption analysis was conducted on biochar samples to determine its surface area, pore volume, and average pore diameter. The N_2 physisorption analysis results are displayed in Table 1. XRD analysis was conducted on the biochar samples to obtain information on its chemical structure. The XRD analysis profile for biochar is displayed in Figure 2. CO_2 adsorption isotherm was generated for biochar samples in order to examine the competition of adsorption sites by this compound. The CO_2 adsorption capacity of biochar was calculated from the adsorption isotherm to be 22.5 mg CO_2 /g biochar. Figure 3 displays the CO_2 adsorption isotherm for biochar. A static adsorption instrument (Autosorb; Quantachrome) was used in conducting the chemisorption and physisorption experiments. N_2 physisorption analysis was conducted on hydrochar samples obtained from Prof. George Philippidis' research group and the results are displayed in Table 2 below. According to Cabrera-Codony et al. (2018). "the porous features of adsorbent media are responsible for siloxanes uptake in competitive adsorption" (pg. 572). Given that the critical diameter of bulky siloxanes like octamethylcyclotetrasiloxane (D4) is 1.08 nm (Cabrera-Codony et al., 2018), the pore diameter of biochar and hydrochar displayed in Table 1 and 2 suggests that these adsorbent materials are capable of adsorbing siloxanes.

Figure 1: Biochar samples.

Table 1: N_2 Physisorption Analysis Result for Biochar (Dr. Ergas Lab at USF)

Biochar	**Specific Surface Area [m2/g]**		**Pore Volume [cc/g]**	**Pore Diameter [nm]**
	S_{BET}	**S_{BJH}**	**V_{BJH}**	**D_{BJH}**
Pellets	467.384	21.007	0.029	3.128

Table 2: N_2 Physisorption Analysis Result for Hydrochar (Dr. Philippidis Lab at USF)

Hydrochar	**Specific Surface Area [m2/g]**		**Pore Volume [cc/g]**	**Pore Diameter [nm]**
	S_{BET}	**S_{BJH}**	**V_{BJH}**	**D_{BJH}**
Powder	1.15	-	0.0028	4.32

