

Master in Chemical Engineering

***Development of a Pressure Swing Adsorption
biogas upgrading plant for CO₂ removal***

A Master's dissertation

of

Ana Beatriz Alves Torgal Pereira

Developed within the course of dissertation

held in

DMT Environmental Technology/ R&D unit



Supervisor at FEUP: Dr. Alexandre Ferreira

Co-supervisors at FEUP: Dr. Ana Mafalda Ribeiro

Prof. Alírio E. Rodrigues

Supervisor at DMT-ET: MSc. Benny Bakker



Department of Chemical Engineering

July, 2018

Acknowledgments

In this section I would like to thank to all those who, in one way or another, contributed for the realization of this work.

To Dr. Alexandre Ferreira I want to express my appreciation for the availability demonstrated to help, clarify and instruct me, even when the distance was not in our favour.

I would like to give my special thanks to my supervisor Benny Bakker for all the assistance, guidance and critical spirit during my work at DMT Environmental Technology. To Dennis Lammeire I owe a very great thanks for all the advices, knowledge and constructive suggestions along the developing of my work.

To my colleagues and friends who made this academic journey even more meaningful, thank you.

To my parents and brother, I want to express my sincere gratitude for all the support and constant presence not only during this work but during my entire life. Thank you.

Abstract

This work is focused in the development of a biogas upgrading Pressure Swing Adsorption (PSA) unit to produce bio-methane with high purity (97%) and recovery (>99%). PSA uses a selective adsorbent material which is submitted to pressure changes in order to adsorb or desorb certain components of a mixture. The selectivity of adsorption is based on different equilibrium capacities (equilibrium based separation) or on different adsorption rates (kinetic based separation). The adsorbent chosen for this case was a carbon molecular sieve with high kinetic selectivity towards CO₂ under certain conditions. This feature allows to use it as a kinetic adsorbent, which means that the CO₂ adsorbs faster than CH₄ in this material. The first design of the adsorption columns was based on the difference between adsorption capacity at high and low pressures, i.e. working capacity, on the fluid velocity inside the adsorber, and after that some simulations were performed the Laboratory of Separation and Reaction Engineering (LSRE). With the simulations for different adsorber dimensions it was possible to do a breakthrough analysis as well as a cycle study to define the best schedule. After different simulations were performed, it was necessary to define the entire process, which is composed of pre-treatment unit, PSA unit to produce bio-methane, and a PSA unit to increase the recovery of bio-methane in the system. By deciding all the equipment necessary for the global process, an estimation of its price and operational costs was made.

Finally, it was defined that the PSA adsorbers are going to be 2 meters of length and 0.8 meters of diameter. This size shows to be the best option regarding the equilibrium and kinetics of adsorption involved to separate CO₂ and CH₄. The PSA for biogas upgrading will be composed of 4 adsorbers working in parallel, in a cycle with 10 minutes, with a capacity to treat 450 Nm³/h. The pressure of adsorption is 8 bar(a) and the pressure of desorption is 0.1 bar(a). It is predicted that the product will have 90% of purity. The second PSA unit to recover bio-methane is placed to achieve a recovery higher than 99%. It is predicted that the cost of a PSA installation with this capacity will probably not be cheaper than a membrane system to produce bio-methane with the same capacity.

Keywords: biogas, bio-methane, adsorption, adsorbent, pressure swing adsorption.

Resumo

Este trabalho foca-se no desenvolvimento de uma unidade de Pressure Swing Adsorption (PSA) para produzir biometano com 97% de pureza e recuperação superior a 99%, a partir de biogás. Este tipo de tecnologia baseia-se na modulação da pressão usando um material adsorvente seletivo com capacidade de adsorver e dessorver certos componentes de uma mistura. O adsorvente escolhido neste caso é um peneiro molecular de carvão (CMS) com alta seletividade para adsorver CO₂ sobre determinadas condições e é caracterizado pelas suas propriedades de separação cinética sendo que o CO₂ é adsorvido mais rapidamente do que o CH₄. Um dimensionamento preliminar dos leitos de adsorção baseou-se na diferença de capacidade de adsorção a alta e a baixa pressão (capacidade de trabalho), na velocidade superficial e, posteriormente, em simulações realizadas pelo Laboratório de Separação e Engenharia das Reações (LSRE). Com simulações realizadas para diferentes dimensionamentos das colunas foi possível analisar as respetivas histórias de rotura e estudar diferentes ciclos de PSA de maneira a definir um ciclo que englobasse 4 colunas a tratar uma corrente de alimentação em contínuo. Depois de estudar todas as simulações foi necessário escolher o dimensionamento final dos leitos de adsorção assim como o processo global composto por uma unidade de pré-tratamento, uma unidade de PSA para produção de biometano e um PSA para aumentar a recuperação e pureza do produto.

Finalmente, foi definido que as colunas de adsorção da unidade terão 2 metros de altura e 0.8 metros de diâmetro. Estas dimensões mostram ser a melhor opção tendo em conta os fatores de equilíbrio e cinética de adsorção envolvidos para separar CO₂ e CH₄. Esta unidade de PSA será composta por 4 colunas de adsorção a produzir biometano continuamente, com um ciclo de 10 minutos de duração, e uma capacidade de tratamento de 450 Nm³/h. A pressão de adsorção será 8 bar(a) e a pressão de dessorção será 0.1 bar(a). É previsto que esta unidade irá produzir biometano com 97% de pureza. Uma segunda unidade de PSA é usada para atingir uma recuperação de biometano superior a 99%. Relativamente ao preço da instalação, é esperado que este não seja menor do que um sistema de membranas para produção de biometano.

Palavras-chave: biogás, biometano, adsorção, adsorvente, adsorção por modulação de pressão

Declaration

I hereby declare, on my word of honor, that this work is original and that all non-original contributions were properly referenced with source identification.

Ana Beatriz Torgal

Index

1	Introduction.....	1
1.1	Framing and presentation work.....	1
1.2	Presentation of the company.....	1
1.3	Contributions of the work.....	2
1.4	Thesis structure.....	2
2	Context and State of the Art	4
2.1	Biogas	4
2.2	Main Technologies used for CO ₂ Removal from Biogas	5
2.2.1	Water Scrubbing.....	5
2.2.2	Physical/Chemical Scrubbing	5
2.2.3	Membranes	6
2.2.4	Pressure Swing Adsorption (PSA)	6
2.3	Fundamental concepts of adsorption	6
2.3.1	Ideal Langmuir Model.....	7
2.3.2	Dual-Site Langmuir (DSL)	8
2.3.3	Sips Model	8
2.4	Fundamental Concepts of Pressure Swing Adsorption	9
2.5	Design of industrial-scale PSA processes	10
2.5.1	Pore diffusion and mass transference	10
2.5.2	Dynamic Studies - Breakthrough Analysis.....	11
2.5.3	Adsorption kinetics	12
3	Technical Description.....	14
3.1	Adsorbent Selection	14
3.2	Mathematical Model to describe Adsorption.....	15
3.3	Biogas Characteristics.....	17
3.4	Bio-methane Requirements	18

3.5	Operational Security Measures and Maintenance	18
4	Results and Discussion	20
4.1	Dynamic study - Breakthrough curves	20
4.2	PSA Cycle Studies	24
4.3	Final Design of the PSA unit	30
4.4	PSA unit to recover bio-methane	33
4.5	Installation and process description.....	34
4.6	Improvements of the system.....	37
4.7	Membrane System vs PSA System - Price analysis	39
5	Conclusions	41
6	Evaluation of the developed work.....	43
6.1	Accomplished Goals	43
6.2	Other tasks developed during the internship	43
6.3	Limitations and recommendations.....	43
6.4	Final Evaluation of the work.....	44
	Appendix 1 - Multicomponent DSL Isotherms	47
	Appendix 2 - MATLAB Model.....	48
	Appendix 3 Flammability Diagram (CH ₄ /O ₂ /N ₂).....	50
	Appendix 4 Parameters used by LSRE to perform the dynamic and PSA cycles simulations	51
	Appendix 5 - Process Flow Diagram (PFD)	52

List of Figures

Figure 1 - Dynamic study of an adsorber ^[19]	12
Figure 2 - Kinetic diameters of the CO ₂ and CH ₄ molecules (Source: wikipedia.org)	14
Figure 3 - Isotherm fitting with different mathematical models (Confidential source and temperature)	16
Figure 4 - Breakthrough performances for different flowrates for case A	21
Figure 5 - Breakthrough curves for 450 Nm ³ /h (left) and 225 Nm ³ /h (right).....	23
Figure 6 - Breakthrough curve for a capacity of 450 Nm ³ /h, 2 m of length and 0.7 m of diameter	24
Figure 7 - Working Schedule for case B.....	25
Figure 8 - Pressure and outlet molar flow rate histories for Case B	26
Figure 9 - Working Schedule for case C.....	27
Figure 10 - Pressure and outlet molar flow rate histories for Case C.1	28
Figure 11 - Outlet volumetric flow rate for a limited blowdown flow of 250 Nm ³ /h and recycle ending when 1 bar is achieved (Case C.2).....	28
Figure 12 - Temperature profile at the end of each step of one cycle at steady state (Case C.2)	30
Figure 13 - General Scheme of the PSA unit for bio-methane production.....	34
Figure 14 - Scheme of a possible configuration of the second PSA unit.....	37
Figure 15 - Multicomponent DSL isotherms for binary mixtures with different compositions at 293 K. 47	
Figure 16 - Multicomponent DSL isotherms for both CH ₄ and CO ₂ pure components at 293 K	47
Figure 17 - Flammability Diagram for a moisture with CH ₄ , O ₂ and N ₂ . ^[19]	50
Figure 18 - Process Flow Diagram of the entire process developed (PFD)	52

List of Tables

Table 1 - Average composition of biogas and natural gas ^[5]	4
Table 2 - CMS-Y standard properties	15
Table 3 - Equilibrium parameters used in the DSL model	16
Table 4 - Dual site Langmuir isotherm parameters for CO ₂ and CH ₄ adsorption on CMS-Y (Equations 2.4 and 2.5).....	17
Table 5 - Parameters calculated by a linear regression of Arrhenius Law at 293 K.....	17
Table 6 - Biogas characteristics and established ranges for each variable.....	18
Table 7 - Bio-methane requirements for grid injection in the Netherlands ^[22]	18
Table 8 - Kinetic analysis regarding the simulations for Case A.....	21
Table 9 - Values used to estimate the diameter of the adsorber	22
Table 10 - Kinetic analysis regarding the simulations for Case B	23
Table 11 - Kinetic analysis regarding the simulations for Case C	24
Table 12 - Working conditions of the PSA cycle for case B	25
Table 13 - Times of each step of the PSA cycle for case B.....	25
Table 14 - Purity, Recovery and productivity of CH ₄	26
Table 15 - Times of each step of the PSA cycle for case C	27
Table 16 - Times of each step of the PSA cycle for case C	27
Table 17 - Purity, recovery and productivity regarding the simulations of case C	29
Table 18 - Volumetric balance for the system simulated in case C.2	29
Table 19 - Velocity studies inside the adsorber	31
Table 20 - Results regarding the kinetics of adsorption	31
Table 21 - Final results regarding different inlet flows ($D = 0.8\text{ m}$, $L = 2\text{ m}$, $t_{feed} = 150\text{ s}$).....	32
Table 22 - Inlet stream conditions for the second PSA unit	33
Table 23 - Inlet stream characteristics (biogas after the pretreatment section)	35
Table 24 - Cases of study in the PSA cost analysis	39
Table 25 - Price analysis and comparison with the base cost of a Carborex MS.....	40
Table 26 - Estimated parameters used in the mathematical model used to perform all the simulations of this work.....	51

Notation

A_s	Superficial area	m^2
C	Concentration	$mol\ m^{-3}$
D	Diameter	m
D_{ax}	Axial dispersion coefficient	$m^2\ s^{-1}$
D_m	Molecular diffusivity	$m^2\ s^{-1}$
d_p	Particle's diameter	m
E_a	Activation energy of micropore diffusion	$J\ mol^{-1}$
F	Molar flow rate	$mol\ s^{-1}$
K_i	Equilibrium adsorption constant of component i	bar^{-1}
$K_{0,i}$	Equilibrium adsorption constant of component i at infinite temperature	bar^{-1}
K_{LDF}	LDF constant	$m^2\ s^{-1}$
$K_{0,LDF}$	LDF constant for infinite temperature	$m^2\ s^{-1}$
L	Length	m
m_{ads}	Mass of adsorbent	kg
N	Number of components of a mixture	-
n	Number of moles	mol
P	Pressure	bar
Q	Volumetric flow rate	$Nm^3\ h^{-1}$
q_i	Amount of component i adsorbed in the solid phase	$mol\ kg^{-1}$
$q_{s,i}$	Maximum amount of component i adsorbed in the solid phase	$mol\ kg^{-1}$
R	Ideal gas constant	$J\ K^{-1}\ mol^{-1}$
Re	Reynolds number	-
Sc	Schmidt number	-
T	Temperature	K
t	time	s
t_b	Breakthrough time	s
t_{diff}	Diffusion time	s
t_{feed}	Feed step time	s
U_{mf}	Minimum fluidization velocity	$m\ s^{-1}$
V_{ads}	Volume of adsorbent	m^3
v_i	Interstitial velocity	$m\ s^{-1}$
v_s	Superficial velocity	$m\ s^{-1}$
v_{sh}	Concentration front velocity (shock wave velocity)	$m\ s^{-1}$
VD	Vessel dispersion number	-
y_i	Molar fraction of component i in a mixture	-

Greek Letters

ϵ_b	Adsorption bed's porosity	-
ϵ_p	Particle's porosity	-
μ_g	Viscosity of the gas	-
ξ_{eq}	Capacity factor for equilibrium phase of adsorption	-
ξ_k	Capacity factor for kinetics phase of adsorption	-
ξ_{nd}	Empirical factor to characterize adsorption	-
ρ_b	Bed's density	$kg\ m^{-3}$
ρ_p	Particle's density	$kg\ m^{-3}$
τ	Residence/Space time	s
ΔH	Isotheric heat of adsorption	$J\ mol^{-1}$

List of Acronyms

CMS	Carbon Molecular Sieve
CAPEX	Capital Expenditure
MTZ	Mass Transference zone
MS	Membrane System
PSA	Pressure Swing Adsorption
TSA	Temperature Swing Adsorption
VPSA	Vacuum Pressure Swing Adsorption

1 Introduction

1.1 Framing and presentation work

The greenhouse gases emissions are nowadays an inevitable theme. Europe has an ambitious goal to achieve that consists in a reduction of 20% of greenhouse emissions until 2020. Thus, not only in Europe but throughout the world, efforts and resources are multiplying to find technologies that take advantage of renewable energies. One of the most promising sources of energy is bio-methane, upgraded from biogas, which is a renewable alternative to natural gas. [1]

Biogas is gas consisting essentially of methane and carbon dioxide, which is formed by the decomposition of biomass through methanogenic bacteria in anaerobic media (without oxygen). Organic waste from landfills, water treatment plants, food and agricultural industries are the main sources of biogas generation. Due to its diverse origins, biogas is a decentralized energy resource and can act as a lever for the development of rural areas. Biogas is a versatile resource and its applications are varied. The most common are the production of heat and electricity in gas engines or turbines (cogeneration systems), and after upgrading it to green gas, it can be injected into the natural gas grid or used as a transport fuel by compressing or liquefying. [2]

This report will focus on the Pressure Swing Adsorption technology (PSA). This kind of system is one of the most established processes for gas separation and its main working principle is based on a selective creation of bonds between a specific porous material (adsorbent) and certain kinds of molecules (adsorbate). Due to the huge variety of adsorbents available in the market nowadays, it possible to adapt a PSA unit for biogas upgrading. [3]

The global objective of this dissertation is to develop and design a PSA installation for biogas upgrading following the logic sequence of work: adsorbent study (equilibrium and kinetics) and selection, dynamic analysis of bed of adsorption, PSA cycle definition, process definition, improvement and description and cost analysis.

