

# Removing CO<sub>2</sub> from Biogas – the Optimisation of a Pressure Swing Adsorption (PSA) Unit Using Breakthrough Curves

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Currently when fossil fuel resources are decreasing and environmental protection is increasing, renewable energy sources are exploited more. Biogas (typically a raw mixture composed of methane, carbon dioxide and other minor components) can be one of the options how to replace some fossil fuel consumption. Specifically, upgraded biogas has the same utilization and advantages as natural gas. Upgrading biogas to biomethane is commonly utilized. In this process the most crucial operation is the separation of carbon dioxide (CO<sub>2</sub>) from biogas, which is carried out by technology based on unit operations like adsorption, absorption or membrane separation. The pressure swing adsorption (PSA) is the most widely used method for the separation of gases. It is a periodic batch process where adsorption is performed at a relatively higher pressure than atmospheric pressure and desorption (regeneration) at lower pressure than atmospheric pressure.

## 1. Biogas

The nature of the raw materials and the operational conditions used during anaerobic digestion determine the chemical composition of the biogas. Raw biogas consists mainly of methane (40 - 75 %) and carbon dioxide (15 - 60 %). A trace amount of other components such as water (5 -10%), hydrogen sulphide (0.005-2 %), ammonia (< 1 %), oxygen (0 - 1 %), carbon monoxide (< 0.6 %) and nitrogen (0 - 2 %) can be present and might be inconvenient when not removed (Persson, 2006).

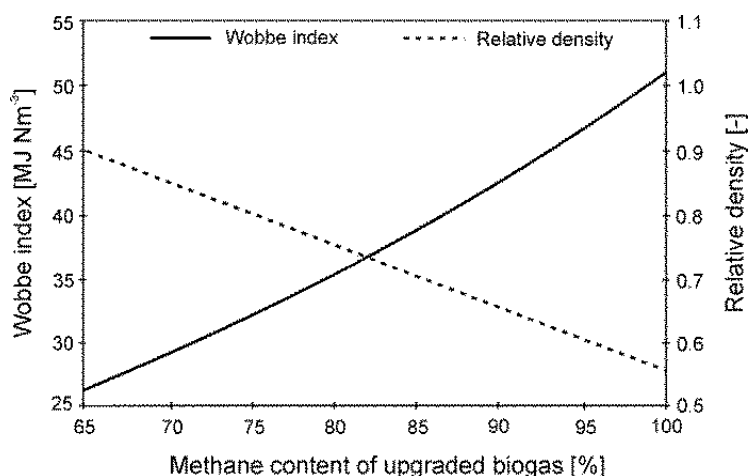


Figure 1: Wobbe index and relative density as a function of methane content of the upgrade biogas

The treatment of biogas is generally aimed at firstly, a cleaning processes, in which the trace components which are harmful to the natural gas grid, appliances or end-users, are removed; secondly an upgrading processes, in which  $\text{CO}_2$  is removed to adjust the calorific value and relative density in order to meet the specifications of the Wobbe Index (see Figure 1). These latter parameters are dependent on both the calorific value and the relative density (Ryckebosh, 2011). The final product after transformation, as referred to as bio-methane typically contain 95-97 %  $\text{CH}_4$  and 1 - 3 %  $\text{CO}_2$ . A number of studies have been published e.g. Cavenatti (2004) concerning the adsorption behaviour of gases ( $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$ ) or vapour on material, including the measurement of equilibrium isotherm for various temperatures.

### 1.1 Breakthrough curves

Adsorption in the fixed bed of the adsorbent has not been a steady process. The concentration of adsorption substance is dependent on both the place and contact time of the bed layer, as the place and time pass of gas through the bed. To begin with, the fresh adsorbent meets with the feed fluid. The main part of the fluid is adsorbed on the adsorbent in the input feed. The concentration of substance decreased exponentially with the direction of fluid flow as far as zero value. The adsorbent is saturated progressively by adsorption substance and the place of saturate adsorbent is increased with direction of fluid flow.

