DESULFURIZATION AND UPGRADING HYDROGEN SULFIDE-RICH BIOGAS: TECHNO–ECONOMIC ANALYSIS

Lappeenranta–Lahti University of Technology LUT

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Examiners: Professor, Mika Mänttäri

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ABSTRACT

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Keywords: Biogas, upgrade, liquefaction, biomethane, H_2S, desulfurization, CBG, LBG

Biogas can be purified and upgraded to biomethane and injected to the gas grid or it can be further refined to liquefied biomethane (LBG) or compressed biomethane (CBG) for vehicle use. Many of commercial scale biogas upgrade systems available designed to remove carbon dioxide from biogas, are extremely sensitive to impurities like hydrogen sulfide (H_2S), and biogas needs to be purified to remove these compounds prior to the upgrade unit.

Aim of this thesis was to help a biogas production company to evaluate and choose an optimal desulfurization and biogas upgrade technology for different manufacturing scenarios where end-products and utility prices vary. The comparison between different technology options for biogas upgrading and liquefaction was based on literature review and quotations received from equipment suppliers. Options for desulfurization technologies were reviewed based on the literature review. Gas composition data from the laboratory scale biogas reactors was reviewed to evaluate the average concentration of hydrogen sulfide in the produced gas. Biogas upgrade and desulfurization technologies were evaluated based on financial as well as from technological perspective.

Best solution for desulfurization of H_2S-rich biogas based on the literature review was found to be the addition of ferric salts or microaeration combined with activated carbon filter. Membrane biogas upgrade system combined with liquefaction unit was found to be the best option for LBG production. Cryogenic upgrading technology could not be recommended due to a fact that the technology is not mature and is still under development.

TIIVISTELMÄ

Lappeenrannan–Lahden teknillinen yliopisto LUT

LUT School of Engineering Science

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Rikkivetypitoisen biokaasun rikinpoisto ja jalostus: teknistaloudellinen analyysi

Kemiantekniikan diplomityö

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Avainsanat: Biokaasu, jalostus, nesteytys, biometaani, H_2S, rikinpoisto, CBG, LBG

Biokaasua voidaan puhdistaa ja jalostaa biometaaniksi, jota voidaan injektoida kaasuverkkoon tai siitä voidaan edelleen jalostaa nesteytettyä (LBG) tai paineistettua biometaania (CBG) liikennekäyttöön. Monet kaupallisen mittakaavan jalostuslaitteistoista, joiden tarkoituksena on poistaa hiilidioksidia biokaasusta, ovat herkkiä biokaasun sisältämille epäpuhtauksille, kuten rikkivedylle (H_2S), jotka täytyy poistaa biokaasusta puhdistamalla ennen jalostusyksikköä.

Tämän työn tarkoituksena on auttaa biokaasualan yritystä arvioimaan ja valitsemaan optimaalinen rikinpoisto ja biokaasun jalostusjärjestelmä eri tuotantoskenaarioille, joissa lopputuotteet ja käyttöhyödykkeiden hinta vaihtelevat. Eri teknologiavaihtoehtoja arvioitiin kirjallisuuskatsauksen sekä biokaasun jalostus- ja nesteytysyksiköistä toimittajilta saatujen laitetarjousten perusteella. Teknologiavaihtoehtoja rikinpoistolle arvioitiin kirjallisuuskatsauksen perusteella. Laboratoriomittakaavan bioreaktoreista mitattua kaasun koostumusta tarkasteltiin, jotta pystyttiin määrittämään rikkivedyn keskimääräinen konsentraatio tuotetussa kaasussa. Biokaasunjalostus- ja rikinpoistoteknologioita arvioitiin taloudellisesta kuten myös teknisestä näkökulmasta.

Paras ratkaisu rikinpoistoon H_2S-rikkaasta biokaasusta kirjallisuuskatsauksen perusteella oli rautasuolojen lisääminen tai mikroilmastus yhdistettynä aktiivihiilisuodatukseen. Membraanitekniikkaan perustuva biokaasun jalostusjärjestelmä yhdistettynä nesteytysyksikköön osoittautui parhaaksi vaihtoehdoksi LBG tuotannolle. Kryotekniikkaan perustuvaa jalostusyksikköä ei voitu suositella teknologian kehittymättömyyden vuoksi.

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SYMBOLS AND ABBREVIATIONS

Roman characters

C	concentration	[M]
K	Henry’s constant	[mol/m^{3}Pa]
p	pressure	[bar, Pa]
J	flux	[mol/m^{2}s]
D	diffusion coefficient	[cm^2/s]
K	sorption coefficient	
l	thickness of membrane	[m]

Greek characters

α	membrane selectivity

Subscripts

0	inflow
1	outflow

Abbreviations

aMDEA	Activated Methyl Diethanolamine
BRS	BioReactor Simulator
CAPEX	Capital Expenses
CBG	Compressed Biomethane
CHP	Combined Heat and Power
CMS	Carbon Molecular Sieves

DEA	Diethanolamine
LBG	Liquefied Biomethane
MAP	Modified Atmospheric Packaging
MDEA	Methyl Diethanolamine
MEA	Monoethanolamide
OPEX	Operating Expenses
PSA	Pressure Swing Adsorption
PZ	Piperazine
RO	Reverse Osmosis
VFA	Volatile Fatty Acid
VOC	Volatile Organic Compound

Chemical abbreviations

CH_4	Methane
CO_2	Carbon dioxide
Fe^{2+}	Iron (II) ion
Fe^{3+}	Iron (III) ion
$FeCl_2$	Ferrous chloride
$FeCl_3$	Ferric chloride
Fe_2O_3	Ferric oxide
$Fe(OH)_3$	Iron hydroxide
FeS	Iron sulfate
FeS_2	Iron disulfide
FeS_3	Ferric sulfide

H^+	Hydrogen ion
H_2O	Water
H_2S	Hydrogen sulfide
H_2SO_3	Sulfurous acid
H_2SO_4	Sulfuric acid
HCl	Hydrogen chloride
HS^-	Bisulfide
KI	Potassium iodide
K_2CO_3	Potassium carbonate
N_2	Nitrogen
NH_3	Ammonia
NO_2^-	Nitrite
NO_3^-	Nitrate
O_2	Oxygen
S	Sulfur
S^0	Elemental sulfur
S^{2-}	Sulfide
S_2	Disulfur
S_8	Octasulfur
SO_2	Sulfur dioxide
SO_3	Sulfur trioxide
SO_4^{2-}	Sulfate
ZnO	Zinc oxide

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1 Introduction

There is a global need to reduce the consumption of fossil fuels in energy production and in traffic sector by replacing them with renewable energy sources. Organic waste streams can be utilized in biogas production to produce biogas which is a renewable energy source and to promote circular economy. (Kymäläinen, Pakarinen, 2015, p.7)

Biogas production as well as biogas upgrading to biomethane for gas grid and vehicle use are increasing in Europe (Scarlat, Dallemand, Fahl, 2018, p.458). Biogas cannot be used without purification to remove impurities such as hydrogen sulfide. When biogas is injected to the gas grid or used as a vehicle fuel it also needs to be upgraded to remove carbon dioxide from it. (Bauer, Hulteberg, 2013a, p.4)

There are multiple commercial technologies currently available in the market for biogas desulfurization and upgrade systems. There are differences between these technologies regarding utility consumption, reliability, and process operation. (Bauer, Hulteberg, 2013, p.4)

There have been multiple previous studies and reports made about the biogas upgrade technologies in the past but as the newer upgrade technologies are constantly being developed the assumptions and conclusions made in these reports can be outdated. The specific investment costs of upgrade technologies are dependent on the scale of the facility (Bauer, Hulteberg, 2013, p.53) and cannot directly be applied to different scale facilities.

