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Influence of Autogenerative Final Pressure on the Specific Methanogenic Yield in a High-Pressure Anaerobic Digestion Process

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In recent years, the development of renewable energy and the improvement of technologies for its production has aroused particular interest. In this perspective, pressurised anaerobic digestion (PAD), i.e. the anaerobic digestion process occurring at a pressure higher than the atmospheric one, has attracted significant attention. PAD enables the production of pressurised biogas, reducing energy costs required for biogas upgrading and injection into the distribution grid. In addition, PAD presents the advantage that by increasing pressure, the solubilisation of CO_2, as compared to CH_4, increases, resulting in the production of biogas with a high content of CH_4 (v/v% $CH_4 \geq 90\%$). Furthermore, results in the literature reported the potential of the autogenerative PAD, in which biogas accumulates in the headspace of the reactor and leads to a gradual increase in autogenerated pressure. In this research, the effect of autogenerated final pressure on the specific methanogenic yield (SMY) was investigated by simulating an autogenerative PAD process of sodium acetate and using a modified ADM1 (Anaerobic Digestion Model No 1) model in batch mode; moreover, the kinetic parameters of the process were assessed. Simulation results showed a good agreement with experimental results and highlighted that SMY increases by increasing the autogenerated final pressure.

1. Introduction

Anaerobic Digestion (AD), consisting of a biological process that converts biodegradable substrates into biogas in the absence of oxygen, is such a process that can reduce the volume and mass of input material and convert this wastage into renewable energy; it does not release any carbon and produces methane-rich biogas which can potentially replace the fossil fuel (Chowdhury, 2021; Zhang et al., 2014).

Additionally, AD produces a nutrient-rich leftover solid and liquid which can be used as a fertilizer for the soil, improving the quality of soil and reducing the use of fertilizers and insecticides for crops (Chowdhury, 2021). So the anaerobic digestion of biodegradable substrates reduces the organic waste from the environment, reduces the greenhouse effect and energy, and beneficial agricultural soil can be recovered (Di Trapani et al., 2019). AD can be developed for different temperature ranges. Conventional anaerobic digestion is carried out at mesophilic temperatures (35°C - 37°C), while the thermophilic temperature (50°C - 60°C) range is worth considering because it will lead to faster reaction rates, higher gas production, and higher rates of the destruction of pathogens and weed seeds than the mesophilic temperature range (Kim et al., 2006). Furthermore, the biogas resulting from AD, mainly composed of methane and carbon dioxide, can be used in internal combustion engines to produce electrical and/or thermal energy (Lombardi et al., 2020; Mao et al., 2015).

The organic waste can be anaerobically digested to methane and subsequently to electricity, with a 33% efficiency, resulting in a potential energy content of 3.6 x 10^6 kWh per kton of organic waste annually treated (Lindeboom et al., 2011).

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Currently, most Italian biogas plants produce electricity even though recent political incentives are promoting biomethane from biogas through its "upgrading" (Murano et al., 2021). In fact, by separating CO_2 from biogas, it is possible to produce biomethane containing high CH_4 gas content ($CH_4 \geq 95\%$) (Ullah Khan et al., 2017; Miltner et al., 2017) and to use it as a substitute for natural gas. Several biogas-upgrading techniques separate CO_2 from CH_4, such as pressure swing adsorption, scrubbing, cryogenic and membrane separations (Martín-Hernández et al., 2020; Baena-Moreno et al., 2020; Molino et al., 2013; Lombardi et al., 2020).

In the last years, particular attention has been paid to pressurised anaerobic digestion (PAD), which consists of an AD occurring at a pressure higher than the atmospheric one that can be achieved in continuous reactors (Gómez Camacho et al., 2019) or batch reactors by the addition of external gas (i.e. N_2 or CO_2), or by accumulating biogas, which leads to a gradual increase in autogenerated pressure in the headspace of the reactor (Autogenerated High pressure Digestion, AHPD) (Lindeboom et al., 2013; Postawa et al., 2021). The higher pressure enables the production of biogas with higher concentrations of methane, even reaching 90%, thanks to the increase of the solubilisation of CO_2, as compared to CH_4 (Bär et al., 2018), which remains in the liquid solution.

AD is a well-established process, but reaching the maximum yields is very challenging due to the substrate variability, microbial consortia complexity, as well as the complicated biochemical, physical and chemical interactions involved in the process (Mulka et al., 2016; Donoso-Bravo et al., 2011), including mass transfer.

