Enhanced ex-situ biomethanation of H_2 and CO_2 for biomethane production using graphene oxide coated carrier

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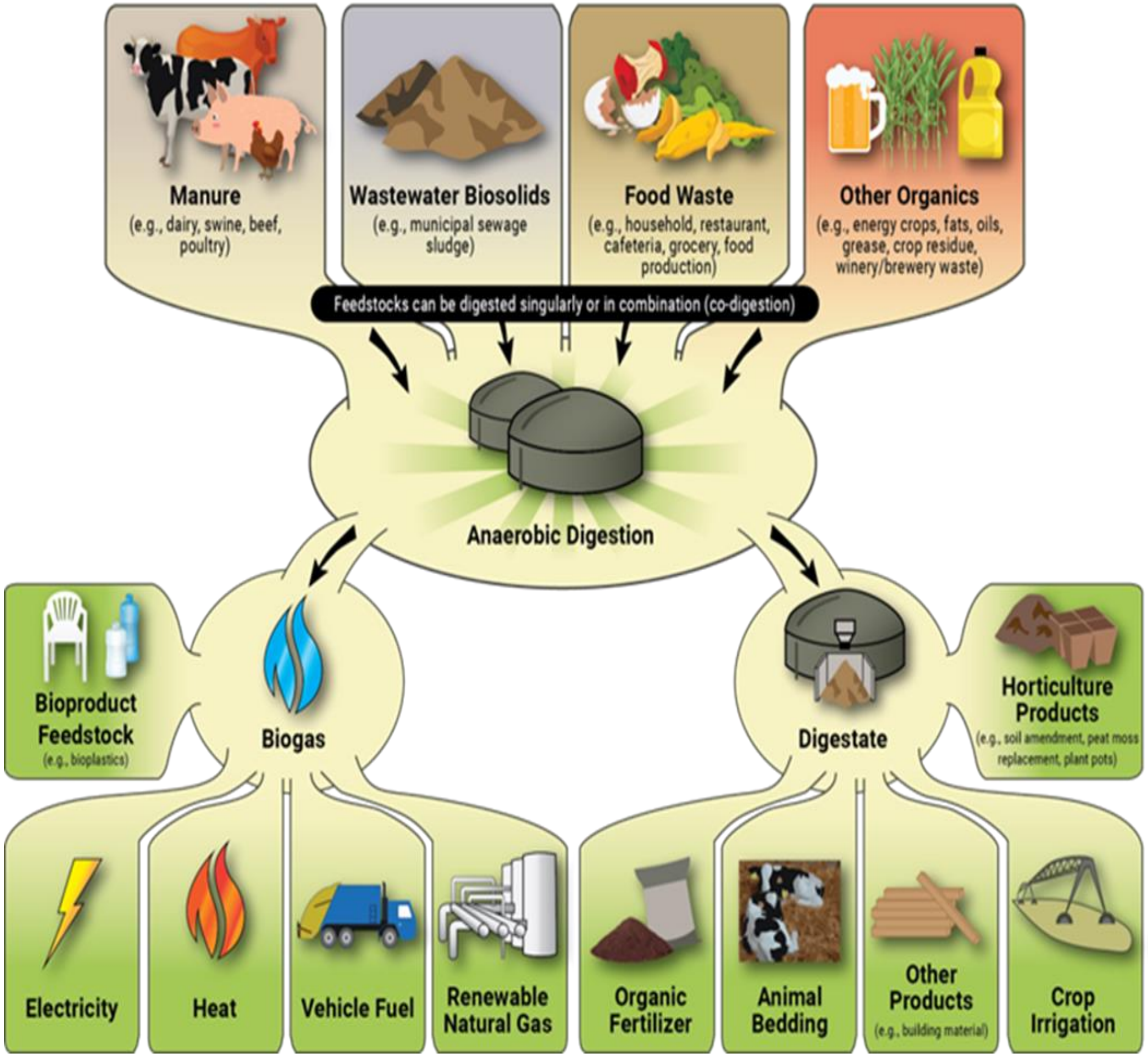
Content

Background

Biogas- a mixture of mainly methane (CH_4) and carbon dioxide (CO_2) produced during anaerobic digestion of organic wastes.