The price for power, heat, chemicals and materials used in the biogas upgrade and liquefaction processes are case sensitive and constantly changing thus the investment decision cannot be based on the previous evaluations found in literature. Also, these base assumptions are not always clearly presented in the previously made reports and studies. In addition, studies that include sensitivity analysis regarding power and heat consumption are rare.

The aim of this thesis is to give an overview of different biogas upgrade and desulfurization technologies and to answer the question of which technology to choose in different project scenarios where product and utility prices vary.

This thesis consists of two sections. In the literature review the main desulfurization and upgrade technologies available for biogas are reviewed. The advantages, disadvantages and the main heat and electricity consumption figures of these technologies are studied. The production process, composition of the produced biogas and possible biogas products are also covered.

In the data analyzation section of the thesis, biogas composition data from a laboratory scale test bioreactor is analyzed to determine an average level of H_2S in the biogas produced to help to select the suitable desulfurization system option for the company's process.

Quotations from equipment suppliers for biogas upgrade and liquefaction units are studied in addition to the literature review. The electricity and heat sensitivity of these systems is evaluated to conclude which technologies are most resistant to the utility price fluctuation.

2 Biogas and biogas production

Producing and utilizing biogas as an energy source has a positive environmental impact because it is a renewable alternative option for fossil fuels, especially for natural gas. Main applications for biogas use are heat and steam production, electricity generation with combined heat and power unit (CHP), injection to gas grid and use as in vehicle fuel. (Ullah Khan et al., 2017, p.287)

2.1 Biogas

Biogas consists mostly of methane (CH_4) and carbon dioxide (CO_2). There are also some impurities like hydrogen sulfide (H_2S), oxygen (O_2) and nitrogen (N_2) but the composition of biogas varies depending on the process conditions and the feedstock mixture used. For example, conventional biogas produced in a bioreactor that uses feedstock like animal manure and other biomasses has a different composition than biogas collected from a landfill. Basic components and their amounts for different cases are presented in table 1. (Petersson, Wellinger, 2013, p.24)

Table 1 Typical compositions of raw biogas (Adapted from Kymäläinen, Pakarinen, 2015, p.128)

Gas Component	Conventional	Landfill
CH_4 (vol–%)	45–75	20–60
CO_2 (vol–%)	20–55	25–50
H_2S (vol–%)	<0.8	<3
O_2 (vol–%)	0–1	0.5–5
N_2 (vol–%)	0–2	4–35

It can be seen in table 1 that biogas produced in a conventional bioreactor has a higher CH_4 content and a lower H_2S compared to biogas produced in a landfill. Biogas produced in a landfill has a higher O_2 and N_2 content because the gas is usually collected by using under pressure which can cause that a small amount of air is mixed with the biogas. (Petersson, Wellinger, 2013, p.24)

2.2 Biogas production process

Biogas is produced under anaerobic conditions from biomass and is based on degradation of organic material by a vast number of microbial species. The microbiological flora of the bioreactor is determined by the conditions such as temperature and pH level of the fermenter. (Kymäläinen, Pakarinen, 2015, pp.60–64)

Decomposition of feedstock and the biogas production can be divided to four main steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis (Kymäläinen, Pakarinen, 2015, pp.60–64). The process steps, feedstocks and products are presented on figure 1.

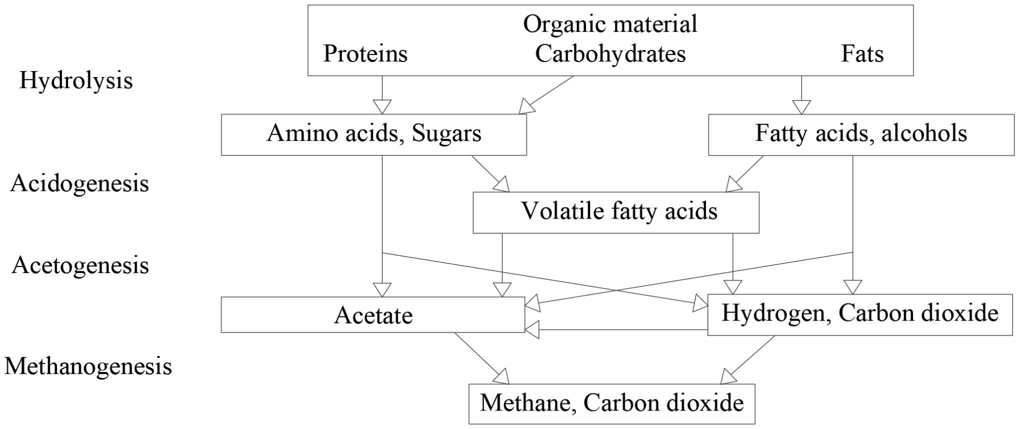

Figure 1 Main steps of organic material decomposition to biogas (Adapted from Kymäläinen, Pakarinen, 2015, p.128)

Hydrolysis is the first step in the decomposition process of organic material to biogas (figure 1). During hydrolysis, large organic compounds like proteins, fats and carbohydrates are broken down to monomers like sugars and amino acids. (Kymäläinen, Pakarinen, 2015, pp.60–64)

In acidogenesis microbes use the compounds produced during hydrolysis to form different acids, such as acetic and propionic acid, which are volatile fatty acids also known as VFAs. Alcohols, ammonia, hydrogen and carbon dioxide are also produced during this step. The share of intermediate products created during acetogenesis depends on the feedstock but also on the specific microbes and conditions in the bioreactor. (Kymäläinen, Pakarinen, 2015, pp.60–64)

In acetogenesis the VFAs are broken down to form acetate, hydrogen, and carbon dioxide from which the methane is produced during methanogenesis by methanogenic bacteria. Methanogens that use acetate to produce methane are called acetotrophic and methanogens that use hydrogen are called hydrogenotrophic. It has been evaluated that over 70% of the methane production happens through acetate. (Kymäläinen, Pakarinen, 2015, pp.60–64)

