

Aspen Plus process-simulation model: Producing biogas from VOC emissions in an anaerobic bioscrubber

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Abstract

A process-simulation model for a novel process consisted of an anaerobic bioscrubber was developed in Aspen Plus[®]. A novel approach was performed to implement the anaerobic reactor in the simulation, enabling it to be connected to the scrubber. The model was calibrated and validated using data from an industrial prototype that converted air emissions polluted with volatile organic compounds with an average daily concentration of 1129 mgC Nm⁻³ into bioenergy for more than one year. The scrubber, which showed a removal efficiency within 83–93%, was successfully predicted with an average absolute relative error of $5.2 \pm 0.08\%$ using an average height-to-theoretical-plate value of 1.05 ± 0.08 m and 1.37 ± 0.11 m for each of the two commercial packing materials used, respectively. The anaerobic reactor, which treated up to 24 kg of chemical oxygen demand m⁻³ d⁻¹ with efficiencies of about 93%, was accurately simulated, both in effluent-stream characteristics and in the biogas stream. For example, the average absolute error between the experimental biogas production and the model values was $19.6 \pm 18.9\%$. The model proved its capability as a predictive tool and an aid in design, resulting in savings of time and money for practitioners. In addition, the approach proposed can be expanded to other bioprocesses that include unit operations.

Keywords: anaerobic reactor, Aspen Plus, biogas, process simulation, scrubber, volatile organic compounds

1 Introduction

Circular economy is attracting more interest from governments, industries, and researchers worldwide. Circular economy is a strategy that attempts to change current linear material- and energy-flow model using a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops (Geissdoerfer et al., 2017). The flexographic sector is one field in which the loops could potentially be closed by recycling waste gases into energy. Flexographic industrial facilities, which can consume up to 1000 t of organic solvents per year, produce waste-gas emissions that have relatively low concentrations (below 5 g m^{-3}) of volatile organic compounds (VOCs), mainly ethanol, ethyl acetate, isopropanol, n-propanol, 1-methoxy-2-propanol, n-propyl acetate, 1-methoxy-2-propyl acetate, acetone, and 1-butanol (Granström et al., 2002). Today, these emissions must be treated to follow the European Directive 2010/75/EU (European Council, 2010). However, recently, a novel process, anaerobic bioscrubber, has offered a circular economy approach that enables these emissions to be transformed into bioenergy (Waalkens et al., 2015). In a previous work (Bravo et al., 2017), an on-site anaerobic bioscrubber installed in a flexographic facility was operated for 484 days, controlling VOC emissions that had an average daily concentration of 1129 mgC Nm^{-3} . The VOC removal efficiency at the scrubber ranged from 83–93%, and the anaerobic reactor showed excellent performance, treating organic loading rates (OLRs) of up to $24 \text{ kg of chemical oxygen demand (COD) m}^{-3} \text{ d}^{-1}$ with efficiencies of about 93% and producing a biogas stream that had methane content of $94 \pm 3 \text{ \% vol}$. This experimental study was the first to demonstrate the potential of this new biotechnology, although more in-depth knowledge of it is necessary to provide an optimized system.

Models are considered useful tools to improve knowledge of bioprocesses, to study their responses against variations in parameters, and to predict their overall performance (Okkerse et al., 1999; Zarook et al., 1997). In fact, process simulators are highly appreciated by industries and researchers because they can perform accurate predictions and sensitivity analyses in less time and much less expensively than can be done in real plants (Al-Rubaye et al., 2017; Rajendran et al., 2014), thereby aiding process design and optimization. One of the most powerful process simulators is Aspen Plus[®], an integrated process engineering software program that performs steady-state and dynamic-process simulations. The software includes equipment-design and cost-evaluation tools and incorporates rigorous property methods, thermodynamic calculations, and the ability to use electrolyte equilibria and a wide range of unit operations.

Regarding the application of simulators to the main unit operations of anaerobic bioscrubbers, Aspen Plus[®] is an established tool for simulating and making predictions about absorption systems (Azahari et al., 2016; Bhoi et al., 2015; Sutanto et al., 2017). Regarding the modeling of anaerobic digestion processes, the Anaerobic Digestion Model no.1 (ADM1), proposed in 2002 (Batstone et al., 2002), is considered the most advanced model for predicting, controlling, and optimizing the production of biogas using anaerobic digestion processes. The ADM1 includes biochemical processes, including disintegration, hydrolysis, acidogenesis, acetogenesis, and methanogenesis, and physicochemical processes, including gas-liquid equilibria and ion dissociations. Some extensions to the ADM1 have been proposed (Batstone et al., 2006), and the model has been used by a number of researchers to simulate various types of biogas-production processes from different substrates for both labs and full-scale biogas plants (Hagos et al., 2017).

However, the complexity of the ADM1 model, with its large numbers of components, has led to the application of both simplified versions of the model and to simpler models (Arzate et al., 2017; Kleerebezem and Van Loosdrecht, 2006). Indeed, the few available studies on the implementation of anaerobic digestion in Aspen Plus® have used simplified approaches to the anaerobic-digestion model. For example, Barta et al. (2010) conducted a techno-economic evaluation of stillage anaerobic treatment in a softwood-to-ethanol process. The author assumed stoichiometric degradation factors of 90% for soluble compounds, 50% for polysaccharides and water-soluble lignin, and 0% for nonsoluble lignin, with a yield of $0.35 \text{ Nm}^3 \text{ kg COD}^{-1}$ for methane production. Nguyen et al. (2014) used the theoretical stoichiometric method based on the Buswell equation to evaluate the products of the anaerobic digestion of food waste for their energy potential. Salman et al. (2017) techno-economically evaluated biomethane production by integrating pyrolysis and anaerobic-digestion processes, using stoichiometric factors for the methane produced from carbohydrates, protein, and lipids. Rajendran et al. (2014) and Al-Rubaye et al. (2017) proposed a similar approach using Aspen Plus® reactor blocks connected in series. Both studies defined the hydrolysis step in a stoichiometric reactor, using different conversion grades for carbohydrates, proteins, and lipids; whereas the acidogenesis, acetogenesis and methanogenesis steps were carried out in continuous stirred tank reactors, defining the degradation kinetics in a homemade calculator block.

The purpose of the present study was to develop a process-simulation model of the anaerobic bioscrubber that would be a useful tool for optimization and design. The simulation model was calibrated and validated using experimental data obtained in a previous study, in which a prototype of anaerobic bioscrubber was operated during 484 days (Bravo et al., 2017). The two main process units, the scrubber and the anaerobic

reactor, were created in Aspen Plus[®], which is capable of defining the gas-liquid equilibriums and the electrolyte chemistry. The anaerobic degradation reaction kinetics of the acidogenesis and methanogenesis steps were assumed as Monod-type expressions. This article includes the assumptions used to implement the anaerobic bioscrubber in Aspen Plus[®]. In addition, a sensitivity analysis evaluated the effect of the model's parameters on the predictions of both units. Finally, a case study showed the model's capability as a design tool.