1.2 Presentation of the company

DMT Environmental Technology was founded in 1987 by Rob Dirkse when the new legislation for environmental clean-up began in the late 80's. However, his son Erwin Dirkse assumed his position in 2001 when he retired. By developing a quality membrane system to produce bio-methane from biogas (Carborex) DMT Environmental Technology achieved a highly respected position in the market of biogas upgrading. Beside the membranes, this company also

delivers technologies such as desulphurization units (Sulfurex) and water treatment systems (TurboTec).

Currently, DMT Environmental Technology employs around 70 employees, maintains a good relationship with several knowledge institutes worldwide and provides quality systems capable to work 24/7. [4]

By developing technology to produce green environmental solutions, DMT Environmental Technology contributes positively to a sustainable and prosperous future of the planet.

1.3 Contributions of the work

During the entire semester a PSA biogas upgrading unit was designed. In the first phase of the internship all kind of research related with adsorption and PSA processes were done, and all the information was being organized step by step. In the second phase, the adsorbent was finally confirmed, and the equilibrium and kinetic studies were developed to estimate the size of the adsorbers. It was previously defined that the PSA unit would be composed of four vessels. After that, due to the absence of an accurate software to simulate and confirm the work that was being developed, the LA /LSRE-LCM in Porto did some simulations according to the given specifications. By analyzing the simulation's data results from LA / LSRE-LCM it was possible to define the final design of the vessels and adjust the entire process to its final configuration. Finally, after the total equipment list was accurate a cost analysis was done comparing the developed PSA unit with the membranes unit.

With the development of this dissertation, DMT Environmental Technology increased its knowledge about Pressure Swing Adsorption technology. This knowledge is described along the report and it will facilitate a future design of a new unit proposition to perform the biogas upgrading through PSA units. The installation will be constructed in the end of 2018.

1.4 Thesis structure

This report is organized in five different sections:

- **Chapter 2 - Context and State of Art:** in this section different technologies used for biogas upgrading are explained succinctly. Besides that, topics like the fundamental concepts of adsorption and PSA technology are explained, as well as the base knowledge to design an industrial PSA installation.
- **Chapter 3 - Technical Description:** this section is mainly to explain the technical information of the project such as the adsorbent selection process, the biogas characteristics and bio-methane requirements, the process description and the bases used to develop the simulation model.

- **Chapter 4 - Results and Discussion:** the main results obtained during the development of the PSA unit are presented in this chapter; such as a cost analysis of the entire process.
- **Chapter 5 - Conclusion:** the results are objectively presented and commented. In this section a general consideration about the entire work developed is presented.
- **Chapter 6 - Final evaluation of the work developed:** a final appreciation about the project is presented.

2 Context and State of the Art

2.1 Biogas

Raw biogas is a gaseous product that is produced by methanogenic bacteria through anaerobic fermentation of organic matter. The main component of biogas is methane, reason why it has a high energetic value. With the proper treatment, it can be converted in bio-methane and used as a fuel to produce electric energy replacing fossil fuels. The use of biogas to produce energy also contributes for the reduction of methane emissions to the atmosphere, which is quite positive since methane has a warming potential 23 times higher than carbon dioxide. ^[5]

Biogas produced specifically by anaerobic digesters contains in average 40-70% of CH₄ and 15-60% of CO₂ in its composition, but also other vestigial compounds like nitrogen, hydrogen sulphide, ammonia and water. Nevertheless, these vestigial compounds usually do not exceed 5% of the total mixture. The following table compares the compositions of biogas with natural gas. ^{[5][6]}

Table 1 - Average composition of biogas and natural gas ^[5]

Compound	Biogas	Natural Gas
Methane (%)	40 - 70	90
Carbon Dioxide (%)	15 - 60	1
Nitrogen (%)	0 - 2	0.3
Oxygen (%)	0 - 1	0
Hydrogen Sulfide (ppm)	0 - 4000	3
Ammonia (ppm)	100	0

Nowadays, Europe is leading worldwide the development of bio-methane market, and the EU's policy promotes the use of this source for energy production. Thus, each bio-methane plant has to be adapted to the local/national standard specifications to be used as an energy resource. In the Netherlands the required purity can be from 90 up to 97 %. Although there is no legal requirement for bio-methane slip, the costumers usually prefer systems with 99% of recovery due to economic reasons. ^[6]

Depending on the biogas upgrading technology used to produce bio-methane, a pre-treatment step to remove some of the vestigial compounds shall be applied in order to produce bio-methane with the highest possible quality.

2.2 Main Technologies used for CO₂ Removal from Biogas

There are several technologies used to remove CO₂ from the raw biogas and to make the right choice about which technology is the most indicated it is necessary to evaluate the feed flowrate, value of utilities, legislation, requirements, investment and operational/maintenance costs. ^[5]

Currently, the most commonly biogas upgrading techniques used in the market are water/chemical/physical scrubbing, membrane separation and pressure swing adsorption (PSA). ^[6]

2.2.1 Water Scrubbing

This process is based on the difference of solubility between CO₂ and CH₄ in water. CO₂ solubility is much higher in water at low temperatures and higher pressures than CH₄. Thus, raw biogas is fed to a column where it is mixed with counter-current water that is sprayed from the top at low temperature. After that, the water rich in CO₂ is pumped to another column in order to proceed with the regeneration process which can be carried out at high temperatures or low pressure (solubility of CO₂ in water decreases again). The purified CH₄ stream should be dried after leaving the scrubber. The H₂S can also be removed along with CO₂ in this type of technology. ^{[5][6]}

2.2.2 Physical/Chemical Scrubbing

The physical scrubbing technologies can be easily compared to water scrubbing since the same principle of difference in solubility to separate CO₂ from CH₄ is used. However, in this case organic solvents like polyethylene glycol are used instead of water to dissolve CO₂. The solubility of CO₂ in water is smaller than in this kind of solvents. Thus, the productivity of a chemical scrubbing system can be higher than the productivity of a water scrubbing system with the same capacity. ^[6]

Chemical scrubbing technology uses solvents such as mono-ethanol amine and di-methyl ethanol amine to dissolve CO₂. However, in this case, a chemical reaction occurs between CO₂ and the solvent and a new solution is created. Amines have high selectivity to CO₂, so with this kind of solvents it is easily possible to achieve high purities and recoveries. The column where the chemical absorbing is occurring is regenerated using vacuum (low pressure) or heat (high temperature). ^[6]

2.2.3 Membranes

A membrane is a material that can be a selective barrier between two phases, remaining impermeable to specific substances when exposed to the action of driving forces (difference of partial pressure between both sides of the membrane). The gas permeability depends on the solubility and diffusivity of the gas into the material of the dense polymeric membrane. Therefore, in this technology the membranes are permeable to CO₂ and to other compounds such as H₂O and NH₃ (they pass from one side of the membrane to the other), while CH₄ has a low permeability and cannot pass through it like the other compounds. Thereby, CH₄ is separated from the rest of the mixture. The process occurs at a range of pressures between 8 to 16 bar and high purities and recoveries can be obtained. ^{[5][6][7]}

2.2.4 Pressure Swing Adsorption (PSA)

PSA technology for biogas upgrading is based on CO₂ separation from CH₄ by adsorption on a specific surface under elevated pressure. The adsorbing material needs to have higher affinity to CO₂ than for CH₄. A PSA unit operates according with a predefined cycle with different steps. The first one is pressurization where the column filled with the adsorbent is pressurized till the high pressure for the production step is achieved. After that, the production step (high pressure) starts and the CO₂ starts adsorbing while the CH₄ is produced. Then, just before CO₂ rupture, a blowdown step starts, in order to prepare the vessel for a regeneration step at low pressure. The regeneration step known by purge is where CO₂ is released from the adsorbent by feeding the column counter-currently with product gas or an inert gas. After this, the column is prepared to perform a new cycle. ^[5]

In the following chapters the adsorption concept behind the PSA process will be explained with detail.

2.3 Fundamental concepts of adsorption

Adsorption is a phenomenon that occurs when a molecule of a fluid (liquid or gas) is in contact with the surface of a specific solid. The solid surface is called adsorbent and the molecules that are retain there are considered the adsorbate. Adsorption is an exothermic spontaneous process and the loading of the adsorbate in the adsorbent depends specifically of the material employed and the operational conditions. ^{[5][8]}

The adsorption processes can be based on two mechanisms: kinetics and equilibrium. Kinetic separations are achieved by the difference of diffusion rates of different molecules into the adsorbent pores. This kind of separation is only possible in kinetic based adsorbents like carbon molecular sieves (CMS). In the other hand, equilibrium separations are based on different abilities of the adsorbent to accommodate different kinds of molecules. Activated

alumina, silica gel and some kinds of zeolites are examples of equilibrium-based adsorbents. [10]

The contact between a molecule and the adsorbent, at a certain temperature and pressure, takes the process to an equilibrium relation between the adsorbed phase and the adsorbate concentration in the fluid phase. This phenomenon is usually represented by adsorption equilibrium isotherms which relate the amount adsorbed per kilogram of adsorbent with the pressure or concentration of the gas. [9]

Regardless of the number of compounds present in a given system, the adsorption equilibrium of the pure compounds is the essential element for understanding how they interact with the adsorbent. This information can be used in the adsorption studies of pure component and multicomponent systems. The performance of an adsorption process can be described by different models based in different assumptions. [8][10]

The next sub-chapters explain some of the several models used for description of gas adsorption equilibrium.

2.3.1 Ideal Langmuir Model

The Langmuir model is one of the simplest isotherms and one of the most useful for both physical and chemical adsorption. This model is based on the following assumptions:

- i) The adsorbed molecule is held at localized sites;
- ii) Each site can only accommodate one molecule or atom;
- iii) The energy of adsorption is a constant over all sites, and there is no interaction between neighboring adsorbates.

Langmuir's theory is based on a kinetic principle in which the adsorption and desorption rates are equal. The *equation 2.1* represents the Langmuir model and it is presented in terms of the amount adsorbed for pure components. [10]

$$q_i = q_{s,i} \frac{K_i P}{1 + K_i P} \quad 2.1$$

Where, q_i is the amount of the component i in the adsorbed phase, $q_{s,i}$ is the maximum amount adsorbed of component i , K_i is the affinity constant and P is the gas pressure. To calculate the affinity constant van't Hoff equation is used (*equation 2.2*).

$$K = K_0 \exp\left(\frac{-\Delta H}{RT}\right) \quad 2.2$$

For multicomponent adsorption both components must be taken into account, whereby the model equation can be extended to include the competition between adsorbate molecules (*equation 2.3*) [10]

$$q_i = q_{s,i} \frac{K_i P}{1 + \sum_{i=1}^N K_i P} \quad 2.3$$

2.3.2 Dual-Site Langmuir (DSL)

In several systems, the Ideal Langmuir Model can give an appropriated answer about the system's behavior at low pressures. However, it has some inconsistencies in the saturation zone where the interaction between the molecules become stronger. Therefore, some deviations can occur due to the heterogeneity of the active sites. [11]

Dual-Site Langmuir is derived from the Ideal Langmuir Model, but it takes into account two different categories of active sites, each one with different energetic parameters.

$$q_i = q_{s1} \frac{K_{1,i} P}{1 + K_{1,i} P} + q_{s2} \frac{K_{2,i} P}{1 + K_{2,i} P} \quad 2.4$$

This model can also be defined for multicomponent adsorption, as expressed in *equation 2.5*. [11]

$$q_i = q_{s1,i} \frac{K_{1,i} P}{1 + \sum_{j=1}^N K_{2,j} P_j} + q_{s1,i} \frac{K_{2,i} P}{1 + \sum_{j=1}^N K_{2,j} P_j} \quad 2.5$$

2.3.3 Sips Model

The Sips model was developed in order to solve the continuous increasing of adsorbed amount with the increasing of pressure in the Freundlich model. Basically, Sips proposed a solution similar to the Freundlich model but with a finite limit at high pressure.

The *equation 2.6* represents the mathematical expression to calculate the amount adsorbed at a certain pressure. [12]

$$q_i = q_{s,i} \frac{(K_i P)^{1/s}}{1 + (K_i P)^{1/s}} \quad 2.6$$

This equation is quite similar to the Langmuir isotherm. The difference resides in the parameter s which characterizes the heterogeneity of the system. Despite it has a finite number at high pressures, this equation shares the same limitation as Freundlich isotherm - being not thermodynamically consistent at low pressures (Henry's zone). [12]

The equation for the multicomponent case is represented in the following expression. [13]

$$q_i = q_{s,i} \frac{(K_i P)^{1/s}}{1 + \left(\sum_{j=1}^N K_j P_j \right)^{1/s}} \quad 2.7$$

2.4 Fundamental Concepts of Pressure Swing Adsorption

PSA systems are not a new concept in the industrial world and actually they are being studied and improved for more than 100 years. The first PSA technology patents were developed in the 30s, however they were revolutionized when a new concept of low pressure purge and also vacuum regeneration were introduced by Skarstrom from one side and Guerin de Montgareuil and Domine from the other, in the late 50s. ^[14]

The operating principle of a PSA unit is relatively simple. First, a mixture of gas is fed to a bed filled with adsorbent particles - adsorption step. Within the PSA column happens a selective separation of the gases, generating a current rich with light product, which is the less adsorbed compound. In the adsorber, there is a zone that contains a concentration gradient from zero to equilibrium known by mass transfer zone (MTZ) and it is where the adsorption is actually occurring at a given moment. The adsorption step is interrupted before the MTZ front runs through the entire column to avoid saturation of the adsorbent and consequent contamination of the product obtained. Then, the column is depressurized allowing the bed regeneration by desorption of the impurities - depressurization step. The regeneration is aided by a purge containing a small amount of light product purified or an inert gas - purge step. Finally, the column is partially pressurized usually with feeding gas to restart the cycle - pressurization step. This simple four-step cycle is known as the Skarstrom cycle and in its most basic state it is applicable to two beds. It is possible to improve this simple cycle by using a sequence of pressure equalization steps. To add pressure equalizations steps to a cycle an extra connection between the top of one column and the bottom of another one has to be settled. After the adsorption step at high pressure, in one bed, and the purge step at low pressure, in the other bed, the equalization of the pressures in both beds can occur. A pressure equalization step is an alternative that can be added to a simple PSA cycle in order to conserve energy and improve the separation efficiency. There is another option known as vacuum pressure swing adsorption (VPSA) in which the low-pressure purge is replaced by a vacuum desorption. By replacing the purge step, the product that would be used to this effect is not lost with the off-gas stream. VPSA systems are a good alternative to reduce product losses despite the higher energy consumption (vacuum pumps are necessary and more energy to regenerate the adsorber is required). ^[14]

PSA technology has advantages such as low energy consumption, non-use of chemicals and low operational costs. Besides, it is a robust and known technology, fully settled in the industrial world with many units in operation. It has also some disadvantages such as the mandatory extra unit to remove H₂S (and water most of the times) before the PSA unit, an extensive process control is needed to regulate the cycles and the maintenance can be quite expensive due to the high number of valves constantly switching in the installation. ^[6]

2.5 Design of industrial-scale PSA processes

To proceed to the design of a PSA unit three main parameters must be considered to evaluate the performance of the cycle configuration used: purity, recovery and productivity.

[4] They are calculated using the following equations: [8]

$$\text{Purity} = \frac{n_{\text{CH}_4}}{n_{\text{CH}_4} + n_{\text{CO}_2}} \quad 2.8$$

$$\text{Recovery} = \frac{n_{\text{CH}_4, \text{product}}}{n_{\text{CH}_4, \text{feed}} + n_{\text{CH}_4, \text{purge}}} \quad 2.9$$

$$\text{Productivity} = \frac{n_{\text{CH}_4, \text{product}}}{t_{\text{total}} m_{\text{ads}}} \quad 2.10$$

Besides, it is necessary to define the characteristics of the gas that will be treated and the specifications of the product.

