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Enhanced Anaerobic Digestion by Graphene-stimulated Direct Interspecies Electron Transfer

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Science Foundation Ireland sfi For what's next

ERI Environmental Research Institute University College Cork

MaREI Centre for Marine and Renewable Energy

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- **2. Promoting Direct IET with Conductive Graphene**
- **3. Future Research**

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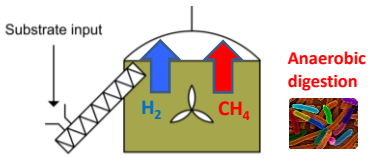
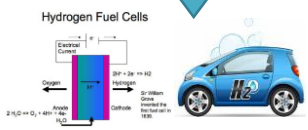
1. Introduction of Anaerobic Digestion

Seaweed, grass, food waste, animal slurry

Needs of alternative energy !

- Exhaustion of fossil fuel
- Global warming





- **Biohydrogen** "Clean energy"
- **Biomethane** "Carbon neutral"
- **Biohythane** "Renewable"

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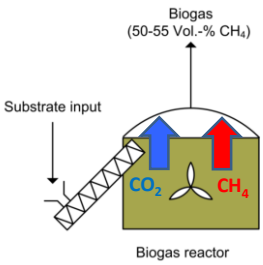
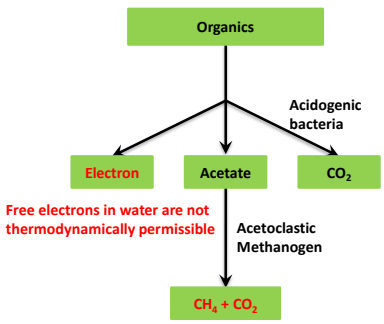
1. Interspecies Electron Transfer in Anaerobic Digestion



Anaerobic digester



Simplified Model for Conversion of Organics to Methane

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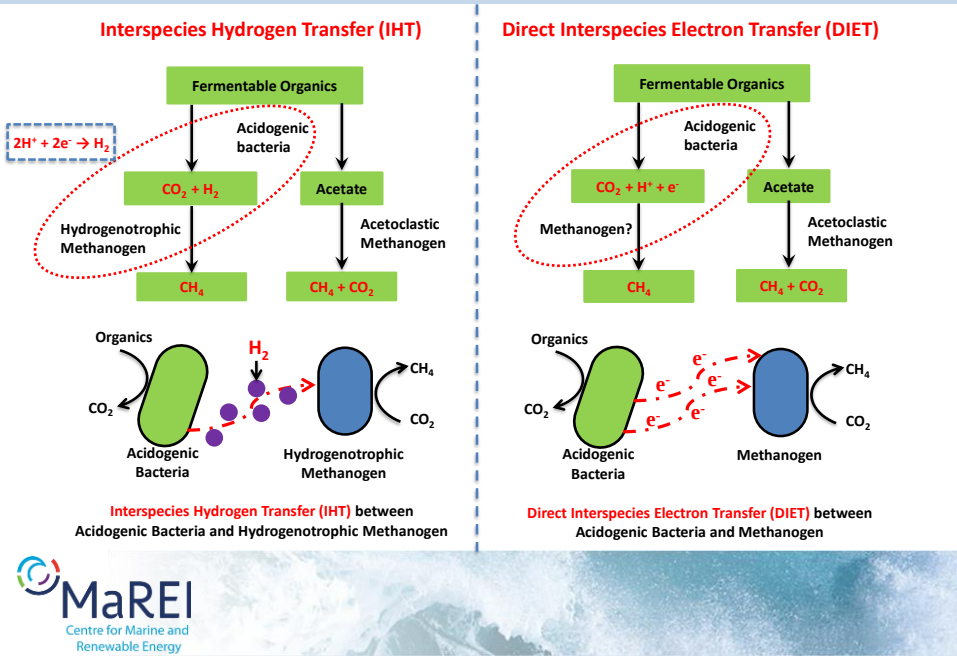
1. Interspecies Electron Transfer in Anaerobic Digestion



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Interspecies Hydrogen Transfer and Direct Interspecies Electron Transfer

Table Reactions and thermodynamics of Ethanol Degradation via IHT and DIET under standard conditions.

Process	Reaction	$\Delta G_0'$ (kJ/mol)
IHT	$CH_3CH_2OH + H_2O \rightarrow CH_3COO^- + H^+ + 2H_2$	+9.7
DIET	$CH_3CH_2OH + 1/2CO_2 \rightarrow CH_3COO^- + H^+ + 1/2CH_4$	-55.7

Positive value of $\Delta G_0'$ indicates the reaction is thermodynamically unfavorable.
Negative value of $\Delta G_0'$ indicates the reaction is thermodynamically favorable.

- IHT can only happen at very low hydrogen concentration due to the thermodynamic limit.
- DIET is thermodynamically more favorable to produce methane.