2 Materials and Methods

2.1 Anaerobic bioscrubber prototype

The process-simulation model developed in this study was calibrated and validated using data obtained previously from an anaerobic-bioscrubber prototype installed on-site in a flexographic printing facility. This system was successfully operated for 484 days to control VOC emissions that were mainly composed of ethanol (ET), ethyl acetate (EA), and 1-ethoxy-2-propanol (E2P) (Bravo et al., 2017). The anaerobic bioscrubber consisted of two interconnected units: a scrubber of 2.0 m in packing-material height and 0.5 m in diameter that was assembled onto a 2-m³ tank and an expanded granular sludge bed anaerobic reactor having a diameter of 1.59 m and a total water volume of 8.7 m³. The reactor was filled with 3 m³ of granular sludge. Figure 1 shows a scheme of the prototype. The flexographic site runs two 8-h shifts each day from Monday through Friday and one 8-h shift on Saturday. A fraction of the VOC emissions from the factory was blown into the scrubber, flowing counter-currently to a water stream. The airflow of this fraction varied from 184–1253 m³ h⁻¹, and the average daily VOC concentration was 1129 ± 460 mgC Nm⁻³. The water stream containing the solvents from the scrubber tank was supplemented with sodium carbonate for pH

control and macro- and micro-nutrients prior to flowing into the anaerobic reactor, which operated at 3 h of hydraulic residence time. The effluent from the reactor was sent to the scrubber unit, meaning that the pilot plant worked in water-closed recirculation. During the study, three different scrubber configurations were tested in the plant, as follows: 1) a cross-flow structured packing material (KFP 319/619, ENEXIO, Germany, named Packing A) was used from days 0–95 (Stage I) and from days 266–484 (Stage V); 2) a vertical-flow structured packing material (KVP 323/623, ENEXIO, Germany, named Packing B) was used from days 96–130 (Stage II) and from days 181–265 (Stage IV); and 3) a spray column was used from days 131–180 (Stage III). More information of the commercial packing materials can be found in supplementary section. Several liquid-to-air volume ratios ranging from 1.9×10^{-3} – 10.1×10^{-3} were set in the scrubber unit, resulting in superficial liquid velocities of from 10.2 – 20.4 m h^{-1} . The organic load (OL) fed to the anaerobic reactor fluctuated according to modifications in the facility and the operation of the scrubber and ranged from 0.37 – $6.96 \text{ kg COD h}^{-1}$.

<<Figure 1>>

2.2 Model description

The process-simulation model of the anaerobic bioscrubber was created in Aspen Plus[®] version 8.0 (Aspen Technology Inc.; Bedford, MA, USA) with the aim of developing a tool useful for predicting the system performance of and designing and optimizing this novel technology. The model was implemented in Aspen Plus[®] under steady-state simulation and was linked to the software MATLAB[®] R2016a (MathWorks; Natick, MA, USA). This connection enabled the transfer of data between the software programs and the use of MATLAB[®] toolboxes (for example, optimization algorithms) for

calibrating and validating the model. The first step in the simulation process involved selecting the thermodynamic package. The Electrolyte NRTL activity coefficient model (ELECNRTL) was selected because it is the recommended option for systems having electrolytes. The ELECNRTL thermodynamic package calculates the properties of the liquid phase from its activity-coefficient model and the properties of the vapor phase from the Redlich-Kwong equation of state. Aqueous and aqueous/organic electrolyte systems are represented with a single set of binary interaction parameters (Aspen Technology, 2013). The second step in the process was specifying the conventional components, including O₂, N₂, H₂O, CO₂, CH₄, H₂, ethanol, ethyl acetate, 1-ethoxy-2-propanol, acetic acid, Na₂CO₃, and the subsequent electrolyte chemistry, with the equilibrium constants being defined by the Aspen Plus[®] database. The electrolyte chemistry reactions considered in the model can be found in Table Sup1 of the supplementary material. Then, the two main units of the anaerobic bioscrubber were created in the simulation environment of the software. Figures 2 (a) and (b) show the flowsheets for the scrubber and the anaerobic unit, respectively. The following two subsections present detailed explanations of both the flowsheets and the simplifications made during the model development.

<<Figure 2>>

2.2.1 Scrubber unit

The scrubber column (SCRUBBER) was modeled using the Aspen Plus[®] rigorous distillation method, RadFrac, and defined as an absorber. As Figure 2 (a) shows, the air stream contaminated with solvents (VOC-AIR) entered at the bottom of the column, and the absorbing water stream (WATER-SC) was introduced at the top. Two outlet streams exited from this block: a solvent-cleaned air stream (CLEANAIR) and a solvent-

polluted water stream (VOCWATER), which went to the anaerobic reactor. The flowrate of the VOC-AIR stream was set by adjusting the flowrate of the AIR stream, its humidity was set by the mass-flow of the HUMIDITY stream, and the VOC concentration was set by specifying the mass-flows of all three solvents streams: ethanol (ET-IN), ethyl acetate (EA-IN), and 1-ethoxy-2-propanol (E2P-IN). The heater (HE-A01) was used to set the temperature of the stream at the required value before it entered the scrubber.

The scrubber unit was calibrated by fitting the experimental concentration of each solvent in the outlet air stream and those in the model predictions (obtained from the CLEANAIR stream) for a set of experimental data. As the Murphree vapor efficiency of individual components was used in the SCRUBBER block, various values could be specified for the equilibrium stages of each solvent. The calibration parameters included the number of equilibrium stages for each solvent (N_{ET} , N_{EA} , and N_{E2P}). The parameter estimation was conducted using the MATLAB[®] algorithm *fminsearch*, to minimize the objective function, which was defined as the sum of the squared deviation between the model prediction and the experimental values. As result, the calibrated number of equilibrium stages for each solvent was transformed into the corresponding value of the Height Equivalent to a Theoretical Plate (HETP).

2.2.2 Anaerobic reactor unit

This process-simulation model for the anaerobic degradation of wastewater containing organic solvents was developed as a simplified model of anaerobic degradation and took into account the following stages: acidogenesis, methanogenesis, and chemical and gas-liquid equilibriums. The following phenomena were considered negligible due to operating conditions and observations throughout the experimental period, for the

reasons explained: 1) sulfate and nitrate reduction, due to the significantly low concentration values of these anions in the inlet water of the anaerobic reactor (always < 5 mg L⁻¹); 2) nutrient limitation, because of sufficient supplementation of macro and micro nutrients; 3) inhibition by pH and other compounds, due to pH being controlled to an average value of 7.4 ± 0.3 and to volatile fatty acids (VFA) concentrations ranging from 43–1154 mg HAc L⁻¹; and 4) biomass growth and decay processes, so granular anaerobic biomass concentration was considered to kept constant.

The reaction set for producing biogas from the degradation of the three solvents was defined according to the literature. Regarding the acidogenesis stage, Kalyuzhnyi et al. (1997) reported that ethanol was decomposed to acetic acid and H₂. Yanti et al. (2014) suggested that methyl ester degraded to carboxylic acids and alcohols. Following this mechanism, ethyl acetate would be transformed into acetic acid and ethanol. Bravo et al. (2017) hypothesized that E2P would be decomposed to ethanol and acetone, and following the mechanism proposed by Platen and Schink (1987), acetone could be transformed into acetic acid. Analysis of the solvent content of the prototype's water streams detected no acetone, so the E2P acidogenesis was simulated as one step. Table 1 details the acidogenic and methanogenic reactions.

<<Table 1>>

As Figure 2 (b) shows, the simulation model of the anaerobic reactor was developed using several Aspen Plus[®] reactor blocks connected in a series, with the reaction temperature set to the value required. The water stream (VOCWAT-2) was defined using the stream coming from the scrubber (VOCWATER), the soluble COD and carbonate species were defined according to the experimental values, and the solvent content of the water was defined by the results of the scrubber simulation. The stream

VOCWAT-2 entered the EA-AC stoichiometric reactor, in which 100% of the EA was converted to ET and acetic acid (HAc). Very fast decomposition of the EA was assumed, given that no EA was detected in the analysis of the solvent content of the water streams during the prototype testing. The outlet stream from the EA-AC went to a succession of two reactors modeled using the RCSRT block. The RCSRT block was a rigorous reactor with a rate-controlled reaction that was based on kinetic expressions. The acidogenesis of the ET and E2P was conducted in the ETE2P-AC reactor. The production of biogas from HAc was addressed in the ACET-MET reactor. The kinetics of the three reactions was assumed to follow the Monod-type equations, resulting in the following expressions for ET, E2P, and HAc, respectively:

$$r_{ET} = v_{max,ET} \frac{S_{ET}}{K_{ET} + S_{ET}} \quad (1)$$

$$r_{E2P} = v_{max,E2P} \frac{S_{E2P}}{K_{E2P} + S_{E2P}} \quad (2)$$

$$r_{HAc} = v_{max,HAc} \frac{S_{HAc}}{K_{HAc} + S_{HAc}} \quad (3)$$

where $v_{max,i}$, K_i , and S_i are the volumetric maximum growth rate, the half-saturation constant, and the liquid concentration of substrate, respectively, for each component ($i =$ ET, E2P, and HAc). The Monod-type kinetic was implemented in Aspen Plus[®] using the Langmuir-Hinshelwood Hougen-Watson reaction type, which mimics a Monod-type expression. The outlet stream from the ACET-MET reactor went to the H2-MET stoichiometric reactor, where 100% of the H₂ produced from previous reactions was fully converted to methane. The gas-liquid-solid separator was simulated by installing a Flash2 block. Two streams exited from this unit: the biogas produced by the degradation of the solvents (BIOGAS) and the water stream (WATER-SC), which passed through a split block to enable recirculation of a part of it to be mixed with the VOCWATER stream and the rest to continue to the scrubber unit.

