Methane from Syngas by Anaerobic Digestion

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Abstract

Anaerobic digestion (AD) is a prominent green technology used for methane production from organic waste. Previous studies have shown that the amount of CH_4 produced during anaerobic digestion can be increased by adding inorganic electron donors such as H_2 and CO, both which can be produced as syngas from wood. Syngas inflow is implemented in the ADM1 model and simulations are carried out with different syngas additions to a well-documented case of wastewater treatment plant sludge AD. Three different compositions; (1) pure hydrogen, (2) 86 vol.% H_2, 7 vol.% CO and 7 vol.% CO_2, and (3) 44.4 vol.% H_2, 33.3 vol.% CO and 22.2 vol.% CO_2 were used for a first set of simulations testing process limitations. The second set of simulations were used to find out how much methane production can be increased for the given case if syngas composition is optimized. The CH_4 production can be increased by 33 % by adding H_2 (1) and was limited by pH going too high. Biogas CH_4 content reached 92 % at this limit. The H_2-rich syngas addition (2) reached 47 % CH_4 production increase with 81 % CH_4 content. The low H_2 syngas case (3) produce more biogas but the CH_4 content is reduced to 42 %. There is a narrow syngas composition range for which methane production can be increased by a factor $>\sim 2.7$, limited by available nitrogen in the treated sludge.

Keywords: Anaerobic digestion, ADM1, Syngas addition, CH_4 production, CO degradation

1 Introduction

The concept of waste to energy from wet organic waste like manure for biogas generation by Anaerobic Digestion (AD) is a prominent green technology since it reduces greenhouse gases and odors (Deublein & Steinhauser, 2011).

Anaerobic digestion is a biochemical process, where microbial activity comes into play and reduce complex organic pollutant by extracellular (disintegration, hydrolysis) and intracellular (acidogenesis, acetogenesis, methanogenesis) (Fig. 1) to produce biogas (Batstone et al., 2002). The generated biogas consists of (55-75) % methane and (25-45) % carbon dioxide (De Mes et al., 2003).

Several techniques are being used for biogas upgrading like water washing, polyglycolic adsorption, pressure swing adsorption and chemical treatment (Osorio & Torres, 2009). These methods are performed outside of the anaerobic reactor for biogas upgrading which requires extra investments. Previous studies have shown that CH_4 in AD can be increased by adding inorganic electron donors such as H_2 and CO (Luo & Angelidaki, 2013). These can, for example, be produced as syngas from wood through a gasification process. Gasification is a thermochemical process where biomass is converted into a mixture of gases that contains H_2, CO and CO_2 (Bridgwater, 2003). The produced syngas can be directly fed into the AD reactor for methane production, making AD a method to convert syngas into methane.

Adding syngas to AD can potentially have significant environmental impact on organic waste handling. It can for instance be a way to obtain more bio-fuel as methane from AD than what is obtainable from the wet organic wastes currently used as feed for biogas production. This study can help estimate how much production can increase and under which conditions. This approach may also serve as a way to mineralize all organic matter in sludge by combining AD and thermal gasification.

Hydrogen can be used to upgrade the methane production directly in the reactor by increasing the hydrogenotrophic methanogenesis (Luo & Angelidaki, 2013), which consumes hydrogen together with CO_2 in the biogas, with methane as product (Luo & Angelidaki, 2012):

$$4\,H_2 + CO_2 \rightarrow CH_4 + 2\,H_2O \qquad (1)$$
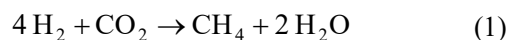
Many degradation paths for CO has been suggested, but experiments have shown acetogenesis to be dominating (Luo et al., 2012) under anaerobic condition at mesophilic temperatures. Acetogens utilize the CO and yields acetate, CO_2, cell material and unrecovered Carbon (Mörsdorf et al., 1992):

$$6.8\,CO \rightarrow CH_3COOH + 3.5\,CO_2 \\ + 0.4\,\text{biomass C} + 0.9\,\text{unrecovered C} \qquad (2)$$
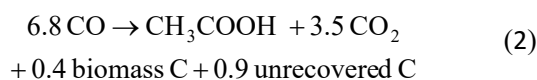
The reaction (Eq. 2) is added to the ADM1 model which is the standard platform of modelling and simulations of AD process developed by IWA in 2002. ADM1 model is a structured model that describes the

