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SCUOLA DI INGEGNERIA INDUSTRIALE
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Executive Summary of the Thesis

First Approach to a Model-based Control System for Optimal Microaeration in Anaerobic Digestion

Laurea Magistrale in Chemical Engineering - Ingegneria Chimica

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Academic year: 2021-2022

1. Introduction

The fight against climate change is the biggest problem the world is confronting in the XXI century. One of the best ways to lessen the influence of carbon dioxide emissions on energy production is to use biomass. Organic material can be converted to a gaseous mixture mainly composed of CH_4 and CO_2 with anaerobic digestion. Along the process, the feedstock undergoes various biochemical reactions, which result in impurities in the final biogas. Among these impurities, the most abundant and critical is hydrogen sulfide, H_2S. This compound corrodes the metallic equipment with which it comes in contact. It can be converted to hazardous sulfur oxides when burnt in a combustion engine, to which the biogas is typically sent.

A possibility to reduce the amount of sulfide present is given by *microaeration*: the injection of minimum oxygen quantity to produce a small aerated environment. It occurs typically in the upper gaseous region of the reactor, the headspace, where sulfides are converted to elemental sulfur by sulfide-oxidizing bacteria. This process is quite innovative and has already found some practical applications, being simple and economically attractive. However, a gap in knowledge about the quantitative impact of the anaerobic digestion process is still present. This lack of information often results in an inappropriate oxygen injection, which ultimate impact is not always assessed [4].

The present work aims to define a model-based approach to control the oxygen dosage in anaerobic systems. The actual models describing the oxygen effects are too heavy to effectively find applications in control systems. A lumped model, named *Anaerobic Digestion Oxygen Control System* (ADOCS), that reproduces the sulfide production during digestion and their removal by biological-mediated oxidation is thus developed and applied in a control algorithm. The present work defines a control action according to the detected sulfide concentration in untreated biogas, resulting from deviations in the influent or the operating conditions. The overall results show how, with a reliable mathematical model, it is possible to keep the hydrogen sulfide concentration in biogas under a given threshold even after a sudden increase.

2. Anaerobic Digestion

Anaerobic Digestion (AD) is one of the available processes to obtain energy from the degra-

dation of organic substrates. It is based on the controlled biological breakdown of the organic matter to produce methane-rich biogas. In general, it is possible to define the most significant phases of the process as hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The first defines the breakdown of organic macromolecules into their more soluble building block, usually enzyme-mediated. Then, these compounds are converted to volatile fatty acids (VFAs) and, finally, to acetate. This compound is finally converted from methanogens microorganisms into methane, carbon dioxide, and hydrogen. In an anaerobic digester, the definitions are not so rigorous, and part of the VFA may be directly converted to the end products by other microbial families. Additionally, sulfates are commonly found in different feedstocks and participate in various metabolic reactions, the most common of which are sulfate reductions (SR) mediated by specific bacterial families. Sulfate directly affects methanogenesis and leads to the formation of hydrogen sulfide, H_2S. When this compound is present in the gas phase in relevant concentration (>300-400 ppm), it can considerably pollute biogas and damage the metallic equipment with which it comes in contact.

2.1. Microaeration

Microaeration, namely the injection of small amounts of air (or oxygen) into an anaerobic digester, is considered a highly efficient, simple, and cost-effective technique for removing hydrogen sulfide from biogas. The presence of small amounts of O_2 can allow the co-existence of facultative and anaerobic bacteria, which will thus not be exposed to oxygen. Indeed, oxygen has also other beneficial effects, such as hydrolysis enhancement or reactor stabilization, maintaining a constant pH by VFA oxidation. Practically, microaeration is not fully deployed due to a general lack of quantitative knowledge of its effects. As a result, oxygen is injected in approximate quantities and timing only after the practical detection of the excessive amount of sulfide. Consequently, part of its beneficial results may not be fully exploited, and some harmful gas goes downstream. Such consequences can be avoided if the oxygen is injected predictively before the actual detection of excessive H_2S is performed.

