Bio-Hydrogen Production via Reforming of Anaerobic Digestion Biogas

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Outline

- Overview/Introduction
- Objective
- Theoretical modeling and setup
- Results and discussion
- Conclusion and path forward

Overview

- The biological pathway to produce H_2 and CH_4 shares similarities.
- Both consist of four generation steps, dominated by different microbial groups, which gives rise to different end products.
- A preliminary major challenge in the utilization of hydrogen is "sustainable production":

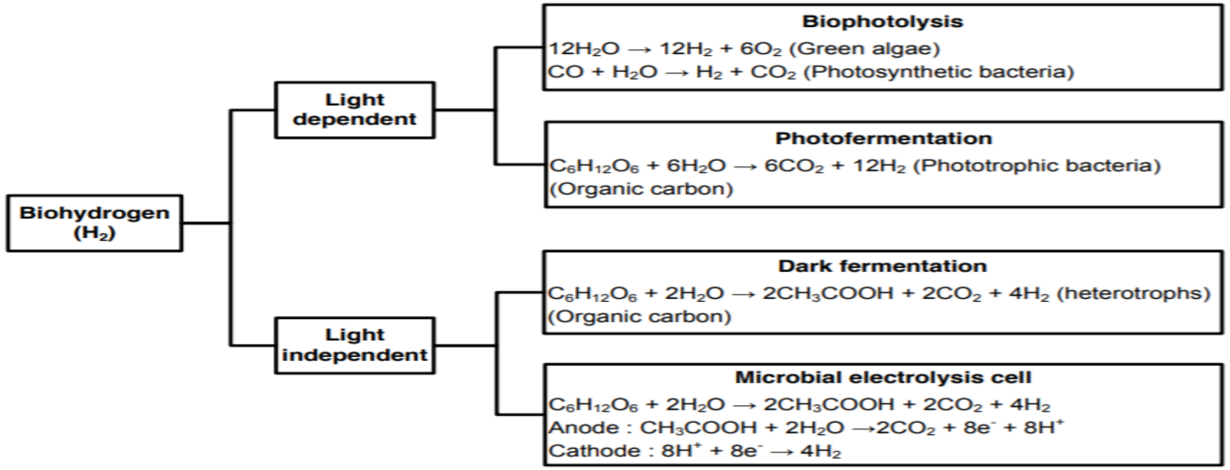
  Current technology to produce hydrogen:

  1. Steam reforming of natural gas!
  2. Gasification of coal!
  3. Electrolysis of water!, and
  4. Steam reforming of CH_4!

  Current Technology involve a significant amount of energy for generating the required heat

- Recent, studies is focusing on low production cost of energy through dark fermentation.
- Bio- hydrogen produced are those follow biological route, termed bio hydrogen (bio H_2), is viewed as a low energy solution particularly considering organic waste source:
  1. Biophotolysis of water,
  2. Photo fermentation and dark fermentation of OM---> least technological complexity, produces comparably high yields (Ntaikou et al., 2010).

Biological pathways for bio H_2 production.