biochemical (Fig.1) and physiochemical reactions that are responsible for methane production (Batstone et al., 2002). The biochemical reactions are the core of this model which includes disintegration of complex organic material to carbohydrates, proteins, and lipids. These are then hydrolysed into sugars, amino acids and long-chain fatty acids (LCFAs) which are further fermented into molecular hydrogen and volatile organic acids (acidogenesis). The acids are broken down to acetate and hydrogen (acetogenesis). The last step is the split of acetate ions into methane and carbon dioxide (acetoclastic methanogenesis). The hydrogenotrophic methanogenesis step (Eq. 1) also produces methane when hydrogen reduces carbon dioxide (Batstone et al., 2002). The hydrogenotrophic methanogens are thus already present in an AD reactor and can grow to handle more hydrogen or syngas. If H_2 is added in excess, it can remove so much CO_2 (Eq. 3) that pH rise too high for efficient methanogenesis (Luo et al., 2012) ultimately causing failure of the reactor. The ratio of added H_2/feed load and effect of composition in the added syngas are therefore evaluated here to evaluate syngas addition limitations.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \qquad (3)$$
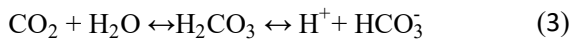
The physiochemical processes are liquid-liquid mass transfer process (i.e. ion dissociation) and liquid-gas exchange (i.e. liquid-gas mass transfer) (Batstone et al., 2002). Inefficient syngas mass transfer can limit its degradation in AD process due to the low solubility of CO and H_2 (Guiot, Cimpoia, & Carayon, 2011) which can result in syngas loss to headspace. In this work it is assumed that such loss is avoided by adding the gas through a membrane by diffusion.
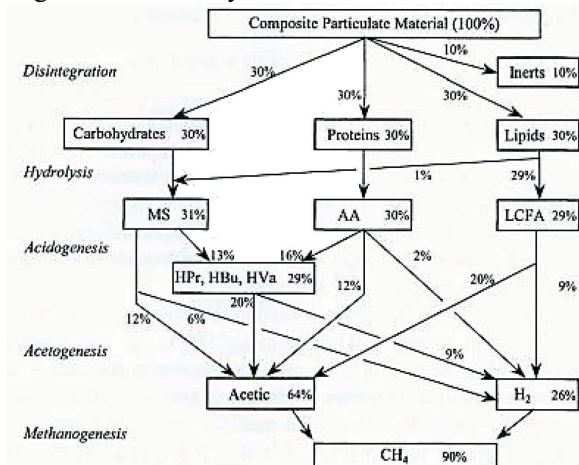

Figure 1. Systematic representation of anaerobic digestion process showing biochemical reactions described in ADM1 model (Batstone et al., 2002).

The purpose of this study is to evaluate effects of syngas composition and quantity on methane production and biogas composition, when added to an AD reactor running on sludge. The ADM1 model implemented in the AQUASIM software is applied and includes:

(1) Implementation of CO degradation in ADM1.
(2) Simulating hydrogen alone or syngas as AD feed supplements.
(3) Evaluation of syngas component effects on the AD reactor performance by adding different ratios of $H_2/CO/CO_2$.

2 Materials and Methods

The ADM1 model was extended by adding CO degradation (Table 1 and 2). H_2 or syngas was supplied as input to the reactor compartment. The simulations were based on a reported sludge digestion experiment with ADM1 simulations (Siegrist et al., 2002), to which H_2 or syngas was added in various amounts. Applicable supply range is assumed to be between zero and the level at which methane production fails.

2.1 Syngas degradation in ADM1

Syngas addition requires two new biochemical reactions to be added into the model. One is the uptake of carbon monoxide to acetate and the second is decay of carbon monoxide degrading organism. The parameters used for uptake are in Table 1 and the rate equations and stoichiometry coefficients are given in Table 2.

Table 1: Parameters used for uptake of CO.