The length of adsorption zone is used for determine of the bed adsorption capacity. If the breakthrough curve is sharp, the area is narrow and the bed adsorption capacity reached maximum is utilized on maximum. The width of adsorption zone is depending on the shape of adsorption isotherm, the velocity of mass transfer and on the axial dispersion. The experiments with breakthrough curves are used for design of adsorption unit (Bai, 2013).

### 1.2 PSA process

PSA is the classical adsorption separation process. The essential requirement, the adsorbent preferentially adsorbs one component from the mixture feed. This selectivity depends on a difference in the adsorption equilibrium or on a difference in the sorption rates (Ruthven, 1993). Adsorption separation process involves two principal steps: adsorption and desorption. High pressure during adsorption and the low pressure during desorption are the basic principle of separation by PSA process. The PSA process is together with scrubbing the most widely used technologies for the biogas treatment in the European region (Niesner, 2013).

## 2. Experiment

The activated carbon was characterized using adsorption isotherm of carbon dioxide ( $\text{CO}_2$ ). Measurement of adsorption isotherm was made by high pressure thermogravimeter TA HP50. Graphical dependence of adsorption capacity on the pressure is shown in Figure 2. Parameters of the adsorption isotherm were calculated by standard equation model - Freundlich, Langmuir and BET (Ruthven, 1984).

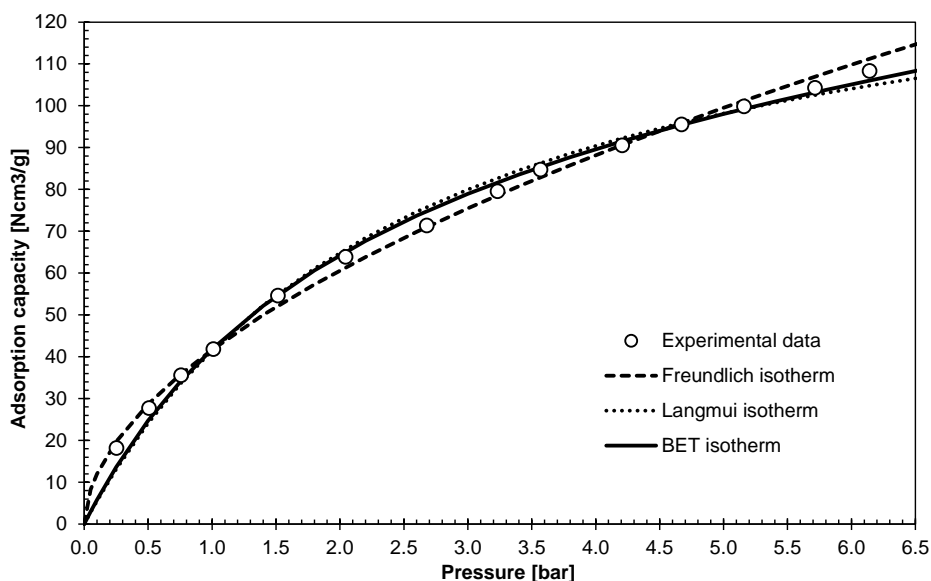


Figure 2: Adsorption isotherms of  $\text{CO}_2$  on the activated carbon

## 2.1 Breakthrough curves

The gas mixtures  $\text{CO}_2\text{-N}_2$  (60 vol. %  $\text{CO}_2$ ) and  $\text{CH}_4\text{-N}_2$  (85 vol. %  $\text{CH}_4$ ) were used for determination of the breakthrough curves. Gas mixture was flowed from flask to the adsorption column with activated carbon. Parameters of the activated carbon are listed in Table 1. Pressure and volumetric flow of the gas mixture were controlled outside the column. Temperature of gas was measured at the output of column. Output gas mixture was analysed using the IR spectrometer, where the composition of upgraded gas was measured. The data of gas concentration were recorded per 1 s. Measurements of the breakthrough curves were made until the dimensionless concentration was not reached to the unity. For measurements of the gas volumetric flow was used the gas flow meter calibrated to air. Values of the gas volumetric flow were corrected by average molar weight of gas mixtures.