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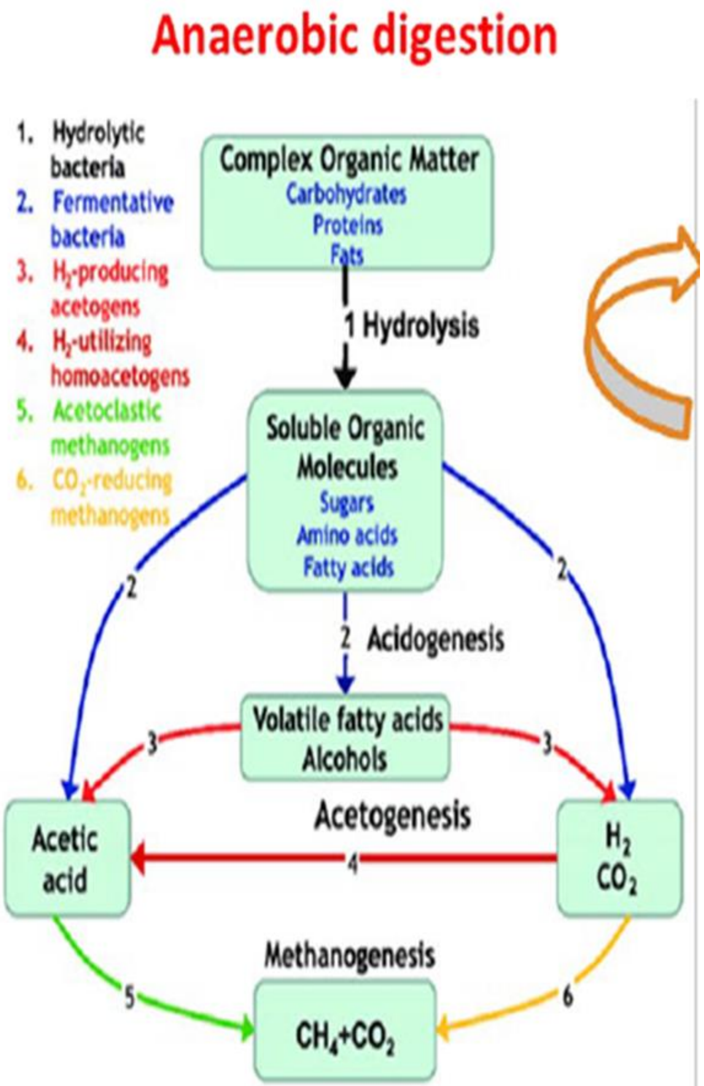
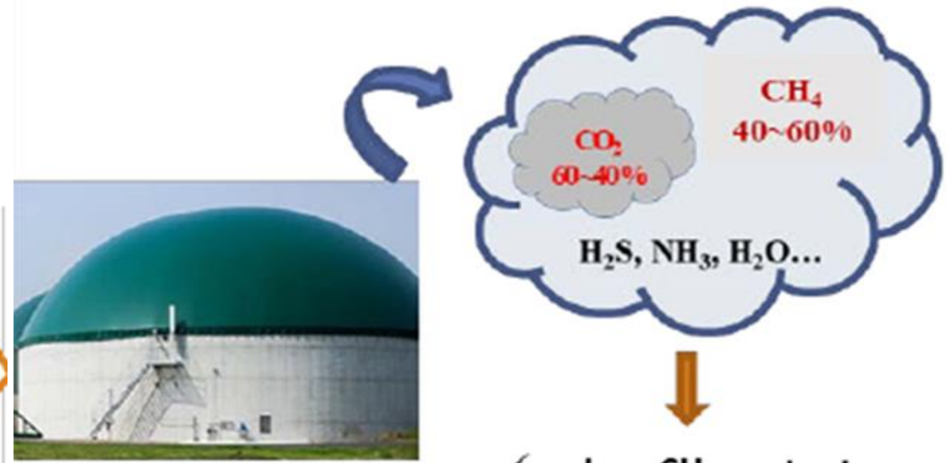




Biogas plant

- ✓ Low CH_4 content
- ✓ Low calorific value
- ✓ Limit use to heat and electricity

❖ What is Biogas Upgrading?

