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Simulation and Optimization of Pressurized Anaerobic Digestion and Biogas Upgrading using Aspen Plus

Davide Scamardella[a], Carmen De Crescenzo[a,*], Antonia Marzocchella[a], Antonio Molino[b], Simeone Chianese[a], Vincenzo Savastano[c], Raffaele Tralice[c], Despina Karatza[a], Dino Musmarra[a]

[a]Department of Engineering, University of Campania “Luigi Vanvitelli”, Via Roma, 29 - 81031 Aversa, Italy
[b]Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Territorial and Production System Sustainability Department, CR Portici Piazzale Enrico Fermi, 1 - 80055, Portici, Italy
[c]Edilgen S.p.a., Via del Pascone, 8/A – 80143, Napoli, Italy
carmen.decrescenzo@unicampania.it

Anaerobic digestion is a technology used to biologically convert organic substrates into biogas in the absence of oxygen. The resulting biogas is a renewable energy source mainly consisting of a mixture of methane (60÷70% v/v) and carbon dioxide (30÷40% v/v), with traces of some minor compounds, such as H_2S and NH_3. Anaerobic digestion takes place through a sequence of four biological phases - hydrolysis, acidogenesis, acetogenesis, and methanogenesis - performed by the action of particular species of bacteria. Operating parameters such as temperature, pH, pressure and organic substrates govern the process and affect the starting biomass transformation and the content of methane into the biogas. The biogas from anaerobic digestion can be upgraded to biomethane by removing CO_2 and the minor compounds. The techniques commonly used for this purpose, like pressure swing adsorption and membrane separation, are energy-intensive as they require the compression of biogas. In this paper, an innovative energy-saving approach for biogas production and its upgrading to biomethane is proposed. The concept is based on anaerobic digestion carried out at a pressure higher than the atmospheric one, called pressured anaerobic digestion (PAD), in order to directly produce high pressure biogas that can be upgraded to high pure biomethane ($CH_4 \geq 95\%$ v/v) avoiding the compression phase during the upgrading. The variation of the main operating parameters has been simulated in order to investigate their effect on biomethane production and composition and to define the best operating conditions. The simulation of the process has been carried out by using Aspen Plus®.

1. Introduction

Environmental pollution is one of the main problems that society faces today, and scientific and technological research is looking for a solution which could allow to reduce contamination and to produce sustainable energy (Molino et al., 2018). One of the most performing processes is represented by Anaerobic Digestion (AD), which produces biogas from the degradation of solid organic waste and biomass, through four biological steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis in which hydrolytic, fermentative bacteria, acetogens and methanogens play distinct roles and differ in physiology, nutritional needs, growth kinetics, and sensitivity to environment (Bonga et al., 2017; González et al., 2018). The biogas is mainly composed by methane (CH_4) and carbon dioxide (CO_2), with traces of other gaseous compounds in concentration depending on the composition of the substrate digested (Adekunle and Okolie, 2015).

The biogas can be used for combined heat and power (CHP) generation or can be upgraded to produce biomethane ($CH_4 \geq 95\%$ v/v), that can be fed in existing natural gas pipelines, after pressurization, or used as vehicle fuel or in fuel cells (Al Seadi et al., 2008). The upgrading of biogas to biomethane consists in removing CO_2 from raw biogas (Barbera et al., 2019; Pellegrini et al., 2015). One of the most used technologies for upgrading biogas is membrane separation, which allows to remove H_2S, CO_2, and other minor compounds forcing biogas to pass through a semipermeable membrane in order to separate CH_4 from the rest of the

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gaseous products (Molino et al., 2016). The driving force of the system is represented by the different partial pressures of compounds (Wellinger et al., 2013). Selected materials for membranes' production able to separate CO_2 and CH_4 are cellulose acetate and polyimide (Angelidaki et al., 2018). Membrane separation represents a very effective process to remove CO_2, H_2S, and other pollutants and exhibits several advantages: fitting to different size of plants; low cost of polymeric material; capability to be used to increase both purity and recovery of CH_4 (Molino et al., 2016). Since the biogas upgrading is a very high energy consumption process, the pressured anaerobic digestion (PAD) could represent a cost-effective technology. PAD process consists of an anaerobic digestion carried out at a pressure higher than the atmospheric one (1.5-5 bar). In this configuration, biogas upgrading uses the pressure at which it is directly available to remove the polluting mixtures and to produce biomethane, fitting characteristics both for the use for vehicles and for the injection into the distribution grid by significantly reducing costs related to the compression of the biomethane. Simulations of both PAD and membrane separation processes have been carried out by using Aspen Plus® software, in order to investigate the effect of variation of anaerobic digestion pressure and temperature on biomethane composition and production.

