QUARTERLY PROGRESSREPORT
February 2024 – April 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:

For this reporting period, we continued the analysis of the amine-supported adsorbents, from Part 1 of this project, and also made progress on the life cycle analysis.

<u>Adsorbent Testing and Analysis:</u>

In the last reporting period, work was done to make a new batch of adsorbent and test again the CO_2 performance of resin-supported PEI adsorbent samples that were made in 2020. A breakthrough experiment was performed with a 50% CO_2 concentration balanced with Ar, and He was used as a tracer.

Fig. 1. shows the results of the measurement. The CO_2 breakthrough and saturated adsorption capacity of the 30PEI-HP2MGL were estimated to be 0.91 and 1.61 $mmol_{CO2}/g_{ads}$. This result is consistent with the CO_2 uptake capacity from the static CO_2 isotherm experiment, where the adsorption capacity measurement was estimated to be ~1.8 $mmol_{CO2}/g_{ads}$. The reduction in the adsorption capacity of the resin-based adsorbent compared to when freshly synthesized (2.7 $mmol_{CO2}/g_{ads}$) is indicative of possible leaching or degradation of amine molecules in the shelfed resin-based adsorbent. A new synthesis effort is being undertaken to prepare a fresh batch of adsorbent and re-evaluate its CO_2 adsorption performance, with the aim of replicating the high adsorption capacity observed in the initially synthesized samples.