2.5.1 Pore diffusion and mass transference

To design an efficient PSA process, it is also necessary to study the mass transference of the gas molecules into the adsorbent particles. The molecules have to diffuse through the “distribution channels” of the adsorbent (macropores) into the micropores. Only then they reach the active center of adsorption. The micropore resistances can be represented by the Linear Driving Force (LDF) model. The LDF constant (K_{LDF}) is composed of the micropore diffusion resistance and the surface barrier at the entrance of the pore. The time that each molecule takes to reach the center of the crystal (t_{diff}) at a certain temperature is given by the inverse of the respective K_{LDF} . [14]

$$K_{\text{LDF}} = K_{0, \text{LDF}} \exp\left(\frac{-E_a}{RT}\right) \quad 2.11$$

$$t_{\text{diff}} = \frac{1}{K_{\text{LDF}}} \quad 2.12$$

The axial dispersion is another important factor to take into account. This factor is directly connected to the molecular diffusion of the molecules in the void space between the particles. Ideally, in the absence of axial dispersion the concentration fronts travel along the vessel as perfect step front (plug flow). However, due to the existence of axial dispersion and the other mass transfer resistances, the front isn't so sharp and the MTZ is generated. The main goal is to have a MTZ as small as possible, in order to avoid big unused length in the adsorber, to increase the time of feed without compromise the purity of the product. [12]

$$\frac{\varepsilon D_{ax}}{D_m} = 20 + 0.55 Sc Re; Re = \frac{\rho_g u dp}{\mu_g}; Sc = \frac{\mu_g}{\rho_g D_m} \quad 2.13$$

There is also a simple correlation to calculate the axial mass dispersion which is only adequate when the particle diameter of the adsorbent is smaller than 3 mm (equation 2.14).

[13]

$$D_{ax} = v_i \frac{d_p}{2} \quad 2.14$$

According with Levenspiel, a Vessel Dispersion Number (VD) can be used to evaluate the axial dispersion contribution to the mass transfer of adsorbate gas in an adsorber (*equation 2.15*). If VD is lower than 0.01, the axial dispersion can be neglected. Otherwise, the axial dispersion needs to be consider. ^[15]

$$VD = \frac{D_{ax}}{v_i L} \quad 2.15$$

Based on the adsorption equilibrium isotherms of pure components, the high pressure of adsorption and the low pressure of desorption can be selected, taking in consideration the working capacity desired. Then, the multicomponent adsorption capacity, the mass transference and diffusion rate shall be evaluated in order to estimate a more precise adsorber's dimensions. ^[12]

2.5.2 Dynamic Studies – Breakthrough Analysis

To choose the dimensions of an adsorption column, beside the factors mentioned previously, it is crucial to do dynamic adsorption studies in fixed bed with different sizes and different feed flowrates, by means of simulation. These studies are usually called adsorption breakthrough experiments or simulations, and they are essentially a concentration history of the outlet stream.

As the MTZ is travelling along the column, the length of the bed which contains fully saturated adsorbent is increasing, until it reaches the end of the adsorbent bed. The instant when that happens is named breakthrough point, where the solute that is being adsorbed is detected at the product composition measurement (5% of the feed concentration). To maintain a high purity of the product the end of the production step shall be shorter than the breakthrough time and the adsorbent should be regenerated. After the breakthrough instant is achieved, it is possible that the MTZ continues to travel along the vessel if the feeding stream is maintained. Thus, the exhaustion instant (t_E) is achieved and it corresponds to the time that is necessary to reach 95% of the solute concentration in the feed. If there is no axial dispersion, a shock wave will describe the advance of the concentration fronts along the vessel instead of the MTZ, for favorable adsorption equilibrium isotherms. Considering this ideal case, the adsorber would be completely saturated immediately after the front reached the end. The instant when it would happen is named as stoichiometric time (t_{st}). If instant equilibrium, favorable adsorption isotherm and no axial dispersion are considered, the 3 times will coincide, due the sharp mass front. ^{[17][18]}

It is possible to calculate the length of the MTZ by using *equation 2.16*. ^[18]

$$LMTZ = \frac{L(t_E - t_b)}{(t_E + t_b)/2} \quad 2.16$$

The following scheme shows a breakthrough study as well as MTZ evolution along the adsorber (Figure 1).

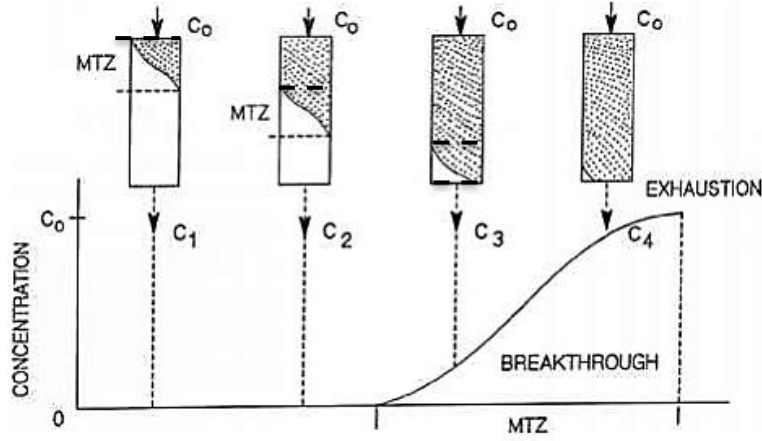


Figure 1 - Dynamic study of an adsorber^[19]

2.5.3 Adsorption kinetics

To confirm the size of the adsorber selected based on the dynamic studies some parameters such as the capacity factor for the equilibrium phase of adsorption (ratio between the retention volume and the dead volume - ξ_{eq}) and capacity factor for the kinetic phase of adsorption (ξ_k) are considered. By calculating an empirical parameter (ξ_{nd}) it is possible to study the dominant regime of the process (adsorption or diffusion) for each component of a mixture analyzing the ratio between both residence and diffusion times. The compound that adsorbs more shall have a bigger ξ_{nd} parameter than the other ones in a scale around of 1 order of magnitude. If ξ_{nd} is higher than 1 the separation is based on equilibrium. Otherwise, it is based on kinetics of adsorption. Based on this, it is possible to have the confirmation if the separation is happening based on an adsorption kinetics or equilibrium.^[17]

$$\tau = \frac{\varepsilon V}{Q} \quad 2.17$$

$$\xi_{eq} = \frac{(1-\varepsilon) q}{\varepsilon c_0} + \frac{(1-\varepsilon)}{\varepsilon} \varepsilon p \quad 2.18$$

$$\xi_k = \frac{t_{diff}}{\tau} = \frac{1}{K_{LDF} \tau} \quad 2.19$$

$$\xi_{nd} = \frac{\xi_{eq}}{\xi_k} \quad 2.20$$

The superficial velocity (v_s) is calculated based on the diameter of the adsorber and the volumetric flow. The minimum fluidization velocity (U_{MF}) of the packed bed (equation 2.21)

must be calculated as well, to guarantee the safety of the adsorbent particles. To have a high efficiency and to avoid fluidization, the superficial velocity shall always be lower than the minimum fluidization velocity. If the opposite happens the gas will have enough velocity to support and drag the adsorbent particles together with the gas. The interstitial velocity (v_i) such the velocity of the shock waves (v_{sh}) are also estimated to evaluate the adsorption kinetics of each compound of the mixture. The interstitial velocity measures the velocity inside the adsorber considering only the void spaces in between the adsorbent. The shock wave velocity for each component measures the advance of the concentration fronts within the column.

$$U_{mf} = 150 \frac{(1-\varepsilon)^2}{\varepsilon} \mu \frac{v_s}{d_p^2} + 1.75 \frac{(1-\varepsilon)}{\varepsilon^3} \rho \frac{v_s^2}{d_p^2} \quad 2.21$$

$$v_i = \frac{v_s}{\varepsilon} \quad 2.22$$

$$v_{sh} = \frac{v_i}{\xi_{eq}} \quad 2.23$$

The ideal ratio between the length and the diameter of the adsorber (L/D) is given by the literature as an empirical way to evaluate the flow distribution and the dead volume. To have an ideal pug flow this parameter shall be higher than 5 but it leads to a high pressure drop thus, in the design of PSA adsorbers this parameter is usually kept lower. ^[12]

3 Technical Description

DMT Environmental Technology, has a particular interest in developing a PSA installation to increase the market opportunity in the sector of biogas upgrading plants. A launching customer for this kind of technology was found and the system needs to meet the requirements to generate bio-methane with the gas grid specifications of the Netherlands.

Therefore, there are several technical aspects that shall be taken into consideration, such as the adsorbent, adsorption equilibrium isotherms, the biogas characteristics, the bio-methane requirements and the operational risks and maintenance of usual PSA installations.

3.1 Adsorbent Selection

The choice of the right adsorbent is crucial for the efficiency of an adsorption-based separation process. There are a big variety of adsorbents, and each one is appropriated for different kind of separations. It is important to define the conditions in which the adsorption process will operate, such as the kind of separation, the composition of the mixture and the final requirements of the product. ^[9]

Carbon molecular sieves (CMS) show to have a good performance for this kind of application. In this type of adsorbents, the separation occurs mainly due to differences in the diffusion rates of different molecules (kinetic separation). CMS have a uniform pore size distribution, a high internal surface area (good pore distribution) and they are usually non-polar adsorbents. A study realized by Qinglin et al. (2003) shows a quite low diffusivity of CH₄ comparing with the diffusivity of CO₂ into the pores of CMS Takeda 3A. CMS-3K (Takeda) also shows a faster diffusion of CO₂ into the micropore structure (Cavenati et al., 2005). The kinetic separation of the moisture CH₄/CO₂ in a CMS adsorbent is characterized by the different of 1 or 2 magnitudes in the rate of adsorption of both gases. ^[14]

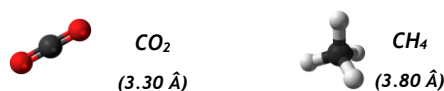


Figure 2 - Kinetic diameters of the CO₂ and CH₄ molecules (Source: wikipedia.org)

The CO₂ molecule has a smaller kinetic diameter than CH₄ (Figure 2), therefore it will pass through the stricture in the entrance of the adsorbent pores more easily than the methane molecule. This results in a high rate of CO₂ adsorption which makes the mass front of this compound much slower along the adsorber than the CH₄ mass front. ^[10]

There are also some equilibrium-based adsorbents like zeolites that can be efficient removing CO₂ from the biogas stream. Zeolites are alumina-silicates adsorbents which have

intracrystalline channels in their structure. These adsorbents show size-selective molecular sieve properties, which means that they exclude larger molecules than a certain critical size defined by their structure (Ruthven, 1981). The CO₂/CH₄ separation was studied by Rolniak and Kobayashi (1980) for zeolite 5A and the results showed high selectivity for CO₂. The same was concluded by Siriwardane et al. (1990) for zeolite 13X, however in this kind of adsorbent the diameter of the pores is even bigger thus the amount of CO₂ adsorbed was slightly higher than in zeolite 5A.

However, the zeolites that contain significant amount of aluminium in their structure are hydrophilic materials. Thus, if the biogas stream contains water in its composition, the adsorbent might not have the best performance since the water molecules can attach permanently to the adsorbent and its structure can even be damaged. Contrary, CMS are less hydrophilic than zeolites and nonpolar adsorbents, reason why they are commonly used when the streams to be treated are humid. [9]

Based on this, for the separation concerned it was selected a CMS adsorbent called CMS-Y (confidentiality reasons), perfect for nitrogen removal from the air and for CO₂/CH₄ separation specifically in PSA installations. The specifications of the selected adsorbent are presented in Table 2.

Table 2 - CMS-Y standard properties

Shape	Cylindrical
d_p (m)	1.8×10^{-3}
ρ_p (kg m ⁻³)	1060
ρ_b (kg m ⁻³)	700
ϵ	0.34
Particle Specific Heat (J mol ⁻¹ K ⁻¹)	880

Note: the references for these values are not presented due to confidentiality reasons.

3.2 Mathematical Model to describe Adsorption

First of all, to describe a PSA process it is necessary to choose one of the several mathematical models (isotherms) to describe adsorption equilibrium. Using the pure component isotherms found in the literature an isotherm fit using different models (Sips and Dual-Site Langmuir) was done and it is presented in Figure 3.

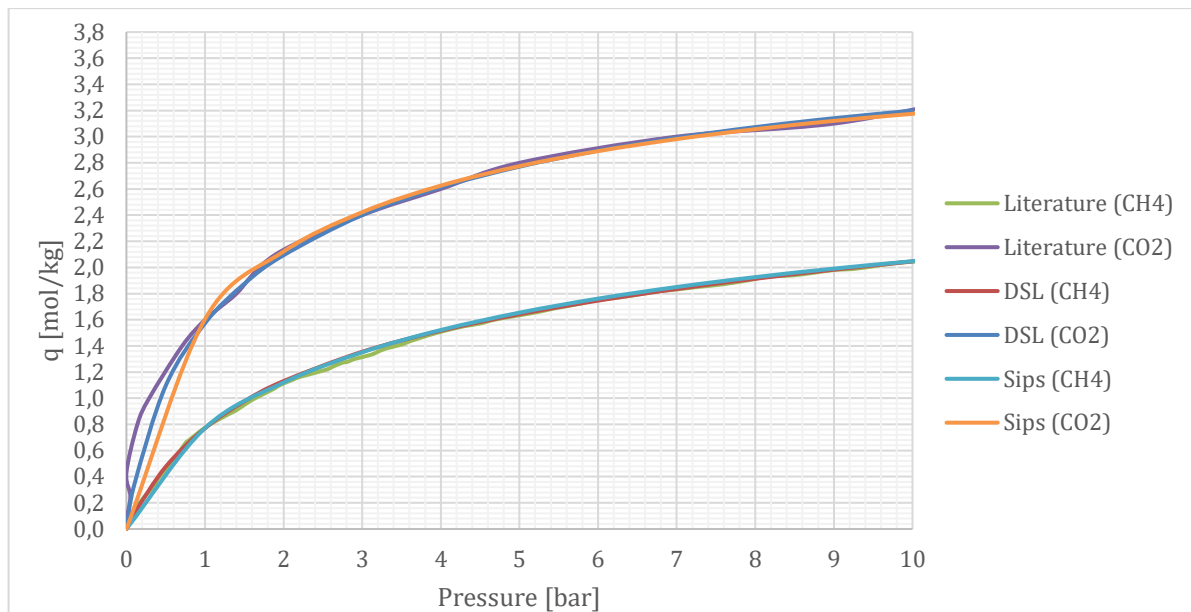


Figure 3 - Isotherm fitting with different mathematical models (Confidential source and temperature)

The dual-site Langmuir model showed the best fit for the isotherms reported in the literature (the references for the isotherms used are not mentioned due to confidentiality). Since the gas is mostly composed of CO₂ and CH₄, a binary system is considered to develop a mathematical model that must be able to predict the multicomponent equilibrium data. Therefore, it was used the extended dual-site Langmuir model (EDSL) (equation 2.5) for the multicomponent equilibrium prediction. The parameters used to obtain the fitting for EDSL are presented in the following table and the isotherms are presented in Appendix 1.

Table 3 - Equilibrium parameters used in the DSL model

		CO ₂	CH ₄
q _{s,1}	mol/kg	2.21	
K _{0,1}	bar ⁻¹	6.3 × 10 ⁻⁷	7.9 × 10 ⁻⁶
ΔH ₁	kJ/mol	-33.5	-21.7
q _{s,2}	mol/kg	1.71	
K _{0,2}	bar ⁻¹	8.9 × 10 ⁻⁴	3.7 × 10 ⁻⁴
ΔH ₂	kJ/mol	-20.1	-19.6

The kinetic parameters used to describe the linear driving force model (LDF) are presented in Table 6.

