

Adsorption

EVALUATION OF SIMPLIFIED PRESSURE SWING ADSORPTION CYCLES FOR BIO-METHANE PRODUCTION

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Abstract:	<p>Pressure Swing Adsorption (PSA) is a mature technique for biogas upgrading. However, it constitutes the most expensive step to obtain fuel-quality bio-methane, particularly in small-scale units. To reduce the cost of upgrading in small-scale plants, we have evaluated different PSA cycles with two and three columns (less than commercial units). An equalization tank was used to perform one asynchronous pressure equalization step and keep the process fed continuous even in the case of two columns. The effect of the purge step was also evaluated.</p> <p>Carbon Molecular Sieve (CMS) was used as adsorbent. The feed composition was 40% CO₂ and 60% CH₄ and pressure swing between 5 and 0.1 bar in the adsorption and blowdown steps, respectively. Four performance indicators (methane purity and recovery, productivity and energy consumption) were used to evaluate the PSA cycles. The mathematical model was effective to predict the PSA performance. Bio-methane with purity higher than 97.5% (specification) and recovery higher than 90% was obtained experimentally using a PSA with two columns and an equalization tank. When a third column is used (implementing an additional pressure equalization), the recovery increases in approx. 4% showing the importance of pressure equalization to reduce methane slip.</p>	

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EVALUATION OF SIMPLIFIED PRESSURE SWING ADSORPTION CYCLES FOR BIO-METHANE PRODUCTION

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ABSTRACT: Pressure Swing Adsorption (PSA) is a mature technique for biogas upgrading. However, it constitutes the most expensive step to obtain fuel-quality bio-methane, particularly in small-scale units. To reduce the cost of upgrading in small-scale plants, we have evaluated different PSA cycles with two and three columns (less than commercial units). An equalization tank was used to perform one asynchronous pressure equalization step and keep the process fed continuous even in the case of two columns. The effect of the purge step was also evaluated.

Carbon Molecular Sieve (CMS) was used as adsorbent. The feed composition was 40% CO₂ and 60% CH₄ and pressure swing between 5 and 0.1 bar in the adsorption and blowdown steps, respectively. Four performance indicators (methane purity and recovery, productivity and energy consumption) were used to evaluate the PSA cycles. The mathematical model was effective to predict the PSA performance. Bio-methane with purity higher than 97.5% (specification) and recovery higher than 90% was obtained experimentally using a PSA with two columns and an equalization tank. When a third column is used (implementing an additional pressure equalization), the recovery increases in approx. 4% showing the importance of pressure equalization to reduce methane slip.

KEYWORDS: Carbon dioxide, pressure swing adsorption, modelling, biogas upgrading, bio-methane.

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2 INTRODUCTION
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5 The global climate has been changing over the last years due to several
6 factors linked to the accumulation of greenhouse gases in the atmosphere. The
7 results of observed climate change are reflected in phenomena like: changes in
8 oceanic levels and currents, volcanic emissions, changes in earth's orbit, etc.
9 (Florides and Christodoulides 2009). The most important greenhouse gases are
10 methane, nitrous oxide, chlorofluorocarbons and carbon dioxide (Lashof and
11 Ahuja 1990). While the greenhouse warming potential of CO₂ is taken as a
12 reference of 1 and is much lower than these other gases (IPCC 2013), the amount
13 of carbon dioxide emitted from burning of fossil fuels is extremely high and for
14 this reason is a priority to reduce its emissions.
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24 Another gas that is important for the greenhouse effect is methane. In this
25 case, reducing its emissions from concentrated source points can result in a win-
26 win situation where methane is not emitted to atmosphere, but can be recovered
27 as a valuable fuel (Wu et al. 2015).
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31 Biogas is an important source of methane that can be considered an
32 alternative to fossil fuels (Poeschl et al. 2012a). Biogas has around 40-70% of
33 methane (Xuan et al. 2009), and its direct use for production of on-site electricity
34 and heat has been favored in many countries (Poeschl et al. 2012b). For using
35 biogas as a transportation fuel or for injecting it in the grid of natural gas, is
36 necessary to upgrade it to bio-methane (Paolini et al. 2018; Pellegrini et al. 2017;
37 Pöschl et al. 2010). Upgrading is the term given to the process of removing bulk
38 carbon dioxide from biogas. Indeed, carbon dioxide is the main contaminant in
39 biogas (Jiang et al. 2017). Its presence increases the energy used for
40 compression and transportation, decrease the calorific power and makes the gas
41 stream corrosive (Wu et al. 2015; Zhang et al. 2013). Adsorption processes like
42 pressure swing adsorption (PSA) are commercially available to remove carbon
43 dioxide (Augelletti et al. 2017). A PSA process uses a regenerable adsorbent,
44 does not use other additional chemicals (that can pollute the environment) and
45 does not demand a heat source (Labus and Machnikowski 2014).
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It is stated in many publications that the most important choice of a PSA unit is the adsorbent material (Cavenati et al. 2006; Grande and Blom 2012). While this statement is true, the optimal operation of a PSA unit is achieved when the "ideal" adsorbent material is coupled with a good process that is designed and tailored for a given application. Several researchers have already focused on studying process conditions for different materials (Bhatt et al. 2016; Effendy et al. 2017; Khurana and Farooq 2016; Ling et al. 2015; Zhang et al. 2008). In this publication we will show the effect of the process design on the performance and utilization of a commercial adsorbent. The motivation for this process simplification is to evaluate the feasibility of economic downscaling PSA units for upgrading biogas in small farms.