The six kinetic parameters, the volumetric maximum growth rate, and the half-saturation constant for the ET, E2P, and HAc were estimated preliminarily by fitting the gas flow-rate of the methane and the VFA concentration in the water effluent predicted by the simulation model against a set of experimental data that covered a wide range of operational conditions. The weighted objective function (OF) was defined as follows:

$$OF = \sum_{i=1}^N \left(10 \cdot \left(\frac{Q-CH_{4,exp} - Q-CH_{4,mod}}{Q-CH_{4,exp}} \right)^2 + \left(\frac{VFA_{exp} - VFA_{mod}}{VFA_{exp}} \right)^2 \right) \quad (4)$$

where Q-CH₄ and VFA are the gas flow-rate of the methane and the VFA concentration in the water effluent, respectively, for the model predictions (mod) and the experimental data (exp). This objective function takes into account both the reactor's performance in degrading the solvent and its stability. A sensitivity analysis using the preliminarily fitted values of the six kinetic parameters had been conducted previously to establish which parameters were determined during the calibration step. This was performed by varying their values by up to ± 20% (step size of 5%) and evaluating the variation in the predicted methane production and VFA concentrations. The calibration step was done by minimizing the objective function defined in Eq. (4) using the MATLAB[®] algorithm *fmincon*.

3 Results and Discussion

3.1 Scrubber model calibration

The scrubber unit was calibrated using data from the industrial prototype, including one set of experimental data (n = 4) for each structured packing material, Packings A and B, respectively. These experiments were conducted using fresh water as the absorbing water stream and using different volume ratios of liquid-to-air to cover the entire range

of operating conditions tested in the prototype. The following parameters were monitored: the temperature, flow rates of the air and liquid streams and the VOC concentration, calculated as the sum of the three solvents in mgC Nm^{-3} , with $C = C_{\text{ET}} + C_{\text{EA}} + C_{\text{E2P}}$. The solvent contents of the inlet and outlet air streams were measured using carbon-sorbent tube and post-gas chromatograph analysis. Table 2 summarizes the experimental data for the calibration and the model predictions for the outlet concentrations of the three solvents and their fitted number of equilibrium stages per meter.

<<Table 2>>

The calibration procedure resulted in values for the number of equilibrium stages per meter that ranged from 0.90–1.10 and 0.64–0.79 for Packings A and B, respectively. The model prediction fit the experimental data, having an average deviation between the observed and predicted outlet VOC concentrations (calculated as the sum of the outlet concentrations of the three solvents) of $12.9 \pm 16.5 \text{ mgC Nm}^{-3}$ (with an average relative error of $6.1 \pm 7.3\%$). The obtained values of the equilibrium stages per meter (N) of both packing materials indicated that Packing A presented better performance than Packing B, with a higher N number indicating greater absorption of the solvents from the water. This behavior was in accord with experimental results in which higher removals were achieved with Packing A, which was selected as the best alternative for the industrial application (Bravo et al., 2017). As similar values of N were obtained for the three solvents in each packing material, to simplify the process-simulation model, it was decided to use the average N value for each packing material, which were $0.96 \pm 0.08 \text{ m}^{-1}$ and $0.74 \pm 0.06 \text{ m}^{-1}$ for Packings A and B, respectively. The N value was transformed into HETP, a more common engineering concept, which yielded $1.05 \pm 0.08 \text{ m}$ and $1.37 \pm 0.11 \text{ m}$ for Packings A and B, respectively.

The model predictions were affected mainly by the calibrated parameter (HETP) and the solvent composition of the polluted gas stream. Therefore, a sensitivity analysis was performed to evaluate the influence of these two factors on the predictions and to assess the robustness of the model. Model sensitivity was gauged by evaluating the variation in the total removal efficiency (RE) of the scrubber when one factor per analysis, either the number of N or the proportion of one solvent composition of the inlet air, was changed by up to $\pm 20\%$ (step size of 5%). The total RE was calculated as follows:

$$Total\ RE\ (\%) = \left[1 - \frac{(C_{out,ET} + C_{out,EA} + C_{out,E2P})}{(C_{in,ET} + C_{in,EA} + C_{in,E2P})} \right] \cdot 100 \quad (5)$$

As an example, the analysis was carried out with Packing A and the following operational conditions: gas load factor (F) = $0.96\ m\ s^{-1}\ (kg\ m^{-3})^{0.5}$ (gas flow rate of $619\ m^3\ h^{-1}$); superficial liquid velocity (v_L) = $15\ m\ h^{-1}$; total inlet VOC concentration = $1129\ mgC\ Nm^{-3}$ ($C_{in,ET} = 734\ mgC\ Nm^{-3}$, $C_{in,EA} = 282\ mgC\ Nm^{-3}$, and $C_{in,E2P} = 113\ mgC\ Nm^{-3}$). The solvent composition of the inlet air stream selected (65.5% ET, 25.4% EA, and 9.1% E2P) corresponded to the average value selected as representative of the 484 days that the prototype was tested (Bravo et al., 2017). Figure 3 shows the variation of the total RE against the change in N (Figure 3 (a)) and against the change in the proportion of each solvent (Figure 3 (b)).

<<Figure 3>>

As Figure 3 (a) shows, the number of equilibrium stages was sensitive, with the variation in the total RE ranging from -7.8–4.5% by a change of $\pm 20\%$ in N, increasing the sensitivity at the low values of the parameter. According to the sensitivity analysis, the use of a constant value of N per packing material caused only a slight variation, $\sim 5\%$, in the total RE. Changes in the E2P composition showed no effect on the total RE. In contrast, the total RE was linearly influenced by changes in the ET and EA

compositions. The higher the ET composition or the lower the EA composition, the higher the removal efficiency obtained in the scrubber. Variations in the solvent content of the polluted gas stream during the experimental period were $\pm 10\%$, and they corresponded to maximum changes in the total RE of $\pm 2\%$, thereby demonstrating the robustness of the proposed model to predict the performance of the anaerobic bioscrubber when treating VOC emissions from flexographic facilities. No literature has been found for the modelling of scrubber treating VOC emissions in Aspen Plus[®], however, other authors have shown the potential of this simulation software to model and simulate absorption process. For example, Ma et al. (2017) modeled in Aspen Plus[®] the biogas upgrading using aqueous choline chloride/urea. In this study, the authors using the capabilities of the simulator optimized the operating parameters such as the liquid-to-air ratio and the number of theoretical stages and showed the improvements in the total energy utilization and the size and the pressure drop in the columns.

