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Modelling Bio-electrochemical CO_2 Reduction to Methane

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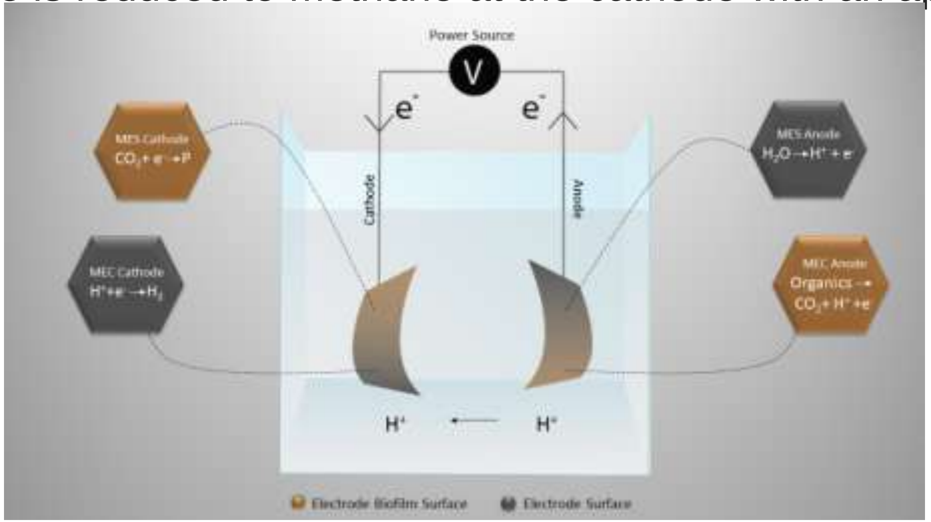
Introduction

- Anaerobic Digestion: Conversion of organic matter to methane and carbon dioxide with help of micro-organisms in the absence of oxygen.
- A typical waste treatment plant in Norway produces biogas with about 60-70% methane and 30-40% CO_2 .
- Biogas needs to be upgraded (separation or utilization of CO_2) to be used as a transport fuel.