The complex mechanisms of the PAD process require modelling investigations that lead to a better understanding and prediction of the behaviour of pressurized digesters, and ultimately design improvements could be proposed. Among existing AD models, the anaerobic digestion model No.1 (ADM1) by Batstone et al., (2002) is the most studied and used for modelling anaerobic digestion processes. Nevertheless, few works simulating the PAD processes in continuous or semi-continuous reactor systems are reported in the literature (Wonneberger, A. M.; Lemmer, A; Chen, Y.; Reimert, 2014; Wonneberger et al., 2011; Scamardella et al., 2019; Bär et al., 2018; Postawa, 2018; Budzianowski et al., 2017; Vavilin et al., 1995), while the PAD in batch reactors has not been specifically simulated in a dynamic modelling framework like the ADM1. De Crescenzo et al. (2022) proposed a model in the batch configuration to predict the dynamic performance of AHPD of acetate as the representative compound of the last step in AD, i.e. the aceticlastic methanogenesis. The model was developed, calibrated, and validated on experimental results by Lindeboom et al. (2011). The model was used to assess the Monod maximum specific uptake rate constant and the half-saturation constant for acetate, and the decay rate constant of microorganism species.

In this research, AHPD process parameters were assessed by simulating experimental conditions of Experiment No. 6 by Lindeboom et al. (2011) and using the modified ADM1 model for autogenerative PAD in batch mode by De Crescenzo et al. (2022).

The model parameters were used to assess the effect of autogenerated final pressure on the specific methanogenic yield (SMY). The simulations were performed at 308.15 K, with a reactor volume of 1.68 L, headspace volume of 0.01 L, and substrate concentration of $14g_{\text{sodium acetate COD}}/L$. Different autogenerated final pressures (40 bar, 58 bar, 80 bar, and 100 bar) were simulated by varying the run time until the autogenerated final pressure was reached.

2. Models and methods

2.1 Equations and parameters of the Autogenerative Pressurised Anaerobic Digestion Modelling

The AD process constitutes a complex system of biochemical series-parallel reactions, which include fast liquid-liquid reactions, i.e. ion association and dissociation reactions; medium-high rates gas-liquid reactions, i.e. gas transfer and medium-low rates liquid-solid reactions, i.e. precipitation and solubilisation of ions. The original ADM1 model included the first two types of reactions and was extended with a module on chemical speciation and precipitation (Flores-Alsina et al., 2016).

The PAD of acetate in a batch reactor under autogenerative regime was simulated by De Crescenzo et al. (2022) by modifying the ADM1 model from a continuous regime to a discontinuous one since the original structure of the ADM1 model was based on the AD of a substrate in a CSTR reactor

The model for acetate digestion consists of eight differential equations in six state variables and two additional variables linked to liquid–gas mass transfer: a soluble substrate (sodium acetate) S_{ac} (kgCOD m^{-3}), soluble methane S_{CH4} (kg_{COD} m^{-3}), soluble inorganic carbon S_{IC} ($kmol_C$ m^{-3}), particulate matter (aceticlastic methanogens) X_{ac} (kg_{COD} m^{-3}), soluble acetate ions S_{ac-} (kg_{COD} m^{-3}), soluble hydrogen carbonate S_{HCO_3-} (kg_{COD} m^{-3}), CH_4 in the gas phase $S_{gas,CH4}$ (kg_{COD} m^{-3}), and CO_2 in the gas phase $S_{gas,CO2}$ ($kmol_C$ m^{-3}).

The following equations describe the biochemical reactions and mass transfer from liquid to gas occurring in the liquid phase in a discontinuous reactor (De Crescenzo et al., 2022)

$$\frac{\mathrm{dS_{ac}}}{\mathrm{dt}} = -\rho_1 \tag{1}$$

$$\frac{\mathrm{dS_{CH_4}}}{\mathrm{dt}} = \nu_{1,s_{CH_4}} \cdot \rho_1 - \rho_{\mathrm{T_{CH_4}}} \tag{2}$$

$$\frac{\mathrm{dS_{IC}}}{\mathrm{dt}} = -(\nu_{1,S_{IC}} \cdot \rho_1) - \rho_{\mathrm{T_{CO_2}}} \tag{3}$$

$$\frac{\mathrm{dX_{ac}}}{\mathrm{dt}} = \nu_{1,Xac} \cdot \rho_1 - \nu_{2,Xac}\,\rho_2 \tag{4}$$

$$\frac{\mathrm{dS_{ac-}}}{\mathrm{dt}} = -\rho_{\mathrm{A_{ac}}} \tag{5}$$

$$\frac{\mathrm{dS_{HCO_3^-}}}{\mathrm{dt}} = -\rho_{\mathrm{A_{HCO_3^-}}} \tag{6}$$

