QUARTERLY PROGRESSREPORT
May 2024 – July 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_2) is produced, by mass, in higher quantities than methane (CH_4), the primary energy carrier, and CO_2 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_2 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, amine-immobilized 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_2 removal into application areas such as bio-methane (i.e., RNG) production via extended stability tests and economic projections and CO_2 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:

Adsorbent Testing and Analysis:

In the last reporting period, polyethyleneimine-modified resin (PEI-HP2MGL) was synthesized as reported by our previous work [1]. The textural properties of the synthesized adsorbent were studied with N_2 physisorption. The surface area and average pore diameter of the adsorbent was 27 m^2/g and 6.5 nm. This is consistent with our previously reported work in the literature. The performance of the adsorbent for CO_2 adsorption and CO_2 separation from biogas stream was also confirmed. In a static CO_2 adsorption experiment, the adsorption capacity of the adsorbent was estimated to be 2.6 $mmol_{CO2}/g_{ads}$. In a biogas

gas stream of CH_4/CO_2/inert at 40/40/20 vol%, the breakthrough capacity was 2.1 $mmol_{CO2}/g_{ads}$ with saturated capacity of 2.3 $mmol_{CO2}/g_{ads}$. This performance is also consistent with already published work on this topic, confirming the reproducibility of the amine-modified polymeric resin.

