Washington University in St. Louis
James McKelvey School of Engineering

# DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

## Project DE-EE0009771: Upgrading Biogas through in situ Conversion of Carbon Dioxide to Biomethane in Anaerobic Digesters


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# Project Overview

**Goal**: develop an innovative system that can accomplish *in situ* biogas upgrading via biological conversion of $CO_2$ to $CH_4$

<u>Alignment with BETO FOA goals and requirements</u>

(1) This project will develop a new technology to convert $CO_2$ in biogas to $CH_4$

(2) A high-quality RNG will be produced to meet pipeline specifications

(3) This project focuses on bench-scale studies and the results will help formulate a strategy for further scaling up

(4) Real biogas will be used as a feedstock to $CO_2$ conversion

(5) Both LCA and TEA will be conducted throughout the project and help identify key issues in the bench system.

# Biological pathways for biogas upgrading

$$CO_2 + H_2 \xrightarrow{Hydrogenotrophic\ methanogens} CH_4 + H_2O$$ ✔

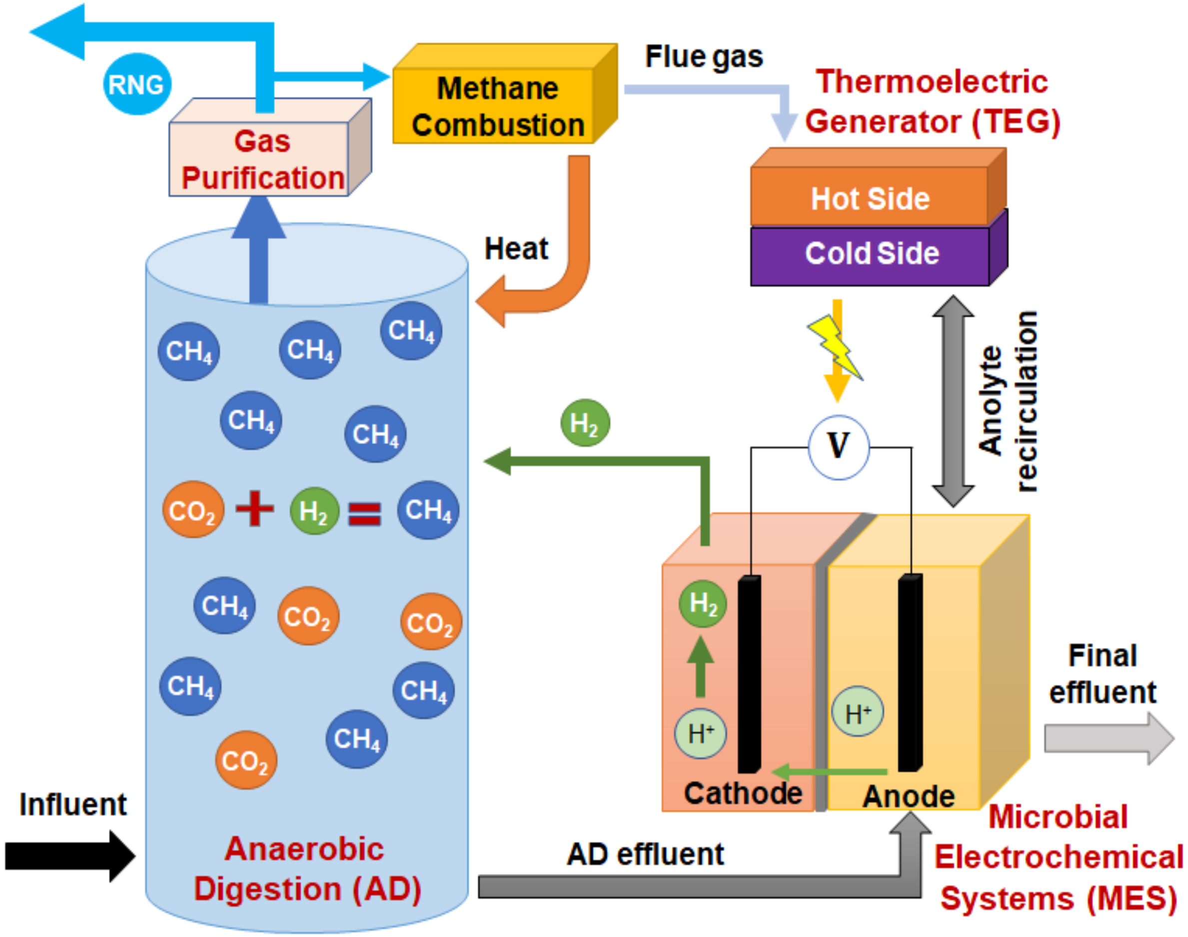
$$CO_2 + H_2 \xrightarrow{Homoacetogenic\ microorganisms} acetic\ acids \xrightarrow{Acetotrophic\ methanogens} CH_4 + H_2O$$ ✘

$$CO_2 + H^+ + e^- \xrightarrow{electrochemical\ (cathode)} CH_4 + H_2O$$ ✘

## *Limitations of current upgrading technologies*

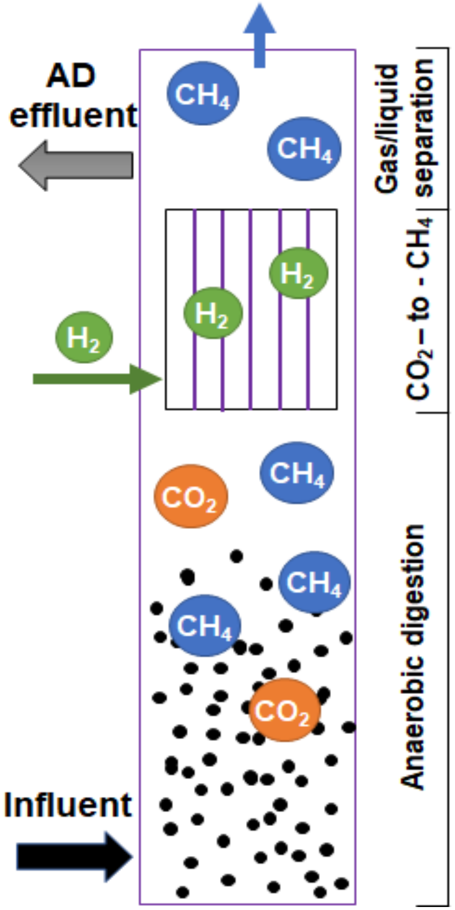
- Mass transfer of $H_2$ in a liquid phase
- Low-cost hydrogen gas
- Negative effects of $H_2$ partial pressure (*in situ* hydrogen supply)
- pH increase due to $CO_2$ removal (*in situ* hydrogen supply)

# Approach - our proposed system




## Novelty

- Integrated "*ex situ*" with "*in situ*"
- Highly-efficient $H_2$ supply
- Simpler operation
- Residue nutrients use by $CO_2$ conversion



# Project Team

**Team Management**

- Bimonthly meetings
- Annual in-person project meetings
- Sub-group communication
- Joint publications/presentations
- Student visits
- Education and outreach to underrepresented community

# Tasks

Task 1: Initial technical verification

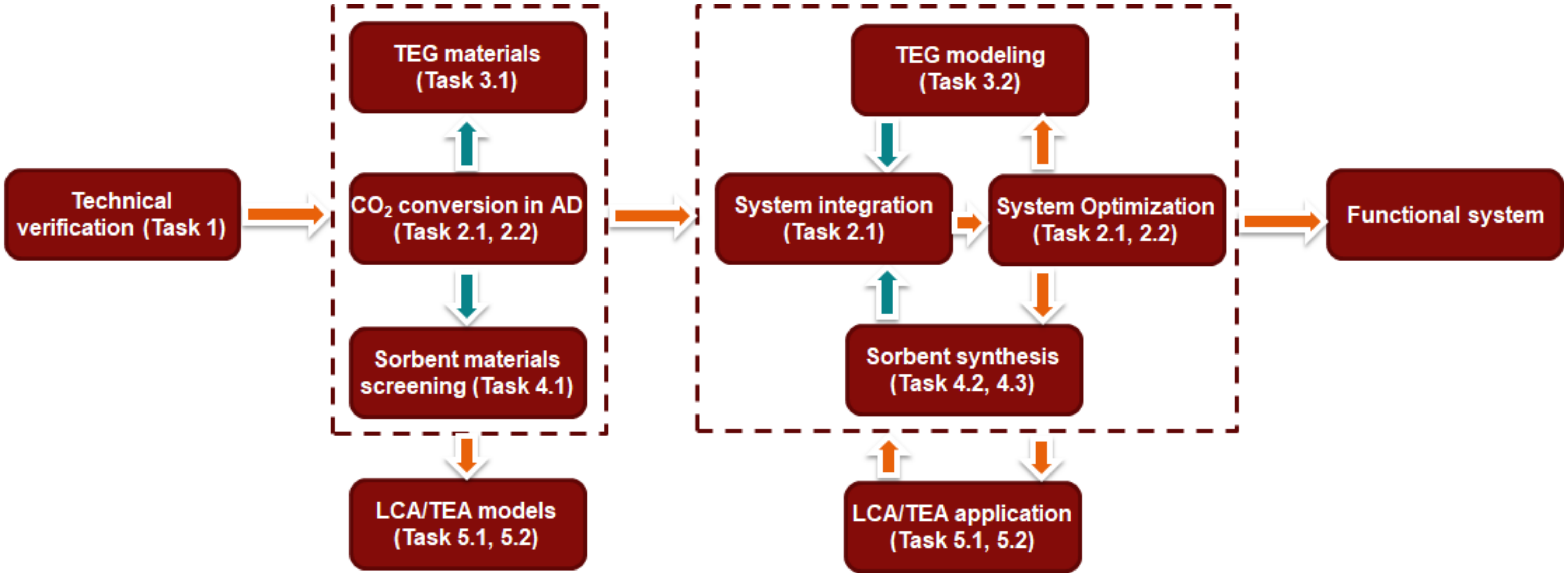
Task 2: Accomplish *in situ* biological $CO_2$ conversion to $CH_4$ with membrane-assisted $H_2$ delivery