3.2 Scrubber model validation

The scrubber model was validated using the experimental data obtained from the scrubber of the prototype while the two structured packing materials were used (days 0–130 and 181–484), providing 291 data points with which to check the model's validity. The model was applied using the calibrated HETP for each packing material, the experimental values for the temperatures and flow rates of the air and liquid inlet streams, and the inlet VOC gas concentration. Figure 4 shows the comparison between the outlet VOC gas concentration predicted by the model (continuous line) and the experimental ones (symbols) throughout the experimental period, together with the evolution of the inlet VOC gas concentration and the gas load factor, F . The model predictions showed trends similar to those found in the experimental data, and good agreement was observed for both Packings A and B. The average absolute relative

errors between the experimental and model values were $2.7 \pm 1.9\%$ and $2.6 \pm 1.7\%$ during Stages I and II, respectively. After Stage III, for the prototype testing, the packing materials were self-assembled into the scrubber to perform Stages IV and V, during which, the average absolute relative errors between experimental and model values were slightly higher: $5.4 \pm 4.0\%$ and $6.9 \pm 5.9\%$, respectively. During these stages, some data points presented large deviations from the model predictions, indicating that the performance of the scrubber could be affected by factors that included the creation of pathways after the self-assembling and growth of the biomass onto the packing surface during the long-term operation, which eventually produced clogging problems in the prototype. The model developed using an average value of N per packing material was able to predict the performance of an industrial prototype that treated VOC emissions that fluctuated in concentration and composition over 433 days with considerably lower differences between the experimental data and the model predictions.

<<Figure 4>>

3.3 Anaerobic reactor model calibration

The six kinetic parameters from the Monod-type kinetics expressions of the ET, E2P, and HAc were preliminarily fitted using a set of experimental data ($n = 5$) selected from the first 95 days of operation of the anaerobic reactor, covering a wide range of inlet OLs. Each inlet OL was derived from the difference between the inlet and outlet VOC air concentrations and was expressed as kg COD h^{-1} . Table 3 summarizes selected data about the experimental OL, CH_4 gas-flow rates, and VFA concentrations in the water effluent, along with the predicted values for methane production and VFA concentrations. According to a previous biodegradation experiment (Lafita et al., 2015),

the volumetric maximum growth rate of the E2P ($v_{\max,E2P}$) adopted was 8.26 times lower than the volumetric maximum growth rate of the ET ($v_{\max,ET}$). In addition, the same value was assumed for the half-saturation constants of the ET, E2P, and HAc (K_{ET} , K_{E2P} and K_{HAc}). This assumption was based on the typical range of half-saturation constants for acidogenic reactions, which ranged from 20–500 mg L⁻¹, and for methanogenic reactions, which ranged from 30–300 mg L⁻¹ (Grady et al., 2011). The preliminary adjustments to the parameters resulted in $v_{\max,ET}$ value of 0.490 kg COD h⁻¹ m³_{reactor}, $v_{\max,HAc}$ value of 0.105 m³ CH₄ h⁻¹ m³_{reactor}, and K value of 50 g COD m⁻³, with a calculated $v_{\max,E2P}$ value of 0.059 kg COD h⁻¹ m³_{reactor}. The difference between the experimental and model values shows an average absolute relative error in methane production and VFA concentrations of $7.7 \pm 7.5\%$ and $13.5 \pm 11.0\%$, respectively. The value obtained for the half-saturation constant is in the same order of magnitude that those found in the literature for the calibration of granular anaerobic reactors. For example, Hirata et al. (2000) calibrated a value of 17.41 g m⁻³ in the treatment of a simulated domestic wastewater in a fluidized bed biofilm reactor. Saravanan and Sreekrishnan (2008) obtained values between 140 and 800 g m⁻³ for the acidogenesis, acetogenesis and methanogenesis steps in the modeling of a hybrid anaerobic reactor with granules under fluidized conditions treating glucose wastewater. For the same steps, Odriozola et al. (2016) used similar range, within 100–500 g m⁻³, in the calibration of a dynamic model for predicting granule development in UASB reactors.

<<Table 3>>

A sensitivity analysis of the three adjusted parameters was performed by varying their values by up to $\pm 20\%$ (step size of 5%) to discern their effect on predicted methane production and VFA concentrations. Figure 5 presents results for OLs of 3 and 6 kg

COD h⁻¹. The $v_{\max,ET}$ and $v_{\max,HAc}$ were the most sensitive parameters, having more influence on the VFA concentrations. For example, when both parameters were changed by $\pm 20\%$, variations of up to 40% were observed in VFA concentrations and variations of up to 10% were observed in CH₄ production. Tartakovsky et al. (2008) validated the ADM1 model for an upflow anaerobic sludge bed reactor treating synthetic wastewater composed of sucrose, butyric acid, yeast extract, and ethanol. They found that the parameters having the largest effects were the maximum specific uptake rates and the half-saturation constants of acetate, propionate, and butyrate/valerate. In contrast, in the present study, the half-saturation constant fixed for the three kinetics was an insensitive parameter, since variations $< 5\%$ were obtained for changes of up to 20%. Therefore, the half-saturation constant was fixed at 50 g COD m⁻³, and $v_{\max,ET}$ and $v_{\max,HAc}$ were chosen as the parameters to be determined by model calibration using the first 95 days of the experimental data obtained in the industrial prototype (Stage I).

<<Figure 5>>

Experimental data included the water flow rate, the OL, T, pH, and alkalinity of the inlet stream; the biogas production, including its CH₄ composition; and the VFA concentrations in the exit stream. The solvent content of the inlet stream to the anaerobic reactor (VOCWAT-2) was set at the value of the solvent content of the exit stream of the scrubber (VOCWATER), which was estimated while validating the scrubber model. The minimization of the objective function that was defined in Eq. (4) resulted in a $v_{\max,ET}$ of 0.520 kg COD h⁻¹ m³_{reactor} and a $v_{\max,HAc}$ of 0.072 m³ CH₄ h⁻¹ m³_{reactor}. From the $v_{\max,ET}$, the $v_{\max,E2P}$ results in 0.063 kg COD h⁻¹ m³_{reactor}. Figure 6 shows the goodness-of-fit between the model prediction and the experimental data for biogas production and VFA concentrations in the water effluent. The simplified

process-simulation model developed by this study was able to predict biogas production with quite good correspondence (average absolute relative error $16.5 \pm 14.2\%$). Other authors have successfully used the strategy of implementing anaerobic digestion using several reactors connected in series in Aspen Plus[®] (Al-Rubaye et al., 2017; do Carmo Precci Lopes et al. (2017); Rajendran et al., 2014). In the case of VFA concentration, the model prediction followed the trend of the experimental data with relatively good correspondence for an OL $< 3 \text{ kg COD h}^{-1}$. For a higher OL, the model deviated from the experimental data values, although it was capable of showing that a VFA $> 150 \text{ mg HAc L}^{-1}$ was expected. Experimental VFA concentrations for an OL $> 3 \text{ kg COD h}^{-1}$ were more dispersed because they were caused by the accumulation when these high OLs were applied for more than one day. The model was developed under a steady state, so it could simulate the overproduction of VFA when the reactor was overloaded (increases from $150 \text{ mg HAc L}^{-1}$ at an OL of 3 kg COD h^{-1} to $450 \text{ mg HAc L}^{-1}$ at an OL of 6 kg COD h^{-1}), but it could not predict the accumulation of VFA in the system caused by intra days accumulation.