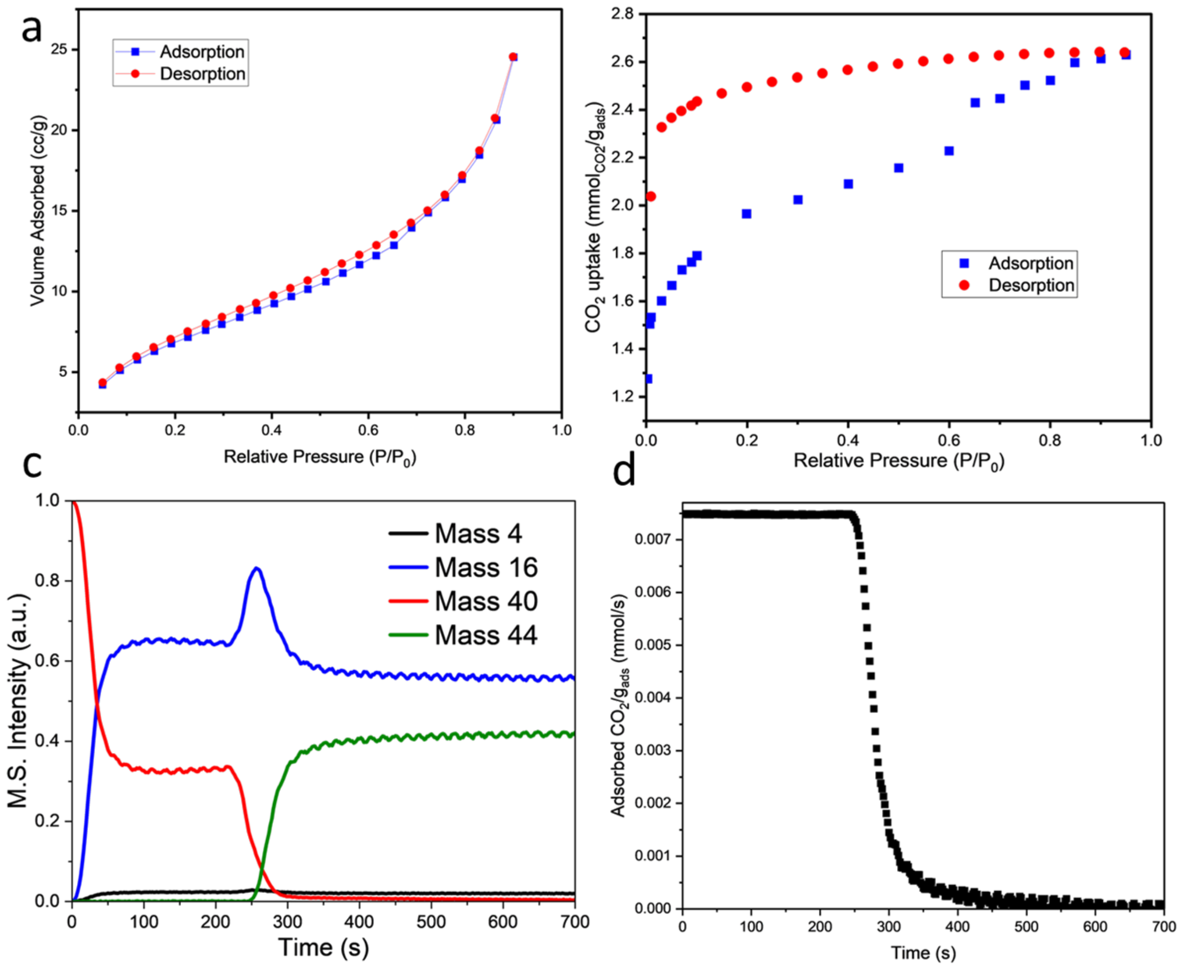

Fig. 1: **(a)** N_2 physisorption **(b)** Static CO_2 adsorption-desorption isotherm **(c)** CO_2 separation from model biogas **(d)** CO_2 breakthrough curve of PEI-HP2MGL

Understanding the pressure drop across the commerical scale adsorber unit is very important as this can affect the flow in the bed and the adsorption pressure. The pressure drop of the temperature swing adsorption unit was estimated to be 3.13 bar across the bed using the Ergun equation given below.

$$\Delta P = \frac{150(1-\emptyset)^2 \mu v}{\emptyset^2 Dp^2} L + \frac{1.75(1-\emptyset)\rho v^2}{\emptyset^3 Dp} L$$

Where,

ΔP= Pressure drop (Pa), $\emptyset$= Adsorbent bed void

μ = Dynamic Fluid Viscosity (Pa.s) , v= Fluid velocity (m/s)

Dp= Particle diameter (m), L= Packed bad length (m)

ρ= Biogas density (kg/m^3)

Consequently, the economic analysis of the system was updated to reflect a new design parameter and account for increasing compressor cost due to pressure drop. Compared to the published economic analysis[1], the system has been updated as follows:

1. Increased Vessel to 3 (15 m^3 each)
2. Increase regeneration cycle to 24 per day (from 12)
3. Vessel pressure drop is 3 bar
4. Change blower to compressor (450 kW rating)
5. Cost adsorbent cooling with N_2 (inlet =20 °C and Outlet = 40 °C)

These changes increased the cost of biomethane production by 30 USD per 1000 m^3, with compressor cost and the operating cost of cooling the adsorber with nitrogen the major cause of this increased production cost, as highlight below in the red text.

Per 1000 m^3 of Biomethane		
	Updated	Old Cost
Operating cost of Steam	$ 36.55	$ 36.55
Annualized Vessel Cost	$ 2.92	$ 2.81
Operating cost of compressor	$ 0.20	$ 0.05
Annualized Compressor Cost	$ 18.83	$ 0.31
Adsorbent capital cost	$ 33.08	$ 33.08
Operating labor cost	$ 21.09	$ 21.09
Waste disposal cost	$ 0.17	$ 0.17
Operating cost of cooling N_2	$ 10.91	-
Overall cost	$ 123.76	$ 94.07

Life Cycle Assessment (LCA)

System boundaries

Update: For this study, system boundaries involving the CO_2 removal from landfill gas to the production of CNG/LNG or no CO_2 capture (flaring – counterfactual scenario) is presented in Figure 2. The functional unit was replaced with **1 MJ of energy** from CNG and LNG. This functional unit helps compare the life cycle emissions with various end products when CO_2 capture is applied to using amine-functionalized supports or not.