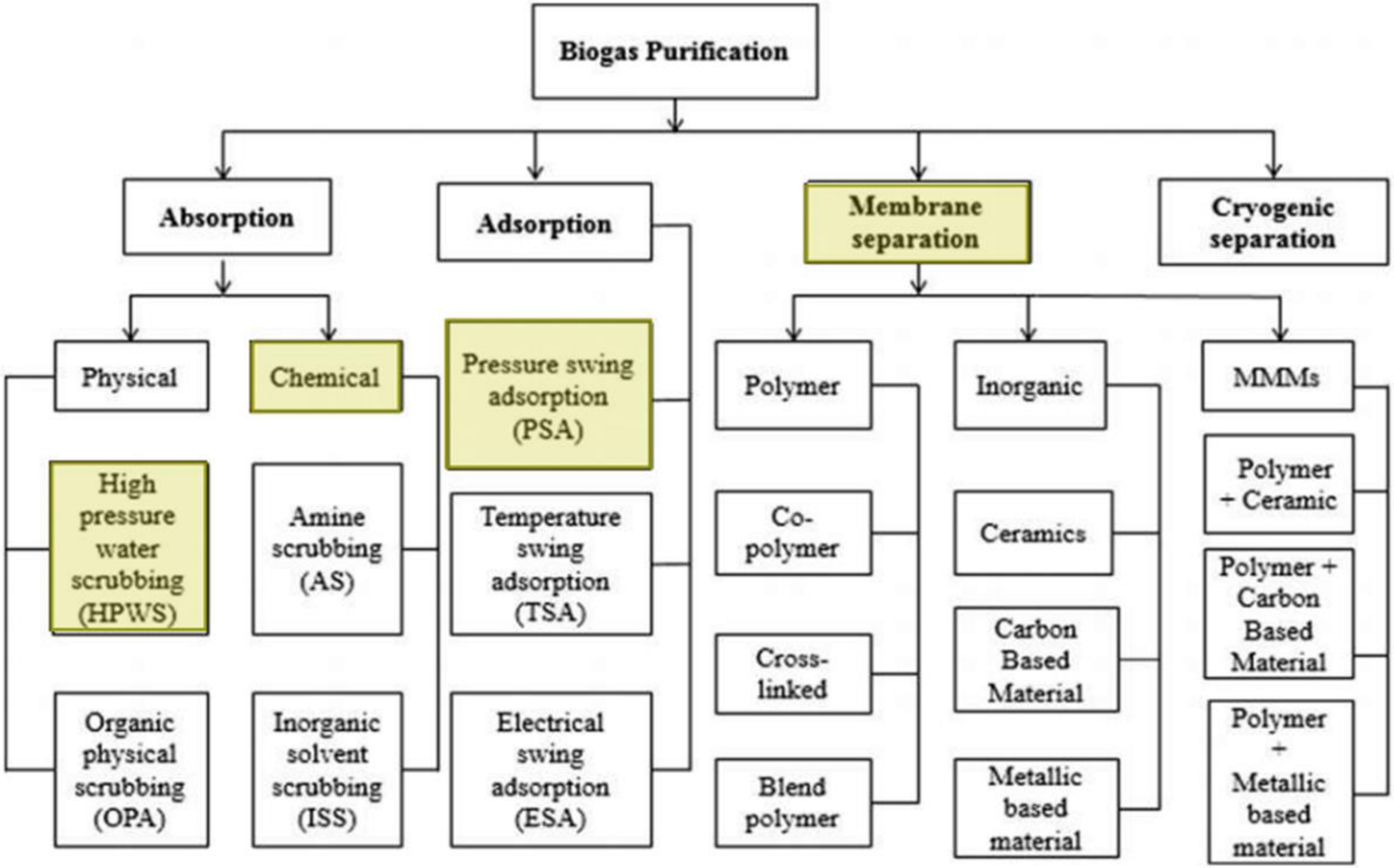
Removal or conversion of CO_2 contained in raw biogas to increase the methane content (> 95%) of the final output gas

Why biogas upgrading?

- ❖ Higher CH_4 content
- ❖ Decrease CO_2 emission
- ❖ Inject into natural gas grid
- ❖ Utilize as transport fuel

Background

Physicochemical biogas upgrading technologies



Khan, I. U., Othman, M. H. D., Hashim, H., Matsuura, T., Ismail, A. F., Rezaei-Dasht Arzhandi, M., & Azelee, I. W. (2017). Energy Conversion and Management, 150, 277-294.

Background

- Currently biogas upgrading technologies are expensive and energy intensive (pressure, chemicals or membrane)
- Upgrading for small and medium scale facilities is not economically feasible
- Losses of CO_2 and CH_4

Efficiency of main physicochemical biogas upgrading technologies

	Cryogenic	Sabatier Process	PSA	Water Scrubbing	Physical Scrubbing	Chemical Absorption	Membrane Separation
Consumption for raw biogas (kWh/Nm^3)	0.76	nf	0.23–0.30	0.25–0.3	0.2–0.3	0.05–0.15	0.18–0.20
Consumption for clean biogas (kWh/Nm^3)	nf	nf	0.29–1.00	0.3–0.9	0.4	0.05–0.25	0.14–0.26
Heat consumption (kWh/Nm^3)	nf	nf	None	None	<0.2	0.5–0.75	None
Heat demand (°C)	−196	270			55–80	100–180	
Cost	High	Medium	Medium	Medium	Medium	High	High
CH_4 losses (%)	2	nf	<4	<2	2–4	<0.1	<0.6
CH_4 recovery (%)	97–98	97–99	96–98	96–98	96–98	96–99	96–98
Prepurification	Yes	Recommended	Yes	Recommended	Recommended	Yes	Recommended
H_2S co-removal	Yes	No	Possible	Yes	Possible	Contaminant	Possible
N_2 and O_2 co-removal	Yes	No	Possible	No	No	No	Partial
Operation pressure (bar)	80	8–10	3–10	4–10	4–8	Atmospheric	5–8
Pressure at outlet (bar)	8–10		4–5	7–10	1.3–7.5	4–5	4–6

Background

- Fluctuating production of electricity from solar panels or wind turbines
- Excess electricity requires solutions
- Difficult to store electricity

