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DEVELOPING A TECHNOLOGICAL CONCEPT FOR THE REMOVAL OF SILOXANES AND VOCS FROM LANDFILL GAS

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Abstract

Biogas is a clean organic fuel that is the result of the organic matter decomposition under anaerobic conditions. It is mainly composed of methane and carbon dioxide, but there are other residue compounds such as NH_3, hydrogens sulfide, siloxanes, and VOCs (volatile organic compounds). These components (in particular sulfur compounds and siloxanes) are detrimental to any processing equipment and can cause health and environmental damage. For these reasons, this energy source must be purified applying gas separation technologies so the desired product, biomethane, can be obtained and utilized as a clean energy.

The first part of this dissertation work consisted of selecting the best pretreatment technology for siloxanes and VOCs removal from landfill gas. A vast research about biogas treatment technologies, and later, about physical absorption and physical solvents was completed. The need to get rid of siloxanes and VOCs is clear and the most suitable physical solvent to serve this purpose was selected: selexol.

Using CHEMCAD software, a water and a selexol scrubber, both with a regeneration step, were simulated and compared along this report. For these simulations, the process is composed by an absorption column followed by a desorption one with a solvent's recycle stream to the first one. The mass transfer model selected for both columns was Billet and Schultes.

Removal efficiencies obtained for selexol were, for most VOCs and siloxanes, higher than 90 % and, for some of them, 99 % was achieved, for instance, 2-butanone, benzene, n-octane, 2-propanol and linear siloxanes (octamethyltrisiloxane also called L3 and decamethyltetrasiloxane known as L4). On the other hand, water could remove NH_3 with a maximum efficiency of 94 % obtained for water option 1 case scenario. Other components such as 2-butanone, ethanol and 2-propanol were also efficiently removed with water.

Keywords (theme): Biogas / Volatile organic compounds / Siloxanes / Physical absorption/ Water scrubber/ Selexol scrubber / Billet and Schultes

Resumo

O biogás é um combustível orgânico limpo resultante da decomposição de matéria orgânica em condições anaeróbias. É, maioritariamente, composto por metano e dióxido de carbono, no entanto, há outros compostos residuais tais como, amoníaco, sulfato de hidrogénio, siloxanos e COVs (compostos orgânicos voláteis). Estes compostos (em particular compostos com enxofre e os siloxanos) são destrutivos para qualquer equipamento processual e podem causar problemas de saúde e ambientais. Por estas razões, esta fonte de energia deve ser purificada através da aplicação de tecnologias de separação para que o produto desejado, o bio metano, seja obtido e utilizado.

A primeira parte desta dissertação consistiu em selecionar a melhor tecnologia de pré-tratamento para a remoção de siloxanos e COVs do gás de aterro. Uma pesquisa alargada sobre tratamento de biogás e, posteriormente sobre absorção física e solventes físicos foi realizada. A necessidade de eliminar os siloxanos e os COVs é evidente assim, o solvente físico escolhido com esse objetivo foi o selexol.

Através da utilização do software CHEMCAD, um processo de absorção com água como solvente e um com selexol, ambos com regeneração, foram simulados e comparados ao longo do relatório. Para estas simulações, o processo é composto por uma coluna de absorção seguida por uma coluna de dessorção com reciclagem do solvente para a primeira. O modelo de transferência de massa selecionado para ambas as colunas foi o modelo Billet and Schultes.

As percentagens de remoção obtidas para o selexol foram, para a maioria dos COVs e siloxanos, superiores a 90 % sendo que, para alguns destes compostos, foi igual a 99 %, como por exemplo para a 2-butanona, benzeno, *n*-octano, 2-propanol e siloxanos lineares (L3 e L4). Por outro lado, a água conseguiu remover o amoníaco com uma eficiência máxima de 94 %, obtida para o caso de estudo "água opção 1". Outros compostos como a 2-butanona, etanol e 2-propanol também foram removidos eficientemente com água.

Palavras-chave (tema): Biogás / Compostos orgânicos voláteis / Siloxanos / Absorção física/ Selexol / Billet and Schultes

Declaration

I hereby declare, under word of honour, that this work is original and that all non-original contributions is indicated and due reference is given to the author and source

06/07/2021

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Notation and Glossary

a	Specific interface area of the dumped packing	$m^2 \cdot m^{-3}$
C	Constant	-
d	diameter	m
D	Diffusion coefficient	$m^2 \cdot s^{-1}$
F_v	Gas load factor	$\sqrt{Pa}$
g	Gravitational acceleration	$m \cdot s^{-1}$
H	Height	m
h_L	Column Holdup	$m^3 \cdot m^{-3}$
K	Wall factor	-
K_0	Overall mass transfer coefficient	-
L	Mass flowrate of the liquid	$kg \cdot h^{-1}$
$\dot{L}$	Molar flowrate of the liquid	$kmol \cdot h^{-1}$
M	Molecular weight	$kg \cdot kmol^{-1}$
m_{yx}	Slope of the equilibrium curve	$kmol \cdot kmol^{-1}$
n	Exponent	-
ΔP	Pressure drop	Pa
Re	Reynolds number	-
T	Temperature	K
u	Velocity with reference to the free column cross section	$m^3 \cdot m^{-2}$
$\bar{u}$	Mean Effective velocity	$m \cdot s^{-1}$
V	Mass flowrate of the gas	$kg \cdot h^{-1}$
$\dot{V}$	Molar flowrate of the gas	$kmol \cdot h^{-1}$
x	Molar concentration in the liquid	$kmol \cdot h^{-1}$

Greek Letters

β	Mass transfer coefficient	$m \cdot s^{-1}$
ε	Void fraction	$m^3 \cdot m^{-3}$
η	Dynamic viscosity	$kg \cdot ms^{-1}$
λ	Stripping factor	-
ν	Kinematic viscosity	$m^2 \cdot s^{-1}$
ρ	Density	$kg \cdot m^{-3}$
σ	Surface tension	$kg \cdot s^{-2}$
ψ	Resistance coefficient	-

Indexes

-	Dimensionless variable
Fl	Flooding point
h	Hydraulic
L	Liquid
O	Total
P	Particles
Ph	Interface
S	Loading point
V	Gas
W	Water

List of Acronyms

-	Dimensionless variable
VOCs	Volatile Organic Compounds
TSA	Thermal Swing Adsorption
PSA	Pressure Swing Adsorption
DEPG	Dimethyl ethers of polyethylene glycol
NMP	N-methyl-2-pyrrolidone
LEL	Lower explosive limit
BF	Bio filters
BTF	Bio trickling filter
DEHA	di-(2-ethylhexyl)adipate
PEG 400	Polyethylene glycol
DMS	Dimethylsulfide
DMDS	Dimethyldisulfide
PDMS	Polydimethylsiloxane
TPPB	two-phase partitioning bioreactor
PSRK	Predictive Soave-Redlich-Kwong
VLE	Vapor-liquid-equilibrium
PFD	Process flow diagram
HSP	Hansen Solubility Parameters
TCO	Total Cost Operation
OPEX	Operational expenditure
CAPEX	Capital expenditure
ROI	Return of investment
LFG	Landfill Gas

1 Introduction

1.1 Framing and presentation of the work

The preoccupation and conscience with the Global Climate Change and Global Warming phenomenon are growing. Efforts to decrease the need for fossil fuels usage are evident. Renewable energies are being explored and growing over time. Wind power, solar power and energy from biomass like biogas supplies around 14 % of total world energy demand [2].

Biogas is a clean organic fuel that is the result of organic matter decomposition under anaerobic conditions. It is mainly composed of methane and carbon dioxide. There are other residue compounds such as NH_3, hydrogens sulfide, siloxanes, and VOCs (Volatile organic Compounds). The concentration of the different gases in the biogas depends on the organic matter composition, the decomposition conditions, and the hydraulic retention time inside the digester.

This energy source has to be optimized by applying gas separation technologies, not only to separate methane and carbon dioxide, but also to remove other impurities as they are detrimental to any processing equipment (in particular sulfur compounds and siloxanes) and they can cause health and environmental damage. The desired product is biomethane and the purpose is to use it to replace natural gas in its applications like vehicles fuel, electricity production or for heat production by direct combustion. The global biogas market has been growing over the past few years and new production technologies are being explored. The Netherlands had, by the end of 2011, 130 biogas plants and 13 biomethane producers. All 13 units inject the biomethane into the natural gas network [2].

Purification technologies for biogas are essential to upgrade it to biomethane and increase its calorific heat. Membranes are the most used gas separation technology. They are used to separate carbon dioxide and methane, but they are not suitable for the trace pollutants in biogas composition to prevent damage. A pretreatment stage is recommended before the biogas is sent to the membrane treatment.

An overview of VOCs and Siloxanes removal technologies was performed to understand the existing possibilities in the market. The evaluation of absorption as a pretreatment step was already initialized by previous students at DMT. Therefore, an extensive research about absorption solvents was also done. An organic physical solvent was selected and compared with a well-known solvent, water. Their performance was compared through an extensive sensitivity analysis and a business case that allowed to have a more realistic perspective regarding the implementation of this technology.

1.2 Presentation of the company

DMT Environmental Technology is a Dutch company, having Theo Zuijdwijk as CEO. With more than 28 years of experience and around 70 employees, it is a market leader in biogas upgrading, with advanced membrane technology, and gas desulphurization. This company is situated worldwide, and it has offices in Europe, the United States and Canada.

Some of the products offered by DMT are Carborex, a multistage membrane configuration that allows obtaining pure methane; Sulfurex, which consists of desulphurization units; and TurboTec, a water treatment system.

1.3 Contribution of the author to the work

In the first part of my thesis work I selected the best pretreatment technology for siloxanes and VOCs removal from landfill gas through a vast research about biogas treatment technologies, and later, about physical absorption and solvents. I understood the need to get rid of Siloxanes and VOCs from the upgrading process and the most suitable solvent for this purpose was selected.

A water scrubber was already modelled for NH_3 removal from landfill gas from the work of a previous student at DMT. In this work, I studied the possibility of adding a solvent's regeneration step to the absorption column. Therefore, I modelled a water scrubber followed by a regeneration step using a chemical software named CHEMCAD, and I further compared with the selected solvent's scrubber, also with regeneration.

With the development of my dissertation, DMT Environmental Technology increased its knowledge about pretreatment technologies, particularly physical absorption, and physical solvents. This knowledge is described along the report, and it will facilitate future studies on this topic.

1.4 Organization of the thesis

This report is organized into 5 different sections:

- **Chapter 2 – Context and State of Art:**

In the first part of this section, a pretreatment technology overview for pollutants removal from biogas is stated. The technologies chosen were specifically for siloxanes and VOCs removal, which is the main target of this work.

Secondly, an absorption solvents overview was performed in order to make a reasoned choice since this solvent would be studied in the following chapters.

- **Chapter 3 – Methods-Computer Application CHEMCAD**

Here, the solvent's choice is justified. Then, some modelling aspects are explained, starting with the presentation of the used software and a description of the process: the equipment characteristics, the streams composition, and the initial operating conditions. It is also presented the models that were selected in CHEMCAD to simulate the process as accurately as possible.

- **Chapter 4 – Results and Discussion:**

  In this chapter, the performed work is described step by step and the results are presented in tables and figures. The chapter is divided into four main parts: Water Option 1, Water Option 2, Selexol and Business Case.

- **Chapter 5 – Conclusion:**

In chapter 5, the conclusions reached during the work are stated. The most relevant results are mentioned and commented.

- **Chapter 6 – Final evaluation of the work developed:**

A final appreciation about the project is presented.

2 Context and State of Art

2.1 Overview of VOCs and Siloxanes Removal Technologies

The VOCs are a group of organic components with high vapor pressure and with a boiling point less than or equal to 250 °C measured at a standard atmospheric pressure of 101.3 kPa [3]. This group includes organic compounds such as terpenes, alkanes, alkenes, cyclical hydrocarbons, aromatic compounds, and furans.

Since VOCs are one of the main sources of photochemical reaction in the atmosphere that leads to various environmental hazards, it is important to remove them before their release into the atmosphere. Besides this, these compounds have carcinogenic properties Although these compounds are harmful to the environment and to human health, they have a good commercial value. So, recovering these compounds would be better than destroying them. Recovered VOCs can be reused within the process, used as wash solvents during equipment cleanup, burned as an alternative boiler fuel, shipped off-site for disposal or resold for reuse by others.

The VOC's removal technologies can be divided into destructive and recovery techniques. The destructive ones include technologies such as oxidation and bio-filtration where microorganisms destroy the pollutants. The technologies that allow recovering the VOCs are varied and include absorption, adsorption, condensation, and membrane separation. These technologies are described in more detail further.

Siloxanes are trace compounds present in landfill gas. When siloxanes are burned, silicon dioxide, a white powder, is formed which can create a problem in gas engines. This is the main reason why siloxanes must be removed from the biogas.

The traditional routes of siloxane removal are either by water scrubbing or by scrubbing with hot sulfuric acid but many other technologies are available.

Many technologies employ a combination of methods in order to increase system performance (i.e., refrigeration/ condensation and activated carbon adsorption; refrigeration/ condensation and gas-liquid absorption and activated carbon).

2.1.1 **Adsorption**

The adsorption process is classified into two types, namely, physical adsorption (or physisorption or Van der Waals adsorption) and chemical adsorption (or chemisorption) based on the strength of the interaction between adsorbate and adsorbent.

Physical adsorption is a reversible process and results from intermolecular forces of attraction between molecules of the solid and the substance adsorbed. Physical adsorption includes continuous processes such as thermal swing adsorption (TSA) and pressure swing adsorption (PSA) [4].

Chemisorption is the result of chemical interaction between the solid and the adsorbed substance. Generally, the strength of the chemical bond is much greater than the physical forces between molecules. This aspect makes the regeneration of the adsorbent challenging.

The preferred adsorbents for VOCs recovery are activated carbon and styrene/divinylbenzene macroporous resins [4]. Although activated carbon provides excellent adsorption, regeneration can be difficult and the expenses for new activated carbon are the predominant part of operating costs. Furthermore, activated carbon has poor stability, humidity control problems, and is chemically reactive with certain contaminants [5].

Regarding siloxanes, in general, siloxane removal from digester gas by adsorption is considered a viable universal solution [6]. This does not hold for landfill gas as VOC concentrations and hydrogen sulfide are significantly higher.

2.1.2 Absorption

Absorption is used to remove VOCs from gas streams by contacting the raw air stream with a liquid solvent. Any soluble VOCs will transfer to the liquid phase. This takes place in an absorber tower designed to provide the liquid-vapor contact area necessary to facilitate mass transfer. To increase the contact area between the two phases, packing, trays and liquid atomization is normally used [4].

Likely adsorption, also absorption can be classified as physical or chemical. In physical absorption, the solute is transferred to the solvent phase through Van der Walls interactions while in chemical absorption solute-solvent reactions occur. The most common absorber types employed in industry are plate columns, packed towers, Venturi cleaning towers and spray chambers.

Physical solvents such as DEPG (dimethyl ethers of polyethylene glycol), NMP (N-methyl-2- pyrrolidone, methanol, and propylene carbonate are becoming increasingly popular as gas treating solvents. Physical solvents tend to be favored over chemical solvents when the concentration of acid gases or other impurities is very high.

“Selexol” is the commercial name for DEPG. It is very promising solvent regarding siloxanes and VOC’s removal. An efficiency of 99 % was reported for siloxanes removal, although no operating pressure has been specified [7].

Physical solvents clearly exhibit some advantages over chemical ones. The regeneration of physical solvents is much easier since it can be done by reducing the pressure without the need for heat unlike chemical solvents that usually need heat to be regenerated. Besides this, physical solvents are non-corrosive, requiring only carbon steel construction.

In chemical absorption, sulfuric acid (95–97 %), nitric acid (65 %), and phosphoric acid (85 %) are used to remove siloxanes [8].

Due to the chemical nature of siloxane, the most suitable absorbents for their removal from biogas are polar organic solvents. Since the absorption process operates better at lower temperatures, the gas is often cooled prior to the absorption stage. A disadvantage of this gas pretreatment method is siloxane desorption because the high volatile siloxanes (such as hexamethyldisiloxane, commonly known as L2) are easily stripped from the solvent at elevated gas flowrates.

