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Simulation and optimization of pressurized anaerobic digestion and biogas upgrading using Aspen Plus

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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 H2S and NH3. 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 CO2 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 (CH4 ≥ 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 (CH4) and carbon dioxide (CO2), 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 (CH4 ≥ 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 CO2 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 H2S, CO2, and other minor compounds forcing biogas to pass through a semipermeable membrane in order to separate CH4 from the rest of the 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 CO2 and CH4 are cellulose acetate and polyimide (Angelidaki et al., 2018). Membrane separation represents a very effective process to remove CO2, H2S, 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 CH4 (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.

* 1. Models and methods
     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 CO2 solubility in the liquid phase, according to the following reactions (Flagiello et al., 2018; Oh and Martin, 2007)

(1)

(2)

(3)

(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.

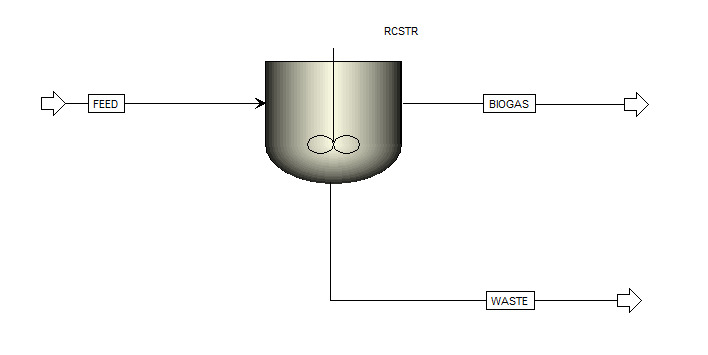


Figure 1: Schematic diagram of RCSTR

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  [m3] | 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 |

* + 1. 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 CH4-rich gaseous stream at a pressure close to the biogas pressure value; and the permeate, which is the CO2-rich gaseous stream and the off-gas of the process (Wellinger et al., 2013).

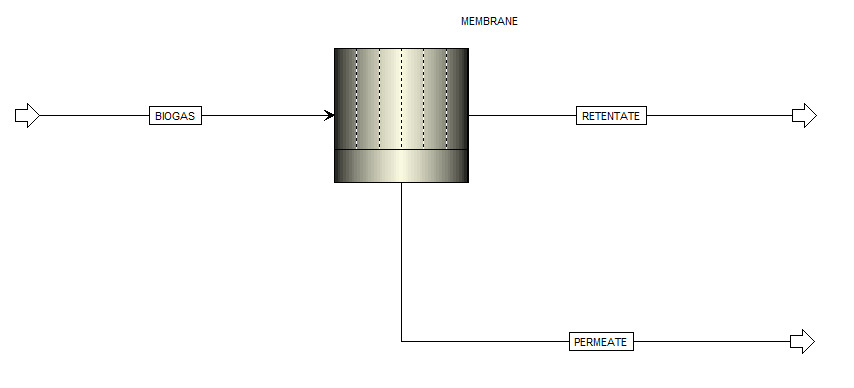


Figure 2: Schematic diagram of membrane system

The main parameters used to determine the efficiency of the separation of methane from the biogas are the CH4 recovery (η), defined as the ratio between the CH4 flow in retentate and the CH4 flow in biogas fed to the membrane, and the purity of retentate flow, i.e. the CH4 volumetric concentration (yR). 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 CO2 and CH4 occurred by using a PEK-A membrane with a selectivity of 28.6 (Molino et al., 2013). CH4 recovery (η) was assumed equal to 30%.

* 1. 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

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Pressure  [bar] | T=35°C | | |  | | T=40°C | | |  | T=45°C | | | |
| Biogas [Nm3/d] | Liquid waste  [t/d] | Biogas Productivity  [Nm3/t] |  | Biogas [Nm3/d] | | Liquid waste  [t/d] | Biogas Productivity  [Nm3/t] |  | Biogas  [Nm3/d] | Liquid waste  [t/d] | Biogas Productivity  [Nm3/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 |

CH4 concentration of the biogas at different operative pressure and temperature values is reported in Figure 3. Increasing operative pressure, CH4 content in biogas stream increases due to the greater solubility of CO2 in liquid phase. According to Henry’s law, CO2 solubility in liquid increases with greater value of its partial pressure in gas phase, and consequently CO2 concentration in the biogas flow decreases (Figure 4). 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 CH4 concentration in the biogas, in accordance with the study by Tian et al., (2018).