The solution

- Excess electricity can be converted to biomethane by ex-situ biomethanation
- Easy to store and transport biomethane where access to natural gas grid

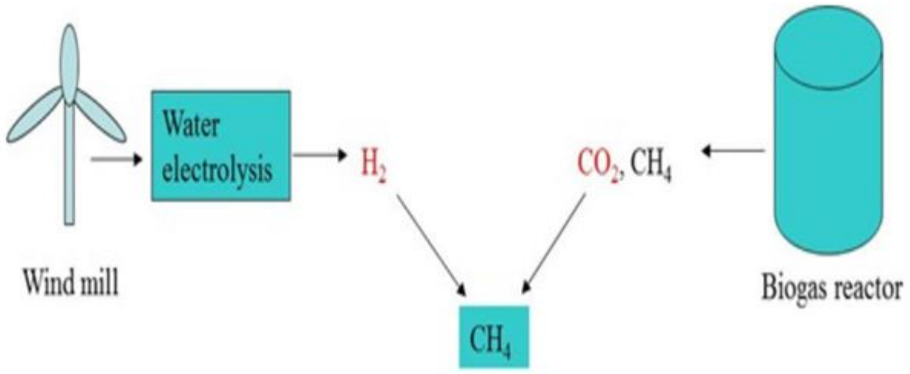
Ex-situ biomethanation

Developed by **Gang Luo**, Postdoc, and **Irini Angelidak**i, Professor

The Principle:
CO_2 together with H_2 could be used by hydrogenotrophic methanogens for CH_4 production

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \quad \Delta G^0 = -130.7 \text{ kJ/mol}$$

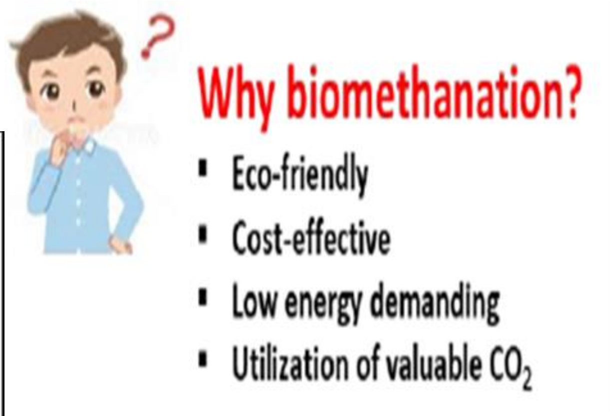
- H_2 as electron donor and CO_2 as electron acceptor and carbon source
- H_2 could be obtained by water electrolysis using surplus renewable electricity (e.g., wind mill, solar panel)
- Power-to-Gas **(PtG)**