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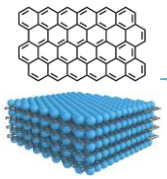
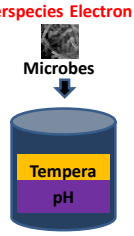
2. Promoting Direct IET with Conductive Graphene

❖ **Hypothesis: Highly conductive nano-graphene promotes Direct Interspecies Electron Transfer?**



- High surface area,
- electron mobility
- thermal conductivity.

Graphene



Anaerobic Digestion

❖ **Research objectives:**

- Assess of AD performance: biomethane yield, production rate, and other kinetic parameters
- Reveal the bacterial and archaeal communities responsible for DIET?
- Calculate the theoretical maximum electron transfer flux of IHT and graphene-based DIET?

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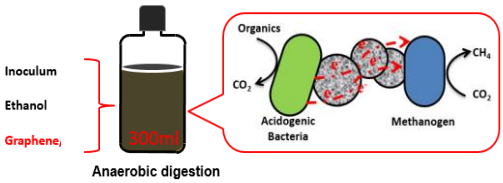
2. Promoting Direct IET with Conductive Graphene



Anaerobic digestion

Batch Biomethane Potential System

Table Experimental design

Group	Inoculum and Substrate	Graphene Concentration
1	250 mL sludge + 2.5 mL Ethanol	No
2	250 mL sludge + 2.5 mL Ethanol	0.5 g/L graphene
3	250 mL sludge + 2.5 mL Ethanol	1.0 g/L graphene
4	250 mL sludge + 2.5 mL Ethanol	2.0 g/L graphene

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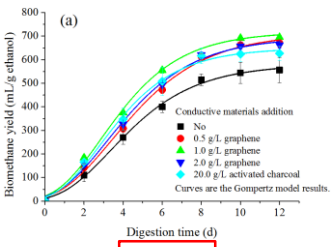
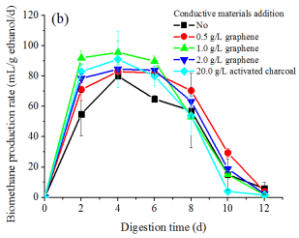
Biomethane production kinetics



CH_4 yield



CH_4 production rate

Graphene concentration	Kinetic model parameters			
	H_m (mL/g)	R_m (mL/g/d)	λ (d)	T_m (d)
No	579.7	86.9	0.89	3.34
0.5 g/L graphene	711.2	99.1	0.81	3.45
1.0 g/L graphene	718.4	116.2	0.60	2.87
2.0 g/L graphene	695.7	102.8	0.70	3.19

Optimal graphene concentration (1 g/L):

- **Biomethane yield +25%;**
- **Peak production rate +20%**
- **Lag-phase time reduced by 48%.**

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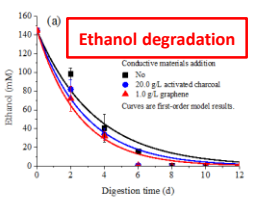
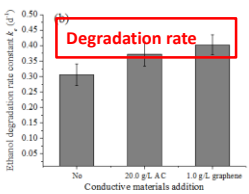
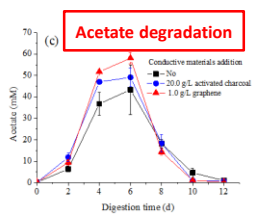
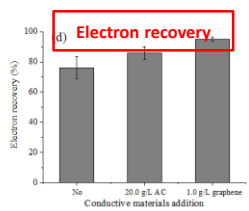
Ethanol degradation and microbial morphology









In the presence of graphene:

- **Ethanol degradation was more rapid,**
- **Acetate generation and consumption were much faster.**

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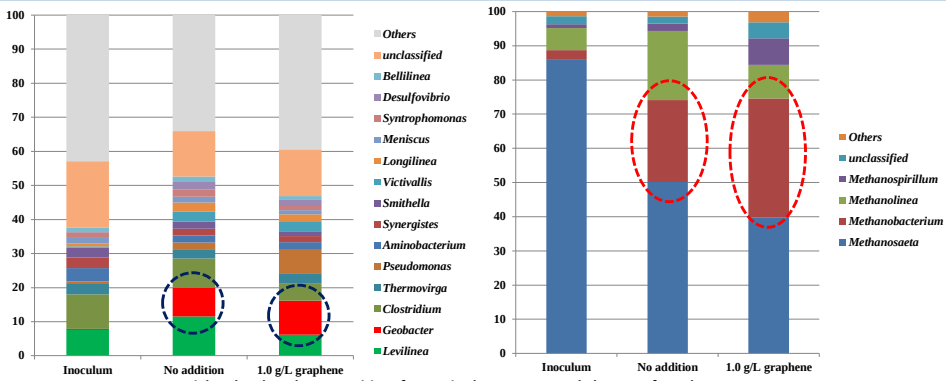
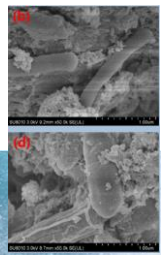
Structures of bacterial and archaeal community



Bacterial and archaeal communities after AD in the presence and absence of graphene

With the addition of graphene in AD,

- ✓ *Geobacter* in bacteria community increased from 6% to 10%. (electrogenic bacteria)
- ✓ *Methanobacterium* in archaea group greatly increased from 24% to 35%.