Task 3: Develop an organic thermoelectric generator that is low cost, scalable, and biocompatible for waste heat conversion to electricity

Task 4: Synthesize custom sorbents in-house featuring a transition metal-oxide nanomaterial for gas cleaning

Task 5: Conduct life cycle analysis and techno-economic assessment of the proposed system.

# Task Integration



# Go/No Go Decision Points

**Budget Period 1 Go/No-Go Decision Point:** (Literature) baseline performance metrics verified.

**Budget Period 2 Go/No-Go Decision Point #2:** Development of individual units with the desired performance in the individual units.

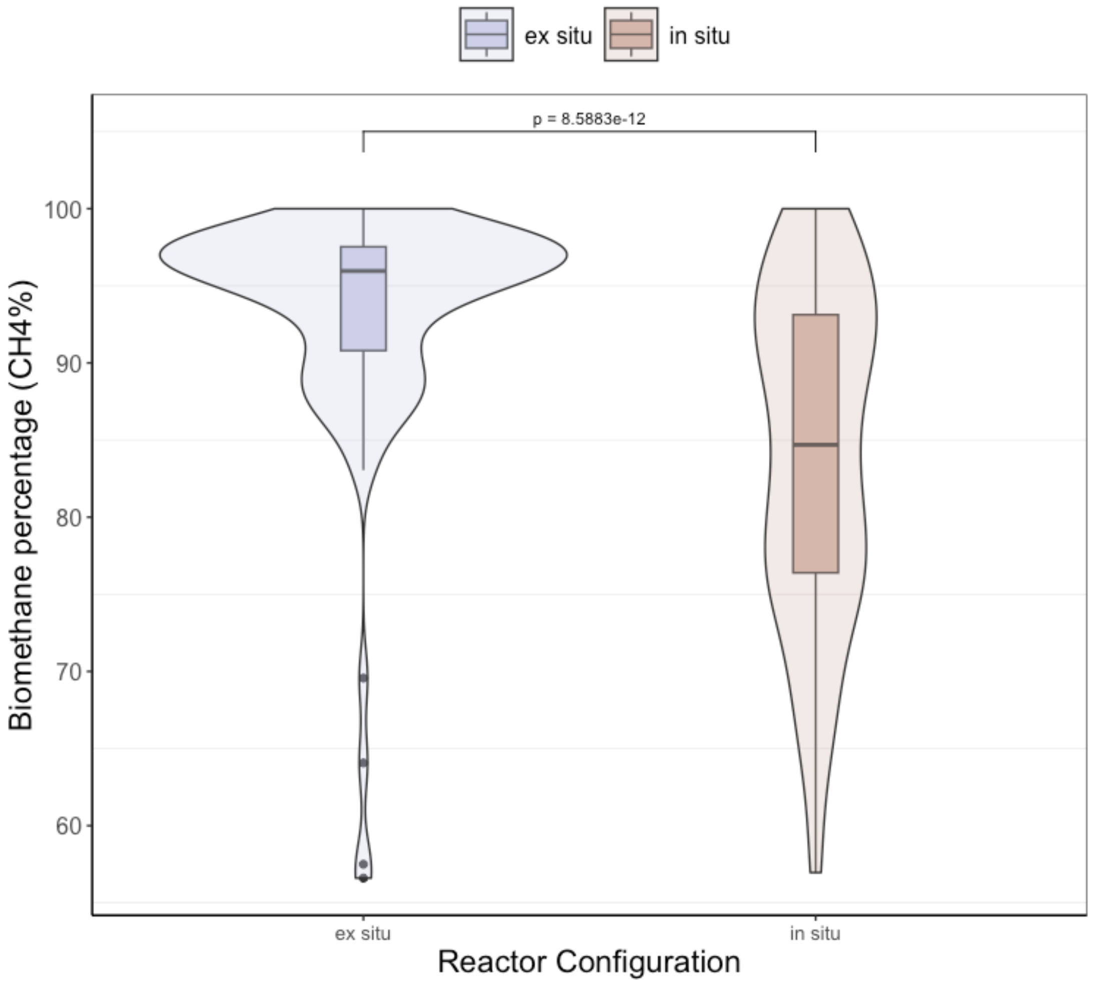
**End of Project Goal:** A scalable and innovative biogas upgrading system at TRL 4 can produce pipeline quality renewable natural gas containing >97% $CH_4$ via two steps, biological $CO_2$ conversion to $CH_4$ that generates a biogas of >95% $CH_4$ and gas cleaning that reduces impurities and further enhances the $CH_4$ content to >97%.

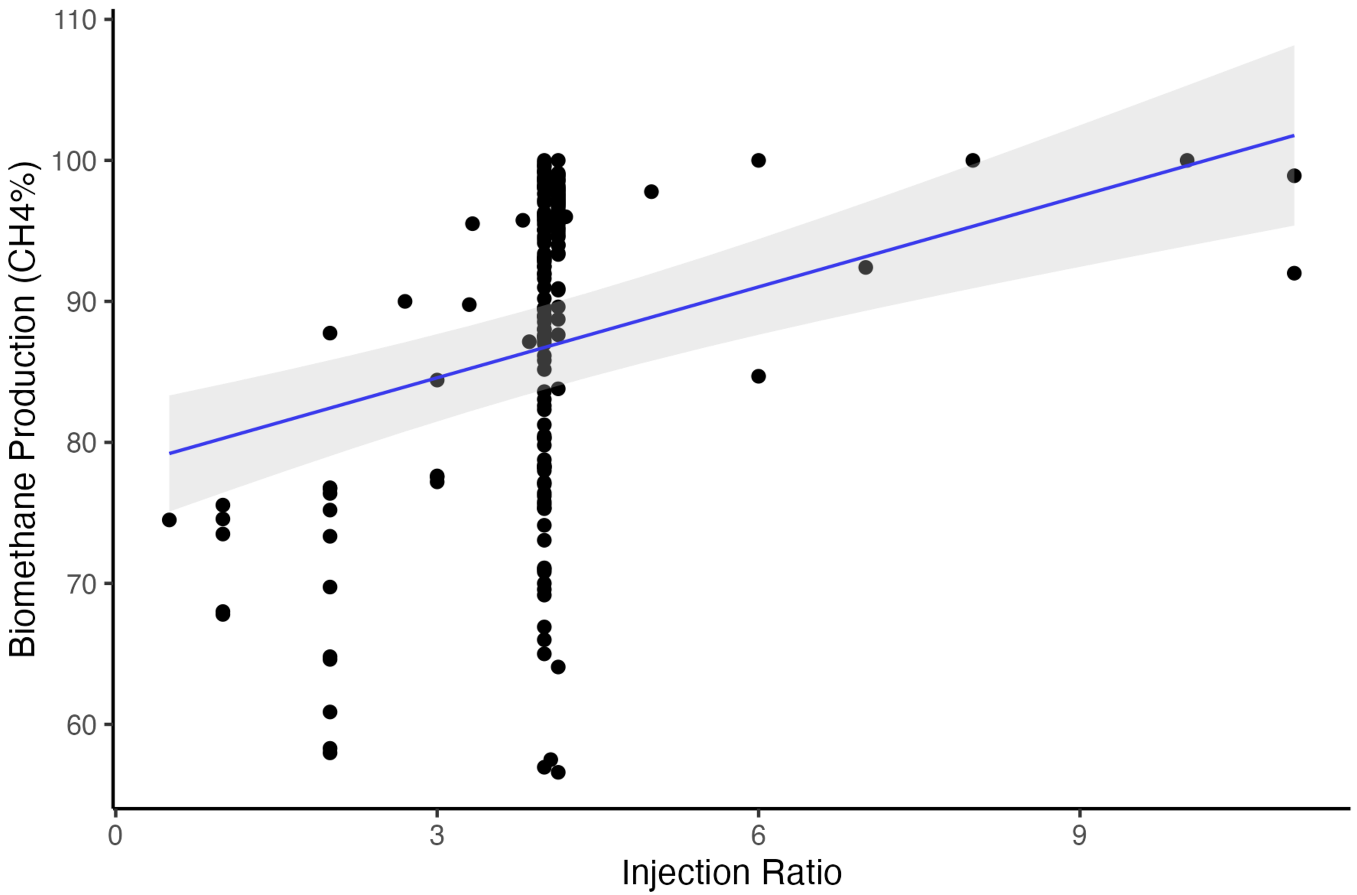
# Progress and Outcome

- Budget Period 1 Go/No-Go Decision Point (FY22Q4)
- [Milestone 2.1.1] Completion of system setup with gas-permeable membrane unit to create different operational zones (FY23Q1)
- [Milestone 5.2.1] Establish a process model for the proposed system based on the experimental data (FY23Q1)
- Patent disclosure filed
- One manuscript submitted