<<Figure 6>>

3.4 Anaerobic reactor model validation

The anaerobic reactor model was validated using the experimental data from days 96–484, providing 211 data points with which to check the model's validity (excluding non-working days and days without water-quality analyses). Figure 7 shows the comparison between the experimental data (symbols) and the model predictions (continuous line) regarding the main parameters used to analyze the anaerobic reactor's performance during the entire experimental period (days 0–484). It plots the OL feeding the reactor, the pH and VFA concentrations of the effluent, and the flow rate of the

biogas produced, including its methane composition. The model was able to successfully predict the performance of an anaerobic reactor with $\sim 9\text{m}^3$ of volume that was treating wastewater polluted with solvents and working under variable compositions and loads over more than one year. The average absolute error between the experimental biogas production and the model values was $19.6 \pm 18.9\%$. The agreement between the experimental and the predictive data shows the proposed model's ability to simulate both the characteristics of the effluent stream (pH, VFA concentration, and COD degradation, among others) and of the biogas stream (flow rate and composition). The deviations observed on some days for both the effluent VFA concentration and the methane percentage in the biogas can be explained by the transient behavior during periods of overload (days 39–64, 181–213, 277–279, and 406–481). The deviations in pH observed can be attributed to the defined electrolyte chemistry of the system, indicating that other acid/base species with effects on anaerobic digestion, including propionate and butyrate, should be included in future versions of the process-simulation model to better predict the pH. Other authors have also observed greater deviations in pH predictions when modeling the anaerobic process (Chen et al., 2009). Saravanan and Sreekrishnan (2008) in the model developed for a hybrid anaerobic reactor obtained good agreement between the experimental values of pH in the liquid phase and the predicted ones considering in its calculation the ionic equilibriums of acetic acid, propionic acid, butyric acid, carbonate, CO_2 , ammonium and phosphate. The novel approach of implementing the anaerobic reactor linked to a scrubber in the Aspen Plus[®] simulation was able to accurately simulate the performance of the system, indicating the approach's potential to predict behavior against changes in industrial emissions and its potential to optimize the process.

<<Figure 7>>

3.5 Process simulation of anaerobic bioscrubber: A design tool

The greatest potential of the process-simulation model developed in this work is to predict and simulate the performance of the two main units, the scrubber and the anaerobic reactor, of the novel technology anaerobic bioscrubber. Therefore, this model can be used to optimize and size anaerobic bioscrubbers under a wide range of conditions. To show the model's potential as a design tool, the present study included a case study in which the polluted air emission was set to a VOC concentration of 1129 mgC Nm⁻³ with a composition of 65.5% ET, 25.4% EA, and 9.1% E2P. Then, three 3-D figures were created for design purposes (Figure 8).

<<Figure 8>>

Figure 8 (a), used for sizing the scrubber, shows the relationship among the 3-D mesh of the predicted total RE of the scrubber and the gas load factor (F), the height of the packing material, and the superficial velocity of the absorbing stream (v_L). Figures 8 (b) and (c) were used for sizing the anaerobic reactor, and they plot the 3-D mesh of the predicted concentration of VFA and the biogas production per volume of the reactor, respectively, against the OLR, which is the OL per volume of the reactor, and the hydraulic retention time (HRT) of the reactor. Figure 8 (a) was used as follows: Once the flow rate and the VOC concentration of the industrial air emission were defined, the value of the RE was set (here, 90% was used, and is indicated by the gray plane) to establish a VOC outlet concentration level below the required value. Then, the 3-D graph was used to determine one of the three design parameters (scrubber diameter, height of the packing material and water-flow rate) when the other two were fixed. Next, the OL was calculated from the mass balance of the scrubber. Figure 8 (b) was used to define a maximum value of VFA concentration in the effluent stream (here, 200

mg HAc L⁻¹ was used, and is indicated by the gray plane) and used the water-flow rate derived from Fig 8 (a) to obtain the reactor volume from the resulting pairs of OLR and HRT. The flow rate of the scrubbing liquid (the anaerobic reactor operates in closed loop) could be changed to modify the HRT and thus the OLR. Then came an iteration process between Figures 8 (a) and 8 (b), in which the height of the packing material was adjusted to retain the RE. Finally, the biogas production was estimated using Figure 8 (c). When F was modified by changes in the industrial air emission, the design tool enabled determination of the main design parameters of the process: the scrubber's diameter and height, the water-flow rate of the absorbing stream, and the anaerobic reactor volume. In addition, the simulation-process model estimates the main characteristics of the liquid stream (pH, VFA concentration, alkalinity, etc.) and inlet and outlet gas streams (flow rate and composition). Therefore, this case study demonstrated the potential of the simulation model implemented in Aspen Plus[®] to aid in designing an anaerobic bioscrubber that converts VOC air emissions into bioenergy.

4 Practical Applications and Future Perspectives

The Aspen Plus[®] simulation model of the anaerobic bioscrubber presented herein was applied successfully to simulate the operation of an industrial installation treating VOC air emissions for more than one year, with good correspondence between the experimental and predicted performances of both main units. The tool developed can be used in a wide range of practical applications, including 1) studying the operational parameters affecting the performance of the system and obtaining system's response changes in these parameters, enabling identification of the variables that should be better controlled; 2) optimizing the system; and 3) as a tool for practitioners designing the anaerobic-bioscrubber process. Using this simulation-process model was cheaper than installing a pilot unit, so the model also saved time and money during preliminary

evaluations of application of this new biotechnology to the flexographic sector or in other industrial sectors. In addition, the process simulation model in Aspen Plus[®] enables to perform easily techno-economic analysis of the process as other authors have shown (García et al., 2017; Hammer et al., 2013), thus, this feature could be applied in future in the anaerobic bioscrubber model. However, the results obtained in this work had some limitations related to simulating transient behavior (no simulation of the VFA accumulation over multiple days) and selecting electrolyte chemistry (deviations in the pH predictions). Therefore, the Aspen Plus[®] model can be improved in future by extending additional components in electrolyte chemistry and by converting the model to a dynamic simulation, which would enable studying the transient response of the system and its stability against perturbations in the operational parameters. Regarding application of the anaerobic reactor simulation model in developing countries, as mentioned previously, its use saves money and time during the evaluation, optimization, and design stages. Circular economy aspects of anaerobic digestion of solid waste was previously discussed (Dahiya et al., 2018; European Commission, 2017; Gikas et al., 2017; Maina et al., 2017). The anaerobic-bioscrubber technology provides another example of circular-economy approach in which a diluted stream (VOC air emissions) is converted into a net output of bioenergy. This could be of interest in developing countries with tropical climates in which warm temperatures facilitate its expansion.

5 Conclusions

This study implemented a process-simulation model for an anaerobic bioscrubber in Aspen Plus[®]. The scrubber unit was successfully predicted using a constant height-to-theoretical-plate for two commercial packing materials. The anaerobic reactor was implemented using a series of stoichiometric and kinetic reactors, and its performance was simulated with a high level of correspondence. The model proved its ability as a

predictive tool and an aid in design, resulting in savings of time and money for practitioners. The approach proposed here can be expanded to other bioprocesses that need to be linked with unit operations.

6 Acknowledgments

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Table 1. Biodegradation reactions included in the model.

Compound	Chemical reaction
<i>Acidogenic reactions</i>	
Ethanol	$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 2H_2$
Ethyl acetate	$C_4H_8O_2 + H_2O \rightarrow C_2H_4O_2 + C_2H_6O$
1-Ethoxy-2-propanol	$C_5H_{12}O_2 + CO_2 + H_2O \rightarrow C_2H_6O + 2C_2H_4O_2$
<i>Methanogenic reactions</i>	
Acetic acid	$C_2H_4O_2 \rightarrow CH_4 + CO_2$
Hydrogen	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

Table 2. Experimental data and their model predictions for calibrating the scrubber unit.