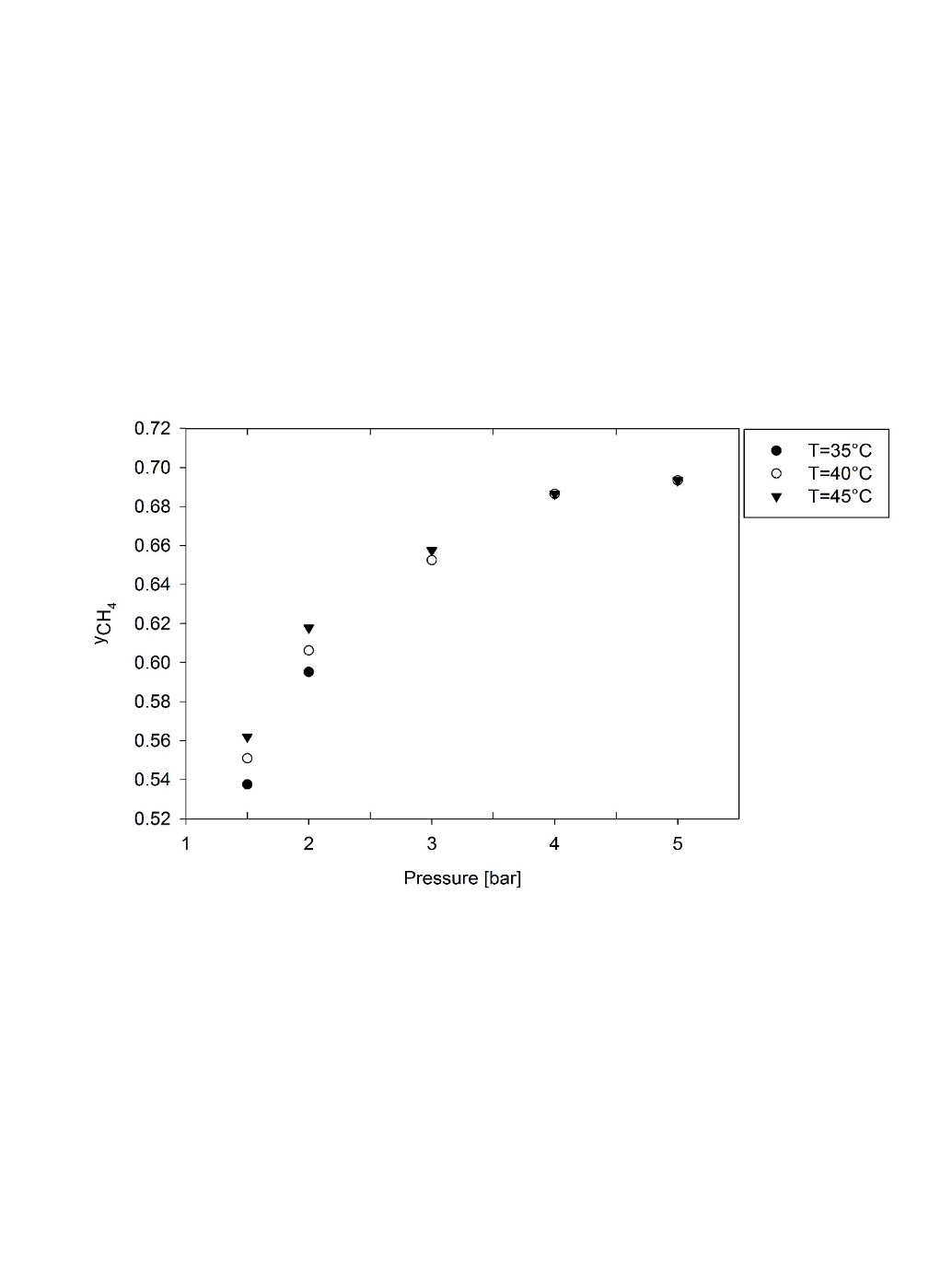


Figure 3: CH4 concentration in biogas as function of pressure at different temperature

