Modelling and Parameter Identification of Ex-Situ Biological Biogas Upgrading

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Abstract: In this paper, a model of ex-situ biological biogas upgrading process is first developed. Then, parameter sensitivity analysis is performed, in order to determine the most relevant parameters for subsequent parameter identification, based on a linear fractional transformation (LFT) reformulation of the model. Biogas composition and volumetric production have been well predicted by the calibrated model, allowing its adoption as a designing tool for start-up operation of experimental pilot-scale activity.

Keywords: Bioenergy production, wastewater treatment processes, modeling and identification, parameter and state estimation, microbial technology.

1. INTRODUCTION

Climate change will bring negative effects on human health, economics, the environment, flora and fauna presence on the planet; for these reasons, the necessity to find and use renewable energy sources is compelling.

Anaerobic digestion provides renewable energy from residual biomass (organic waste, wastewater sludge, manure, crop waste from agriculture etc.), converting organic fraction into biogas, composed by methane (CH_4), in a range of 50–70% and carbon dioxide (CO_2), at a concentration of 30–50%. In recent years, biogas upgrading to biomethane has been promoted in Europe and Italy since policies, like the European Green Deal, highlights the need to reach climate neutrality before 2050 and to make European economy sustainable.

There are several upgrading technologies available, from the well-known physical/chemical technologies for separation/transformation of CO_2, to the newest biological process. Biological biogas upgrading methods have been experimentally proved and are still on an early pilot or full scale implementation (Angelidaki et al. (2018)). External hydrogen must be provided to make the process feasible, however, to make the process sustainable, hydrogen must derive from renewable sources, i.e., water electrolysis during renewable energy surplus. Therefore, the process is called power-to-gas (P2G). The major advantage of these processes is that the CO_2 is converted into other energy (CH_4) instead of being simply removed from the main flux and then disposed of.

Biological biogas upgrading has been tested on two main configurations: *in-situ* and *ex-situ*. In the in-situ application, hydrogen is injected directly in an existing anaerobic

digester to be co-digested with CO_2 produced by metabolic processes from anaerobic organic degradation. On the other hand, the ex-situ biogas upgrading technology is based on the provision of external CO_2 with H_2 in a dedicated anaerobic reactor. Even though, a new reactor is needed, the main advantage of the ex-situ configuration is that H_2 addition does not inhibit the anaerobic organic degradation, which remains the main aim of anaerobic digestion. Moreover, in the ex-situ configuration it is possible to reach higher CH_4 content ($> 95\%$ in volume) in the final product (Angelidaki et al. (2018)).

Models dealing with biological biogas upgrading, very limited up to now, could effectively support experimental research that still needs optimization and could speed-up future full-scale applications.

This work reports a model for ex-situ configuration, and it consists of a set of differential equations including biomass, substrate, gas-liquid mass transfer and acid-base.

A sensitivity analysis, based on the OpenModelica sensitivity optimization tools OMSens (Fritzson et al. (2020)), has been performed to assess the key parameters of the model. The sensitivity analysis showed that the gas-liquid mass transfer coefficient of H_2 ($k_L a_{O_2}$) is the parameter of interest to obtain high CH_4 concentration in the final biogas, since the efficiency of the process depends on the availability of dissolved H_2 for hydrogenotrophic methanogens. Other relevant parameters are the maximum specific uptake of hydrogenotrophic methanogens (km_{H_2}) and the half-saturation constant of dissolved hydrogen (K_{S,H_2}).

Then, these parameters have been calibrated by experimental parameter identification, based on a linear fractional transformation (LFT) reformulation of the model (Lee and Poolla (1999); Hsu et al. (2008b); Casella and

Lovera (2008); Hsu et al. (2008a)). Theil's Inequality Coefficient (TIC) (Theil (1961)) has been used to evaluate the goodness of the model: biogas composition and volumetric production have been well predicted by the model, TIC range from 0.042–0.072, allowing its adoption as a designing tool for start-up operation of experimental pilot-scale activity.

The paper is organized as follows. In Section 2 the model is developed; Section 3 illustrates the results of the sensitivity analysis; in Section 4 LFT-based parameter identification is recalled and the model is reformulated in a LFT form, while in Section 5 the results of parameter identification are discussed; finally, some conclusions are given in Section 6.

2. PROCESS MODEL

The process exploits the action of hydrogenotrophic methanogens (*Archaea*), that can utilise H_2 to convert CO_2 into CH_4 based on the following reaction:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \ , \ \Delta G^0 = -130.7 \frac{kJ}{mole}$$
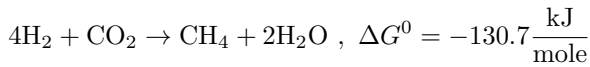
The process model is based on the Anaerobic Digestion Model No. 1 (ADM1) (Batstone et al. (2002)), while not including all the processes regarding organic degradation, such as disintegration, hydrolysis and acidogenesis. This means that the only microbial population included is the hydrogenotrophic methanogens X_{H_2}.