Table 4 - Dual site Langmuir isotherm parameters for CO₂ and CH₄ adsorption on CMS-Y (Equations 2.4 and 2.5)

Temperature (K)	K _{LDF} CO ₂ (s ⁻¹)	K _{LDF} CH ₄ (s ⁻¹)
293	0.01005	6.94 × 10 ⁻⁶
313	0.01273	1.91 × 10 ⁻⁵
333	0.01481	5.77 × 10 ⁻⁵
353	0.01759	1.12 × 10 ⁻⁴

Doing a linear regression based using the logarithm form of the Arrhenius law, it is possible to obtain the activation energy and the pre-exponential factor (*Table 5*).

Table 5 - Parameters calculated by a linear regression of Arrhenius Law at 293 K

	CO ₂	CH ₄
Ea (kJ/mol)	7.9	40.7
K _{0,LDF} (s ⁻¹)	0.25	126

A MATLAB model was developed by DMT Environmental Technology to describe the dynamic behaviour of CO₂ and CH₄ in a fixed bed and also to simulate the PSA cycle performance. However, the model is not accurate enough in order to be the used as a correct simulation model since the simulations performed were showing considerable inconsistencies in the dynamic and PSA cycles studies. Even so, the assumptions used in the MATLAB model such as equations are presented are presented in *Appendix 2*.

3.3 Biogas Characteristics

For this project, the biogas specifications delivered by the client to the product development department are described in *Table 6*. However, it is necessary to consider a range for each variable to consider future projects with different requirements. Due to economic factors, the bio-methane recovery of the system shall be higher than 99%.

Table 6 - Biogas characteristics and established ranges for each variable

		MIN	MAX	NOM
Pressure	[mbar(g)]	10	30	20
Temperature	[°C]	25	40	37
Dew-point	[°C]	25	40	37
Relative humidity	[%]	100	100	100
Flow	[Nm ³ /h]	300	500	450
CH ₄	[v/v %]	50	65	55
CO ₂	[v/v %]	35	50	45
N ₂	[v/v %]	0	2	1
O ₂	[v/v %]	0,15	1	1
H ₂ S	ppm(v)	-	200	-
NH ₃	ppm(v)	-	100	-

3.4 Bio-methane Requirements

The bio-methane produced must be in line with the Dutch grid requirements represented in Table 7. Only if these specifications are covered the biogas can be introduced in the grid and all the design of the PSA installation should be based on it.

Table 7 - Bio-methane requirements for grid injection in the Netherlands^[22]

		MIN	MAX	NOM
Temperature	[°C]	0	35	20
Dew-point	[°C @70 bar(a)]	-	-	-8
CH ₄	[mol %]	84.8	97	90
CO ₂	[mol %]	0	10.3	10
O ₂	[mol %]	0	0.5	< 0.5
H ₂ S	ppm(v)	-	200	< 200

3.5 Operational Security Measures and Maintenance

The entire process will have a sophisticated control system previously programmed to react to all the needs of the system that will be working 24/7.

It is important to consider that the bio-methane in combination with O₂ has a potential risk of forming an explosive mixture. In order to create explosive mixtures, around 5-15% of CH₄ has to be in contact with the O₂ rich surroundings. The leakage points present the highest

risks. Therefore, it is important to adopt measures to avoid this kind of issue like, for example, adding lower explosion limit (LEL) detectors inside the containers where the installation is allocated. ^[20] In *Appendix 3* it is represented the ternary flammability diagram for CH₄/O₂/N₂ mixtures. ^[21]

Since the PSA process works with big variations of pressure in a short period of time the equipment (adsorption beds, pipelines, valves) shall be selected to resist to these conditions. Stainless steel adsorbers and pipelines may be the best solution to maximize the life time of the installation but also because it is a resistant material to pressure fluctuations. It is recommended to introduce safety and relieve valves in the top of each vessel or in the product pipelines to prevent pressure deviations (higher pressure than the necessary).

The maintenance of the installation will mainly be focused in the valves that make the switching of each step of the PSA process. The lifetime of the valves used in PSA processes is directly related with the duration of the PSA cycle. Shorter the cycle, bigger is the number of cycles done per year. Special PSA valves have a lifetime higher than 500 000 cycles (for example, a cycle with 10 minutes has a lifetime around 10 years). The adsorbent selected is known by its long-life time in this kind of processes, therefore it is estimated a period of 8 years until it is necessary to replace it.

4 Results and Discussion

Due to the lack of resources to confirm if the PSA unit for bio-methane production was being designed accurately it was necessary to create some external partnerships. One of them was made with the Faculty of Engineering of University of Porto, in specific with its I&D unit the Associate Laboratory LSRE-LCM. The mathematical model used to describe the dynamic behavior of a fixed bed multicomponent adsorption column results in ordinary differential equations system (ODE) with respect to time. Then, based on that simulations it was possible to define the final design of the adsorbers.

4.1 Dynamic study - Breakthrough curves

To design a column of adsorption, it is necessary to predict the breakthrough curve and adsorption capacity of the adsorbent for the selected adsorbate under the given set of operating conditions. The parameters used by LSRE in the mathematical model to perform the simulations are presented in *Appendix 4*.

Based on equilibrium assumptions (adsorption capacity of 2.0 mol/kg for 8 bar) and taking into account the ratio L/D, a first estimation of the sizing of an adsorber filled with CMS-Y adsorbent was done. By estimating the mass and volume of adsorbent needed the first sizing the adsorber considered was 1.5 meters of height and 0.3 meters of diameter and the value of the ratio L/D calculated was 5 - expected plug flow behaviour. Thus, it was asked to LA/LSRE-LCM to perform dynamic studies for this design (Case A) in order to confirm the veracity of it. The breakthrough curves were performed for different flowrates and the results are presented in the following figure.

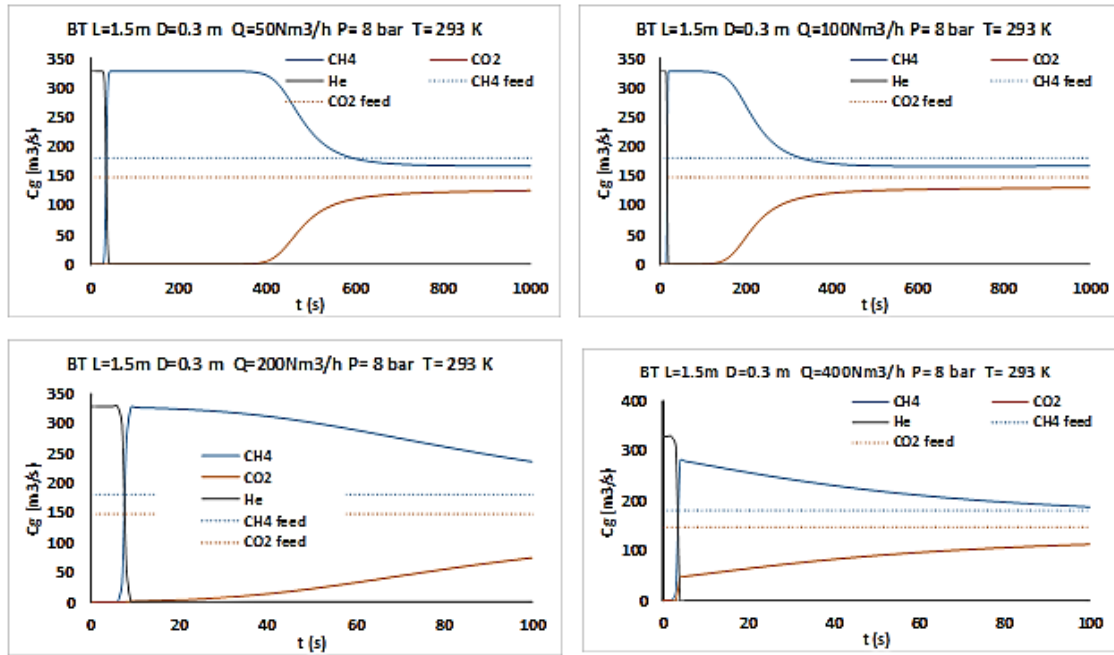


Figure 4 - Breakthrough performances for different flowrates for case A

Observing the several breakthrough curves it is possible to conclude that for the highest flowrate of 400 Nm³/h the breakthrough of both components happens immediately and simultaneously. Therefore, it was possible to conclude that the adsorption of both components was controlled by the adsorption kinetics. Since CMS-Y is a kinetic adsorbent, the fastest adsorbing component (the heavy one) must be able to adsorb (controlled by equilibrium) and not have kinetic limitations. An analysis to the velocities and kinetics was done to understand the dynamic behaviour presented in Figure 4 (Table 8).

Table 8 - Kinetic analysis regarding the simulations for Case A

Q (Nm ³ /h)	Q (m ³ /h)	v _s (m/s)	v _i (m/s)	τ (s)	t _{diff} (s)	t _b (s)
50	6.7	0.026	0.077	19.4	99.5	390
100	13.4	0.053	0.154	9.7	99.5	130
200	26.8	0.105	0.309	4.8	99.5	10
400	53.6	0.211	0.620	2.4	99.5	5

As it is possible to observe, the simulations regarding the 50 Nm³/h and 100 Nm³/h flowrates are the only ones that showing separation based on the adsorption. For these flowrates the breakthrough point happens 390 and 130 seconds (respectively) after the beginning of the feed step. For all the other cases the breakthrough of CO₂ is premature, due to the high velocities and low residence times of the gas inside the adsorber (MTZ travels too fast) and there is no time for an efficient adsorption of the CO₂). The 50 Nm³/h case was

considered has a good result. However, this flowrate is around 1/8 of the desired flowrate that the PSA unit will have to treat. Then, new calculations were done in order to design the adsorber and determine its dimensions.

The adsorption capacity of the adsorber was predicted based on an assumption considering the adsorption capacities for 8 bar (adsorption pressure) and 0.1 bar (desorption pressure):

- 8bar: $y_{CO_2} = 0.45$, $q_{CO_2} = 2.52$ mol/kg;
- 0.1 bar: $y_{CO_2} = 0.05$, $q_{CO_2} = 0.27$ mol/kg;

$$\text{Adsorption capacity} = 2.52 - 0.27 \quad 4.1$$

These compositions were defined according to the biogas characteristics and the adsorption capacities were based on the CMS-Y binary mixture isotherm for CO₂ (EDSL isotherm). The overall working capacity calculated was 2.25 mol/kg.

The diameter was estimated based on the superficial velocity that should never be higher than the minimum fluidization velocity of the adsorption step (v_{mf}). For the selected adsorbent specifications, the v_{mf} is 0.211 m/s. To estimate the maximum superficial velocity, it was considered that it should be 80% of the v_{mf} in order to prevent fluidization.

Table 9 - Values used to estimate the diameter of the adsorber

$v_{s, \max}$ (m/s)	0.169
Q (Nm ³ /h)	450
F (m ³ /h)	60.3
A_s (m ²)	0.099
D_{minimum} (m)	0.4

The diameter calculated based on the maximum superficial velocity is the minimum diameter that the vessel can be. Otherwise, there is a high risk of fluidization during the adsorption step. Since the superficial velocity can be lower for a better adsorption performance the diameter was fixed at 0.5 meters ($v_s = 0.085$ m/s).

A length of 2 m was chosen taking into account a ratio L/D of 4.

After the calculations to estimate a second size for the adsorber, it was requested a second simulation (case B), this time using 2 m of length and 0.5 meters of diameter (L/D = 4).

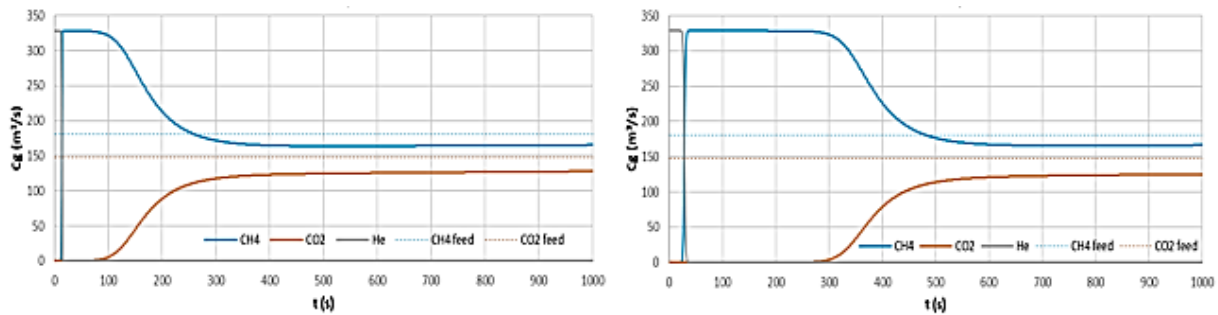


Figure 5 - Breakthrough curves for 450 Nm³/h (left) and 225 Nm³/h (right)

Table 10 - Kinetic analysis regarding the simulations for Case B

Q (Nm ³ /h)	Q (m ³ /h)	v _s (m/s)	v _i (m/s)	τ (s)	t _{diff} (s)	t _b (s)
450	60.3	0.085	0.251	8.0	99.5	90
225	30.2	0.043	0.126	15.9	99.5	290

In this case, the breakthrough point elapses at 90 seconds for the 450 Nm³/h flowrate case. Since in the PSA installation the adsorption time shall be lower than the breakthrough time (to preserve product’s purity), in this case the feed step would have to be lower than 90 and consequently the cycle would have to be quite fast. Regarding the valves maintenance it is preferred larger cycles to decrease the number of switches per year. To solve this problem LA/LSRE-LCM laboratory proposed a solution: two PSA units (with 4 vessels each) working in parallel each one with 225 Nm³/h of capacity. Although it was an efficient alternative the cost of an installation with that disposition was considered too high.

Finally, a last adsorber’s design was estimated in order to request a last simulation regarding an adsorber working efficiently with 450Nm³/h. Studying the previous simulations, it was observed that for big residence times (and low superficial velocities) the breakthrough point occurs later. If the velocity of the gas is directly connected to the breakthrough time, it means that the diameter of the vessel is a critical point to obtain a good general performance. Thus, the diameter was increased to 0.7 meters in order to maintain the superficial velocity of 0.043 m/s obtained for the 225 Nm³/h capacity in case B. The simulation was done for 2 meters of height and 0.7 meters of diameter (case C) and the dynamic result is presented on Figure 6. The ratio L/D is 3 in this case.

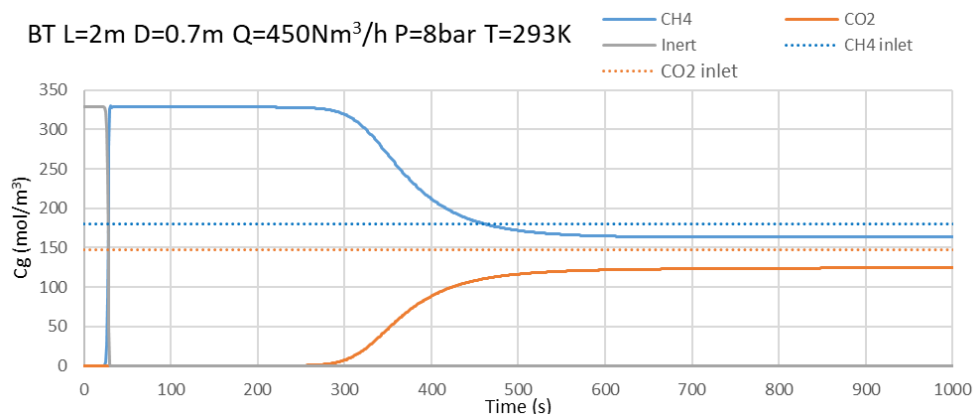


Figure 6 - Breakthrough curve for a capacity of 450 Nm³/h, 2 m of length and 0.7 m of diameter

This last simulation is in line with the predictions previously done. In *Table 11* it is possible to observe the characteristic times analyses for the process in this case.