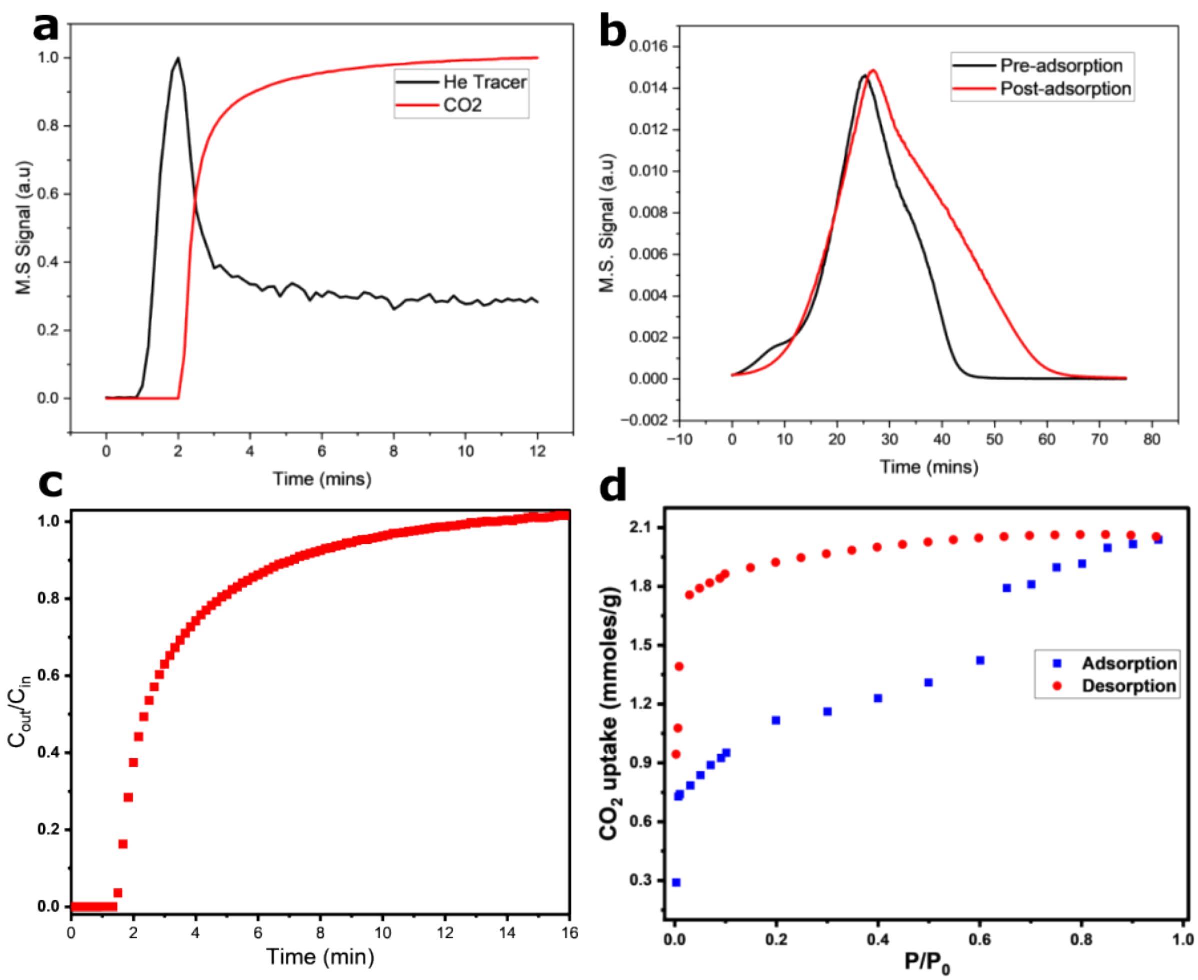

Figure 1: CO_2 adsorption capacity measurement. (a) 50% CO_2 breakthrough experiment with He Tracer (b) CO_2 effluent with time during temperature-induced desorption before and after CO_2 breakthrough experiment; (c) CO_2 breakthrough adsorption curves (d) Static CO_2 adsorption isotherm

<u>Systems Level Modeling and Comparison of Methods:</u>

There has been a notable increase in the number of studies focused on the Life Cycle Assessment of absorption techniques to assess the environmental impacts and emissions related to the technologies developed, such as membrane and cryogenic separations, pressure swing adsorption, and chemical scrubbing, among others [1]. Upgrading technologies to landfill gas has various advantages, such as the reduction of the dependence on natural gas (through the development of another source of methane), and the environmental impacts that can be reduced by offering a renewable source of energy, fuels, and chemicals production [2].

The Life Cycle Assessment of CO_2 recovery technologies (e.g., chemical adsorption, membrane separation, cryogenics, and pressure swing adsorption) was analyzed by several authors [3-5]. Khoo and Tan (2006) analyzed the generation of 1 MWh (functional unit) from a coal-fired power plant and the impact assessment for the CO_2 capture technologies obtained are reported in Table I [4].

Table I – Summary of comparative results for CO_2 capture technologies.

Env. impact categories	Chemical absorption (MEA)	Membrane separation	Cryogenics	Pressure swing adsorption
GWP (g-CO_2-eq)	7.87×10^4	1.86×10^5	1.79×10^5	1.72×10^5
Human toxicity water (m^3/g)	4.02×10^{-4}	8.53×10^{-5}	8.53×10^{-5}	1.95×10^{-4}
Ecotoxicity (m^3/g)	2.20×10^{-2}	4.66×10^{-3}	3.99×10^{-2}	1.06×10^{-2}
Acidification (g-SO_2-eq)	3.42×10^2	7.25×10^1	6.21×10^2	1.66×10^2
Human toxicity air (m^3/g)	7.24×10^4	1.54×10^4	1.32×10^5	3.51×10^4

Source: [4], GWP = global warming potential.

From the results, it can be inferred that according to the GWP, chemical absorption using MEA, followed by pressure swing adsorption is the technology with a smaller global warming potential. Cryogenics recover a large amount of CO_2 but account for a large energy consumption that results in greenhouse gas emissions. The acidification and human toxicity to air impacts are displayed by cryogenics, chemical absorption, and PSA [4]. Carbon dioxide capture technologies have several environmental impacts that come from infrastructure production and the formation of chemical by-products. All these aspects can be taken into account to define the environmental impacts of the CO_2 capture processes [6].

CO_2 absorption using amine-based solvents, such as monoethanolamine (MEA) has stood out as one of the effective ways to capture carbon dioxide. On the other hand, the increased use of amine-based solvents has increased the concern about the negative environmental impacts of human toxicity [5]. In addition, the use of corrosion inhibitors (such as vanadium pentoxide) when added to the amine solvent is related to the biggest impact of the solid waste [7]. In this scenario, the use of ammine functionalized supports without corrosion inhibitors can advance the CO_2 separation through a selective and efficient process.

There are three major landfill gas (LFG) use pathways that are usual throughout the United States that include: 1) flaring without energy recovery, 2) combustion for electricity generation, and 3) conversion to renewable natural gas (RNG) [8, 9]. Several studies examined the life-cycle impacts of different LFG management pathways on the environment and carbon capture processes, as can be seen in Table II.

Table II – Literature review on LCA studies for carbon capture technologies.