The first PSA process was designed by Skarstrom with four steps (pressurization, adsorption, blowdown and purge) (Skarstrom 1960). A variation of the PSA process was designed by Guerin de Montgareuil and Domine with the same four step, but adding two column equalization steps to save energy (Pierre Guérin de Montgareuil, Paris 1964). The use of pressure equalization steps also contribute in improving the recovery of the heavy or most adsorbed compound (Delgado and Rodrigues 2008; Grande et al. 2017; Yavary et al. 2015). While the Skarstrom cycle works very well for purification of light (or less adsorbed) gases, the performance for recovery of heavy compounds is normally poor (Webley et al. 2017). Also, in a two-column PSA with an equalization step, the process suffers a discontinuity for feed processing; when the two columns are connected for pressure equalization, the feed should be stopped. For this reason, other solutions to transform the PSA into a continuous process for downstream and upstream equipment should be found. Using another column is one of several possibilities (Stark and Morrish 1966).

An alternative to improve the PSA recovery and keep the process continuity is to use a tank to receive and provide pressure equalization (Chahbani et al. 2017; Krishnamurthy et al. 1989; Santos et al. 2011). The "equalization tank" can also be used to provide a purge flow with the intention of improve the recovery of PSA process (Krishnamurthy et al. 1989). Maximizing the performance of a PSA process require tailoring of several operating parameters like step arrangement and duration, flow rates and additionally for this arrangement, the volume of the

1 equalization tank (Ribeiro et al. 2008; Siqueira et al. 2017; Wu et al. 2015).
2 Experimental determination of good operating conditions with so many unknowns
3 is difficult. For this reason, mathematical modeling is a powerful tool to optimize
4 and fine-tune PSA processes (Bhadra and Farooq 2011; Jiang et al. 2017). It
5 should be noted that to validate the results, is beneficial if experimental
6 verification can be done (Marx et al. 2015; Schell et al. 2013).
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11 In this work, we have performed PSA simulations and experiments for
12 biogas upgrading using a constant synthetic gas composition (40% CO₂ and 60%
13 CH₄). Experiments were made in a fully automated setup at 30° C. The unit can
14 be operated with different modes and in this work, we have used two different
15 process configurations: PSA experiments with two and three columns (plus
16 equalization tank). The two-column PSA experiments were performed with
17 different equalization tank volumes and purge flows. The experimental data
18 obtained was used to validate the mathematical modeling, which is fully
19 predictive.
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31 MATERIALS AND METHODS

32 33 34 35 **Experimental**

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37 The PSA experiments were performed in a four-column PSA unit. The PSA
38 unit can run in diverse modes simply not using one or more columns for its
39 operation. In order to use a two-column PSA with continuous feed, one of the
40 columns was replaced by a tank (and one column was not used). Three columns
41 were packed with CMS KP 407 (Japan EnvironChemicals). The temperature
42 behavior inside the columns was monitored by four thermocouples located in the
43 center of each column at 0.11, 0.26, 0.41 and 0.56 m from the feed gas inlet at
44 the bottom of the column.
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53 A total of 20 different experiments were performed. Experiments were made
54 inside an oven at 303K, between 5.0 and 0.1 bar for feed and blowdown,
55 respectively. CMS sample was activated overnight under vacuum and presence
56 of a small flow of helium (0.10 SLPM) at 150° C. The composition and the feed
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flowrate were 60% methane and 40% carbon dioxide, and 0.62 SLPM, in all cases. Equalization time in all cases was 30 s and purge time was 60 s when this step was performed.

The other operation conditions of the PSA experiments are shown in Table 1. Gases with high purity and without further treatment were used (all provided by Yara Norway): He with purity >99.996%, Ar with purity > 99.996%, CO₂ with purity > 99.9992% and CH₄ with purity > 99.9995%.

To protect the membrane vacuum pump used for the blowdown step, the experimental blowdown step was divided into two sub-steps: "high-pressure" blowdown from the intermediate pressure until 1.05 bar and not passing through the pump and "low-pressure" blowdown from 1.05 bar to vacuum.

The PSA cycle with two columns runs with six steps: pressurization, feed, depressurization, blowdown, purge and equalization. The cycle with three columns has seven steps, being removed the purge step and added two new steps: second depressurization and second equalization. The scheme of the PSA unit with 2 and 3 columns as well as the cycle scheduling for each case are shown in Fig 1 and Fig 2, respectively.