2.1.3 **Membranes**

Membranes are selective barriers where the driving force is the pressure difference between the permeate and the retentate side of the membrane.

Membrane based gas treatment techniques are primarily used in removing CO_2 and VOCs from landfill gas. However, these membranes remove siloxanes and VOCs as well and usually these systems have promising results. Nevertheless, many adaptability factors determine the process efficiency. Some of these factors are the large range of VOCs to be retained; the significant cost; the availability of the membranes; the demanding maintenance because membranes are very susceptible to the operating conditions, fouling and bacterial growth; the slow process rate; short life of the membrane; the environmentally challenging disposal; the presence of liquid that constitutes an extra resistance and the flow patterns.

The costs of a membrane process are directly linked to the power needed for compressors or vacuum pumps to establish a sufficiently high partial pressure difference across the membrane to induce contaminant permeation. Hence, this process was identified as a non-competitive treatment due to its operating costs and its sensibility linked to membrane fouling [9].

For VOC's permeation, rubbery membrane composed of polydimethylsiloxane or polyoctylmethylsiloxane are used. These membranes come in a number of configurations, including spiral-wound modules, round flat sheet membranes in a membrane envelope, and hollow fiber membranes having plasma-polymerized silicone membranes. Typically, membrane systems contain a condenser, compressor, and a membrane. Some membrane suppliers are MTR, Inc., GKSS, Inc. and AMT, Inc. [5].

Some of the possible configurations of membrane processes are 1) membrane-based absorption and stripping process; 2) flow swing membrane permeation; and 3) vacuum driven vapor permeation process [5].

2.1.4 Condensation

The driving force for condensation is the over-saturation, which is achieved by chilling or pressurisation (or both) of the gas stream. Condensation is most efficient for VOCs with boiling points above 37.8 °C at relatively high concentrations above 5,000 ppm [5]. Low-boiling VOCs can require extensive cooling or pressurisation, which sharply increases operating costs.

One significant disadvantage in these systems is that exceeding the LEL (lower explosive limit) is common. This is dangerous, because the concentration will likely fall through the explosive range during the condensation process.

Best suited for mono solvent systems, condensation produces a liquid product that must be treated to remove condensed water and possibly to separate various chemical species.

In the case of siloxanes removal, due to relatively high investment and operating costs, condensation is generally regarded as economically suitable only at high flowrate and elevated siloxane load. The more volatile the siloxane, the more difficult it is to condense. In order to reach higher removal efficiencies, condensation could theoretically be performed at higher pressures.

2.1.5 Biological Removal

Biological processes are an important technology when it comes to VOCs removal at large scale. They can be subdivided into bio scrubbers, bio filters (BF) and bio trickling filter (BTF).

The bio scrubber consists of a two-stage system composed of a physical countercurrent absorption column and a biological regeneration step of the loaded liquid phase.

The biofilter is a biologically active fixed bed where compounds are absorbed and then mineralized by a fixed community of bacteria and fungi. A difficulty is the acidification that occurs in greater extent in the presence of alcohols, aldehydes, organic acids, and esters, and to a lesser extent with ketones, ethers, aromatics, and unsubstituted aliphatic hydrocarbons, since the volatile components of the exhaust air are bio transformed into organic acids as storage substances.

The bio trickling filter takes an intermediate position between the bio scrubber and the bio filter, consisting of an absorber column and a rudimentary swamp [10]. Bio trickling filters for siloxanes removal were tested on lab scale, but the results were not very promising. Both aerobic and anaerobic conditions were tested. It was concluded that the availability of octamethylcyclotetrasiloxane (D4) to the microorganisms was limited by low mass transfer

coefficients. Furthermore, the subsequent use of a second organic phase to enhance D4 availability to the microorganisms did not result in higher D4-removal [6].

2.1.6 Oxidation

Oxidation processes can be divided into thermal and catalytic oxidation. Thermal Oxidation consists of superheating the pollutants. As it requires heat for its application, it is not an environmentally friendly technique because it involves burning off large quantities of fossil fuels, and very little of the thermal energy can be recovered. Catalytic oxidation relies on the chemical effectiveness of advanced catalytic activity to oxidize the pollutant concentrations and to remove these problematic substances from exhaust streams [11].

In Table 1, some of the process options for removing VOCs are presented and their respective maximum pollutant concentration and removal efficiency.

Table 1- Operating characteristics of different techniques of VOC control [4, 5].

Process		Maximum Feed Pollutant Concentration / ppm	Maximum Removal / %
Adsorption (Activated Carbon)		700 to 10 000	greater than 99
Absorption		500 to 15 000	90 to 98
Membranes		nearly unlimited	90 to 98
Cooling/ Condensation		unlimited	50 to 75
Biological Removal		<5000	85
Oxidation	Thermal	100 to 2000	95 to 99
	Catalytic	100 to 2000	90 to 95

2.2 Overview of Absorption Solvents

In this project, absorption will be studied. Some common solvents that may be useful for volatile organics include water, mineral oils, or other non-volatile petroleum oils [12].

The most commonly used solvent is water because it is the cheapest and easy to handle and operate. However, most VOCs present in biogas are non-polar and hydrophobic compounds. Adding to this, is also difficult to strip VOCs from saturated water due to the loss of water by evaporation during the stripping operation [12].

For siloxanes and VOCs removal, absorption by an organic solvent seems to be a promising alternative [13]. The solubility is a key parameter for choosing the solvent because it will determine the absorption capacity of a solvent *versus* the solute. Besides this, cost, recycle ability and disposal method are also parameters to consider.

As mentioned before, there are mainly two types of absorption processes: chemical and physical absorption. Physical absorption is favored when the purpose is to remove impurities and other trace compounds [14]. Physical solvents have some advantages over the chemical ones, such as the fact that they are non-corrosive and that the regeneration step is easier because physical solvents can easily be stripped of impurities without heat and just reducing the pressure.

Some popular physical solvents for gas treatment are DEPG, NMP, methanol, and propylene carbonate. From these physical solvents the ones that have proven efficient removing hydrocarbons are DEPG and methanol. These solvents are more often referred to by the process name where they are used for instance DEPG is denominated by “Selexol”, methanol by “Rectisol” or “Ifpexol” and NMP by “Purisol” [14].

It has also been investigated the option of recycling waste oils as solvents.

2.2.1 DEPG/ Selexol

DEPG is a mixture of dimethyl ethers of polyethylene glycol ($CH_3O(C_2H_4O)_nCH_3$) with n between 2 and 9 [15].

An efficiency of 99 % was reported for siloxanes removal in a continuous pilot plant of landfill gas (Mountain Gate, USA) but, unfortunately, no operating pressure was specified [7].

For VOCs removal, selexol has also shown to be a good solvent, removing aliphatic hydrocarbons very well. Hydrocarbon’s solubility in selexol increase with increasing molecular weight. These characteristics have led to the development of selexol solvent applications for removing hydrocarbons and/or water from natural gas, e.g., simultaneous hydrocarbon and water dew point control [16].

Solvents containing DEPG are licensed and/or manufactured by several companies including Coastal Chemical Company, Dow and UOP. In total there are 32 commercial plants built using selexol as a solvent [14]. These are advantages because it is a well-known solvent and there is a lot of data available about this process.

Some of the advantages regarding the usage of selexol as an absorption solvent are its low vapor pressure that limits its losses to the treated gas; low viscosity to avoid large pressure drop; high chemical and thermal stability; the fact that it is nontoxic, non-corrosive and inherently non-foaming; its high flash column point ensures ease and safety in handling and a fairly wide range of operating temperature (-18 to 175 ºC) allowed. Also, it has low heat requirements for regeneration since the regeneration step for selexol can be carried out by either thermally, or flashing, or stripping gas depending on the process design [17].

The major drawback is the need for refrigeration in order to increase the solubility of acid gases and minimize the solvent circulation rate [16].

2.2.2 Methanol/ Ifpexol

Methanol can be used to remove hydrocarbons in a process called Ifpexol. The overall system involves two separate processes (IFPEX-1 and IFPEX-2) that may be used independently or in combination. IFPEX-1 removes condensable hydrocarbons from the feed gas, while IFPEX-2 accomplishes acid gas removal and recovery [16]. Using methanol is an advantage due to the available information and the know-how of this solvent usage.

2.2.3 Vegetable and Lubricant oils

Fresh and waste oils like vegetable oil and lubricant oil have been studied as VOCs absorbents (specifically in thisbenzene, carbontetrachloride, methanol and toluene). Vegetable oils are glycerin esters of fatty acids (glycerides) and lubricant oils are basically long changed alkanes [12].

Efficiencies of 70 to 95 % were reported [12]. This is very promising since waste oils are reused, therefore reducing the amount of waste oil entering the wastewater treatment plants, while VOCs are being removed. These efficiency results can be explained by the chemical rule “like dissolves like”. It is expected that non-polar solvents, like these oils, have bigger absorption capacities for VOCs than water, for example.

The major obstacle of this technology is to find the values for physical properties of the used oils in literature. Modelling an absorption process with this lack of information is challenging.

DEHA, *n*-hexadecane, Oleyl alcohol and PEG400

Other organic solvents such as di(2-ethylhexyl) adipate (DEHA), *n*-hexadecane, oleyl alcohol and polyethylene glycol (PEG 400) were considered for the VOCs removal. These solvents exhibit interesting properties for instance, low viscosity (high mass transfer rate), low volatility (limitation of solvent losses due to evaporation) and density close to that of water (less energy required for recycling) [13].

The VOCs evaluated were dimethylsulfide (DMS), dimethyldisulfide (DMDS) and toluene. From this study, PEG 400 was the most efficient solvent regarding toluene absorption. However, since it is miscible with water, it makes the solvent recycle difficult, so *n*-hexadecane showed to be the best choice for the VOCs studied [13]. These results should be confirmed by implementing the solution in a scrubber, such as a packed column.

Silicone oils- PDMS 5 and PDMS 50

Another possible way to remove such pollutants is to use an absorption–biodegradation process. The absorption process uses Silicone oils as absorbents of VOCs. After the absorption, there is a biodegradation step in a Two-Phase Partitioning Bioreactor (TPPB) where the destruction of VOCs takes place. The solvent regeneration is carried out in a gravity separator [18].

The main drawback is the viscosity of oils and the instability of processes using microorganisms. Depending on the packing type of the column, the viscosity problem can be overcome.

Efficiencies of 100 % were obtained experimentally for both polydimethylsiloxane (PDMS). However, the volatility of PDMS 5 inhibits its implementation in the proposed process. As a result, PDMS 50 can be a relevant absorbing liquid for the treatment of toluene in the absorption–biodegradation process [18].

3 Methods- Computer Application CHEMCAD

3.1 Solvent selection

Besides all the factors mentioned before, the availability of vapor/liquid equilibrium data for the specific organic solvent system is an important factor to consider when choosing the solvent. Such data is necessary for the design of absorber systems and to validate the results obtained; however, it is not immediately available for uncommon organic compounds. Another consideration is the treatment or disposal method of the material removed from the absorber. Since selexol is a widely used solvent and has reported good efficiencies removing both siloxanes, and VOCs it will be studied in this work.

This solvent physical and thermodynamic properties are summarized in the table below (Table 2). These values were obtained from the Computer Application CHEMCAD described in the next section.

Table 2- Selexol properties (from CHEMCAD library values).

	Selexol Properties	
Density at 25 °C	1034	$Kg \cdot m^{-3}$
Vapor pressure at 25 °C	0.093	Pa
Freezing Point	-22 to -28	°C
Normal Boiling Point	275.8	°C
Specific Heat at 25 °C	2113.2	$J \cdot kg^{-1} \cdot K^{-1}$
Viscosity at 25 °C	0.0058	Pa·s
Flash Point	151	°C
Molar Mass	266.3	$g \cdot mol^{-1}$

3.2 Computer Application

The software used was CHEMCAD as DMT owns a license for this program. CHEMCAD is widely used and allows to simulate most chemical processes and so, it fits into the chemical engineering workflow. It is very intuitive and easy to handle. This program can be compared with Aspen Plus software.

3.3 Modelling considerations

To start, a water scrubber with regeneration was studied in order to validate the process before changing to a more complex solvent, such as selexol.

DMT had already a designed absorption column from previous studies, using water as a solvent. But in this process, there was no solvent regeneration, making it very expensive and

not sustainable. Therefore, a solvent regeneration step was added to the water scrubber and further sensitivity studies were performed.

The studied parameters are the air flowrate of the stripping column, the regeneration temperature, the absorber's inlet water flow, the dimensions of both columns and the solvent recycle rate. Since the inlet composition is not fixed, because it depends on the waste composition, it was also studied. The operation of absorption, desorption, and rectification columns with loads over 80 % of the flooding load is uneconomical [19]. For all these sensitivity analyses the flooding percentage was kept between 20-30 and 60-70 %.

Packed towers are widely used for gas-liquid absorption operations [20]. The designed absorption column consists of a packing-bed tower with 30 segments, operating in counter-current, in which the gas flows upward and the liquid trickles down through the packed bed. A packing bed tower example and the packing type plastic Pall Ring are represented in Figure 1. The description of the packing of both columns is presented in *Table 3*.

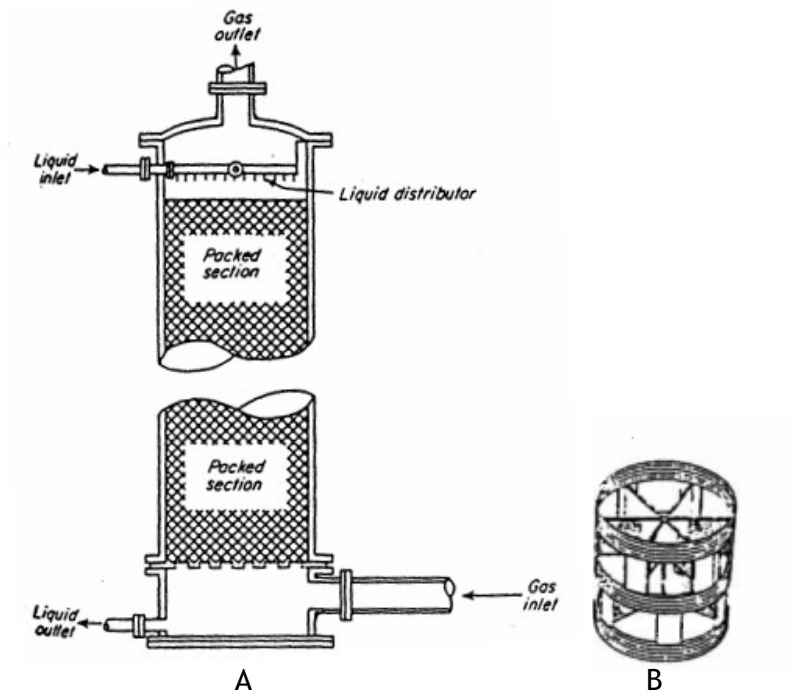

Figure 1- Packed tower and plastic Pall Ring packing [1].

Table 3- Packing material characteristics.

Packing	
Type	Random
Name	Pall Ring
Material	Plastic
Size (mm)	25
Surface ($m^2 \cdot m^{-3}$)	225
Void fraction	0.887

The regeneration step consisted of one desorption column where the solvent enriched with contaminants is cleaned. This desorption column was designed with these same characteristics as the absorption column.

The removal efficiencies presented in the results are calculated between the inlet raw biogas composition and the composition obtained in the clean gas stream.

It is important to refer that all simulations were performed in steady state.

3.4 Water simulation methodology

The sensitivities studies were carried out in separate columns, so it would be easier to draw conclusions regarding the parameter's influence in the simulation. Another advantage is that the time that each simulation takes with just one column is also shorter.

It is important to refer that for the water simulations, the focus was the removal of NH_3. Water scrubbers are usually used to remove NH_3 and hydrogen sulfide, mainly. Since DMT's process already includes one removal step for sulfur compounds (SULFUREX), the focus was just on NH_3.