The intermediate products from previous steps are the feedstock for the next steps. In a well–functioning bioreactor these process steps are in balance and there is no build–up of intermediate products that would cause a risk of inhibition. (Kymäläinen, Pakarinen, 2015, pp.60–64)

2.3 Impurities

Biogas has several other compounds besides CO_2, called impurities, that need to be removed partially or completely depending on the end use of the gas (Ullah Khan et al., 2017). Biogas purification means the removal of any impurities that might cause operational problems or damage the process equipment, whereas the process of removing CO_2 and other possible inert gases that lower the calorific value of the gas but oppose no operational threat, is called upgrading. (Kymäläinen, Pakarinen, 2015, pp 126–127)

The amount and concentration of the impurities in the raw biogas depend on the source of the biogas. (Ullah Khan et al., 2017, p.287) For example, biogas produced in landfills has more components than biogas produced from other feedstock materials. But generally, the amount of impurities combined in raw biogas is almost always less than 1 volume percentage, whereas the amount of inert gases is dozens of volume percentages. (Kymäläinen, Pakarinen, 2015, pp.126–127)

Biogas can be used for example in power generation, fuel for boilers or vehicle use. Different equipment has different requirements for individual components of the biogas but generally the cleaner the biomethane, less cleaning and maintenance of the equipment is needed. On the other hand, the costs of the biogas upgrading and purification increase as the obtained product gas purity increases. (Deng, Liu, Wang, 2020, pp.205–207)

When using biogas to produce heat with boilers, H_2S, siloxanes and particles need to be removed prior to combustion, even though some boilers are certified to use raw untreated biogas. When biogas is used to produce heat on site, it is usually needless to upgrade it. (Kymäläinen, Pakarinen, 2015, pp.126) When used as a vehicle fuel generally the compounds to remove are water, halogen, and carbon compounds as well as hydrogen sulfide. (Deng et al., 2020, pp.205–207)

2.3.1 Carbon dioxide (CO_2)

Carbon dioxide is one of the major compounds, besides CH_4, in raw biogas. The amount of CO_2 varies typically between 20–55% depending on process conditions and feedstock. CO_2 doesn't affect the combustion process itself or the equipment involved when the biogas is utilized in the energy production, but it decreases the calorific value of the gas which increases the storage space needed and costs from possible transportation. When the high volumetric energy content of the produced gas is important, like when methane is injected to the gas grid or used as a vehicle fuel, CO_2 needs to be removed. When raw biogas is used to generate heat at the plant site, CO_2 doesn't usually cause problems for the process nor the equipment. (Deng et al., 2020, p.202)

2.3.2 Hydrogen sulfide (H_2S)

Hydrogen sulfide is a toxic, inflammable, colorless gas and has a strong smell of rotten eggs. There are sulfur–containing components present in the biogas of which H_2S is the most common one. H_2S levels present in the raw biogas depend strongly on the feedstock used. Feedstock with high sulfate or protein levels result higher H_2S levels in raw biogas produced. (Deng et al., 2020, p.204)

Because H_2S is highly poisonous it can cause serious health risks. The severity of the symptoms depends on the concentration of the gas as well as exposure time which are listed in table 2.

Table 2 Symptoms of H_2S poisoning with associated gas concentration and contact time (Deng et al., 2020, p.204)

Concentration of H_2S (mg/m^3)	Contact time	Reaction/symptoms
0.035		H_2S starts to smell
0.4		Strong odor
4–7		Strong odor
30–40		Strong odor
70–150	1–2 h	Respiratory tract and eye irritation, olfactory fatigue causes inability to smell
300	1 h	Eye irritation after 8 min, longer exposure causes emphysema
760	15–60 min	Emphysema, bronchitis, pneumonia, headache, dizziness, nausea
1000	Seconds	Acute poisoning, respiratory paralysis
1400	Instantly	Coma and respiratory paralysis

On low concentrations it causes eye and respiratory track irritation. H_2S has a distinguished smell but on concentrations of 100–150 ppm it paralyses the sense of smell which increases the risk of exposure (Table 2). Higher concentrations can cause nerve damage, loss of consciousness or even death. (Deng et al., 2020, p.203)

H_2S forms sulfuric acid with water and can cause corrosion to the pipelines, valves, compressors, and other process equipment reducing their lifespan and increasing the maintenance costs and possible downtime of the process. (Deng et al., 2020, pp.202–204)

2.3.3 Ammonia (NH_3)

In the same way as H_2S, NH_3 causes corrosion in the pipelines and process equipment when it reacts with water. This can cause untimely wearing of the equipment and possible process malfunctions. In high concentrations, NH_3 can also cause inhibition of methanogenesis in the fermenter which lowers methane yield of the biogas process. (Deng et al., 2020, pp.202–204) In addition to the problems mentioned earlier, nitrogen oxide emissions are formed during combustion of ammonia (Adapted from Allegue, Hinge, 2020, pp.26–27).

2.3.4 Water

Part of the water used in anaerobic digestion will evaporate and the raw biogas leaving the reactor will be saturated with water. The amount of water present in the gas depends on the temperature and the pressure inside the reactor. Water in the raw biogas can cause corrosion in process equipment, valves and piping because it reacts with other components in biogas such as H_2S and CO_2 to form different acids. Water present in the biogas will also lower the calorific value of the biogas if it’s not removed prior to combustion process. Water vapor can also increase fluid resistance or condense and accumulate to pipelines and cause problems. (Bragança et al., 2020, pp.2–3)

2.3.5 Siloxanes

Siloxanes are compounds found in several cosmetic products, textiles, and pharmaceuticals. During the biogas production process siloxanes volatilize and end up in the produced biogas (Abatzoglou, Boivin, 2009, p.55) The amount of siloxanes present in the raw biogas depend on the source and feed material of the biogas (Abatzoglou, Boivin, 2009, p.55). Compared to biogas produced with traditional fermentation process that doesn’t contain any or contains only non–existent amounts of siloxanes, biogas collected from landfills has usually higher level of siloxanes and can be up to 50 mg/m^3. (Abatzoglou, Boivin, 2009, p.55)

Siloxanes produce microcrystalline silica during combustion and cause fouling in the equipment use to burn the biogas and reduce the efficiency of the machinery and increase the possibility of malfunction (Deng et al., 2020, pp.202–203). The formed crystalline deposits accumulate on valves, pistons and cylinder heads and the formed layer of impurities can be several millimeters thick and are hard to remove with mechanical or chemical techniques (Accettola, Guebitz, Schoeftner, 2008, pp.211–212)

2.3.6 Nitrogen (N_2) and oxygen (O_2)

Nitrogen is an inert gas that dilutes the biogas lowering its energy density, in the same way that CO_2. O_2 is an unwanted compound in the biogas because it may create an explosive mixture with the methane. O_2 and N_2 are normally not present in the raw biogas, except in biogas that has been collected from landfills, and are indicators of a leak in the process.