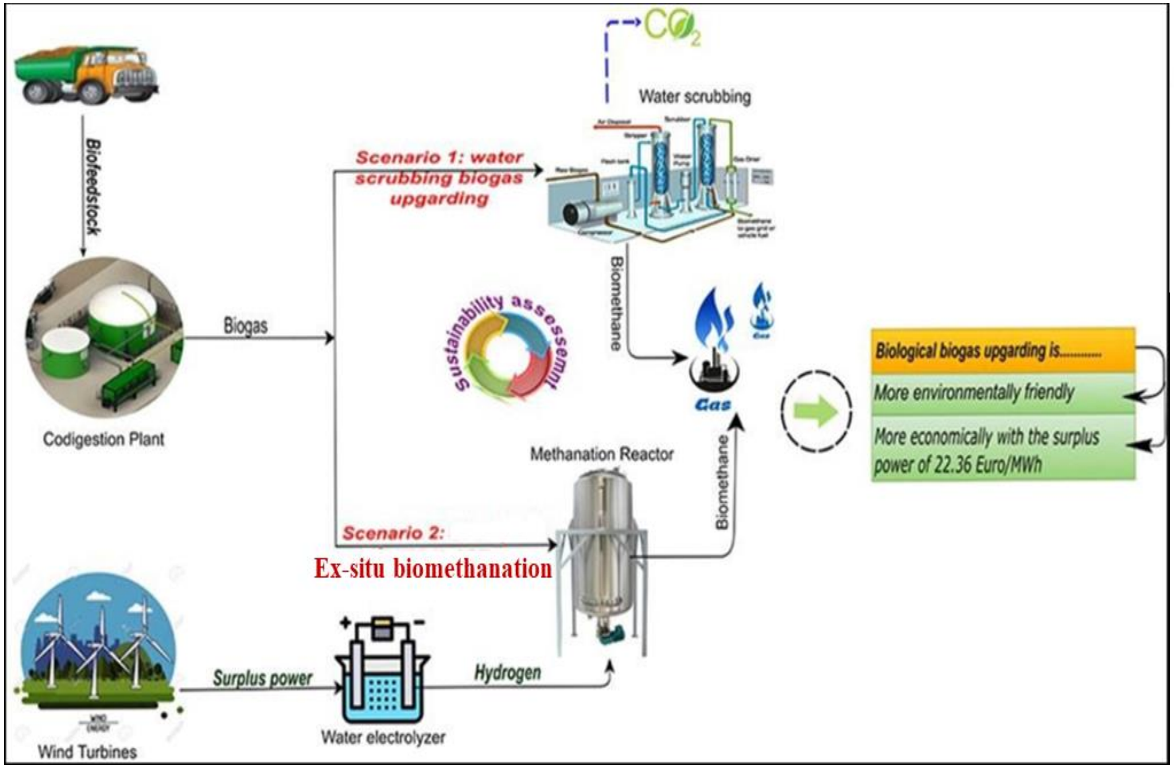


Ex-situ biomethanation

Why ex-situ biomethanation ?

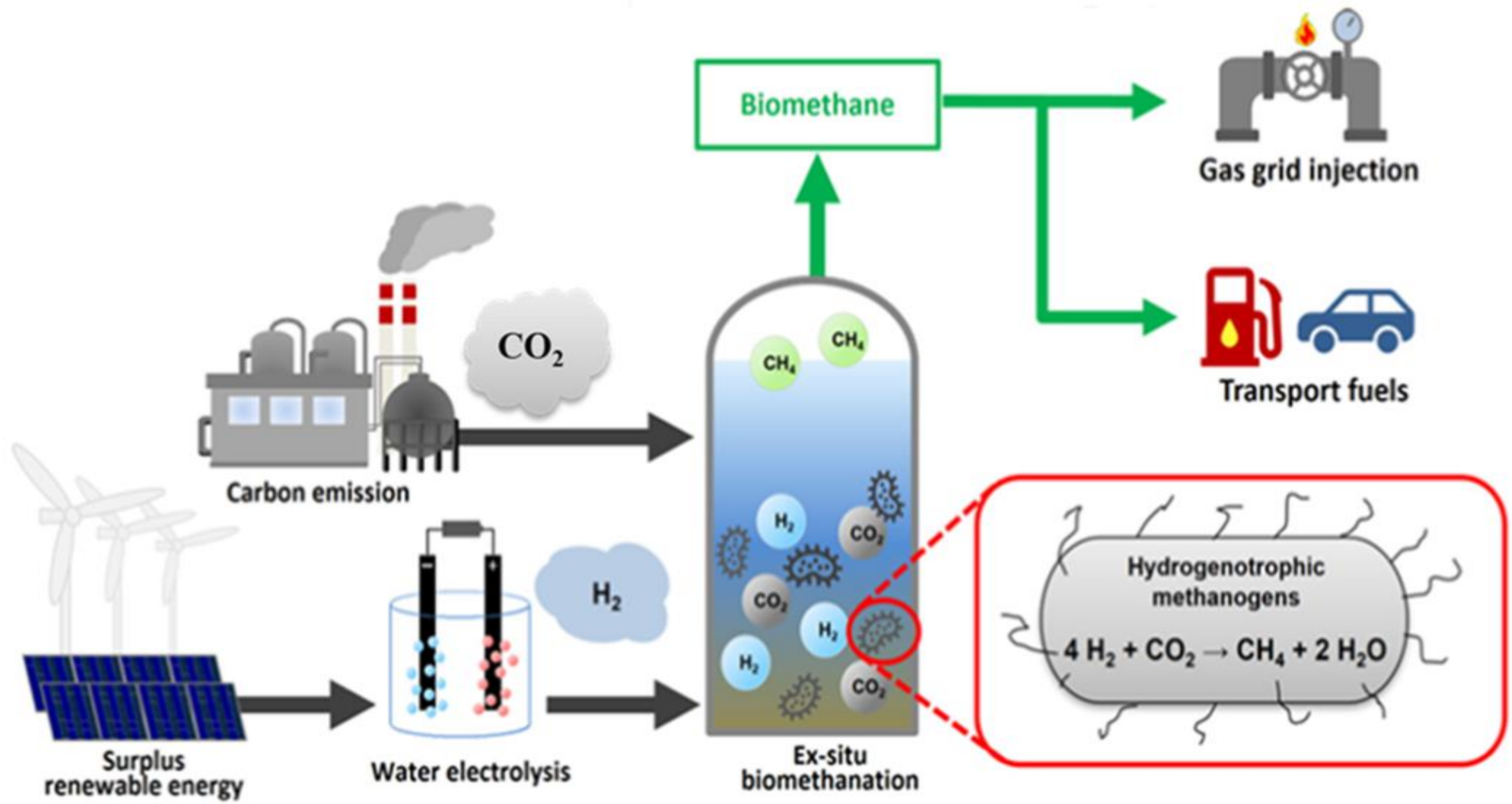
- ❖ Operation at ambient conditions (atmospheric pressure and moderate temperature) without use of catalyst and chemicals
- ❖ Utilization of CO_2 instead of removal to increase CH_4 content in output gas
- ❖ Higher resistance to gas impurities like H_2S, organic acids, NH_4