It was decided to divide the water study into two parts: Water Option 1 and Water Option 2. The Water Option 1 is a simulation where heating and cooling equipment is used to keep different temperatures in the absorption and desorption columns. The Water Option 2 simulates a process where both columns operate at the same temperature.

For Water Option 1, the first step was to simulate the desorption column to determine the most suitable air flowrate for different inlet NH_3 compositions. This sensitivity study was performed at 50 °C, the initially estimated temperature. Next, it was performed an evaluation of influence of the desorption temperature change for each air flowrate determined in step 1. The air flowrate and column height were adjusted with additional sensitivity studies.

In Water Option 2, the temperature in the absorber and the desorber was kept equal and constant. The temperatures simulated were 10 and 30 °C, respectively. The diameter, liquid flowrate and air flowrate were studied and determined.

To allow independent modelling of the absorber and desorber, a flash column was used to estimate the component's equilibrium concentrations with the limit concentrations in the treated/clean biogas stream.

3.5 Selexol simulation methodology

For selexol the goal was to remove mostly VOCs and siloxanes present in the biogas as these components are not removed with water. For this analysis, the same approach described for water was taken concerning the usage of a flash column. The absorption and desorption columns were also studied separately. Concerning the column's dimensions, since it was already a parameter studied previously, the same values were used: they were set constant and equal to 1 meter diameter and 4 meters height. For both columns, the inlet gas flowrate and liquid temperature were analyzed.

3.6 Inlet conditions

The operating conditions for the first sensitivity study (Water Option 1) and inlet biogas composition are described in Table 4 and Table 5, respectively. For DMT, the highest pollutant levels detected was 300 ppm(v), so this was the main study case, although it was also evaluated the influence of the inlet composition in the process.

Table 4- Operating conditions.

Parameters	Absorber	Desorber
Constant		
Packing Type	Pall Ring - Plastic, 25	Pall Ring - Plastic, 25
Pressure / Pa	101325	101325
Variable		
Temperature / °C	10	50
Make-up water / $StdLm^3 \cdot h^{-1}$	0.2	0
Total inlet liquid flowrate / $StdLm^3 \cdot h^{-1}$	8	8
Total inlet gas flowrate / $Nm^3 \cdot h^{-1}$	1450	1450
Flooding / %	27	28
Diameter / m	1	1
Height / m	4	8
Recycling Rate / %	97.50	

Table 5-Inlet raw biogas composition.

Raw Gas Composition			
Bulk	Methane	vol%	57.58
	Carbon dioxide	vol%	40.95
	Nitrogen	vol%	0.75
	Oxygen	vol%	0.18
Inorganic (traces)	NH_3	ppm(v)	300
	Hydrogen Sulfide	ppm(v)	300
VOC's (traces)	2-Butanone	ppm(v)	300
	Toluene	ppm(v)	300
	Ethanol	ppm(v)	300
	Benzene	ppm(v)	300
	Ethylbenzene	ppm(v)	300
	n-Hexane	ppm(v)	300
	n-Pentane	ppm(v)	300
	n-Octane	ppm(v)	300
	D-Limonene	ppm(v)	300
	α-Pinene	ppm(v)	300
	2-Propanol	ppm(v)	300
	ß-Pinene	ppm(v)	300
Siloxanes (traces)	D4	ppm(v)	300
	D5	ppm(v)	300
	L3	ppm(v)	300
	L4	ppm(v)	300

3.7 Thermodynamic and Calculation Models

3.7.1 **K-Value Model**

For the water simulation, the used thermodynamic model for heat and mass balance was the Henry's Law Constant. The Henry's law model was chosen because the solute gas is very diluted in the liquid phase (water); This process, as mentioned before, is a physical process, thereby, no reaction occurs. Furthermore, the operating conditions like temperature and pressure are low and the temperature is kept relatively constant during the process.

In the landfill gas composition, there are some components that constitute electrolytes for instance CO_2 and NH_3. The electrolytes are present in very low concentrations, except the CO_2. Since they are weak electrolytes, they partially ionize in aqueous solution, so it was considered that an Electrolyte Model was not necessary.

On the other hand, CHEMCAD has a Sour Water Model that is applied when H_2S, CO_2 and NH_3 are dissolved in water. This model was also tested for the final operating conditions obtained with Henry's law model but it was possible to see that the result values were very similar. The Henry's law model was used for the report.

Selexol is included in CHEMCAD's library and a K-value model suitable for this component is PSRK-Predictive Soave-Redlich-Kwong model. It combines an equation of state approach with an activity coefficient, and it has the main advantage that vapor-liquid-equilibrium (VLE) can be predicted for a large number of systems without introducing new model parameters that must be fitted to experimental VLE data [21].

3.7.2 H-Enthalpy Model

The models were selected according to CHEMCAD manuals and guiding documents [21, 22]. The Enthalpy models employed were the Latent Heat with the Henry's Law K-Value Model and the SRK with the Sour Water. In combination with PSRK K-value model, Latent Heat should be used as the enthalpy model.

3.7.3 Packed Column Mass transfer

The simulation model selected was Packed Column mass transfer model. CHEMCAD's mass transfer model needs input in the liquid flowrate model, heat transfer option and the calculation model. The selected models for both columns were Plug Flowrate, Heat transfer mode and Billet and Schultes, respectively.

The plug flowrate assumes that the liquid composition in the segment changes with height.

The Heat transfer mode considers the heat transfer calculation for each segment. The heat transfer coefficients are derived using the Chilton-Colburn analogy (this information was taken from CHEMCAD).

Billet and Schultes model calculate the mass transfer coefficients, pressure drop inside the column, loading and flooding points and the liquid holdup of the packing. The basis of this calculation is a model which assumes that empty space of packing can be replaced for theoretical considerations by vertical flowrate channels where the liquid trickles equally distributed [19]. The model is descripted in Annex A- Billet and Schultes [19]. It is important to refer that this model was selected as one of the inputs in the software, but it was not directly used.

4 Results and Discussion

In this section, the main part of the work performed is discussed. The followed procedure is described, and its results presented and explained. This section is divided into four sub-sections: the three approaches taken (Water Option 1, Water Option 2 and Selexol) and at the last sub-section the results of a business case.

4.1 Water Option 1

4.1.1 Flash Column

The limit concentration of pollutants in the clean biogas, i.e., after the pretreatment process, was established as 50 ppm(v). To ensure that this value is respected, a limit of 20 ppm(v) for the simulations was used, instead.

To allow independent modelling of the absorber and desorber, a flash column was used, and a mass balance calculated (Appendix A) to estimate the equilibrium concentrations. This study was focused in the NH_3 concentration only. The implemented flowsheet to simulate the flash column is represented in Figure 2.

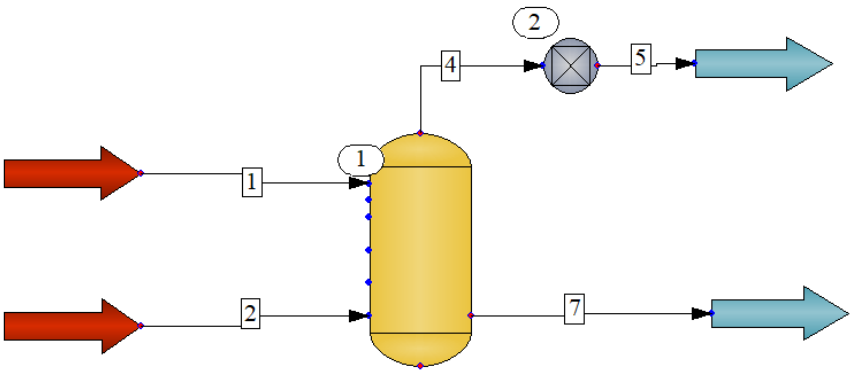

Figure 2- Flowsheet implemented for the flash column.

The flash column represents the absorber in the process. The feed backward controller (equipment number 2 in Figure 2) changes the liquid flowrate of stream 1, so the NH_3 concentration in stream 5 is equal to 20 ppm(v).The obtained NH_3 concentration in stream 7 of the flash column was 4.54×10^{-5} mole fraction, which corresponds to 334 $g \cdot h^{-1}$ (NH_3 mass flowrate).

4.1.2 Process Flow diagram of the overall process

The process flow diagram (PFD) for this simulation is shown below (Figure *3*). The process is composed of two columns: column number 2, which is where the absorption takes place, and column number 6, which is the stripping column for solvent's regeneration. The raw biogas (stream 2) enters through the bottom of the absorber and flows upwards, contacting with the solvent and granting the absorption of some pollutants. The clean biogas, which is the desired product from this process, is obtained at the top of the absorption column (stream 4). The stripping gas, atmospheric air, enters in stream 8 and contacts with enriched solvent (with pollutants in its composition) that comes from absorber (stream 12). The liquid outlet from desorber (stream 6) should be lean solvent, therefore it can be recycled to the first column.

This option includes two heat exchangers, represented respectively by equipment number 5 and number 7. The former heats the liquid until the desired desorption temperature, while the latter cools it down again for the absorption. Since not all solvent is recycled there is the need to add an amount of pure solvent (stream 1). To avoid flooding in the process, there is also an outlet stream (stream 11).

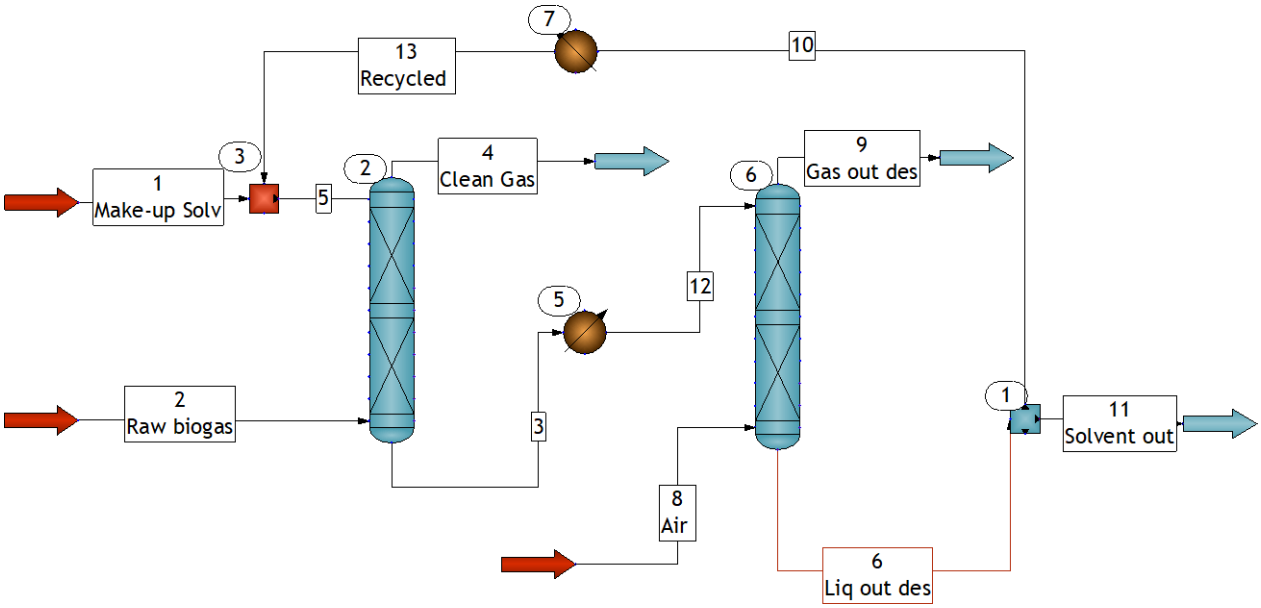

Figure 3-Flowsheet of the *overall process implemented for Water Option 1.*

4.1.3 Sensitivity Studies

Air flowrate of the Desorber

To be able to study solely the air flowrate influence the desorber's efficiency, the diameter of the column was set constant and equal to 1 meter. If the air flowrate is too high for the column dimensions, it will bring with it, the liquid which is intended to run downwards in the column, resulting in flooding [23]. To avoid this problem and allow the study of a great range of gas flowrates, the desorption column was oversized. Therefore, a diameter of 1 meter and a column's height of 8 meters was selected.

The liquid flowrate was calculated, and it corresponds to 8 $m^3 \cdot h^{-1}$ since the selected liquid load was 10 $m^3 \cdot m^{-2} \cdot h^{-1}$ and the straight section area was obtained for a diameter of 1 meter. In Figure 4 the desorption column PFD is represented.

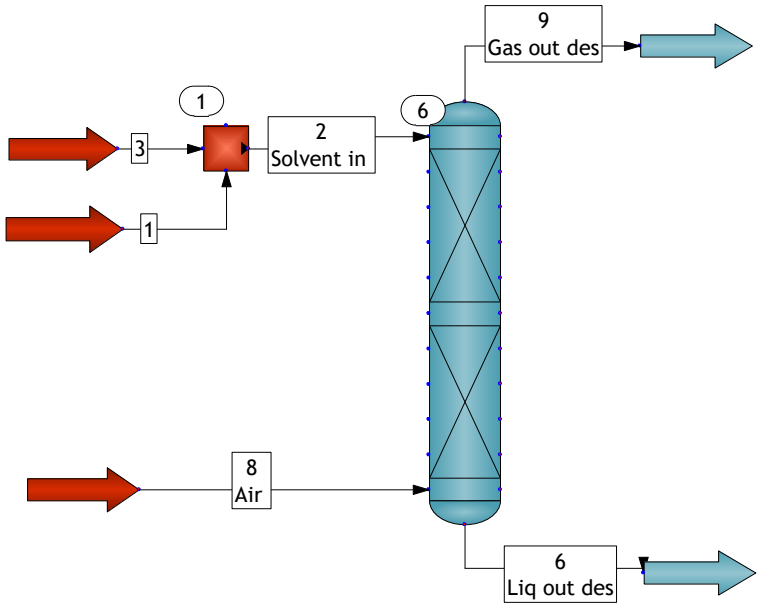

Figure 4- *Flowsheet* implemented for the desorption column.

The liquid desorber inlet stream (stream 2) corresponds to the liquid absorber outlet stream. The NH_3 quantity fed to the desorber has two sources: the one coming from the NH_3 quantity in the recycling stream (stream 13 in Figure 3) correspondent to the 334 $g \cdot h^{-1}$ determined with the flash column) and the other is the difference between the clean gas and the raw biogas NH_3 quantities (streams 4 and 2 in Figure 3, respectively). These two sources are represented in Figure 4 by stream 3 and stream 1, respectively. Atmospheric air enters in stream 8 and flows upwards in countercurrent with the liquid allowing to strip the pollutants from the liquid that leaves the column in stream 6.

In Figure 5, the NH_3's liquid outlet mass flowrate from the desorber (stream 6 in Figure 4) is plotted as a function of the inlet air flowrate (stream 8 in Figure 4) for different NH_3 concentrations in raw biogas (stream 2 in Figure 3) in order to study the influence of the inlet

composition in the required stripping gas flowrate. To simulate the different inlet composition of NH_3 in raw gas (stream 2 in Figure 3), stream 3 (Figure 4) was kept at the equilibrium concentration, 4.54×10^{-5} mole fraction or 334 g·h^{-1} in mass flowrate; and stream 1 (Figure 4) was varied in the sensitivity study between 90 and 1100 g·h^{-1}. These values were projected to correspond to an NH_3 raw biogas composition of 100 to 1000 ppm(v) since in CHEMCAD it was only possible to select flowrate units for this sensitivity variable.