2. Models and methods

2.1 PAD model

PAD was simulated by means of RCSTR using Aspen Plus® V10 software. RCSTR models a continuous-stirred tank reactor (Aspen Plus® User Guide, 2000). Reaction kinetics were obtained from previous ADM 1 model, which was investigated by several research groups (Angelidaki et al., 1999; Batstone et al., 2002; Rajendran et al., 2014). ELECNRTL method was used for rigorously modeling electrolyte systems and it allowed to simulate dissociation equilibria that affect the CO_2 solubility in the liquid phase, according to the following reactions (Flagiello et al., 2018; Oh and Martin, 2007)

$$CO_{2(l)} \leftrightarrows CO_{2(g)} \tag{1}$$

$$2H_2O \leftrightarrows H_3O^+ + OH^- \tag{2}$$

$$CO_{2(l)} + 2H_2O \leftrightarrows HCO_3^- + H_3O^+ \tag{3}$$

$$HCO_3^- + H_2O \leftrightarrows CO_3^{2-} + H_3O^+ \tag{4}$$

In order to evaluate the composition of the biogas obtained by PAD, the main compounds reported in literature as intermediate and final products of the hydrolysis, acidogenesis, acetogenesis, and methanogenesis reactions, are selected in Aspen Plus®. A schematic diagram of RCSTR used for simulations is represented in Figure 1.

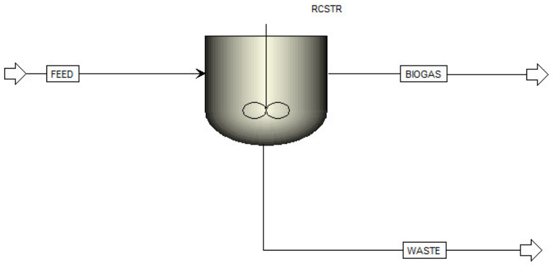

Figure 1: Schematic diagram of RCSTR

In Table 1 input parameters of PAD reactor are reported. Feeding composition was kept constant and detailed in Table *2*, while operating pressure and temperature were varied in the range 1.5-5 bar and 35-45 °C (mesophilic condition), respectively.

Table 1: *PAD input parameters*

Reactor volume [m^3]	Feeding mass flow [t/d]	Operating pressure [bar]	Temperature [°C]	Retention time [d]
60	2	1.5-5	35-45	30

In this validation, fruit waste was used as a substrate in the reactor with following composition:

Table 2: *Feeding composition*

Sugar [% w/w]	Protein [% w/w]	Fatty acids [% w/w]	Water [% w/w]	Others [% w/w]
42	5.8	1.2	49.9	1.1

2.2 Membrane separation

In gas separation processes gas components are separated according to different gas permeability of membrane materials. Aspen Plus® enables to simulate membrane separation using a user-defined model (user 2 block), interfacing the block with an Excel file.

Biogas upgrading by membrane separation process was simulated by means of Fick's law with diffusive model assumptions. In Figure 2, a schematic diagram of membrane system is represented. From membrane, two streams are produced: the retentate, which is the CH_4-rich gaseous stream at a pressure close to the biogas pressure value; and the permeate, which is the CO_2-rich gaseous stream and the off-gas of the process (Wellinger et al., 2013).