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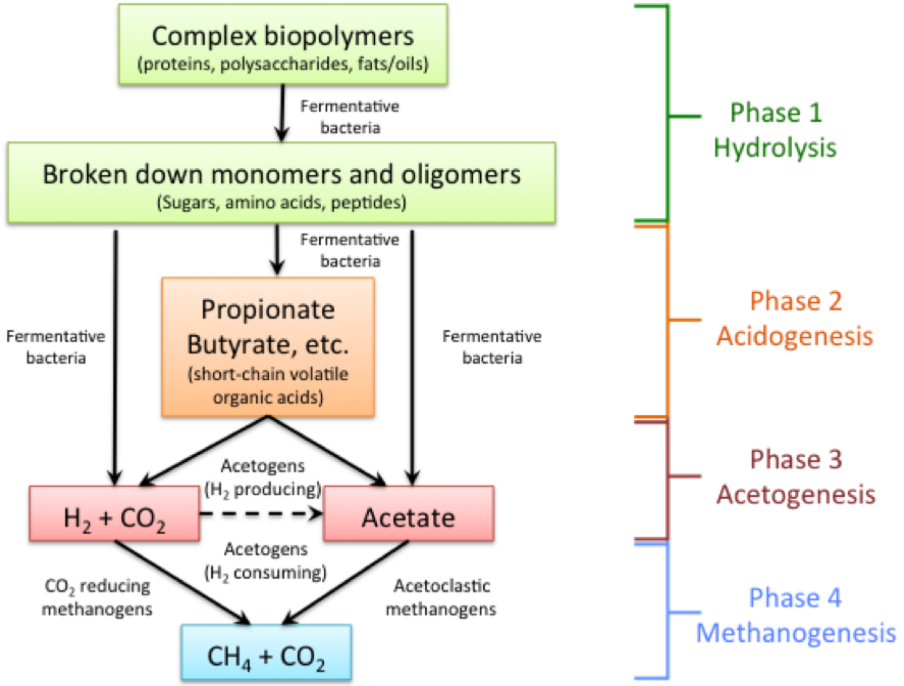
Overview (Cont'd)

- Fermentation or anaerobic digestion (AD) is a complicated dynamic biological process which involves multiple physicochemical and biochemical reactions in sequential and parallel pathways.
- The AD process is governed by different microbes with varied specific cell growth rates, substrate consumption capabilities and preferred environmental conditions, such as pH and temperature.
- This complexity renders the sensitivity of the AD to changes in environmental conditions and, thus, parameters will need to be carefully monitored to prevent process failure.
- Generally, AD is characterized by four distinct phases: *Hydrolysis; Acidogenesis; Acetogenesis; Methanogenesis*
- Hydrolysis of carbohydrates, protein and lipid has a theoretical CH_4 yield of 415 L CH_4/ kg VS, 496 L CH_4/ kg VS and 1014 L CH_4/ kg VS, respectively.

The four major steps during the AD of complex organic substrates



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Objective

- Because the biogas composition depends on the source:
  - Sewage digesters —> 55%-65% CH_4, 35%-45% CO_2 and <1% nitrogen by volume;
  - Organic waste digesters —> 60%-70% CH_4, 30%-40% CO_2 and <1% nitrogen
  - Landfills —> 45% -55% CH_4, 30%-40% and N_2 5% -15% [Jönsson O, et al 2013].

Typically, biogas also contains hydrogen sulphide and other sulphur compounds such as siloxanes, aromatic and

Biogas	CH_4 (%)	CO_2 (%)	O_2 (%)	N_2 (%)	H_2S (ppm)	Benzene(mg m^{-3})	Toluene(mg m^{-3})	Ref.
Landfill	47-57	37-41	<1	<1-17	36-115	0.6-2.3	1.7-5.1	S. Rasi et al. 2007
Sewage Digester	61-65	36-38	<1	<2	b.d.	0.1-0.3	2.8-11.8	S. Rasi et al. 2007
From Biogas Plant	55-58	37-38	<1	<1-2	32-169	0.7-1.3	0.2-0.7	S. Rasi et al. 2007
Landfill	59.4-67.9	29.9-38.6	n.a.	n.a.	15.1-427.5	21.7-35.6	83.3-171.6	Shin H-C et al. 2002
Landfill	37-62	24-29	<1	n.a.	n.a.	<0.1-7	10-287	Allen MR et al. 1997
Landfill	55.6	37.14	0.99	n.a.	n.a.	3.0	55.7	Eklund B et al. 1998
Landfill	44	40.1	2.6	13.2	250	n.a.	65.9	Jaffrin A et al 2003
Sewage digester	57.8	38.6	0	3.7	62.9	n.a.	n.a.	Spiegel RJ, Preston JL 2003
Organic Waste digester	62.6	37.4	n.a.	n.a.	n.a.	n.a.	n.a.	Stern SA et al 1998
Sewage digester	58	33.9	0	8.1	24.1	n.a.	n.a.	Spiegel RJ, Preston JL 2000

- Because there is no studies considering the reforming of biogas with compositional variation and the impact on the metrics.