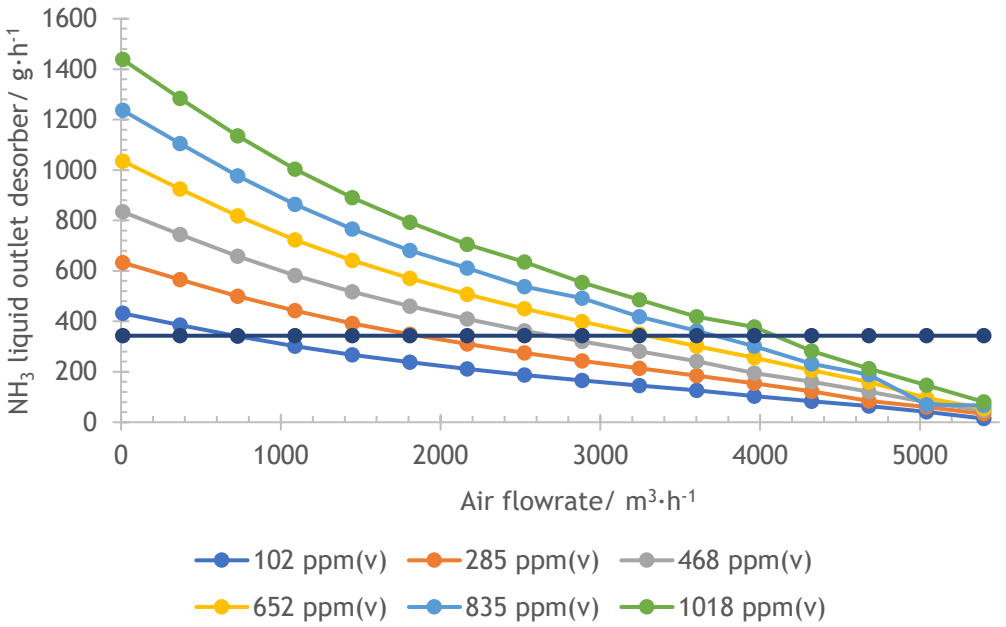

Figure 5- NH_3 liquid desorber outlet flowrates for different air flowrates.

The NH_3 amount in stream 6 (Figure 4) should be less than or equal to 342 g·h^{-1}. This value was determined in Appendix A . For the different inlet compositions of NH_3, the necessary air flowrate, for a NH_3 outlet flowrate equal to 342 g·h^{-1} (straight line in the graphic), was calculated through linear regression. These values are summarized in Table 6.

Table 6- Calculated air flowrate for the respective inlet concentration of NH_3.

NH_3 raw biogas concentration	**NH_3 Stream 1 Desorber**	**Air Flowrate Stream 8 Desorber**
ppm(v)	g·h^{-1}	Nm^3·h^{-1}
102	90	713
285	292	1861
468	494	2695
652	696	3296
835	898	3719
1018	1100	4094

The relation between the calculated air flowrates and the inlet concentration of NH_3 is represented in Figure 6.

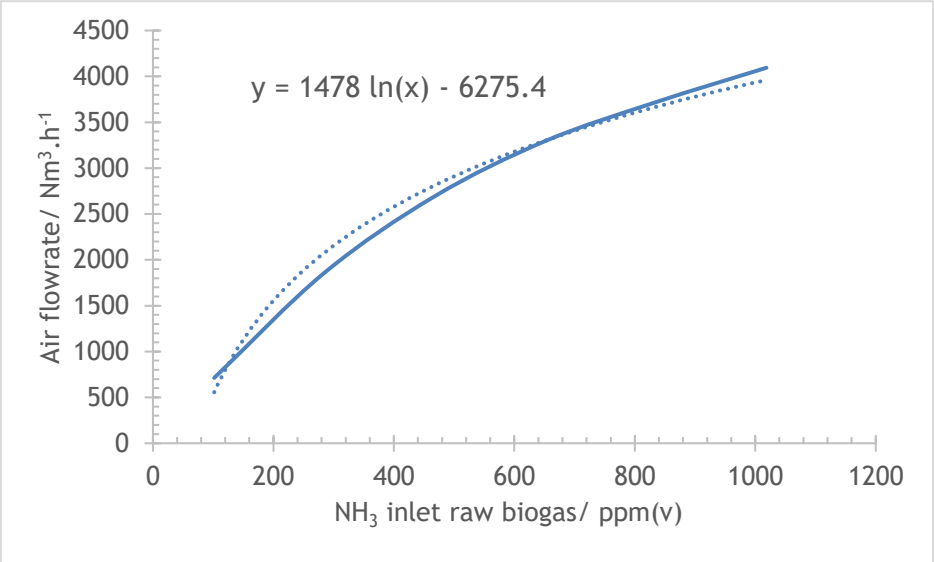

Figure 6- Correlation between air flowrate and inlet NH_3 concentration and the correspondent trendline.

It is possible to see that with increasing NH_3 inlet raw biogas concentration, it is necessary a higher air flowrate to strip this pollutant until the intended limit. Using expression (1), the predicted air flowrates are shown in Table 7. These are the values used for the following sensitivity studies.

$$y = 1478 \ln(x) - 6275.4 \qquad (1)$$

Where, x is the inlet raw biogas concentration in ppm(v) and y is the correspondent air flowrate.

Table 7- Predicted Air flowrate for the respective NH_3 inlet.

NH_3 raw biogas concentration ppm(v)	Air flowrate $Nm^3 \cdot h^{-1}$
100	531
200	1555
300	2155

This approximation was used for the following work, but it was posteriorly noticed that it was a fragile estimation of air flowrates. It would be preferable to calculate the exact inlet mass flowrate of stream 1 corresponding to 100 to 1000 ppm(v) and use those values for the air flowrate sensitivity study shown in Figure 5.

Regeneration Temperature

The regeneration temperature, i.e., the temperature inside the stripper, can be changed by changing both inlet streams (gas and liquid) or just the liquid stream. This was tested, and it was possible to conclude that the air temperature does not have much influence.

So, to simplify the system, and to avoid the need of an extra equipment, the air stream was kept at 10 ˚C, since it is the average temperature in the Netherlands [24]. The inlet liquid temperature was studied, and the values varied between 10 ˚C and 80 ˚C.

The desorber inlet flowrates used for this sensitivity analysis are shown in Table 8 for each case of NH_3 inlet concentration. The air flowrates were set constant and equal to the values reported in Table 7.

Table 8- Desorber NH_3 Inlet liquid flowrates

NH_3 raw biogas concentration ppm(v)	**Stream 1 $g.h^{-1}$**	**Stream 3 $g.h^{-1}$**
100	88	334
200	198	334
300	308	334

The results from this sensitivity analysis are show in two different variables in Figure 7. Increasing the regeneration temperature, the amount of NH_3 in the desorber liquid outlet (stream 6 from Figure 4) decreases and the removal efficiency (calculated between the desorber gas inlet concentration and desorber gas outlet concentration) increases. This means that increasing the regeneration temperature, the desorption process is improved.

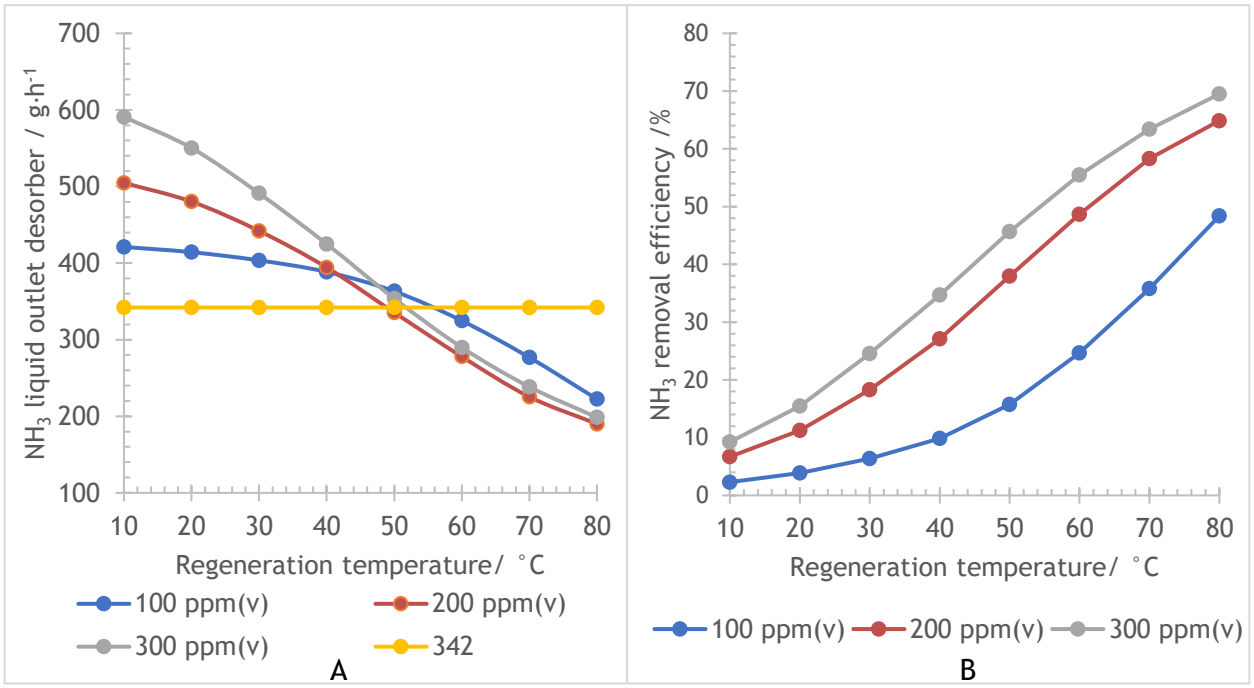

Figure 7- NH_3 desorber outlet with regeneration temperature change. a) NH_3 desorber liquid outlet mass flowrate; b) NH_3 desorber removal efficiency

From the Figure 7 analysis, the minimum temperatures can be determined and are shown in Table 9.

Table 9- Minimum temperatures required.

NH_3 raw biogas concentration ppm(v)	Temperature ˚C
100	60
200	50
300	60

For an NH_3 concentration of 300 ppm(v), the minimum temperature possible is 60 ˚C. If the air flowrates were established the same for the three inlet composition scenarios, it was expected that, increasing raw biogas pollutant's quantities, the required desorption temperature would increase.

Air flowrate for a regeneration temperature of 60 ˚C

The air flowrate was readjusted for the 60 ˚C and a raw biogas composition of NH_3 equal to 300 ppm(v). The liquid inlet mass flowrates were 308 $g \cdot h^{-1}$ (stream 1) and 334 $g \cdot h^{-1}$ (stream 3), in accordance with Table 8. Besides NH_3, another component was taken into consideration for this analysis. Ethanol was chosen because it has a high solubility in water compared with NH_3. This way, two different behaviors are studied. The results are represented in Figure 8.

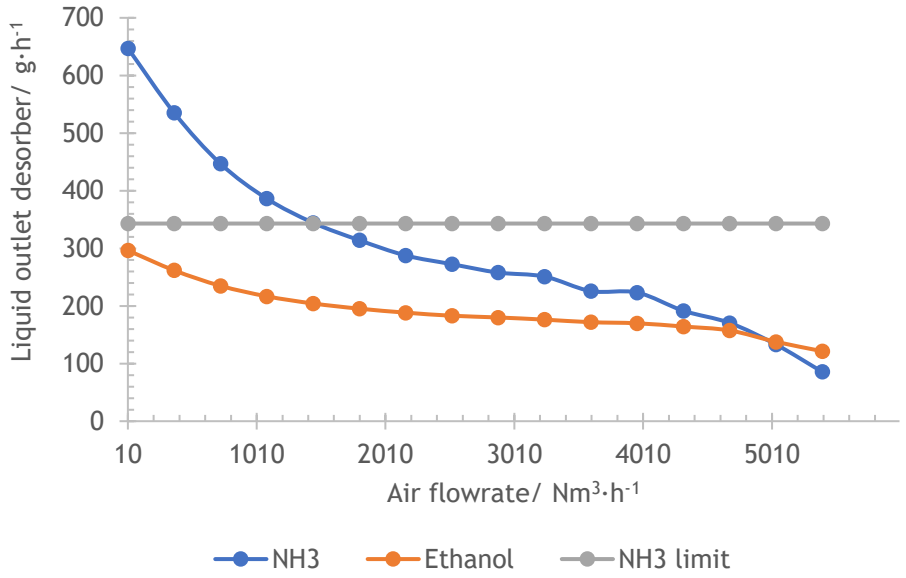

Figure 8- Desorber liquid outlet mass flowrates for different air flowrates at 60 ˚C.

From Figure 8, it can be seen that ethanol does not need very high air flowrates because its liquid outlet mass flowrate tends to be relatively constant after 1500 $Nm^3 \cdot h^{-1}$ (approximately). The minimum air flowrate correspondent to the NH_3 limit value of 342 $g \cdot h^{-1}$ is around 1500 $Nm^3 \cdot h^{-1}$. This flowrate value is used for the next sensitivity analysis.

Desorption Column Height

The conditions shown in Table 10 are the result of the previous studies. These conditions were used to study the desorption column's height.

Table 10- Operating conditions used for desorption column height study.

Conditions	
Temperature /˚C	60
Pressure / Pa	101325
Columns Diameter / m	1
Columns straight section area / m^2	0.79
Liquid flowrate / $StdLm^3 \cdot h^{-1}$	8
Liquid load / $m^3 \cdot m^{-2} \cdot h^{-1}$	10.19
Air flowrate / $Nm^3 \cdot h^{-1}$	1500
Trace compounds raw biogas / ppm(v)	300
Raw gas flowrate / $Nm^3 \cdot h^{-1}$	1450

In this sensitivity study the column's height was changed between 1 and 8 meters and the other parameters were kept constant. The results are shown in Table 11.

Table 11- NH_3 desorption removal efficiencies for different heights.

Desorber's Height / m	NH_3 liquid out (Stream 6) / $g \cdot h^{-1}$	NH_3 liquid in (Stream 2) / $g \cdot h^{-1}$	NH_3 Removal / %
1	561	651	14
2	503	651	23
3	460	651	29
4	**424**	**651**	**35**
5	397	651	39
6	374	651	43
7	355	651	45
8	339	651	48

An appropriate heigh for the desorption column would be 4 meters. Analyzing the data from Table 11, to have a 4 meters column, the outlet of NH_3 in clean biogas would be 25 ppm(v), because it is the corresponding concentration to the 424 $g \cdot h^{-1}$ obtained (see Appendix B). Since 25 ppm(v) is still lower than the 50 ppm(v), some adjustments were made to have a 4 meters column instead. It was determined that the absorber's inlet gas flowrate should be 1100 $Nm^3 \cdot h^{-1}$ rather than 1450 $Nm^3 \cdot h^{-1}$ to match the 25ppm(v). These calculations are presented in Appendix B .

4.1.4 Water-Option 1 final operating conditions

The conditions obtained through the previous described sensitivity studies are summarized in Table 12.

Table 12- Final column operating conditions and dimensions for the case study Water Option1.

Parameters	Absorber	Desorber
Constant		
Packing Type	Pall Ring - Plastic, 25	Pall Ring - Plastic, 25
Pressure / Pa	101325	101325
Variable		
Temperature / °C	10	60
Make-up water / $StdLm^3 \cdot h^{-1}$	0.2	0
Total inlet liquid flowrate / $StdLm^3 \cdot h^{-1}$	8	8
Total inlet gas flowrate / $Nm^3 \cdot h^{-1}$	1100	1500
Flooding / %	22	30
Diameter / m	1	1
Height / m	4	4
Recycling Rate / %	97.50	

The removal efficiencies obtained for these final conditions are presented in section 4.4 with the following study case's removal efficiencies.

4.2 Water Option 2

4.2.1 PFD- Overall Process

The Water Option 2 PFD is illustrated below (Figure 9). It is very similar to the one in *Figure 3*. The main difference is that no heat exchangers are used.