Methanogens X_{H_2} consume the substrate, dissolved hydrogen S_{H_2}, to produce methane S_{CH_4}, and their decay term is described by a first order kinetic, having k_{dec} (d^{-1}) as constant, and becoming increasingly important at high hydraulic retention time t_{HR}.

S_{IC} is the total inorganic carbon in the liquid phase, and it is assumed to be the sum of carbon dioxide and bicarbonate ion. Inorganic carbon is used for methane generation, knowing carbon content in methane C_{CH_4} (mole gCOD^{-1}). It is also used for biomass growth, depending on carbon content in biomass C_{bac} (mole gCOD^{-1}) and it is respectively released into the reactor liquor during biomass decay.

The last liquid variable is the inorganic nitrogen (S_{IN}), that is an indicator for nutrients availability, and it is used by microorganisms for their growth N_{bac} (mole gCOD^{-1}).

All the liquid variables are expressed in term of COD (chemical oxygen demand), except for S_{IC} and S_{IN} that are expressed in molar terms (mole L^{-1}).

The gas-phase set of equations, that include H_2, CH_4 and CO_2, has been then modified to consider an input gas flowrate that is not common in anaerobic digestion.

Finally, gas-liquid mass transfer coefficient of each gas $i = \{H_2, CH_4, CO_2\}$ has been derived from Pauss's law of gas diffusivity (Pauss et al. (1990)):

$$k_L a_i = k_L a_{O_2} \sqrt{\frac{D_i}{D_{O_2}}}$$

where $k_L a_{O_2}$ (d^{-1}) is the gas-liquid mass transfer coefficient, D_i (cm^2 s^{-1}) is the diffusivity if the gas i, and D_{O_2}

is the diffusivity of O_2. Diffusivity values can be found in literature and are function of temperature. The reason of this formulation is that it is easier to experimentally derive, with a blank test, dissolved oxygen concentration, and thus $k_L a_{O_2}$.

The gas-liquid transfer for H_2, CH_4 and CO_2 is expressed by the combination of Henry's law and the two-film theory of Whitman (Whitman (1962)). Therefore, for gaseous components the gas-liquid mass transfer rate is present in the gas equation and in the corresponding liquid variable; in the following model (1–9) a positive gas-liquid transfer means that the transfer of i component is from the liquid phase (S_i) to the gas phase ($S_{i,gas}$).

The ex-situ biological biogas upgrading model is thus defined by 8 differential equations: 1 for the microorganisms (X_{H_2}), 1 for the substrate (S_{H_2}), 1 for the product (S_{CH_4}), 2 for inorganic carbon (S_{IC}) and nitrogen (S_{IN}), and finally 3 for the gaseous components ($S_{H_2,gas}$, $S_{CH_4,gas}$ and $S_{CO_2,gas}$):

$$\frac{dX_{H_2}}{dt} = \frac{1}{t_{HR}} \left(X_{H_2,in} - X_{H_2} \right)$$
$$+ Y_{H_2} km_{H_2} \frac{S_{H_2}}{S_{H_2} + K_{S,H_2}} X_{H_2} - k_{dec} X_{H_2} \quad (1)$$

$$\frac{dS_{H_2}}{dt} = \frac{1}{t_{HR}} \left(S_{H_2,in} - S_{H_2} \right) - km_{H_2} \frac{S_{H_2}}{S_{H_2} + K_{S,H_2}} X_{H_2}$$
$$- k_L a_{O_2} \sqrt{\frac{D_{H_2}}{D_{O2}}} \left(S_{H_2} - RT_{op} KH_{H_2} S_{H_2,gas} \right) \quad (2)$$

$$\frac{dS_{CH_4}}{dt} = \frac{1}{t_{HR}} \left(S_{CH_4,in} - S_{CH_4} \right)$$
$$+ (1 - Y_{H_2}) km_{H_2} \frac{S_{H_2}}{S_{H_2} + K_{S,H_2}} X_{H_2}$$
$$- k_L a_{O_2} \sqrt{\frac{D_{CH_4}}{D_{O_2}}} \left(S_{CH_4} - RT_{op} KH_{CH_4} S_{CH_4,gas} \right) \quad (3)$$

