#### QUARTERLY PROGRESSREPORT

November 2023 – January 2024

# PROJECT TITLE: Carbon Capture from Gaseous Landfill Emissions, Part 2: System Designs for Carbon Purposing

#### PRINCIPAL INVESTIGATOR(S):

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#### **Research Description:**

Landfill gas (LFG) is increasingly used and proposed for a variety of Waste-to-Energy (WTE) technologies either developed or in the process thereof. A challenge for all of these processes is that carbon dioxide (CO<sub>2</sub>) is produced, by mass, in higher quantities than methane (CH<sub>4</sub>), the primary energy carrier, and CO<sub>2</sub> amounts tend to increase from aging landfills. Thus, this low energy content either hinders the performance of the WTE process (e,g, electricity generation) or necessitates purification for value-added products. The high costs of purification are especially prohibitive for production of renewable natural gas (RNG) for pipeline quality natural gas, due to the stringent requirements.

In this work, we propose to apply the efficient adsorbents for CO<sub>2</sub> removal from biogas that were developed in Part I of this project. In our earlier Part I of the project funded by the Hinkley Center, amineimmobilized adsorbents prepared and demonstrated to purify biogas (both surrogate and real LFG) to pipeline/vehicle grades. In the present effort, we propose to employ the materials to integrate CO<sub>2</sub> removal into application areas such as bio-methane (i.e., RNG) production via extended stability tests and economic projections and CO<sub>2</sub> recovery and sequestration. The proposed effort leverages previous and ongoing efforts on research and demonstration of LFG to diesel fuel through thermochemical catalytic processes, contaminant removal from LFG, and economic and environmental impact from WTE technologies, which have been funded by the Hinkley Center, Florida Energy Systems Consortium (FESC), the Department of Energy, VentureWell and T2C-Energy, LLC.

# Work accomplished during this reporting period:

For this reporting period, we initiated the synthesis of the amine-supported adsorbents, characterization of samples from Part 1 of this project, and initiated the life cycle analysis. Unfortunately, all of the paperwork to allow the start of the project was not finalized until the middle of this quarter.

# Adsorbent Synthesis and Characterization:

The synthesis and characterization have been initiated. We have begun acquiring precursors to validate synthetic procedures and started benchmark characterization. To date, we have not experienced any technical issues. We will be able to start presenting performance data in the next quarter.

#### Systems Level Modeling and Comparison of Methods:

Landfill gas (LFG), a mixture of mainly methane, carbon dioxide, and contaminants (such as siloxanes and hydrogen sulfide) is a product of the anaerobic decomposition of municipal solid waste in landfills [1]. The low energy content of LFG happens because of the high concentrations of  $CO_2$ , and it can be enriched by removing the  $CO_2$  to the production of renewable natural gas (RNG), a feedstock to the production of fuels, which enables a circular economy. Due to the interest in replacing fossil natural gas, the use of renewable natural gas (RNG) has increased the discussion of decarbonization based on its viability [2]. In this scenario, several technologies for up-grading the biogas have been developed to improve efficiency and reduce costs [3].

Cherubini et al., [4] studied four different strategies of utilization of landfill gas which included no treatment, treated and burnt landfill to produce electricity, separation of organic and inorganic materials followed by production of electricity and biogas, and incineration to produce electricity. The authors found that sorting a plant coupled with electricity and biogas production is the best option for waste management, providing the reduction of ecological footprint.

To valorize biogas, the production of heat and electricity through engines is usually done. On the other hand, there are sustainable alternatives to biogas combustion such as the production of biomethane and hydrogen [3, 5]. In this sense, the use of Life Cycle Assessment (LCA) methodologies is a valuable tool to help in strategic decisions and to provide the understanding of environmental impacts [4], such as the comparison between the capture of  $CO_2$  from the LFG from silica supported amine adsorbents and business-as-usual scenarios without purification. The LCA is used to quantify the environmental performance of goods and processes, referring to the whole life cycle, from production to the end-of-life [6].

Kotagodahetti et al. [7] studied the main methods of production of RNG, considering the anaerobic digestion to generate biogas. According to them, some upgrade technologies are used to achieve the methane concentration to be blended into natural gas pipelines. Between these technologies, pressure swing adsorption (PSA), chemical scrubbing, high-pressure water scrubbing (HPWS), and membrane separation are commonly used and were analyzed [8]. These authors did not take into account technologies such as cryogenic separation (sublimation or condensation of CO<sub>2</sub> at varying temperatures), gas cleaning using hot potassium carbonate, or other methods such as the CO<sub>2</sub> purification through amine functionalized supports. The results showed that LFG-based RNG production with PSA stood out in comparison with the other technologies due to higher efficiencies and lower methane loss from an eco-friendly perspective.

Ardolino et al. [6] conducted a study focusing on the comparison of the most common techniques used to get high-quality biomethane through biogas from anaerobic digestion. The Life Cycle Assessment was used to compare the membrane separation, water scrubbing, chemical absorption with amine solvent, and pressure swing adsorption. The authors identified that the performance of the techniques is dependent on site-specific conditions (injection pressure, commercial strategies, among others). In this work, the authors analyzed the use of chemical absorption (CA) with amine solvents such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA) and diglycolamine (DGA) [3] since they are selective in absorbing CO<sub>2</sub>. They found that membrane separation provides the best performances, based on site-specific conditions.