(Bragança et al., 2020, pp.2–3) Large quantities of O_2 can also inhibit the anaerobic biogas fermentation process (Deng et al., 2020, pp.202–203).

2.3.7 Volatile organic compounds (VOC)

Volatile organic compounds (VOC) include for example hydrocarbons, alcohols and esters. Some of them are corrosive. (Bragança et al., 2020, pp.2–3) The VOC level in the produced biogas depends on the feedstock used. The amount of VOC is higher in the biogas produced in landfills compared to the amounts produced from manure or other farm–based feedstock materials. (Hoyer et al., 2016, pp.39–40) Some VOCs are toxic and can cause corrosion in the process equipment and piping (Bragança et al., 2020, p.3).

2.3.8 Summary of impurities in biogas

The raw biogas has multiple impurities that can cause damage and process failure (Ryckebosch, Drouillon, Vervaeren, 2011, p.1634). The most common impurities and their possible effects for the biogas production process and downstream processes are listed in table 3.

Table 3 Impurities in biogas and possible process problems and consequences (1) Bragança et al., 2020, pp.2–3; 2) Ryckebosch et al., 2011, p.1634)

Impurity	**Impact**
CO_2	Lowers the biogases calorific value (1,2, forms acid with water causing corrosion of pipelines and process equipment (2
H_2S	Causes corrosion (1,2, toxic (1,2, SO_2 and SO_3 formation during combustion which also cause corrosion and are toxic (1
NH_3	Causes corrosion when reacts with water (1,2
Water	Condensation and/or freezing, accumulation to pipelines (1,2, causes corrosion when reacts with H_2S, NH_3 and CO_2 (1,2
Siloxanes	Formation of SiO_2 and microcrystalline during combustion and deposits on equipment components such as spark plugs, valves etc. and can cause malfunction (1,2
N_2	Lowers biogases calorific value (2
O_2	Creates an explosive mixture with CH_4 (1,2, can inhibit the biogas production process in large concentrations
VOC	Some are toxic and can cause corrosion (2

Most of the impurities either reduce the calorific value of the biogas thus increasing handling costs or cause direct problems to the process. Most common of these are the corrosion and fouling of the process equipment. (Table 3)

3 Biogas products

The raw biogas can be purified, upgraded and injected to the gas grid or refined to high value products such as compressed biomethane (CBG) by elevating its pressure, or liquefied biomethane (LBG) by cooling it to liquid form (Tabatabaei, Ghanavati, 2018, p.169). Liquefaction and compression both reduce the volume of the product and reduce the transportation and storage costs (Allegue, Hinge, 2020, pp.30–31). The CO_2 fraction of the biogas removed during the upgrade process can also be utilized as a product when purified. (Bauer, Hulteberg, 2013, p.4)

3.1 Injection to gas grid

When biogas is utilized as vehicle fuel or injected to the gas grid, different countries have different quality standards. Different gas quality standard values for gas grid injection are presented in table 4.

Table 4 Country specific biogas quality standards for grid injection (Adapted from Allegue, Hinge, 2020, pp.26–27)

Country	France	Germany	Sweden	California
Calorific upper value	38.5-46.1	30.2-47.2		36.9-42.8
Wobbe index	48.2-56.5	46.1-56.5	44.7-46.4	47.6-51.6
CH_4 (%)			97	
CO_2 (%)	<2.5	<6	<3	3
O_2 (%)	<0.01	<3	<1	<0.2
Total sulfur (mgS/m^3)	<30	<30	<23	265
H_2S (mg/m^3)	<5	<5	<15.2	88
NH_3	<3 mg/m^3	<20 mg/m^3	<20 mg/m^3	<0.001 mol-%
Siloxanes				<0.1 mgSi/m^3
VOCs (ppmv)				<0.1
Dust	<5mg/m^3		<1µm	Free

The quality requirement standards are very similar between different European countries that are presented in table 4. Standard used in California has similar values except for allowing a larger amount of total sulfur as well as H_2S to the natural gas grid system.

For grid injection the methane content of the upgraded biogas needs to be 97–98% in Europe but this varies depending on the country, for example in Netherland the Wobbe index limitations are lower. Wobbe index is used to define the calorific value of the gas by using the ratio between the density of the gas and density of air. (Bauer, Hulteberg, 2013, p.28)

3.2 Compressed biomethane, CBG

In ambient pressure the energy density of biomethane is rather low and is usually compressed to 200–300 bar (Allegue, Hinge, 2020, pp.30–31). The pressure of the biomethane is elevated with a series of compressors and because the first compression stages require more work, it is possible to decrease the power consumption by deploying a biogas upgrading technology that produces biomethane stream which is already in elevated pressure. (Hoyer et al., 2016, p.62)

On the other hand, the amount of work is directly proportional to the volume of the gas compressed. When compressing raw biogas, also the CO_2 contained in the gas is compressed. Compressing upgraded biomethane can be roughly estimated to require half of the energy compared to compressing raw biogas. The amount of energy used to compress biomethane to 200 bar is about 2–3% of the biomethanes energy content. (Hoyer et al., 2016, pp.39–40)

Over–the–road transportation of the compressed biomethane is an option when connection and transportation by natural gas grid or dedicated pipelines is impossible or extremely expensive. To make the over–the–road transportation economically feasible the pressure of the biomethane needs to be elevated to over 200 bar which is also a minimum requirement for CBG fueling stations. This way of transportation needs compression equipment in the plant site as well as at the destination point and the transportation equipment. Therefore, this solution is generally not considered to be cost–efficient nor a long–term method, but it can be used temporarily in some cases. (Allegue, Hinge, 2020, pp.30–31) The design pressure for CBG storages can be up to 350 bar to increase refueling and transport efficiency (Hoyer et al., 2016, pp.39–40).

3.3 Liquefied biomethane, LBG

The boiling point of CH_4 is very low and to produce LBG the biogas needs to be cooled significantly. To avoid process problems due freezing and plugging, most of the CO_2, water and H_2S need to be removed prior to the liquefaction process. (Hoyer et al., 2016, pp.58–66)

LBG can be produced with a combination of conventional upgrading technologies with separated liquefaction unit, or with a cryogenic upgrading process where the produced biomethane stream is already in low temperature. These technologies are described in more detail in chapter 5 of this thesis. The model where a liquefaction unit is linked with an upgrade unit is currently more common. (Spoof-Tuomi, 2020, pp.7–9)

One of the biggest challenges is LBG production is the scale of the process. The technologies used in large scale application are usually not economical nor practical when applied to small scale facilities. (Spoof-Tuomi, 2020, pp.7–9)

One cubic meter of LBG is equivalent to approximately 600 Nm^3 of biomethane in gaseous form in ambient environment (Allegue, Hinge, 2020, pp.30–31). This means that LBG has a higher energy density compared to CBG which makes the transportation more efficient. The pressure of the LNG is only about 1.5–10 bar depending on the system design, and the temperature is kept very low, under –100 °C. The storage time of the LBG should be minimized because possible rise in temperature in the storage unit results loss of the fuel due evaporation through the tanks release valve. (Allegue, Hinge, 2020, pp.30–31)

The filling stations for LBG usually have lower investment cost and energy consumption compared to CBG stations. (Hoyer et al., 2016, pp.58–66) Other advantage of LBG is that it can be used in both LNG ad CNG vehicles (Allegue, Hinge, 2020, pp.30–31).