Parameters	Description	units
km_CO_ac	Maximum uptake rate for CO degrading organisms.	kg COD S kg^{-1} COD X d^{-1}
X_CO_ac	CO degrading organisms.	kg COD m^{-3}
Ks_CO_ac	Half-saturation constant for CO degradation (same as for H_2 degradation).	kg COD m^{-3}
I_ph_CO_ac	pH inhibition of CO to acetate degrading organisms (same as for propionate degradation).	-
I_H2_CO_ac	Hydrogen inhibition for CO to acetate degrading organism.	-
kdec_x_CO_ac	Decay rate for CO degrading organisms	d^{-1}
Y_CO_ac	Yield of biomass on the uptake of CO to acetate.	kg COD kg^{-1} COD
S_CO	Total carbon monoxide.	kg COD m^{-3}
KH_CO	Non-dimensional Henry's law constant for CO	M (liq) M^{-1} (gas)

Table 2: Uptake rate of CO and decay rate of CO degrading organism in the model.

| Dynamic process	Rate equation
uptake_CO_ac	km_CO_ac*X_CO_ac*S_CO/(Ks_CO_ac+S_CO)*I_ph_CO_ac*I_H2_CO_ac*I_NH_limit
decay_CO_ac	X_CO_ac*kdec_x_CO_ac

Estimations of k_m and Y for CO uptake are based on reported experimental results (Mörsdorf et al., 1992) and the observed stoichiometric reaction of CO utilization (Eq. 4).

$$6.8\,CO \rightarrow CH_3COOH + 3.5\,CO_2$$
$$+\,0.4\,biomass\,C + 0.9\,unrecovered\,C \qquad (4)$$
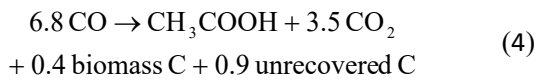
The unrecovered carbon is here assumed to be divided between acetate and CO_2 in the same way as the recovered part observed by Mörsdorf et al. (1992), according to (Eq. 5).

$$6.8\,CO \rightarrow 1.15\,CH_3COOH + 4.1\,CO_2$$
$$+\,0.4\,biomass\,C \qquad (5)$$

Eq.5 is further converted into COD basis (Eq. 6) using 5 mole carbon per mole biomass and 160 g COD mole-1 for biomass (Batstone et al., 2002).

$$108.8\,CO \rightarrow 73.6\,CH_3COOH + 0\,CO_2$$
$$+\,12.8\,biomass \qquad (6)$$
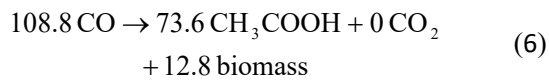
From equation 6, it can be seen that biomass yield per g COD of CO is obtained by:

$$Y = \frac{12,8}{108,8} = 0,12\,g\,COD\,biomass\,g^{-1}\,COD\,CO$$

The relation between maximum uptake rate of substrate (k_m) and maximum specific growth rate (μ^{max}) per day is (Eq. 7):

$$k_m = \frac{\mu^{max}}{Y} \qquad (7)$$

Where Y is the yield of biomass and μ^{max} of the organism can be calculated from doubling times under batch exponential growth condition (Eq. 8).

$$\mu^{max} = ln2/doubling\,times \qquad (8)$$

The reported doubling times for acetogenesis bacteria which shows the fastest growth on CO is 0.125 day (Mörsdorf et al., 1992).

This gives

$$\mu^{max} > \frac{ln2}{0,125} = 5.54\,d^{-1}$$

Now,

$$k_m = \frac{5.54}{0,12} = 46.20\,kg\,COD\,S\,kg^{-1}\,COD\,X\,d^{-1}$$

The values km_CO_ac = 46.20 kg COD S kg-1 COD X d-1 and Y_CO_ac = 0.12 kg COD biomass kg-1 COD CO are used in all simulations.