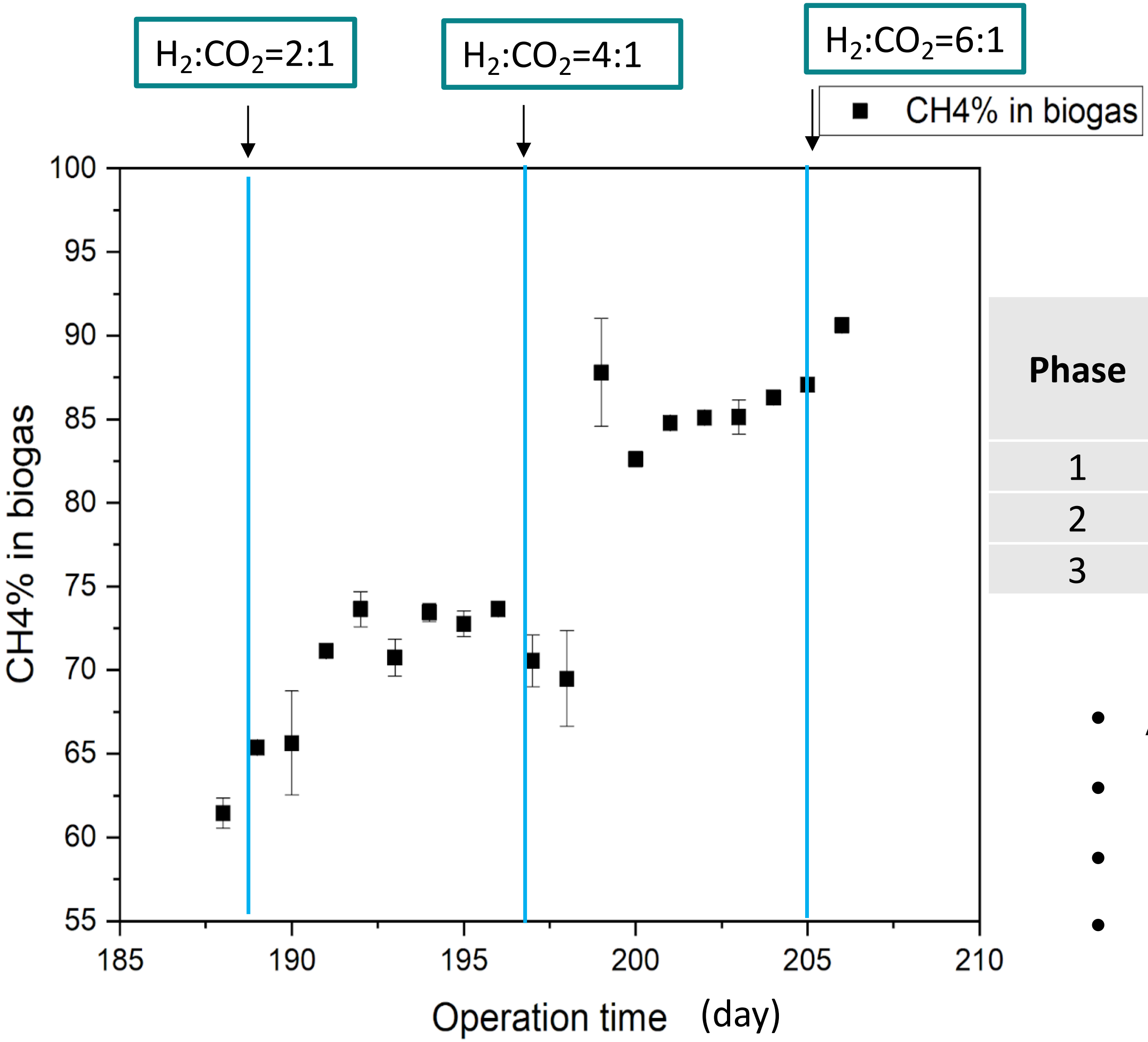

- [Milestone 2.1.2] Achieve 85% conversion of $CO_2$ to $CH_4$ and 90% of $H_2$ utilization efficiency
- [Milestone 3.1.1] Virtually screen the conjugated polymers using supervised machine learning with a large molecular space to focus on minimizing thermal conductivity while maximizing the power factor to produce a record (material) zT value
- [Milestone 4.1.1] Establish metrics and reference performance data
- [Milestone 5.1.1] Draft version of GREET with pathway for the proposed system

# Meta Analysis of Biogas Upgrading



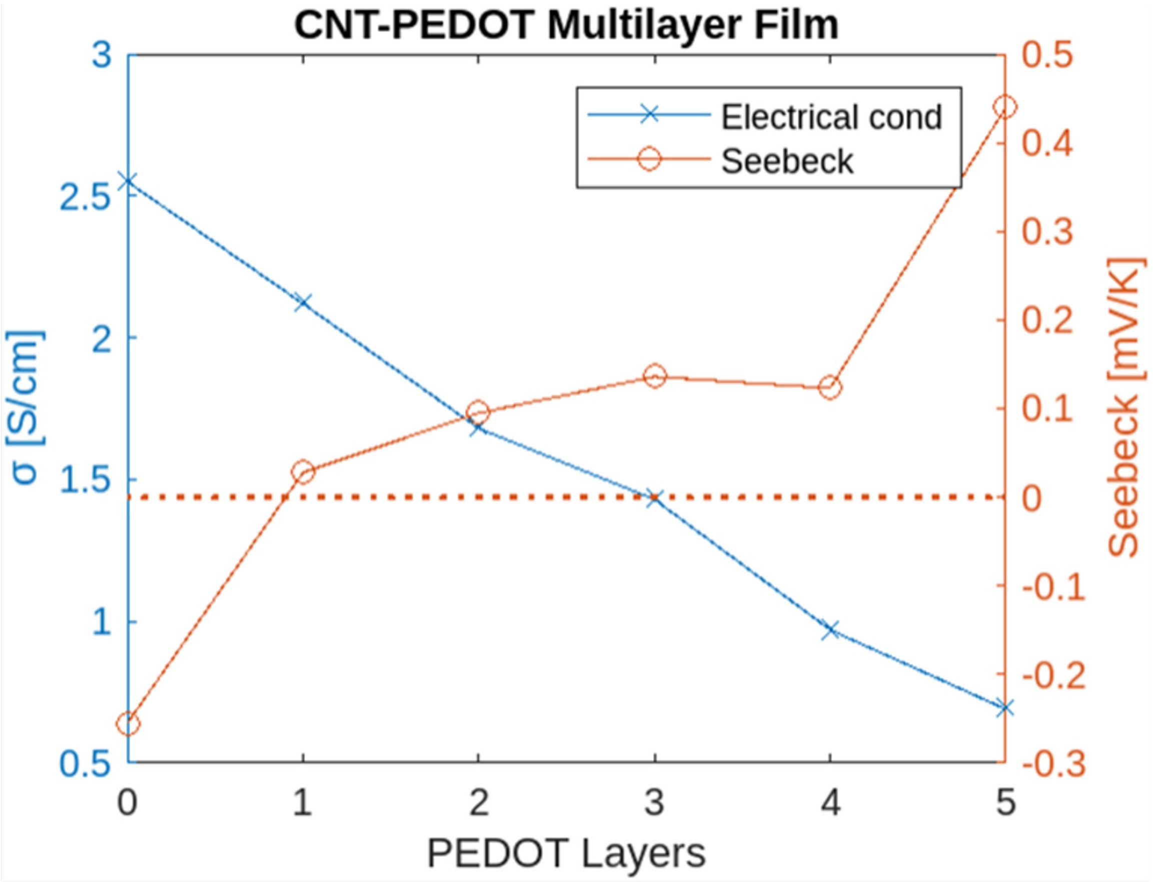
# Task 2: System performance: methane production




| Phase | Hydrogen flow rate (mL/min) | Biogas production rate (mL/L_reactor/day) | $CH_4$ in biogas (%) | $CO_2$ in biogas (%) |
|---|---|---|---|---|
| 1 | 0.421 (2:1) | 1113.68±72.23 | 70.50±0.99 | 30.46±0.79 |
| 2 | 1.419 (4:1) | 1274.04±108.41 | 83.03±1.08 | 18.71±0.48 |
| 3 | 2.130 (6:1) | 1478.95 | 90.62 | 9.36 |