3.4 CO_2 utilization

CO_2 is the other major component in biogas alongside with CH_4 (Petersson, Wellinger, 2013, p.24). Biogas upgrade systems provide an option to capture CO_2 rather that dispose it to the atmosphere. CO_2 can be a valuable product and utilizing it can help to reduce the biogas plants total carbon footprint (Monteiro et al., 2015, pp.1–5).

CO_2 can be used as a feedstock material to produce chemicals or fuels such as methanol and biodiesel. It can be used to make inorganic carbonates like potassium and calcium carbonates or in production of polymers. It can also be utilized as it is for example in greenhouses and food industry. (Monteiro et al., 2015, pp.1–5)

CO_2 can be used in greenhouses to increase the growth rate of the plants to increase the production efficiency. Some plants can increase their growth rate almost 50% when CO_2 is added to the greenhouse. Commonly CO_2 levels are increased by using a burner with a carbon–based fuel, but this method has problems due incomplete combustion and contaminants. (Hoyer et al., 2016, pp.63–65)

CO_2 is used in food industry for example to produce carbonated drinks and in modified atmospheric packaging (MAP) to replace O_2 to increase the shelf life of certain products. Purity of CO_2 needs to be 99,9% which can be achieved with cryogenic distillation process. Since cryogenic process is considered to be high–priced, the production of food–grade CO_2 as a side product in biogas upgrading is usually not economically appealing. (Hoyer et al., 2016, pp.63–65)

Liquid CO_2 can be used as a refrigerant which is non–flammable and non–toxic. It can be used for example in air conditioning equipment and heat pumps. When CO_2 is in solid form, also known as dry ice, it can be used as a cooling medium for frozen food products while transportation. When used as a refrigerant, CO_2 has the same purity requirement of 99.9% when used in food industry and it is not economically interesting due to high cost mentioned above. (Hoyer et al., 2016, pp.63–65)

CO_2 can be obtained for example from fertilizer plants and natural gas processing or CO_2 gas streams of for example steel and power plants (Sun et al., 2015, p.529). Captured CO_2 needs to be liquidized by cooling and pressurizing for transportation if it is not directly used at the plant site (Øi et al., 2016, pp.500–501). High quality CO_2 in high volumes can also be transported via pipelines (Sun et al., 2015, p.529).

4 Desulfurization technologies

There are several methods to remove H_2S from biogas. They can be divided to three groups according to table 5.

Table 5 Desulfurization methods (Bailon Allegue, Hinge, 2014, p.5)

Adsorption	Activated carbon Iron oxides
Absorption	Iron salts Water scrubbing Physical scrubbing
Biotechnology	Biofilter, Biotrickling filter Bioscrubber Microaeration

It can be seen from table 5 that desulfurization technologies can be divided to adsorption, absorption and biotechnology based on their operating principle. H_2S can be easily oxidized, it reacts easily with alkali and is very soluble in organic solvents. It can react with metal ions and oxides to produce low solubility sulfides (Deng et al., 2020, p.203). Some technologies used to upgrade biogas by removing the CO_2, can also be used to remove H_2S. These technologies are presented separately in chapter 5 of this thesis.

4.1 Iron salts

H_2S can be dissociated by adding different iron salts that contain iron ions (Fe^{2+} or Fe^{3+}), like iron chloride, oxide or phosphate directly to the biogas fermenter or along with the feed. These ions react with H_2S forming nearly insoluble iron sulfide salts that can be removed from the biogas process along with the digestate. Ferrous chloride ($FeCl_2$) is the most common chemical, but also ferric chloride ($FeCl_3$) and iron hydroxide ($Fe(OH)_3$) can be used. (Bailon Allegue, Hinge, 2014, p.7) The dosing of these salts varies and should be determined case–by–case (Petersson, Wellinger, 2013, p.7). The main reactions are:

$$Fe^{+2} + S^{-2} \rightarrow FeS \qquad (1)$$

$$2Fe(OH)_3 + 3HS^{-} + 3H^{+} \rightarrow 2FeS + S + 6H_2O \qquad (2)$$

$$2FeCl_3 + 3H_2S \rightarrow 2FeS + S + 6HCl \qquad (3)$$

(Bailon Allegue, Hinge, 2014, p.7)

Addition of iron salts is effective in reducing H_2S concentration in the raw biogas, but it is challenging to keep H_2S at a steady level. It is able to achieve 100–200 ppm of H_2S in the raw biogas by this method but to be able to achieve lower concentrations larger amount of chemical must be used. (Bailon Allegue, Hinge, 2014, p.7)

Adding iron salts directly to the anaerobic digester is a rather common method for H_2S removal in biogas production because of its simple operation and due to the fact that the chemical reaction occurs in the digester and there is no need for a separate desulfurization vessel. Storage tank and a dosing pump are required for the addition of the ferric salt. Mixing of the sludge increases the desulfurization efficiency by increasing the rate of which H_2S is released from the gas phase to the liquid phase. (Díaz, Ramos, Fdz-Polanco, 2015, p.281)

Even though desulfurization by using this method is common due to its simplicity, it has several disadvantages. Whereas addition of ferric salt doesn't require large investments in additional process equipment, operating costs can be high depending on the price of the chemical. Due to the parallel reactions the consumption of the chemical is increased thus adding the total operating costs. (Díaz et al., 2015, p.281) The operational costs are directly proportional to the amount of H_2S in the process. When using feedstock material with high protein content, iron salts as a desulfurization technology are estimated to be high. (Bailon Allegue, Hinge, 2014, p.7)

It is possible that ferric salt accumulates in the process and increases the amount of total iron in the digestate (Díaz et al., 2015, p.281). Addition of chemicals to the digester may have an undesired effect on the microbiological activity resulting in declining methane yield (Okoro, Sun, 2019, p.19).

4.2 Iron sponge

Iron ions can be introduced to the process also in a form of iron oxides or hydroxides. These chemicals are not dosed to the reactor, but raw biogas is blown through a bed that contains the iron compounds (Deng et al., 2020, pp.218–219). Iron oxide used in the reaction is hydrated iron oxide Fe_2O_3 (Bailon Allegue, Hinge, 2014, p.13).