2.2   Reactor operation

A 28 m³ reactor was fed wastewater treatment plant sludge continuously for 50 days (Fig. 2) with feed step increases at day 16 and 37 (Siegrist et al., 2002).
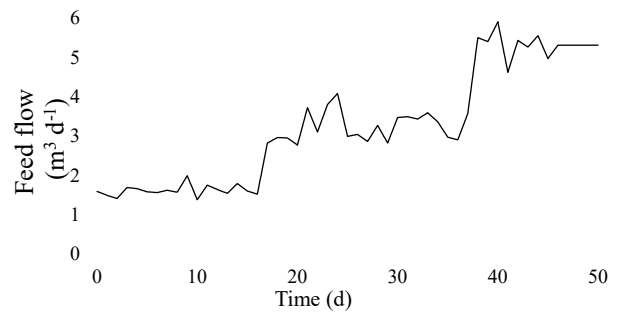

Figure 2: Sludge feed flow to the pilot reactor (Wang et al., 2013).

The feed composition of amino acid, fatty acid, sugar and composite organic material are in Table 3.

Table 3: Feed composition (Wang et al., 2013).

Components in reactor feed	Concentration (kg COD m⁻³)
Amino acids	4.2
Fatty acids	6.3
Monosaccharides	2.8
Composite material	10
Total	23.3

The average feed flow the first 16 days is 1.61 m³ d⁻¹ or 37.5 kg COD d⁻¹. The average is 3.2 m³ d⁻¹ at days 17-36 and 5.24 m³ d⁻¹ during days 37-50.

2.3   H₂/syngas additions simulated

Three main cases with increasing gas supply complexity are simulated: 1) pure hydrogen, 2) two selected compositions of syngas and 3) a wider range of gas mixtures. Syngas composition depends on the gasification process and the two chosen here for case 2 are from steam based gasification processes (Pfeifer et al., 2009): 1) Gasification included capture of CO_2 produces synthesis gas with high hydrogen content, called H₂-rich syngas i.e. 86 vol.% H₂, 7 vol.% CO and 7 vol.% CO_2. 2). Gasification without CO_2 capture produces syngas that consists of 44.4 vol.% H₂, 33.3 vol.% CO and 22.2 vol.% CO_2 (Pfeifer et al., 2009). These compositions are used in the simulations here (Table 4). For these simulations (1, 2 and 3 in Table 4) the load of hydrogen and syngas are in Table 5.

Four different syngas compositions were used during the third simulation case (simulation 4-7), to search for the AD process syngas load limitation. Process capacity limits are found by increasing the load of hydrogen until failure of the AD process. The load of CO and CO_2 is according to the composition ratio in Table 4.

Table 4: Composition of gas feed during simulations.

Gas	Vol.%							
	Ref[1]	Sim 1	Sim 2	Sim 3	Sim 4	Sim 5	Sim 6	Sim 7
H_2	0	100	86	44.4	80	74	70	60
CO	0	0	7	33.3	10	13	15	20
CO_2	0	0	7	22.2	10	13	15	20

Table 5: Load of wastewater, pure H_2, and syngas.

	Load H_2 (kg COD d^{-1})	Load CO (kg COD d^{-1})	Load WW feed (kg COD d^{-1})
Ref	0	0	37.5
Sim 1	10.43	0	37.5
Sim 2	10.43	0.849	37.5
Sim 3	10.43	7.82	37.5

3 Results and discussion

The hydrogen and various syngas additions to the AD process simulated strongly influence the conditions in the reactor and thereby the produced biogas.

3.1 Biogas production

The biogas production rate for 50 days of reactor operation increases with increase in the organic loading rate (Fig. 3). The constant addition of pure hydrogen or H_2-rich syngas shows only a small variation in biogas production rate while syngas with low H_2 concentration almost doubled the biogas production.
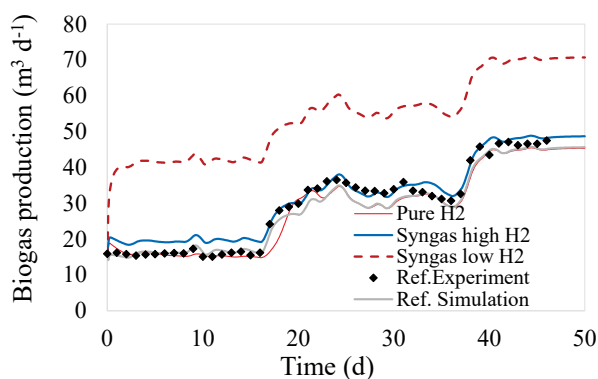
Figure 3: Biogas production rate of AD reactor added pure H_2 or two compositions of syngas. Included reference (Siegrist et al., 2002) experimental and simulated result.