2.2. Modeling

Modeling AD has always been challenging and complex, and it still is in most cases. The fundamental reason for this challenge is that AD systems frequently differ in operating parameters and—more significantly—regarding the substrates and microorganisms involved.
As a result, many methods can be considered to create models of AD processes, implying an increasing understanding of the existing system. The most common approach is the one that represents the reactor as a white box and seeks to capture all processes taking place in the digester precisely. The Anaerobic Digestion Model No. 1 (ADM1) represents the state-of-the-art AD modeling among all the solutions created throughout the years [1]. The International Wastewater Association (IWA) established it to offer a workable foundation for practical and industrial applications. Although being created initially for wastewater treatment, it is currently used with specific modifications on various substrates and process conditions. The model structure comprises biological and physicochemical conversion processes, which are usually interdependent. The results are consequently defined within an algebraic differential equations (DAEs) system. Many equations, more than thirty, and almost a hundred parameters make it challenging to use models like ADM1 in control systems due to their complexity and sensitivity. In fact, for this latter application, models must be able to explain any change significant to the specific control system in various contexts with a minimal number of inputs. This result can be obtained by combining several parameters and various reactions into broader families, working on global mass balances, and model reactions. This process produces hybrid and semi-mechanistic models that can bridge the gap between accuracy, complexity, stability, and adaptability. This method tries to accurately depict the process with minimal experimental data requirements and possibly in various situations.
A reduced model is affirmed on these foundations as the most widespread solution for more direct applications in AD control systems. This model, named Anaerobic Digestion Model No. 2 (AM2) or AMOCO, from the commission which produces it, includes only two bacterial populations, namely the acidogenic (X_1) and the

methanogenic (X_2) microorganisms. Furthermore, two general reactions of acidogenesis from a solubilized substrate and methanogenesis from acetate are used as model equations [2]. This model comprises only six differential equations and an additional set of simple algebraic equations to determine all the relevant process variables. Moreover, it provides a simple identification procedure for its parameters, with linear regressions on retrievable steady-state measurements at different reactor dilution rates.

$$\frac{dX_1}{dt} = (\mu_1 - \alpha D - k_{d,1})X_1 \tag{1}$$

$$\frac{dX_2}{dt} = (\mu_2 - \alpha D)X_2 \tag{2}$$

$$\begin{aligned}\frac{dZ}{dt} &= D(Z_{in} - Z) + \\ &+ (k_1 N_{S1} - N_{bac})\mu_1 X_1 - N_{bac}\mu_2 X_2 + \\ &+ k_{d,1} N_{bac}\mu_{1,max} X_1 + k_{d,2} N_{bac}\mu_{2,max} X_2\end{aligned} \tag{3}$$

$$\frac{dX_T}{dt} = D(X_{T,in} - X_T) - k_{hyd} X_T \tag{4}$$

$$\frac{dS_1}{dt} = D(S_{1,in} - S_1) - k_1\mu_1 X_1 + k_{hyd} X_T \tag{5}$$

$$\frac{dS_2}{dt} = D(S_{2,in} - S_2) + k_2\mu_1 X_1 - k_3\mu_2 X_2 \tag{6}$$

$$\frac{dC}{dt} = D(C_{in} - C) - q_C + k_4\mu_1 X_1 + k_5\mu_2 X_2 \tag{7}$$

AM2 found applications in different contexts and has been improved over the years. In particular, the addition of nitrogen dynamics and the hydrolysis stage substantially enhanced the model's predictions. This latter model is named AM2HN [3], stating the additions to the original AM2. Its equations, which definitions are detailed in the models' presentation, are given in 1- 4. The parameter calibration has also been modified to derive AM2 parameters from experimental measurements and regressions on ADM1 simulation steady-state data. This solution implies that adequate inputs should be previously given to ADM1, but those do not need to be so detailed as long as the interest is only in the ultimate result and not the whole dynamics. Consequently, as long as ADM1 provides reasonable values, those can calibrate the AM2 model by running different steady-state simulations.