$$\frac{dS_{IC}}{dt} = \frac{1}{t_{HR}} \left(S_{IC,in} - S_{IC} \right)$$
$$- C_{CH_4} (1 - Y_{H_2}) km_{H_2} \frac{S_{H_2}}{S_{H_2} + K_{S,H_2}} X_{H_2}$$
$$- C_{bac} \left(Y_{H_2} km_{H_2} \frac{S_{H_2}}{S_{H_2} + K_{S,H_2}} X_{H_2} - k_{dec} X_{H_2} \right)$$
$$- k_L a_{O_2} \sqrt{\frac{D_{CO_2}}{D_{O_2}}}$$
$$\cdot \left(S_{IC} \frac{10^{-pH}}{10^{-pH} + Ka_{CO_2}} - RT_{op} KH_{CO_2} S_{CO_2,gas} \right) \quad (4)$$

$$\frac{dS_{IN}}{dt} = \frac{1}{t_{HR}} \left(S_{IN,in} - S_{IN} \right)$$
$$- N_{bac} \left(Y_{H_2} km_{H_2} \frac{S_{H_2}}{S_{H_2} + K_{S,H_2}} X_{H_2} - k_{dec} X_{H_2} \right) \quad (5)$$

$$\frac{dS_{H_2,gas}}{dt} = \frac{q_{gas,in}S_{H_2,gas,in}}{V_{gas}} - \frac{q_{gas,out}S_{H_2,gas}}{V_{gas}}$$
$$+ \frac{V}{V_{gas}}k_La_{O_2}\sqrt{\frac{D_{H_2}}{D_{O_2}}}\left(S_{H_2} - RT_{op}KH_{H_2}S_{H_2,gas}\right) \quad (6)$$

$$\frac{dS_{CH_4,gas}}{dt} = \frac{q_{gas,in}S_{CH_4,gas,in}}{V_{gas}} - \frac{q_{gas,out}S_{CH_4,gas}}{V_{gas}} \quad (7)$$
$$+ \frac{V}{V_{gas}}k_La_{O_2}\sqrt{\frac{D_{CH_4}}{D_{O_2}}}\left(S_{CH_4} - RT_{op}KH_{CH_4}S_{CH_4,gas}\right)$$

$$\frac{dS_{CO_2,gas}}{dt} = \frac{q_{gas,in}S_{CO_2,gas,in}}{V_{gas}} - \frac{q_{gas,out}S_{CO_2,gas}}{V_{gas}}$$
$$+ \frac{V}{V_{gas}}k_La_{O_2}\sqrt{\frac{D_{CO_2}}{D_{O_2}}}$$
$$\cdot \left(S_{IC}\frac{10^{-pH}}{10^{-pH} + Ka_{CO_2}} - RT_{op}KH_{CO_2}S_{CO_2,gas}\right) \quad (8)$$

$$q_{gas,out} = q_{gas,in}$$
$$+ \frac{RT_{op}Vk_La_{O_2}\sqrt{\frac{D_{H_2}}{D_{O_2}}}}{p_{gas} - p_{gas,H_2O}}\frac{S_{H_2} - RT_{op}KH_{H_2}S_{H_2,gas}}{16}$$
$$+ \frac{RT_{op}Vk_La_{O_2}\sqrt{\frac{D_{CH_4}}{D_{O_2}}}}{p_{gas} - p_{gas,H_2O}}\frac{S_{CH_4} - RT_{op}KH_{CH_4}S_{CH_4,gas}}{64}$$
$$+ \frac{RT_{op}Vk_La_{O_2}\sqrt{\frac{D_{CO_2}}{D_{O_2}}}}{p_{gas} - p_{gas,H_2O}}$$
$$\cdot \left(S_{IC}\frac{10^{-pH}}{10^{-pH} + Ka_{CO_2}} - RT_{op}KH_{CO_2}S_{CO_2,gas}\right) \quad (9)$$

where Y_{H_2} ($gCOD_{X_{H_2}}\,gCOD_{S_{H_2}}^{-1}$) is the growth yield of hydrogenotrophic methanogens, km_{H_2} (d^{-1}) is the maximum specific uptake rate of hydrogenotrophic methanogens, k_{dec} (d^{-1}) is the first order decay coefficient of the biomass, K_{S,H_2} ($gCOD\ L^{-1}$) is the half-saturation constant of dissolved hydrogen, KH_i is the Henry's constant of gas i (mole L^{-1} bar^{-1}), p_{gas} and p_{gas,H_2O} (bar) are the total headspace pressure and the water vapour pressure respectively. Other physical parameters are Ka_{CO_2} (mole L^{-1}) that is inorganic carbon dissociation constant, R (bar L mole^{-1} K^{-1}) is the ideal gas constant and T_{op} (K) is the operating temperature inside the reactor, V (L) is the working volume of the reactor, and V_{gas} the headspace volume. The quantities $X_{H_2,in}$, $S_{H_2,in}$, $S_{CH_4,in}$, $S_{IC,in}$, $S_{IN,in}$ are the concentrations of each liquid component in the influent stream, while, $S_{H_2,gas,in}$, $S_{CH_4,gas,in}$, $S_{CO_2,gas,in}$, $q_{gas,in}$ are the gas inputs.