The purge step was performed with gas coming from the equalization tank. The experiments with the two-column configuration were performed using three different tank volumes for the equalization step and three different purge conditions, one of which is equal to zero (no purge).

Mathematical Modeling

The mathematical model employed to describe the PSA behavior comprises mass, energy and momentum balances coupled with thermodynamic state equations for gas phase (ideal gas law) and adsorbed phase. The complete model is shown in the supplementary information section. This model was also employed in other PSA works (Canevesi et al. 2018; Rocha et al. 2017; Da Silva et al. 1999). The mathematical model was solved using gPROMS (PSE Enterprise, U.K.). The third-order orthogonal collocation on finite elements

method with 50 elements was used to discretize in the axial direction. The DAE system was solved with DASOLV method.

A theoretical extension of the Multisite Langmuir (MSL) Model for multicomponent adsorption equilibrium was used to describe the behavior of the multi-component system. The values of MSL and the kinetics parameters employed in this study are shown in Table 2 (Canevesi et al. 2018).

In this work, the whole PSA unit was simulated, including all the columns, tanks and valves. The performance of the different PSA configurations was quantified by four performance indicators: methane recovery, product purity, unit productivity and energy consumption (E.C.). From the modelling results it is possible to define the performance indicators in a traditional way (in terms of performance of one column) or from the overall PSA performance. We have calculated both approaches and verified that the error is within the second decimal (88.62% against 88.68% in one example). The following equations were used for calculating the performance parameters on the column-level.

The product (bio-methane) purity is defined by the following equation:

$$\text{Purity} = \frac{\int_0^{t_{feed}} C_{CH_4}|_{z=L} \cdot u|_{z=L} dt}{\int_0^{t_{feed}} C_T|_{z=L} \cdot u|_{z=L} dt} \quad (1)$$

where t_{feed} is the time of the feed step, C_T and C_{CH_4} are the total and methane concentrations respectively, z is the axial direction, L is the column length and u is the fluid velocity.

The methane recovery is given by:

$$\text{Recovery} = \frac{\int_0^{t_{feed}} C_{CH_4}|_{z=L} \cdot u|_{z=L} dt + \int_0^{t_{eqD}} C_{CH_4}|_{z=L} \cdot u|_{z=L} dt}{\int_0^{t_{feed}} C_{CH_4}|_{z=0} \cdot u|_{z=0} dt + \int_0^{t_{eqP}} C_{CH_4}|_{z=L} \cdot |u|_{z=L} dt + \int_0^{t_{purge}} C_{CH_4}|_{z=L} \cdot |u|_{z=L} dt} \quad (2)$$

where t_{eqD} , t_{purge} and t_{eqP} are respectively depressurization equalization time, purge time and pressurization equalization time.

The PSA productivity is calculated by:

$$\text{Productivity} = \frac{\int_0^{t_{feed}} C_T|_{z=L} \cdot u|_{z=L} dt}{t_{TOTALWAds}} \quad (3)$$

where t_{TOTAL} was the total time of PSA cycle and w_{Ads} was the weight of adsorbent in each column of the PSA.

The energy consumption is defined as the required energy for compression of the different streams and the energy requirements of the PSA unit; it is calculated by adiabatic compression given by

$$EC = \frac{3.6\gamma R_g}{\eta(\gamma-1)N_{CH_4}} T_{feed} \left[\left(\frac{P_{EQ}}{P_{Low}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \int_0^{t_{Blow}+t_{purge}} C_T|_{z=0} |u|_{z=0} dt \quad (3)$$

where EC is the energy consumption, P_{EQ} and P_{low} are the pressure in *the column* at the end of equalization step and at the end of blowdown step respectively, t_{Blow} and t_{Purge} are the blowdown and purge step time respectively, N_{CH_4} is the total amount of bio-methane produced in a PSA cycle, T_{feed} is the temperature in the feed stream, R_g is the universal gas constant, η is the mechanical efficiency, which was assumed as 0.8 and γ is defined by $\gamma = \tilde{C}_p / \tilde{C}_v$.

RESULTS AND DISCUSSION

A summary with the conditions of the experiments performed as well as the results of the performance indicators (purity, recovery and productivity) is shown in Table 3.

Two-column PSA unit

Different experiments with two-columns and one pressure equalization (with or without purge step) were executed. When employed, the flow of the purge step was extracted from the equalization tank. The idea was to promote a larger pressure differential and thus be able to reduce the pressure of the equalization step further.

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Cyclic steady state takes aprox. 100 cycles to be reached. The reason for such a long time is the very slow diffusion of methane. However, the changes between cycle 15 and cyclic steady state are very small: once the thermal profiles are consolidated, the performance of the cycle does not change significantly. The volumetric gas flows and pressure profiles, together with the prediction of the mathematical model after 21 cycles are shown in Figure 3. Similar figures for other PSA experiments (runs 1, 3, 5 and 8) are shown in the Supporting information. The observed differences between experimental data and the values predicted with the mathematical modeling are very small.