Background

Ex-situ biomethanation with Power-to-gas concept for biomethane production



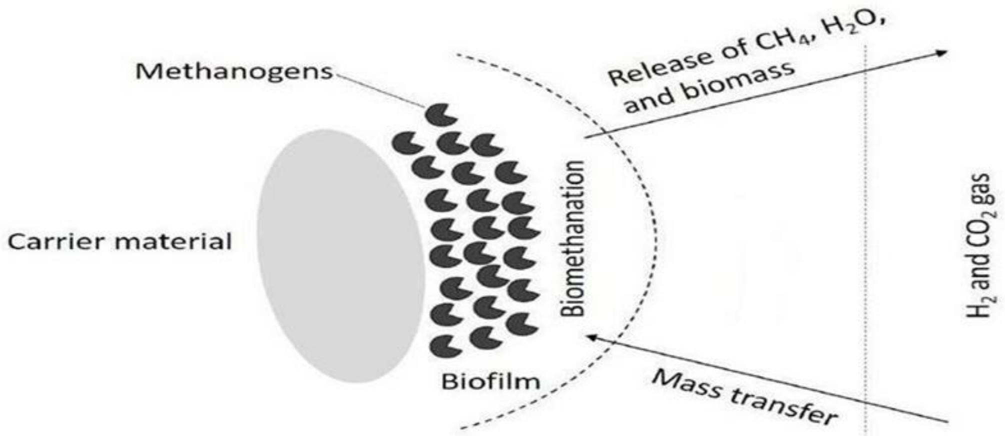
- ❖ **H_2 production** using surplus renewable electricity (windmills or solar panels) through **water electrolysis**
- ❖ Power-to-Gas (P2G)

Research gaps

- Low H_2 gas-liquid mass transfer
- Biofilm detachment under high gas loading rate (H_2/CO_2)
- Dilution of methanogens (from metabolic H_2O production during hydrogenotrophic methanogenesis)
- Stability of ex-situ biomethanation process under intermittent gas supply

Hypothesis

- Carrier material coated by conductive material (e.g., graphene oxide) can offer various benefits:
- Robust and dense biofilm formation (High microbial biomass)
- High specific surface area for microbes (biofilm)-gas-liquid phase interaction, which ultimately increase H_2 gas-liquid mass transfer and enhance biomethane production
- Prevent risk of dilution of methanogen from metabolic water production (No loss of microbes)
- Prevent loss of conductive materials



Objective

Main objective

- To enhance biomethane production using ex-situ biomethanation trickle bed reactor setup

Specific objective

- To investigate performance of graphene oxide coated carrier materials for H_2 gas-liquid mass transfer and biomethane production & apply in trickle bed reactor setup

Experimental setup

Preparation of coated carrier materials for biomethane production

- ❖ Graphene oxide (GO) was prepared by Hummer's method with some modifications.
- ❖ GO coated carrier was prepared from the solution deposition method.