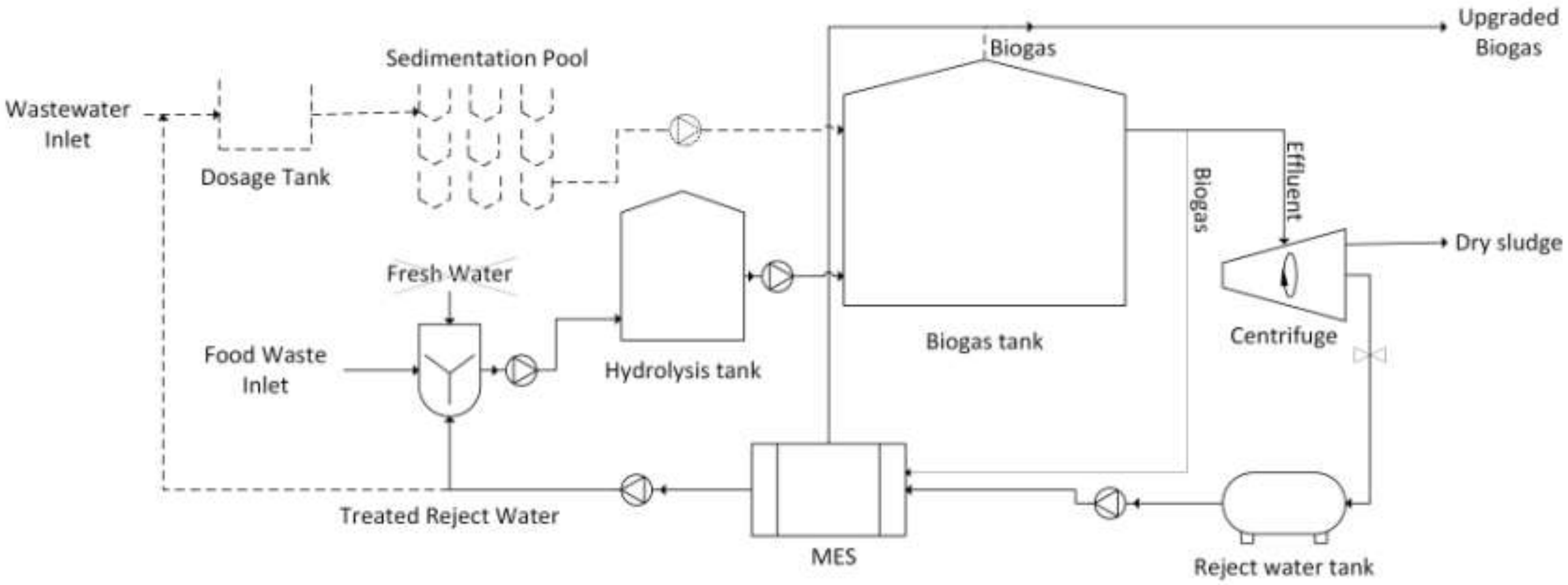
Microbial Electrosynthesis System

- Convert electrical energy to chemical energy with help of microorganisms as catalysts.
- Carbon dioxide is reduced to methane at the cathode with an applied potential.



(Nelabhotla et. al., 2018).

MES Integration with AD

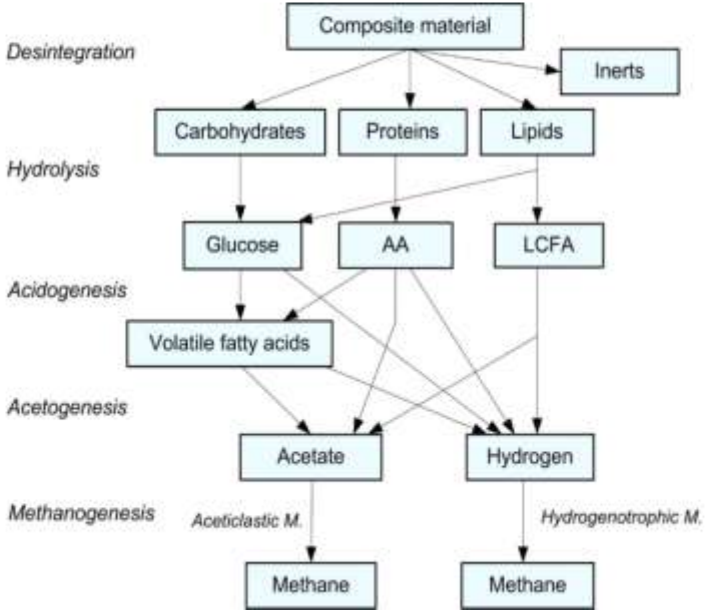


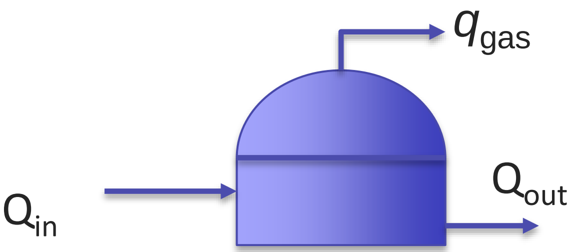
(Nelabhotla et. al., 2019)

Model Development and Method

The reaction system in an anaerobic digester is complex with a number of sequential and parallel steps.

- Biochemical reactions mediated by bacteria
- Physico-chemical reactions (*e.g.,* pH), and gas-liquid transfer.





MES Model Development and Method

$$\rho_{c1} = k_{\mathrm{m}}^{0} X \frac{S_a}{K_a + S_a} \frac{S_d}{K_d + S_d}$$

Electrochemical substrate limitation

$$CO_2 + 8H^+ + 8e^- \xrightarrow{\rho_{c1}} CH_4 + 2H_2O$$

$$\frac{S_d}{K_d+S_d} = \frac{1}{1+exp\left[-\frac{F}{RT}\eta\right]}$$

$$\frac{S_a}{K_a + S_a} = \frac{S_{CO_2}}{K_{CO_2} + S_{CO_2}}$$

The electron-donor and the electron-acceptor substrates together limit the overall reaction