Table 11 - Kinetic analysis regarding the simulations for Case C

Q (Nm ³ /h)	Q (m ³ /h)	v _s (m/s)	v _i (m/s)	τ (s)	t _{diff} (s)	t _b (s)
450	60.3	0.043	0.128	15.6	99.5	290

4.2 PSA Cycle Studies

After studying the adsorption dynamic behaviour of the mixture in the adsorbent it was decided to study the cycles for the cases B and C, since they showed the most promising results in the dynamic studies. For each case the LA/LSRE-LCM used the same model to develop a PSA cycle and its respective multicolumn, and then all the variables were studied to finally decide what the best design for the PSA.

In case B the behaviour of an installation with two units with four vessels working in parallel was studied, each one processing 225 Nm³/h. Otherwise, in case C a PSA cycle with four columns processing the total flow of 450 Nm³/h was studied. The goal between cases B and C studies is different, since in case B it is studied a cycle producing CH₄ with 97% of purity and in case C a cycle producing 90% of CH₄. In both cases the feed stream is divided in Feed 1, which represents the total flow entering in the adsorption bed, and Feed 2 which is the flow that is entering in the adsorber when the pressurization step of the other vessel starts.

The working conditions for case B are presented in *Table 12*.

Table 12 - Working conditions of the PSA cycle for case B

	Case B
Flow (Nm ³ /h)	225
High Pressure (bara)	8
Low Pressure (bara)	0.1
Temperature (K)	293
y CH ₄	0.55
y CO ₂	0.45
Length (m)	2
Diameter (m)	0.5

The working schedule and times of each step for case B are presented on *Figure 7* and *Table 13*.

Feed 1	Feed 2	Eq. D	Blowdown	Purge		Eq. P	P
Eq. P	P	Feed 1	Feed 2	Eq. D	Blowdown	Purge	
Purge		Eq. P	P	Feed 1	Feed 2	Eq. D	Blowdown
Eq. D	Blowdown	Purge		Eq. P	P	Feed 1	Feed 2

Figure 7 - Working Schedule for case B

Table 13 - Times of each step of the PSA cycle for case B

	Case B (s)
Feed	150
Equalization Depressurization	90
Blowdown	70
Purge	140
Equalization Pressurization	90
Pressurization	60

The outlet molar flows and the pressure histories along the whole PSA cycle are presented in *Figure 8*.

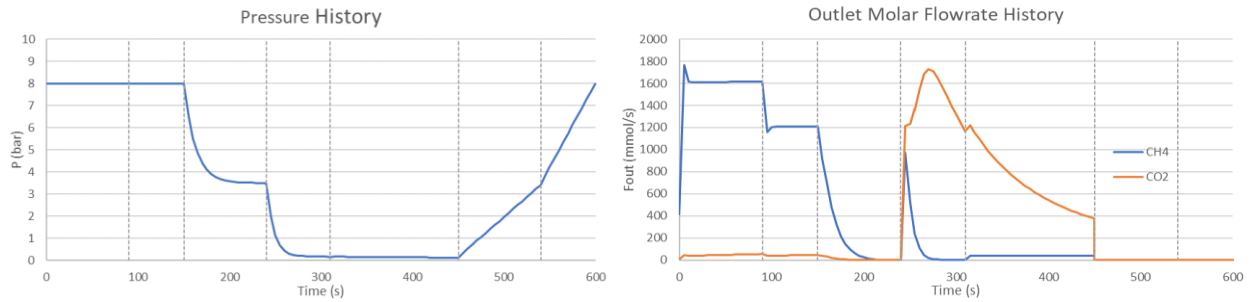


Figure 8 - Pressure and outlet molar flow rate histories for Case B

As it is possible to observe in *Figure 8*, a considerable amount of CH₄ is going together with the off-gas flow in the blowdown and purge steps (it affects the recovery of bio-methane of the system). Thus, to reduce the CH₄ loss in the blowdown, a recycle on the first 10 seconds of this step was added. The recycle is performed until the pressure of 1 bar is achieved in order to have a smaller vacuum pump to perform the regeneration of the columns. The purge is performed with product gas entering counter-currently with a flow rate of 9.65 Nm³/h.

The purity, recovery and productivity are presented in *Table 14*.

Table 14 - Purity, Recovery and productivity of CH₄

	CH ₄
Purity (%)	97.10
Recovery (%)	91.40
Productivity (mol/kg _{ads} h)	4.38

According to the previous simulations the CH₄ purity achieved for this PSA configuration is indeed around 97%. However, the recovery is far from the 99% defined as a goal for the PSA installation, fact that can be explained by the CH₄ used in the purge step. To reduce the methane losses in this case it would be necessary a second stage (PSA or membrane) to recover the methane slip of the first PSA unit. Other option to consider is a purge step performed with an inert gas instead of product gas.

Case B was not considered as an option due to the high number of vessels required which implies a considerable higher price of the unit. However, it was possible to evaluate the behaviour of the adsorber for this cycle configuration regarding the 97% of purity. With this simulation it was also possible to study the influence of the purge step and recycle in the blowdown in the global efficiency of the process.

The second simulation is related to case C which is performed as VPSA unit. The regeneration of the adsorber is achieved by using a single blowdown (no purge) for a design of 2 m of length and 0.7 m of diameter.

Feed 1	Feed 2	Eq. D	Blowdown			Eq. P	P
Eq. P	P	Feed 1	Feed 2	Eq. D	Blowdown		
Blowdown		Eq. P	P	Feed 1	Feed 2	Eq. D	
Eq. D	Blowdown			Eq. P	P	Feed 1	Feed 2

Figure 9 - Working Schedule for case C

Table 15 - Times of each step of the PSA cycle for case C

	Case C
Flow (Nm ³ /h)	450
High Pressure (bara)	8
Low Pressure (bara)	0.1
Temperature (K)	293
Y CH ₄	0.55
Y CO ₂	0.45
Length (m)	2
Diameter (m)	0.7

Table 16 - Times of each step of the PSA cycle for case C

	Case C (s)
Feed	150
Equalization Depressurization	90
Blowdown	210
Purge	-
Equalization Pressurization	90
Pressurization	60

The outlet molar flows and the pressure histories along the whole PSA cycle are presented in *Figure 10*.

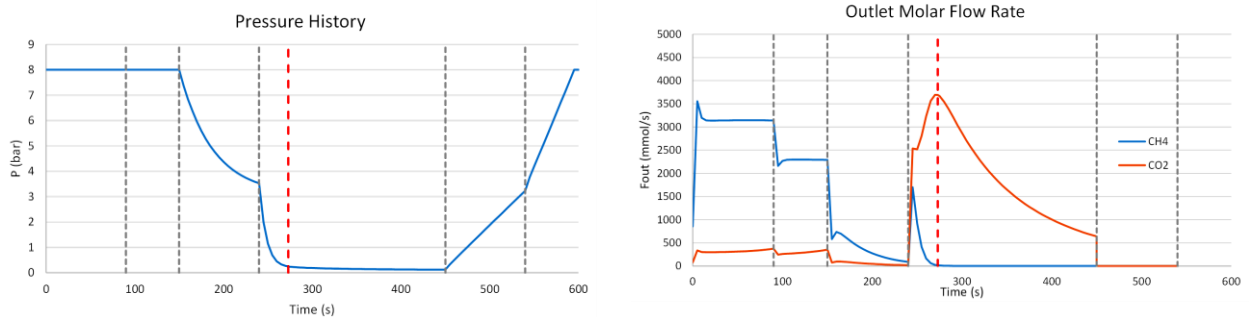


Figure 10 - Pressure and outlet molar flow rate histories for Case C.1

The red dotted line (*Figure 10*) points out the recycle time in the beginning of the blowdown step which is 30 seconds. However, it is preferred that the recycling blowdown doesn't drop below 1bar, otherwise an additional vacuum pump would be required in the process due to the overlapping of flows in the recycle and blowdown steps in different adsorbers. The pressure of 1 bar as the end pressure of the recycle is also chosen based on the pressure of the buffer where the gas is being stored, before being mixed with fresh feed.

The vacuum pump choice is an important factor since it is deeply related with the flowrates of the recycle and blowdown. Focusing on the blowdown step it is possible to observe a peak in the outlet flow due to the quick drop of pressure (3.5-0.1 bar) in a short period of time. A vacuum pump that can handle of the observed flowrates is inevitably big and expensive, since it must work in a large range of flowrates. Therefore, it was decided that the volumetric outlet flow in the blowdown should never be higher than 250 Nm³/h to enable the choice of a smaller vacuum pump.

Thus, a last simulation was performed taking into account the end of the recycle at 1 bar and the maximum outlet flow of 250 Nm³/h in the blowdown step (*Figure 11*).

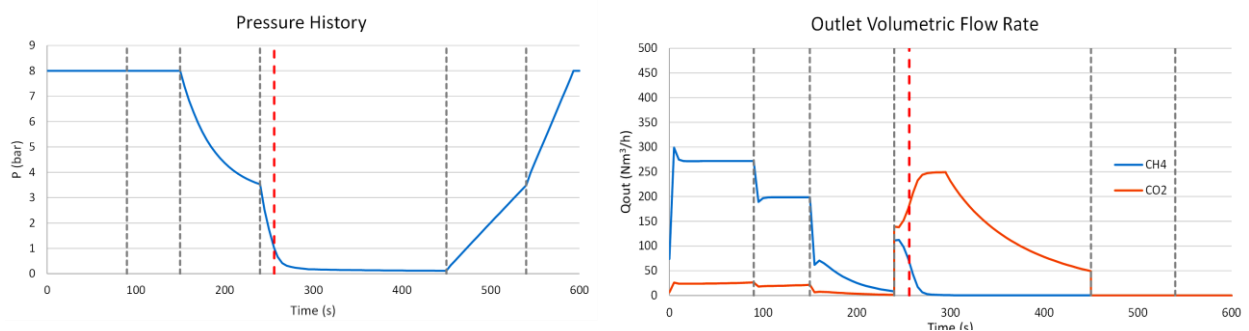


Figure 11 - Outlet volumetric flow rate for a limited blowdown flow of 250 Nm³/h and recycle ending when 1 bar is achieved (Case C.2)

In this case, the recycle time considered was 16 seconds. This time corresponds to the time necessary to achieve 1 bar inside the vessel. Since the recycle time is shorter, the CH₄ retained in the bottom of the vessel after the adsorption step is not recovered so efficiently and a part of it goes out in the blowdown step together with the off-gas. This factor causes a decrease in the bio-methane recovery of this PSA unit. The purity doesn't change substantially although for the case C.2 it is a little bit higher. The purity, recovery and productivity for both cases are presented in *Table 17*.

Table 17 - Purity, recovery and productivity regarding the simulations of case C

CH ₄	Case C.1	Case C.2
Purity (%)	90.00	91.5
Recovery (%)	99.80	98.6
Productivity (mol/kg _{ads} h)	4.78	3.47

Since the last configuration simulated was the most promising one regarding the requirements of the installation, a volumetric balance to the system was elaborated considering that the four vessels are working at the same time (*Table 18*).

Table 18 - Volumetric balance for the system simulated in case C.2

	Case C.2								
	Flow (Nm ³ /h)			y CH ₄ (%)			y CO ₂ (%)		
	Min	Max	Average	Min	Max	Average	Min	Max	Average
Recycle	159	270	227	11.9	33.3	19.4	66.7	88.1	80.6
Blowdown	57.0	307	153	0.00	19.4	1.00	80.7	100	99.0
Product	214	304	269	67.8	98.4	91.8	1.63	32.2	8.16

It is important to consider that the recycle line is not working continually, thus the values presented in the previous table are only related to the 16 seconds of blowdown. The vacuum pump chosen can handle 210 m³/h. It means that when a recycle step in one adsorber is happening at the same time as a blowdown step in another one, the flow easily exceeds this value. In that sense, considering that the global off gas flow of the system can achieve a value around 500 Nm³/h (with the adsorbers working at the same time), three vacuum pumps with 210 Nm³/h of capacity were considered as the best solution regarding the price and cycle performance.

4.3 Final Design of the PSA unit

After analysing all the simulations done by LA/LSRE-LCM in Porto, the case C.2 seemed to be the most promising study. Thereunto, it was necessary to calculate some parameters such as the mass of adsorbent necessary and the kinetic parameters to make sure that the adsorption of the CO₂ is being performed efficiently.

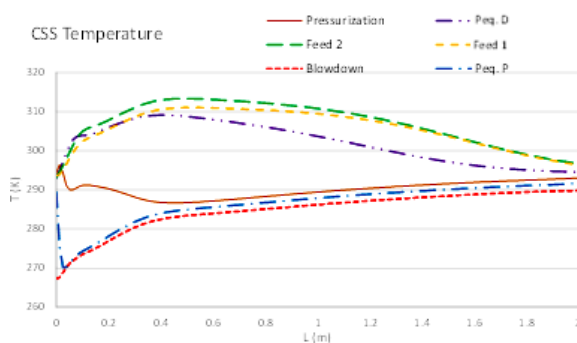


Figure 12 - Temperature profile at the end of each step of one cycle at steady state (Case C.2)

The adsorption step is an exothermic process and that explains why the temperature increases along the vessel during this step. The inverse occurs during the blowdown, since energy is required to break the bonds between the CO₂ and the active center of the adsorbent. In this case a decrease in the temperature happens. It is necessary to take into account that the temperature in the desorption step can drop below zero. If the gas contains water in its composition, it can condensate or even form ice crystals and the adsorbent might be damaged. In this case, even if the feed stream contains water in its composition it is estimated that it would not substantially adsorb in the CMS-Y (nonpolar adsorbent). However, a small amount of water might be adsorbed and consequently stay inside the adsorber in the blowdown step. Considering that the adsorber's volume is totally filled with adsorbent, the total mass of adsorbent that is actually in each vessel can be calculated taking into account the adsorbent bed density. The total mass of adsorbent in each adsorber for this design is 538.8 kg.

It is also important to study the velocities associated to this adsorption process since it is mainly a kinetic separation. The desorption velocity regarding the average flowrate of the blowdown for this case (150 Nm³/h) were also calculated to ensure that crushing is never achieved.

Table 19 - Velocity studies inside the adsorber

$V_{s,adsorption}$ (m/s)	0.043
$V_{i,adsorption}$ (m/s)	0.128
$V_{sh_CO_2}$ (m/s)	0.004
$V_{sh_CH_4}$ (m/s)	0.019
$V_{s,desorption}$	1.161

As it is possible to see in *Table 19* the CH₄ concentration front is faster than the CO₂ concentration front. It means that the CH₄ will go through the column much faster while the CO₂ stays retained for a longer interval of time. Thus, each CH₄ molecule will take around 71 seconds to reach the exit of the adsorber, while the CO₂ would take around 586 seconds. This is a positive result, since the main goal is to maintain the CO₂ inside the vessel as much is possible while the CH₄ is passing through.

Finally, to confirm the pre-defined design, the characteristics times of the process, such as the diffusional time and the space time, were calculated. For that the concentrations and kinetic constants of CO₂ and CH₄ are required. The results are presented on *Table 20*.

Table 20 - Results regarding the kinetics of adsorption

	CO ₂	CH ₄
C (mol/m ³)	147.8	180.6
ξ_{eq}	34.8	6.84
t_{diff} (s)	99.5	1.4×10^5
τ (s)	15.6	15.6
ξ_{nd}	5.5	7.4×10^{-4}

Comparing both capacity factors, it is obvious that the kinetics are favoring the CO₂ adsorption in this adsorbent, since the factor is much bigger for this component. The empirical parameter (ξ_{nd}) was applied to analyze which process, adsorption or diffusion, is the dominant one. Considering the *Equation 2.20*, the component that is most likely adsorbed shall be largely bigger than the other one. Observing the values presented on *Table 20* it is possible to conclude that the kinetic separation will happen successfully at the pre-defined conditions.