- This work fills this gap and undertakes the reforming modeling of biogas considering two different anaerobic digesting sources, i.e. landfill and Sewage Digester and benchmarks the analysis against natural gas reforming.
- Process metrics such as conversion percentage as well as thermal process efficiency will be delineated and compared.

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Theoretical Modeling and setup

- Reforming of biofuel is a series of homogeneous reactions and involves many species and their intermediates.

Reforming reaction of the main species and their corresponding heat of reactions

Reaction#	Reaction Stoichiometry	Reaction energy (kJ/mol)	Description
R1	$CH_4 + H_2O \rightarrow CO + 3H_2$	+206	Methane steam reforming I
R2	$CO + H_2O \rightarrow CO_2 + H_2$	−41	CO Shift
R3	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	+165	Methane steam reforming II

- Determine the molar o… d streams (CH_4 source to steam source) as well a… s (as well as pressures).
- An equilibrium based model is developed by considering three reaction constants, elemental mass balance and chemical/formation and thermal/sensible energy balance.
- The main assumption is that the process takes infinite residence time, occurs under chemical and thermodynamic equilibrium, neglecting reaction kinetics, no intermediate species, ideal mixing and fixed spatial distribution of species.
- Feed 1 can be a pure CH_4 or combination of CH_4 rich species as in the case of natural gas (CO, H_2, C_2H_4, C_3H_6, C_4H_{10} and C_5H_{12}) and the outcome of the digestion process (CH_4 and CO_2).
- Total of 8 unknowns are generated governed by 8 equations and these are the 4 elemental balance of each of C, O, H, and N, the (one) total heat balance, the three equilibrium reaction of Steam Reforming (R1), CO-shift (R2) and Steam Reforming II (R3). Each reaction is associated with equilibrium equation in terms of the concentration Kc (or the partial pressure Kp) as follows:

$$K_c(T) = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad k_c(T) = A_r T^{\beta_r} e^{-\frac{E_r}{RT}}$$

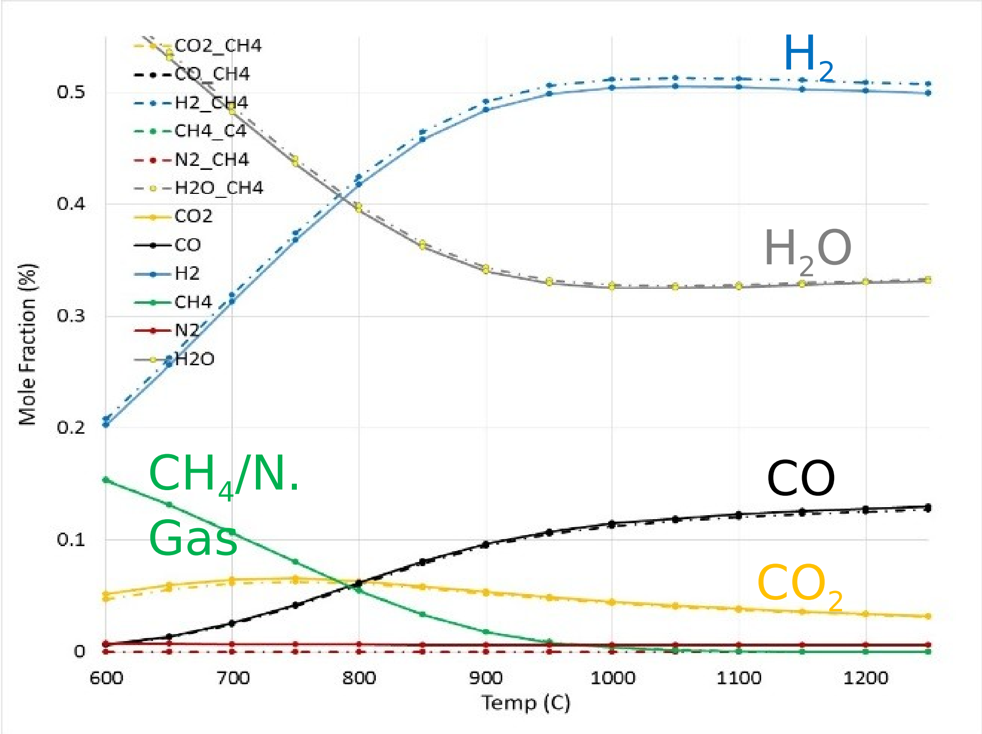
$$\sum_{i=1}^{n\,product} \dot{n}_i\, h_i = \sum_{i=1}^{n\,react} \dot{n}_i\, h_i + \dot{Q}$$