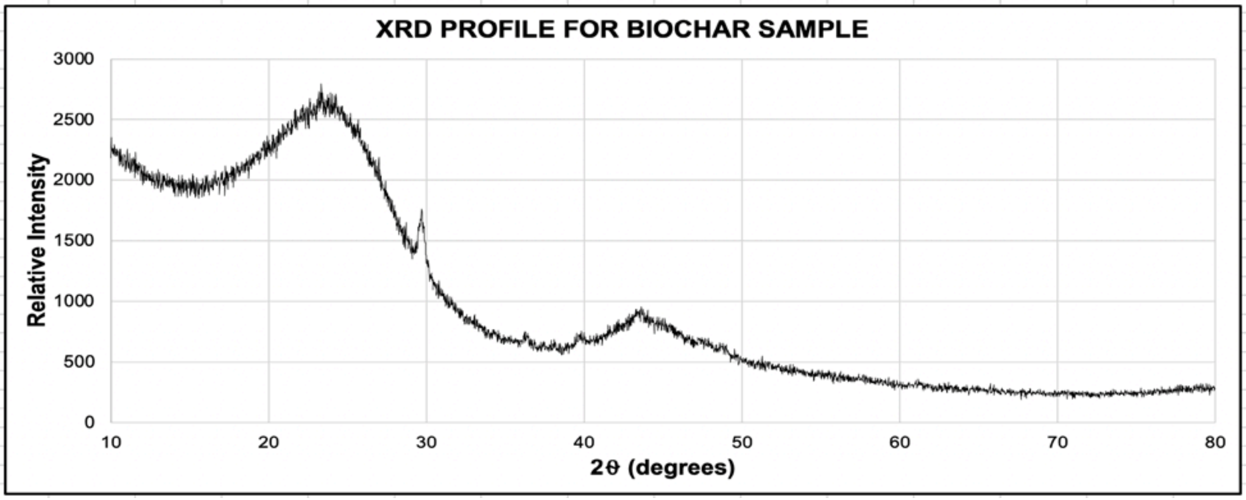

Figure 2: XRD Analysis Profile for Biochar

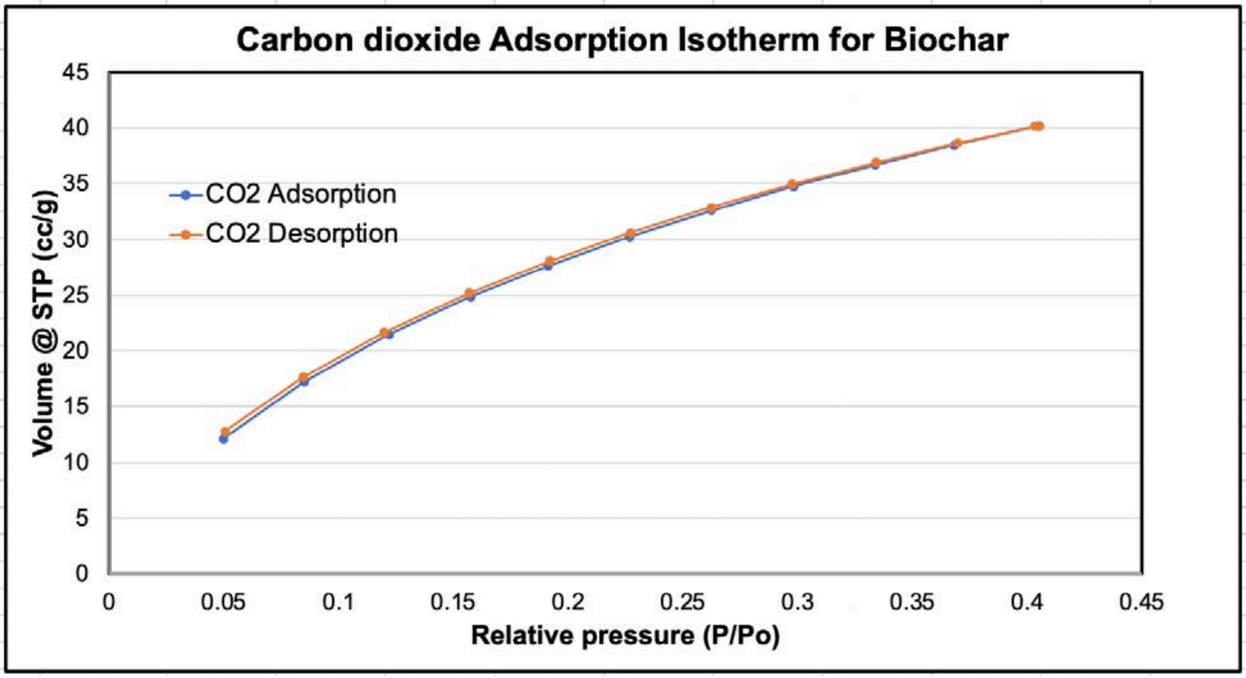

Figure 3: CO_2 Adsorption Isotherm for Biochar.

Techno-economic Analysis

A preliminary techno-economic analysis was conducted for a siloxane removal process utilizing a consumable media as an adsorbent which is replaced once saturated with siloxane. To ensure a continuous process, two adsorption chambers are used in this system. LFG flows through the adsorbing packed bed till it is saturated with siloxane after which the operation of the two packed beds between saturated/fresh media is switched by a valve.