Table 1: Parameters of the activated carbon and layer of the fixed bed

activated carbon	
Shape	cylinder
density [ $\text{kg/m}^3$ ]	472.2
porosity [-]	0.577
eq. diameter [mm]	4.92
bed of adsorbent	
height [mm]	300
diameter [mm]	106
volume [ $\text{cm}^3$ ]	2,646
weight [g]	1,249

## 2.2 PSA process

The gas mixture  $\text{CH}_4\text{-CO}_2$  (65 vol. %  $\text{CH}_4$ ) was used. Parameters of the activated carbon and bed of adsorbent in the column are listed in table 1. On the start of PSA process, the vacuum pump was use for blowdown and purge of the adsorption column. Pressurization process was started, when pressure in the column was 0.12 bar. Pressurization of the column was stopped, when pressure in the column was 1 bar. After that, the feed part was begun. The volumetric flow of synthetic biogas was  $0.095 \text{ Nm}^3/\text{h}$ . This value was used with respect to neglect of axial dispersion in the adsorbent bed, at which it can be neglected. Upgraded biomethane was flowed through the IR analyser until to the breakthrough of  $\text{CO}_2$ . Then, the vacuum pump was used again and cycle of PSA process was repeated. The data of gas concentration were recorded per 1 second. Measurements of  $\text{CO}_2$  breakthrough curves were stopped when the dimensionless concentration was reached to the unity. The schema of experimental apparatus is show in Figure 3.

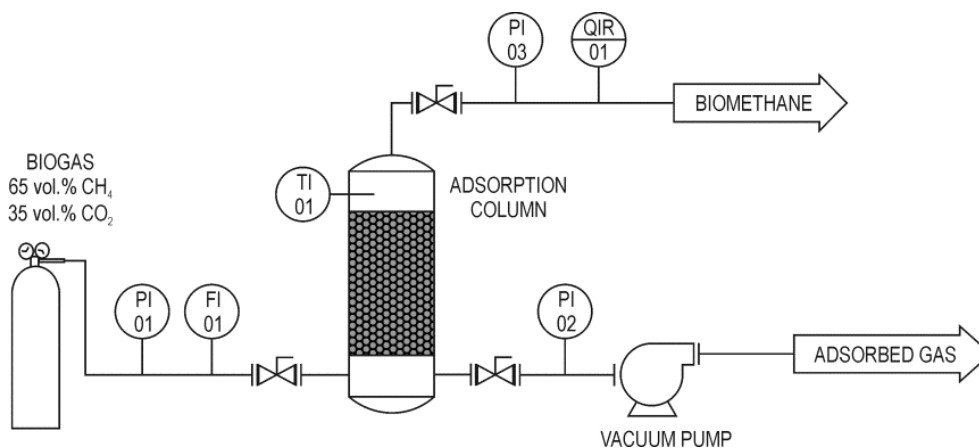


Figure 3: Schema of experimental apparatus (prepare for PSA cycle with gas mixture  $\text{CH}_4\text{-CO}_2$ )

### 3. Results

#### 3.1 Breakthrough curves

The adsorption capacities of active carbon for  $\text{CO}_2$  and  $\text{CH}_4$  were measured on the laboratory experimental apparatus, very similar to apparatus on Figure 3. The adsorption capacity (volume of adsorbed gas) was calculated using breakthrough curve. Ratio of the gas volumetric flow and breakthrough time (time at  $C/C_0 = 0.01$ ) is volume of adsorbed gas. Results of breakthrough curves measurement for various gas volumetric flows are shown in Figure 4 and Figure 5. Volume of adsorbed carbon dioxide was  $20,600 \text{ Ncm}^3$  ( $16.5 \text{ Ncm}^3/\text{g}$ ), approximately. Volume of adsorbed methane was  $10,400 \text{ Ncm}^3$  ( $8.3 \text{ Ncm}^3/\text{g}$ ), approximately. Ratio of the adsorption capacity was 2, but concentrations of substance ( $\text{CO}_2$  or  $\text{CH}_4$ ) in gas mixture were not same. Dependence of the adsorption capacity (volume of adsorbed gas) on the gas volumetric flow was not measured, because the laboratory apparatus is not ready for measurements in such sensitivity, which needs for this.