The experimental data of the equalization tank pressure is shown in Figure 4. It is possible to see how much time was necessary to equalization tank reach the steady state. The larger the volume of the tank, the longer it takes to reach a repeatable pressure pattern. Also, is verified that the equalization tank steady state pressure does not had a strong dependence with the tank volume.

The results in Figure 5 indicate that in all cases bio-methane was obtained with purity greater than 97.8%. However, results in Figure 6 showed that the methane recovery increases with the absence of a purge step and longer feed times. The effect of the size of the equalization tank in methane purity and recovery (shown in Figures 5 and 6) was less pronounced than then effect of the feed time in the methane recovery.

Also, the purge step contributed to increase the purity of the bio-methane around 0.5% in all cases. In fact, using purge step it is possible to increase the feed flow rate or the feed time without compromising the product quality.

Another interesting result was the PSA productivity behavior shown in Figure 7. The productivity is not strongly influenced by the equalization tank volume. In Table 3 we show that the productivity of two-column PSA unit is around 40% larger than in the three-column configuration. The productivity in this work is a measure of the performance of the adsorbent in each of the configurations. It should not be directly used as a measure of the footprint of the unit, once that in the calculation of this parameter, the volume of the tanks is not used.

1 The mathematical modeling was used to predict how much energy is
2 necessary to operate the different PSA cycles. The estimated energy
3 consumption for all cases is shown in Figure 8. These results show that the
4 energy consumption decreases with longer feed times since more gas is
5 produced per cycle decreasing the overall energy used per mol of product.
6 Energy consumption also increases with the absence of purge steps once that
7 the equalization pressure was bigger. The effect of equalization tank volume is
8 not very relevant in terms of energy consumption when the volume was greater
9 than 600 mL.
10

11 The three-column PSA cycle with two equalizations (equalization tank of
12 600 mL and without a purge step), showed a higher methane recovery than the
13 two-column configuration: 93.5% and 92.1% with purity of 97.2 and 98.4%,
14 respectively for feed times of 15 min and 13 min. The purity levels obtained with
15 three columns was lower than the ones obtained in two-column PSA
16 configurations. Since there are two equalizations, more CO₂ is recycled to the
17 top portion of the column exiting with the bio-methane obtained as product. The
18 recovery level when using three-column units are around 2-4% larger than PSA
19 units with two columns. The two equalizations steps in a three-column PSA cycle
20 caused a decrease in the methane losses at blowdown steps, and for this reason
21 the methane recovery was increased. Reducing the amount of CH₄ lost in the
22 CO₂-rich stream is very important in countries where the regulation of "methane
23 slip" imposes a minimum level for the unit recovery.
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25 With these results, we showed that is possible to obtain bio-methane with
26 high quality and good recovery using simplified PSA schemes and carbon
27 molecular sieves. Also, a PSA with two-columns and continuous feed can be
28 used without significant losses in purity and recovery. The replacement of a
29 column by an equalization tank can be a successful step in reducing the
30 implementation cost in cases where the cost of the adsorbent is large. This can
31 be an alternative solution for materials that are slightly more expensive than the
32 commercial ones but that have a much better performance to perform this
33 separation.
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CONCLUSIONS

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4 In this work, we have evaluated the effect of different configurations of PSA units
5 for bio-methane upgrading. The use of an equalization tank for asymmetric
6 pressure equalizations in two-column and three-column PSA schemes was
7 studied experimentally. A mathematical model was used to describe the whole
8 PSA unit including all columns, tanks and valves. The two and three-column PSA
9 cycles showed potential to produce bio-methane with pipeline quality (purity
10 >97.5%). The mathematical model showed good prediction of the experimental
11 data. The experimental results showed that the methane purity, recovery,
12 productivity and energy consumption were mainly controlled by the feed time.
13 The presence of a purge step had great influence in product purity. The
14 equalization tank volume does not have a major influence in any performance
15 parameter. The reason is that the pressure equalization does not differ much for
16 the different volumes used. These reported results showed that is possible to
17 simplify the design a small PSA unit to operate in continuous feed, with lower
18 costs and good productivity to be used in small farms.
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SUPPORTING INFORMATION