Reference	Scenarios studied	Functional unit
[8]	1)Flare the LFG (diesel to power the tractor-trailers); 2) Generate electricity from the LFG (diesel to power the tractor-trailers); 3) Refine the LFG to RNG and use to power CNG tractor-trailers; 4) Generate electricity from the LFG and use to power electric tractor-trailers.	Total net annual emissions (in kg/year) of each type of pollutant generated (CO_2 was the major pollutant of interest).
[10]	1) The current MSW management system in the central district of Tianjin; 2) LFG utilization to produce electricity; 3) Incineration; 4) Materials recycling; 5) Centralized composting; 6) Anaerobic digestion; 7) Integrated system.	Disposal of the MSW collected by the central districts of Tianjin city in 2006 (909,160 tons).
[6]	Life cycle emissions of post-combustion CO_2 capture technologies based on membrane separation and amine absorption processes.	Capture of 1 tonne of CO_2.
[5]	1) Conventional solvent absorption process with monoethanolamine (MEA); 2) The UNO MK 3 process with potassium carbonate absorbent and stainless-steel absorption and regeneration columns; 3) The UNO MK 3 process with potassium carbonate absorbent and concrete absorption and regeneration columns.	Capture of 1 tonne of CO_2.
[11]	1) Landfilling; 2) Biogas burned to produce electricity; 3) a combination of incineration and anaerobic digestion; 4) gasification and anaerobic digestion; 5) incineration; 6) direct gasification.	1 tonne of solid waste treated.
[12]	1) Landfilling without any further treatment; 2) biogas treated and burnt to produce electricity; 3) electricity, biogas (from anaerobic digestion) and compost are produced; 4) incineration to produce electricity.	The amount of waste produced in 2003 by the city of Rome.

[13]	Power generation of five pulverized coal-based steam power plants, which differ in the year of installation, the conversion efficiency, and in the ability and efficiency to capture CO_2 (MEA).	1 kWh net electricity produced
[14]	Municipal solid waste incineration (MSWI) with and without carbon capture and storage (CCS) via MEA.	1 tonne of wet MSW as received at the incinerator.
[15]	Municipal solid waste (MSW) grate incineration power plants: 1) without CO_2 capture; 2) with CO_2 capture including (MEA) absorption; 3) pressure/vacuum swing adsorption (P/VSA), and 4) oxy-fuel combustion (Oxy).	1 tonne of MSW
[16]	1) Post-combustion CO_2 recovery through chemical absorption with MEA; 2) alternative post-combustion technologies (membrane separation, cryogenic, PSA); 3) pre-combustion CO_2 recovery with Selexol; 4) oxy-fuel technology.	1 kWh of net electricity produced

Methodology

For the development of this life cycle assessment (LCA), the ISO 14040/14044 will be used, because they represent standardized steps for LCA [1, 2]. The steps that will be followed are i) goal and scope definition, ii) inventory modeling, iii) impact assessment, and iv) interpretation of the results. Well-to-wheels (WTW) analysis will be performed using The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET ®) model developed by Argonne National Laboratory. In summary, in a WTW analysis, the areas covered include the feedstock recovery (well) to end use (wheels). In addition, the WTW is divided into well-to-pump (WTP), which includes feedstock recovery, fuel production, transportation, and distribution, and pump-to-wheels (PTW), which represents fuel combustion in a vehicle [17].

Goal and scope

The goal of this study is to compare the environmental impact of capturing CO_2 from landfill gas with various end products. The comparison with scenarios without CO_2 purification will also be included. Three LCAs will be conducted: i) Compressed Natural Gas (CNG) production through the use of amine-functionalized supports to CO_2 adsorption from landfill gas, ii) LNG production instead of CNG, iii) electricity production without no CO_2 capture, and iv) CO_2 purification through pressure-swing-adsorption to produce CNG. The functional unit serves as a reference for the comparative analysis of the environmental impact of different systems/studies. The functional unit is selected according to the purpose of the research. The functional unit for a LCA is usually defined in terms of the system's output, in other words, the product. On the other hand, for the development of an LCA focused on waste management, the functional unit must be defined in terms of the system's input, for example, the quantity of specific waste, or the total waste of a defined region in a specific time (year) [15]. Since the major function of the system proposed in this work is to purify CO_2 from landfill gas, the functional unit used is 1 SCFM of LFG. For studies in which the main goal is to compare benefits of CO_2 separation methods, a CO_2-based functional unit facilitates the comparison taking into account the uptake efficiency [18].