The size of 2 meters height and 0.7 diameter seems to be in line for the specifications considered. However, to design an industrial scale PSA unit it is necessary to consider an

engineering margin to make sure that the installation will still work if some variables change. The flowrate that is going to be fed to the PSA unit can variate since it always depends on how much biogas the digester produces and also on the amount of gas that is recycled in the system. These variations directly affect the superficial and interstitial velocities. The increasing of the inlet flowrate, and consequently of the velocities has a negative impact on the purity of the product as the mass transference zone for CO₂ will travel faster through the bed.

Therefore, a diameter of 0.8 m was defined instead of 0.7 m. This alteration in the diameter results in a larger amount of adsorbent required (total mass is 704 kg for each adsorber), in a higher working capacity and in a larger breakthrough time of the vessel (for the same flow of 450Nm³/h). The results regarding velocities and kinetics are presented for different inlet flows in *Table 21*.

Table 21 - Final results regarding different inlet flows (D = 0.8 m, L = 2 m, t_{feed} = 150 s)

Q (Nm ³ /h)	450	500	550
v _{s,adsorption} (m/s)	0.0333	0.0370	0.0407
v _{i,adsorption l} (m/s)	0.0981	0.1090	0.1199
v _{sh_CO2} (m/s)	0.0028	0.0031	0.0034
v _{sh_CH4} (m/s)	0.0144	0.0159	0.0175
ξ _{CO2,eq}	34.8	34.8	34.8
ξ _{CH4,eq}	6.84	6.84	6.84
t _{diff} (s)	99.5	99.5	99.5
τ (s)	20.4	18.4	16.7
ξ _{nd,CO2}	7.1	6.4	5.8
ξ _{nd,CH4}	9.7 × 10 ⁻⁴	8.7 × 10 ⁻⁴	7.9 × 10 ⁻⁴

For these three different cases, the superficial velocity of adsorption never exceeds the velocity related to the 290 seconds of breakthrough case previously simulated and analyzed in the dynamic studies. It means that for the same length, if the velocity is lower than 0.043 m/s (*Table 11*), the breakthrough will take more time to be achieved. Thus, the adsorber with this design can work properly for higher feed flows with the same working schedule without compromising the adsorption process.

The final size of the adsorber was finally defined as 2 m of length and 0.8 m of diameter.

4.4 PSA unit to recover bio-methane

As it was mentioned before, the bio-methane recovery of the entire system shall be higher than 99%. However, to achieve 97% of CH₄ purity, it is necessary to perform an efficient regeneration step by purging the vessel with product gas. In that case, the amount of product used to purge will be lost with the off gas and the recovery will not be high enough.

To solve this problem, a second PSA unit to recover bio-methane was considered to treat the off gas coming from the blowdown and purge steps of the first PSA unit. The same methods of design were applied to estimate a size of the adsorbers of the second PSA. In the future, LA/LSRE-LCM will provide to DMT Environmental Technology the simulations for this PSA unit.

The same adsorbent is considered as well as the same isotherm model (multicomponent DSL model). The main goal of this PSA is to produce gas with 50% of CH₄ and 50% of CO₂ that will be forwarded as a recycle to the pre-treatment to be treated again. The off gas of this PSA cycle will be forwarded to a stack and will have around 99.9% of CO₂ in its composition. The inlet stream characteristics considered to design this PSA adsorber are represented in *Table 22*. The flowrate taken into account is based on the volumetric balance done to the simulation C.2, but a margin was considered to make sure that the unit works in case of flow variations (like a purge flow added to the off-gas flow or bigger inlet flow in the first PSA). The average flow that is coming out in the blowdown step of the first PSA is around 150 Nm³/h. Therefore, the second unit will be designed to handle a maximum of 250 Nm³/h.

Table 22 - Inlet stream conditions for the second PSA unit

Q (Nm ³ /h)	250
P (bar)	3
T (K)	293
y _{CO₂} (%)	95
y _{CH₄} (%)	5

Considering that the inlet flow characteristics of this PSA and the low purity required, it is expected a simple Skarstrom cycle composed of two adsorbers working at low pressures. Regarding the composition of the inlet gas, the high working pressure chosen is 3 bar and the low pressure is 0.7 bar, since for these pressures the adsorption capacity shows to be enough (2.9 mol/kg at 8 bar and 1.7 mol/kg at 0.7 bar). The working capacity estimated considering the pressures of adsorption and desorption is around 1.2 mol/kg.

It will only be possible to define the correct size of the adsorber and the best cycle configuration after the LSRE provides the simulations for this second PSA unit to recover bio-methane.

4.5 Installation and process description

The whole system is divided in three main sections: raw biogas pretreatment, PSA unit for bio-methane production and PSA unit for bio-methane recovery.

First, the raw biogas delivered directly from the anaerobic digester is going to a pre-treatment unit. The pre-treatment starts with a drying step where part of the water present in the biogas stream is removed. In this section, a dew point of -3°C must be achieved to prevent condensation at low temperatures in the blowdown step of the first PSA. After that, the gas is boosted to pass through a desulphurization process composed of two activated coal columns. They are lined up in such way that the outlet flow of the first coal filter is the feed towards the second filter. To achieve the working pressure required for the PSA unit there is a compression section where the biogas is compressed to a range between 8 and 10 bar(a). The compression section is followed by a filter system to remove traces of oil and particles that can be released during the compression section. In the end of the pre-treatment the biogas finally has the required conditions to enter in the PSA unit for bio-methane production.

The Pressure Swing Adsorption section is composed of four columns filled with CMS-Y working at the same time with a combined schedule that allows a continuous bio-methane production. This unit has been designed to produce a bio-methane stream composed by CH₄ and CO₂ with a methane content of at least 97 %.

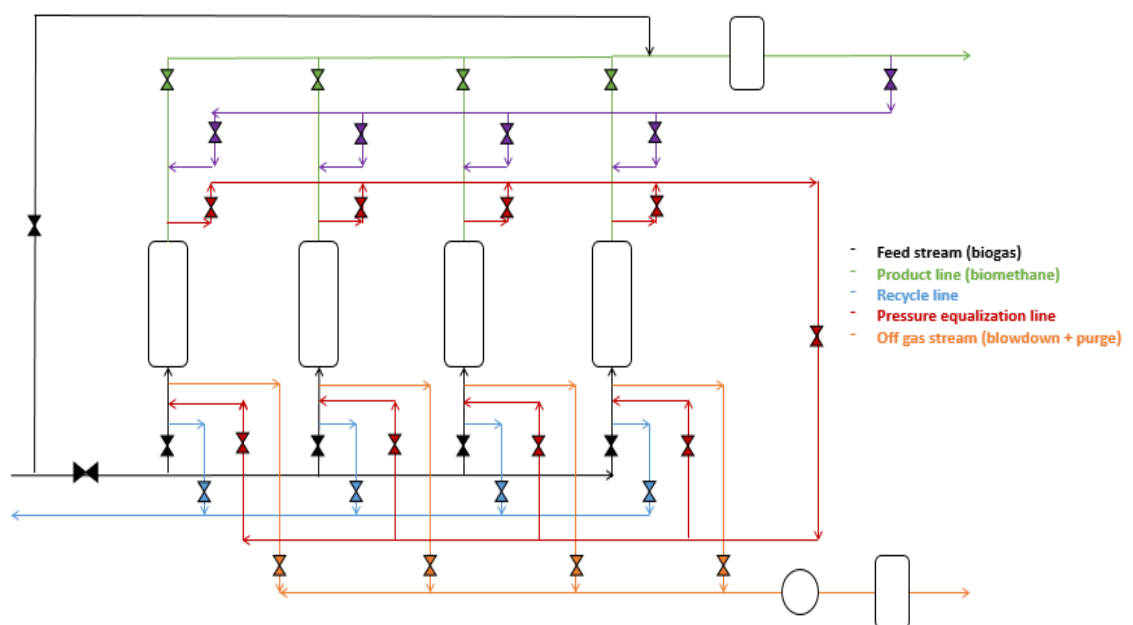


Figure 13 - General Scheme of the PSA unit for bio-methane production

The PSA unit is composed of four adsorber vessels filled with CMS-Y. The beds are interconnected, which means that if one vessel is stopped for some reason the others will be also impacted and the total process will shut down. The biogas stream characteristics after the pre-treatment are presented in *Table 26*.

Table 23 - Inlet stream characteristics (biogas after the pretreatment section)

Q (Nm ³ /h)	450	P (bara)	8
Q (m ³ /h)	60.3	T (K)	293
y CH ₄	0.55	y CO ₂	0.45

The cycle is divided in six different steps:

- 1. Feed:** where the adsorption of the CO₂ occurs. This step has two phases, since in the first 90 seconds the flow that is being fed is the total flow coming from the pre-treatment (Feed 1), and the 60 seconds after 26% of that flow is being forward to pressurize another vessel (Feed 2). While the CO₂ is being retained in the adsorbent, the CH₄ continues to pass through the column exiting the top and heading to the product line. Adsorption is an exothermic process, so it is normal that the temperature increases in this step.
- 2. Equalization depressurization (Eq. D):** after the adsorption step it is common to do an equalization of the pressure. It can contribute for a higher recovery and also saves energy consumption. In this case, the pressure inside the vessel is 8 bar(a) in the beginning of the step and in the end (after 90 seconds) it shall be 3.5 bar(a). The gas that is leaving the vessel in the equalization depressurization is used to do the equalization pressurization (see step number 5) in another vessel. It means that the number of moles that is coming out from a vessel in the equalization depressurization step is the same as the number of moles that is entering in the equalization pressurization step of another vessel. These two steps happen simultaneously.
- 3. Blowdown:** in this step the low pressure of 0.1 bar(a) is achieved using three vacuum blowers for the effect during 70 seconds. To reduce the losses of CH₄ along this step it is possible to do a recycle during 16 seconds in the beginning of the step, the recycled stream will be mixed with fresh feed. It is also possible to do a larger blowdown (210 seconds) to replace the purge step (see step number 4). In this case a VPSA configuration will be used.
- 4. Purge:** at the end of the blowdown, CO₂ molecules are both in the adsorbed and gas phases. Thus, it is possible to remove them by feeding a purge gas (usually a small amount of product gas) counter-currently in the vessel (from the top to the bottom).

This purge stream decreases the partial pressure of CO₂ to improve the adsorbent regeneration and its specific way (counter-current) avoids the contamination of the top of the bed where pure gas exits. The purge occurs during 140 seconds at a low pressure of 0.1 bar(a) with a flowrate of about 10 Nm³/h. The system is also configured to replace this step for a larger blowdown as it was mentioned previously (VPSA configuration).

5. **Equalization pressurization (Eq. P):** this step is used with the same propose than equalization depressurization, but an increase of pressure happens instead of a decrease of it. In the beginning of Eq. P. the pressure is 0.1 bar(a) and in the end it is 3.5 bar(a).
6. **Pressurization:** the pressurization step is when the high pressure of 8 bar(a) is achieved again to begin a new cycle. This step is made with 26 % of the feed flow that is at high pressure. It takes around 60 seconds to be complete.

The product gas is sent to a buffer and then to a TSA drying unit where it is dried until the required dew point of -8 °C @70bar is achieved. After that, the bio-methane has finally all the specifications required to be introduced in the gas grid.

It is estimated that to produce bio-methane with high purities (around 97%) the purge step is necessary to do a better regeneration of the adsorbers. If the purge step is being performed with product gas, some of the product will be lost with the off gas from the PSA and consequently the overall recovery of the process will decrease below 99%. To solve this problem, two different solutions were considered: a nitrogen injection to purge the bed or a second PSA unit to recover bio-methane.

The nitrogen purge has the goal of replacing the product purge step performed, since it is the main cause for the decrease of the recovery in the system. If the purge is performed with nitrogen, a small amount of it will stay inside the vessel in the end of the step. However, the adsorbent chosen has also high selectivity to adsorb nitrogen. Therefore, the small amount of nitrogen retained in the adsorber will be adsorbed in the pressurization and feed steps together with the CO₂. The nitrogen can be produced by a unit that captures nitrogen from the air. It will be tested in the first plant constructed by DMT Environmental Technology.

Beside the nitrogen injection unit, a second PSA unit is placed to treat the off gas coming from the first PSA.

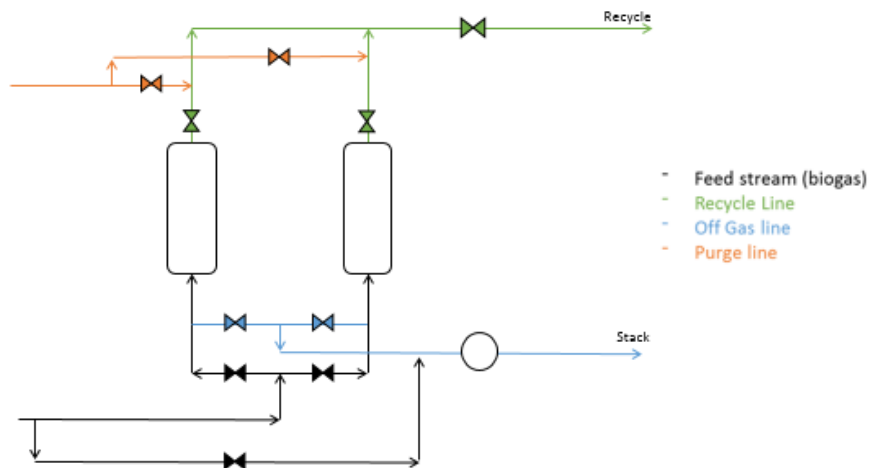


Figure 14 - Scheme of a possible configuration of the second PSA unit

This PSA unit will probably follow a simple Skarstrom cycle (2 adsorbers) with four steps: pressurization, feed, blowdown and purge (it will be confirmed by the simulations from LA/LSRE-LCM). It will treat a flow around 250 Nm³/h with 95% of CO₂ and 5% of CH₄. The goal for the product line is to achieve a stream with 50% of CH₄ and 50% of CO₂ so then it can be forwarded as a recycle to the pretreatment of the system without compromise significantly the composition of the predefined biogas coming from the digester. The production step will occur in a range of pressures between 3 and 4 bar(a). The regeneration of the adsorber will be performed by purging with a small amount of nitrogen or exclusively with a larger blowdown at a range of pressures between 0.5 and 0.7 bar(a). The off gas will be released to the atmosphere through a stack. This second PSA unit shall never be used when the first PSA is being purged with nitrogen. If that happens, the nitrogen will be accumulated in the system due to the stream rich in methane and hence nitrogen which is being sent upfront to the pretreatment. This PSA unit needs to be confirmed with accurate dynamic studies.

The process flow diagram (PFD) of the entire process is available in the *Appendix 5* of this report.

4.6 Improvements of the system

Regarding the client requirements for this installation, the purity of 90% and recovery higher than 99% shall be accomplished for bio-methane. For future clients the probability of the purity required be 97% is high. As the requirements can change, the installation will be developed and tested in order to be able to produce bio-methane in a range of 90% to 97% of purity. For the cases where the purity required is lower than 97% a by-pass that conducts pre-treated biogas to the product stream was added to the system. Doing this the purity can be controlled to the required point (if it is too high after the first PSA unit).

If the purity of the gas is not sufficient it is possible to increase it by performing the following solutions:

- Decrease the temperature of the inlet biogas. This causes an increasing of the adsorption capacity according to the isotherm tendency;
- Increase the pressure of the production step (higher adsorption capacity). The pressure influences directly the velocity of the gas inside the adsorber. The higher the pressure, the lower the velocity and hence the longer the residence time of the molecules inside the adsorber. It will allow a better adsorption of the CO₂ molecules;
- Perform a better regeneration step by increasing the purging flow and time. This will result in a more efficient adsorption step, since more CO₂ molecules will be removed from the active centers of the adsorbent. The adsorption capacity will increase.