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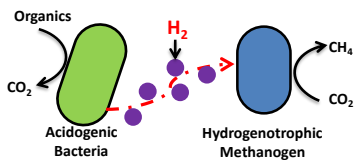
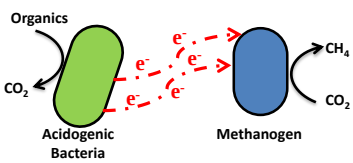
Calculation of Theoretical Maximum Electron Transfer of IHT and DIET



Interspecies Hydrogen Transfer (IHT) between Acidogenic Bacteria and Hydrogenotrophic Methanogen



Direct Interspecies Electron Transfer (DIET) between Acidogenic Bacteria and Methanogen

Interspecies Hydrogen Transfer
Or
Graphene-stimulated Direct Electron Transfer?

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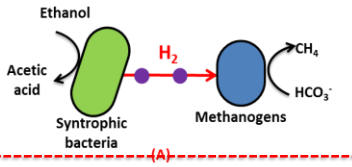
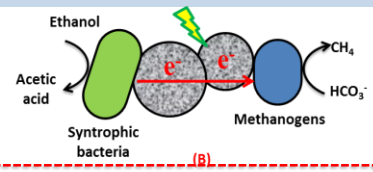
Calculation of Theoretical Maximum Electron Transfer of IHT and DIET





$$i = D_f \bullet \frac{S_{cell}}{d} \bullet ([H_2]_{highest} - [H_2]_{lowest}) \bullet n \bullet F$$

$$i = k \bullet \frac{S_{conduit}}{d} \bullet (E_{Met} - E_{syn})$$

i=Electric current associate with electron carrier flux
D_f=Diffusion coefficient of H_2 in water
S_{cell}=Surface area of the cells
d=Distance between cells
$[H_2]_{highest}$=Highest H_2 concentration produced by syntrophic bacteria
$[H_2]_{lowest}$=Lowest H_2 concentration reached by methanogen
n=mol of electrons per mol of H_2
F=Faraday's constant

i=Electric current associate with electron carrier flux
k=Electrical conductivity of conductive materials
$S_{conduit}$=Cross-sectional area of the electron conduit
d=Distance between cells
E_{Met}=Redox potential of ethanol oxidation reaction
E_{syn}=Redox potential of bicarbonate reduction reaction

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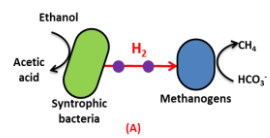
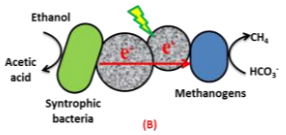
Calculation of Theoretical Maximum Electron Transfer of IHT and DIET



$$i = D_f \bullet \frac{S_{cell}}{d} \bullet ([H_2]_{highest} - [H_2]_{lowest}) \bullet n \bullet F$$



$$i = k \bullet \frac{S_{conduit}}{d} \bullet (E_{Met} - E_{syn})$$

The highest H_2 concentration :

$$\Delta G' = \Delta G^{0'} + RTln\frac{[\text{Acetate}] \cdot pH_2^2}{[\text{Ethanol}]}$$

In a similar way, the lowest H_2 concentration:

$$\Delta G' = \Delta G^{0'} + RTln\frac{pCH_4^{1/2}}{pCO_2^{1/2} pH_2^2}$$

The maximum driving force for direct electron transfer is given by the redox potential ($\Delta E = \Delta E_{met} - \Delta E_{ace}$) of the overall reaction ($CH_3CH_2OH + 1/2CO_2 \rightarrow 1/2CH_4 + CH_3COO^- + H^+$, $\Delta G^{0\prime} = -55.67$ kJ/mol).

❖ **Graphene-based DIET sustains much higher electron transfer flux (up to 6 orders of magnitude) than conventional IHT.**

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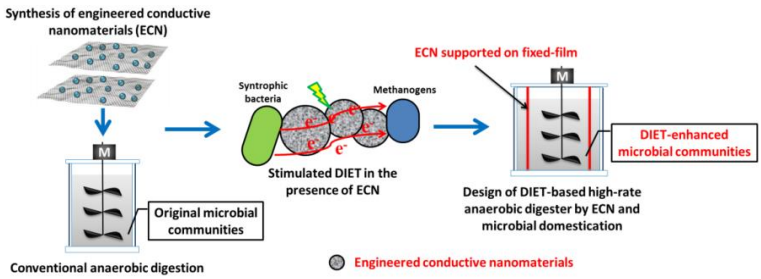
3. Future Research



- Highly-conductive graphene is capable of promoting DIET, and enhancing AD (up to 25.0%).
- Future work:
  - To develop continuous DIET-based anaerobic digester.
  - To assess the renewable feedstocks (such as seaweed, grass) for DIET-AD.
  - To reutilize graphene to make the process economically more viable. (Conductive Biochar)

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Thanks for your attention!

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