3. ADOCS Model

The proposed model aims to adequately describe the sulfide oxidation processes occurring in the reactor's headspace. Consequently, relevant additions should be provided to models such as AM2 or AM2HN, starting from the sulfate reduction along the methanogenesis to the gaseous phase modelization. To accomplish this goal, the digester is divided into different segregated blocks, where the output of one is the input of the subsequent. The liquid region is defined accordingly to the AM2HN model, with more accurate parameter estimation. Consequently, a fictitious vapor-liquid separation unit establishes how the species distribute between the two phases. To complete the description of the equilibrium, the addition of influent water content is added to the system. Consequently, also the estimation of the digester liquid level is performed. The latter addition is also considered to determine the headspace volume, which is used to quantify sulfide oxidation reactions when oxygen is injected.

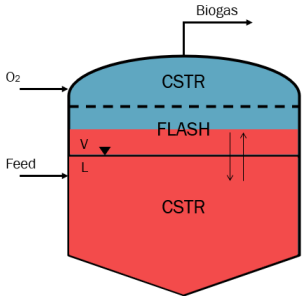

Figure 1: Correspondence between digester areas and model blocks considered.

3.1. Empowered AM2 Identification

AM2 provided a reliable identification procedure, updated by the AM2HN model due to the additional variables present. It is noted that the parameters obtained with the most recent approach provide effective results concerning adimensional variables $y^*(t) = y(t)/y_0$, but fail in predicting the absolute value of essential variables, such as methane composition in biogas. A new procedure is presented in this work To overcome this issue. The approach adopted follows the original AM2 model, deriving the six yield coefficients for the reactions involved in a dual-step sequence. Moreover, as further improvement, a different manipulation of the equations for the kinetic coefficients is performed, leading to slightly more stable regressions. It also added a more detailed estimation of the CO_2 Henry's constant to be used in the liquid-gas transport equation. In the pre-

vious models, it is considered constant with a value of $K_H = 16\ [mmol\, L^{-1}\, atm^{-1}]$. Its derivation from empirical equation commonly used in chemical engineering leads, however, to a range of $K_H = 26.5 - 21.5\ [mmol\, L^{-1}\, atm^{-1}]$, according to the temperature considered. The results for biogas composition obtained with the new estimated parameters are shown in figure 2, compared to the ones obtained with the AM2HN method and with ADM1 outputs as reference. It is possible to note that the obtained value for methane fraction is now closer to the ADM1 result and thus to reality. The better accuracy in absolute values does not substantially reduce the model's precision in predicting the relative deviations. Moreover, the value obtained with the AM2HN approach led to an utterly irrealistic result of carbon dioxide fraction in biogas larger than 70%. Consequently, the new approach can be successfully implemented and has to be used in further developments of the model.

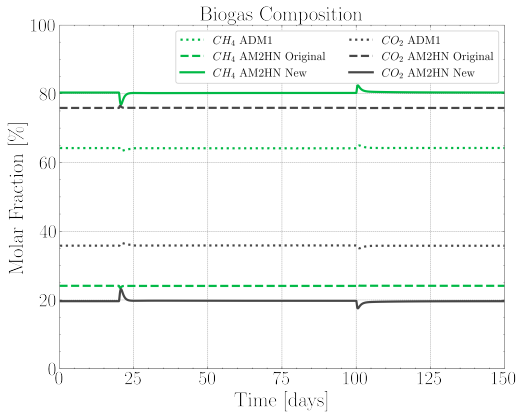

Figure 2: Comparison of results for gaseous outlet composition.*ADM1*: results PyADM1 simulation; *Original*: results AM2HN with parameters from [3]; *New*: results AM2HN with parameters from the new identification method.