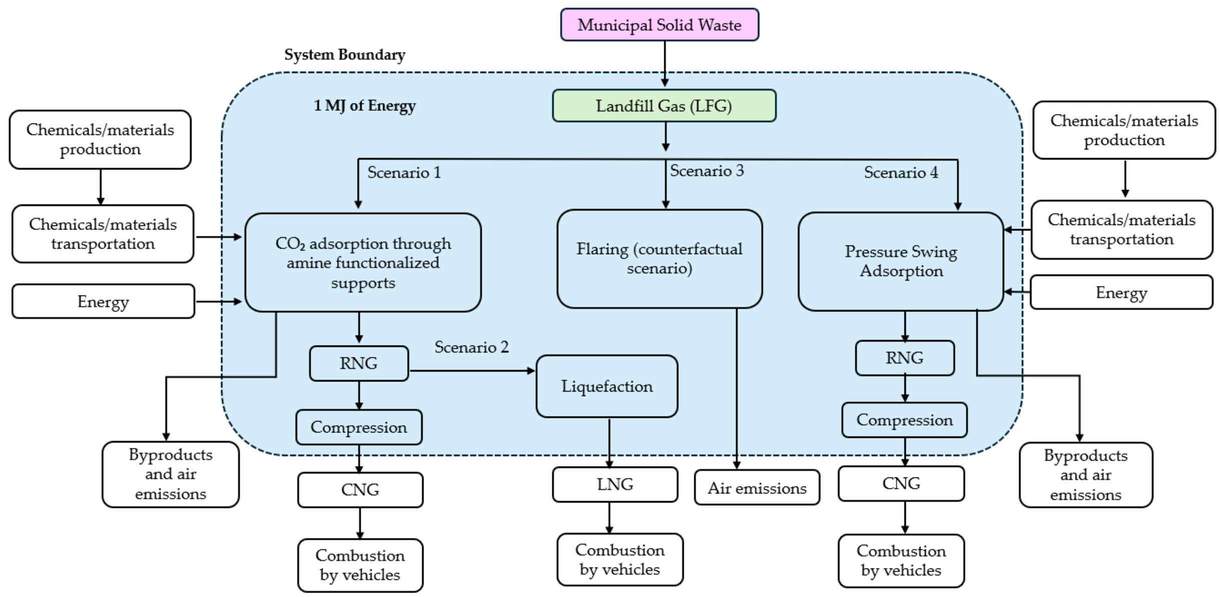

Fig. 2: Updated system boundaries for the LCA of CO_2 removal from landfill gas using amine- functionalized supports.

Process Flow Diagram

In this study, the composition of biogas is modeled as 56.7 % methane, 40.5 % carbon dioxide [1] as major constituents and it is used as the only feedstock for this process. The adsorption the CO_2 from biogas using amine functionalized supports proposed in this project is represented in the process flow diagram (PFD) reported in Figure 3. Three bed systems (leg-lead for two of them and one in regeneration) are used. Figure 3 a) represents the first regeneration mode in which the first two bed systems will be used in the process while the third one will be regenerated with N_2 flow (cooling step) and steam (flash vessel for separation of CO_2 and water). Figure 3 b) and c) are also modes of operation of the system.