Regarding the bio-methane recovery of the system some different solutions were considered:

- The adsorbers of the first PSA are being purged with product gas in order to achieve an efficient regeneration (when high purities as 97% are required), and the second PSA is used to recover the bio-methane lost in that step;
- The adsorbers of the first PSA are being purged with nitrogen to avoid the loss of product in this step and still achieve high purities up to 97%;
- The adsorbers of the first PSA are being regenerated without purge but with a larger blowdown (VPSA configuration). High recoveries achieved however the purity is lower since the regeneration step is not so efficient in the absence of purge gas (suitable when low purities such as 90% are required).

In the last two cases it is recommended a recycle in the beginning of the blowdown to recover the methane that is stuck in the column after the production step. A line for this recycle was also added to the process configuration. The second PSA unit shall never be used when the first PSA unit is being purged with N₂ (it will cause an accumulation of nitrogen in the system).

Another important factor is the TSA drying unit, since it is an expensive section of the system. First, the TSA was allocated before the first PSA unit (pretreatment) to remove water from the mixture before it enters in the production section. It would be the best solution, since the adsorption capacity of the vessel would not be compromised by the possibility of water adsorption. However, before the PSA the gas is still considered acid due to the high concentration of CO₂ and H₂O in the raw biogas. Therefore, the corrosion of the equipment is an issue and leads to stainless steel equipment and hence high costs. Since the CMS-Y is a non-polar adsorbent, it is expected that if the gas which is being treated is humid, the water would not be substantially adsorbed. ^[14] Thus, if the gas is not completely dried before the first PSA

unit, it is expected that almost all the water present in the mixture will pass through the adsorber together with the CH₄. Even if some water adsorbs together with the CO₂, a dew point of -3°C is guaranteed to prevent condensation in the blowdown step by using the water trap placed in the pre-treatment. Based on this, the most promising alternative to reduce the cost of the TSA unit is to allocate it in the product gas stream mainly composed of bio-methane (no acid gas). Furthermore, in this case the flow of humid gas to be dried will be almost half of the total flow entering in the system. With this solution the TSA drying unit can be smaller and there is no need to choose stainless steel equipment which decreases in a big scale the price of the unit.

All these options were added in the design of the installation (*Appendix 5*) and it is up to the client and DMT Environmental Technology to test and choose the most efficient method taking into account the requirements of the whole system.

4.7 Membrane System vs PSA System - Price analysis

After designing the whole PSA system, quotations for the necessary equipment were requested and an equipment list was made to predict the price of the total installation. This equipment list includes the costs for the pre-treatment (dewatering, gas boosting, desulphuration, compression section), TSA drying unit (before or after the PSA1), PSA for bio-methane production (PSA1), PSA for bio-methane recovery (PSA2), extras (piping, container, control cabinet, PED certificate, etc.), project hours, transport and commissioning.

Different section arrangements were considered to analyze the price of the total installation since the simplest case to the most complex. The cases are presented in *Table 24*.

Table 24 - Cases of study in the PSA cost analysis

	Pre-treatment	TSA before PSA	PSA1	PSA2	TSA after PSA	N ₂ injection	Extras	Project Hours
Case 1.1	x	x	x				x	x
Case 1.2	x		x		x		x	x
Case 2.1	x	x	x	x			x	x
Case 2.2	x		x	x	x		x	x
Case 3.1	x	x	x			x	x	x
Case 3.2	x		x		x	x	x	x
Case 4.1	x	x	x	x		x	x	x
Case 4.2	x		x	x	x	x	x	x

As it was mentioned before, DMT Environmental Technology’s main technology in the market is a biogas upgrading membrane system (Carborex MS). The price for a membrane system with the same capacity as the PSA developed was considered. It was taken into account in order to make a comparison between the price of both systems since the PSA unit shall not be more expensive than the MS but similar or even cheaper.

Table 25 - Price analysis and comparison with the base cost of a Carborex MS

	Comparing to MS (%)
Case 1.1	+ 31
Case 1.2	+ 19
Case 2.1	+ 45
Case 2.2	+ 33
Case 3.1	+ 34
Case 3.2	+ 22
Case 4.1	+ 48
Case 4.2	+ 37

The most promising cases regarding the costs are 1.2 and 3.2, more 19% and 22% than MS price, respectively, mainly due to the TSA system in the product stream. In all the evaluated cases the cost of a PSA system is higher than an MS system. It is important to consider that the cost of the PSA system is not completely accurate and probably it will suffer some alterations that can increase or decrease the total cost of the total installation estimated until the present moment. Anyway, it is expected that for a PSA technology with this capacity and quality the investment cost will be higher than a membrane system.

Based on the energetic consumption that each cubic meter of raw biogas requires to be treated in this installation (estimated as 0.3 kWh/Nm³) and on the industrial electricity price in the Netherlands (around 0.08 €) the estimated operational costs are 96,973.20 €/year.

5 Conclusions

Doing an overview of the results obtained with the realization of this work it is possible to say that the PSA installation is almost ready to be constructed and tested.

After the adsorbent CMS-Y was selected, it was possible to proceed with the equilibrium and kinetic simulation studies. To choose the mathematical model to describe the adsorption process an isotherm fitting was made taking into account previous studies documented in the literature. The model with the best fitting result was Dual-Site Langmuir. Based on that, a multicomponent Dual-Site Langmuir was used to predict the competition between both species.

The design of the vessel was divided in several steps and performed at LA/LSRE-LCM. The simulations for the dynamic studies were done for different sizes (1.5-0.3 m; 2-0.5 m; 2-0.7 m). For the required feed flowrate (450 Nm³/h) the most promising design was taking in consideration the 2m length and a diameter of 0.7 m. The breakthrough point for this design occurs around 290 seconds after the feeding step starts with a superficial velocity of 0.043 m/s. The production time defined is 150 seconds, to ensure that the breakthrough point is not achieved. In order to give some engineering margin to the installation in case of working conditions variations it was decided that the final design of the adsorber will be 0.8 m of diameter and the 2 m of length. Maintaining the flow rate at 450 Nm³/h the superficial velocity of the adsorption step will be around 0.033 m/s. These velocities are lower than the minimum fluidization velocity which is an important fact to preserve the adsorbent properties. The dynamic simulation studies for the CMS-Y were very promising. Analyzing mass front velocities, it is possible to conclude that the CO₂ concentration front is slower than the CH₄ front because its faster adsorption kinetics. The equilibrium capacity factor (ξ) is considerable higher for CO₂ (34.8) than for CH₄ (6.8). The inverse happens with the characteristic diffusion time since it is much lower for the CO₂ (99.5 s) than for CH₄ (1.4 x 10⁵ s). The residence time in the adsorber is around 20 seconds.

Since the beginning until the current moment several improvements to first design were made, in all sections (pre-treatment, PSA1, recovery unit). To increase the recovery of the system 3 solutions were adopted: a second PSA to treat the off gas coming from the PSA1, adding a recycle in the beginning of the blowdown to recover some CH₄ that is retained in the bottom of the vessel after the production step and purging with N₂ (inert gas) to reduce the product losses. To increase the purity in cases when it is not in line with the requirements it is recommended to reschedule the cycle times increasing the regeneration time. It is also possible to increase the purity by decreasing the temperature or increasing the pressure of the feeding gas. To achieve the dew point required a TSA drying unit before PSA1 was considered. However,

after the cost analysis was done it was decided to allocate the TSA unit in the product line. Therefore, the dryer equipment does not need to be in line with corrosive gas characteristics and it can also be smaller due to the lower flow which leads to a lower price.

Finally, a comparison between the PSA installation and the membrane unit prices was done. Some different dispositions of the equipment in the PSA installation were considered to study the price general costs. In all the cases the PSA system is more expensive than the MS. The best case of study is a disposition only composed of pre-treatment, PSA1 and TSA in the product line. For this case, the estimated price is 19% higher than the MS price. The second-best price was obtained for a disposition with pre-treatment, PSA1, N₂ injection unit to purge and TSA in the product line. In this case the price estimated is 22% higher than the MS. The case considering all the sections (pre-treatment + TSA, PSA1, N₂ injection unit, PSA2) presents the most expensive option, with a CAPEX 48% higher than the MS unit. For all the cases in study the ones with a second PSA to recover bio-methane show the most expensive results. After this study, it is recommended to study all the equipment in order to reduce as much as possible the costs. Regarding the energy consumption it estimated that it will have a cost of 96,973.20 €/year.

6 Evaluation of the developed work

6.1 Accomplished Goals

In order to develop a PSA unit to upgrade biogas the following goals were achieved during the internship:

- Equilibrium and kinetic study of the adsorbent selected;
- Design of the adsorbers was defined based on the dynamic and kinetic analysis of each component of the mixture in the adsorbent;
- The PSA cycle was defined according with the specifications required;
- The global configuration of the installation including pre-treatment, recovery units and product gas treatment was decided.

6.2 Other tasks developed during the internship

During the internship some additional work was done such as:

- The improvement of the MATLAB model developed by DMT Environmental Technology to simulate dynamics of adsorption and PSA cycles;
- A detailed process description;
- Analysis of the competitors of DMT Environmental Technology in the PSA for biogas upgrading market;
- Research about equipment suppliers;
- Equipment list and price analysis for different case scenarios of the process.

6.3 Limitations and recommendations

During the internship some limitations were found such as the lack of proper software to simulate the theoretical calculations that were being developed. In that sense, the partnership with the LA/LSRE-LCM from University of Porto was essential to the development of the work although the waiting time required to have the results of each simulation performed. However, some performances need to be ordered to study the second PSA and to make a scale-up of the entire installation for higher capacities.

It might be a good idea to invest in a pilot installation (laboratorial scale) in order to have practical studies regarding the equilibrium and kinetics of the adsorption process as well as to test different conditions of operation of the PSA unit to allow a correct scale-up for future projects. A pilot installation would increase DMT's autonomy in the subject of PSA technology since it would allow practical studies without a need of partnerships for that.

Finally, after analyzing the prices regarding the PSA, it might be a good idea to focus in one of the following points:

1. High purity and high recovery: first PSA (purging with bio-methane) and second PSA or first PSA and N₂ purge,
2. High purity and low recovery: first PSA (purging with biomethane) and cogeneration system to produce energy with the CH₄ lost in the first PSA unit;
3. Low purity and high recovery: first PSA (VPSA);
4. Low purity and low recovery: first PSA (VPSA without recycle line in the beginning of the blowdown).

Considering these four options, the one presented in point 2 might be a good solution to reduce the costs of the installation by adding value to the system, since energy can be produced and the operational costs can be covered.

6.4 Final Evaluation of the work

The developed work regarding the design of a PSA unit to upgrade biogas was found challenging and also enriching to the general knowledge of DMT Environmental Technology about adsorption and PSA designing. The main goals were achieved, and the installation will be built and tested in the end of 2018 and beginning of 2019.

References

- [1] European-biogas.eu. (2018). Biomethane in transport. [Online] Available at: <http://european-biogas.eu/wp-content/uploads/2016/05/BiomethInTransport.pdf> [Accessed 1 Jun. 2018].
- [2] Deublein, D. and Steinhauser, A. (2008). Biogas from waste and renewable resources. Weinheim [Germany]: Wiley-VCH.
- [3] Ugelletti, R., Conti, M. and C. Annesini, M. (2016). Pressure swing adsorption for biogas upgrading. A new process configuration for the separation of biomethane and carbon dioxide. Rome, Italy: Journal of Cleaner Production.
- [4] DMT Environmental Technology. (2018). DMT Environmental Technology, Biogas upgrading, Waste to Energy. [Online] Available at: <https://www.dmt-et.nl/> [Accessed 1 Jun. 2018].
- [5] A. Grande, C. (2011). Biogas Upgrading by Pressure Swing Adsorption. Oslo, Norway: SINTEF Materials and Chemistry.
- [6] Allegue, L. and Hinge, J. (2012). Biogas and bio-syngas upgrading. Aarhus, Denmark: Danish Technological Institute.
- [7] Huertas, J., Giraldo, N. and Izquierdo, S. (2011). Removal of H₂S and CO₂ from Biogas by Amine Absorption. Mass Transfer in Chemical Engineering Processes. Monterrey, Mexico: InTech.
- [8] Silva Santos, M. (2011). Advanced Modelling of PSA Processes for Biogas Upgrading. Porto, Portugal: Laboratory of Separation and Reaction Engineering, Faculty of Engineering of University of Porto.
- [9] T. Yang, R. (1986). Gas Separation by Adsorption Processes. Stoneham, USA: Butterworth.
- [10] Do, D. (2008). Adsorption analysis: Equilibria and Kinetics. London: Imperial College Press.
- [11] Moulijn, J. and Cybulski, A. (2005). Structured Catalysts and Reactors. 2nd ed. New York [etc.]: Marcel Dekker.
- [12] Narin, G., M.Ribeiro, A., Ferreira, A., Hwang, Y., Loureiro, J., Chang, J. and E. Rodrigues, A. (2014). Propylene/Nitrogen Separation in a By-Stream of the Polypropylene Production: From Pilot Test and Model Validation to Industrial Scale Process Design and Optimization. Industrial & Engineering Chemistry Research.
- [13] Möller, A., Eschrich, R., Reichenbach, C., Guderian, J., Lange, M. and Möllmer, J. (2017). Dynamic and equilibrium-based investigations of CO₂-removal from CH₄-rich gas mixtures on microporous adsorbents. New York, USA: Springer Science + Business Media.
- [14] Ruthven, D. M. et al. Pressure swing adsorption. VCH Publishers, New York, 1994.
- [15] Levenspiel, O. (1999) Chemical Reaction Engineering. 3rd Edition. John Wiley & Sons, New York, 54.
- [16] Santos, M., Grande, C. and Rodrigues, A. (2011). New cycle configuration to enhance performance of kinetic PSA processes. Porto, Portugal: Elsevier Ltd.

- [17] Labvirtual.eq.uc.pt. (2018). Portal de Engenharia Química - Fundamentos e Princípios Físico-Químicos. [Online] Available at: <http://labvirtual.eq.uc.pt/siteJoomla/index.php>
- [18] Guo, J. and Cong Lua, A. (2002). Textural and Chemical Characterizations of Adsorbent Prepared from Palm Shell by Potassium Hydroxide Impregnation at Different Stages. Glasgow, Scotland; Singapore, Republic of Singapore: Journal of Colloid and Interface Science.
- [19] Notorecycling.us. (2016). Adsorption capacity - Removal and Degradation - Alberto Noto Recycling. [Online] Available at: <https://www.notorecycling.us/removal/adsorption-capacity.html> [Accessed 30 May 2018].
- [20] En.wikipedia.org. (2018). Limiting oxygen concentration. [online] Available at: https://en.wikipedia.org/wiki/Limiting_oxygen_concentration [Accessed 1 Jun. 2018].
- [21] Commons.wikimedia.org. (2011). Category:Flammability diagrams - Wikimedia Commons. [online] Available at: https://commons.wikimedia.org/wiki/Category:Flammability_diagrams [Accessed 1 Jun. 2018].
- [22] Wetten.overheid.nl. (2018). wetten.nl - Regeling - Regeling gaskwaliteit - BWBR0035367. [online] Available at: <http://wetten.overheid.nl/BWBR0035367/2016-04-01> [Accessed 18 Jun. 2018].