Leonzio et al. [3] analyzed the up-grading processes of biogas to bio-methane using chemical absorption processes. They simulated the comparison using an aqueous solution of MEA (mono-ethanolamine), NaOH (sodium hydroxide), and KOH (potassium hydroxide) and found that MEA solution provides good performance with a low required amount of absorbent solution and through LCA they found that KOH solution is responsible for low environmental impacts.

Starr et al. [9] conducted the life cycle assessment (LCA) to analyze the biogas upgrading using commercial technologies and two pilot-scale technologies: alkaline absorption with regeneration (AwR) process and bottom ash from municipal solid waste incinerators to capture CO<sub>2</sub> in a direct gas/solid contact, called (BABIU) process. They found that BABIU had the lowest impact in 8 of the 12 categories, using the CML 2001 method. The authors also pointed out that 93% of the Global Warming Potential of the BABIU process came from the transport of the bottom ash.

The chemical absorption (CA) processes are commonly researched due to the benefits of simultaneously removing  $CO_2$  and  $H_2S$ . In addition, amine solvents are more selective in absorbing  $CO_2$  with respect to water, ensuring smaller units of up-grading [6, 10]. The process happens through the penetration of gas in the liquid phase [3]. In addition, the process also requires energy for regeneration of the amine to avoid loss of efficiency.

The membrane separation (MS) technique takes the use of materials like <u>polysulfone</u>, polyimide, or <u>polydimethylsiloxane</u> that show a good selectivity to  $CO_2$  and  $CH_4$ . It means that  $CO_2$  is filtered using a membrane, in a way that gases and impurities penetrate the micro-pores of the membrane while methane passes through it [6, 7, 9].

The water scrubbing (WS) technique is used in low temperatures and high pressures and is defined by the difference in solubility of carbon dioxide in water, since when comparing the solubility of  $CO_2$  and methane in water at 25 °C there is a big difference between them. In some configurations, before using the WS, it is necessary to treat the biogas to remove the H<sub>2</sub>S, in the same way that can happen in configurations of MS [6, 11]. The high-pressure water scrubbing (HPWS) happens with a two-stage technique, in which the initial step includes the biogas (desulfurized and pressurized) flowing and carbon monoxide being dissolved in water. The second and last step includes the  $CO_2$  being degassed [2, 7].

Pressure swing adsorption (PSA) technology has as a feature the ability to adsorb some molecules from a gas mixture and release them by applying different pressures. The molecular dimensions differences of carbon monoxide and methane are responsible for making the adsorption of one preferable in comparison with the other according to the cavities of the adsorbent material. Activated carbon is commonly used in this technique. In this configuration, usually the use of a technique to remove  $H_2S$  is utilized [6, 12].

While many LCA studies quantify the environmental benefits of various biogas up-grading techniques, the studies using amine functionalized supports for the removal of CO<sub>2</sub> from methane should be explored. The objective of this study is to assess and compare the environmental impact through the LCA of using the supported amine sorbents (SAS) of our lab studies with commercial technologies (PSA, HPWS, MS, and CA using solvents).

# **References for this Section**

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# TAG meetings:

The  $1^{st}$  TAG meeting was held on Feb. 2 . The full list of members is found at the website link. We were pleased to have ~ 15 of the TAG members be able to join. The website will be updated soon to reflect the meeting took place and the slides will be uploaded there. Matt Yung, Devin Walker, and Tony Elwell were not in attendance.

# Future Tasks:

The future work would be to compare the reproducible synthesis of the candidate silica supported amine adsorbents, plus additional characterization and initial performance testing. We will also update the process economics of using amine functionalized materials for  $CO_2$  adsorption as new data is obtained.

Impact of various factors such as adsorption capacity and degradation rate on separation costs will be examined. The lifecycle assessment will also be continued.

# **METRICS REPORTING**

1. Summarize input provided by the TAG during this period.

We recently completed our kickoff TAG meeting. As mentioned above, we had ~ 15 TAG members present. After ~ 25 min presentation, TAG members asked ~ 5 questions, which helped us refine the explanations and scope of work. We anticipate also receiving feedback via email.

2. List research publications resulting from THIS Hinkley Center project. Has your project been mentioned in any research and/or solid waste publication/newsletters/magazines/blogs, etc.?

None.

3. List research presentations resulting from (or about) THIS Hinkley Center project. Include speaker presentations, TAG presentations, student posters, etc.

"Landfill gas upgrading using amine-functionalized silica sorbents" by O. Johnson at AICHE National Meeting, Orlando FL, Nov. 23.

4. List who has referenced or cited your publications from this project. Has another author attributed your work in any publications?

None.

5. How have the research results from THIS Hinkley Center project been leveraged to secure additional research funding? What additional sources of funding are you seeking or have you sought? Please list all grant applications and grants and/or funding opportunities associated with this project. Indicate if additional funding was granted.

Multiple (pre)proposals on CO2 capture and conversion are pending. One is to ARPA-E, and another to DOE. A USF internal CREATE (<u>https://www.usf.edu/provost/initiatives-special-projects/create.aspx</u>) proposal along similar lines has been invited, in which the PI is also leading.

6. What new collaborations were initiated based on THIS Hinkley Center project? Did any other faculty members/researchers/stakeholders inquire about this project? Are you working with any faculty from your institution or other institutions?

None.

7. How have the results from THIS Hinkley Center funded project been used (not will be used) by the FDEP or other stakeholders? (1 paragraph maximum). Freely describe how the findings and implications from your project have been used to advance and improve solid waste management practices.

None.

PICTURES: The most recent pictures have been uploaded to the website (linked above).