Adsorption/Sacrificial bed process

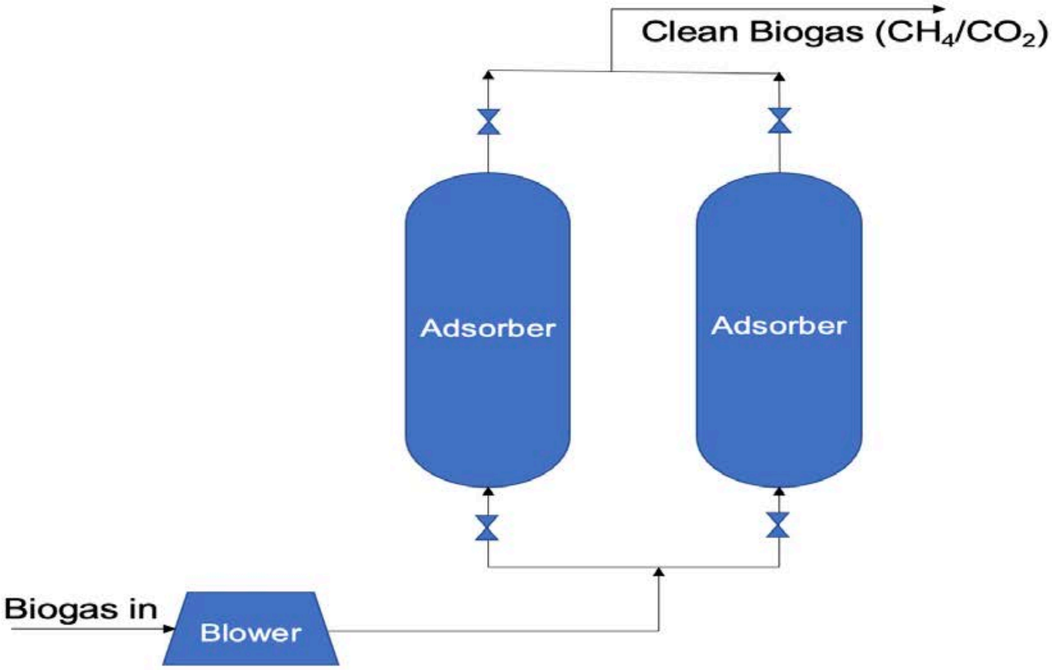

Figure 4: Schematic of Siloxane Removal System using Adsorption/Sacrificial bed process

Table 3: Equipment Needed for Siloxane Removal System

Equipment	**Quantity**
Process Vessel	2
Blower	1

The use of activated carbon and clinoptilolite as consumable media were compared in this study. Preliminary TEA was conducted based on the literature values of the adsorption capacity of octamethylcyclotetrasiloxane (D4) on clinoptilolite and activated Carbon. D4 was chosen as the target siloxane as it is the most occurring siloxane type in biogas (Tran et al., 2019). The adsorption capacity values are displayed in table 4 below.

Table 4: Adsorption capacity for Activated Carbon and Clinoptilolite

Adsorbent media	**Adsorption Capacity at Room Temperature (mg D4/g adsorbent)**
Activated Carbon	53 (Sigot et al., 2014)
Clinoptilolite	11.2 (Cabrera-Codony et al., 2017)

The biogas flowrate and the siloxane concentration in the biogas/LFG are two very important factors that affects the size of the siloxane removal system needed which in turn directly affects the cost of the siloxane removal system. In this report, a base case with siloxane concentration of 15 mg/m^3 was studied since this concentration falls within the typical range of siloxane concentration (5 to 15 mg/m^3) as suggested by Elwell et al. (2018). The biogas flowrate studied in this report ranges from 500 to 3500 SCFM. The cost of raw materials used in this study was gotten from (Alibaba, n.d.-a) and (Alibaba, n.d.-b) and is displayed in table 5 below.

Table 5: Cost of Raw Materials

Adsorbent Material	**Cost ($/ton)**	**Cost ($/kg)**
Activated Carbon (Coconut based)	1350	1.49 (Alibaba, n.d.-a)
Clinoptilolite	113	0.12 (Alibaba, n.d.-b)

Some of the assumptions used for the estimation of the cost of siloxane removal system is displayed in table 6 below:

Table 6: Assumptions used for estimation of capital, operating and maintenance costs for siloxane removal system (Tansel & Surita, 2019).

Item	**Value**
Auxiliary equipment	5% of equipment cost
Freight	5% of equipment cost
Sales Tax	10% of equipment + freight
Foundation and structural support	8% of total equipment cost (TEC)

Handling and erection	8% of TEC
Electrical	4% of TEC
Piping	2% of TEC
Insulation	1% of TEC
Painting	1% of TEC
Siloxane System Periodic Testing	$24,000 per yr.
Indirect costs (for labor + maintenance)	60%
Insurance	1% of total capital investment
Administration	2% of total capital investment
Interest rate	7%
Amortization period	10 years

Figure 5 shows the total capital investment (TCI) comparison between siloxane removal system using clinoptilolite media and activated carbon media. It can be seen that a siloxane removal system that uses activated carbon media has a much greater TCI than a siloxane removal system that uses clinoptilolite media.