- $k_m{}^0$ - maximum growth rate
- X – micro org. con.
- S_a , S_d - two "limiting-substrate" con.
- K_a , K_d - half-maximum rate con. for substrates S1 and S2.

a – electron acceptor
d – electron donor

MES Model Parameters

$$\frac{S_d}{K_d+S_d} = \frac{1}{1+exp\left[-\frac{F}{RT}\eta\right]}$$

- local potential(η) is defined = E_{KA} - $E_{cathode}$
- E_{KA} is the potential in which the substrate consumption rate will reach half of the maximum substrate consumption (analogous to K_d).
- η accounts the electro active part of the rate expression
- The current study, E_{KA} is taken as the reference potential (*i.e.,* E_{KA} =0)
- R = ideal gas law constant
- T = absolute temperature
- F = faraday constant

Model Assumptions

- Hydrogenotrophic methanogens (X_H$_2$) catalyse methane production from CO_2 via direct interspecies electron transfer (DIET).
- Complete mixed cathode compartment.
- Non- limiting flow of proton, and electron current supplies with separate anode compartment.
- The heterotrophic biogas production follows the ADM1 model.

Overall redox reactions

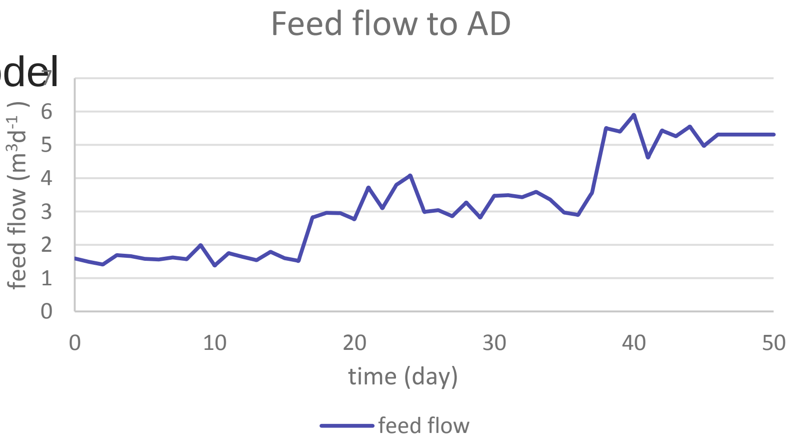
Oxidation reaction : $\frac{1}{2}H_2O \rightarrow H^+ + e^- + \frac{1}{4}O_2$

Reduction reaction : $\frac{1}{8}CO_2 + H^+ + e^- \rightarrow \frac{1}{8}CH_4 + \frac{1}{4}H_2O$

Simulation Result – Anaerobic Digestion

Conventional AD for baseline data – Batstone Model

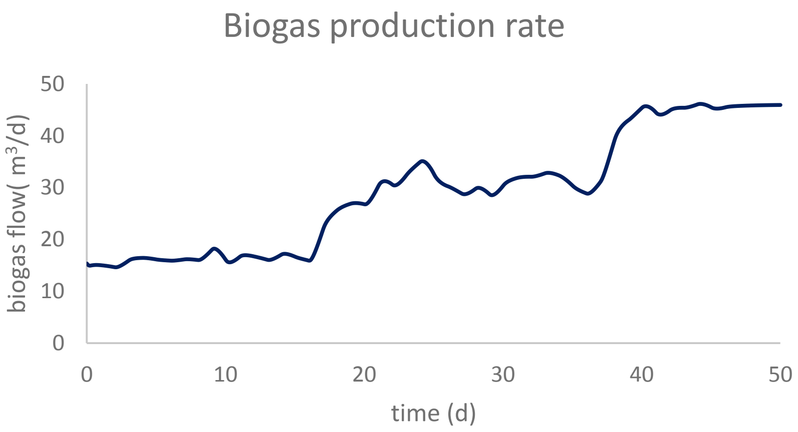
- CSTR reactor
- 50 days
- Feed step increases at day 16 and 37
- Feed composition