- A functional biosystem is established
- Initial feasibility is demonstrated
- Upgrading is accomplished with synthetic WW
- Residue nutrients use by $CO_2$ conversion

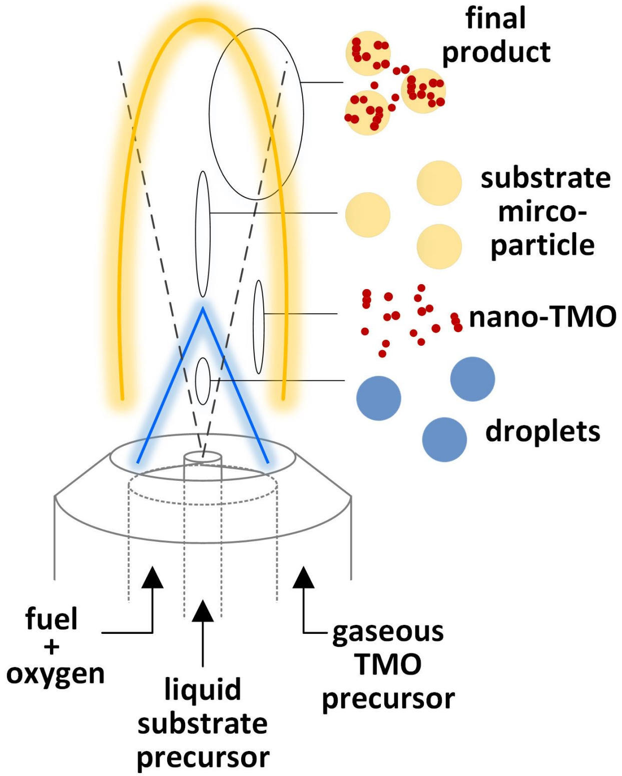
# Task 3: TEM material development



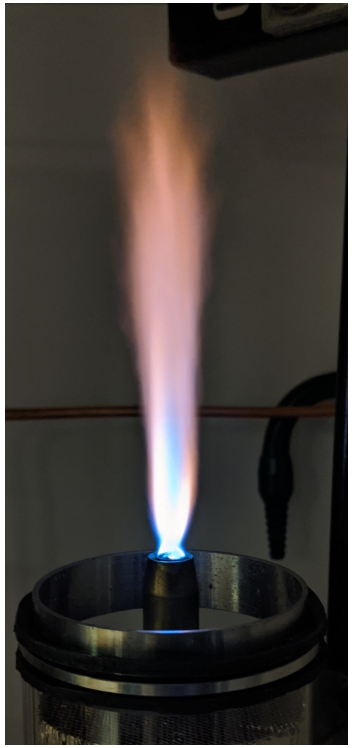

- P-type: The 10 vol% Formic Acid as dopant and post-treatment with DMSO achieved both higher electrical conductivity and Seebeck coefficient. The highest value of power factor is about 110 uW $m^{-1}$ $K^{-2}$ which reached our intermediate target.

- N-type: We manufactured PEDOT solution and CNT solution in the lab, and confirmed that filtered PEDOT solution showed improved electrical conductivity and Seebeck coefficients.

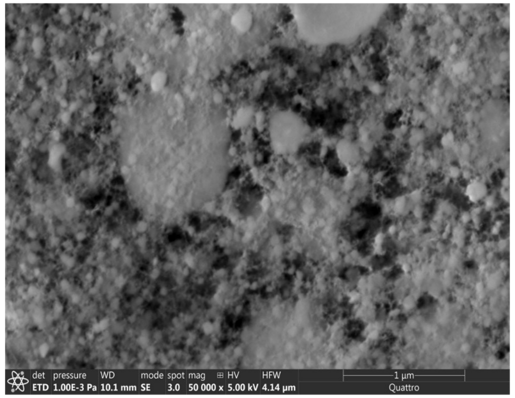
# Task 4: Flame spray synthesis of sorbents




proposed concept



Test Burn w/ MgO precursor

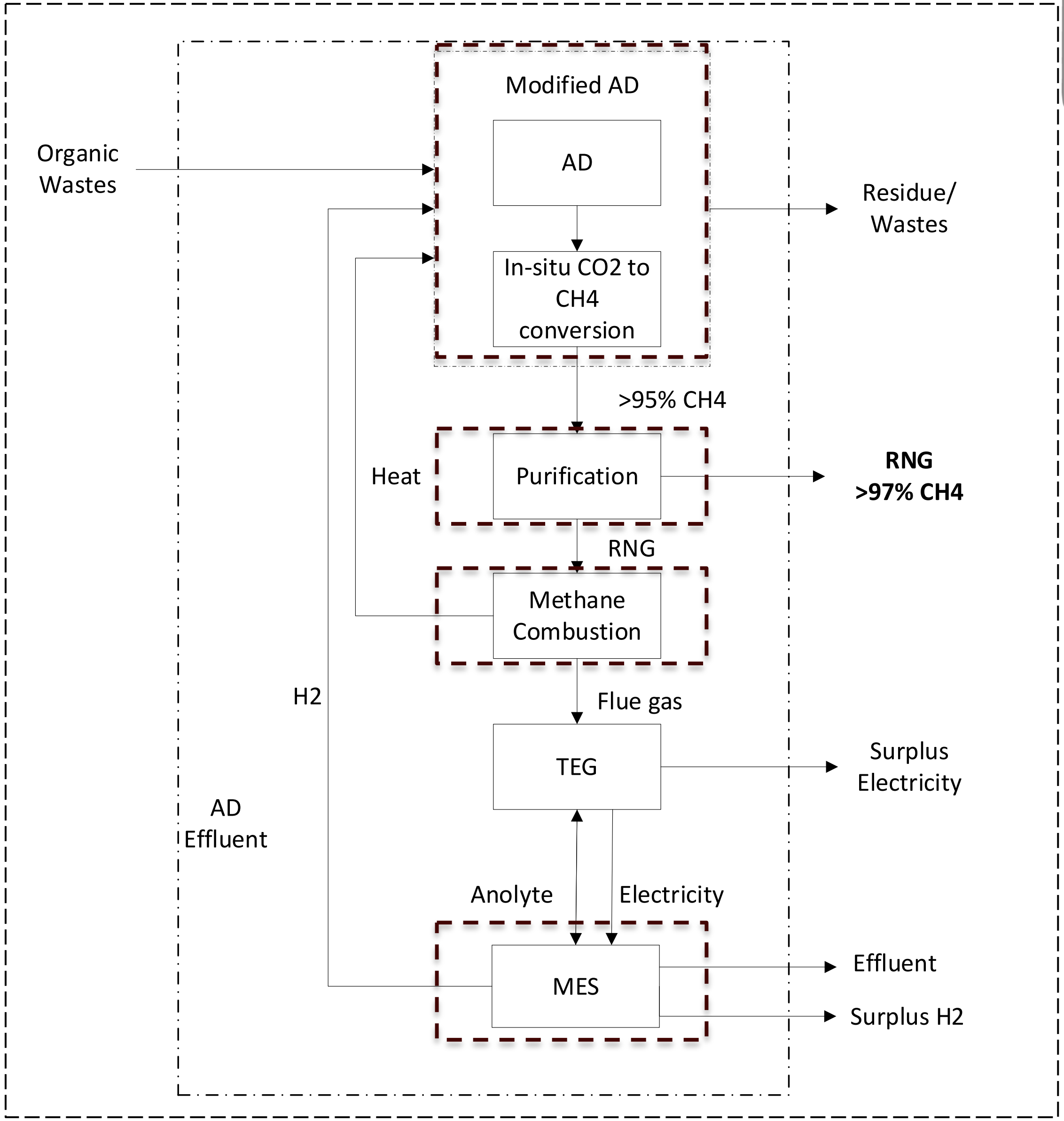


MgO powder

- Building database of adsorbant properties reported in literature
- Designed an improved two-fluid nozzle (2nd Gen).
- Magnesium oxide (MgO) was successfully synthesized using the flame spray pyrolysis system (MgO is a relatively well-established mesoporous material for CO2 adsorption for both high and low temperature applications and will serve as a baseline for more complex mixed-metal oxides to be synthesized in the future).
- Single-particle pyrolysis model is being developed.