3. SENSITIVITY ANALYSIS

The model depends on many parameters, a part of them can be taken from literature (Batstone et al. (2002)), while others (especially the ones depending on reactor configuration as $k_La_{O_2}$) need further investigation. Thus, a sensitivity analysis is firstly performed on the model to assess the most significant parameters which need identification and optimization.

The perturbed parameters in the sensitivity analysis are $k_La_{O_2}$ and hydrogenotrophic methanogens kinetic and stoichiometric parameters: Y_{H_2}, km_{H_2}, k_{dec}, and K_{S,H_2}. Initial values of these parameters are taken from ADM1 recommended values and are reported in Table 1, except for $k_La_{O_2}$ which is assumed to be 200 d^{-1}, a coherent value for batch activity test of the process.

Table 1. Initial values of the parameters

$k_La_{O_2}$ (d^{-1})	Y_{H_2} ($\frac{gCOD_{X_{H_2}}}{gCOD_{S_{H_2}}}$)	km_{H_2} (d^{-1})	k_{dec} (d^{-1})	K_{S,H_2} (mgCOD L^{-1})
200	0.06	35	0.02	0.007

Hydrogen transfer rate $r_{t,H2}$ and methane production rate Φ, defined as

$$r_{t,H_2} = k_La_{O_2}\sqrt{\frac{D_{H_2}}{D_{O_2}}}\left(S_{H_2} - RT_{op}KH_{H_2}S_{H_2,gas}\right)$$

$$\Phi = (1 - Y_{H_2})km_{H_2}\frac{S_{H_2}}{S_{H_2} + K_{S,H_2}}X_{H_2}$$

are the keys for biological biogas upgrading process optimization, therefore, their maximization is evaluated through the sensitivity analysis.

The sensitivity analysis is performed with the OpenModelica sensitivity optimization tools OMSens (Fritzson et al. (2020)). An individual parameter-based sensitivity analysis has been performed and the Root Mean Square (RMS) index is used to evaluate the differences between the values assumed by a variable (along with the whole simulation) with and without a parameter perturbation. Four simulations have been reported, with parameters perturbations range from -50% to $+50\%$, results are shown in Fig. 1.
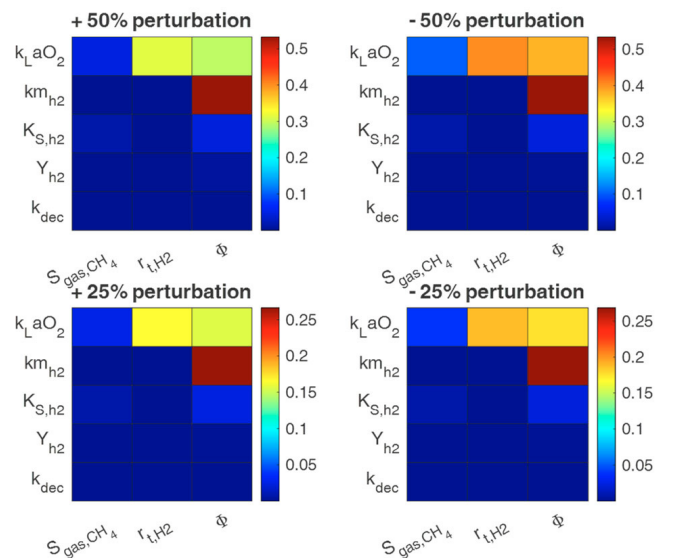

Fig. 1. Results of the sensitivity analysis.

Methane production rate is highly influenced by the maximum specific uptake of hydrogenotrophic methanogens, km_{H_2}, the gas-liquid mass transfer coefficient of oxygen

$k_L a_{O_2}$ and the half-saturation constant on dissolved hydrogen K_{S,H_2}. The gas-liquid mass transfer coefficient is a key parameter to enhance H_2 dissolution and thus, hydrogenotrophic methanogenesis. Therefore, the parameters selected for identification are: $k_L a_{O_2}$, km_{H_2} and K_{S,H_2}.

4. LFT MODELLING AND PARAMETER IDENTIFICATION

Consider a nonlinear, time invariant, multi-input multi-output, continuous-time system

$$\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}(t), \mathbf{u}(t), \boldsymbol{\delta}) \\ \mathbf{y}(t) = \mathbf{g}(\mathbf{x}(t), \mathbf{u}(t), \boldsymbol{\delta}) \tag{10}$$

where $\mathbf{x} \in \mathbb{R}^n$, $\mathbf{y} \in \mathbb{R}^p$, are the state and noise-free output vectors, respectively, $\mathbf{u} \in \mathbb{R}^m$ is the input vector, $\boldsymbol{\delta} \in \mathbb{R}^q$ is a vector of unknown parameters, and assume as output observation equation

$$\check{\mathbf{y}}(t_k) = \mathbf{y}(t_k) + \boldsymbol{\varepsilon}(t_k)$$

where t_k, $k = 1, \ldots, N$, is the sampling instant, and $\varepsilon_i(t_k)$, $i = 1, \ldots, p$, is a discrete-time, zero-mean, white noise of variance σ_i^2. Denote with $\boldsymbol{\delta}^o \in \mathbb{R}^q$ the true value of parameters $\boldsymbol{\delta}$.