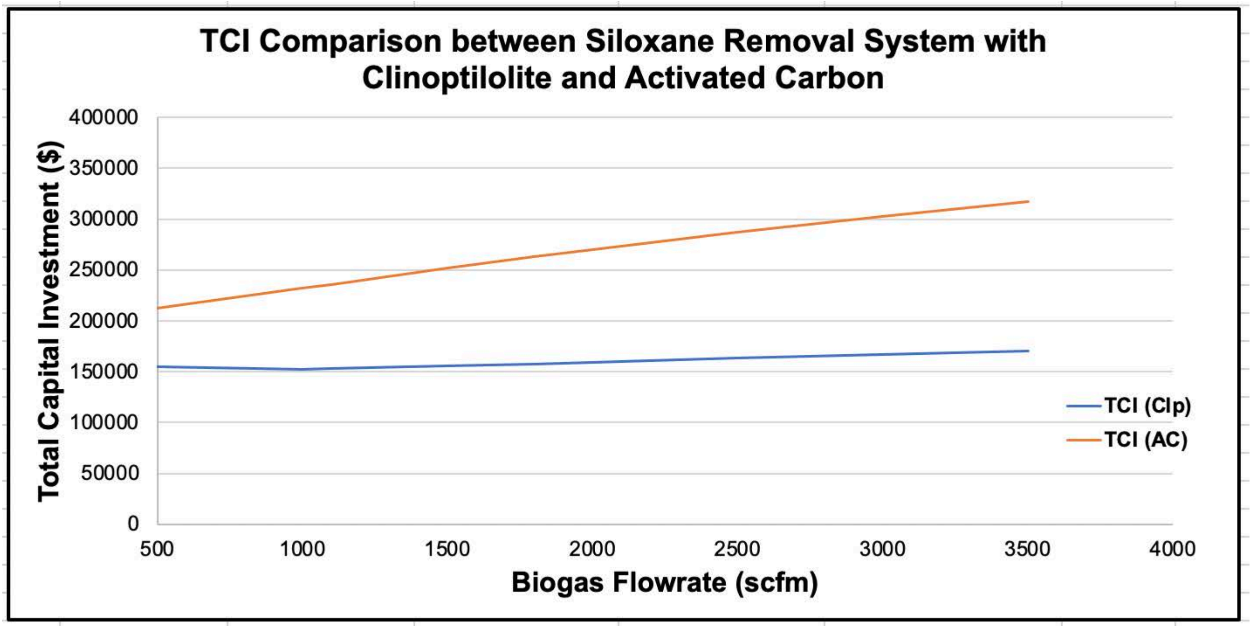

Figure 5: Total Capital Investment (TCI) comparison between Siloxane Removal System with Clinoptilolite and Activated Carbon (Base case: 15 mg/m^3 D4 concentration).

TCI was calculated using Eq. (1) (Hill, 2014) below:

TCI = DCC + ICC + Project contingency + Retrofit cost

Where:
TCI – Total Capital Investment
DCC – Direct Capital Cost
ICC – Indirect Capital Cost

Figure 6 shows the total annual cost comparison between an LFG plant that installs a siloxane removal system using activated carbon media and clinoptilolite media, and an LFG plant without siloxane removal system installed. It can be seen from the graph that installing siloxane removal system in LFG facilities operating at biogas flowrate capacities less than 1000 scfm is not economically feasible as the TAC associated with the siloxane removal system exceeds the maintenance cost for facilities with no siloxane removal system installed. However, for facilities with biogas flowrate capacities exceeding 1000 scfm, it becomes economically feasible to install a siloxane removal system. The maintenance cost used for this comparison was gotten from Tansel & Surita (2019).

TAC was calculated using Eq. (2) (Hill, 2014) below:
TAC = DOC+IOC-RC
Where:
DOC – Direct Operating Cost
IOC – Indirect Operating Cost
RC – Recovery Credits