Pure hydrogen addition in AD process enhances the hydrogenotrophic methanogenesis process (Eq. 1) and increases production of methane while consuming carbon dioxide.

In the case of H_2-rich syngas (composition 86 % H_2, 7 % CO and 7 % CO_2), biogas production rate increases

slightly more than pure H_2; since syngas also contains some CO and CO_2.

In the case of syngas composition of 44.4 %, 33.3 % CO and 22.2 % CO_2, the biogas production rate is higher than pure H_2 and H_2-rich syngas because of the higher CO and CO_2 addition to the reactor.

During both the syngas additions, the fast degradation of CO to acetic acid and CO_2 avoid loss of CO to headspace and result in almost zero CO concentrations in the produced gas.

3.2 Methane production

The methane production rate is 14.3 m^3d^{-1} for pure H_2, 15.7 m^3d^{-1} for high H_2 syngas and 17.9 m^3d^{-1} for low H_2 syngas at days 1-16 when adding gases, which is more than the pilot case without gas supply (10.7 $m^3 d^{-1}$ in Fig. 4, the experimental values presented by black diamonds). The methane production rate increased by 33 % and 47 % by adding pure H_2 and H_2-rich syngas and by 67 % by adding syngas with low H_2 concentration.
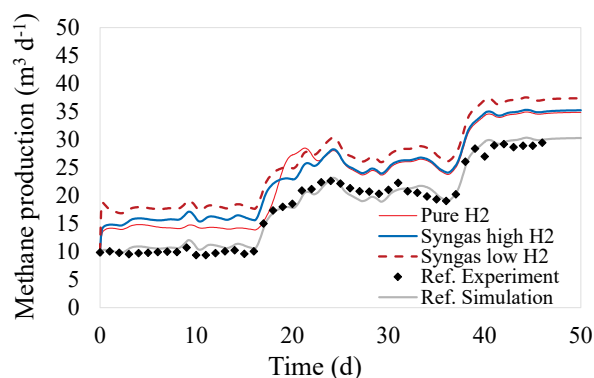
Figure 4: Methane production rate of AD reactor added pure H_2 or two compositions of syngas. Included reference (Siegrist et al., 2002) experimental and simulated results.

3.3 pH and inhibition effects

NH_3 is increased because of pH increase in the reactor (Eq. 9), especially pronounced when pure H_2 is supplied. pH (Fig. 5) increase as supplied hydrogen leads to CO_2 consumption, which reduces the acid concentration in the reactor due to the equilibrium reaction between CO_2 and water (Eq. 3).

[1]Reference simulations were based on a reported sludge digestion experiment with ADM1 simulations (Siegrist et al., 2002).
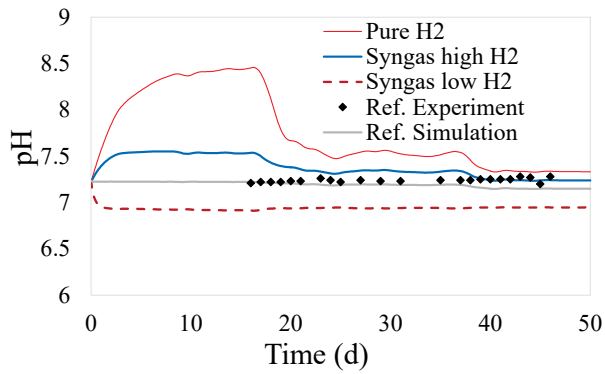
Figure 5: pH of bulk reactor volume for AD reactor added pure H_2 or two compositions of syngas. Included reference (Siegrist et al., 2002) experimental and simulated result.