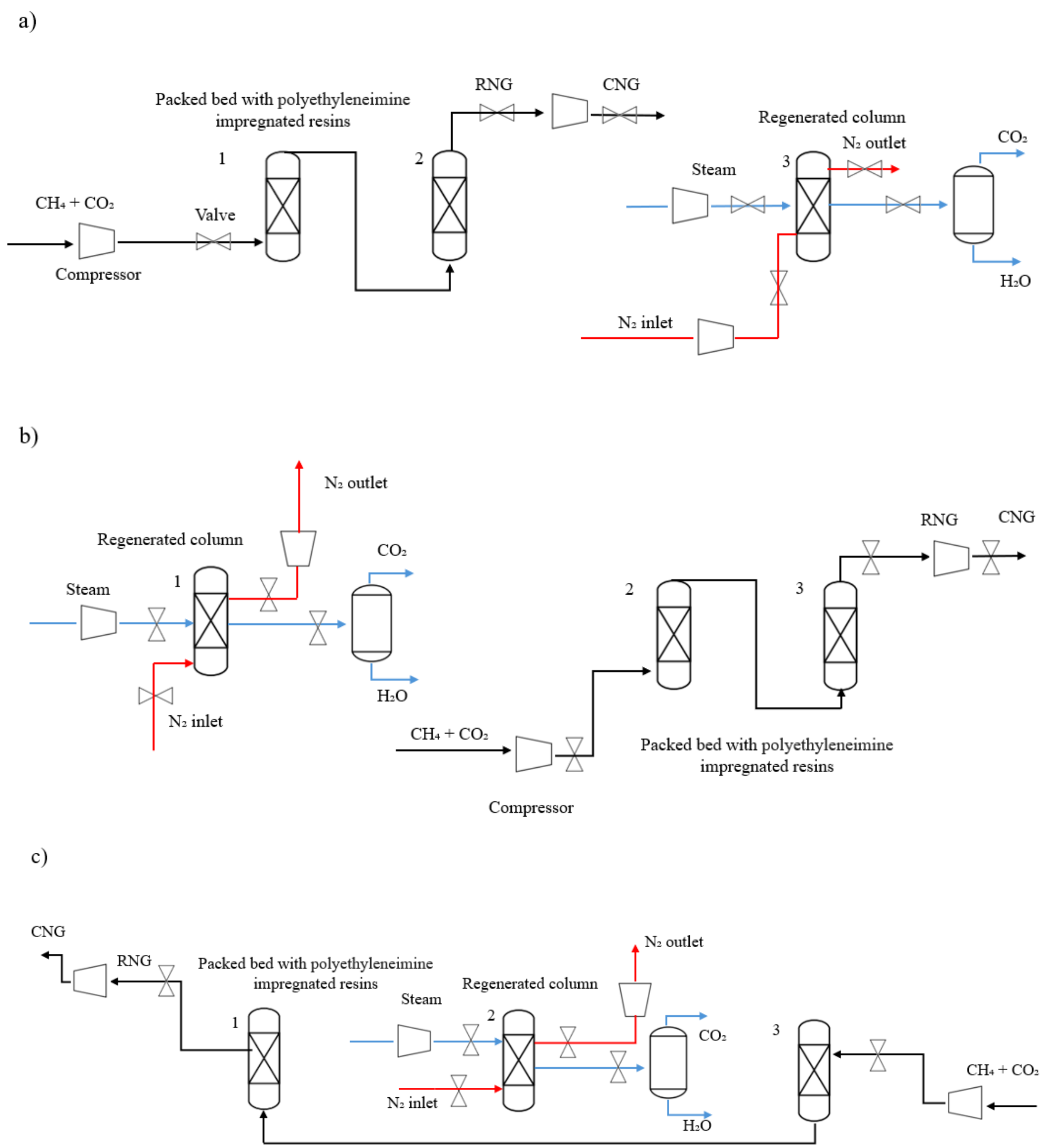

Fig. 3: **(a)** First regeneration mode for the system using two beds, **(b)** second regeneration mode and **(c)** third regeneration mode.

Model assumptions

This study assumes that the facility containing the three beds with amine functionalized supports for CO_2 adsorption from landfill gas is located with the landfill site. In addition, it was assumed that the feedstock is biogas derived from landfill gas. The life cycle GHG emissions might vary within the operation of the process proposed, mainly due to the composition ratio of CH_4:CO_2 of the biogas, as reported elsewhere [2]. Life cycle analysis (LCA) results are computed for 4 different scenarios, according to the defined system boundaries. These scenarios include landfill gas to production of CNG using amine functionalized supports for CO_2 adsorption (scenario 1), the use of LFG for generation of LNG (scenario 2), flaring – counterfactual (scenario 3) and CNG using Pressure Swing Adsorption (scenario 4). The GREET 2023 model [3] is used in this study to perform the life-cycle analysis.

GREET scenarios for simulation

Using the GREET 2023 model, new pathways were created to simulate the CO_2 capture from biogas using the PEI (polyethyleneimine) impregnated resins developed in our research group [1]. In addition to the nitrogen, electricity, biogas and water, the inputs of scenario 1 and 2 that use PEI have methyl amine and methacrylate ester resin to form the CO_2 adsorbents with a defined carbon capture ratio based on our experimental results. Compressed natural gas and liquefied natural gas are produced as main outputs, respectively (Figures 4 and 5).