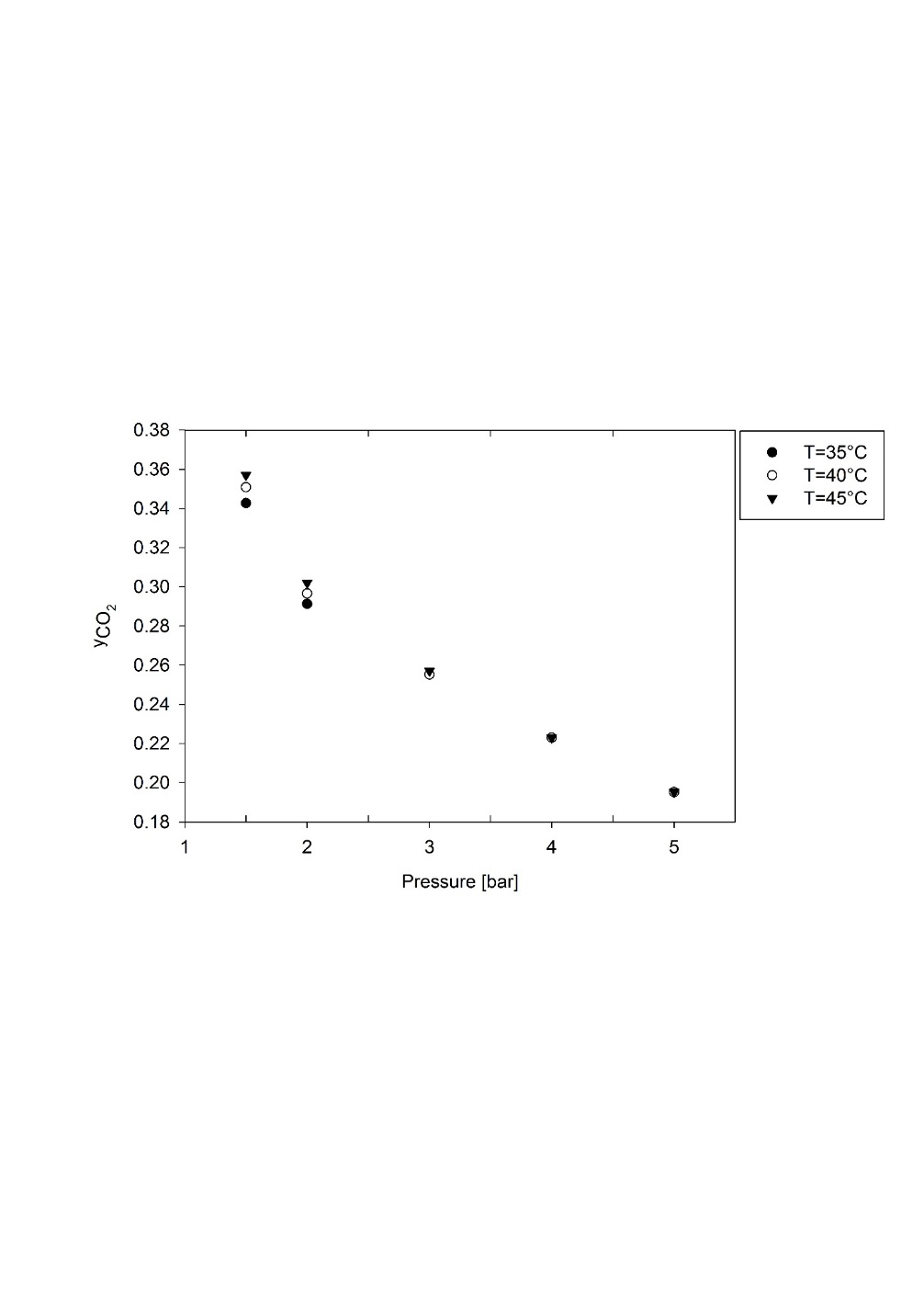


Figure 4 : CO2 concentration in biogas as function of pressure at different temperature