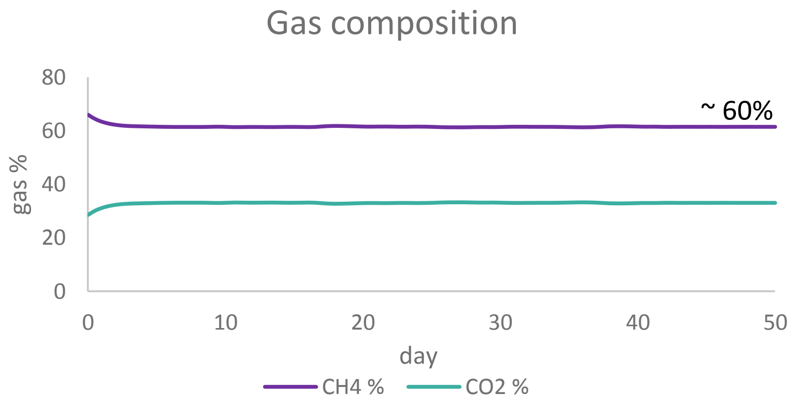


Components in the feed	Concentrations kg COD
Amino acids	4.2
Fatty acids	6.3
Monosaccharides	2.8
Complex particulates	10
Total	**23.3**

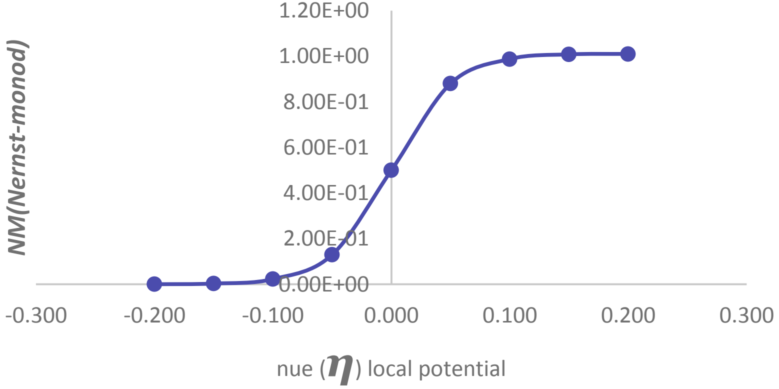
Batstone, et al. (2002). The IWA Anaerobic Digestion Model No 1 (ADM1). *Water Science and Technology*, *45*(10), 65-73.