Two liquid-gas dynamic equations for CH_4 and CO_2 for a discontinuous reactor are written as in the following:

$$\frac{\mathrm{dS_{gas,CH_4}}}{\mathrm{dt}} = \rho_{\mathrm{T_{CH_4}}} \cdot \frac{\mathrm{V_{liq}}}{\mathrm{V_{gas}}} \tag{7}$$

$$\frac{\mathrm{dS_{gas,CO_2}}}{\mathrm{dt}} = \rho_{\mathrm{T_{CO_2}}} \cdot \frac{\mathrm{V_{liq}}}{\mathrm{V_{gas}}} \tag{8}$$

Rates ρ_j of the *j-th* process and the stoichiometric coefficients $\nu_{i,j}$ of *i-th* component in *j-th* process of equations (1)-(8) are explicated in the Petersen matrix reported in Table 5 of De Crescenzo et al. (2022).
p_{CH4} and p_{CO2} (bar) are CH_4 and CO_2 partial pressures in biogas, respectively, and are calculated according to the state equation of ideal gases.
V_{liq} and V_{gas} (m^3) are the volumes of the liquid and the gas in the reactor, respectively.
The equations mentioned above differ from the ADM1 model because they do not consider inlet and outlet liquid flows and biogas outlet flow since they are written for a discontinuous reactor to simulate the autogenerative pressurized environment.
The pH was kept constant at 7, as was experimentally highlighted by Lindeboom et al.(2012).
All the parameters used in the model simulations were assumed or calculated according to the scientific literature (Nguyen, 2014; Danielsson, 2014; Rosen et al., 2006; Batstone et al., 2002).

2.2 Process simulation

The initial amount of acetate substrate (S_{ac}) was set equal to $14\mathrm{g}_{\text{sodium acetate COD}}\ \mathrm{L}^{-1}$, according to the Experiment No. 6 by Lindeboom et al. (2011); the particulate composite matter (X_{ac}) was assumed equal to 0.5% of the total sodium acetate substrate; $S_{gas,CH4}$ and $S_{gas,CO2}$ were zero. Simulations were performed by implementing the model equation system in the MATLAB environment (MATLAB R2021). The simulations were performed at 308.15 K, with a reactor volume of 1.68 L and a headspace volume of 0.01 L. The values of autogenerated final pressures simulated are 40 bar, 58 bar, 80 bar, and 100 bar. Run time was varied until the autogenerated final pressure was reached and was set equal to 68 h, 96 h, 127 h, and 153 h, respectively.
The ADM1 kinetic parameters obtained from the calibration of the model and used for the present simulations are $k_{m,ac} = 5.9\ \mathrm{kg_{COD}\ (kg_{COD}\cdot d)^{-1}}$, $K_{S,ac} = 0.05\ \mathrm{kg_{COD}\ m^{-3}}$ and $k_{dec,Xac} = 0.02\ \mathrm{d^{-1}}$ (De Crescenzo et al., 2022).
The above-mentioned parameters were added to the equations allowed to solve the problem.
The SMY was calculated according to the following equation (Lemmer et al., 2017):

$$SMY = \frac{\mathrm{n_{gas,CH4}\ R\ T_{STP}}}{\mathrm{P_{STP}\ S_{COD\ added}}} \tag{9}$$

where $n_{gas,CH4}$ is the CH_4 mole number in accumulated gas (kmol), T_{STP} is the standard temperature (273.15 K) and P_{STP} standard pressure (1 bar), R is the ideal gas constant (0.083145 bar M^{-1} K^{-1}), and $S_{COD\ added}$ (0.0234 kgCOD) is the mass of COD added to the reactor.

3. Results and discussion

Simulation results showed that the higher the run time, the higher the biogas accumulated and the pressure in the reactor headspace. Consequently, CH_4 concentration in the biogas increased because of the reduced solubilisation of CH_4 compared to CO_2.