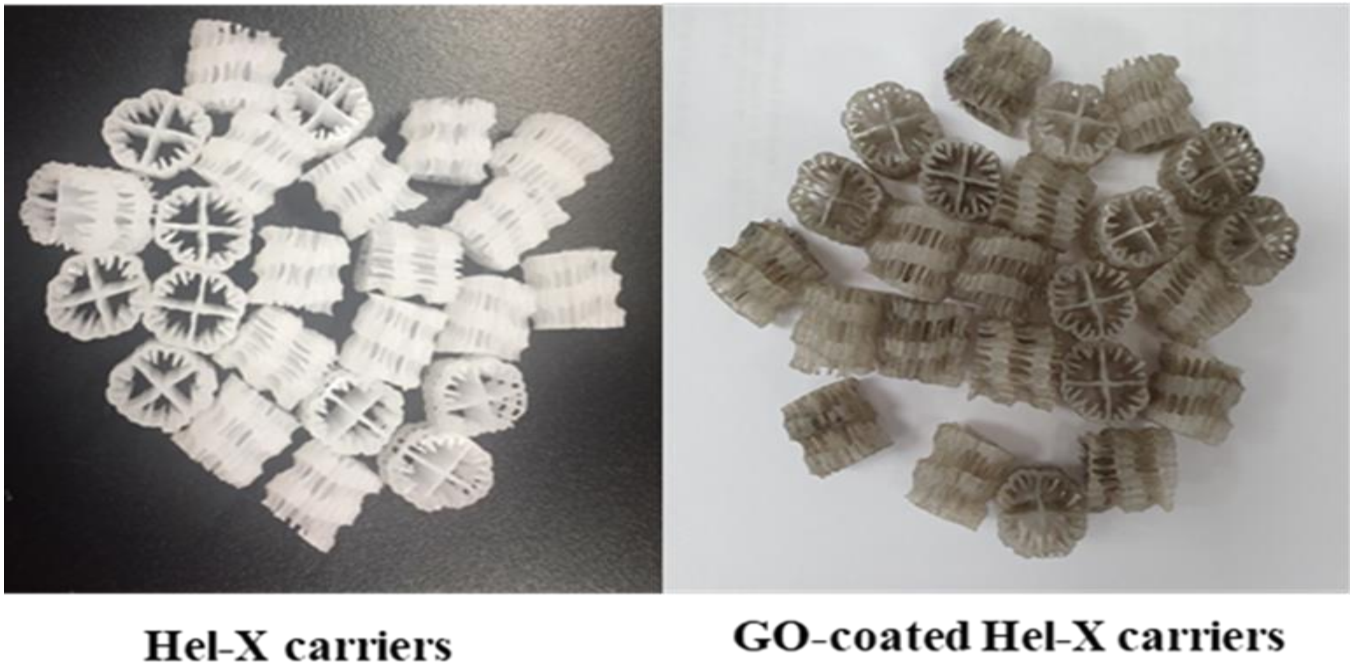
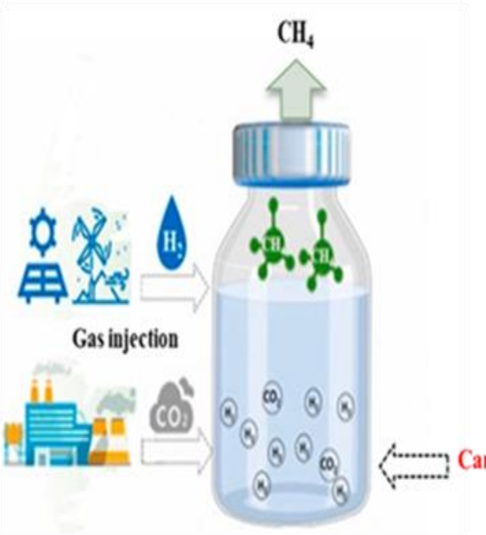


Fig. Photos of conventional Hel-X carriers and graphene oxide (GO)-coated Hel-X carriers

Experimental setup



Carrier material (Hel-X)

Serum bottle

Serum bottles kept at shaking incubator (37 ° C, 150 rpm)