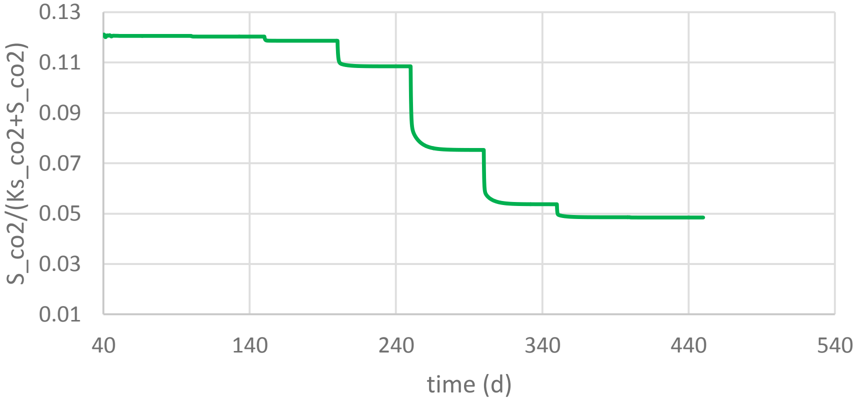
Conventional AD for baseline data





Saturated Potential and Substrate Limitation

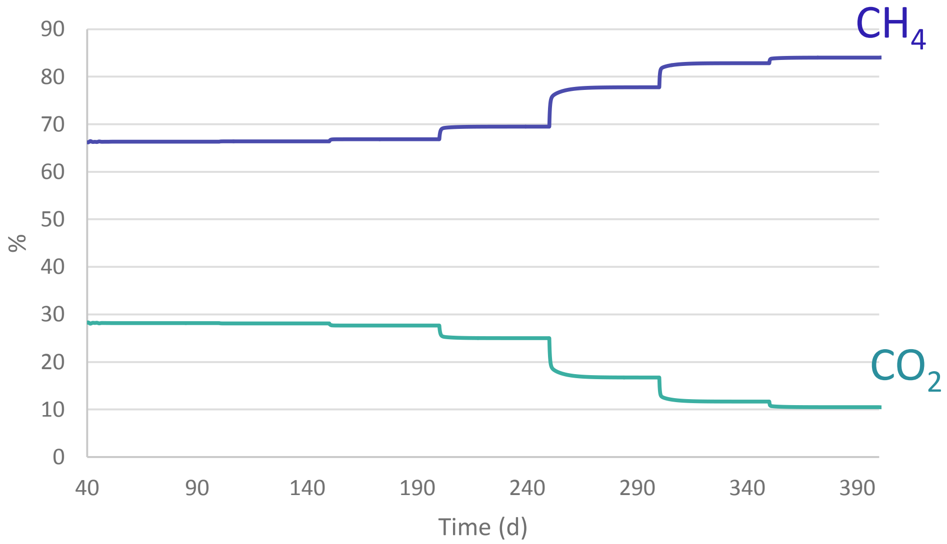




Local potential (η) is increased from -0.2 to +0.2 v stepwise.

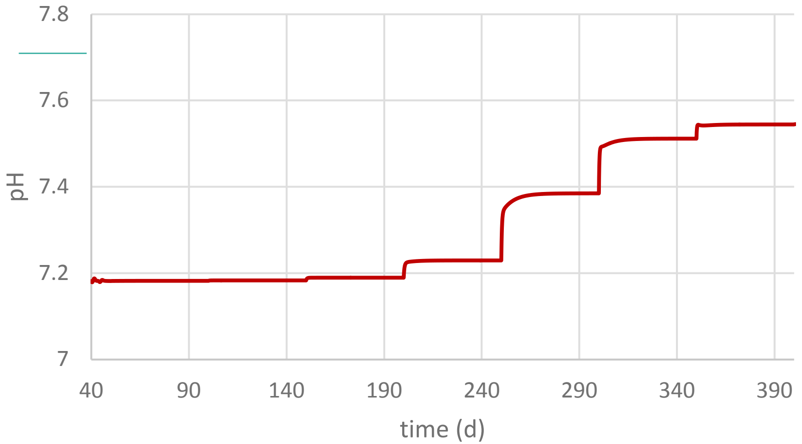
$$r = k_m^0 X \underbrace{\frac{1}{1 + exp\left[-\frac{F}{RT}\eta\right]}}_{\textit{Electrode}} \underbrace{\frac{S_{co2}}{K_{s\_co2} + S_{co2}}}_{\textit{Soluble substrate}}$$

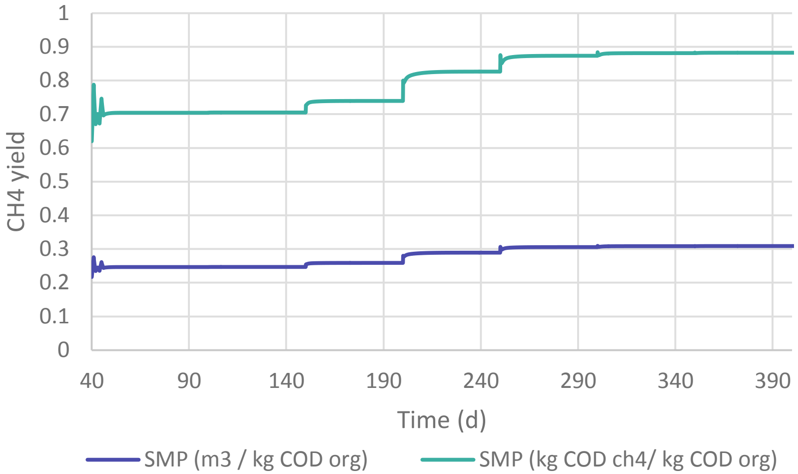
Biogas Composition



- Biogas methane content rise up to 85 % from 65 %.
- Further increase of η does not result in rise of methane content.
- Substrate limitation (S_CO_2)