The identification problem can be formulated as follows: given the sampled data $\{\mathbf{u}(t_k), \check{\mathbf{y}}(t_k)\}_{k=1}^N$, find the values of the unknown parameters $\boldsymbol{\delta}$ minimizing the cost function

$$J(\boldsymbol{\delta}) = \frac{1}{2N} \sum_{k=1}^N \mathbf{e}^T(t_k, \boldsymbol{\delta}) \mathbf{W} \mathbf{e}(t_k, \boldsymbol{\delta})$$

i.e.,

$$\tilde{\boldsymbol{\delta}} = \underset{\boldsymbol{\delta} \in \mathbb{R}^q}{\arg\min} \, J(\boldsymbol{\delta})$$

where

$$\mathbf{e}(t_k, \boldsymbol{\delta}) = \check{\mathbf{y}}(t_k) - \hat{\mathbf{y}}(t_k, \boldsymbol{\delta})$$

is the prediction error between the measured output $\check{\mathbf{y}}(t_k)$ and the output $\hat{\mathbf{y}}(t_k, \boldsymbol{\delta})$, predicted by model (10) using parameters $\boldsymbol{\delta}$ instead of the true parameters $\boldsymbol{\delta}^o$, and $\mathbf{W}$ is a weight matrix.

As it is well known, $\tilde{\boldsymbol{\delta}}$ is a *maximum-likelihood* estimate of the model parameters $\boldsymbol{\delta}$ for output-error plants (Ljung (1999)), and can be determined through well-known iterative optimization procedures such as, for example, the Gauss-Newton algorithm

$$\hat{\boldsymbol{\delta}}(\nu + 1) = \hat{\boldsymbol{\delta}}(\nu) - \alpha(\nu) \hat{\mathbf{H}}^{-1} \left(\hat{\boldsymbol{\delta}}(\nu) \right) \mathbf{g} \left(\hat{\boldsymbol{\delta}}(\nu) \right)$$

where ν is the iteration number, $\alpha(\nu)$ is the step size, $\mathbf{g}(\boldsymbol{\delta}) : \mathbb{R}^q \to \mathbb{R}^q$ and $\hat{\mathbf{H}}(\boldsymbol{\delta}) : \mathbb{R}^q \to \mathbb{R}^{q \times q}$ are the gradient vector and a positive semi-definite approximation of the Hessian of the cost function with respect to the unknown parameters, respectively.

In turn, rewriting model (10) in a Linear Fractional Transform (LFT) formulation allows for a direct computation by simulation of the gradient and approximated Hessian of the cost function (Della Bona et al. (2015))

$$\dot{\mathbf{x}}(t) = \mathbf{A}\mathbf{x}(t) + \mathbf{B}_1\mathbf{w}(t) + \mathbf{B}_2\boldsymbol{\zeta}(t) + \mathbf{B}_3\mathbf{u}(t) \\ \mathbf{z}(t) = \mathbf{C}_1\mathbf{x}(t) + \mathbf{D}_{11}\mathbf{w}(t) + \mathbf{D}_{12}\boldsymbol{\zeta}(t) + \mathbf{D}_{13}\mathbf{u}(t) \\ \boldsymbol{\omega}(t) = \mathbf{C}_2\mathbf{x}(t) + \mathbf{D}_{21}\mathbf{w}(t) + \mathbf{D}_{22}\boldsymbol{\zeta}(t) + \mathbf{D}_{23}\mathbf{u}(t) \\ \mathbf{y}(t) = \mathbf{C}_3\mathbf{x}(t) + \mathbf{D}_{31}\mathbf{w}(t) + \mathbf{D}_{32}\boldsymbol{\zeta}(t) + \mathbf{D}_{33}\mathbf{u}(t) \\ \mathbf{w}(t) = \boldsymbol{\Delta}\mathbf{z}(t) = \text{diag}\{\delta_1\mathbf{I}_{r_1}, \ldots, \delta_q\mathbf{I}_{r_q}\}\mathbf{z}(t) \\ \boldsymbol{\zeta}(t) = \boldsymbol{\Theta}(\boldsymbol{\omega}(t))$$