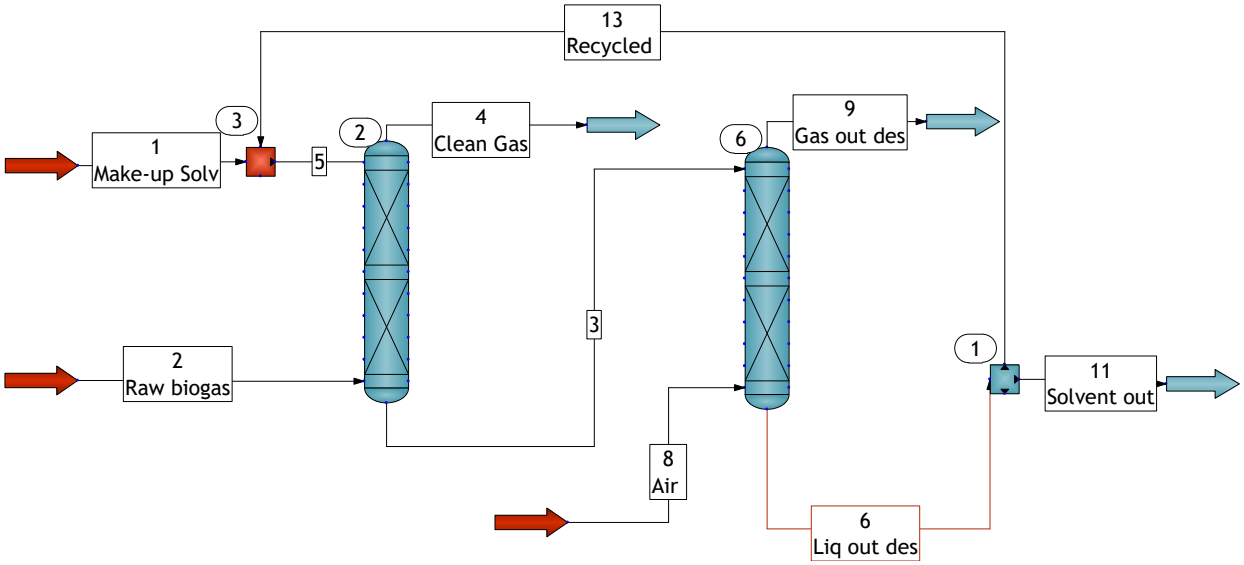

Figure 9- Flowsheet of the overall process implemented for Water Option 2.

4.2.2 Sensitivity Studies

Another approach was used to optimize the system with no need for heat exchangers. The temperature in the absorber and the desorber was kept equal and constant.

The biogas from the digester is at approximately 30 ˚C (mesophilic average temperature) and the biogas from dewatering is at 10 ˚C [25]. So, these were the chosen study temperatures. The equilibrium concentration obtained with the flash column depends on the temperature, therefore, the equilibrium concentrations were also calculated for 30 ˚C, as it can be seen in Table 13.

Table 13- Equilibrium Concentrations obtained with the flash column.

	10˚C		30˚C	
Stream 4 Absorber	**Stream 13 Absorber**	**Stream 6 Desorber**	**Stream 13 Absorber**	**Stream 6 Desorber**
ppm(v)	mole fraction	$g \cdot h^{-1}$	mole fraction	$g \cdot h^{-1}$
20	$4.5x10^{-05}$	342.3	$1.7x10^{-05}$	128.8
50	$1.1x10^{-04}$	856.5	$4.3x10^{-05}$	322.0

The air flowrate was adjusted using CHEMCAD so it would correspond to a flooding percentage between 30 and 70 %. To do this, the program utilizes the Billet and Schultes model selected and shown in Annex A- Billet and Schultes [19].

For both 10 ˚C and 30 ˚C, it was not possible to achieve the 20 ppm(v) limit, even for the highest air flowrates. The 50 ppm(v) was used instead. For this case, only for 30 ˚C and an inlet concentration of 100 ppm(v) was possible to meet the limit. These results are shown in Appendix C. Consequently, for this approach it was considered a limit of 50 ppm(v) in the clean biogas.

Liquid Load Desorption Column

The following study consisted of changing the liquid load, either by changing the diameter of the column or the inlet liquid flowrate (Table 14). Different liquid loads were studied and the necessary air flowrate to achieve the concentrations stated in Table 13 was determined.

Table 14- Air flowrate ranges allowed for different liquid loads and inlet composition.

Diameter / m	**Liquid flowrate / $StdLm^3 \cdot h^{-1}$**	**Liquid Load / $m^3 \cdot m^{-2} \cdot h^{-1}$**	**Air flowrate range / $Nm^3 \cdot h^{-1}$**	
			Raw biogas NH_3 / ppm(v)	
			100	300
1	8	10	1700-4800	3560-4800
1	16	20	1282-4250	4250
0.7	8	21	1030-2050	-
0.7	16	41	1054-1750	-

From Table 14, it can be seen that for the liquid load values of 21 and 41 $m^3 \cdot m^2 \cdot h^{-1}$ and a NH_3 composition in raw biogas for 300 ppm(v), it is not possible to achieve the limit concentrations stated in Table 13 for any air flowrate. The liquid load that allows having a larger range of air flowrates is 10 $m^3 \cdot m^{-2} \cdot h^{-1}$. This value was studied in more detail and the results are condensed in Table 15.

Table 15- Air flowrate ranges allowed for 10 $m^3 \cdot m^{-2} \cdot h^{-1}$ and different inlet compositions.

Diameter / m	Liquid flowrate / $StdLm^3 \cdot h^{-1}$	Liquid Load / $StdLm^3 \cdot m^{-2} \cdot h^{-1}$	Air flowrate range / $Nm^3 \cdot h^{-1}$			% Max Removal Desorber
			Raw biogas NH_3 / ppm(v)			
			100	200	300	
0.70	3.85	10	1120-2400	2080-2400	2400	57.72
1.00	8.00		1700-4800	2320-4800	3560-4800	56.11
1.25	12.30		2700-7300	2700-7300	4540-7300	54.82
1.50	17.70		3500-10800	3500-10800	4960-10800	56.42

It would be preferable to have the lowest column dimensions, from an economic perspective. However, for the first option shown in Table 15 (diameter equal to 0.7 m and liquid flowrate equal to 3.85 $StdLm^3 \cdot h^{-1}$) there is only one possible air flowrate for the target inlet composition of 300 ppm(v). For the second case diameter equal to 1 m and liquid flowrate equal to 8 $StdLm^3 \cdot h^{-1}$), the air flowrate range is wider for 300 ppm(v) so this was the chosen option.

4.2.3 Water-Option 2 final operating conditions

The final operating conditions and equipment dimensions are represented in the next table (Table 16).

Table 16- Final column operating conditions and dimensions for the case study Water Option2.

Parameters	Absorber	Desorber
Constant		
Packing Type	Pall Ring - Plastic, 25	Pall Ring - Plastic, 25
Pressure / Pa	101325	101325
Variable		
Temperature / °C	30	30
Make-up water / $StdLm^3 \cdot h^{-1}$	0.2	0
Total inlet liquid flowrate / $StdLm^3 \cdot h^{-1}$	8	8
Total inlet gas flowrate / $Nm^3 \cdot h^{-1}$	1100	4800
Flooding / %	30	70
Diameter / m	1	1
Height / m	4	4
Recycling Rate / %	97.50	

4.3 Selexol

The process flow diagram of the overall process implemented for the case that uses selexol as a solvent is the same as the one shown in *Figure 3*, only the selected solvent is different.

4.3.1 Sensitivity Studies

Raw gas flowrate in the absorption column

In order to determine the most suitable raw gas flowrate, a sensitivity study was performed. This consisted of varying the raw gas flowrate and analyzing the consequences in the pollutant's outlet concentrations in the clean gas stream. For this study, the flowsheet presented in Figure 10 was implemented, in which equipment number 2 represents the absorption column. The total liquid inlet is composed by two streams: stream 1 is the inlet make-up solvent and stream 13 is the recycle stream that is part of the liquid outlet from the desorber. The stream number 2 is the inlet raw biogas. The clean gas (stream 4) is the desired product and, stream 3 is the liquid outlet from absorber that will enter in the desorption column for stripping out the pollutants from this stream.

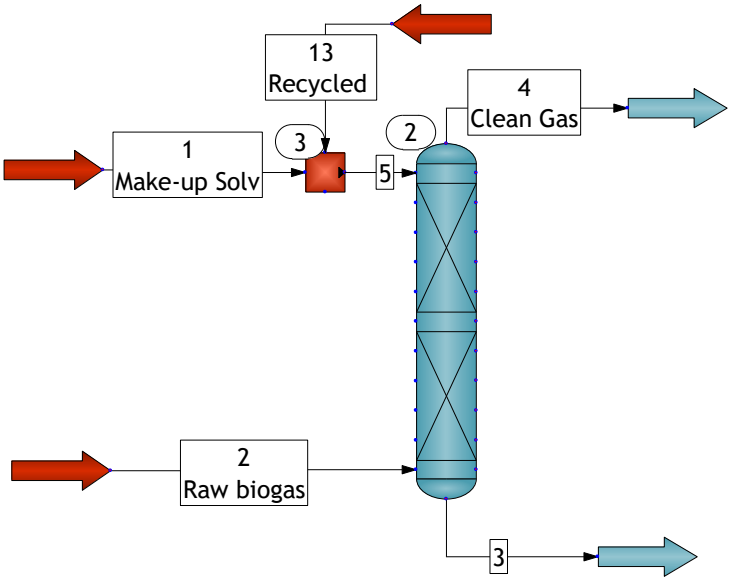

Figure 10-Flowsheet *implemented for the absorption column.*

Since the liquid inlet in the absorber is a mixture of make-up solvent and the recycled stream coming from the desorber (stream 13 in Figure 10), this last stream needs to be considered for the absorber sensitivity studies. The composition of the recycle stream is shown in the following table (Table 17) and has been determined with the flash column methodology, as mentioned before. Once again, a limit of 20 ppm(v) was set for the trace components. Since the raw biogas trace components concentration is 300 ppm(v), a removal efficiency of 83 % is expected for them, especially the target pollutants, siloxanes and VOCs.

Table 17- Recycle stream composition.

Recycle Stream			
Component	**mole fraction**	**Component**	**mole fraction**
Water	0	Ethanol	1.12×10^{-05}
Methane	1.75×10^{-03}	Benzene	1.12×10^{-05}
Carbon Dioxide	9.25×10^{-03}	Ethylbenzene	1.12×10^{-05}
Nitrogen	2.02×10^{-06}	*n*-Hexane	1.11×10^{-05}
Oxygen	2.17×10^{-06}	*n*-Pentane	1.07×10^{-05}
NH3	1.04×10^{-05}	*n*-Octane	1.12×10^{-05}
Hydrogen Sulfide	1.03×10^{-05}	2-Propanol	1.12×10^{-05}
2-Butanone	1.12×10^{-05}	Siloxane D4	1.12×10^{-05}
Toluene	1.12×10^{-05}	Siloxane D5	1.12×10^{-05}
D-Limonene	1.12×10^{-05}	Siloxane L3	9.77×10^{-06}
α-Pinene	1.12×10^{-05}	Siloxane L4	9.94×10^{-06}
ß-Pinene	1.12×10^{-05}	Selexol	0.99

The raw gas flowrate range for this sensitivity analysis is between 1700 $StdLm^3 \cdot h^{-1}$ to 4800 $StdLm^3 \cdot h^{-1}$ correspondent to 30 and 70 % of flooding, respectively and the temperature inside the absorption column is 10 °C. The absorber behavior is shown in Figure 11.

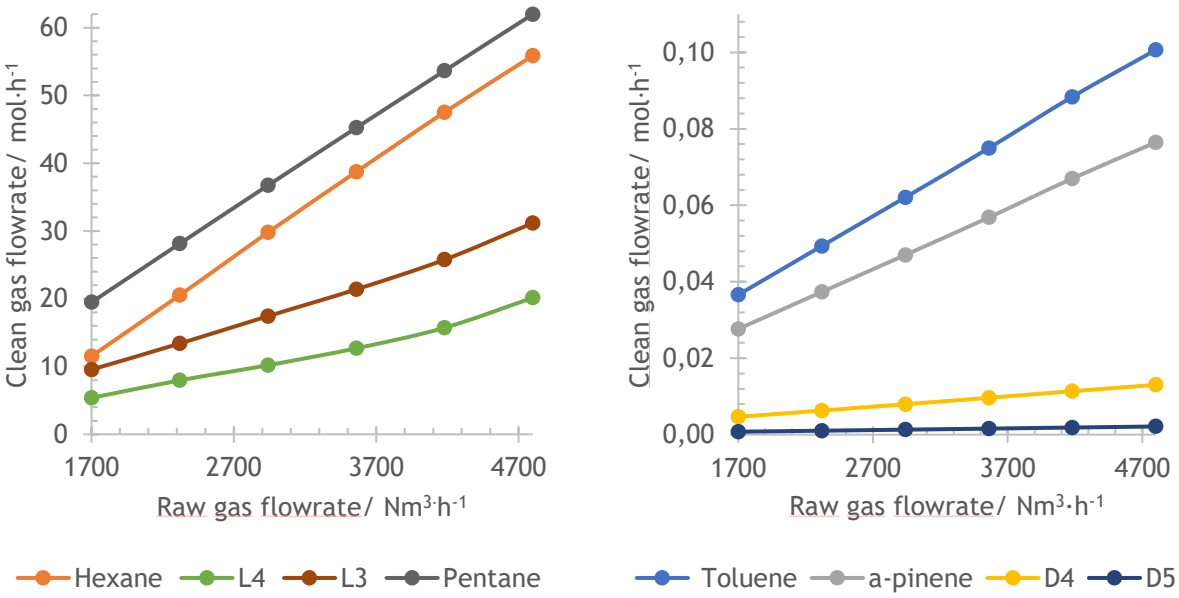

Figure 11 - Clean gas molar flowrates for different VOCs and siloxanes and raw gas flowrates.

With the aim of supporting the results obtained in this study, the solubility of each compound in selexol was investigated. Available data concerning pollutant's solubility in selexol was hard to find for some components. Alternatively, a solubility software based on Hansen Solubility Parameters (HSP) was used and allowed to list the components by increasing solubility in Table 18. [26]. Although siloxanes HSP's were not available in the literature, it was possible to estimate their position in Table 18 from the sensitivity analysis results obtained in Figure 11.

This calculation is explained in more detail in Appendix D.

Table 18- Components listed by increasing solubility in selexol.

Increasing Solubility
Pentane
Hexane
Octane
Siloxane L3
Siloxane L4
Benzene
Ethylbenzene
Toluene
ß-Pinene
α-Pinene
Limonene
Siloxane D4
Siloxane D5

Looking at Figure 11 all component's gas outlet flowrates increased with increasing raw gas flowrate but in different ranges. The components with higher solubility leave the column with the liquid, consequently, the concentration in the clean gas is reduced.

N-Pentane, *n*-hexane, and linear siloxanes (siloxanes L3 and L4) are the less absorbed compounds. For this reason, they are present in higher concentration in the clean gas, exceeding the 20 ppm(v) limit established. These results are in accordance with the solubility order prediction of Table 18.

The absorption is better at lower raw gas flowrates as can be seen in Figure 11, since the pollutants are easily stripped of from the solvent at elevated gas flowrates. The minimum flowrate is 1700 $StdLm^3 \cdot h^{-1}$ equivalent to 30 % of flooding inside the scrubber.

Absorption Temperature

An absorption temperature of 20°C was simulated in this part, in order to compare it with the 10 °C simulation and evaluate the absorption temperature effect. The removal efficiencies (calculated considering quantities in the clean gas and the raw gas stream) for 10 and 20 °C are displayed in Table 19.

Table 19- Absorber removal efficiencies for 10 °C and 20 °C.

Component	Removal Efficiency / %	
	10°C	20°C
2-Butanone	99.58	99.52
Toluene	99.84	99.82
D-Limonene	99.96	99.95
α-Pinene	99.88	99.86
ß-Pinene	99.94	99.93
Ethanol	99.57	99.49
Benzene	99.62	99.59
Ethylbenzene	99.94	99.93
n-Hexane	49.68	32.50
n-Pentane	14.78	10.08
n-Octane	99.63	99.54
2-Propanol	99.74	99.66
Siloxane D4	99.98	99.97
Siloxane D5	100.00	99.99
Siloxane L3	58.45	45.48
Siloxane L4	76.88	70.65

Temperature can be applied as a variable to enhance solubility when needed. Comparing these two temperatures, the overall impact is rather small, except for the components with lower solubility like the smaller hydrocarbons. For *n*-hexane, for example, the difference between removal efficiencies reached 17 %. In this work, 10 °C was applied as the base case to facilitate pre-drying of the gas.