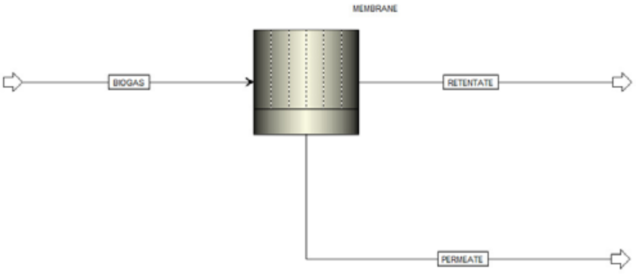

Figure 2: Schematic diagram of membrane system

The main parameters used to determine the efficiency of the separation of methane from the biogas are the CH_4 recovery (η), defined as the ratio between the CH_4 flow in retentate and the CH_4 flow in biogas fed to the membrane, and the purity of retentate flow, i.e. the CH_4 volumetric concentration (y_R). Another key parameter used to design gas separation membrane process is the membrane selectivity, which is the ratio of permeabilities of the components to be separated. It depends on the membrane materials to be used. For this study, separation of CO_2 and CH_4 occurred by using a PEK-A membrane with a selectivity of 28.6 (Molino et al., 2013). CH_4 recovery (η) was assumed equal to 30%.

3. Results and discussion

In this work the effects of variation of pressure (1.5-5 bar) and temperature (35°C-45°C) of PAD on biomethane production and composition were investigated. In Table 3, biogas and liquid waste flow rates resulting from PAD process are reported. In addition, biogas productivity, i.e. ratio between produced biogas and feeding flow rate, is shown. As it can be seen, produced biogas decreases with higher pressure values; meanwhile it increases with increasing of temperature. The liquid waste does not exhibit relevant variation varying temperature and pressure of the process.

Table 3: Biogas, liquid waste flow rates and biogas productivity from PAD

	T=35°C			T=40°C			T=45°C		
Pressure [bar]	Biogas [Nm^3/d]	Liquid waste [t/d]	Biogas Productivity [Nm^3/t]	Biogas [Nm^3/d]	Liquid waste [t/d]	Biogas Productivity [Nm^3/t]	Biogas [Nm^3/d]	Liquid waste [t/d]	Biogas Productivity [Nm^3/t]
1.5	149	1.89	74.5	152	1.89	76.0	157	1.88	78.5
2.0	144	1.90	72.0	148	1.89	74.0	154	1.89	77.0
3.0	135	1.90	67.5	145	1.90	69.5	145	1.89	72.5
4.0	131	1.91	65.5	142	1.90	68.0	142	1.90	71.0
5.0	127	1.91	63.5	139	1.91	66.0	139	1.90	69.5

CH_4 concentration of the biogas at different operative pressure and temperature values is reported in Figure 3. Increasing operative pressure, CH_4 content in biogas stream increases due to the greater solubility of CO_2 in liquid phase. According to Henry's law, CO_2 solubility in liquid increases with greater value of its partial pressure in gas phase, and consequently CO_2 concentration in the biogas flow decreases (Figure 4**Errore. L'origine riferimento non è stata trovata.**). Furthermore, pH value in the liquid phase decreases with increasing of pressure, as reported in Figure 5, confirming results presented in Al-Rubaye et al., (2017) and Chen et al., (2014). The increase of temperature from 35 °C to 45 °C implies higher CH_4 concentration in the biogas, in accordance with the study by Tian et al., (2018).

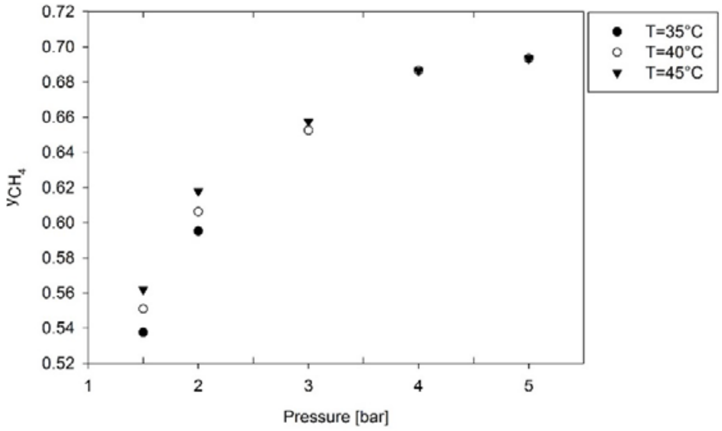

Figure 3: CH_4 concentration in biogas as function of pressure at different temperature