where $\mathbf{z} \in \mathbb{R}^{n_z}$, $\boldsymbol{\omega} \in \mathbb{R}^{n_\omega}$, $\mathbf{w} \in \mathbb{R}^{n_w}$, $\boldsymbol{\zeta} \in \mathbb{R}^{n_\zeta}$ are vectors of auxiliary variables, $\mathbf{A}$, $\mathbf{B}_i$, $\mathbf{C}_i$, $\mathbf{D}_{ij}$ are 16 known constant matrices, r_i are the sizes of the corresponding identity matrices $\mathbf{I}_{r_i}$ in the $\boldsymbol{\Delta}$ block, and $\boldsymbol{\Theta}(\boldsymbol{\omega}) : \mathbb{R}^{n_\omega} \to \mathbb{R}^{n_\zeta}$ is a known nonlinear vector function.

Further information on the implementation of the LFT-based identification algorithm can be found in Della Bona et al. (2015). A MATLAB™ Toolbox for parameter identification of nonlinear LFT models is available, as well [1].

Table 2. Aggregated parameters

d	a	b
$\frac{1}{t_{HR}}$	$\sqrt{\frac{D_{H_2}}{D_{O_2}}}$	$\sqrt{\frac{D_{CH_4}}{D_{O_2}}}$
c	p	D
$\sqrt{\frac{D_{CO_2}}{D_{O_2}}}$	$\frac{10^{-pH}}{10^{-pH} + Ka_{CO_2}}$	$\frac{RT_{op}V}{p_{gas} - p_{gas,H_2O}}$

Defining the aggregated parameters as in Table 2 and the following input $\mathbf{u}$, state $\mathbf{x}$, output $\mathbf{y}$ and parameters vectors $\boldsymbol{\delta}$:

$$\mathbf{u} = \begin{bmatrix} X_{H_2,in} \\ S_{H_2,in} \\ S_{CH_4,in} \\ S_{IC,in} \\ S_{IN,in} \\ S_{H_2,gas,in} \\ S_{CH_4,gas,in} \\ S_{CO_2,gas,in} \\ q_{gas,in} \end{bmatrix}, \, \mathbf{x} = \begin{bmatrix} X_{H_2} \\ S_{H_2} \\ S_{CH_4} \\ S_{IC} \\ S_{IN} \\ S_{H_2,gas} \\ S_{CH_4,gas} \\ S_{CO_2,gas} \end{bmatrix}, \, \mathbf{y} = \begin{bmatrix} x_5 \\ q_{gas,out} \\ x_6 \\ x_7 \\ x_8 \end{bmatrix}$$

$$\boldsymbol{\delta} = \begin{bmatrix} Y_{H_2} & km_{H_2} & K_{S,H_2} & k_{dec} & k_L a_{O_2} \end{bmatrix}^T$$

model (1–9) can be reformulated into a LFT as follows:

$$\dot{\mathbf{x}} = \begin{bmatrix} -dx_1 + du_1 + w_1 - w_4 \\ -dx_2 + du_2 - w_2 - w_5 \\ -dx_3 + du_3 + w_2 - w_1 - w_6 \\ \begin{bmatrix} -dx_4 + du_4 + C_{CH_4}(w_1 - w_2) \\ + C_{bac}(w_4 - w_1) - w_7 \end{bmatrix} \\ -dx_5 + du_5 + N_{bac}(w_4 - w_1) \\ \frac{1}{V_{gas}}(\zeta_2 - \zeta_5 + Vw_5) \\ \frac{1}{V_{gas}}(\zeta_3 - \zeta_6 + Vw_6) \\ \frac{1}{V_{gas}}(\zeta_4 - \zeta_7 + Vw_7) \end{bmatrix}$$

$$\mathbf{y} = \begin{bmatrix} x_5 \\ u_9 + D\left(\frac{w_5}{16} + \frac{w_6}{64} + w_7\right) \\ x_6 \\ x_7 \\ x_8 \end{bmatrix}, \, \mathbf{w} = \begin{bmatrix} \delta_1 z_1 \\ \delta_2 z_2 \\ \delta_3 z_3 \\ \delta_4 z_4 \\ \delta_5 z_5 \\ \delta_5 z_6 \\ \delta_5 z_7 \end{bmatrix}$$

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[1] See https://github.com/looms-polimi/LFTSolver.