The reactions for desulfurization are following:

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \tag{4}$$

$$Fe_2S_3 + \frac{3}{2}O_2 \rightarrow Fe_2O_3 + 3S \tag{5}$$

(Abatzoglou, Boivin, 2009, p.55)

The H_2S removal efficiency depends on the contact time and the flowrate of the biogas through the bed material. Reaction will be more efficient the smaller the flow rate and the longer the contact time. The optimum temperature for the reaction is 25–50 °C. (Deng et al., 2020, pp.218–219)

Wood chips impregnated with iron oxide are commonly used as a bed material, but also red mud pellets can be used. Pellets are more expensive compared to woodchips but have a larger surface area compared to volume. It has been evaluated that 100 g of pellets can remove up to 50 g of sulfide when the concentration of H_2S in the biogas is 1000–4000 ppm. Stoichiometrically 64 g of H_2S can be removed with 100 g of Fe_2O_3. (Bailon Allegue, Hinge, 2014, pp.13–14)

As the bed material starts to become covered with elemental sulfur the removal efficiency of H_2S decreases (Deng et al., 2020, pp.218–219). The bed material can be regenerated with O_2 by aerating but the rection is exothermic and can result to a self-ignition of the wood chips. It has been evaluated that the bed material can be regenerated only a couple of times before replacing is needed as the activity of the material reduces by 1/3 with every regeneration. The problematic disposal of the wood chips or pellets saturated with sulfur is one of the main disadvantages of this technology. (Bailon Allegue, Hinge, 2014, pp.13–14)

Removing H_2S with iron oxides and hydroxides has low investment costs, simple operation and has a high removal efficiency (Deng et al., 2020, pp.218–219). Iron sponge is considered to be a mature technology (Bailon Allegue, Hinge, 2014, p.14). Even though ferric oxide is cheap and easy to obtain, the removal costs of H_2S can be high with this method (Deng et al., 2020, pp.218–219).

4.3 Activated carbon

Use of active carbon filtration in H_2S removal is based on adsorption. H_2S forms a thin layer on top of the pores of active carbon (Petersson, Wellinger, 2013, p.7). Activated carbon is used for desulfurization when low H_2S levels are needed. When oxygen is present also oxidization of H_2S occurs in addition to physical adsorption and the formed elemental sulfur is retained within the activated carbon. (Bailon Allegue, Hinge, 2014, pp.11–12) The reaction is flowing:

$$2H_2S + O_2 \rightarrow \frac{1}{4}S_8 + 2H_2O \qquad (6)$$

(Bailon Allegue, Hinge, 2014, p.11)

The efficiency of the removal process will slowly decrease as the sulfur builds up to activated carbon. When activated carbon is saturated with sulfur it can be regenerated or replaced. (Persson, Jönsson, Wellinger, 2006, p.22) Regeneration is usually done by applying a high temperature with inert gas or steam (Salvador et al., 2015, p.259).

The operation time for activated carbon filter varies between 4000–8000 hours depending on the H_2S content and the filter design. When the H_2S levels are over 3000 ppm more frequent regeneration cycle is needed. (Bailon Allegue, Hinge, 2014, pp.11–12)

The removal efficiency can be increased with transforming H_2S to elemental sulfur which is adsorbed to activated carbon quicker compared to H_2S. In practice this is achieved with impregnating the activated carbon with catalyst such as zinc oxide (ZnO), potassium iodide (KI) or potassium carbonate (K_2CO_3). (Petersson, Wellinger, 2013, p.7) The removal capacity of the activated carbon is normally 10 – 20 kg H_2S/m^3 carbon but 120–140 kg H_2S/m^3 carbon for impregnated carbon (Bailon Allegue, Hinge, 2014, pp.11–12).

The main drawback in using impregnated carbon is that after its saturated it needs to either be disposed and replaced or regenerated. Re-impregnation has high costs and the process itself is exothermic which creates a risk of ignition in the bed material. (Bailon Allegue, Hinge, 2014 pp.11–12)

4.4 Biological desulfurization

Biological H_2S removal is carried out with bacteria under aerobic or anaerobic process conditions. Chemolithotrophic bacteria, for example Thiobacillus, can be used oxidize H_2S to elemental sulfur under aerobic of anaerobic conditions. When desulfurization is done under anaerobic conditions nitrite NO_2^- or nitrate NO_3^- is used as electron acceptor instead of oxygen. (Okoro, Sun, 2019, pp.11–15) The describing reactions are the following:

$$5S^{2-} + 2NO_3^- + 12H^+ \rightarrow 5S^0 + N_2 + 6H_2O \quad (7)$$

$$5S^0 + 6NO_3^- + 2H_2O \rightarrow 5SO_4^{2-} + 3N_2 + 4H^+ \quad (8)$$

$$5S^{2-} + 8NO_3^- + 8H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O \quad (9)$$

(Deng et al., 2020, p.222)

In aerobic biological H_2S removal, a small amount of air or oxygen is introduced to a separated desulfurization system. Aerobic conditions can also be created inside the fermenter by microaeration where a small amount of air or oxygen is injected directly to the biogas fermenter. H_2S reacts with oxygen and forms elemental sulfur or sulfate with Thiobacillus bacteria as catalysts. Thiobacillus bacteria are autotrophic and a natural part of a bioreactor's flora. (Deng et al., 2020, pp.221–222) Reactions are as followed:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O \quad (10)$$

$$H_2S + 3O_2 \rightarrow 2H2SO_3 \quad (11)$$

(Deng et al., 2020, p.220)

The bacteria can be cultivated in a packing material of biofilters, biotrickling filters or bioscrubbers. In the biofilter and the biotrickling filter system raw biogas is blown through a separated reactor containing the microbes. The difference between biofilter and biotrickling filter is the carrier material of which surface the bacteria grow. The carrier material in biofilter is organic and inert in a biotrickling filter. A process media is used in biotrickling filter to provide the bacteria with nutrients and moisture. (Bailon Allegue, Hinge, 2014, pp.21–23)

4.4.1 Biofilter and biotrickling filter

Bacteria used in biofilters and biotrickling filters are usually aerobic and air is injected to the gas stream. Pure oxygen needs to be used instead of oxygen when biomethane is used for vehicle fuel or gas grid injection. (Bailon Allegue, Hinge, 2014, p.21)

A nutrient solution is needed for biotrickling filter. The solution is sprayed from the top of the biotrickling filter and the H_2S-rich biogas is pumped from the bottom of the column. The H_2S is dissolved to the biofilm on the packing material and microbes use it as an energy source. (Deng et al., 2020, pp.221–222) Mainly sulfur and sulphate are produced during the process (Bailon Allegue, Hinge, 2014, p.21).

In a report made by Bailon Allegue & Hinge some commercial biotrickling filters for desulfurization of biogas are reviewed (Bailon Allegue, Hinge, 2014, p.21). The main figures of these technologies are presented in table 6.