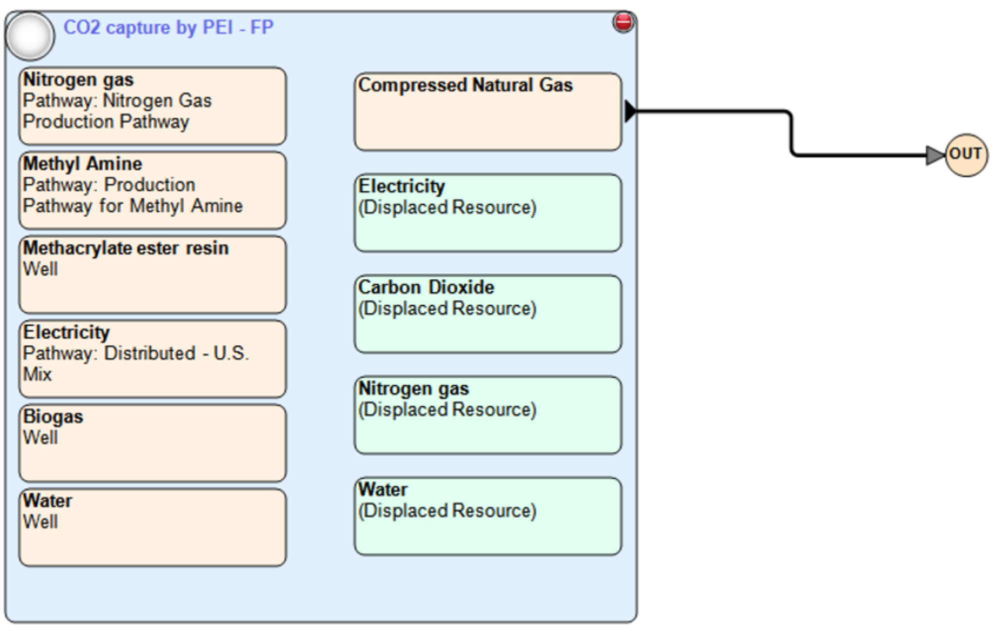

Fig. 4: Scenario 1- landfill gas to production of CNG using amine functionalized supports for CO_2 adsorption.

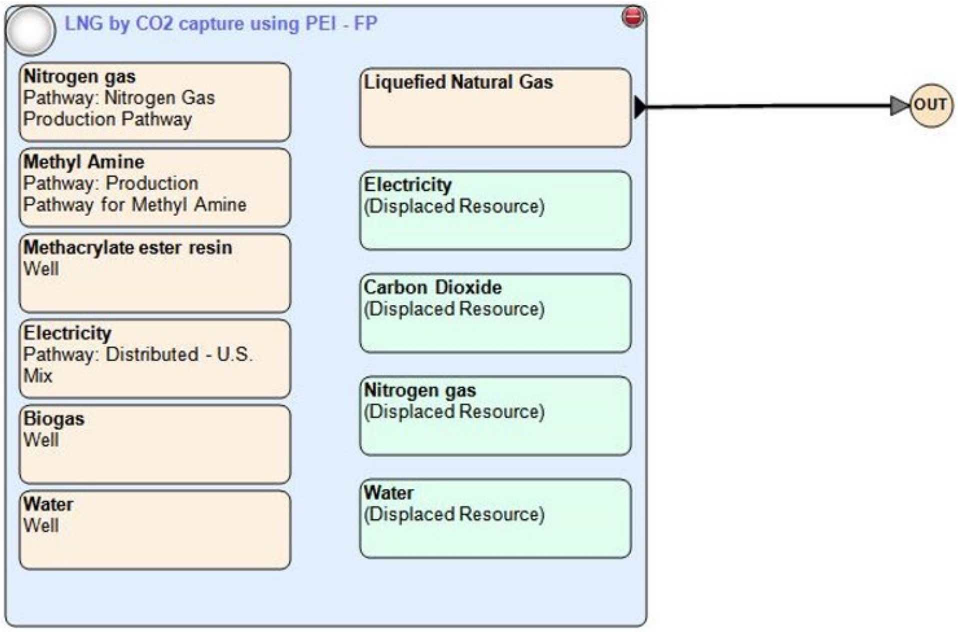

Fig. 5: Scenario 2 - landfill gas to production of LNG using amine functionalized supports for CO_2 adsorption.

The counterfactual scenario used for comparison in this project is flaring of biogas, a common option for management of LFG in waste-to-energy product pathways. Scenario 3 is represented in Figure 6.

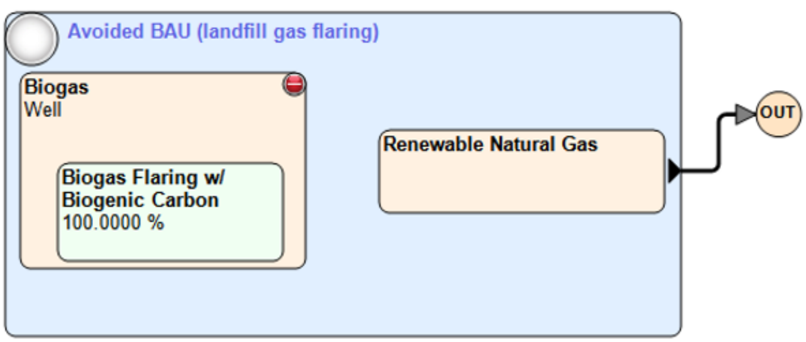

Fig. 6: Scenario 3 - landfill gas to flaring (counterfactual scenario).