pH





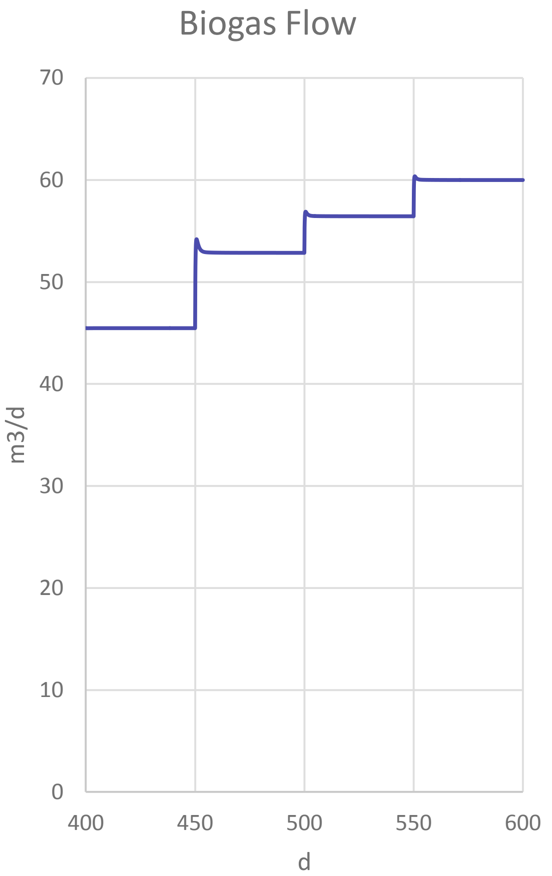
- pH of the digester rises due to depletion of headspace CO_2 and depletion of protons.
- The rise of pH inhibits heterotrophic biogas production.
- However, the methane yield (MY) increases, due to electrochemical contribution.