3.2. Sulfate Reduction Processes

Due to a lack of detailed biological knowledge of the system, the sulfate reduction processes are modeled following a mathematical approach. This solution allows keeping the simplicity of the original differential equation system and the addition of SR processes *a posteriori*. Consequently, the dynamics of the concentration of sulfate-reducing bacteria $X_{srb}\ [g\, L^{-1}]$ is modeled accordingly to an adjusted version of the Gompertz equation, commonly used for microbial growth (Equation 8). With that variable, it is possible to compute the concentration of dissolved sulfide $S_s\ [mmol\, L^{-1}]$ from the balance on the consumed substrate accounting for the yield coefficient $Y_{srb}\ [g\, mmol^{-1}]$, as stated in equation 9.

$$X_{srb}(t) = X_{s,max}\ \exp\left\{-\exp\left[\frac{K_{z,srb}\, e}{X_{s,max}}\,(-t) + 1\right]\right\} \quad (8)$$

$$S_s(t) = \frac{1 - Y_{srb}}{Y_{srb}}\, X_{srb}(t) \quad (9)$$

The parameters of the Gompertz equation are related to the methanogens population ($K_Z = \Delta X_2 / \Delta t$, the growth parameter) and the sulfate content in the influent converted to the available substrate for the SRB, on a COD basis ($S_{s,max}(t) = \gamma_{S,in}(t) \cdot S_2(t) \cdot 1000/64$). There, $\gamma_{S,in}\ [-]$, defines the sulfate content present in the influent and can potentially be available to the SRB. The maximum value for microbial population $X_{s,max}(t)$ is obtained by inserting the expression of $X_{s,max}(t)$ in 9. Indeed, a term accounting for substrate uptake has to be subtracted from equation 6:$\rho_{uptake} = -1/Y_{srb} \cdot \mu_{srb}$. There, $\mu_{srb}(t) = \mu_2(t) \cdot X_{srb}(t)/X_2(t)\ [g\, L^{-1}\, d^{-1}]$ stands for the SRB growth rate, defined, accordingly to the similarity between the reactions considered, as proportional to the respective methanogens rate μ_2.

3.3. Headspace Modeling

The essential addition of the ADOCS model is headspace modeling. The sulfide oxidation process usually takes place there. The region requires defining the gaseous volume above the liquid phase and the respective composition to be correctly accounted for. The modeling approach is relatively simple and considers the headspace behaves like a CSTR reactor, as shown in figure 1.

3.3.1 Digester Level

The first is described by defining the liquid level from the influent flow rate, according to reactor design and system characteristics, as defined by equation 10. The liquid volume $V_{liq}\ [m^3]$ can be easily computed by assuming a cylindrical shape. Finally, the actual gaseous volume is computed as $V_{gas} = V_{headspace} + (V_{reactor} - V_{liq})$. $V_{headspace}\ [m^3]$ is that region which is always in the gaseous phase, and $V_{reactor}\ [m^3]$ is the one

corresponding to the maximum allowed liquid level.

$$h(t) = \frac{\dot{Q}_{in}(t)}{S_R\, D}\left(1 - e^{-Dt}\right) + H_0\, e^{-Dt} \tag{10}$$

3.3.2 Vapor-Liquid Equilibrium

Since water is included as non-reactive species to compute the liquid level effectively, its impact on the vapor-liquid equilibrium has to be assessed. Consequently, it is assumed that the species flow rates computed from the biochemical reactions are entering, along with the water stream, a fictitious vapor-liquid separation modeled as an isothermal and isobaric flash unit. The outlet flows are computed using the Rachford-Rice equation (11), solved for the vapor fraction $\alpha = V/F$. Then, it is possible to manipulate the mass balances to get values for the vapor fraction y_i and x_i. From that, the vapor (V) and liquid (L) streams can be computed for each species as $V_i = y_i\, V$ and $L_i = x_i\, L$.