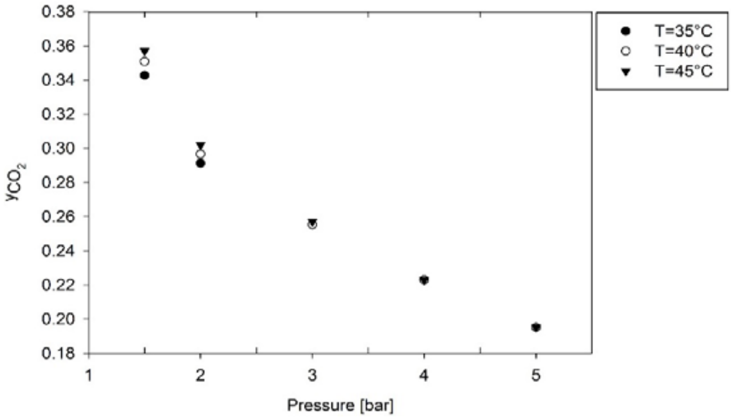

Figure 4 : CO_2 concentration in biogas as function of pressure at different temperature

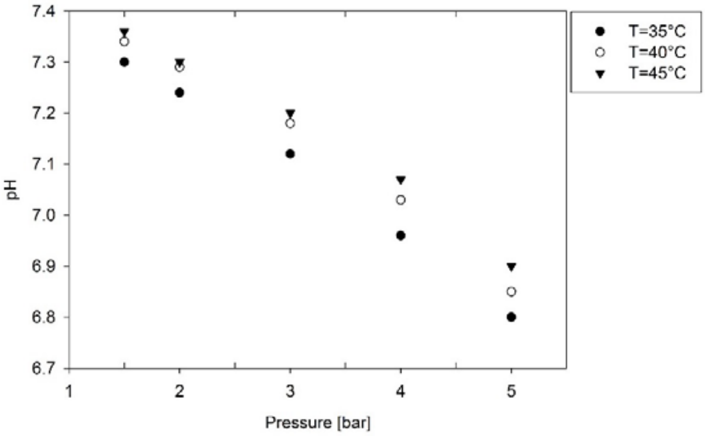

Figure 5: pH in the liquid phase as function of pressure at different temperature

The effects of operating pressure of PAD on the performances of upgrading process of biogas were studied assuming CH_4 recovery (η) equal to 30% and considering the biogas produced at 45 °C, because of the higher CH_4 concentration for all the pressures investigated (Figure 3). In Table *4*, biogas, retentate, permeate flow rates and CH_4 volumetric concentrations in retentate (methane purity y_R) and permeate are reported (y_R). By increasing pressure, biogas, retentate and permeate flow rates decreased while methane purity (y_R) increased; in particular a pressure of 3 bar resulted sufficient to produce a retentate flow rate with a CH_4 purity higher than 95% (y_R = 0.97). CH_4 concentration in the permeate stream (y_P) also increased with pressure, highlighting the possibility to further process the permeate for biomethane production or for energy recovery.

Table 4: *Mass flow rates and composition of retentate and permeate streams from biogas upgrading*

Pressure [bar]	Biogas [Nm^3/d]	y_R	y_P	Retentate [Nm^3/d]	Permeate [Nm^3/d]
1.5	157	0.75	0.52	35.3	121.7
2.0	154	0.90	0.54	31.7	122.3
3.0	145	0.97	0.57	29.5	115.5
4.0	142	0.98	0.60	29.8	112.2
5.0	139	0.99	0.61	29.2	109.8

4. Conclusions

In this work, anaerobic digestion was simulated at pressure higher than the atmospheric one, in the range 1.5-5 bar, in order to use the pressure of resulting biogas for the upgrading through membrane separation. Results show that the higher the pressure the higher the CH_4 concentration in the biogas stream for all temperatures investigated. This finding can be justified by Henry's law under which CO_2 solubility in liquid increases with greater value of its partial pressure in gas phase. Produced biogas decreases with higher pressure values and increases with higher temperatures.

In addition, the effects of operating pressure on CH_4 purity of retentate stream from the upgrading process of the biogas obtained at 45°C, assuming CH_4 recovery equal to 30%, were investigated. As shown, the higher the pressure the higher the CH_4 purity, with values higher than 95% at a pressure of 3, 4 and 5 bar. Similarly, the higher the pressure, the higher the CH_4 concentration in permeate stream. On the basis of this finding, CH_4 concentration in permeate flow is still relevant and it should be expected to use permeate as a feeding to CHP (combined heat and power) system in order to guarantee self-sustainability of whole process, and to avoid the climate-change methane emissions in the atmosphere.

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