Inhibition (Fig. 6) following pH increase (Fig. 5) is explained by more NH_3 (Eq. 9). The biomass responsible for methane production from acetate belongs to the archaeal group (aceticlastic methanogens) and is inhibited by NH_3 and slows down the conversion of acetate to methane (Bergland et al., 2011).

$$NH_4 \leftrightarrow H^+ + NH_3 \qquad (9)$$
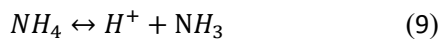
The inhibition is reduced after the step increase in organic feed supply on day 16 (Fig. 6). This can also be observed as acetate concentration reduction during the same time (Fig. 7). During the initial stage i.e. day (0-16), the acetate concentration rises due to inhibition (Fig. 7). During the initial stage, pH rises to 8.5. (Fig. 5) at pure H_2 addition. After day 16, the increase in wastewater addition increases the organic loading rate resulting in more CO_2 available through degradation of feed, the pH goes down and the reactor stabilize.
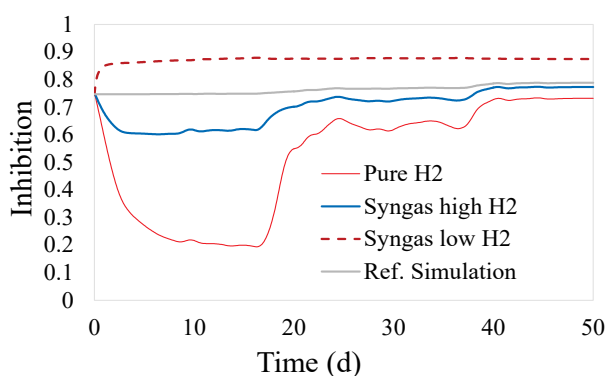

Figure 6: NH_3 inhibition for AD reactor added pure H_2 and two different syngas composition. Included reference (Siegrist et al., 2002) simulated result.

The two syngas additions follow a similar path for methane production as the experimental values. The acetate concentrations are low during both syngas additions because NH_3 is low and does not much inhibit the methanogens (Fig. 6). The extreme pH effect of

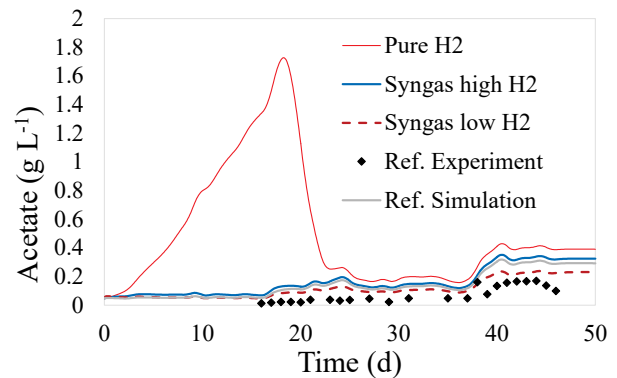adding hydrogen alone is avoided when CO and CO_2 are also supplied.

Figure 7: Acetate concentration of AD reactor added pure H_2 or two compositions of syngas. Included reference (Siegrist et al., 2002) experimental and simulated result.

The inorganic carbon simulations show decrease (Fig. 8) corresponding to acetate increase (Fig. 7) and inhibition (Fig. 6). The loads applied before and after 16 days of the pure hydrogen case indicates how much hydrogen to organic load ratio such AD can handle. The simulated pH (~8.5) is close to the pH 9 observed experimentally under similar conditions (Wang et al., 2013).
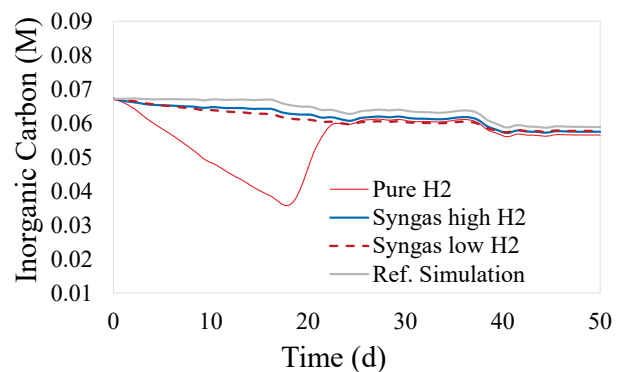

Figure 8: Inorganic carbon curve for AD reactor added pure H_2 and two different syngas composition. Included reference (Siegrist et al., 2002) simulated result.

