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In-situ biogas upgrading process: Modeling and simulations aspects

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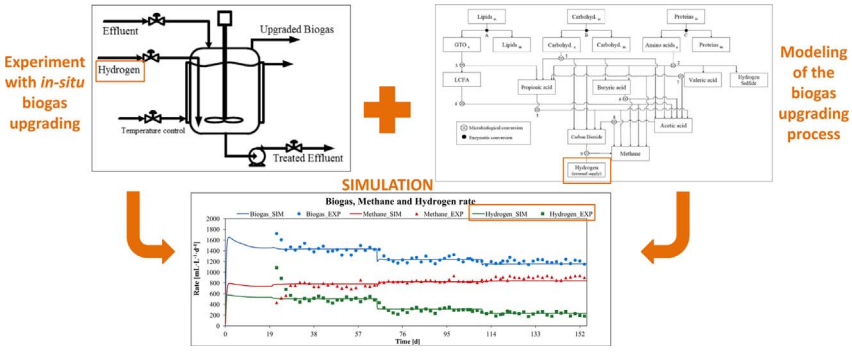
GRAPHICAL ABSTRACT



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ABSTRACT

Biogas upgrading processes by *in-situ* hydrogen (H_2) injection are still challenging and could benefit from a mathematical model to predict system performance. Therefore, a previous model on anaerobic digestion was updated and expanded to include the effect of H_2 injection into the liquid phase of a fermenter with the aim of modeling and simulating these processes. This was done by including hydrogenotrophic methanogen kinetics for H_2 consumption and inhibition effect on the acetogenic steps. Special attention was paid to gas to liquid transfer of H_2. The final model was successfully validated considering a set of Case Studies. Biogas composition and H_2 utilization were correctly predicted, with overall deviation below 10% compared to experimental measurements. Parameter sensitivity analysis revealed that the model is highly sensitive to the H_2 injection rate and mass transfer coefficient. The model developed is an effective tool for predicting process performance in scenarios with biogas upgrading.

1. Introduction

Anaerobic digestion (AD) is a biological process performed in the absence of oxygen to degrade and stabilize organic matter while producing biogas, a mixture formed mainly of methane (CH_4) and carbon dioxide (CO_2) (typically it contains 50–70% CH_4, 30–50% CO_2, < 1% N_2, and 10–2000 ppm H_2S). Biogas can be used for a number of purposes, including electricity production (most common), heat generation and as a raw product for industries (Angelidaki et al., 2006; Mata-Alvarez et al., 2014).

Currently, there is a growing interest in employing biogas coming from the AD treatment as an alternative to natural gas. By removing the CO_2 present in biogas the energy content is increased so that it can be used as vehicle fuel or be injected into natural gas distribution grids

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(Sun et al., 2015). Therefore, "biogas upgrading" is the process that involves the removal of CO_2 and water vapor, as well as typical contaminants such as hydrogen sulfide, siloxanes, dust and particles. The final gas is called "biomethane" if it is purified to natural gas standards (Kougias et al., 2017).

Traditional methods for biogas upgrading include membranes, water physical scrubber, pressure swing adsorption, polyglycol adsorption, chemical treatments and cryogenic upgrading (Osorio and Torres, 2009). These are performed outside the anaerobic reactor and require investments in external equipment such as compressors, pumps, membranes, etc. (Luo and Angelidaki, 2013) and consume considerable amounts of electricity and/or heat. Based on the process technology used, the cost of biogas upgrading has been estimated to be in the range of 0.12–0.44 €/Nm^3 of biogas (Hullu et al., 2008).

As an alternative to the conventional biogas upgrading process, biogas can also be upgraded by biological coupling of hydrogen (H_2) with CO_2 present in the biogas to convert it to CH_4. For this purpose, H_2 can be produced by water electrolysis using the surplus of electricity generated from wind mills or photovoltaic facilities (Ursua et al., 2012). The biochemical reaction between H_2 and CO_2 is performed by a group of microorganisms known as hydrogenotrophic methanogenic archaea that use CO_2 as carbon source and H_2 as electron donor to produce CH_4 (Muñoz et al., 2015). Recent studies have documented that the injection of H_2 into a conventional biogas reactor can result in up to 45% increase in CH_4 productivity, as the result of the carbon dioxide conversion present in the biogas to additional CH_4 (Bassani et al., 2016; Luo et al., 2012; Luo and Angelidaki, 2013).

The hydrogen injection can be performed in two different ways: (i) *in-situ*, in which H_2 is injected directly into the liquid phase of a conventional AD reactor where it will couple with endogenous (internally produced by the process) CO_2 and (ii) *ex-situ*, in which (exogenous from external sources) CO_2 and H_2 are injected inside the liquid phase of a reactor containing enhanced hydrogenotrophic cultures (Kougias et al., 2017).