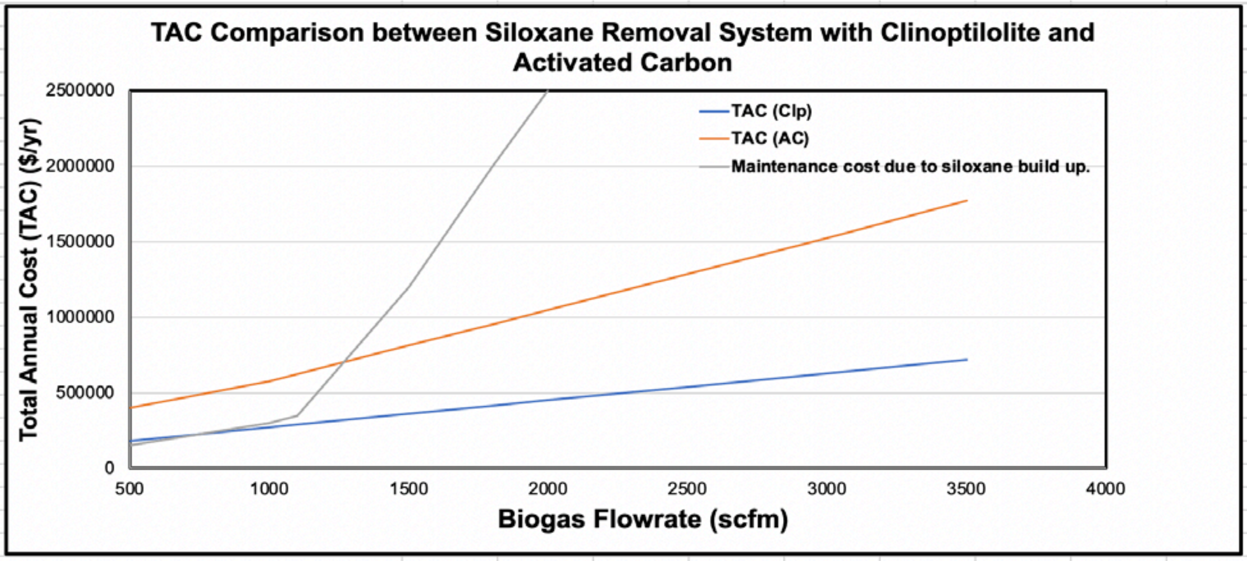

Figure 6: Total Annual Cost (TAC) Comparison between Siloxane Removal System with Clinoptilolite and Activated Carbon Media (Base case: 15 mg/m^3 D4 concentration).

The pie charts displayed in figure 7 and figure 8 shows the capital and operating cost distribution for siloxane removal system using activated carbon and clinoptilolite media. The base case used in this illustration is a biogas flowrate of 1000 scfm and siloxane (D4) concentration of 15 mg/m^3. It can be seen from figure 7 and figure 8 that the direct operating cost (DOC) accounts for more than 50% of the total cost. Once the DOC is broken down, it shows that the replacement of the siloxane removal system media accounts for the majority of the cost. This is expected as the siloxane removal system modelled in this study uses a consumable media without regeneration.

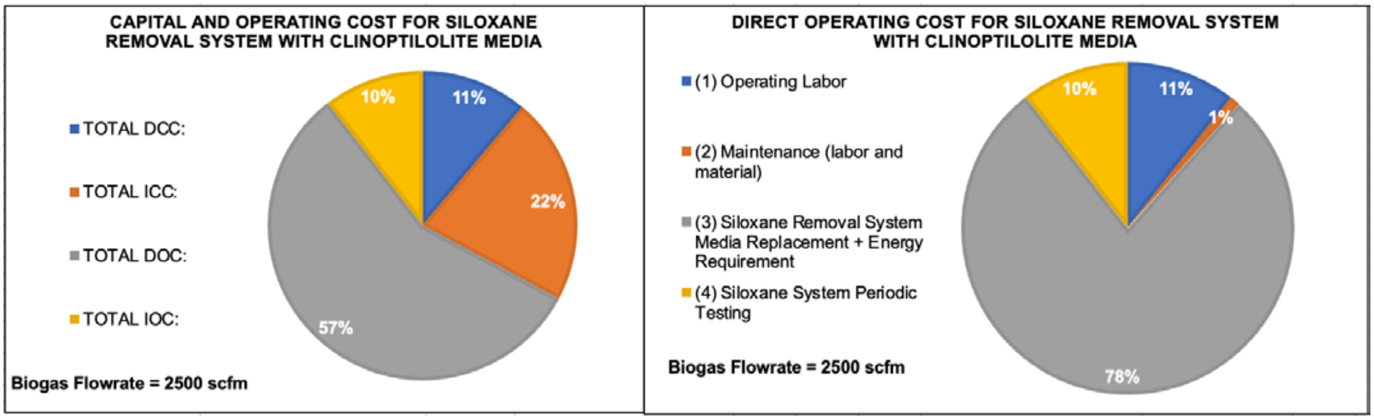

Figure 7: Breakdown of Capital and Operating Cost for Siloxane Removal System using Clinoptilolite Media (Base case: 1000 scfm biogas flowrate, 15 mg/m3 siloxane (D4) concentration).