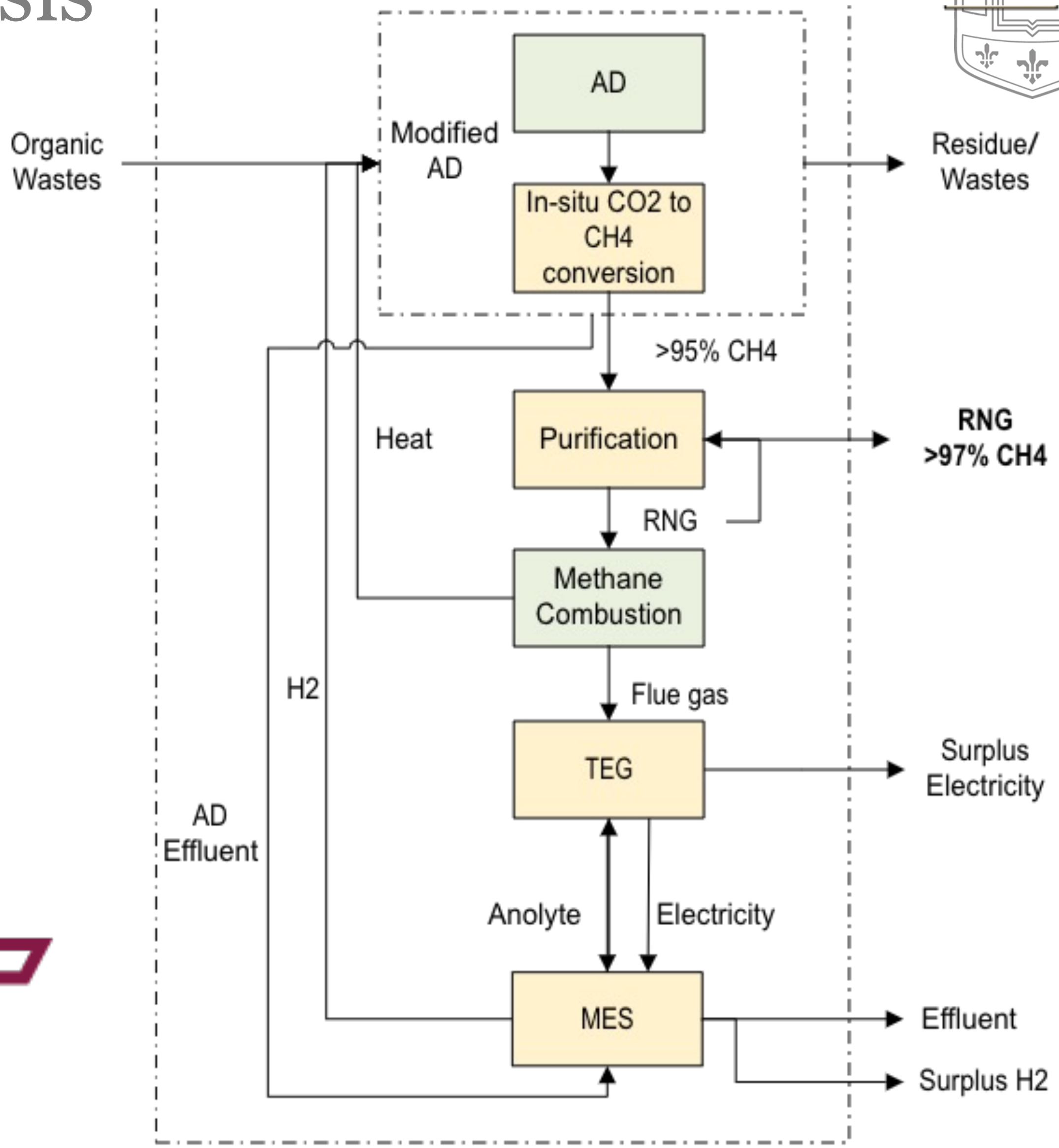
# Task 5: Life cycle assessment

- Draft LCA model is being developed based on initial assumptions and available inventory data.
- Model will be updated and refined as project progresses.
- Experimental data for mass and energy flow rates are being collected.
- Coordinate input and output data with the TEA team for alignment.



# Task 5: Techno-Economic Analysis

- The 1st version of TEA model is developed
- The process model framework is being expanded to include the microbial electrochemical cell
- Initial TEA results showed that the estimated biomethane production cost is about $1.33/m3.
- Close interaction with LCA teams to discuss the harmonized approach between TEA and LCA

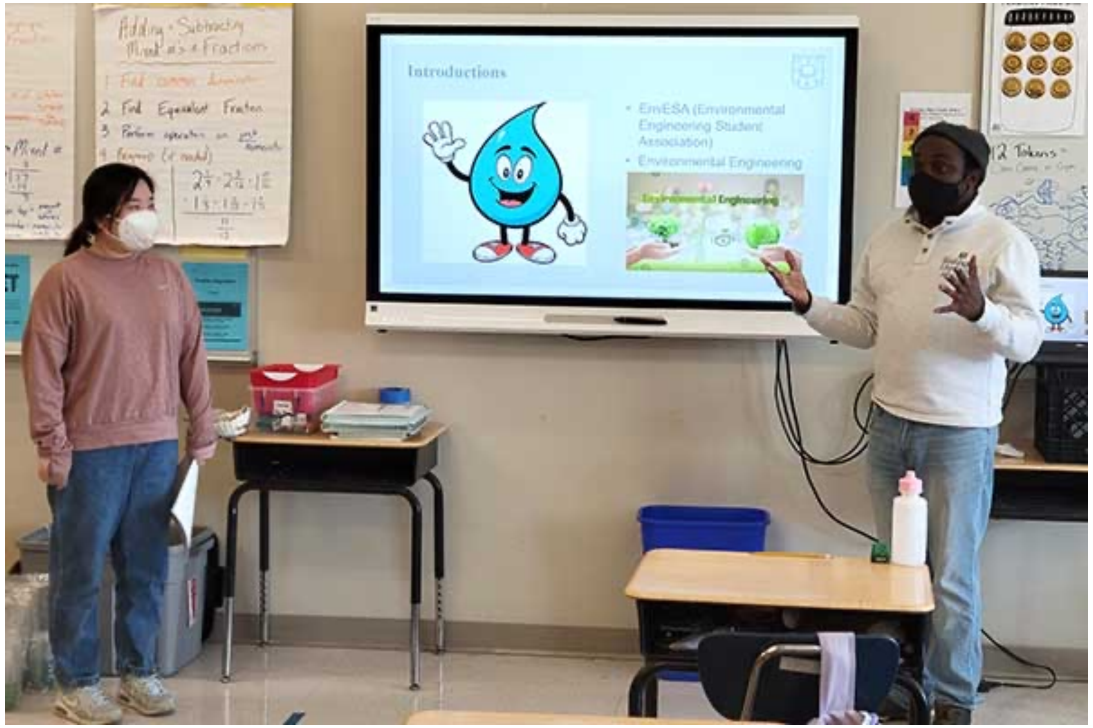


# Impacts

- A new strategy for converting waste into bioenergy that will contribute to "Decarbonizing Transportation Fuel".
- Reduce carbon emission through utilizing $CO_2$ for upgrading biogas.
- New business opportunities may be created to allow the developed system to be adopted by a wide range of potential users of treating food/beverage wastewater, livestock wastes, and municipal wastes.
- Strategic partnership(s) will be established with the end users that may provide resources to further develop the system to TRL 6 (beyond this DOE project) towards commercialization.
- This project will also advance TEG technology for the applications with low temperature gradients and introduce it into the field of waste conversion to bioenergy.

# Education Outreach and DEI

- >50% trainees (graduate students and postdocs) are from the underrepresented groups
- Provide a hands-on water education program to the 5th graders at the School District of University City, which has 90% of its students identified as minority.
- Establish a connection with Lincoln University of Missouri, a historically black college, and explore the opportunities of research collaboration and student recruitment.



# Summary

- This project has successfully passed the Verification.
- The initial results have demonstrated that the proposed system can upgrade biogas to >90% methane while treating a synthetic wastewater.
- Both P- and N-Type TEG materials exhibited enhanced properties.
- Initial absorbent material synthesis and LCA/TEA models are being developed.
- The project is moving forward as scheduled in the Budget Period 2

# Quad Chart Overview

## Timeline
- *Project start date: Oct. 1, 2021*
- *Project end date: April 30, 2025*

| | FY22 Costed | Total Award |
|---|---|---|
| **DOE Funding** | *$121,715* | *$2,300,000* |
| **Project Cost Share** | *$59,621* | *$581,916* |