Although biological biogas upgrading may be economically advantageous compared to conventional methods, H_2 mediated *in-situ* biogas upgrading still involves some technical challenges that need to be solved. For instance, direct H_2 injection into the AD reactor can lead to a substantial decrease of pH – primarily due to CO_2 uptake by hydrogenotrophic methanogens – thereby affecting process stability negatively. Along with this, H_2 mass transfer to the liquid phase still remains the limiting step (Bassani et al., 2015; Luo et al., 2012; Luo and Angelidaki, 2013). Thus, it is of major importance to address these challenges to obtain optimal and stable process operation of this technology in the long term.

Mathematical models can provide insights into understanding and analyzing important aspects (inhibition pathways, policies for start-up, operation and optimization) associated with the anaerobic digestion process. Also, the use of reliable mathematical models minimizes experimental effort, risk and cost (Angelidaki et al., 1999). Therefore, the aim of the present work was to model and simulate the biogas upgrading process by *in-situ* hydrogen injection accurately. The range of application of a mathematical model for anaerobic bioconversion of complex substrates was extended by incorporating the hydrogenotrophic pathway into the model kinetics as well as the H_2 mass transfer process. Two case studies were used for the validation of the extended bioconversion model. Finally, a parameter sensitivity analysis was performed to investigate the influence of the new set of parameters included in the model (kinetic constants for hydrogenotrophic methanogens and hydrogen inhibition, global mass transfer coefficient (k_La) of the main gases and volumetric flowrate injection of hydrogen) on the output variables of the model (biogas, methane, carbon dioxide and hydrogen rates, pH, and total ammonium nitrogen concentration).

2. Material and methods

2.1. Modeling approach

2.1.1. BioModel description

The core bioconversion model, namely "BioModel" in this work, was developed by Angelidaki et al. (1999, 1993) and recently extended by Kovalovszki et al. (2017) for modeling and simulation of various co-digestion scenarios. The BioModel describes complex substrates degradation with the co-digestion of different types of organic wastes. The substrates are described in terms of their basic organic components' composition (carbohydrates, lipids, and proteins), organic acids and inorganic components (ammonia, phosphate, cations, anions, etc.). The model includes three enzymatic hydrolytic processes and eight bacterial steps. It involves 19 chemical compounds, together with a detailed description of pH and temperature characteristics. Free ammonia, volatile fatty acids (VFAs) and long chain fatty acids (LCFAs) constitute the primary modulating factors. Inhibitions, interactions, and stoichiometry of the components and equations applied in the model are described in Angelidaki et al. (1999) and can be found in the Supplementary material provided in this paper. The current model uses the optimal kinetic and yield parameters estimated by Kovalovszki et al. (2017) for Angelidaki's model, which are also provided in the Supplementary material.

Fig. 1 shows the main pathways of the process. The model involves the following enzymatic processes: (A) hydrolysis of undissolved lipids (based on Weinrich and Nelles, 2015), (B) hydrolysis of undissolved carbohydrates, and (C) hydrolysis of undissolved proteins, and the bacterial groups: (1) glucose-fermenting acidogens, (2) amino acid-degrading acidogens, (3) glycerol trioleate (GTO)-degrading acidogens (4) long chain fatty acids (LCFA)-degrading acetogens, (5) propionate, (6) butyrate, (7) valerate-degrading acetogens, (8) aceticlastic methanogens and, finally, (9) hydrogenotrophic methanogens for the biogas upgrading that were included in the model.

The biochemical reactions and yield coefficients derived from stoichiometry of all steps can be found in the Supplementary material.

2.1.2. Incorporation of hydrogenotrophic pathway and gas mass transfer rates

It is important to note that, in the original BioModel, hydrogen kinetics were merged into other steps (omitted), as endogenous hydrogen utilization is faster compared to the other metabolic pathways and therefore this pathway was not considered as a separate kinetic step (Lima et al., 2016). Therefore, in the current model development, in order to couple the CO_2 present in biogas with an external H_2 supply the BioModel has been expanded by incorporating the hydrogenotrophic pathway (Eq. (1)) proposed by Hill (1982):

$$H_2 + 0.0058\,NH_3 + 0.2644\,CO_2 \rightarrow 0.0058\,C_5H_7NO_2 + 0.2355\,CH_4 + 0.5171\,H_2O \quad (1)$$

Although hydrogenotrophic methanogenesis, homoacetogenesis, syntrophic acetogenesis and synthrophic acetate oxidation are competing pathways, the former prevails because the injection of hydrogen close to microbial communities inhibits syntrophic acetogenesis and syntrophic acetate oxidation, as these processes are getting less energetically favourable. Between hydrogenotrophic methanogenesis and homoacetogenesis, the first is more energetically favourable and it has been shown to be the dominant process in reactors feed with H_2 (Garcia-Robledo et al., 2016).

The kinetics for the hydrogenotrophic methanogens (μ_{X_9} – Eq. (2)) were based on Batstone et al. (2002) and Siegrist et al. (2002), considering Monod type kinetics for hydrogen and ammonium (primary substrates), non-competitive inhibition by LCFA and the effect of pH on the growth rate was modelled by the Michaelis pH function described in Angelidaki et al. (1993). Expressions in square brackets represent the