$$f(\alpha) = \sum_{i=1}^{NC} \frac{z_i\,(K_i - 1)}{1 + \alpha\,(K_i(T) - 1)} = 0 \tag{11}$$

3.3.3 Sulfide Oxidation Process

The sulfide oxidation is modelled comparing the headspace to a CSTR reactor, as is commonly the case for anaerobic digestion processes. This reactor has two influent streams, represented by the products of anaerobic digestion and the oxygen injected to guarantee the microaerobic conditions for SOBs. Then, a single mixed stream will leave the digester after a specific residence time $\tau_{headspace}$ $[h]$, defined as the ratio between gaseous volume V_gas $[m^3]$ and the headspace influent volumetric flowrate, properly obtained from V $[mol\, h^{-1}]$.
The equations representing the system are derived from the classical CSTR balance in molar terms. Non-reactive species are CH_4 and CO_2, whereas the other species participate in the sulfide oxidation process, according to the model reaction in Eq. 12

$$2\,H_2S + O_2 \longrightarrow 2\,S_x + 2\,H_2O \tag{12}$$

S_x is the solid elemental sulfur produced, which either deposits on headspace walls or falls into the liquid phase. The complete set of equations for the reactive species is given as follows:

$$\frac{d\dot{n}_S}{dt} = V_S - \dot{n}_{S,OUT} - \frac{r_{SOB}\, V_{gas}}{MW_S} \tag{13}$$

$$\frac{d\dot{n}_W}{dt} = V_W - \dot{n}_{W,OUT} + \frac{r_{SOB}\, V_{gas}}{MW_S} \tag{14}$$

$$\frac{d\dot{n}_O}{dt} = \dot{n}_{O,IN} - \dot{n}_{O,OUT} - \frac{r_{SOB}\, V_{gas}}{MW_{O_2}\, R_b} \tag{15}$$

$$\frac{dn_{Sx}}{dt} = +\frac{r_{SOB}\, V_{gas}}{MW_S} \tag{16}$$

The reactive term is defined with a power-law kinetic mechanism, dependent on the mass concentration of the reactants (Eq. 17).

$$r_{SOB} = k_{SOB}\; w_S^{\alpha}\; w_O^{\beta}\; [g_S\, m^{-3}\, h^{-1}] \tag{17}$$

This mechanism is usually valid for chemical oxidation, whereas biochemical oxidation is commonly modeled from the SOB population according to Monod-type kinetic mechanisms. However, since chemical oxidation accounts for almost 40% of the total and, in some cases, the power-law approach is also applied in the microbial-mediated kinetic mechanism, this more direct kinetic relationship is applied in the present case [5]. The results for the base-case study considered are shown in figure 3. Trends of CH_4 and CO_2, resulting from influent deviations, are consistent with the ones of the AM2 model. It is possible to notice the significant reduction in H_2S concentration (shown in $[ppm]$, as it is commonly done) thanks to SOB activity. Being the influent oxygen defined as a constant flow, it is less abundant in the outlet stream when a more considerable amount of sulfide is present in the influent.

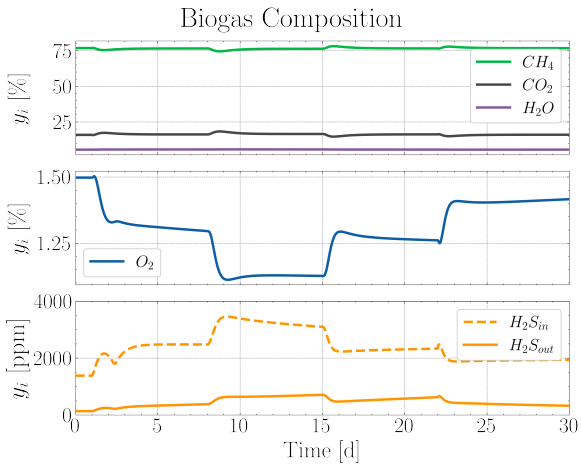

Figure 3: Headspace exiting biogas stream composition. *Full lines*: digester outlet; *dashed lines*: headspace influent.