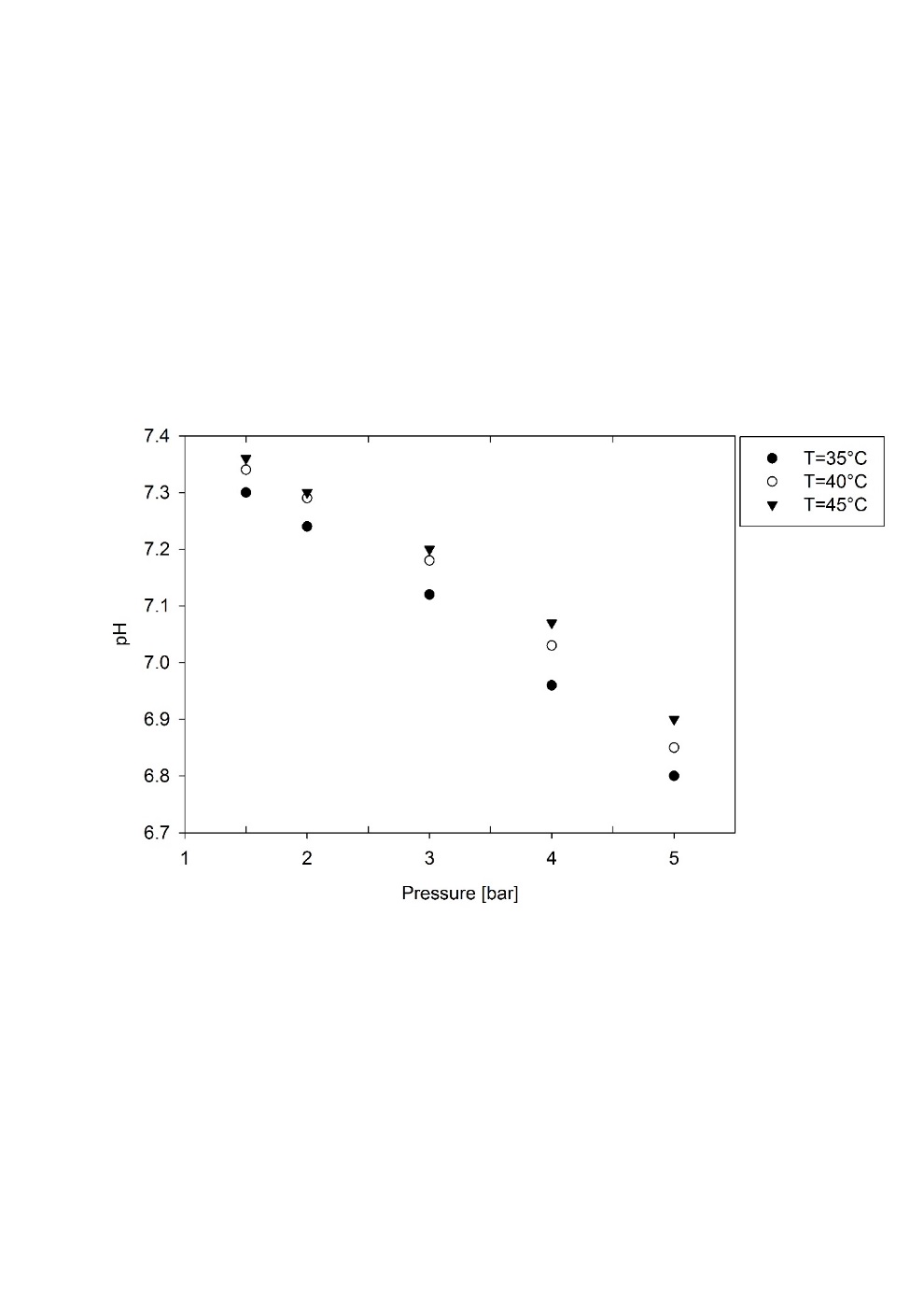


Figure 5: pH in the liquid phase as function of pressure at different temperature

The effects of operating pressure of PAD on the performances of upgrading process of biogas were studied assuming CH4 recovery (η) equal to 30% and considering the biogas produced at 45 °C, because of the higher CH4 concentration for all the pressures investigated (Figure 3). In Table 4, biogas, retentate, permeate flow rates and CH4 volumetric concentrations in retentate (methane purity yR) and permeate are reported (yR). By increasing pressure, biogas, retentate and permeate flow rates decreased while methane purity (yR) increased; in particular a pressure of 3 bar resulted sufficient to produce a retentate flow rate with a CH4 purity higher than 95% (yR = 0.97). CH4 concentration in the permeate stream (yP) 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  [Nm3/d] | yR | yP | Retentate  [Nm3/d] | Permeate  [Nm3/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 |

* 1. 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 CH4 concentration in the biogas stream for all temperatures investigated. This finding can be justified by Henry’s law under which CO2 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 CH4 purity of retentate stream from the upgrading process of the biogas obtained at 45°C, assuming CH4 recovery equal to 30%, were investigated. As shown, the higher the pressure the higher the CH4 purity, with values higher than 95% at a pressure of 3, 4 and 5 bar. Similarly, the higher the pressure, the higher the CH4 concentration in permeate stream. On the basis of this finding, CH4 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.