$$
\boldsymbol{\omega} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \\ x_6 \\ x_7 \\ x_8 \\ w_3 \\ w_5 \\ w_6 \\ w_7 \\ u_6 \\ u_7 \\ u_8 \\ u_9 \end{bmatrix}, \quad
\boldsymbol{\zeta} = \begin{bmatrix} \dfrac{\omega_1 \omega_2^2}{\omega_2^2 + \omega_9} \\ \omega_{16}\omega_{13} \\ \omega_{16}\omega_{14} \\ \omega_{16}\omega_{15} \\ \omega_6 \left[\omega_{16} + D\left(\dfrac{\omega_{10}}{16} + \dfrac{\omega_{11}}{64} + \omega_{12}\right)\right] \\ \omega_7 \left[\omega_{16} + D\left(\dfrac{\omega_{10}}{16} + \dfrac{\omega_{11}}{64} + \omega_{12}\right)\right] \\ \omega_8 \left[\omega_{16} + D\left(\dfrac{\omega_{10}}{16} + \dfrac{\omega_{11}}{64} + \omega_{12}\right)\right] \end{bmatrix}
$$

$$
\mathbf{z} = \begin{bmatrix} w_2 \\ \zeta_1 \\ x_2 \\ x_1 \\ a\left(x_2 - RT_{\mathrm{op}}KH_{H_2}x_6\right) \\ b\left(x_3 - RT_{\mathrm{op}}KH_{CH_4}x_7\right) \\ c\left(px_4 - RT_{\mathrm{op}}KH_{CO_2}x_8\right) \end{bmatrix}
$$

Note that, even if only the three parameters considered after the sensitivity analysis have been identified, the LFT formulation has been developed considering 5 parameters (while considering the other two fixed), in order to make the LFT formulation more flexible for future applications.

Of course, it assumed that all inputs and outputs are measurable or can be assumed to be null i.e. $X_{H_2,\mathrm{in}}$, $S_{H_2,\mathrm{in}}$, and $S_{CH_4,\mathrm{in}}$.

5. EXPERIMENTAL PARAMETER IDENTIFICATION

The LFT calibration has been performed with two datasets, (Bassani et al. (2017)) and own unpublished data. The study of Bassani et al. (2017) considers a thermophilic ($T = 55$ °C) up-flow (UF) reactor for ex-situ biogas upgrading, operating conditions of this reactor can be found in the paper.

Own experimental work is composed of a Continuous Stirred Tank Reactor (CSTR) with a working volume $V = 380$ L and 460 L of headspace, where hydrogen cylinder and biogas (or just pure cylinder carbon dioxide) are injected. Figure 2 reports the input flowrate of the gases expressed in $L_N\ d^{-1}$. For all the experiments, the stoichiometric $H_2 : CO_2 = 4 : 1$ ratio has been kept constant. Results from LFT calibration of both configurations are reported in Table 3.
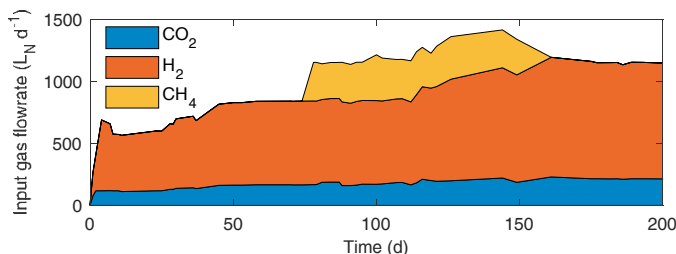
Fig. 2. Input flowrates of gases.

As expected, UF configuration reports a high $k_La_{O_2}$ than the CSTR configuration. In fact, the diffusion gas system of UF is proved to be more efficient with respect to CSTR configuration where it is more difficult to enhance turbulence and thus, gas-liquid mass transfer. The half saturation constant K_{S,H_2} is higher in the case of the CSTR configuration probably due to a limited availability of substrate (S_{H_2}) for microorganisms (X_{H_2}), and this is related to limited gas-liquid mass transfer of H_2. The maximum specific uptake rate km_{H_2} is higher in the UF configuration since the process is more efficient in this configuration and hypothetically temperature is influencing results. It is well known in literature that thermophilic microorganisms have higher kinetics constants (Batstone et al. (2002)).
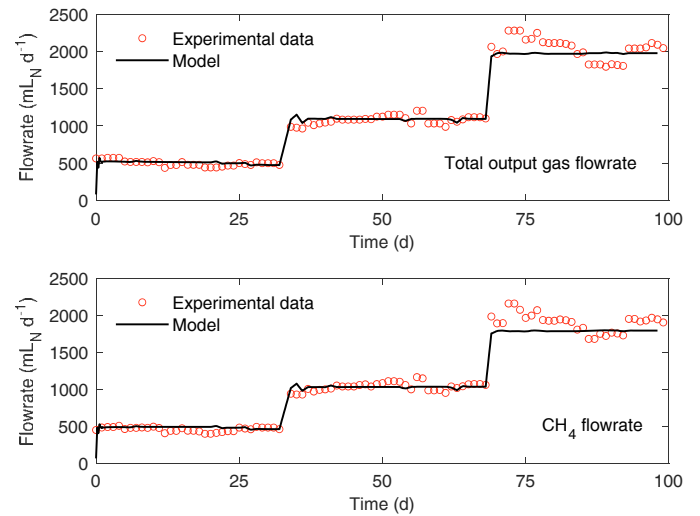
Fig. 3. UF configuration: fitting results (methane and total gas flowrates).