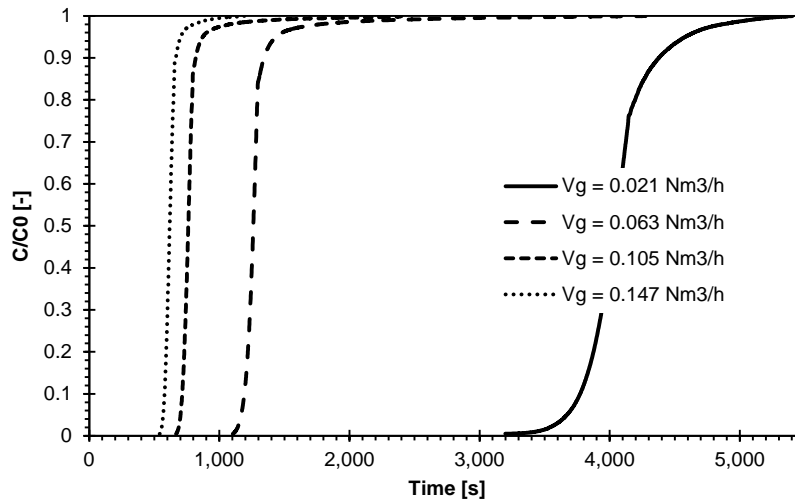


Figure 4: Experimental breakthrough curves for  $\text{CO}_2\text{-N}_2$  mixture

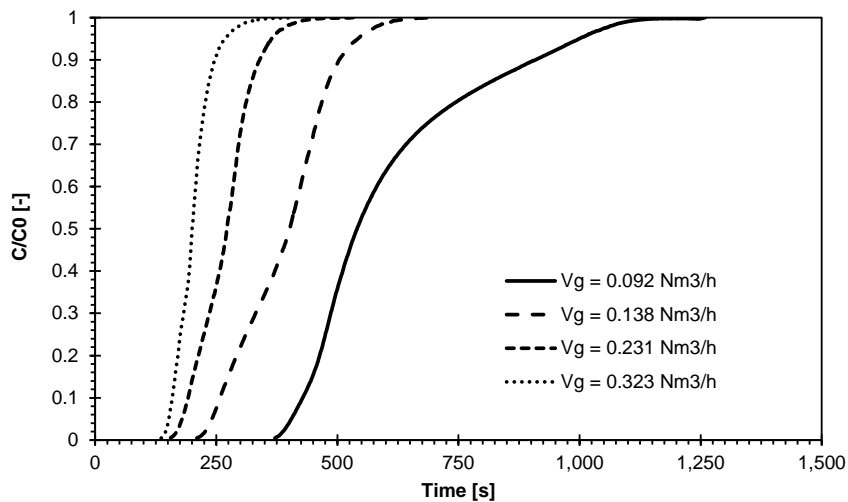


Figure 5: Experimental breakthrough curves for  $\text{CH}_4\text{-N}_2$  mixture

Table 2: Balance of separation process of the synthetic biogas

	Input gas	Output gas	Adsorbed gas
$V_g$ [Ncm <sup>3</sup> ]	23,159	11,786	11,373
$V_{CH_4}$ [Ncm <sup>3</sup> ]	15,053	11,607	3,446
$x_{CH_4}$ [vol.%]	65	98.5	30.3
$V_{CO_2}$ [Ncm <sup>3</sup> ]	8,106	179	7,927
$x_{CO_2}$ [vol.%]	35	1.5	69.7