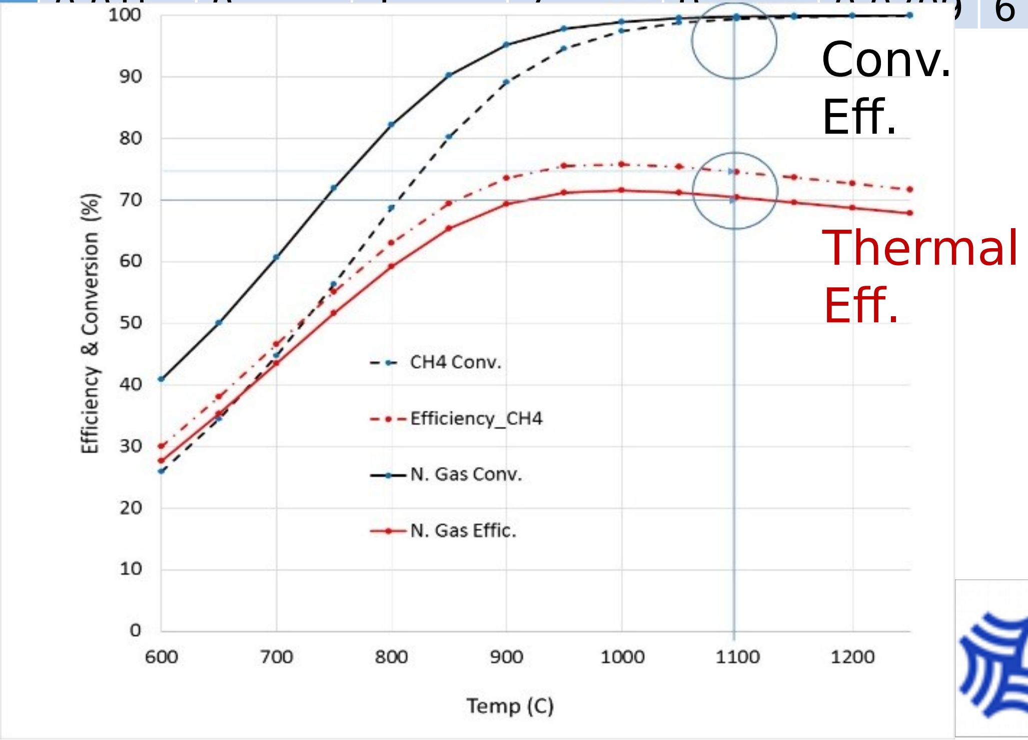
Results and discussion

- Baseline analyses are carried at fixed pressure of 30 bars and sweeping values of temperature 650°C-1250°C.
- Additional to species evaluation, the conversion and reforming efficiencies are evaluated:
  - The conversion efficiency: the ratio of the remaining CH_4 mass to the feed CH_4 mass
  - The reforming/thermal efficiency is the heating value of H_2 to the feed stream heating value+ added process heat.