Pressure Swing Adsorption is used in Scenario 4 (Figure 7) for life cycle GHG emissions comparison with the proposed project.

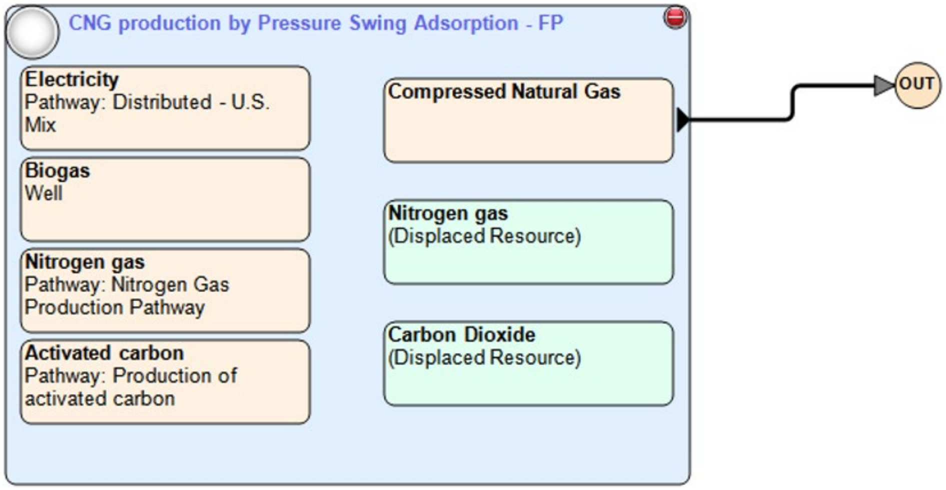

Fig. 7: Scenario 4 – CNG production using Pressure Swing Adsorption.

Life Cycle Inventory Data

The mass and energy data associated with the biogas used as feedstock in this proposed project are reported in Table I. Carbon ratio and sulfur ratio indicate the mass ratio of carbon or sulfur atoms in the molecules of the gas, respectively.

Table I. Landfill Gas composition.

Biogas properties	Unit	Value
Density	g/ft^3	22
Low Heating Value (LHV)	Btu/ft^3	544.56
High Heating Value (HHV)	Btu/ft^3	605.49
Sulfur Ratio	%	$6\ x\ 10^{-6}$
Carbon ratio	%	53.57

The process inputs and outputs using amine adsorbents are based on the performance results achieved in our research group. Table II summarizes more considerations used for the comparison of scenarios.

Table II. Considerations for simulation.

Data used	Unit	Value
Biogas energy flow	Btu/h	100
Flaring efficiency	%	98 [2]

A complete detailed description of all inputs and outputs flow for the four scenarios will be provided in the next report, including the Life Cycle GHG Emission Results and the discussion, analysis, and recommendations.

References for this section

1. Johnson, O., B. Joseph, and J.N. Kuhn, *CO2 separation from biogas using PEI-modified crosslinked polymethacrylate resin sorbent.* Journal of Industrial and Engineering Chemistry, 2021. **103**: p. 255-263.
2. Poddar, T.K., et al., *Life Cycle Analysis of Fischer-Tropsch Diesel Produced by Tri-Reforming and Fischer-Tropsch Synthesis (TriFTS) of Landfill Gas.* Environ Sci Technol, 2023. **57**(48): p. 19602-19611.
3. Wang, M., et al., *Summary of Expansions and Updates in R&D GREET® 2023.* 2023.

TAG meetings:

There was not a TAG meeting during this quarter.

Future Tasks:

In the next reporting period, we plan to conduct cyclic performance testing of the adsorbent in real landfill gas from the Sarasota County to study the long-term performance and the effect of impurities such as siloxane and sulfides among others on the performance. We will also complete the LCA in the next quarter.

METRICS REPORTING

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

   There was minimal input from the TAG during this quarter.

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.

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

   None during this quarter, though we have several accepted for this fall.

   "Landfill gas upgrading using amine-functionalized silica sorbents" by O. Johnson at AICHE National Meeting, Orlando FL, Nov. 2023.

   "Amine-Impregnated Hyper-Cross-Linked Polymeric Resins for Economically Viable CO_2 removal" by O. Johnson at ACS meeting, Denver CO, August 2024.

   "Amine-Infused Adsorbents for Biogas Purification to RNG" by O. Johnson at AICHE National Meeting, San Diego CL, Oct. 2024.

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 proposals are pending.

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).