The absorber removal efficiencies shown in Table 19, correspond to a simulation with no water in the recycle stream composition. This is not fully realistic as water is also part of the raw gas composition; moreover, air for stripping has typically a humidity of 60 %, resulting in a carry-over of water into the solvent. Therefore, the process was also simulated including water. The results indicate that removal efficiency with and without a water fraction in the solvent does not differ much. These results are shown Appendix E.

Desorption Temperature

The considered stripping temperature range is 60 °C to 120 °C, in accordance with literature data [27]. The desorption temperature was considered as the desorber liquid inlet temperature. The process flow diagram of the desorption column is represented in Figure 4.

Air at 10 °C was used to strip the pollutants from the enriched solvent stream. The column exhibited high sensitivity to the inlet air flowrate, having flooding issues when increasing it. The air flowrate was set constant and equal to 1700 $StdLm^3 \cdot h^{-1}$ for this reason.

The desorber outlet gas (stream 9 in Figure 4) flowrate values are plotted as function of the liquid inlet (stream 2 in Figure 4) temperature in Figure 12.

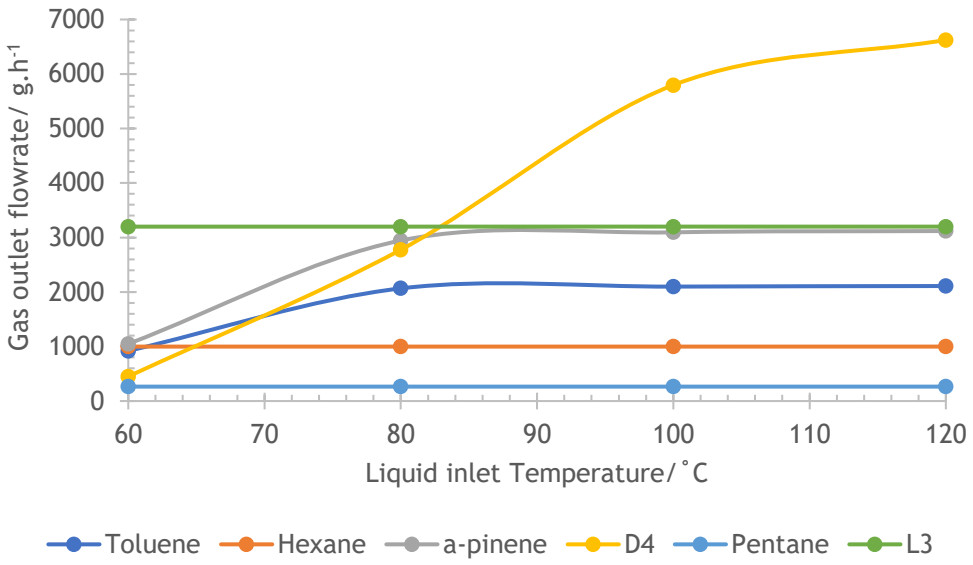

Figure 12- Desorber outlet gas flowrates with increasing desorption temperature.

The pollutant's desorber gas outlet flowrates increased with increasing temperature for the most soluble pollutants in selexol and remained relatively constant for the less soluble ones. The less soluble components are not a problem in the desorption column since they are easily desorbed from selexol. Therefore, the desorption temperature was chosen according to the desorber performance for highly soluble components. If the inlet absorber composition of highly soluble pollutants is reduced, it increases the driving force for the other pollutants.

Analysing in more detail, the outlet gas flowrate values for siloxane D4, toluene and α-pinene increase with temperature but toluene and α-pinene are constant after 80 ˚C as it can be seen in the following figure (Figure 13).

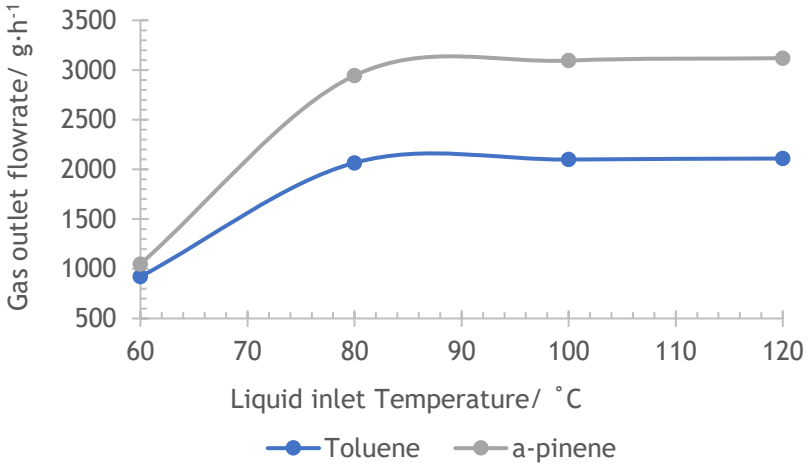

Figure 13- Toluene and α-pinene desorber gas outlet flowrates with desorption temperature.

The selected temperature for the liquid inlet was 80 ˚C since for higher temperatures there are no significant variations for toluene and α-pinene.

Recycle Rate

All the previous studies were performed assuming a recycling rate of 97.50 %. The goal is to increase this rate as much as possible since it reduces the costs considerably. Then, the whole process, i.e., absorption and desorption columns connected, was simulated for two recycling ratios, 97.50 % and 99.75 %. The removal efficiencies are presented below (Table 20).

Table 20- Removal efficiencies for different temperatures and recycling rates.

Removal efficiencies / %		
Recycle / %	97.50	99.75
Temperature / ˚C	**80**	**80**
2-Butanone	99.55	99.43
Toluene	95.25	94.62
D-Limonene	91.10	90.16
α-Pinene	94.32	93.62
ß-Pinene	92.01	91.25
Ethanol	99.89	99.81
Benzene	99.18	98.98
Ethylbenzene	91.36	90.57
n-Hexane	52.37	53.02
n-Pentane	16.88	17.04
n-Octane	99.42	99.28
2-Propanol	99.83	99.76
Siloxane D4	93.99	93.22
Siloxane D5	96.56	95.32
Siloxane L3	97.01	99.93
Siloxane L4	98.96	99.89

From the results observed in Table 20, the removal efficiencies for the two recycling rates do not differ much for all components and for some components like *n*-pentane, *n*-hexane, and linear siloxanes (L3 and L4), the removal efficiency values increased slightly.

The amount of pure solvent required per hour with a higher recycling rate is reduced, reducing expenses of acquisition and discharge. For this reason and the results in Table 20, a recycling rate of 99.75 % is more advantageous.

4.3.2 Selexol final operating conditions

The final operating conditions and column dimensions obtained according to the sensitivity studies performed, and shown in the previous sections, are summarized below (Table 21).

Table 21- Final operating Conditions for Selexol Process.

Parameters	Absorber	Desorber
Constant		
Packing Type	Pall Ring - Plastic, 25	Pall Ring - Plastic, 25
Pressure / Pa	101325	101325
Variable		
Temperature / ˚C	10	80
Make-up water / $StdLm^3 \cdot h^{-1}$	0.02	0
Total inlet liquid flowrate / $StdLm^3 \cdot h^{-1}$	8	8
Total inlet gas flowrate / $Nm^3 \cdot h^{-1}$	1700	1700
Flooding / %	30	30
Diameter / m	1	1
Height / m	4	4
Recycling Rate / %	99.75	

4.4 Removal efficiencies for all study cases

The results of this report can be summarized in Table 22, where all removal efficiencies are presented.

Table 22- Removal efficiencies summary- all Study Cases.

Component		Removal efficiencies / %			
		300 ppm(v)			100 ppm(v)
		Water Option 1	Water Option 2	Selexol	Water option 2
Inorganic (traces)	NH_3	94.04	89.82	14.53	90.18
	Hydrogen Sulfide	2.38	1.78	8.13	1.97
VOCs (traces)	2-Butanone	98.36	98.09	99.43	98.12
	Toluene	8.62	2.42	94.62	2.49
	D-Limonene	40.63	3.44	90.16	0.00
	α-Pinene	20.71	1.24	93.62	0.00
	ß-Pinene	31.27	2.25	91.25	0.14
	Ethanol	98.12	83.84	99.81	81.65
	Benzene	7.46	3.01	98.98	3.24
	Ethylbenzene	14.46	2.41	90.57	2.03
	n-Hexane	0.10	0.00	53.02	0.00
	n-Pentane	0.00	0.00	17.04	0.00
	n-Octane	1.02	0.09	99.28	0.00
	2-Propanol	98.82	84.36	99.76	84.25
Siloxanes (trace)s	D4	6.04	1.64	93.22	0.00
	D5	8.25	7.16	95.32	0.00
	L3	3.20	0.52	99.93	0.00
	L4	8.25	4.28	99.89	0.00

Regarding to the results presented in this table (Table 22) there are some straightforward conclusions:

- NH_3 is only sufficiently removed with water as a solvent. For selexol it shows a low removal efficiency value. NH_3 is not very soluble in selexol compared with the other components present in the raw biogas. More information regarding component's solubilities in selexol is presented in Appendix D;
- Comparing Water Option 1 with Water Option 2, the first has higher removal efficiency values for all components. This is because the absorption and desorption columns operate at different temperatures since the absorption process is improved at lower temperatures while the opposite goes of the desorption process;
- There are some components that are removed with both solvents such as 2-butanone, ethanol and 2-propanol;
- Most VOCs are highly removed with selexol except the light hydrocarbons like *n*-pentane and *n*-hexane. The solubility of hydrocarbons in selexol increase with increasing molecular weight.
- All siloxanes are well removed with selexol.

These removal efficiencies results show that the goal of removing NH_3 in case of water, and VOCs and siloxanes in the case of selexol was achieved.

4.5 Business Case

The actual DMT's system for upgrading landfill gas consists of a 4-step process. The pretreatment is composed of a Sulfurex system, to remove the sulfur compounds, followed by an adsorption media of activated carbon. After compression, it starts the treatment phase with a 3-stage membrane system (Carborex System) [28]. The absorption-desorption technology explored in this work would constitute the first step of the existing pre-treatment. Although one more step is added to the process, this could reduce the total costs in a long-term perspective, mainly due to the maintenance costs associated with activated carbon bed replacement.

Therefore, to evaluate the techno-economic feasibility of the different biogas pretreatment applications, a business case has been set up. The business case is providing a total cost of ownership calculation of four applications, respectively the reference case with activated carbon only (AC), the system based on water scrubbing with and without regeneration process, as well as a selexol based scrubber with regeneration step. The water and selexol processes with regeneration were previously studied in this report. Their operating conditions used for this business case calculation were described in the previous chapters and are condensed into Table 12, Table 16 and Table 21.

Feedstock pollutant levels typically strongly depend on the digester feedstock composition. The chosen scenario for the pollutant load is based on a moderate case. The concentration values used can be found in Table 23.

Table 23- Concentration input for the business case.

Pollutant	Raw gas concentration / ppm(v)	Pollutant	Raw gas concentration / ppm(v)
NH_3	100	Ethylbenzene	10
Hydrogen Sulfide	100	*n*-Hexane	10
2-Butanone	20	*n*-Pentane	10
Toluene	10	*n*-Octane	10
Limonene	10	2-Propanol	20
α-Pinene	10	Siloxane D4	5
ß-Pinene	10	Siloxane D5	5
Ethanol	10	Siloxane L3	5
Benzene	10	Siloxane L4	5

4.5.1 Business case assumptions

The main assumptions used for the business case are shown in Table 24. The production hours were fixed as 8672 hours per year which corresponds to an uptime of 99 %. Labor intensity has been increased with added complexity of the applied technology. Power consumptions are based on engineering calculations for the circulation pumps, air blowers and, in the case of the selexol scrubber, heating and cooling utilities. The activated carbon costs were based on input from DMT's purchase manager. The selexol price was adapted from literature values are corrected based on inflation (1,5% per year) and converted from dollar to Euro against exchange rate of 0,84 [29].

Table 24- Business Case assumptions.

	AC only	Water scrubber without regeneration + AC polishing	Water scrubber with regeneration + AC polishing	Selexol scrubber with regeneration + AC polishing	Units
Depreciation period	15	15	15	15	year
Interest	7	7	7	7	%
Maintenance	2.5	2.5	2.5	2.5	% of investment
Production hours	8672	8672	8672	8672	$h \cdot year^{-1}$
Operator wage	62.5	62.5	62.5	62.5	$€.h^{-1}$
Labour intensity	0.02	0.07	0.07	0.12	FTE
Power consumption	0	0.0018	0.0138	0.0061	$kWh \cdot (Nm^3 gas\ in)^{-1}$
Power	0.09	0.09	0.09	0.09	$€ \cdot (kWh)^{-1}$
Chemicals (selexol)	3660	3660	3660	3660	$€ \cdot ton^{-1}$
Chemical's disposal	100	100	100	100	$€ \cdot ton^{-1}$
Water	1	1	1	1	$€ \cdot m^{-3}$
Water disposal	0.44	0.44	0.44	0.44	$€ \cdot m^{-3}$
Activated Carbon	3-5	3-5	3-5	3-5	$€ \cdot kg^{-1}$
Carbon discharge	50	50	50	50	$€ \cdot ton^{-1}$

4.5.2 Results and conclusions

Capital cost estimates for the activated carbon vessels and scrubbers have been based on input from DMT's calculation & procurement office. Operational costs have been quantified based on the assumptions stated in Table 24. Activated carbon consumption rates and cost levels are calculated based on DMT's activated carbon bed engineering tool (Engineering Assist Tools 0.07). The pollutant inlet concentrations of the carbon beds after passing through the water and selexol based scrubber, have been calculated using the removal efficiencies determined with the simulation activities described in the previous chapters. In Appendix F the removal efficiencies as used are displayed.

OPEX and CAPEX cost have been stated as yearly cost and summarized to display the plants yearly TCO (Total cost of ownership) for fair comparison. In addition, cost have been normalized to display the TCO per Nm^3 of raw biogas treated. Return of investment (ROI) calculations have been added to indicate the payback period of the additional investment required.

The main parameters of the business case are summarized in Table 25. In Appendix F, a more detailed description can be found. The values were rounded to simplify the interpretation.

Table 25- Business Case Calculation results.

Main parameters	AC-only	Water scrubber without regeneration + AC polishing	Water scrubber with regeneration + AC polishing	Selexol scrubber with regeneration + AC polishing
TCO Summary				
TCO / €·year^{-1}	339680	327260	309110	203270
€·Nm^{-3} pretreated	0.039	0.038	0.036	0.023
Annual saving	-	12420	30580	136410
ROI / years	-	16	8	2
CAPEX (Investment)				
Total investment / €	150000	350000	400000	450000
Depreciation / €·year^{-1}	10000	23330	26670	30000
Interest / €·year^{-1}	5250	12250	14000	15750
OPEX (Investment)				
1. Total raw materials / €·year^{-1}	313470	257900	234460	130930
2. Total services / €·year^{-1}	4610	15930	14880	6240
3. Maintenance / €·year^{-1}	3750	8750	10000	11250
4. Operating labour / €·year^{-1}	2600	9100	9100	9100

Selexol scrubber with regeneration has the lowest TCO value, mainly due to the raw materials and services costs. Although selexol is more expensive than water, the make-up water volume used is 10 times higher (0.2 $m^3 \cdot h^{-1}$ of water, compared with 0.02 $m^3 \cdot h^{-1}$ of selexol). The recycling rate used for the water scrubber was 97.50 %. Although, at first sight, is a high percentage, it is still a significant daily make-up water volume, implying considerable acquisition and disposal costs. For this reason, a higher recycling rate should be studied, but considering that the make-up volume needs to compensate for solvent losses due to evaporation effects, and in the outlet steams. For selexol, a larger recycling rate was studied, 99.75 % and proved to be an efficient process.

Within these 4 options, selexol process proved to be an advantageous pretreatment step. However, the water recycling rate should still be assessed, and it can change the conclusions of this business case.