$n_{gas,CH4}$ and $n_{gas,CO2}$ the CH_4 and CO_2 mole numbers, respectively, in accumulated gas as a function of the autogenerated final pressure in the headspace, are reported in Table 1

Table 1: CH_4 mole number in gas accumulated in the headspace

	Autogenerated final pressure [bar]			
	40	58	80	100
$n_{gas,CH4}$ [kmol]	1.54e-5	2.16e-5	2.91e-5	3.97e-5
$n_{gas,CO2}$ [kmol]	7.56E-07	1.06E-06	1.43e-6	1.94e-6

For all cases simulated, CH_4 and CO_2 volume fraction in the accumulated biogas is about 95.3% and 4.7%, respectively. This achievement agrees with the experimental results (Lindeboom et al., 2011; Bär et al., 2018; Merkle et al., 2017).

In particular, SMY resulted in being equal to 15 $L_{CH4}/kg_{sodium\ acetate,COD}$, 21.3 $L_{CH4}/kg_{sodium\ acetate,COD}$, 28.3 $L_{CH4}/kg_{sodium\ acetate,COD}$, and 38.5 $L_{CH4}/kg_{sodium\ acetate,COD}$ for autogenerated final pressure in the headspace equal to 40 bar, 58 bar, 80 bar, and 100 bar, respectively. In addition, SMY from simulations are confirmed by the experimental one obtained by Lindeboom et al. (2011); in particular, simulated SMY with an autogenerated final pressure equal to 58 bar (21.3 $L_{CH4}/kg_{sodium\ acetate,COD}$) matches the experimental value of 21.5 $L_{CH4}/kg_{sodium\ acetate,COD}$.

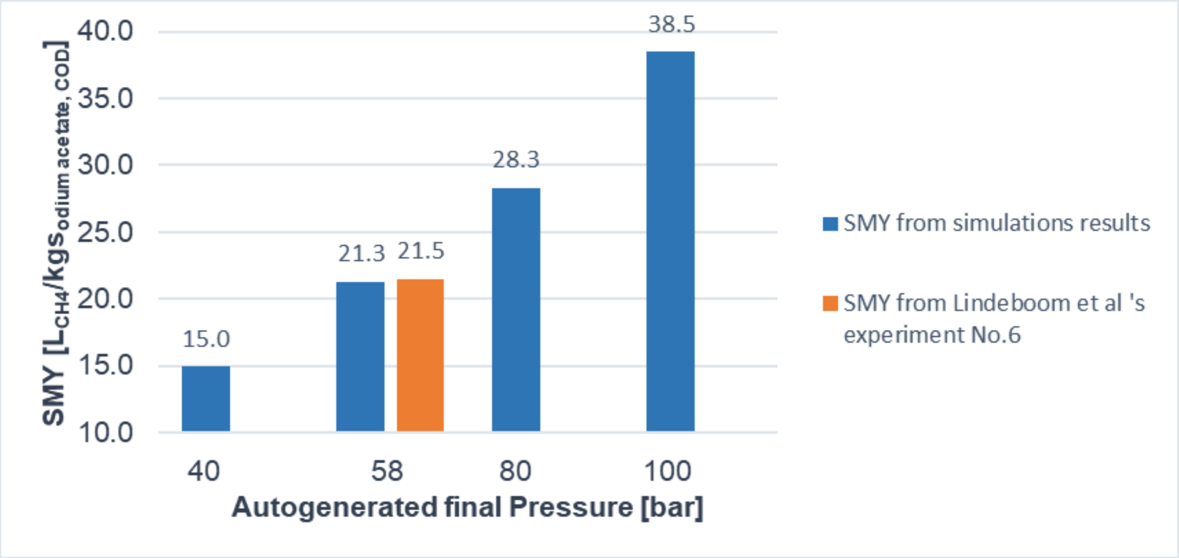

Figure 1: Effect of autogenerated final pressures on SMY

4. Conclusions

The modified ADM1 model for autogenerative PAD in batch mode allows for assessing the kinetic parameters of the process. Moreover, it is possible to evaluate the variation of the autogenerated pressure as a function of the runtime and the composition of the pressurized biogas. For all cases investigated, the volume fraction of the CH_4 and CO_2 in the accumulated biogas is about 95.3% and 4.7%, respectively. Simulations for different run times and, consequently, for different autogenerated final pressure showed an increasing SMY with a higher value of final pressure in the headspace of the digester. The simulated SMY equal to 21.3 $L_{CH4}/kg_{sodium\ acetate,COD}$ for a pressure value of 58 bar resulted in being in agreement with experimental results obtained by Lindeboom et al. (2011) that was found to be equal to 21.5 $L_{CH4}/kg_{sodium\ acetate,COD}$.

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