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Figures

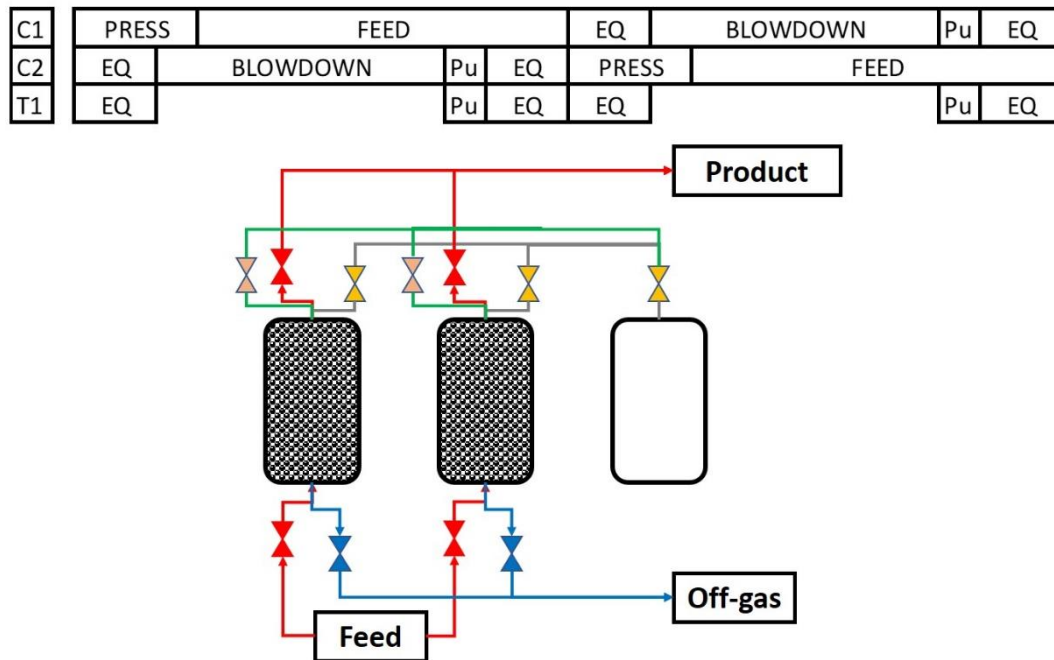


Figure 1. Operation schedule and configuration of the two columns PSA unit.

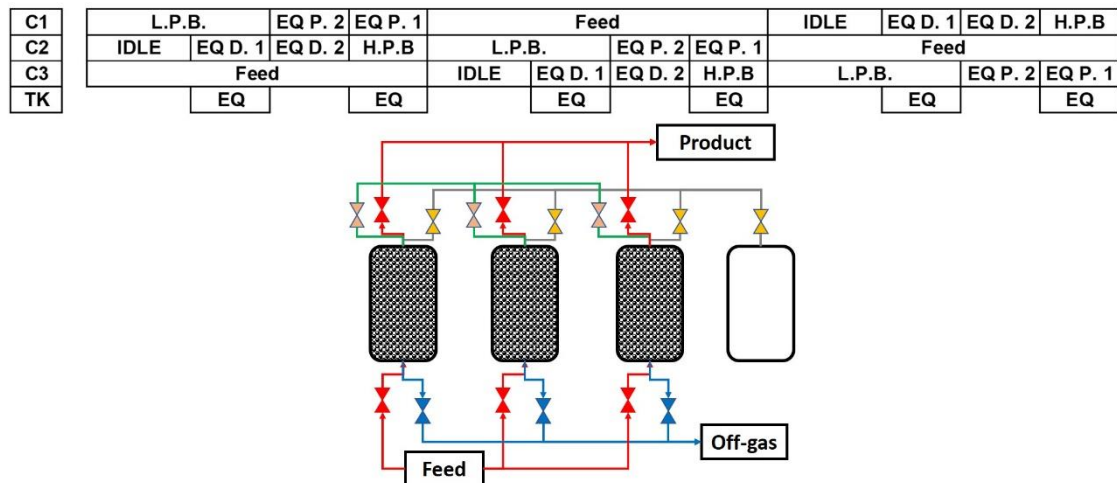


Figure 2. Operation schedule and configuration of the three columns PSA unit.