Experimental											Model					
Data	F ^a	v _L ^b	T _a (°C) ^c	T _w (°C) ^c	C _{in,ET} ^d	C _{in,EA} ^d	C _{in,E2P} ^d	C _{out,ET} ^d	C _{out,EA} ^d	C _{out,E2P} ^d	C _{out,ET} ^d	C _{out,EA} ^d	C _{out,E2P} ^d	N _{ET} ^e	N _{EA} ^e	N _{E2P} ^e
Packing A																
1	2.3	12.6	40	25	887	287	97	61	210	3	60	209	4	1.00	0.85	0.98
2	2.0	15.3	40	25	1395	352	514	52	225	32	57	227	12	1.08	0.95	0.91
3	1.1	13.0	40	25	288	125	30	19	65	1	24	65	2	0.90	0.90	0.97
4	1.0	25.3	40	25	1797	1014	132	91	267	9	89	267	6	0.98	1.10	0.90
Packing B																
5	2.0	15.4	53	17	599	238	49	81	137	7	81	161	7	0.78	0.79	0.75
6	1.3	10.5	52	17	635	279	54	113	105	6	113	154	6	0.70	0.77	0.81
7	1.3	15.1	50	17	330	145	28	65	68	3	61	68	3	0.67	0.69	0.77
8	1.3	25.4	51	19	639	253	52	127	98	6	128	98	6	0.64	0.68	0.77

^aF: gas load factor, (m s⁻¹ (kg m⁻³)^{0.5})

^bv_L: superficial liquid velocity, (m h⁻¹)

^cT_a and T_w: temperature of inlet air and water stream, respectively, (°C)

^dAir solvent concentrations of inlet: C_{in} and outlet: C_{out}, (mgC Nm⁻³)

^eNumber of equilibrium stages per meter for each solvent

Table 3. Experimental data and their model predictions for preliminarily calibrating the anaerobic reactor.

Data	Experimental			Model	
	OL (kg COD h ⁻¹)	CH ₄ production (m ³ h ⁻¹)	VFA (mg HAc L ⁻¹)	CH ₄ production (m ³ h ⁻¹)	VFA (mg HAc L ⁻¹)
1	1.61	0.50	74	0.60	56
2	2.89	0.81	109	0.83	119
3	4.34	1.02	315	1.05	330
4	5.02	1.02	671	1.12	514
5	6.13	1.14	640	1.18	661

Figure Captions

Figure 1. Scheme of the anaerobic bioscrubber prototype.

Figure 2. Process flowsheet for the anaerobic bioscrubber in Aspen Plus[®]. (a) Scrubber unit, (b) Anaerobic reactor unit.

Figure 3. Sensitivity analysis of the scrubber model. (a) Change in the number of equilibrium stages per meter, (b) change in the proportion of each solvent.

Figure 4. Experimental evolution of the scrubber's inlet and outlet air VOC concentrations and the gas load factor (F), along with the model predictions.

Figure 5. Sensitivity analysis of the anaerobic reactor model based on changes in kinetic parameters for OLs of 3 and 6 kg COD h⁻¹.

Figure 6. Comparison between the experimental and the modeled biogas production and VFA concentrations from the model's calibration.

Figure 7. Experimental evolution of the OL feeding of the reactor, the pH and VFA concentrations of the effluent, and the flow rate of the biogas produced, including its methane composition, along with the model's simulations.

Figure 8. 3-D figures for anaerobic bioscrubber design. (a) Scrubber unit: 3-D mesh of removal efficiency against the gas load factor (F), the height of the packing material, and the superficial velocity of the absorbing stream (v_L). (b) and (c) Anaerobic reactor: 3-D mesh of the VFA concentration and biogas production per volume of the reactor, respectively, against the organic loading rate (OLR) and the hydraulic retention time (HRT).

Figure 1 (1 column)

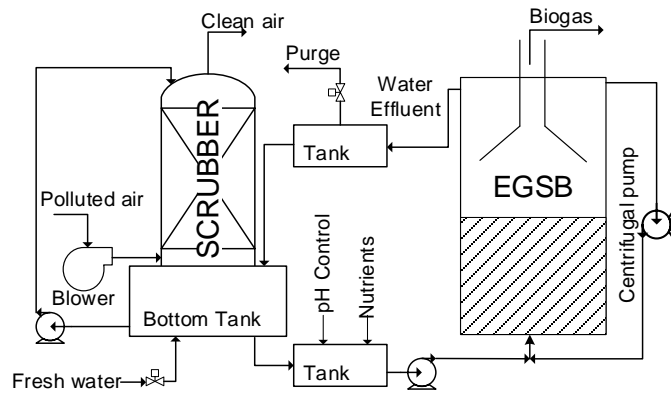
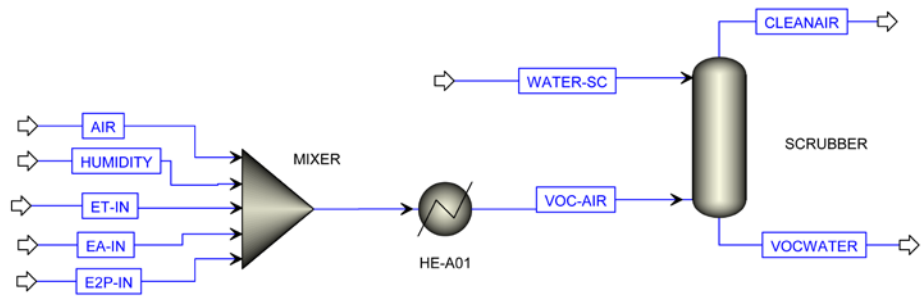


Figure 2 (1.5 column)

a)



b)

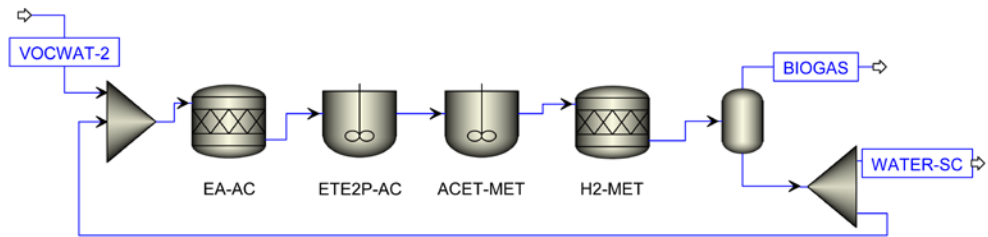


Figure 3 (1 column)

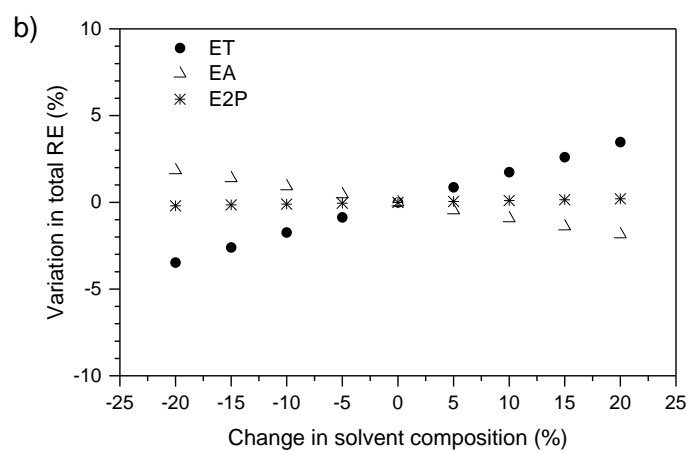
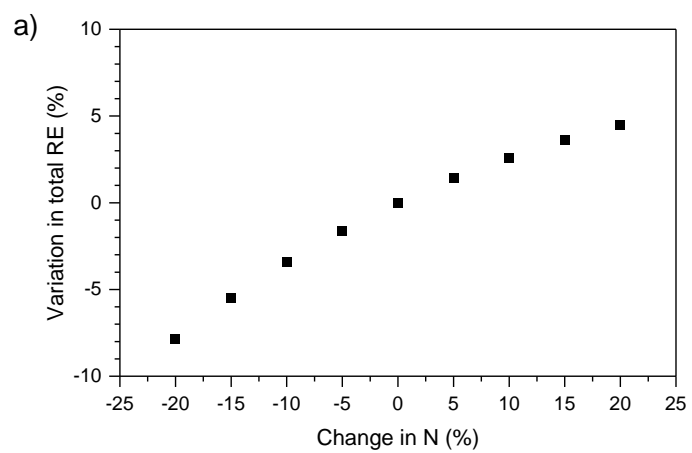


Figure 4 (1.5 column)