5 Conclusions

Landfill gas (LFG) emissions make up for a large portion of the human-related methane emissions [28]. Upgrading this biogas to biomethane (or green gas) reduces odour as well as health and safety hazards associated with the emissions. Besides this, biomethane can be used to replace fossil fuels and natural gas. One of the possible futures for biogas is to be used as vehicle fuel [30]. To meet the characteristics and properties imposed for these future possibilities, landfill gas has to be upgraded.

The pretreatment of LFG is indispensable to remove harmful impurities that affect utilization as an energy source. Moreover, there are components that damage the process equipment, for instance sulfur compounds and siloxanes.

The absorption process studied in this work proved to be an efficient pretreatment step that can be added to DMT's LFG upgrading process eradicating some operational issues.

The addition of a solvent regeneration step to the organic scrubber makes a huge difference since the process was not feasible before in monetary and sustainable terms. The desorption column, as a regeneration step, gave satisfactory results. Nevertheless, in future work, it can be compared with other regeneration options such as evaporation by reducing pressure or heating it up.

The raw gas composition depends on the waste composition. For the water scrubber, 100 and 300 ppm(v) impurities composition were simulated. The NH_3 removal efficiency for 100 ppm(v) was higher. The higher the concentration of impurities, the lower the removal will be.

The gas flowrates are a limiting parameter for the columns because if the air flowrate is too big for the column dimensions, it will bring with it, the liquid which is intended to run downwards in the column, resulting in flooding issues. For all simulations, the flooding percentage was kept between 30 and 70 %. At elevated gas flowrates, there's not enough time for the mass transfer to occur and besides that, the pollutants can be stripped of from the solvent. To improve the mass transfer, the size of the column can be increased since it would allow more transfer area.

Regarding to gas temperature, it should be noted that its influence is not relevant, so it is preferable to adjust the liquid streams temperature instead and to apply heat/cooling equipment to these streams. Absorption processes are more efficient at lower temperatures and the opposite goes for desorption. Keeping all the other parameters constant, it is expected that decreasing temperature in absorption column and increasing it in desorption would

improve the overall process. Temperature can be applied as a variable to enhance solubility when needed.

An interesting perspective was taken regarding to the system's temperature. It was evaluated the option of having both columns, scrubber and the regeneration step, at the same temperature (presented as Water Option 2 in results). Comparing for 300 ppm(v), this approach exhibits an NH_3 removal efficiency 4 % inferior to the approach with different absorption and desorption temperatures (Water Option 1). This is not a significant difference since the limit concentration in clean biogas is respected in both situations.

Selexol is a more complex solvent compared with water but it allows to remove the trace components that are not removed using water, more specifically some VOCs and siloxanes. On the other hand, for NH_3 removal it was not effective.

The components with lower solubility in selexol are *n*-pentane, *n*-hexane and linear siloxanes like L3 and L4. The solubility of hydrocarbons in this solvent increase with molecular weight. These components are easily stripped out from the solvent and removed in desorber. The opposite behavior is observed for highly soluble components such as cyclic siloxanes, limonene, α and ß pinene and toluene.

Increasing the recycle rate is advantageous regarding to saving pure solvent needs and money. The recycle rate cannot be 100 % due to solvent losses by evaporation and outlet streams.

Removal efficiencies obtained for the selexol were, for most VOCs and Siloxanes higher than 90 % and for some of them 99 % was achieved for instance 2-butanone, benzene, *n*-octane, 2-propanol and linear siloxanes (L3 and L4). On the other hand, water could remove NH_3 with a maximum efficiency of 94 %, this value was obtained for Water Option 1 case scenario. Other components such as 2-butanone, ethanol and 2-propanol were also efficiently removed with water.

The addition of this pretreatment step to the overall upgrading system can reduce the total costs in a long-term perspective, mainly due to the maintenance costs associated with activated carbon bed and membranes replacement. Selexol scrubber with regeneration has the lowest TCO value, mainly due to the raw materials and services costs. This is mainly a consequence of the make-up solvent volume used in this study since it is much higher for water than selexol. For this reason, a higher recycle rate for water should be studied. Within the four options presented in the business case, selexol proved to be an advantageous pretreatment step.

For further studies in this matter, the option of having a batch process, instead a continuous as it is right now, can be considered. It would also be very interesting to analyze the loss of solvent and methane during the process.

It is also important to notice that if H_2S concentrations in the raw gas are too big, air should not be used as the stripping gas since it could lead to elemental sulfur formation resulting in corrosion problems.

6 Assessment of the work

6.1 Objectives Achieved

- Overview of the pretreatment techniques used for siloxanes and VOCs removal;
- Overview of solvents used for absorption processes and selection of the solvent suitable for siloxanes and VOCs removal;
- Design and modelling of a physical absorption process with regeneration and recycle using CHEMCAD software;
- Process optimization through many sensitivity studies performed for water and selexol simulations with the aim of reducing pollutants concentration on biogas before membranes treatment;
- For the water scrubber, two cases were studied and compared. Both gave high values of NH_3 removal efficiency;
- Selexol proved to be a good choice for the siloxanes and VOCs removal showing efficiencies of 99 % for some pollutants;
- A business case was performed to understand if the addition of this pretreatment step is lucrative to the overall biogas upgrading process. It also allowed to compare the three cases studied and the water scrubber without regeneration as a pretreatment stage.

6.2 Final Assessment

The work performed during this internship demonstrates that this pretreatment technology can be profitable for the company. If the main goal is to remove VOCs and siloxanes, selexol should be used rather than water. Selexol proved to be an interesting solvent which absorbs most of the harmful and equipment-damaging pollutants.

For these reasons, further studies in this subject should focus in increasing as much as possible the recycle rate to reduce the costs. Also, for the selexol process, the removal efficiency values of light hydrocarbons should be improved, specifically for *n*-pentane and *n*-hexane.

7 References

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Annex A- Billet and Schultes [19]

The calculation model by Billet and Schultes is a physically proven model for the advanced calculation of mass transfer in columns with dumped or arranging packings. This model allows calculating gas and liquid mass transfer coefficients, the pressure drop of dry or irrigated packings, their loading and flooding points as well as their liquid holdup.

Mass transfer coefficients

The height of the mass transfer unit is calculated according to the HTU-NTU model. According to this, in the case of systems with predominantly gas-phase mass transfer resistance, the product is formed from the overall height of a gas-phase mass transfer unit HTU_{OV} and the number of gas-phase mass transfer units NTU_{OV} for the calculation of the height H, see equation (1).

$$H = HTU_{OV} NTU_{OV} \quad (1)$$

If the mass transfer resistance is situated mainly in the liquid phase, the previous equation is re-written as equation (2).

$$H = HTU_{OL} NTU_{OL} \quad (2)$$

The variables of equations (3) and (4) are linked by the stripping factor λ. This factor is described by the quotient formed by the gradient of the equilibrium curve m_{yx} and the molar phase ratio $\dot{L}/\dot{V}$.

$$HTU_{OL} = HTU_{OV}/\lambda \quad (3)$$

$$NTU_{OL} = \lambda\, NTU_{OV} \quad (4)$$

The loading capacity of the packing determines the column diameter and thus the flowrate velocity and the residence time.

The effectiveness of the mass transfer between phases is decided by the geometric surface area of the packing and its ability to create turbulent flowrate.

The following statements apply to systems with predominantly gas-phase resistance. However, they can be applied to systems with predominantly liquid-phase resistance by means of equations (3) and (4).

The overall height of a gas-phase mass transfer unit, HTU_{OV}, is subdivided into the height of a gas-phase mass transfer unit HTU_V and the height of a liquid-phase mass transfer unit HTU_L, which are defined by the gas and liquid velocities u_V and u_L with reference to the empty column cross−sections and the volumetric mass transfer coefficients $\beta_v a_{ph}$ and $\beta_L a_{ph}$, see equation (5).

The volumetric mass transfer coefficients are calculated from equations (6) to (11). Furthermore, a_{ph} , describes the specific interface area between the phases and d_h, the hydraulic diameter of the dumped packings.

$$HTU_{OV} = HTU_V + \lambda HTU_L = \frac{u_V}{\beta_v a_{ph}} + \frac{m_{yx}}{\frac{\dot{L}}{\dot{V}}} \frac{u_L}{\beta_L a_{ph}} \tag{5}$$

$$\beta_L a_{ph} = C_L 12^{1/6} \bar{u}_L^{1/2} \left(\frac{D_L}{d_h}\right)^{1/2} a \left(\frac{a_{ph}}{a}\right) \tag{6}$$

The effective liquid velocity $\bar{u}_L$ is calculated from the velocity $u_L$with reference to the column cross-section and the column holdup, $\boldsymbol{h_L}$:

$$\bar{\boldsymbol{u}}_{\boldsymbol{L}} = \frac{\boldsymbol{u_L}}{\boldsymbol{h_L}} \tag{7}$$

$$\beta_v a_{ph} = C_v \frac{1}{(\epsilon - h_L)^{\frac{1}{2}}} \frac{a^{\frac{3}{2}}}{d_h^{\frac{1}{2}}} D_V \left(\frac{u_V}{a v_v}\right)^{\frac{3}{4}} \left(\frac{v_V}{D_v}\right)^{\frac{1}{3}} \left(\frac{a_{ph}}{a}\right) \tag{8}$$

Next, α_{Ph} describes the specific interface area between the phases and d_h the hydraulic diameter of the dumped packings.

$$\frac{a_{ph}}{a} = 1.5\,(a d_h)^{-0.5} \left(\frac{u_L d_h}{v_L}\right)^{-0.2} \left(\frac{u_L^2 \rho_L d_h}{\sigma_L}\right)^{0.75} \left(\frac{u_L^2}{g d_h}\right)^{-0.45} \tag{9}$$

$$d_h = 4\frac{\epsilon}{a} \tag{10}$$

$$h_L = \left(12\,\frac{1}{g}\frac{\eta_L}{\rho_L}\mu_L a^2\right)^{\frac{1}{3}} \; for\; u_v \leq u_{v,s} \tag{11}$$

These equations apply to load conditions up to the loading point of a two-phase counter-current flowrate: $u_v \leq u_{v,s}$.

Above the loading point, the shear stress of the gas countercurrent is large enough to dam up the falling film so that the column holdup and the size of the interface increase and the effective flow velocity of the falling film decreases. This condition was taken into account in equations (12) to (16).

$$h_L = h_{L,S} + (h_{L,Fl} - h_{L,S}) \left(\frac{u_V}{u_{V,Fl}}\right)^{13} \tag{12}$$

$$h_{L,Fl}^3 \left(3h_{L,Fl} - \epsilon\right) = \frac{6}{g} a^2 \epsilon \frac{\eta_L}{\rho_L} \frac{L}{V} \frac{\rho_V}{\rho_L} u_{V,Fl} \; with \; \frac{\epsilon}{3} \leq h_{L,Fl} \leq \epsilon \tag{13}$$

$$\frac{a_{Ph}}{a} = \frac{a_{Ph,S}}{a} + \left(\frac{a_{Ph,Fl}}{a} - \frac{a_{Ph,S}}{a}\right) \left(\frac{u_V}{u_{V,Fl}}\right)^{13} \tag{14}$$

$$\frac{a_{Ph,Fl}}{a} = 10.5 \left(\frac{\sigma_L}{\sigma_W}\right)^{0.56} (ad_h)^{-0.5} \left(\frac{u_L d_h}{v_L}\right)^{-0.2} \left(\frac{u_L^2 \rho_L d_h}{\sigma_L}\right)^{0.75} \left(\frac{u_L^2}{g d_h}\right)^{-0.45} \quad (15)$$

$$\bar{u}_L = \left(\frac{g\rho_V^2 u_V^2}{12\eta_L a^2 \rho_L}\right)^{1/3} \left(\frac{L}{V}\right)^{2/3} \left[1 - \left(\frac{u_V - u_{V,S}}{u_{V,Fl} - u_{V,S}}\right)^2\right] for\ u_{V,S} \leq u_V \leq u_{V,Fl} \quad (16)$$

Pressure drop.

The pressure drop depends on the geometric surface (α), the void volume of the column packings (ϵ), the gas load factor (F_V), calculated from the gas velocity (u_V) and the square root of the gas density (ρ_V), and the wall factor K. The wall K factor, the resistance coefficient ψ_0, and the particle diameter are calculated by equations (18)-(21).

$$\frac{\Delta P_0}{H} = \psi_0 \frac{a}{\epsilon^3} \frac{F_v^2}{2} \frac{1}{K} \quad (17)$$

$$\frac{1}{K} = 1 + \frac{2}{3} \frac{1}{1 - \epsilon} \frac{d_p}{d_s} \quad (18)$$

$$\psi_0 = C_{p,0} \left(\frac{64}{Re_v} + \frac{1.8}{Re_v^{0.08}}\right) \quad (19)$$

$$Re_v = \frac{u_v d_p}{(1-\epsilon)v_v} K \quad (20)$$

$$d_p = 6 \frac{1-\epsilon}{a} \quad (21)$$

Calculation of the load limits.

Below the loading point, the liquid film trickles from the top of the column to the bottom without any influence of the gas countercurrent flowrate. The column holdup is merely a function of the liquid load. Increasing the gas velocity, the shear stress at the surface of the liquid increases, so that the velocity of the liquid film at the phase boundary layer drops. At the loading point, the velocity at the interface is zero, and thus the loading point is derived according to equation (22).

If the flowrate parameter, given by $\frac{L}{V}\sqrt{\frac{\rho_V}{\rho_L}}$, is smaller than 0.4, the liquid trickles downwards as a disperse phase, while if it is greater than 0.4, the liquid load and thus the column holdup reach such large values that the empty spaces within the bed close up and the liquid flowrates downwards as a continuous phase. The gas phase then rises up through the liquid in the form of bubbles.

The resistance coefficient at the loading point ψ_S is determined by equation (23). The exponent n_S is dependent on the given flowrate parameter (equations (25) and (26)) which characterizes the load condition for the phase inversion in the column.

$$u_{V,S} = \sqrt{\frac{g}{\psi_s}} \left[\frac{\epsilon}{a^{1/6}} - a^{1/2} \left(12 \frac{1}{g} \frac{\eta_L}{\rho_L} u_{L,S} \right)^{1/3} \right] \times \left(12 \frac{1}{g} \frac{\eta_L}{\rho_L} u_{L,S} \right)^{1/6} \times \sqrt{\frac{\rho_L}{\rho_V}} \quad (22)$$

$$\psi_s = \frac{g}{C_s^2} \left[\frac{L}{V} \sqrt{\frac{\rho_V}{\rho_L}} \left(\frac{\eta_L}{\eta_V} \right)^{0.4} \right]^{-2n_S} \quad (23)$$

$$u_{L,S} = \frac{\rho_V}{\rho_L} \frac{L}{V} u_{V,S} \quad (24)$$

$$for \ \frac{L}{V} \sqrt{\frac{\rho_V}{\rho_L}} \leq 0.4 : \ n_s = -0.326 \ ;$$
$$for \ \frac{L}{V} \sqrt{\frac{\rho_V}{\rho_L}} \geq 0.4 : \ n_s = -0.723 \quad (25)$$

$$C_s = 0.695 \, C_{S,Tab.2} \left(\frac{\eta_L}{\eta_V} \right)^{0.1588} \quad (26)$$

Above the loading point, the flowrate of the liquid is impeded and the column holdup increases. If the shear stress is sufficient to entrain the entire liquid to the top of the column then the flooding point is reached. Mathematically, this means that the velocity gradient of the liquid film becomes zero at the interface of the dumped packing. Flooding condition calculations are derived by equations (27) to (31).

$$u_{V,Fl} = \sqrt{2} \sqrt{\frac{g}{\psi_{Fl}}} \frac{(\epsilon - h_{L,Fl})^{3/2}}{\epsilon^{1/2}} \sqrt{\frac{h_{L,Fl}}{a}} \sqrt{\frac{\rho_L}{\rho_V}} \quad (27)$$

$$\psi_{Fl} = \frac{g}{C_{Fl}^2} \left[\frac{L}{V} \sqrt{\frac{\rho_V}{\rho_L}} \left(\frac{\eta_L}{\eta_V} \right)^{0.2} \right]^{-2n_{Fl}} \quad (28)$$

$$u_{L,Fl} = \frac{\rho_V}{\rho_L} \frac{L}{V} u_{V,Fl} \quad (29)$$

$$for \ \frac{L}{V} \sqrt{\frac{\rho_V}{\rho_L}} \leq 0.4 : \ n_{Fl} = -0.194;$$
$$for \ \frac{L}{V} \sqrt{\frac{\rho_V}{\rho_L}} \geq 0.4 : \ n_{Fl} = -0.708 \quad (30)$$

$$C_{Fl} = 0.6244 \, C_{Fl,Tab.2} \left(\frac{\eta_L}{\eta_V} \right)^{0.1028} \quad (31)$$

Appendix A

Mass balance to both columns

The PFDs of the absorption and desorption columns as presented before in Figure 10 and Figure 4 are here repeated (**Figure 14**) to facilitate the understanding of the mass balance. In these flowsheets, the different streams are:

- Absorber:
    - Stream 1: Make-up solvent, with no pollutants in its composition;
    - Stream 13: Recycling stream. The NH_3 composition was determined with the flash column as it is explained in section 4.1.1, and it represents the equilibrium concentration;
    - Stream 5: The sum of stream 1 and 13;
    - Stream 2: Raw gas stream. For this case the NH_3 composition is 300ppm(v);
    - Stream 4: Clean biogas. The NH_3 composition was target as 20ppm(v);
    - Stream 3: This stream is determined by: (Stream 5+ Stream 2)-Stream 4;.
- Desorber:
    - Stream 1: This stream is calculated by the difference between the outlet and inlet gas streams from the absorber, i.e., (Stream 2 Absorber-Stream 4 Absorber);
    - Stream 3: Corresponds to Stream 5 from absorber;
    - Stream 2: This stream has to be the same as stream 3 from absorber;
    - Stream 6: This stream is calculated by dividing stream 13 from absorber by 0.975, which is the recycling rate;
    - Stream 8: Air inlet stream;
    - Stream 9: Calculated by the difference between the inlet and the outlet of this column (Stream 2+Stream 8)-Stream 6.