As shown in Fig. 3, a good fitting is obtained for UF configuration, confirmed by the values of Theil's Inequality Coefficient (TIC) (Theil (1961)): TIC = 0.0420 for total output gas flowrate and TIC = 0.0454 for methane flowrate.

A good fitting is also obtained for CSTR configuration (Fig. 4): TIC = 0.072 for total output gas flowrate and TIC = 0.043 for methane flowrate.

Figure 5 compares volatile solids concentration (gVS L^{-1}) (TIC = 0.035), a derived variable from hydrogenotrophic methanogens concentration, and ammonium concentration (S_{IN}) (TIC = 0.104). Regarding ammonium concentration there are some differences between model and the experimental data. This is probably due to ammonification of residual organic nitrogen in the inoculum, a process that is not included in the model. In the last part of the experimental activity an increase in nitrogen concentration is revealed due to ammonium bicarbonate (NH_4HCO_3)

Table 3. LFT calibration results

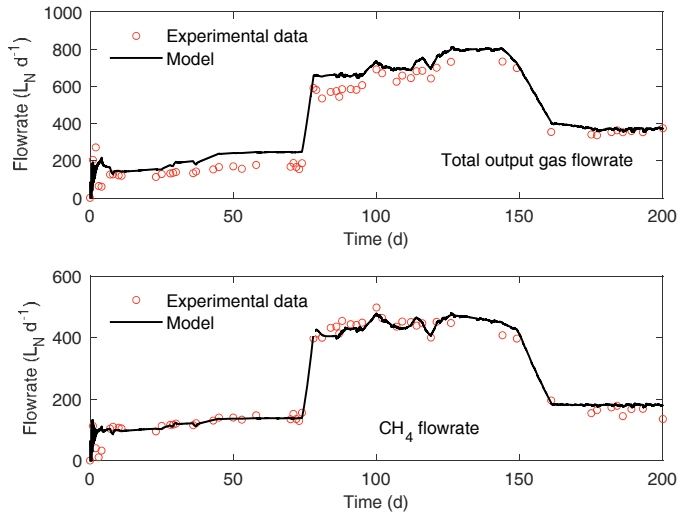| Parameter	Optimal value (UF)	Optimal value (CSTR)
km_{H_2}	160	101
$k_La_{O_2}$	1532	247
K_{S,H_2}	1.1047×10^{-3}	5.6763×10^{-2}

Fig. 4. CSTR configuration: fitting results (methane and total gas flowrates).
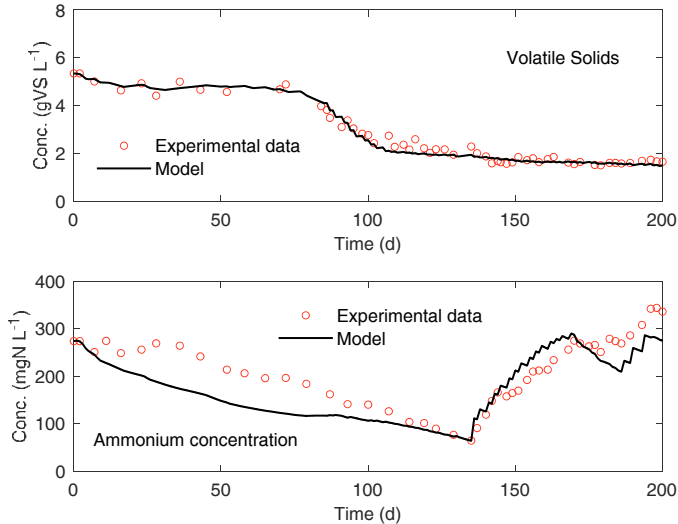

Fig. 5. CSTR configuration: fitting results (volatile solids concentration and ammonium concentration).

dosing, to restore nitrogen availability for microorganisms' growth.

6. CONCLUSION

In this paper, a model of ex-situ biological biogas upgrading has been presented. The model can predict methane flow rate output of two different configurations: a thermophilic up-flow reactor and a continuous stirred tank reactor. Sensitivity analysis using OpenModelica has been performed in order to identify the parameters which needs further optimization. Parameter identification based on Linear Fractional Transformation (LFT) has proven to be a valuable tool for the calibration of the model's parameters. Identification results demonstrate a good model accuracy, even though it should be compared with more datasets, to increase its strength and applicability. Finally, the model can be extended including other dissolved hydrogen consumption pathways such as homoacetogenesis, introducing new parameters and state variables.

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