Natural gas composition

Species	CO_2	CO	H_2	CH_4	N_2	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
M.Concent	0.015	0	0.0642	0.7877	0.0370	0.0709	0.0166	0.0016	0.0379





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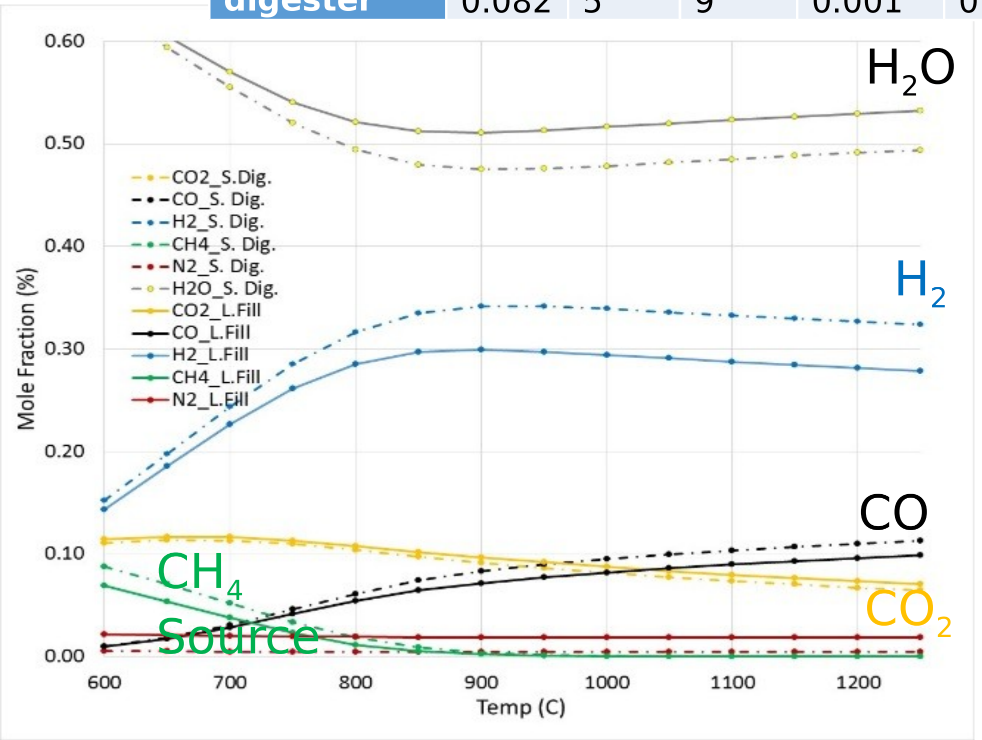
Results and discussion