3.3.4 Inhibition constants

The effect of inhibitors of methanogens is added to the equation of the AM2 describing their function. The approach follows the one of ADM1 and defines two inhibition functions I_O and I_S, accounting for oxygen and sulfate effects, respectively. The two functions are included in the methane production rate of AM2, as in Eq. 18.

$$q_M = k_6 \cdot \mu_2 \cdot X_2 \cdot I_S \cdot I_O \tag{18}$$

Their shape is defined according to literature references. Their evaluation leads to a value of 0 and 1, with $I_i = 1$ defining an uninhibited reaction.

4. Oxygen Injection Control

The model is finally inserted within a complete control algorithm to use it for practical purposes effectively. The sequence starts with collecting influent data and, according to those, deciding whether to perform the parameter identification. Subsequently, the simulation of anaerobic digestion with the ADOCS model is performed for the desired time horizon, considering any default oxygen injection. If the prediction is satisfactory, in terms of final H_2S concentration in biogas, nothing changes, and the algorithm is recalled for the new time horizon (typically, the day after). Conversely, if the model retrieves a sulfide concentration exceeding the threshold defined, it triggers a control action.
The entity of this response is defined according to its impact on the system. The model can predict the result of a deviation in the influent flow rate, which can typically increase the final H_2S concentration before it occurs. Given this prediction, it anticipates the action so that excessive concentration is never reached. Figure 4 refers to an example case study in which the concentration of H_2S entering the headspace increases sharply, leading to an excessive amount of sulfide if it is not adequately treated. The result of the control action shows how the sulfide concentration does not present an overshoot above the threshold if the oxygen is injected before the excessive concentration is detected. Moreover, a maximum value for the injected flow rate is defined. This tolerance can be due to a physical limit of the system or to keeping a maximum ratio between oxygen and total biogas flow rate.

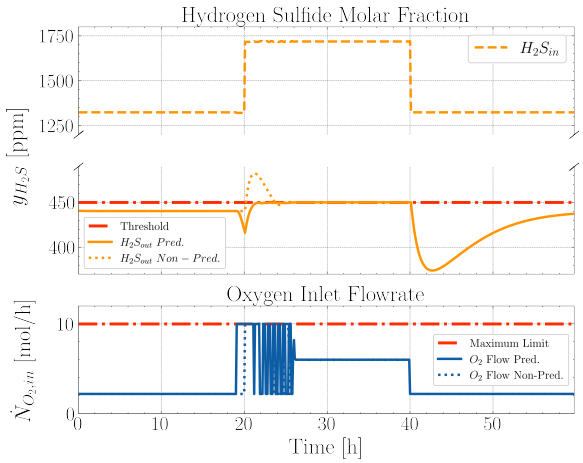

Figure 4: Headspace H_2S fraction and oxygen injection. *Full lines*: Predictive injection; *dotted lines*: Non-predictive injection.

5. Conclusions

The model presented successfully represents the general behavior of an anaerobic digestion system with sulfate reduction and sulfide oxidation processes. The results are successfully compared with referenced literature values regarding the untreated molar fraction of sulfide and the microaeration effects [4]. A further comparison with industrial data regarding a plant of the *Thöni* company shows good accuracy of the predictions even in the case that the available measurements are deficient. Moreover, the model application within a complete control algorithm successfully proves the efficacy of a preventive O_2 injection to keep the values of H_2S concentration below a given threshold.
Further advances should include a more detailed estimation of the oxidation kinetic parameters, here determined from the literature for a power-law kinetic mechanism. Furthermore, a complete characterization of the control system's physical characteristics is fundamental for a practical on-field application and additional experimental validations.

6. Acknowledgements

The author would like to thank the company *Thöni Italia S.r.l.* for the courtesy of the data provided.

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