Table 6 The key figures of commercial biotrickling filters for desulfurization of biogas (Bailon Allegue, Hinge, 2014, p.21)

Biotrickling filter	
Removal efficiency of H_2S	90–99%
Loading rate of H_2S	1000–15 000 ppm
Power consumption	0.21 kWh/kg/ H_2S removed
Total operational costs	0.10–0.25€kg/ H_2S removed

It can be seen from table 6 that the efficiency is evaluated to exceed over 90%. Disadvantage of these systems is that when the raw biogas treated has a high H_2S content there might be a need to use multiple parallel biological filter systems to achieve the desired removal efficiency. Another disadvantage is that when biogas is upgraded for grid injection or vehicle use a secondary H_2S system is needed in addition of the biofiltration system since maintaining a steady H_2S level of low concentrations cannot be guaranteed. (Bailon Allegue, Hinge, 2014, p.21)

One of the disadvantages of biofilters is the pH drop in the process media due to the H_2S which forms sulfuric acid. Filter media can be washed with water, alkaline compounds can be added or a carrier material that is alkaline can be used to prevent operational issues due to the drop in pH. As biotrickling filter is continuously washed with the nutrient solution there is no threat of pH drop since sulfur compound are continuously removed from the process. (Bailon Allegue, Hinge, 2014, p.21)

4.4.2 Bioscrubber

Bioscrubber consists of a scrubber unit and a bioreactor unit. The raw biogas is injected from the bottom part of the scrubber column and bioreactor liquid is sprayed down from the top part. This results the H_2S from the raw biogas is absorbed to the water phase from the gas phase. (Bailon Allegue, Hinge, 2014, p.21) A simplified process diagram is presented in figure 2.

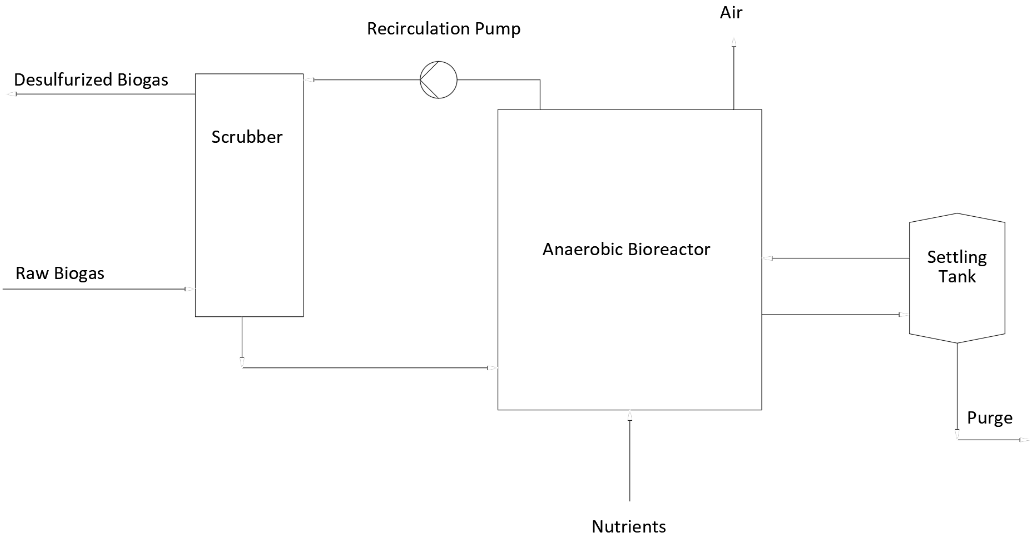

Figure 2 Simplified process diagram of a bioscrubber system (Adapted from, Bailon Allegue, Hinge, 2014, p.24)

The bioreactor is filled with microorganism that consume the H_2S and produce sulfate and elemental sulfur. Nutrients are added to the bioreactor unit to maintain stable growth and microbiological activity in the reactor. (Bailon Allegue, Hinge, 2014, p.23)

The raw biogas is not directly in contact with the desulfurization microbes. Biomass is constantly purged along with the sulfur compounds from H_2S degradation (Figure 2). This prevents the accumulation sulfate and elemental sulfur to the process. (Bailon Allegue, Hinge, 2014, p.23)

The H_2S removal efficiency of bioscrubbing system can reach 99% when system is optimized. The advantage of a bioscrubber system is that it doesn't require air or oxygen to be injected along with the gas stream.(Bailon Allegue, Hinge, 2014, p.23)

4.4.3 Microaeration

In microaeration a small amount of air or oxygen is injected directly to the fermenter or a biogas storage unit. The H_2S in the biogas is aerobically oxidated to elemental sulfur by Thiobacillus bacteria (Bailon Allegue, Hinge, 2014, p.9) described in the reactions 10 and 11. To promote the growth of the bacteria, a mechanical structure can be installed on the top part of the bioreactor. Oxidation of H_2S to elemental sulfur occurs in both gas and liquid phases. The elemental sulfur is removed from the bioreactor along with the digestate. (Deng et al., 2020, pp.221–222)

The amount of oxygen needed for desulfurization depends on the initial H_2S level but usually, the required amount of air injected to the bioreactor varies between 2–6% air in biogas (Persson et al., 2006, p.22). The final product of the chemical reaction depends on the H_2S to oxygen mole ratio, even though elemental sulfur seems to be most common one (Okoro, Sun, 2019, p.10-11). Not all oxygen is consumed during the desulfurization process and the concentration O_2 varies between 0.5 – 1.8 vol.% (Bailon Allegue, Hinge, 2014, p.9).

The removal efficiency can vary depending on the reaction time, temperature and the amount and place of the air injected (Persson et al., 2006, p.22). The desulfurization process with microaeration is considered to be efficient and over 99% removal rates have been established in laboratory scale processes. Efficiencies over 90% have been reported from large–scale facilities. (Okoro, Sun, 2019, p.10-11) It is possible to optimize the O_2 injection rate so that the O_2 concentration in the biogas stays as low as 0,1% (v/v) while the desulfurization efficiency is 97–99%. (Díaz et al., 2015, p.273)

Concentration levels of H_2S achieved can be as low as 20–100 ppm but, most real life systems are less efficient. A report by Bailon Allegue & Hinge mentions research where the removal efficiencies of several industrial scale microaeration systems were studied. In over half these systems, the treated biogas had H_2S levels of over 500 ppm after the desulfurization regardless of the amount of oxygen fed to the system. (Bailon Allegue, Hinge, 2014, p.9).

The advantages of this method are that the process doesn't use any chemicals, it has high efficiency and low energy consumption (Deng et al., 2020, pp.221–222). Microaeration is evaluated to be the least expensive desulfurization system for facilities where no upgrading is needed (Bailon Allegue, Hinge, 2014, p.9).

There are several disadvantages with microaeration. The removal of H_2S is challenging to keep steady in case of H_2S concentration peaks. Another disadvantage is that the oxygen injection to the bioreactor can create an explosion hazard if oxygen feed amount is not carefully monitored and regulated. (Deng et al., 2020, pp.221–222) Methane is explosive when in the range of 5–15% in air (Persson et al., 2006, p.22).