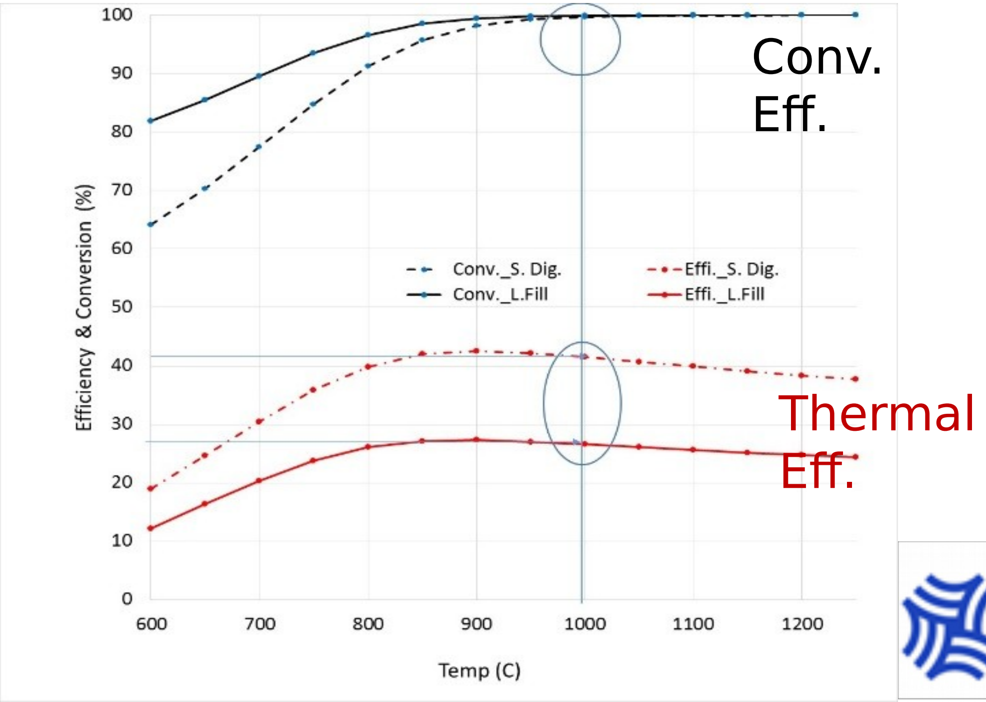
- Condition of anaerobic digestion at fixed pressure of 30 bars and at sweeping values of temperature 650°C-
- Species evaluation, the conversion and reforming efficiencies are evalu

Anaerobic digestion cond.

Species	CO_2	CH_4	N_2
Landfill	0.4	0.5	0.1
Anaerobic Digester	0.375	0.6	0.025

Species	CO_2	CO	H_2	CH_4	N_2	H_2O	Power	Heat (MJ)	Efficiency	Conversion
Landfill	0.088	0.082	0.294	0.000	0.019	0.517	3.672	140.883	26.566	99.894
An. digester	0.082	0.095	0.339	0.001	0.005	0.479	3.808	157.278	41.514	99.672





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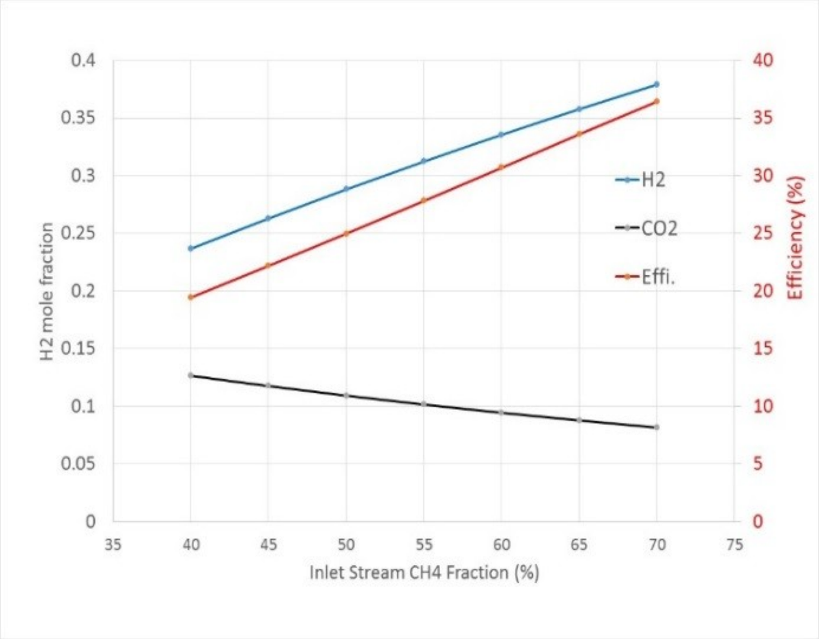
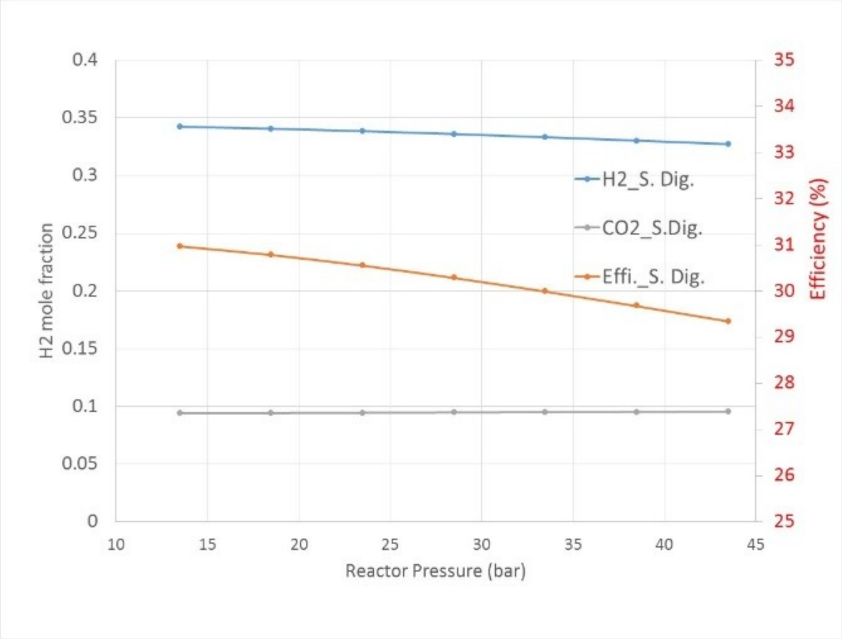
Results and discussion