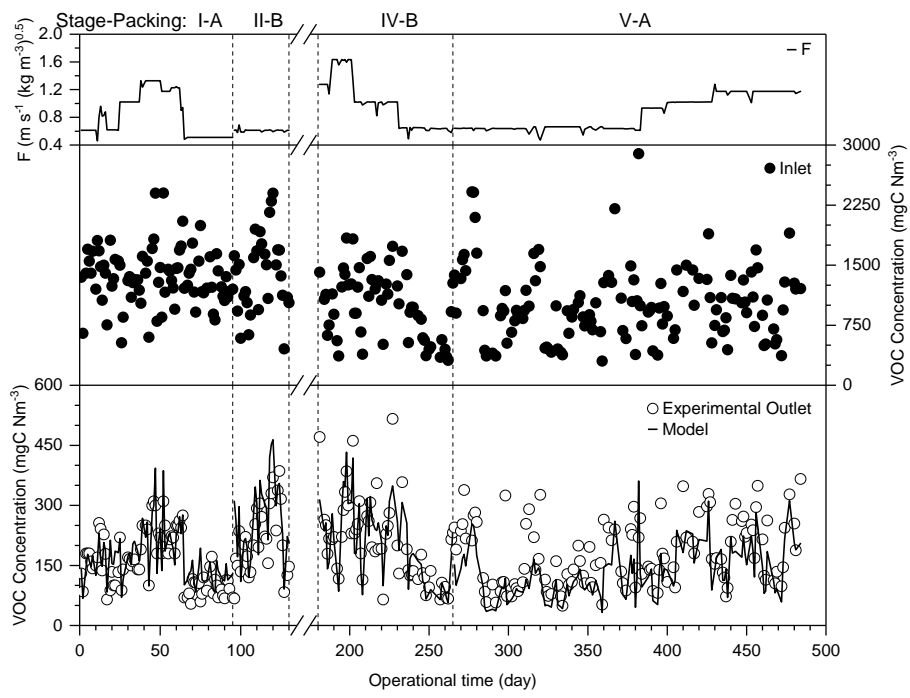


Figure 5 (1.5 column)

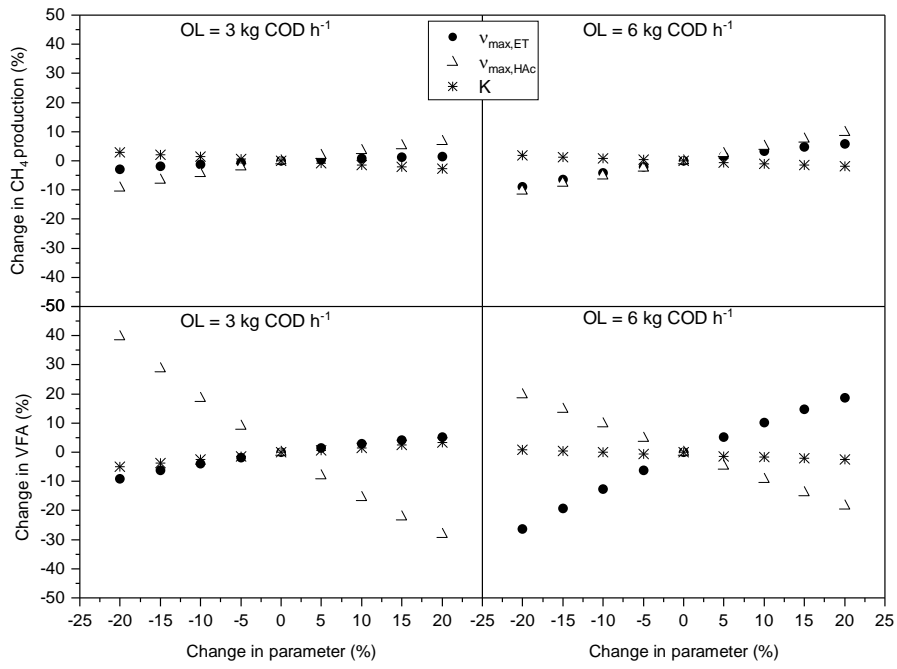


Figure 6 (1 column)

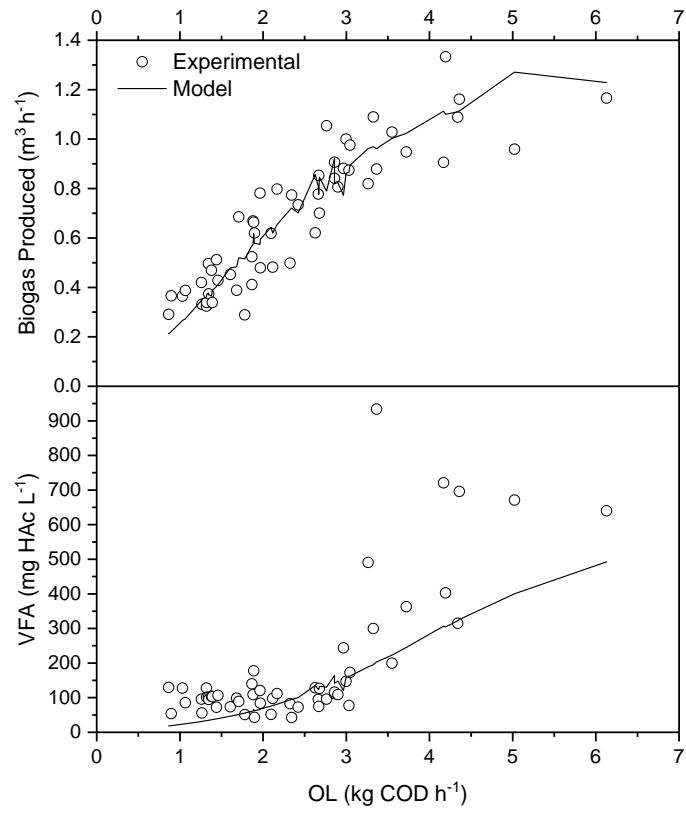


Figure 7 (1 column)