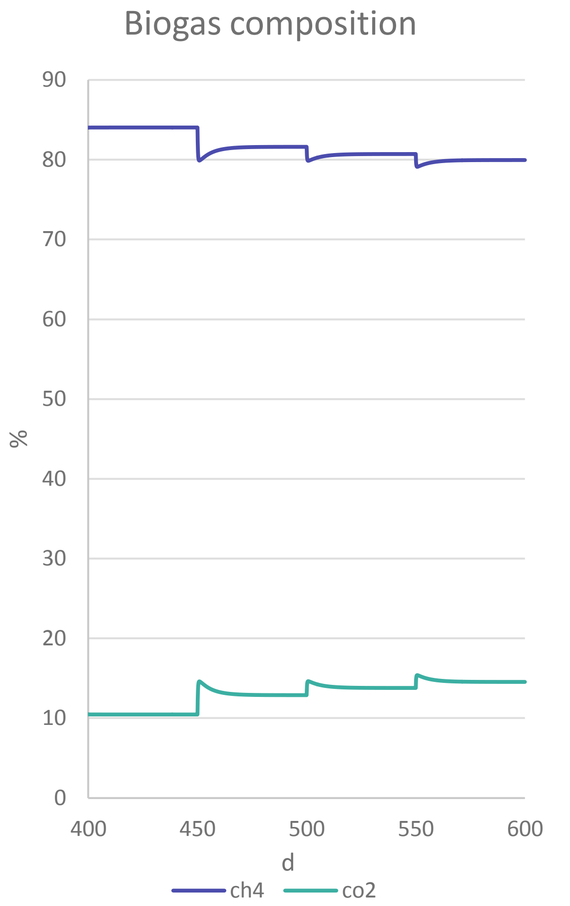
External CO_2 Source

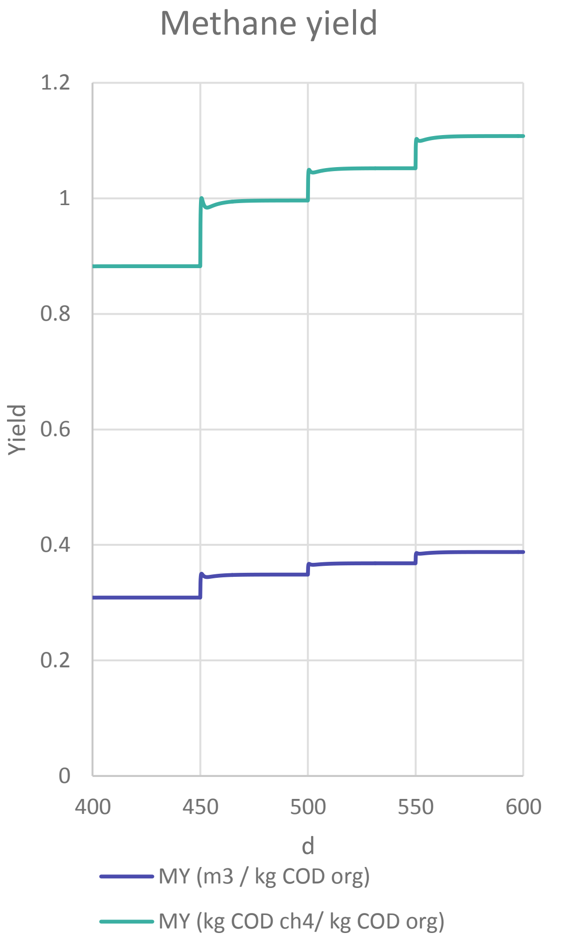
- Overcome the substrate limitation (S_CO_2)
- Reduce the pH inhibition
- It will increase the specific CH_4 yield
- Utilisation of CO_2 as opposed to capture for storage

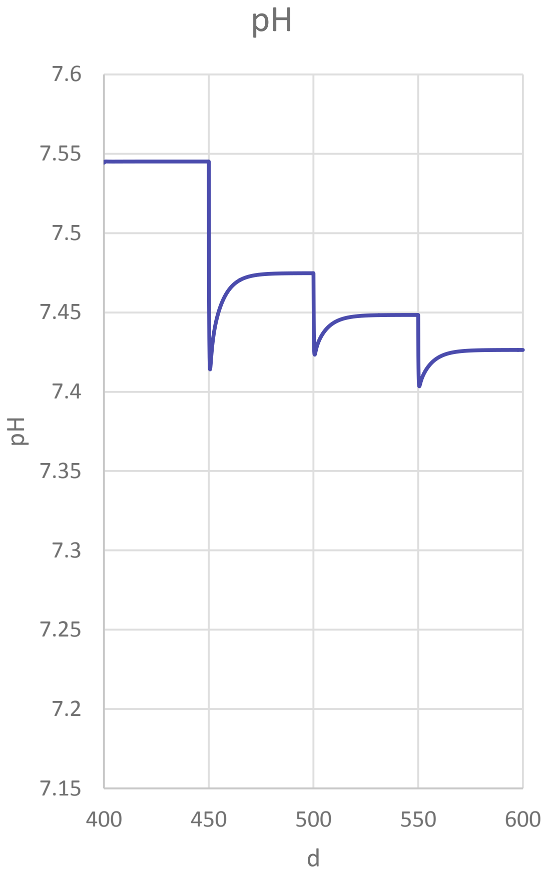
CO_2 loading conditions

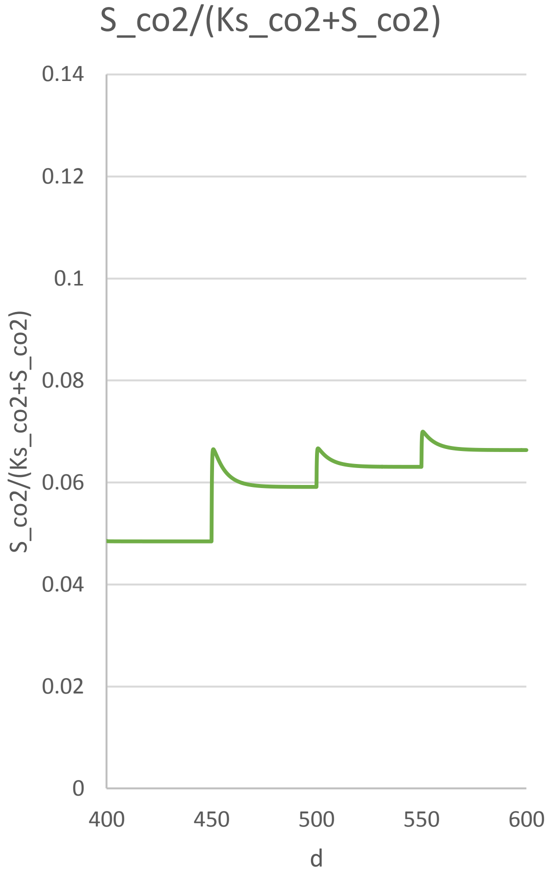
Duration (d)	CO_2 loading ($M.\ d^{-1}$)
400-450	0
450-500	0.01
500-550	0.015
550-600	0.02