The simulated percentage of methane (Fig. 9A) in produced biogas rises very high for the pure H_2 case and reaches up to 92 %. The carbon dioxide concentration follows a similar but opposite behavior (Fig. 9B). The addition of hydrogen enhances the produced biogas concentration of methane. Syngas composition with low H_2 concentration gives less methane percentage than no gas, pure H_2 and H_2-rich syngas supply since it contains more carbon dioxide (CO_2).
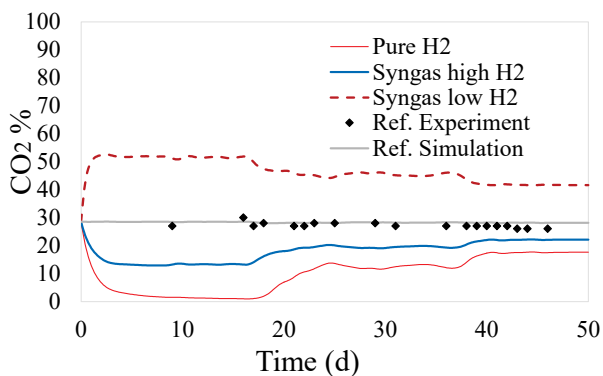
A
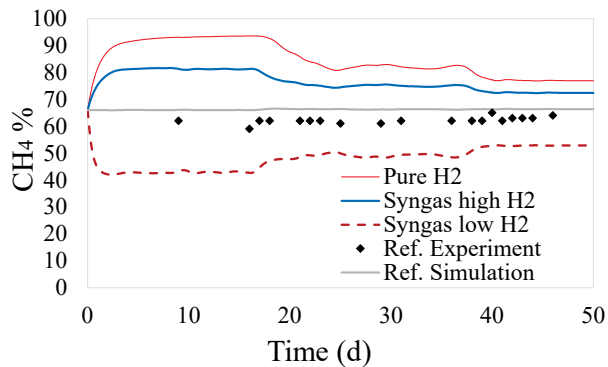
B

Figure 9: Percentage of biogas in the headspace (A) methane and (B) carbon dioxide of AD reactor added pure H_2 or two compositions of syngas. Included reference (Siegrist et al., 2002) experimental and simulated result.

The methane percentage is around 92 % (Fig. 9A) with pure H_2, around 81 % with H_2-rich syngas and at least 42 % with syngas with low hydrogen concentration due to the different H_2/CO_2 ratios in the added gas.

The yield of methane as kg COD methane kg^{-1} COD feed (wastewater + gas addition) was for days 1-16 0.72, 0.75, 0.82, and 0.81 for reference (Siegrist et al., 2002), pure H_2, syngas with high H_2 and syngas with low H_2. This shows that the yield was almost similar for the syngas with high H_2 and syngas with low H_2 concentration. The high CO_2 content of produced biogas is however a drawback for further processing of the biogas when syngas with low H_2 is added. These simulations suggest that there is some optimal range of syngas supply, defined by gas composition and amount relative to organic feed.

3.4 Loading ratio and syngas supply limitation

Steady state simulations of four different syngas compositions (Table 4) operated close to failure of the AD process are summarized in Fig. 10. 70 – 80 % hydrogen in the supplied syngas evidently can sustain

much higher total methane production than lower and higher fractions. Methane production is approximately proportional to the gas to organic feed ratio (abscissa in Fig. 10), explained using loading with pure H_2 as example.

The production rate can be increased (by a factor of ~ 2.7) with 74 % hydrogen content in the added syngas. The reason for failure of the AD reactor for H_2 content higher than 74 % is lack of available CO_2 while pH drop limits the process when the H_2 content is lower than 74 %, due to high CO_2 concentration in the reactor. pH remains stable at 74 % hydrogen content in the added syngas and production is nutrient (N) limited.
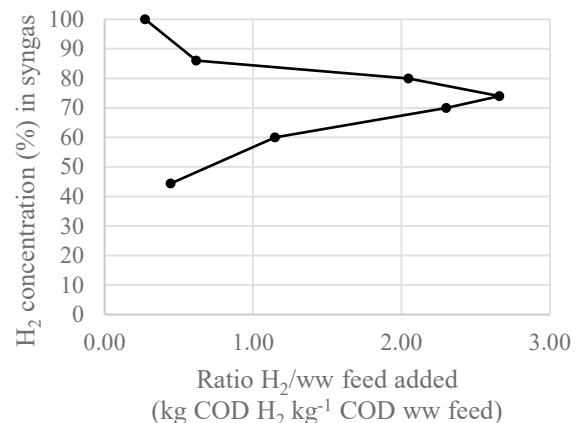

Figure 10: Threshold limit for ratio of hydrogen load and load of wastewater feed as a function of H_2 concentration (%) in added syngas.