References

Adekunle, K.F., Okolie, J.A., 2015, A Review of Biochemical Process of Anaerobic Digestion, Advances in Bioscience and Biotechnology, 6, 205–212. DOI:10.4236/abb.2015.63020

Al-Rubaye, H., Karambelkar, S., Shivashankaraiah, M.M., Smith, J.D., 2017, Process Simulation of Two-Stage Anaerobic Digestion for Methane Production, Biofuels, 1–11. DOI:10.1080/17597269.2017.1309854

Al Seadi, T., Rutz, D., Prassl, H., Köttner, M., Finsterwalder, T., Volk, S., Janssen, R., 2008, Advantages of biogas technologies, in: Biogas Handbook. University of Southern Denmark Esbjerg, Niels Bohrs Vej 9-10, DK-6700 Esbjerg, Denmark, pp. 10–14

Angelidaki, I., Ellegaard, L., Ahring, B.K., 1999, A comprehensive model of anaerobic bioconversion of complex substrates to biogas, Biotechnology and Bioengineering, 63, 363–372. DOI:10.1002/(SICI)1097-0290(19990505)63:3<363::AID-BIT13>3.0.CO;2-Z

Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., Kougias, P.G., 2018, Biogas upgrading and utilization: Current status and perspectives, Biotechnology Advances, 36, 452–466. DOI:10.1016/j.biotechadv.2018.01.011

Aspen Plus User Guide, 2000, Aspen Plus ® User Guide, Aspen Plus ® User Guide,

Barbera, E., Menegon, S., Banzato, D., D’Alpaos, C., Bertucco, A., 2019, From biogas to biomethane: A process simulation-based techno-economic comparison of different upgrading technologies in the Italian context, Renewable Energy, 135, 663–673. DOI:10.1016/j.renene.2018.12.052

Batstone, D.J., Keller, J., Angelidaki, I., Kalyuzhnyi, S., Pavlostathis, S.G., Rozzi, A., Sanders, W., Siegrist, H., Vavilin, V., 2002, Anaerobic Digestion Model No. 1, Water Science and Technology, 45, 65–73. DOI:org/10.2166/wst.2002.0292

Bonga, C.P.C., Lima, L.Y., Leea, C.T., Hoa, W.S., Klemešb, J.J., 2017, The Kinetics for Mathematical Modelling on the Anaerobic Digestion of Organic Waste- A Review, Chemical Engineering Transactions, 61, 1667–1674. DOI:10.3303/CET1761276

Chen, Y., Rößler, B., Zielonka, S., Lemmer, A., Wonneberger, A.M., Jungbluth, T., 2014, The pressure effects on two-phase anaerobic digestion, Applied Energy, 116, 409–415. DOI:10.1016/j.apenergy.2013.11.012

Flagiello, D., Erto, A., Lancia, A., Di Natale, F., 2018, Experimental and modelling analysis of seawater scrubbers for sulphur dioxide removal from flue-gas, Fuel, 214, 254–263. DOI:10.1016/j.fuel.2017.10.098

González, J., Sánchez, M.E., Gómez, X., 2018, Enhancing Anaerobic Digestion: The Effect of Carbon Conductive Materials, Journal of Carbon Research, 4, 1–19. DOI:10.3390/c4040059

Molino, A., Iovane, P., Migliori, M., 2016, Biomethane production by biogas with polymeric membrane module, in: Membrane Technologies for Biorefining. Woodhead Publishing, Cambridge, UK, pp. 465–482. DOI:10.1016/C2014-0-03660-X

Molino, A., Larocca, V., Chianese, S., Musmarra, D., 2018, Biofuels production by biomass gasification: A review, Energies, 11, 1–31. DOI:10.3390/en11040811

Molino, A., Nanna, F., Iovane, P., 2013, Test sperimentali con membrane polimeriche per la purificazione del biogas da CO2 e H2S

Oh, S.T., Martin, A.D., 2007, Thermodynamic equilibrium model in anaerobic digestion process, Biochemical Engineering Journal, 34, 256–266. DOI:10.1016/j.bej.2006.12.011

Pellegrini, L.A., De Guido, G., Consonni, S., Bortoluzzi, G., Gatti, M., 2015, From Biogas to Biomethane: How the Biogas Source Influences the Purification Costs, Chemical Engineering Transactions, 43, 409–414. DOI:10.3303/CET1543069

Rajendran, K., Kankanala, H.R., Lundin, M., Taherzadeh, M.J., 2014, A novel process simulation model (PSM) for anaerobic digestion using Aspen Plus, Bioresource Technology, 168, 7–13. DOI:10.1016/j.biortech.2014.01.051

Tian, G., Yang, B., Dong, M., Zhu, R., Yin, F., Zhao, X., Wang, Y., Xiao, W., Wang, Q., Zhang, W., Cui, X., 2018, The effect of temperature on the microbial communities of peak biogas production in batch biogas reactors, Renewable Energy, 123, 15–25. DOI:10.1016/j.renene.2018.01.119

Wellinger, A., Murphy, J., Baxter, D., 2013, Biogas upgrading to biomethane, in: The Biogas Handbook: Science, Production and Applications. Woodhead Publishing Limited, Cambridge, UK, pp. 342–378. DOI:10.1533/9780857097415