- Sensitivity of anaerobic digestion at different press and temp pressure Species evaluation, the conversion and reforming efficiencies are

Anaerobic digestion cond.

Variable	CO_2	CH_4	N_2	Pressure (bar)	Variable	Pressure(bar)	CO_2	CH_4	N_2
Biogas Concentration	0.3	0.69	0.01	28.5	Process Pressure	13.5	0.4	0.59	0.01
	0.35	0.64	0.01	28.5		18.5	0.4	0.59	0.01
	0.4	0.59	0.01	28.5		23.5	0.4	0.59	0.01
	0.45	0.54	0.01	28.5		28.5 (baseline)	0.4	0.59	0.01
	0.50	0.49	0.01						
	0.55	0.44	0.01						
	0.60	0.39	0.01						





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Conclusion

- In this work, bio H_2 production through biogas reforming is carried out from two sources the landfill and anaerobic digester. The main difference in these streams are the concentration of the CH_4.
- A reforming model that is based on equilibrium was developed and is validated with respect to the two conventional streams, namely natural gas and pure CH_4.
- The model is then used to assess the molar concentration of the hydrogen produced and reforming efficiency under different conditions including the methane concentration and reactor temperature and pressure.
- Results shows that methane concentration has the most pronounced influence on the produced hydrogen and, consequently, the reforming efficiency.
- These values are around 0.5 molar fraction for H_2 and reforming efficiency nearly 75% for conventional stream, while are near 0.3 molar fraction and best reforming efficiency near 36%.
- Although this work states the technical feasibility of reforming the biogas stream, low efficieny is clear drawback is that needs further research to improve it.
- *Under progress is high fidelity modelling:*

Activation energies and pre-exponential factors for SMR process via reactions 1 (SMR), 2 (WGS) and 3 (SMR/							
2 (WGS) and 3 (SMR/WGS) over 18 wt. % NiO/a-Al2O3. Reaction parameters of this work (S.Z. Abbas*, V. Dupont, T. Mahmud) vs Xu and Froment [22]							
R1	CH4+ H2O=CO+ 3H2 DH298+206 kJ/mol	E1 [kJ/mol] 257.01* 240.10	Ao,1 [mol bar0.5 /g.s] 5.19e9* 1.17e12				
	CO+ H2O=CO2+H2 DH298-41	E2 [kJ/mol] 89.23*	Ao,2 [mol/ bar.g.s] 9.90e3*				