Appendix 1 - Multicomponent DSL Isotherms

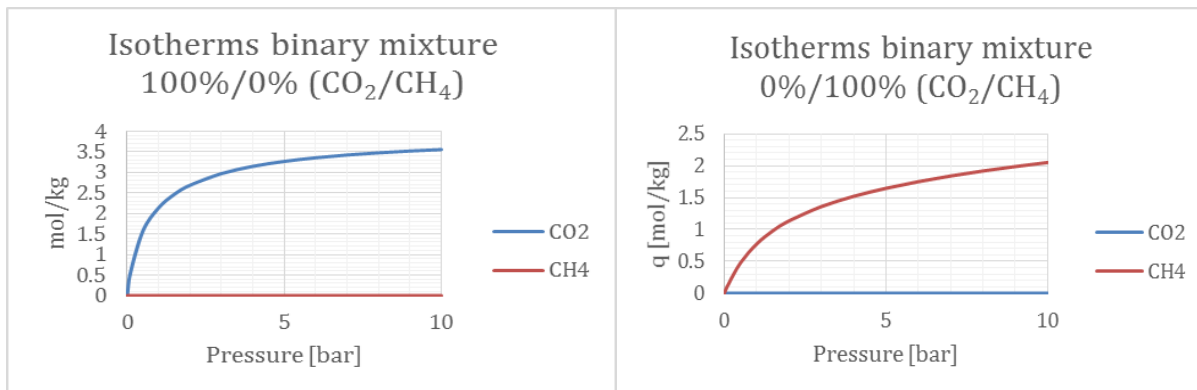


Figure 16 - Multicomponent DSL isotherms for both CH₄ and CO₂ pure components at 293 K

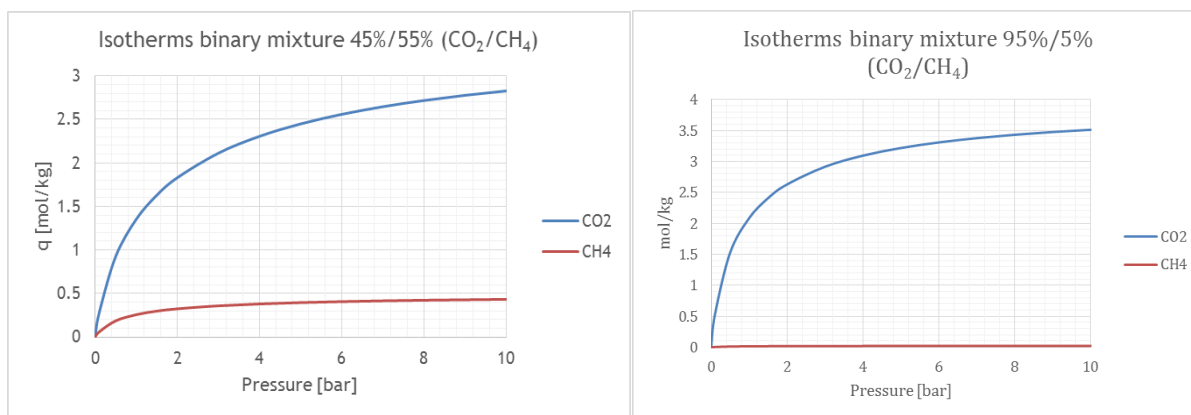


Figure 15 - Multicomponent DSL isotherms for binary mixtures with different compositions at 293 K

Appendix 2 - MATLAB Model

The mathematical model developed to describe the behaviour of the PSA adsorbers during the adsorptive separation is based on the following assumptions:

- i. Ideal gas behaviour of adsorption along the adsorber;
- ii. Mass, heat and velocity gradients in the radial direction are negligible;
- iii. No temperature gradient inside the adsorbent particles;
- iv. Bed porosity is constant along the bed;
- v. Heat conduction through the adsorber walls is neglected;
- vi. Plug-flow with axial dispersion;
- vii. Mass transfer according with LDF model;
- viii. Neglected external mass transfer effect;
- ix. Thermal equilibrium between the gas and the adsorbent;
- x. Constant heat transfer coefficients are considered.

The total mass balance for the gas phase in the adsorption column is described in the next equation: ^[13]

$$\frac{\partial c_i}{\partial t} - D_{ax} \frac{\partial^2 c_i}{\partial z^2} + \frac{(1-\varepsilon)}{\varepsilon} \rho_s \sum_{i=1}^N \frac{\partial q_i}{\partial t} + C_i \frac{\partial u}{\partial z} = 0 \quad 2.1$$

The partial mass balance is presented in equation 2.2.

$$\frac{\partial c_i}{\partial t} - D_{ax} \frac{\partial^2 c_i}{\partial z^2} + \frac{\partial u c_i}{\partial z} + \frac{1-\varepsilon}{\varepsilon} \rho_s \frac{\partial q_i}{\partial t} = 0 \quad 2.2$$

Considering the assumptions *vii* and *viii* the adsorption rate can be written as follows:

$$\frac{\partial q_i}{\partial t} = K L D F_i (q_{eq,i} - q_i) \quad 2.3$$

The energetic balance in terms of gas considering the assumptions *iii*, *v*, *ix* and *x* is defined by equation 2.4. ^[13]

$$\rho_b \sum_{i=1}^N (-\Delta H_i) \frac{\partial q_i}{\partial t} - (C_{ps} \rho_b + C_{pg} \varepsilon \rho_g) \frac{\partial T}{\partial t} - u C_{pg} \varepsilon \rho_g \frac{\partial T}{\partial z} - T C_{pg} \varepsilon \rho_g \frac{\partial u}{\partial z} + \lambda \varepsilon \frac{\partial^2 T}{\partial z^2} - k_{in} \frac{4}{d_i} (T - T_w) = 0 \quad 2.4$$

The heat of adsorption is an indicator to the strength of interaction between the adsorbent and the adsorbate and it has a big impact for modelling adsorption processes. The higher the temperature the lower will be the adsorbent capacity as the isotherms can indicate. Thus, it is important to correctly define the isotheric heat of adsorption and in this case the equation is adapted to the multicomponent DSL model considering the partial pressures of each component (equation 2.5). ^[10]

$$-\Delta H_i = \frac{q_{s1} \frac{K_{1,i} \Delta H_{1,i}}{(1+K_{1,i} y_i P)^2} + q_{s2} \frac{K_{2,i} \Delta H_{2,i}}{(1+K_{2,i} y_i P)^2}}{q_{s1} \frac{K_{1,i}}{(1+K_{1,i} y_i P)^2} + q_{s2} \frac{K_{2,i}}{(1+K_{2,i} y_i P)^2}} \quad 2.5$$

The energy balance regarding the adsorber wall is ^[13]:

$$(d_i WS + WS^2) c_{pw} \rho_w \frac{\partial T_w}{\partial t} = h_g d_i (T_g - T_w) - h_w (d_i + 2WS) (T_w - T_{env}) \quad 2.6$$

Appendix 3 Flammability Diagram (CH₄/O₂/N₂)

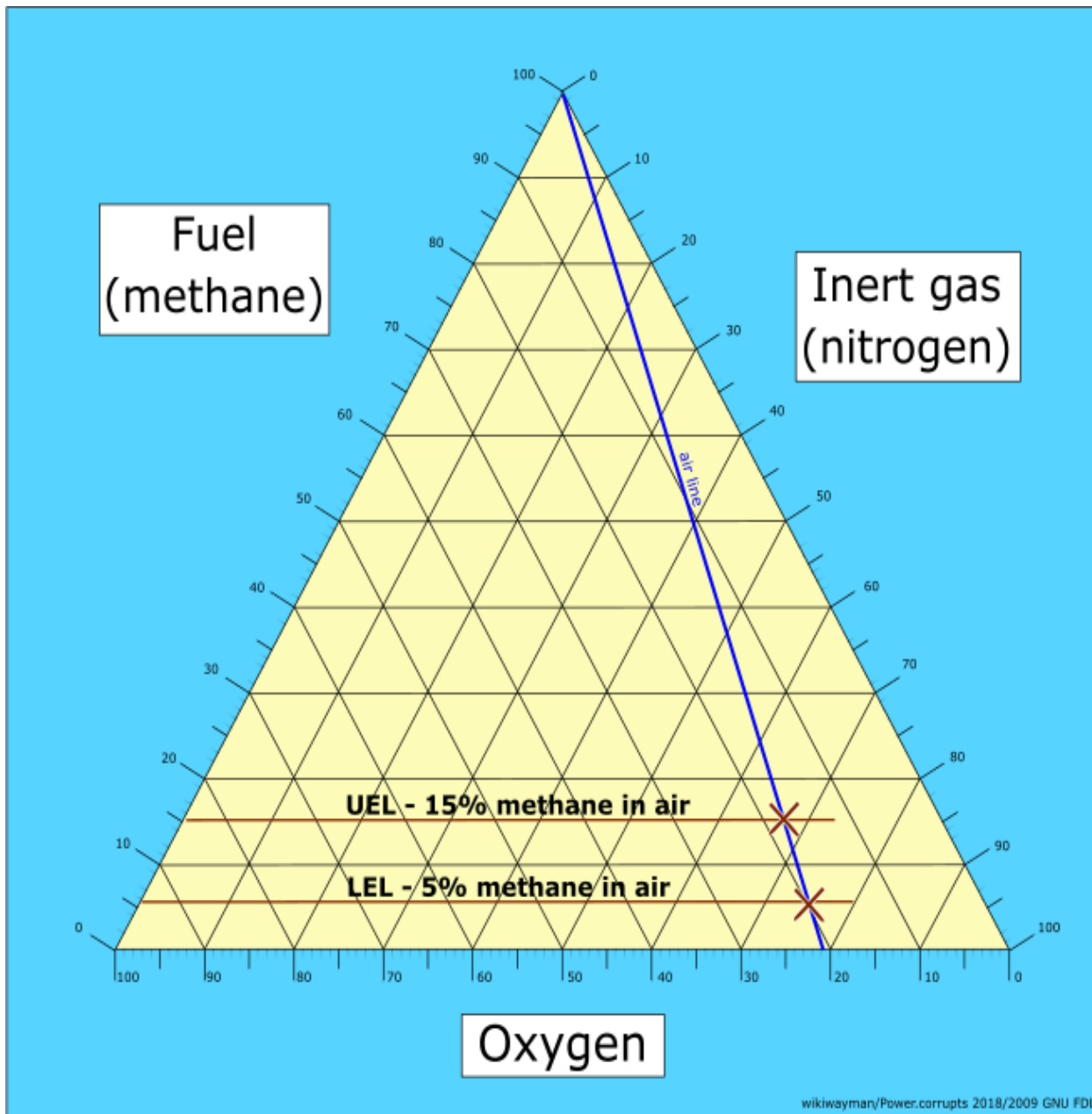


Figure 17 - Flammability Diagram for a mixture with CH₄, O₂ and N₂. [19]

Appendix 4 Parameters used by LSRE to perform the dynamic and PSA cycles simulations

Table 26 - Estimated parameters used in the mathematical model used to perform all the simulations of this work

Outside Temperature	293	K
Void Fraction	0.34	-
Averaged Viscosity	1.35×10^{-5}	Pa.s
Bulk Density	700	kg/m ³
Particle Density	1060	kg/m ³
Particle Radius	9×10^{-4}	m
Particle Specific Heat	880	Jmol ⁻¹ K ⁻¹
Particle Porosity	0.23	-
Adsorbent Mass	539	kg
Wall Density	8328	kg/m ³
Wall Specific Heat	500	Jmol ⁻¹ K ⁻¹
Wall Thickness	2×10^{-3}	m
Molecular Diffusivity	2.04×10^{-6}	m ² s ⁻¹
Axial Dispersion Coefficient	2.40×10^{-4}	m ² s ⁻¹
Film Mass Transfer Coefficient	1.48×10^{-2}	m.s ⁻¹
Thermal Conductivity	2.39×10^{-2}	Wm ⁻¹ K ⁻¹
Thermal Axial Dispersion Coefficient	6.51×10^{-1}	Wm ⁻¹ K ⁻¹
Film Heat Transfer Coefficient	174	Wm ⁻² K ⁻¹
Wall Heat Transfer Coefficient	300	Wm ⁻² K ⁻¹
Overall Heat Transfer Coefficient	43	Wm ⁻² K ⁻¹
Ratio of the Internal Surface Area to the Volume of the Wall	498	-
Ratio of the Log Mean Surface Area to the Volume of the Wall	500	-

Appendix 5 - Process Flow Diagram (PFD)

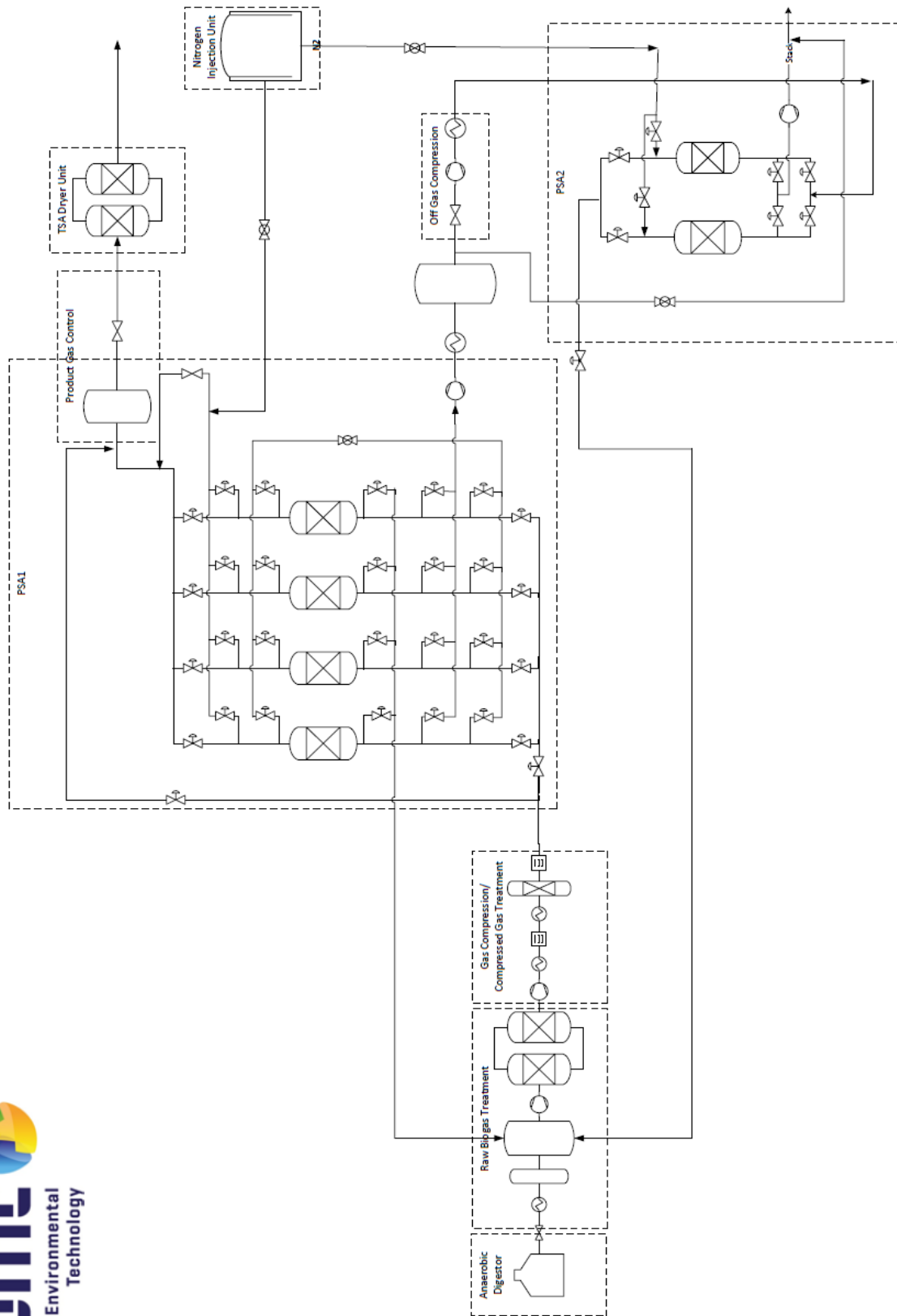


Figure 18 - Process Flow Diagram of the entire process developed (PFD)