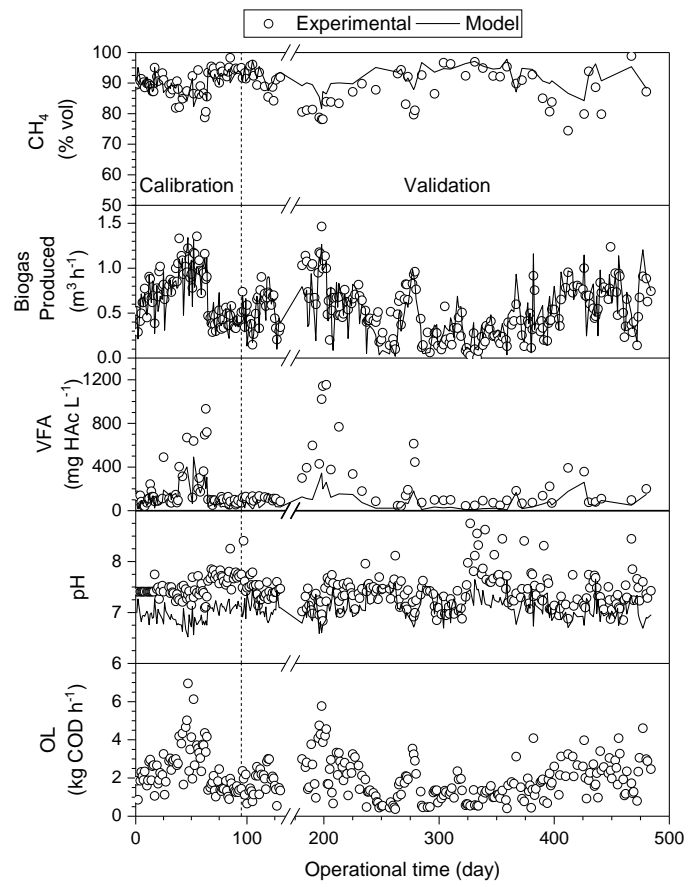
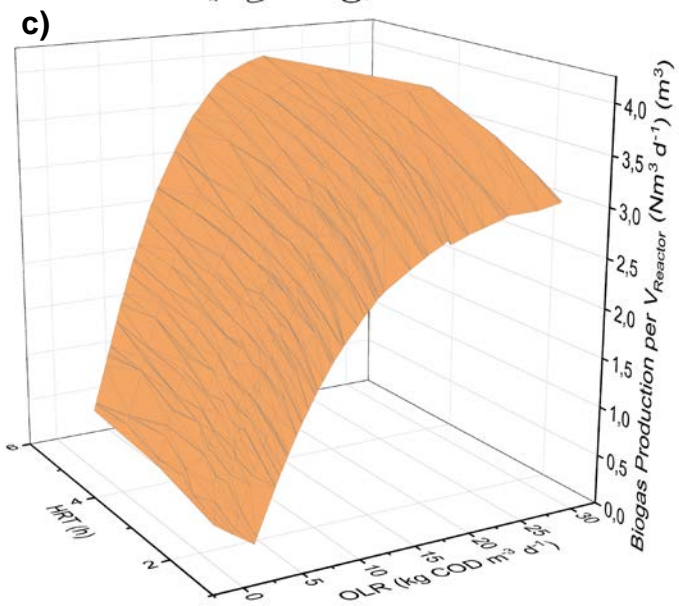
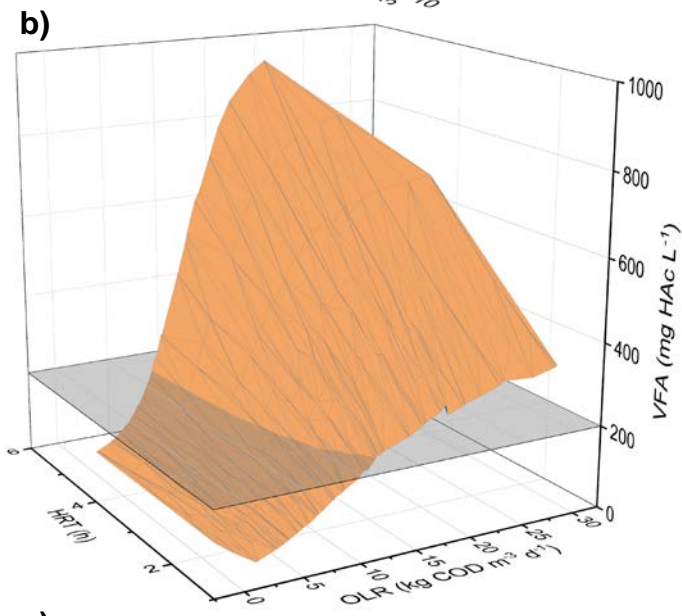
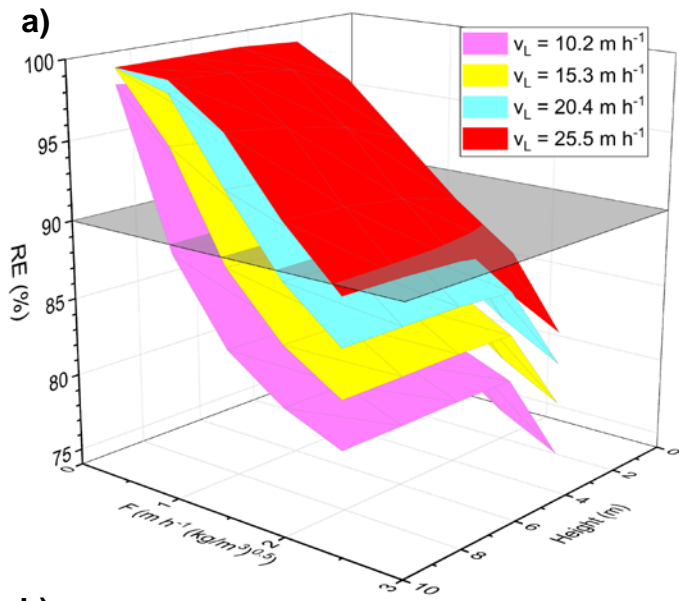


Figure 8 (1 column)



Supplementary material

Links to the e-brochures of the commercial packing materials:

- Packing A: cross-flow structured packing material, KFP 319/619, ENEXIO, Germany.

http://www.enexio.com/fileadmin/user_upload/media/2h_components_solutions/GB-2H-PLASdek-Cross-fluted-fills.pdf

- Packing B: vertical-flow structured packing material KVP 323/623, ENEXIO, Germany.

http://www.enexio.com/fileadmin/user_upload/media/2h_components_solutions/GB-2H-PLASdek-Vertical-Flow-Fills.pdf

Table Sup1. Electrolyte chemistry and biodegradation reactions considered in the Aspen Plus[®] model.

Electrolyte chemistry reactions	
<i>Equilibrium</i>	$C_2H_4O_2 + H_2O \leftrightarrow CH_3COO^- + H_3O^+$
<i>Equilibrium</i>	$HCl + H_2O \leftrightarrow Cl^- + H_3O^+$
<i>Equilibrium</i>	$HCO_3^- + H_2O \leftrightarrow CO_3^{2-} + H_3O^+$
<i>Equilibrium</i>	$CO_2 + 2H_2O \leftrightarrow HCO_3^- + H_3O^+$
<i>Equilibrium</i>	$2H_2O \leftrightarrow OH^- + H_3O^+$
<i>Salt</i>	$NaOH_{(s)} \leftrightarrow OH^- + Na^+$
<i>Salt</i>	$C_2H_3NaO_{2(s)} \leftrightarrow CH_3COO^- + Na^+$
<i>Salt</i>	$C_2H_3NaO_2 \cdot 3H_2O_{(s)} \leftrightarrow CH_3COO^- + Na^+ + 3H_2O$
<i>Salt</i>	$NaOH \cdot H_2O_{(s)} \leftrightarrow H_2O + OH^- + Na^+$
<i>Salt</i>	$NaHCO_{3(s)} \leftrightarrow HCO_3^- + Na^+$
<i>Salt</i>	$C_4H_3Na_5O_{12(s)} \leftrightarrow CO_3^{2-} + 3HCO_3^- + 5Na^+$
<i>Salt</i>	$C_2H_3Na_3O_{8(s)} \leftrightarrow CO_3^{2-} + HCO_3^- + 2H_2O + 3Na^+$
<i>Salt</i>	$Na_2CO_3 \cdot 10H_2O_{(s)} \leftrightarrow CO_3^{2-} + 2Na^+ + 10H_2O$
<i>Salt</i>	$Na_2CO_3 \cdot 7H_2O_{(s)} \leftrightarrow CO_3^{2-} + 2Na^+ + 7H_2O$
<i>Salt</i>	$Na_2CO_3 \cdot H_2O_{(s)} \leftrightarrow CO_3^{2-} + 2Na^+ + H_2O$
<i>Salt</i>	$Na_2CO_{3(s)} \leftrightarrow CO_3^{2-} + 2Na^+$
<i>Salt</i>	$NaCl_{(s)} \leftrightarrow Cl^- + Na^+$
Biodegradation reactions	
<i>Ethanol</i>	$C_2H_6O + H_2O \rightarrow C_2H_4O_2 + 2H_2$
<i>Ethyl Acetate</i>	$C_4H_8O_2 + H_2O \rightarrow C_2H_4O_2 + C_2H_6O$
<i>1-Ethoxy-2-propanol</i>	$C_5H_{12}O_2 + CO_2 + H_2O \rightarrow C_2H_6O + 2C_2H_4O_2$
<i>Acetic acid</i>	$C_2H_4O_2 \rightarrow CH_4 + CO_2$
<i>Hydrogen</i>	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$