4 Conclusion

Addition of pure H_2 and different compositions of syngas (down to 44.4 % H_2) to an AD treating sludge are simulated in an ADM1 model extended to include CO reactions. Comparisons of experimental and simulated results suggest realistic simulations.

Addition of syngas with high or low H_2 concentration to the sludge fed AD reactor showed a methane production increase of respectively 47 and 67 % while the methane content in the produced biogas was 81 and 42 % (66 % without gas addition).

Addition of pure H_2 gives the highest methane content (up to 92 % which is close to vehicle fuel quality) but overall biogas production is limited by available CO_2 in the AD reactor. Low CO_2 caused pH increase leading to NH_3 inhibition of methanogenesis and the methane production could only be increased by 33%.

The best syngas composition to feed AD processes for enhanced methane production has a hydrogen content of 70-80 %. It can more than triple methane production compared to organic feed only and is nitrogen (as nutrient for biomass growth) limited.

References

Bastone, D.J., et al., The IWA anaerobic digestion model no 1 (ADM1). *Water Science and Technology, 2002. 45*(10): p. 65-73.

Bridgwater, A. V., Renewable fuels and chemicals by thermal processing of biomass. *Chemical Engineering Journal, 2003. 91*(2): p. 87-102.

De Mes, T., et al, Methane production by anaerobic digestion of wastewater and solid wastes. *Bio-methane & Bio-hydrogen*, 2003: p. 58-102.

Deublein, D. and A. Steinhauser, *Biogas from waste and renewable resources: an introduction 2011*: John Wiley & Sons.

Guiot, S. R., R. Cimpoia, and G. Carayon, Potential of wastewater-treating anaerobic granules for biomethanation of synthesis gas. *Environmental science & technology, 2011. 45*(5): p. 2006-2012.

Luo, G. & I. Angelidaki, Integrated biogas upgrading and hydrogen utilization in an anaerobic reactor containing enriched hydrogenotrophic methanogenic culture. *Biotechnology and bioengineering, 2012. 109*(11): p. 2729-2736.

Luo, G. and I. Angelidaki, Co-digestion of manure and whey for in situ biogas upgrading by the addition of H2: process performance and microbial insights. *Applied microbiology and biotechnology, 2013. 97*(3): p. 1373-1381.

Luo, G., et al., Simultaneous hydrogen utilization and in situ biogas upgrading in an anaerobic reactor. *Biotechnology and bioengineering, 2012. 109*(4): p. 1088-1094.

Mörsdorf, G., et al., Microbial growth on carbon monoxide. *Biodegradation, 1992. 3*(1): p. 61-82.

Osorio, F. and J. Torres, Biogas purification from anaerobic digestion in a wastewater treatment plant for biofuel production. *Renewable energy, 2009. 34*(10): p. 2164-2171.

Pfeifer, C., B. Puchner, and H. Hofbauer, Comparison of dual fluidized bed steam gasification of biomass with and without selective transport of CO2. *Chemical Engineering Science, 2009. 64*(23): p. 5073-5083.

Siegrist, H., et al., Mathematical model for meso-and thermophilic anaerobic sewage sludge digestion. *Environmental science & technology, 2002. 36*(5): p. 1113-1123.

Wang, W., et al., Performance and microbial community analysis of the anaerobic reactor with coke oven gas biomethanation and in situ biogas upgrading. *Bioresource technology, 2013. 146*: p. 234-239.

Bergland, W., Botheju, D., Dinamarca, C., Bakke, R., Considering Culture Adaptations to High Ammonia Concentration in ADM1. *In proceedings of the 52nd International Conference of Scandinavian Simulation Society: SIMS. 2011.*