In Table 26 the results of NH_3 molar and mass balances for the absorber at 10 °C, a recycling rate of 97.5 %, NH_3 raw gas concentration of 300 ppm(v) and the limit NH_3 clean gas concentration established as 20 ppm(v) are summarized.

Table 26- Molar and Mass balance for the absorption and the desorption column specific case.

Absorber								
Variable	Liquid					Gas		
	In			Out	Units	In	Out	Units
	Stream 1	Stream 13	Stream 5	Stream 3		Stream 2	Stream 4	
Total flowrate	0.2	7.8	8	8	$m^3.h^{-1}$	1450	1450	$m^3.h^{-1}$
NH_3 composition	0	$4.5x10^{-05}$	$4.4x10^{-05}$	$8.5x10^{-05}$	mole fraction	300	20	ppm(v)
NH_3 molar flowrate	0	19.6	19.6	37.7	$mol.h^{-1}$	19.4	1.3	$mol.h^{-1}$
NH_3 mass flowrate	0	333.8	333.8	642.3	$g.h^{-1}$	330.5	22	$g.h^{-1}$
Desorber								
Variable	Liquid					Gas		
	In			Out	Units	In	Out	Units
	Stream 1	Stream 3	Stream 2	Stream 6		Stream 8	Stream 9	
NH_3 molar flowrate	18.1	19.6	37.7	20.1	$mol.h^{-1}$	0	17.6	$mol.h^{-1}$
NH_3 mass flowrate	308.5	333.8	642.3	342.4	$g.h^{-1}$	0	299.9	$g.h^{-1}$

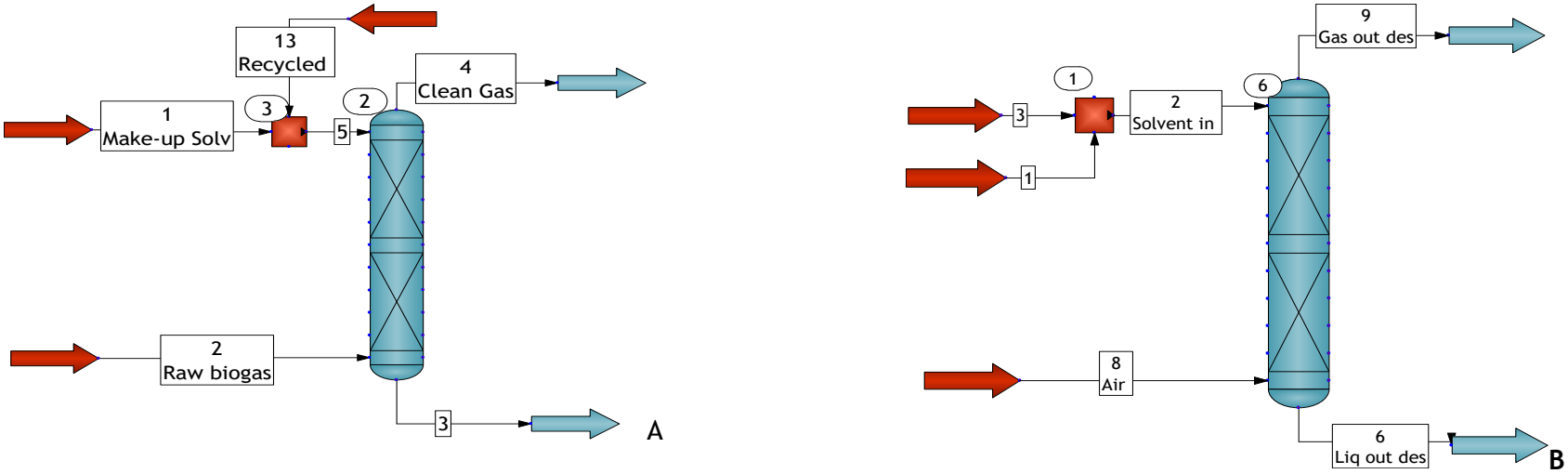

Figure 14- Process flow diagrams implemented for the mass balance. A) Absorption column; B) Desorption column.

Appendix B

Calculation of inlet Raw Gas Flowrate for 4 meters column height

In order to have a 4 meters column height, the raw gas flowrate had to be adjusted so that the NH_3 liquid outlet (stream 6) from the desorber equal to 424 $g \cdot h^{-1}$ (value obtained in results- chapter 0).

First, the NH_3 raw gas composition in ppm(v) correspondent to the NH_3 liquid outlet mass flowrate value of 424 $g \cdot h^{-1}$ was determined. This value was obtained through a trendline. The NH_3 equilibrium concentrations for 20, 50 and 100 ppm(v) were determined with the flash column. In Table 27, these values are summarized.

Table 27- NH_3 concentration in ppm(v) calculation.

Raw gas Stream 4 Absorber	**Equilibrium concentration** Stream 13 Absorber	**Liquid out** Stream 6 Desorber
ppm(v)	mol fraction	$g \cdot h^{-1}$
20	$4.54x10^{-05}$	342.33
50	$1.14x10^{-04}$	856.58
100	$2.27x10^{-04}$	1713.22
	TRENDLINE	
25	$5.62x10^{-05}$	423.79

As it can be seen in Table 27, the correspondent NH_3 concentration is 25 ppm(v).

Applying, the mass balance presented before in Appendix A , it was determined that the new value for the raw gas flowrate was 1100 $Nm^3 \cdot h^{-1}$. The mass balance was calculated in the reverse direction to determine the raw gas flowrate that would allow having 25 ppm(v) of NH_3 in stream 4 of absorber and a NH_3 mass flowrate equal to 423.79 $g \cdot h^{-1}$ in stream 6 of the desorber.

Appendix C

Water Option 2 results for 10°C and 30°C

The NH_3 limits for different temperatures are summarized in Table 28. The results presented in Table 29 are for 100 ppm(v) inlet concentration of NH_3, an inlet liquid flowrate of 8 $m^3.h^{-1}$, a desorption column with a diameter of 0.7 meters and column's height equal to 4 meters and a variable air flowrate.

Table 28- NH_3 desorber liquid outlet (stream 6) mass flowrates for 10 and 30 °C.

	10°C		30°C	
Stream 4 Absorber	**Stream 13 Absorber**	**Stream 6 Desorber**	**Stream 13 Absorber**	**Stream 6 Desorber**
ppm(v)	mole fraction	$g{\cdot}h^{-1}$	mole fraction	$g{\cdot}h^{-1}$
20	$4.5x10^{-05}$	342.3	$1.7x10^{-05}$	128.8
50	$1.1x10^{-04}$	856.5	$4.3x10^{-05}$	322.0

Table 29- Water Option 2 results for 10 and 30 °C.

Air flowrate / $Nm^3.h^{-1}$	**NH_3 desorber liquid outlet flowrate / $g{\cdot}h^{-1}$**			
	20 ppm(v) 10°C	20 ppm(v) 30°C	50 ppm(v) 10°C	50 ppm(v) 30°C
10	432.78	218.49	945.53	411.42
214	428.87	213.45	936.99	401.04
418	425.03	208.60	928.58	391.05
622	421.26	203.92	920.34	381.41
826	417.49	199.19	912.11	371.66
1030	413.73	195.81	903.91	361.93
1234	409.99	189.78	904.39	352.23
1438	406.25	185.07	887.55	342.52
1642	403.40	180.38	879.39	332.83
1846	398.77	175.67	871.23	323.13
2050	395.04	170.99	863.08	**313.52**

From the values stated in Table 29, only for an air flowrate of 2050 $Nm^3{\cdot}h^{-1}$ and for the case of 50 ppm(v) and 30 °C it was possible to respect the limit NH_3 desorber liquid outlet flowrate of 322 $g{\cdot}h^{-1}$.

Appendix D

Solubility Prediction with HSP

An Excel Solver add-in was used for the determination of Hansen's solubility parameters (HSP), to have an idea of which components are more soluble in selexol. These parameters are δD, δP and δH corresponding to dispersion, polar and hydrogen bonding forces respectively.

HSPs of more than a thousand compounds are reported in the literature. Yet, for selexol, it was not possible to find them. The HSPs of ethylene glycol monomethyl ether were used instead (δD = 16; δP = 8.2; δH = 15) since it was the most similar found solvent to selexol.

The affinity, that is, an indirect measurement of the ability to dissolve a certain compound, is measured by the so-called distance between the solvent (a) and the solute (b), usual called Ra. This distance can be determined by the following expression [31].

$$Ra = [4 \cdot (\delta_{Da} - \delta_{Db})^2 + (\delta_{Pa} - \delta_{Pb})^2 + (\delta_{Ha} - \delta_{Hb})^2\ ]^{1/2} \qquad (32)$$

The biggest the Ra value, the lower the solubility.

In Table 30, it is presented the HSPs for some biogas components and their respective distance to ethylene glycol monomethyl ether.

Table 30- Distance between solvent and solute (Ra) calculation.

Solute		HSP			Ra
		dD	dP	dH	
Terpenes	Limonene	17.2	1.8	4.3	12.70
	α-Pinene	16.9	1.8	3.1	13.63
	ß-Pinene	16.23	0.95	1.78	15.08
Aromatics	Benzene	18.4	0	2	16.10
	Ethylbenzene	17.8	0.6	1.4	15.99
	Toluene	18	1.4	2	15.21
Hydrocarbons	*n*-Hexane	14.9	0	0	17.24
	n-Pentane	15.6	0	0	17.36
	n-Octane	15.5	0	0	17.12

Siloxanes HSP's were not available in the literature; even so, it is possible to estimate their position in Table 18 from the sensitivity analysis results obtained.

Appendix E

Removal Efficiencies of Selexol Simulation with and without water

The simulation "without water" consists in the absorption column with a liquid inlet composition stated in Table 17, simulating the composition coming from desorber. The simulation "with water" is the complete system (two columns connected). Results can be found in Table 31.

Table 31- Removal efficiencies of Selexol simulation with and without water,

Component	% Removal	
	Without Water	With water
2-Butanone	99.58	99.69
Toluene	99.84	96.11
D-Limonene	99.96	92.62
α-Pinene	99.88	95.30
ß-Pinene	99.94	93.22
Ethanol	99.57	99.94
Benzene	99.62	99.41
Ethylbenzene	99.94	92.63
***n*-Hexane**	49.68	52.95
***n*-Pentane**	14.78	17.13
***n*-Octane**	99.63	99.58
2-Propanol	99.74	99.90
Siloxane D4	99.98	95.22
Siloxane D5	100.00	97.82
Siloxane L3	58.45	76.86
Siloxane L4	76.88	89.62

Appendix F

Descriptive Business Case

Table 32 describes with more detail, the business case calculations.

Table 32- Complete Business Case.

Main parameters	AC-only	Water scrubber without regeneration + AC polishing	Water scrubber with regeneration + AC polishing	Selexol scrubber with regeneration + AC polishing
TCO Summary				
TCO / €·year^{-1}	339680	327260	309110	203270
Total Capital costs / €·year^{-1}	15250	35580	40670	45750
Total Operational costs / €·year^{-1}	324430	291680	268440	157520
€·Nm^{-3} pretreated	0.039	0.038	0.036	0.023
Annual saving	-	12420	30580	136410
ROI / years	-	16	8	2
CAPEX (Investment)				
Total investment / €	150000	350000	400000	450000
AC vessel Cost / €	150000	150000	150000	150000
Scrubber Cost / €	n.a	200000	250000	300000
Depreciation / €·year^{-1}	10000	23330	26670	30000
Interest / €·year^{-1}	5250	12250	14000	15750
OPEX (Investment)				
1. Total raw materials / €·year^{-1}	313470	257900	234460	130930
Virgin Carbon usage / €·year^{-1}	258470	216050	216050	24800
Impregnated Carbon usage / €·year^{-1}	12940	12690	12690	11890
NH_3Carbon usage / €·year^{-1}	42050	4130	4130	35940
Water usaged / €·year^{-1}	0	25030	1590	0
Chemicals usaged / €·year^{-1}	0	0	0	58290
2. Total Utilities (services) / €·year^{-1}	4610	15930	14880	6240
Electricity	0	1420	10790	3580
Chemicals disposal	0	0	0	1590
Carbon Discharge	4610	3390	3390	1070
Water disposal	0	11120	710	0
3. Maintenance / €·year^{-1}	3750	8750	10000	11250
4. Operating labour / €·year^{-1}	2600	9100	9100	9100

The removal efficiencies used for the business case presented above, are shown in the following table (Table 33).

Table 33- Removal efficiencies- Business Case.

Component	Removal efficiencies / % (From this Report)				Removal efficiencies / % (Comparison Case)	
	300 ppm(v)			100 ppm(v)	100 ppm	300 ppm
	Water Option 1	Water Option 2	Selexol	Water option 2	Water no Regeneration	
NH_3	94.04	89.82	14.53	90.18	92.41	89.41
Hydrogen Sulfide	2.38	1.78	8.13	1.97	0.09	0.08
2-Butanone	98.36	98.09	99.43	98.12	78.40	78.40
Toluene	8.62	2.42	94.62	2.49	1.63	1.63
D-Limonene	40.63	3.44	90.16	0	0.51	0.51
α-Pinene	20.71	1.24	93.62	0	0.19	0.19
ß-Pinene	31.27	2.25	91.25	0.14	0.17	0.17
Ethanol	98.12	83.84	99.81	81.65	98.03	98.03
Benzene	7.46	3.01	98.98	3.24	1.87	1.87
Ethylbenzene	14.46	2.41	90.57	2.03	1.62	1.62
***n*-Hexane**	0.10	0	53.02	0	0.00	0.00
***n*-Pentane**	0	0	17.04	0	0.00	0.00
***n*-Octane**	1.02	0.09	99.28	0	0.00	0.00
2-Propanol	98.82	84.36	99.76	84.25	97.42	97.42
Siloxane D4	6.04	1.64	93.22	0	0.00	0.00
Siloxane D5	8.25	7.16	95.32	0	0.00	0.00
Siloxane L3	3.2	0.52	99.93	0	0.00	0.00
Siloxane L4	8.25	4.28	99.89	0	0	0