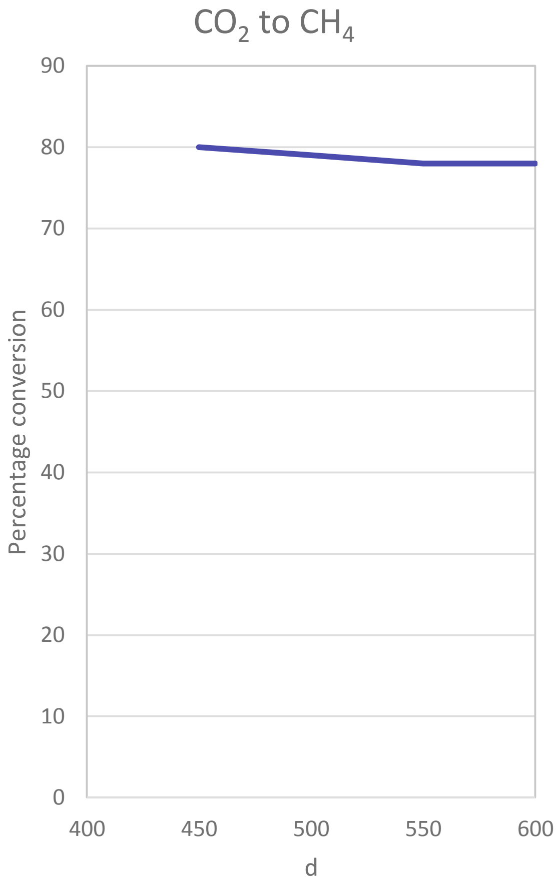

Biogas Flow
m3/d
d
70
60
50
40
30
20
10
0
400
450
500
550
600


Biogas composition
%
d
90
80
70
60
50
40
30
20
10
0
400
450
500
550
600
ch4
co2


Methane yield
Yield
d
1.2
1
0.8
0.6
0.4
0.2
0
400
450
500
550
600
MY (m3 / kg COD org)
MY (kg COD ch4/ kg COD org)


pH
7.6
7.55
7.5
7.45
7.4
7.35
7.3
7.25
7.2
7.15
400
450
500
550
600
d
pH


S_co2/(Ks_co2+S_co2)
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
400
450
500
550
600
d
S_co2/(Ks_co2+S_co2)


CO_2 to CH_4
90
80
70
60
50
40
30
20
10
0
400
450
500
550
600
d
Percentage conversion

Restrictions on the Model

- Electron flow or current (internal and external resistance, overpotential of anodic oxidation reactions, conductivity)
- Electrode area (geometry, which depends on space available in the reactor)
- Morphology of the biofilm on the cathode (availability of the specific micro-organism on the cathode biofilm)
- Electron transfer coefficient (all electrons which flow to the cathode are not available for this specific reaction, *e.g.,* parallel reduction reactions, cell synthesis)
- Mass transfer in the biofilm on the cathode.

Conclusion

- AD with MES can increase the biogas methane content from 65 % to 80-90 % (v/v).
- The rate of reaction can be controlled by the substrate concentration and local potential.
- It is necessary to maintain a buffer system to prevent pH inhibition.
- Addition of external CO_2 to an ADMES, operated under limited organic loading could achieve simultaneous bio-methanation of CO_2 20%.
- Industrial CO_2 emissions can also be reduced to methane which increases the methane yield without decreasing methane concentration to less than 80%.

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