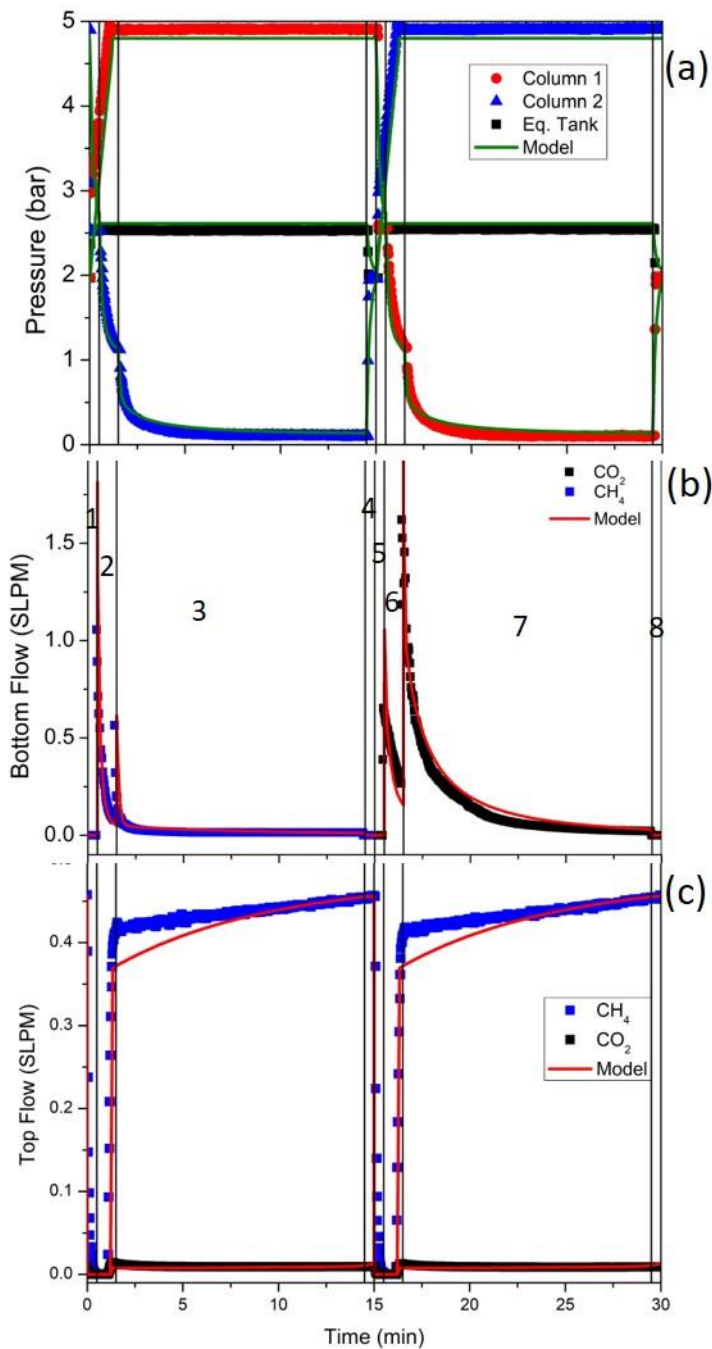


Figure 3. Pressure (a), exiting flow from the bottom of the Columns (b) and exiting flow from the top of the Columns (c). PSA cycle operation conditions are shown in Table 3 (run 2). Step sequence: (1) feed in column 1 and equalization depressurization in column 2; (2) feed in column 1 and high pressure blowdown in column 2; (3) feed in column 1 and low pressure blowdown in column 2; (4) feed in column 1 and equalization pressurization in column 2; (5) equalization depressurization in column 1 and feed in column 2; (6) high pressure blowdown

in column 1 and feed in column 2; (7) low pressure blowdown in column 1 and feed in column 2; (8) equalization pressurization in column 1 and feed column 2.

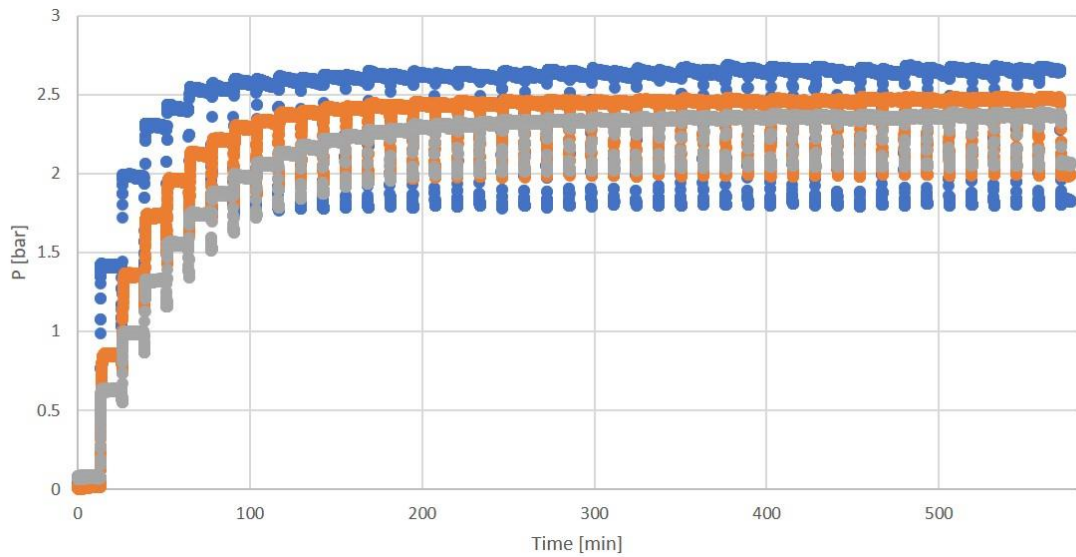


Figure 4. Pressure history of different volumes of equalization tanks for two-column PSA configurations: ● 1000 mL (run 12), ● 600mL (run 11), and ● 300mL (run 10).