TRL at Project Start: 2
TRL at Project End: 4

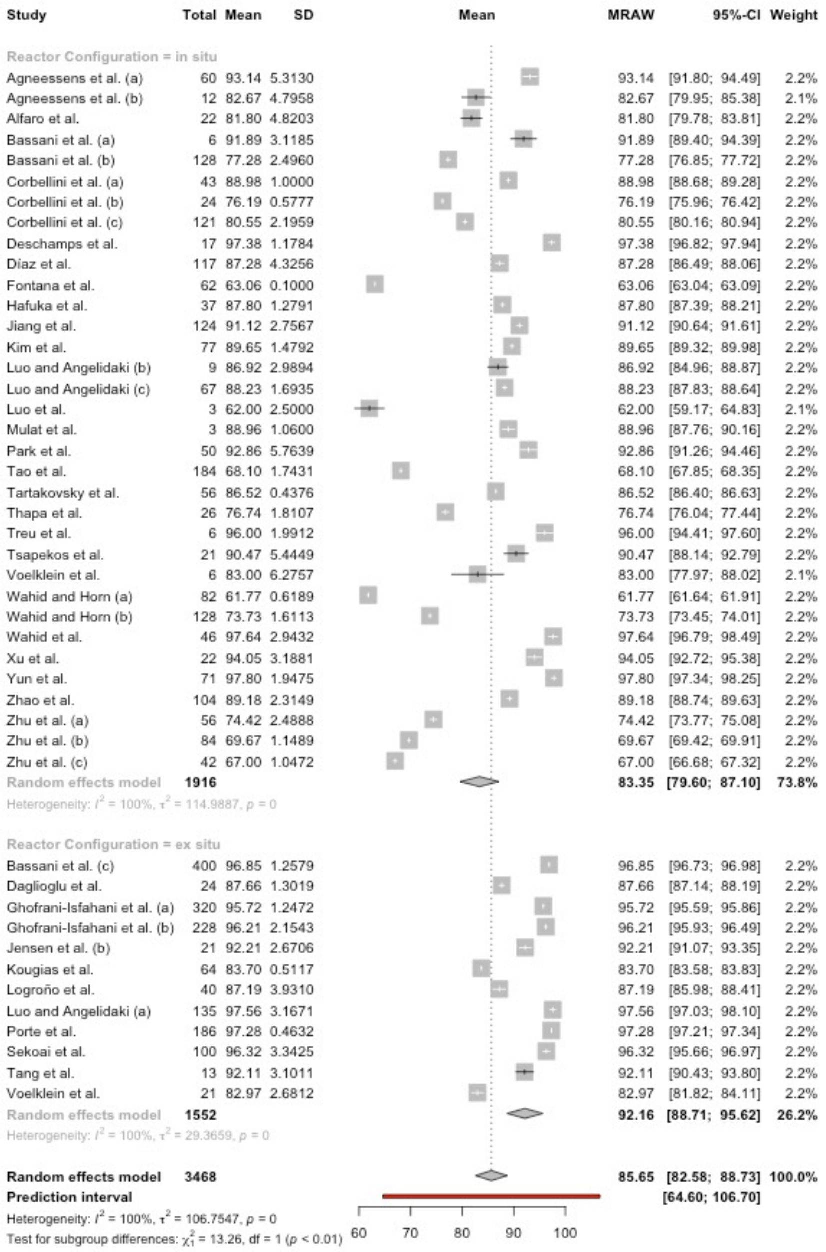
## Project Goal
*This project aims to develop an innovative system that can accomplish in situ biogas upgrading via biological conversion of $CO_2$ to $CH_4$.*

## End of Project Milestone
- *Pipeline quality renewable natural gas containing >97% $CH_4$*
- *The target $CO_2$ concentration in the final RNG is <1%.*
- *The $H_2S$ content will be kept below 5.7 mg/Nm3 (or 0.25 grain/110 scf).*
- *Comprehensive model involving both biofilm model and system*
- *Finalized LCA and TEA models*

## Funding Mechanism
*FY21 BETO Scale-up and Conversion FOA DE-FOA-0002396*

## Project Partners
- *Anheuser-Busch Companies*

# Additional Slides



Study Total Mean SD Mean MRAW 95%-CI Weight
Reactor Configuration = in situ
Agneessens et al. (a) 60 93.14 5.3130 93.14 [91.80; 94.49] 2.2%
Agneessens et al. (b) 12 82.67 4.7958 82.67 [79.95; 85.38] 2.1%
Alfaro et al. 22 81.80 4.8203 81.80 [79.78; 83.81] 2.2%
Bassani et al. (a) 6 91.89 3.1185 91.89 [89.40; 94.39] 2.2%
Bassani et al. (b) 128 77.28 2.4960 77.28 [76.85; 77.72] 2.2%
Corbellini et al. (a) 43 88.98 1.0000 88.98 [88.68; 89.28] 2.2%
Corbellini et al. (b) 24 76.19 0.5777 76.19 [75.96; 76.42] 2.2%
Corbellini et al. (c) 121 80.55 2.1959 80.55 [80.16; 80.94] 2.2%
Deschamps et al. 17 97.38 1.1784 97.38 [96.82; 97.94] 2.2%
Díaz et al. 117 87.28 4.3256 87.28 [86.49; 88.06] 2.2%
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Kim et al. 77 89.65 1.4792 89.65 [89.32; 89.98] 2.2%
Luo and Angelidaki (b) 9 86.92 2.9894 86.92 [84.96; 88.87] 2.2%
Luo and Angelidaki (c) 67 88.23 1.6935 88.23 [87.83; 88.64] 2.2%
Luo et al. 3 62.00 2.5000 62.00 [59.17; 64.83] 2.1%
Mulat et al. 3 88.96 1.0600 88.96 [87.76; 90.16] 2.2%
Park et al. 50 92.86 5.7639 92.86 [91.26; 94.46] 2.2%
Tao et al. 184 68.10 1.7431 68.10 [67.85; 68.35] 2.2%
Tartakovsky et al. 56 86.52 0.4376 86.52 [86.40; 86.63] 2.2%
Thapa et al. 26 76.74 1.8107 76.74 [76.04; 77.44] 2.2%
Treu et al. 6 96.00 1.9912 96.00 [94.41; 97.60] 2.2%
Tsapekos et al. 21 90.47 5.4449 90.47 [88.14; 92.79] 2.2%
Voelklein et al. 6 83.00 6.2757 83.00 [77.97; 88.02] 2.1%
Wahid and Horn (a) 82 61.77 0.6189 61.77 [61.64; 61.91] 2.2%
Wahid and Horn (b) 128 73.73 1.6113 73.73 [73.45; 74.01] 2.2%
Wahid et al. 46 97.64 2.9432 97.64 [96.79; 98.49] 2.2%
Xu et al. 22 94.05 3.1881 94.05 [92.72; 95.38] 2.2%
Yun et al. 71 97.80 1.9475 97.80 [97.34; 98.25] 2.2%
Zhao et al. 104 89.18 2.3149 89.18 [88.74; 89.63] 2.2%
Zhu et al. (a) 56 74.42 2.4888 74.42 [73.77; 75.08] 2.2%
Zhu et al. (b) 84 69.67 1.1489 69.67 [69.42; 69.91] 2.2%
Zhu et al. (c) 42 67.00 1.0472 67.00 [66.68; 67.32] 2.2%
Random effects model 1916 83.35 [79.60; 87.10] 73.8%
Heterogeneity: $I^2$ = 100%, $\tau^2$ = 114.9887, $p$ = 0
Reactor Configuration = ex situ
Bassani et al. (c) 400 96.85 1.2579 96.85 [96.73; 96.98] 2.2%
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Ghofrani-Isfahani et al. (a) 320 95.72 1.2472 95.72 [95.59; 95.86] 2.2%
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Jensen et al. (b) 21 92.21 2.6706 92.21 [91.07; 93.35] 2.2%
Kougias et al. 64 83.70 0.5117 83.70 [83.58; 83.83] 2.2%
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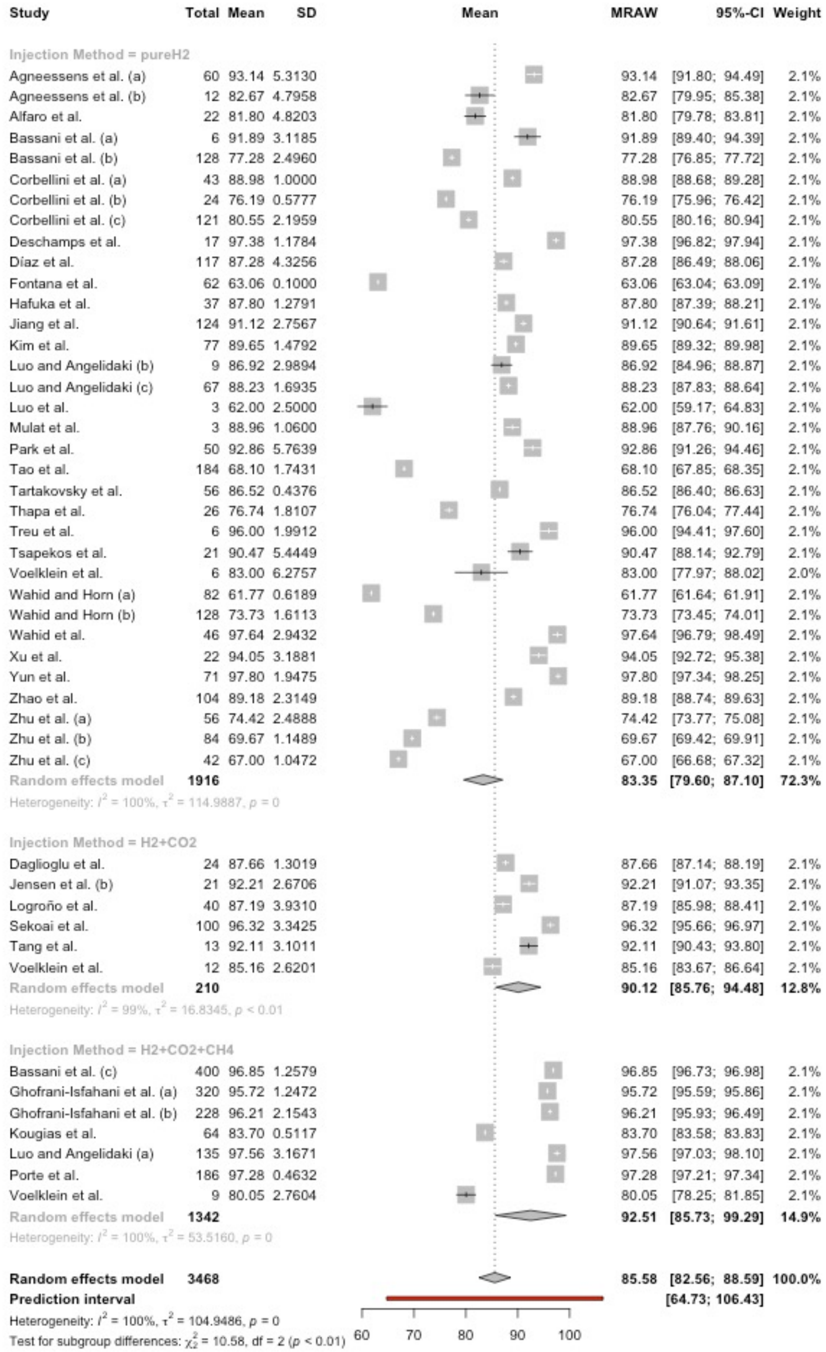
Tang et al. 13 92.11 3.1011 92.11 [90.43; 93.80] 2.2%
Voelklein et al. 21 82.97 2.6812 82.97 [81.82; 84.11] 2.2%
Random effects model 1552 92.16 [88.71; 95.62] 26.2%
Heterogeneity: $I^2$ = 100%, $\tau^2$ = 29.3659, $p$ = 0
Random effects model 3468 85.65 [82.58; 88.73] 100.0%
Prediction interval [64.60; 106.70]
Heterogeneity: $I^2$ = 100%, $\tau^2$ = 106.7547, $p$ = 0
Test for subgroup differences: $\chi^2_1$ = 13.26, df = 1 ($p$ < 0.01)
60 70 80 90 100