System boundaries

It is well known that system boundaries change according to the goals of the study. In this sense, simplification of system boundaries can be used in complex systems to help keep the focus of the study. Infrastructure had been reported as having a negligible impact on the Life Cycle Global Warming potential for carbon capture projects [19, 20] and will not be taken into account in this study. In addition, it is defined that processes with environmental impact inferior to 1 % can be ignored [21].

For this study, system boundaries involving the CO_2 removal from landfill gas to the production of CNG/LNG or no CO_2 capture to produce electricity as outlined in Figure 2. The assumptions applied to the LCA, as well as the inventory of the materials and energy used, and emissions released to the environment, will be present in the life cycle inventory.

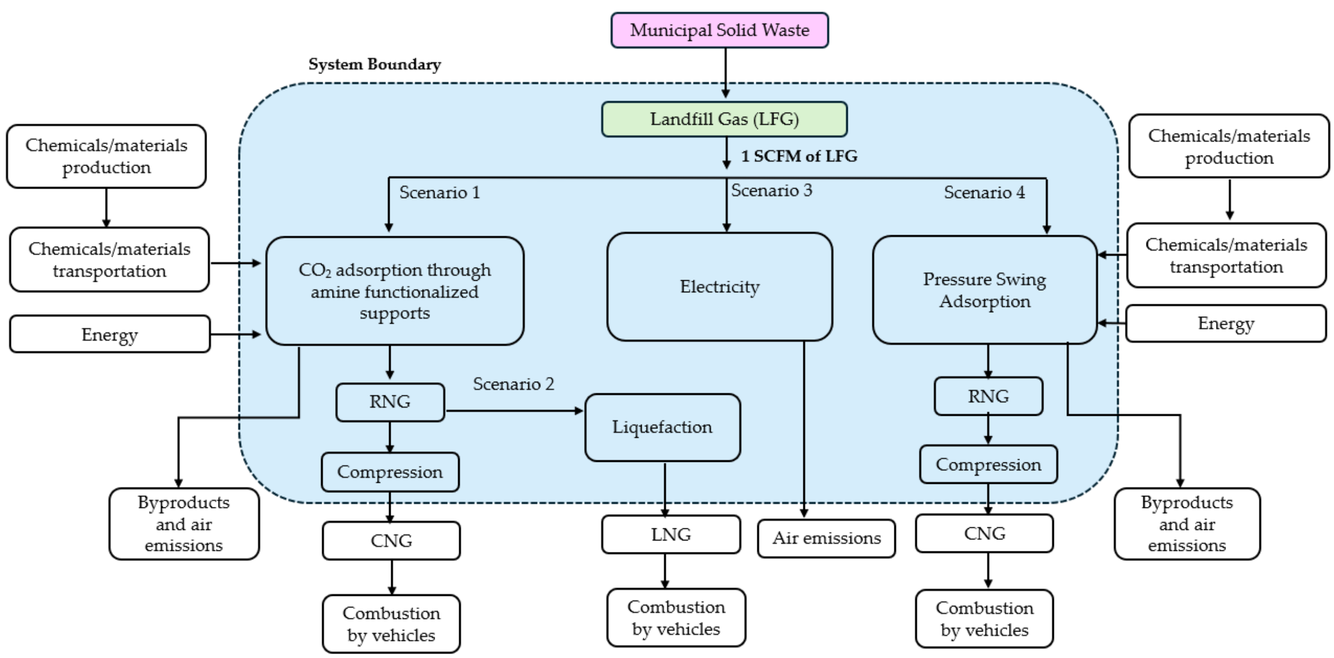

Figure 2. System boundaries for the LCA of CO_2 removal from landfill gas based on amine functionalized supports.

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TAG meetings:

There was not a TAG meeting during this quarter.

Future Tasks:

In the next quarter, we will test the CO_2 separation performance of the reproduced samples under simulated and real biogas conditions. We will also assess the effect of pressure drop study on bed design and economic analysis. In addition, we will continue on the LCA of the scenarios presented in this report.

METRICS REPORTING

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

   We received a couple follow up emails from TAG members, after the first TAG meeting last 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 submitted multiple abstracts for conferences this fall.

   "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 proposals on CO_2 capture and conversion are pending. One is to ARPA-E, and another to DOE. A USF internal CREATE (https://www.usf.edu/provost/initiatives-special-projects/create.aspx) 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).