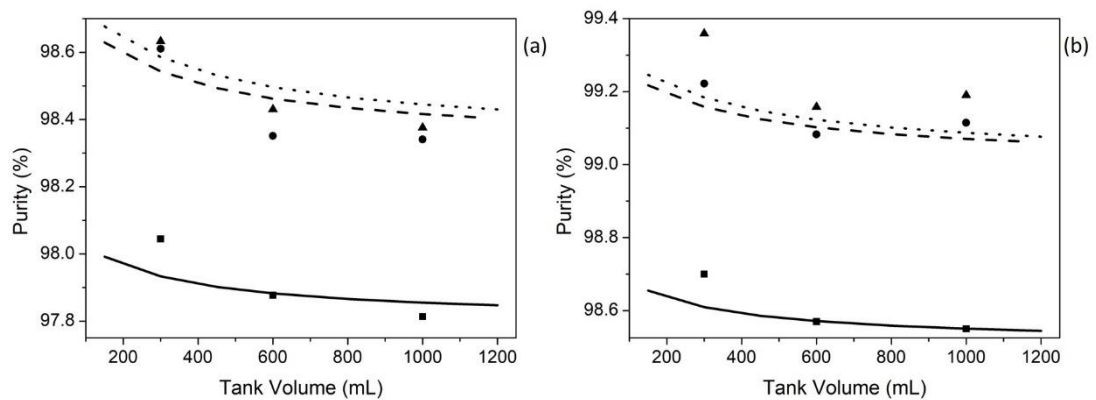


Figure 5. Methane purity for feed times of 15 min (a) and 13 min (b) for different equalization tank volumes and different purge flow rates (experimental data: ■)

highest purge flow, ● lowest purge flow, and ▲ without purge; modeling: ... highest purge flow, -- lowest purge flow, and — without purge).

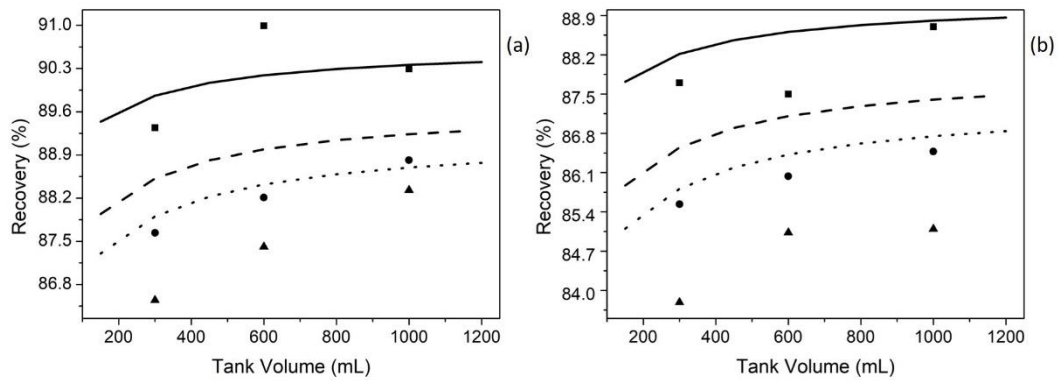


Figure 6. Methane recovery for feed times of 15 min (a) and 13 min (b) for different equalization tank volumes and different purge flow rates (experimental data: ■ highest purge flow, ● lowest purge flow, and ▲ without purge; modeling: ... highest purge flow, -- lowest purge flow, and — without purge).

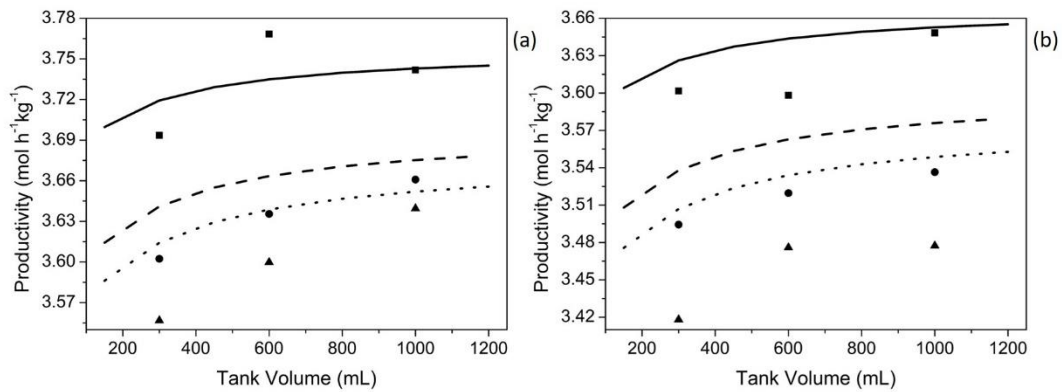


Figure 7. Productivity per weight of adsorbent for feed times of 15 min (a) and 13 min (b) with different equalization tank volume and different purge flow rates (experimental data: ■ highest purge flow, ● lowest purge flow, and ▲ without purge; modeling: ... highest purge flow, -- lowest purge flow, and — without purge).