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Injection Method = H2+CO2
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Random effects model 210 90.12 [85.76; 94.48] 12.8%
Heterogeneity: $I^2$ = 99%, $\tau^2$ = 16.8345, $p$ < 0.01
Injection Method = H2+CO2+CH4
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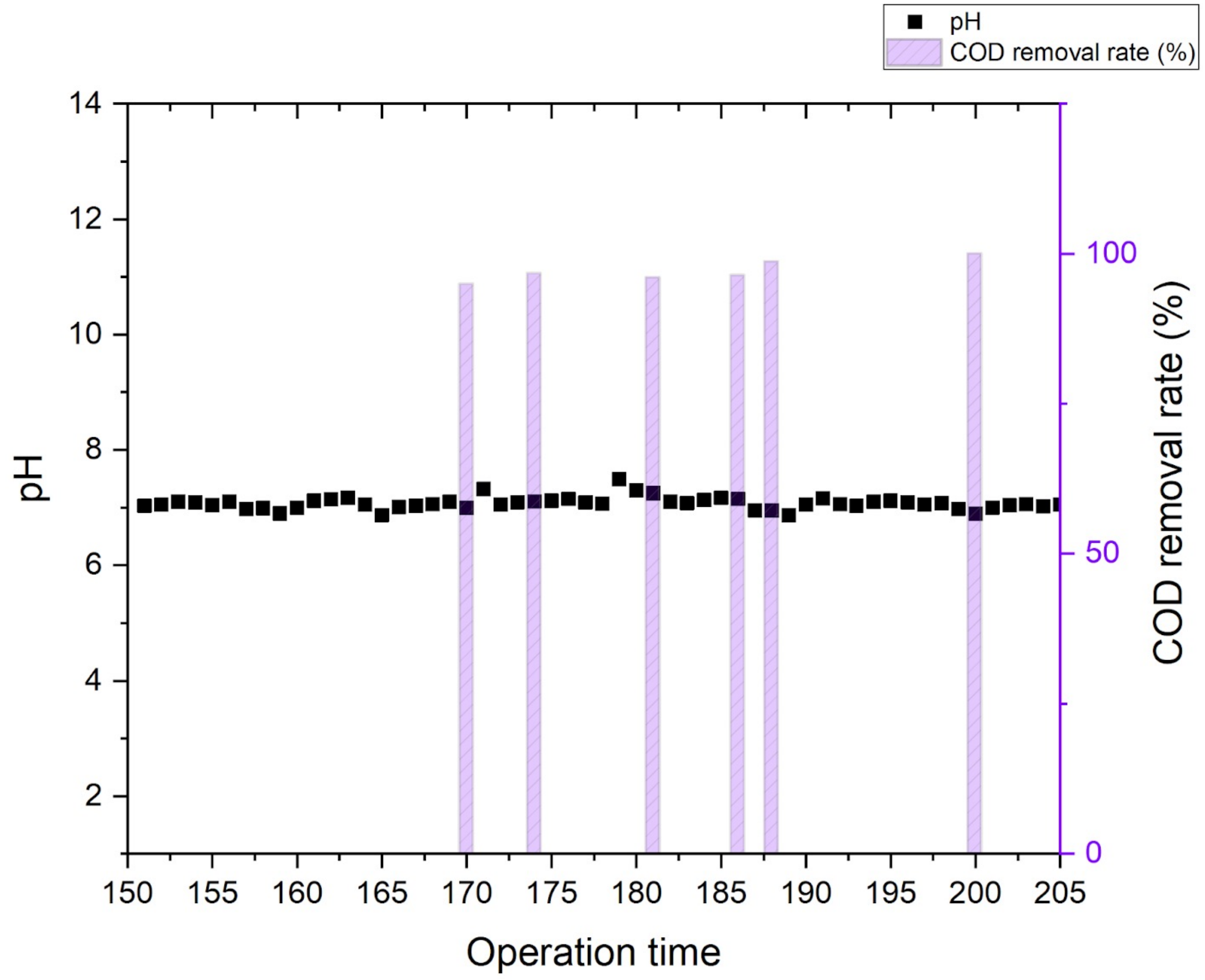
Voelklein et al. 9 80.05 2.7604 80.05 [78.25; 81.85] 2.1%
Random effects model 1342 92.51 [85.73; 99.29] 14.9%
Heterogeneity: $I^2$ = 100%, $\tau^2$ = 53.5160, $p$ = 0
Random effects model 3468 85.58 [82.56; 88.59] 100.0%
Prediction interval [64.73; 106.43]
Heterogeneity: $I^2$ = 100%, $\tau^2$ = 104.9486, $p$ = 0
Test for subgroup differences: $\chi^2_2$ = 10.58, df = 2 ($p$ < 0.01)
60 70 80 90 100

# Reactor performance: pH & COD




pH observation is stable, within the optimal range, 6.8-7.2.

- Current results:

The addition of 2, 4, and 6 equivalents of $H_2$ relative to $CO_2$ was investigated.;