Hel-X carriers

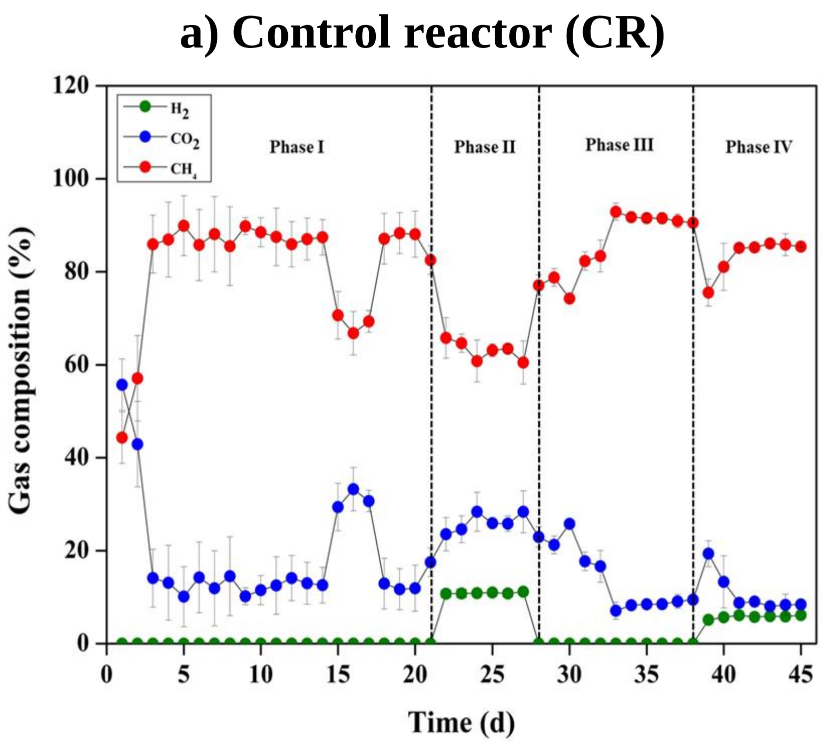
GO-coated Hel-X carriers

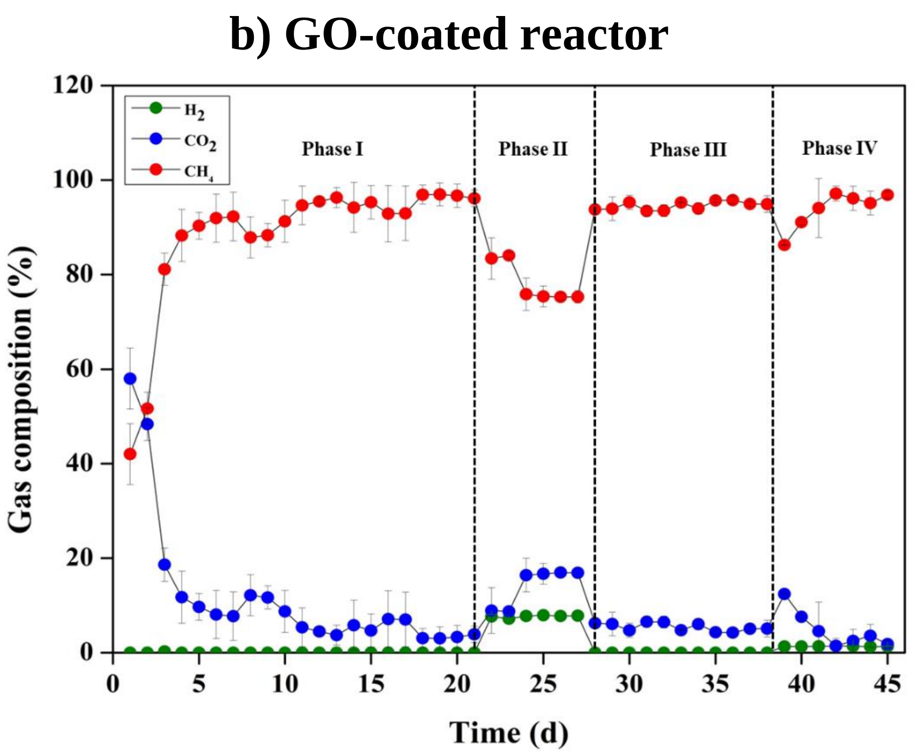
Analytical equipment

Gas chromatography

HPLC

Experimental results





- CH_4 content reached >98% in GO coated reactor
- Dramatic reduction in CH_4 content in CR than GO under stressful condition (i.e., high H_2 loading rate)
- Complete conversion of H_2 for reducing CO_2 to CH_4

Figure. Biogas composition of **a)** Control reactor filled with Hel-X carrier and **b)** Reactor filled with graphene oxide (GO)-coated Hel-X carrier. The lines represent mean values (n=3) and error bars denote the standard deviation.

Experimental results

Table. Reactors performance at different phases under steady-state conditions

Phase	I		II		III		IV	
Parameter	**CR**	**GO**	**CR**	**GO**	**CR**	**GO**	**CR**	**GO**
H_2 loading rate ($L/L_R.d$)	3.2		4.8		3.2		3.2	
CO_2 loading rate ($L/L_R.d$)	0.8		1.2		1.2		1.2	
Gas retention time (h)	24		24		24		18	
CH_4 production rate ($L/L_R.d$)	**0.46 ± 0.08**	**0.65 ± 0.07**	**0.56 ± 0.07**	**0.68 ± 0.11**	**0.53 ± 0.03**	**0.69 ± 0.01**	**0.50 ± 0.02**	**0.69 ± 0.02**
Biogas composition (%)								
H_2	0.00 ± 0.00	0.00 ± 0.00	10.98 ± 0.19	7.83 ± 0.19	0.00 ± 0.00	0.00 ± 0.00	5.99 ± 0.28	1.31 ± 0.08
CO_2	13.31 ± 5.51	4.93 ± 2.81	26.67 ± 2.40	16.84 ± 1.58	9.27 ± 1.25	5.08 ± 1.10	8.39 ± 1.49	2.69 ± 1.52
CH_4	**86.69 ± 5.52**	**95.07 ± 2.84**	**62.35 ± 2.31**	**75.33 ± 1.77**	**90.73 ± 1.27**	**94.92 ± 1.12**	**85.62 ± 1.27**	**96.00 ± 1.60**
ηH2 (%)	100 ± 0.00	100 ± 0.00	97.96 ± 0.07	98.52 ± 0.06	100 ± 0.00	100 ± 0.00	98.91 ± 0.04	99.71 ± 0.05

- **GO-coated reactor** performed better in terms of **CH_4 production rate (38% ↑) & CH_4 content (13% ↑)** than **control reactor (CR)**
- **GO-coated reactor** showed **resilience** even under 18 h gas retention time than CR
- GO facilitated **Direct interspecies electron transfer (DIET) for high CH_4 content due to its high electrical conductivity and large specific surface area**

Conclusion

- Performance of GO-coated Hel-X carriers were evaluated for ex-situ biomethanation
- **GO-coated reactor** performed better in terms of **CH_4 production rate & CH_4 content** than **control reactor**
- GO-coated carrier enhanced gas conversion efficiency and increased CH_4 production
- GO act as an electron mediator, accelerated DIET for enhanced bioconversion of CO_2 and H_2
- Coupling of H_2 and CO_2 in GO-coated reactor met natural gas quality CH_4 content (>95%)

THANK YOU

MERCI