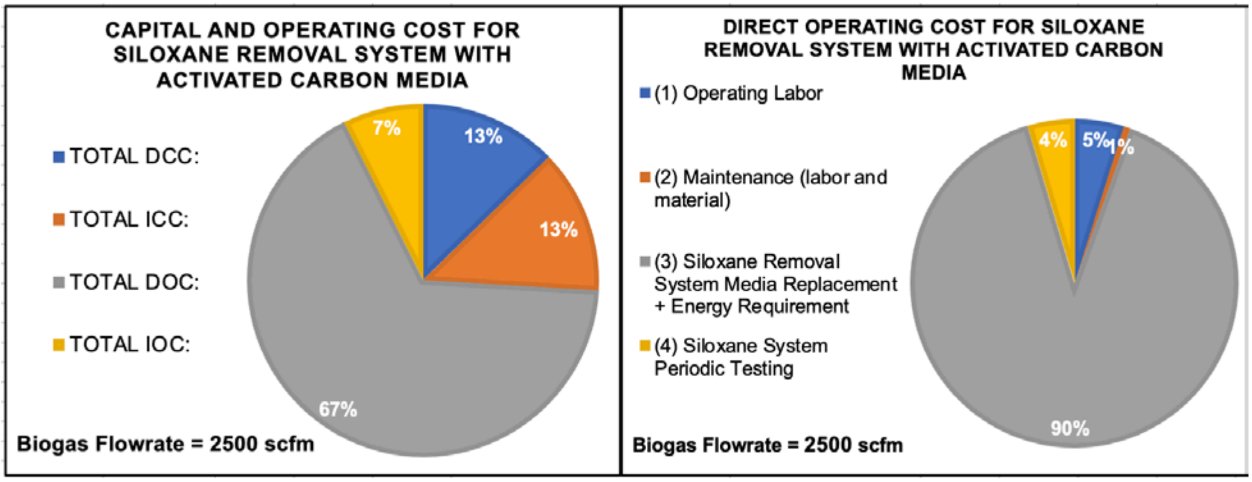

Figure 8: Breakdown of Capital and Operating Cost for Siloxane Removal System using Activated Carbon Media (Base case: 1000 scfm biogas flowrate, 15 mg/m3 siloxane (D4) concentration).

According to Elwell et al. (2018), “siloxane concentration in LFG can vary greatly depending on location, age, weather, source, and components in the landfill and have been stated to be anywhere from 1 to 136 mg/m^3” (Pg. 190). In order to study the effect of siloxane concentration on the cost of siloxane removal system, the concentration of D4 was varied from 5 to 50 mg/m^3 while holding biogas flowrate constant at 1000 scfm. The TAC comparison as a function of siloxane (D4) concentration between siloxane removal systems using activated carbon and clinoptilolite media is displayed in Figure 9 below.