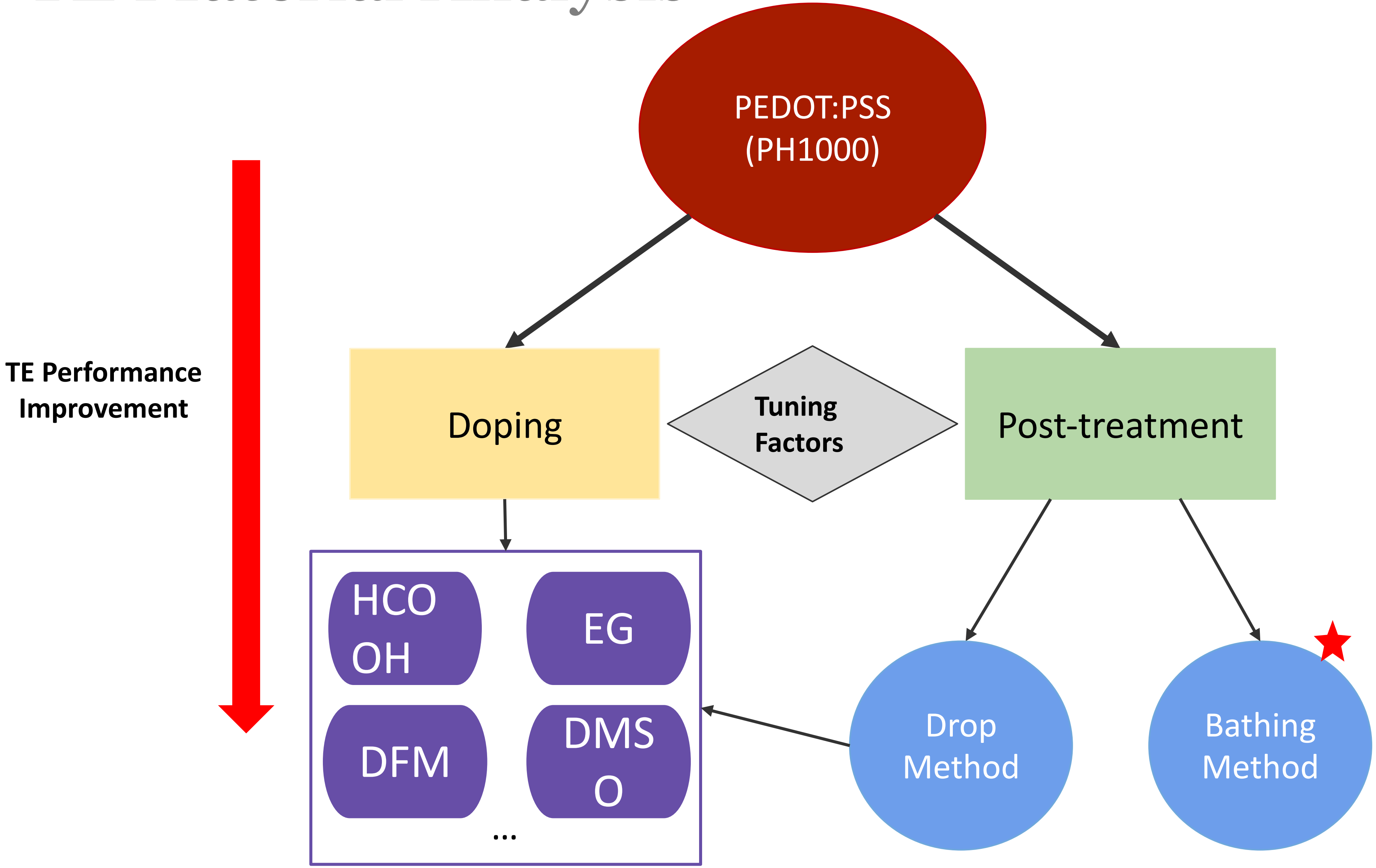
Change the calculation method for methane content:
Relative $CH_4$%
=$CH_4$%/($CH_4$%+$CO_2$%)

>90% methane production was achieved;

$N_2$% was under detect limit;

The amount of $CO_2$ dropped after hydrogen gas injected and no $H_2$ was detected in the outlet gas.

# P-type TE Material Analysis



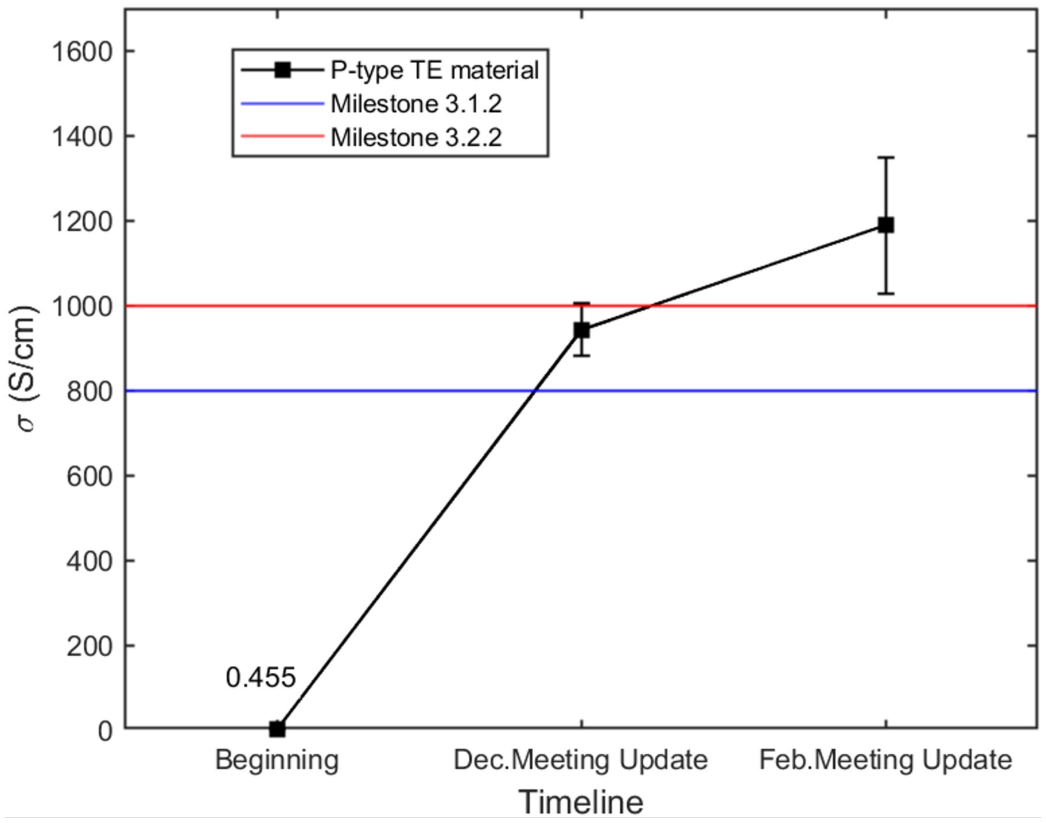
# P-type TE Material Analysis

- Organic polymer used
  - **PEDOT:PSS (PH1000)**

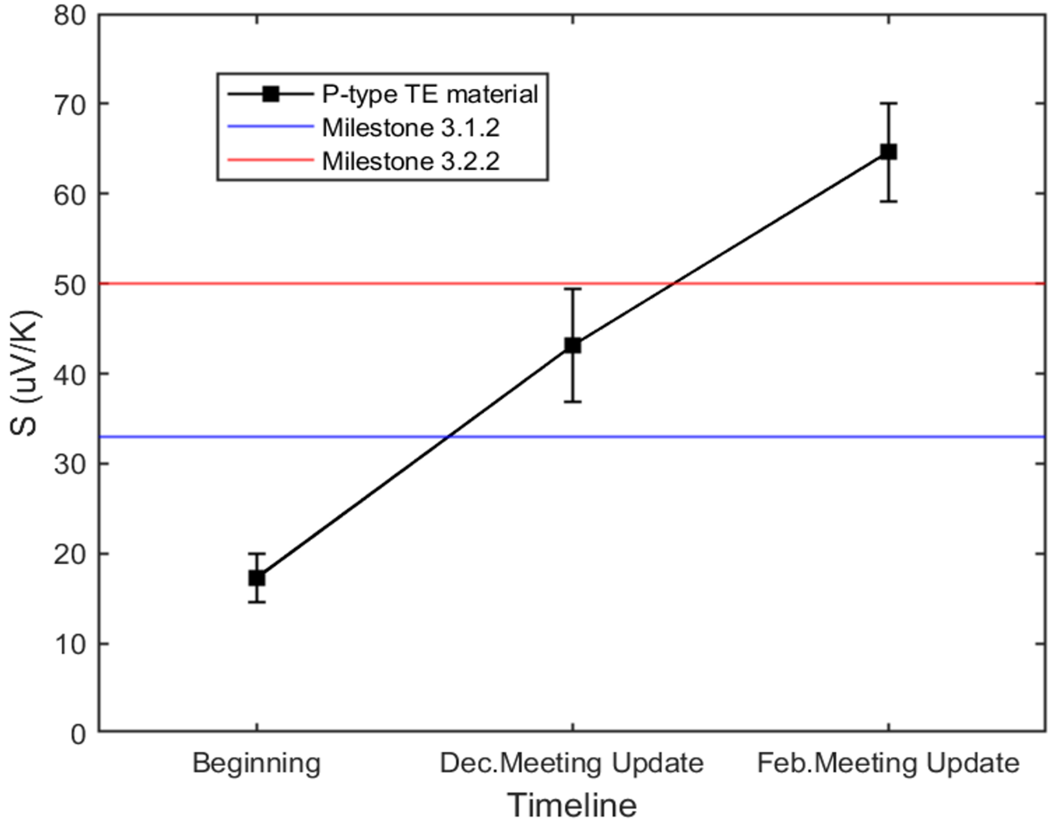
- TE performance improving process:
  - Step1: Doping (DMSO,EG)
  - Step2: EG Bathing

- Referenced Paper
  - https://doi.org/10.1038/nmat3635

# P-type TE material development




*Electrical Conductivity Improvement for PEDOT:PSS*




*Seebeck Coefficient Improvement for PEDOT:PSS*