### 3.2 PSA process

PSA process was measured according to the description in section 2.2. Result of separation process is listed in Table 2. The one PSA cycle was 26 min, approximately. In this time, adsorption bed with 2,646 cm<sup>3</sup> of activated carbon processed 23,159 Ncm<sup>3</sup> of synthetic biogas. The biomethane with 98.5 vol. % content of CH<sub>4</sub> and volumes 11,786 Ncm<sup>3</sup> was obtained. The efficiency of separation process was 77.0 %. The dissipation of CH<sub>4</sub> in the adsorbed gas presents 23.0 %.

The adsorption capacity of carbon dioxide was 2.3 times higher than the adsorption capacity of methane at pressure 1 bar and at the same gas volumetric flow ( $V_g = 0.1$  Nm<sup>3</sup>/h approximately). Similar result was published by Bonnot et al. (2006). The one PSA cycle, mainly the swing pressure is shown in Figure 6. Increase and decrease of temperature was affected by the adsorption heat.

## 4. Conclusion

The cogeneration is most widely used technology for biogas processing. Upgrading biogas to biomethane is very important for biogas pre-processing, because Wobbe index increase with methane content (see figure 1). Adsorption process is classical method for the processing, PSA (Pressure Swing Adsorption) process particularly. It is a periodic batch process where adsorption is performed on a high pressure and desorption (regeneration) at low pressure. High pressure is 6-8 bar, obviously. But, it requires complex equipment with semi- or fully-automatised unit. Adsorption pressure 1 bar and desorption pressure 0.12 bar were used in our laboratory experiment. The adsorption capacity at pressure 1 bar was 2.4 times smaller than at pressure 6 bars (according to adsorption isotherm), but the swing of pressure was kept. Efficiency of adsorption process on laboratory PSA unit was 77 %, as compared with adsorption isotherm. The adsorption capacity depends on the adsorption isotherm and pressure (see Figure 2). The adsorption capacity increase with volume of adsorbent linearly. The kinetics of adsorption process generally depends on the type of material (Rashidi, 2013), not on the amount. The breakthrough time is function of the gas volumetric flow, which seems to be logical. The Peclet number (ratio of advection and diffusive transport rate) and axial dispersion are very important parameters for prediction of flow condition through the adsorption column (Kubonova, 2011). Peclet number for our laboratory experiment was about 100, it is a low bound of condition, where axial dispersion can be neglected.

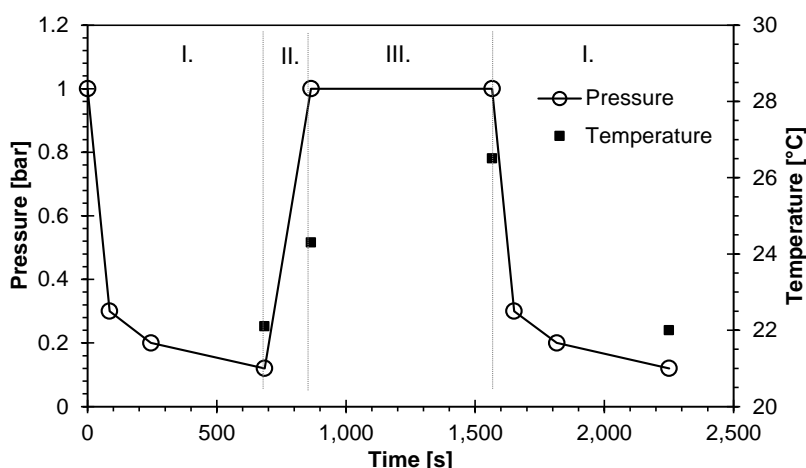


Figure 6: Changes of pressure and temperature during the PSA cycle (I. – blowdown and purge, II. – pressurization, III. - feed)

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