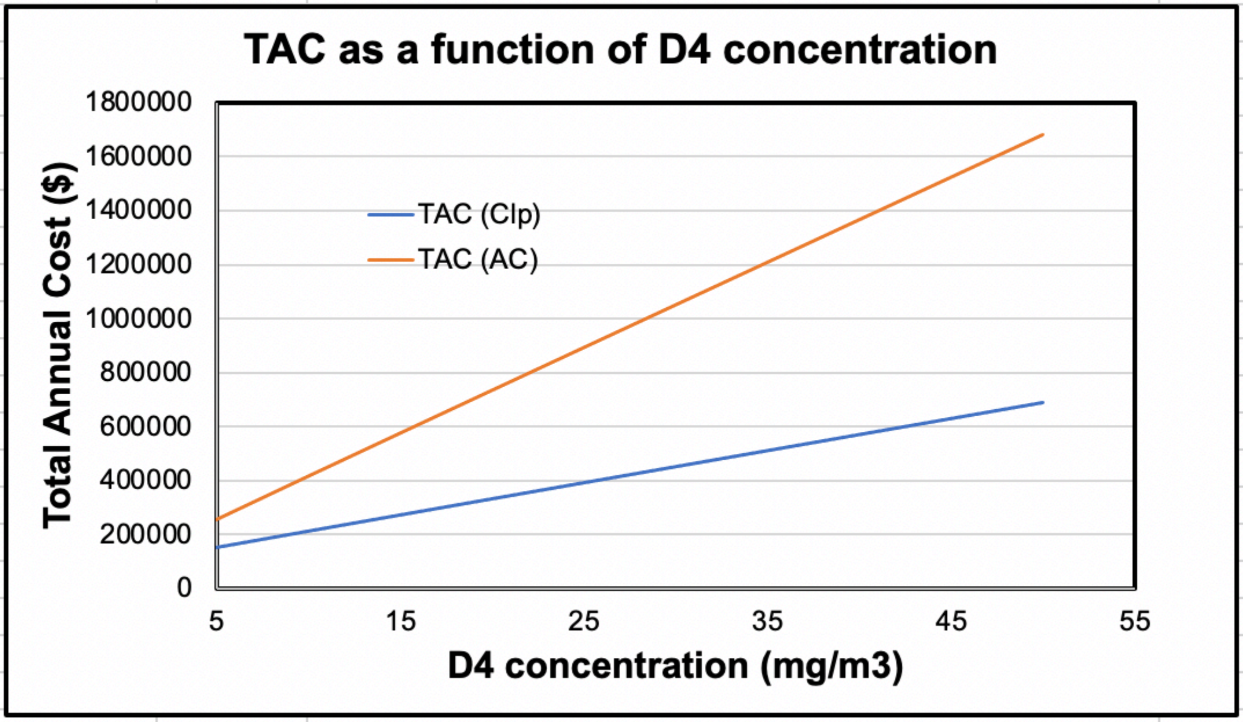

Figure 9: Total Annual Cost (TAC) Comparison as a function of D4 concentration between Siloxane Removal System with Clinoptilolite and Activated Carbon Media (Base case: 1000 scfm biogas flowrate).

Future Task

The future work will involve:

- Determining the adsorption capacity and regeneration ability of chosen adsorbents for selected siloxanes in inert and surrogate LFG.

- Designing a process flowsheet and conducting technoeconomic analyses and life cycle assessment of the siloxanes' adsorbents evaluated in this project.

TAG meeting:

The first TAG meeting occurred on March 4, 2020 (Video can be found here: https://youtu.be/bWuNFECMvTg). The second TAG meeting is estimated to occur in January 2021.

Metrics:

*1. List research publications resulting from **THIS** Hinkley Center projects.*

None up to this point.

*2. List research presentations resulting from **THIS** Hinkley Center project.*

Amaraibi, R. J. (2020, March). *Assessment of Low-Cost Adsorbents for Siloxanes Removal from Landfill Gas*, Paper presented at the TAG meeting, USF, Tampa.

Amaraibi, R. J. (2020, September). *Assessment of Low-Cost Adsorbents for Removal of Siloxanes from Landfill Gas*, Paper presented at the meeting of NOBCChE, Virtual Conference.

Kuhn, J. N. (2020, October). *Assessment of Low-Cost Adsorbents for Removal of Siloxanes from Landfill Gas*, Paper presented at the meeting of SWANA Hinkley Center Research Symposium, Zoom.

Amaraibi, R. J. (2020, November). *Assessment of Low-Cost Adsorbents for Removal of Siloxanes from Landfill Gas*, Paper presented at the meeting of AICHE, Virtual Conference.

3. List who has referenced or cited your publications from this project?

None up to this point.

4. Provide an explanation of how the research results from this Hinkley Center project and previous projects have been leveraged to secure additional research funding.

None up to this point.

5. List new collaborations that were initiated based on this Hinkley Center project.

We are collaborating with Prof. George Philippidis. His group is producing biochar and hydrochar from waste materials. These materials will be tested as additional low-cost adsorbents.

6. *Provide an explanation of how the results from this Hinkley Center funded project have been used (not will be used) by the FDEP or other stakeholders?*

To date, the results have not been used by the shareholders.

Pictures:

A compilation of current pictures can be found here: (**http://www.eng.usf.edu/~jnkuhn/Hinkley2019.html**)

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