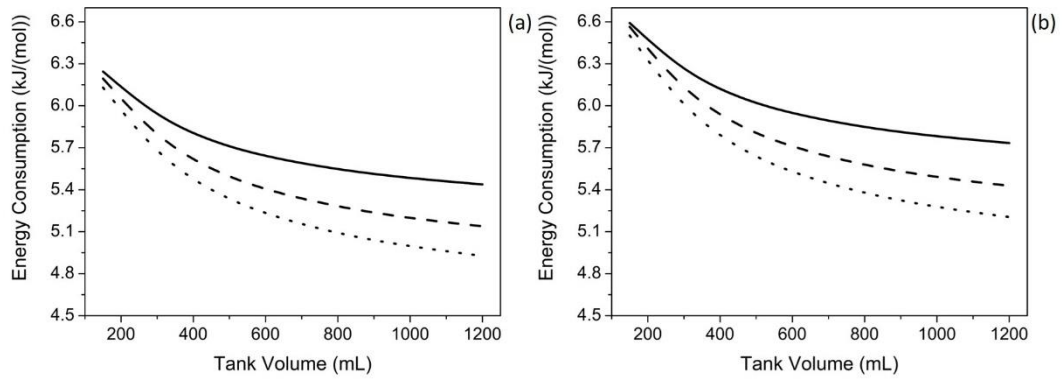


Figure 8. Energy Consumption for feed times of 15 min (a) and 13 min (b) with different equalization tank volume and different purge flow rates (modeling: ... highest purge flow, -- lowest purge flow, — without purge). .

Tables

Table 1. Operating conditions and properties of the material used for the PSA experiments made in this work.

Column Proprieties	
Length (m)	0.56
Internal Diameter (m)	0.0211
External Diameter (m)	0.0254
Bed Void (%)	37.7
Adsorption Pressure (bar)	5.0
Desorption Pressure (bar)	0.1
Feed Temperature (K)	303
Wall Temperature (K)	303
Adsorbent Proprieties	
Diameter (m)	9.0 10 ⁻⁴
Length (m)	1.8·10 ⁻³
Shape	Cylindrical
Particle Density (kg m ⁻³)	1060
Particle Void (%)	46

Table 2. Equilibrium and Kinetics Parameters used in the PSA simulations.

Equilibrium Parameters					
	q_{max} [mol kg ⁻¹]	K_0 [bar ⁻¹]	$-\Delta H$ [kJ mol ⁻¹]	α	$\alpha \cdot q_{max}$ [mol kg ⁻¹]
CH ₄	4.03	1.31 x 10 ⁻⁴	20.065	2.77	11.15
CO ₂	4.71	5.15 x 10 ⁻⁵	23.387	1.84	11.15
Kinetics Parameters					
	D_{μ} [s ⁻¹]	k_b [s ⁻¹]	K_{μ} [s ⁻¹]		
CH ₄	5.00 x 10 ⁻⁰⁶	7.00 x 10 ⁻⁰⁵	3.62 x 10 ⁻⁵		
CO ₂	1.05 x 10 ⁻⁰³		1.58 x 10 ⁻²		

Table 3. PSA process performance for CH₄/CO₂ separation using CMS-KP-407 for different configurations and feed/purge conditions.

Run	Feed Time (min)	Tank Volume (mL)	Number of Columns	Purge valve CV (SLPM Pa ⁻¹)10 ⁸	Purity (%)	Recovery (%)	Productivity (mol h ⁻¹ kg ⁻¹)
1	15	300	2	0	98.04	89.3	3.74
2	15	600	2	0	97.88	91.0	3.82
3	15	1000	2	0	97.81	90.3	3.79
4	15	300	2	0.8	98.61	87.6	3.65
5	15	600	2	0.8	98.35	88.2	3.68
6	15	1000	2	0.8	98.34	88.8	3.71
7	15	300	2	1.3	98.63	86.5	3.60
8	15	600	2	1.3	98.43	87.4	3.65
9	15	1000	2	1.3	98.38	88.3	3.69
10	13	300	2	0	98.70	87.7	3.65
11	13	600	2	0	98.57	87.5	3.64
12	13	1000	2	0	98.55	88.7	3.70
13	13	300	2	0.8	99.22	85.5	3.54
14	13	600	2	0.8	99.08	86.0	3.57
15	13	1000	2	0.8	99.11	86.5	3.58
16	13	300	2	1.3	99.36	83.8	3.46
17	13	600	2	1.3	99.16	85.0	3.52
18	13	1000	2	1.3	99.19	85.1	3.52
19	15	600	3	0	97.20	93.50	2.63
20	13	600	3	0	98.40	92.10	2.56



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Supplementary Material

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