If the feed amount of oxygen is higher than required for H_2S removal, the efficiency of the anaerobic digestion process can decrease due to a disturbance in the methanogenesis (Deng et al., 2020, pp.221–222). This leads to decreased methane yield from the process (Bailon Allegue, Hinge, 2014, p.9).

Elemental sulfur can be further oxidized to sulfates which can inhibit the production process of methane. There is also a risk that elemental sulfur can clog the oxygen supply pipeline. (Okoro, Sun, 2019, p.11)

The presence of O_2 and N_2 in the desulfurized biogas is also a disadvantage if biogas is upgraded to biomethane for vehicle use or grid injection. Separating these gas compounds from the gas stream in considered to be expensive since most biogas upgrade technologies are unable to remove them. The amount of these gas components allowed to the gas grid vary between countries. (Bailon Allegue, Hinge, 2014, p.9)

To avoid the diluting effect of N_2 pure oxygen can be used instead of air but this increases the operating costs. Therefore, large biogas facilities generate oxygen on site instead of buying and importing it to the plant site. (Bailon Allegue, Hinge, 2014, p.9)

4.5 Summary of desulfurization technologies

Choosing desulfurization method depends on the initial H_2S level as well as the intended end use of the biogas. Some systems are used just to prevent problems caused by corrosion and some to purify the biogas to meet gas grid requirements regarding the H_2S concentration. (Bailon Allegue, Hinge, 2014, p.9)

4.5.1 Advantages and disadvantages

Different desulfurization systems differ regarding initial investment costs, operating costs as well as reliability, complexity, and efficiency of the process (Bailon Allegue, Hinge, 2014, p.4-26). The advantages and disadvantages of different desulfurization methods are presented in table 7.

Table 7 The advantages and disadvantages of different desulfurization methods (1) Bailon Allegue, Hinge, 2014, pp.7–14; 2) Deng et al., 2020, pp.218-222–222; 3) Díaz et al., 2015, p.281; 4) Okoro, Sun, 2019, p.19)

Desulfurization Technology	Advantages	Disadvantages
Iron salts	• Low investment costs(4 • Simple (4 • Well know technique(4	• To achieve low H_2S levels a vast amount of surplus chemical is needed (1 • Chemical price determines the operating costs (4 • High H_2S concentrations require more chemical (1 • Chemical can inhibit the methanogenesis (4
Iron sponge	• Low investment costs(2 • Simple operation (2 • High removal efficiency (2 • Mature technology (2	• Expensive disposal of bed material (1 • Hazardous regeneration of the bed material (1
Activated carbon	• High removal efficiency (1 • Reliable (1	• Expensive especially when concentration of H_2S is high (4
Biofilter		• Unstable (1 • Needs a secondary system (1 • Acidification of the process media (1 • Not suitable when biogas upgraded for vehicle or grid use (1
Biotrickling filter		• Unstable (1 • Needs a secondary system (1 • Not suitable when biogas upgraded for vehicle or grid use (1
Bioscrubber	• Doesn't require oxygen injection to the gas stream(1	• Unstable (1 • Needs a secondary system (1
Microaeration	• Low costs (1 • No chemicals (1 • Low energy consumption(1	• Unstable (1 • Insufficient efficiency possible (1 • Explosion hazard (2 • Inhibition of methanogenesis (2 • Possible clogging by elemental sulfur (4 • Pure oxygen needed if biomethane for vehicle use or gas grid(1

It can be seen from table 7 that all biotechnology based systems are known to be unstable and a secondary desulfurization system is needed. Biofilter and biotrickling filter do not have any specific advantages compared to other desulfurization systems. Compared to other biotechnology desulfurization method, bioscrubber has the advantage that oxygen doesn't come to direct contact with the treated biogas. (Table 7)

Iron based system are both mentioned to have low costs and simple operation. The disadvantages of adding iron salts is the high chemical consumption if the initial H_2S concentration is high or the required level of H_2S is low. These disadvantages can also increase the operating costs which are directly proportional to the chemical consumption. (Table 7)

Activated carbon filter is mentioned to be reliable and to have high efficiency, but also to be an expensive option when the concentration of H_2S is high. Microaeration is evaluated to be low cost system but has multiple process related problems. Process is mentioned to be unstable and to possibly have insufficient removal efficiency. There is also an explosion hazard when oxygen is mixed with the biogas. Also, it is possible that the methanogenesis is disturbed because the oxygen is directly injected to the fermenter. (Table 7)

4.5.2 Economical comparison

In a study made by Okoro and Sun the costs for different desulfurization units were collected from literature (Okoro, Sun, 2019, p.19).These figures are presented in table 8.

Table 8 Cost evaluation figures and capacities for different desulfurization methods (1) Bailon Allegue, Hinge, 2014, pp.26–29; 2) Okoro, Sun, 2019, pp.18–19)

Desulfurization Technology	Capital costs (€/m^3 raw biogas)	Operating costs (€/m^3 raw biogas)	Total costs (€/m^3 raw biogas)	Capacity kg S/day
Iron salts			0.009(2	112(1
Iron sponge			0.069(1	<110(1
Activated carbon	1.116(2	0.008(2	1.158(2	<9(1
Biofilter	0.084(2	0.028(2	0.114(2	
Biotrickling filter	1.376(2	0.009(2	1.427(2	
Bioscrubber	0.149(2	0.019(2	0.172(2	8–450(1
Microaeration			0.015(2	

Because the cost evaluations were collected from different sources from literature, they are not directly comparable, as there is no information available for the initial assumptions, such as initial concentration of H_2S or the removal efficiency, made for these cost evaluations. Okoro and Sun stated that the results would still give an overall impression of the costs for different desulfurization technologies (Okoro, Sun, 2019, p.4).

Desulfurization by dosing iron salt directly to the biogas process was found to be the most economical method for biogas desulfurization followed by microaeration. Biotrickling filter was found to be the most expensive option followed by activated carbon. The price estimate for microaeration, presented in table 8, was evaluated as a mean value from three different cases where different oxygen concentration of 100%, 95% and 21% were used. (Okoro, Sun, 2019, p.19) The total costs of biotrickling filter were the highest followed by activated carbon unit. (Table 8)

The removal capacities for different desulfurization technologies are presented in table 8. The activated carbon has the lowest capacity of all the methods. Bioscrubbing system has a large variety regarding removal capacity. (Table 8.)

In a study made by Diaz and Ramos, costs of three different microaeration systems were evaluated. First system utilized pure O_2 that was purchased and stored in cryogenic tanks. Second system used 95% O_2 which was produced with a pressure swing adsorption (PSA) generator. The third option was the injection of air to the digester. (Díaz et al., 2015, pp.285–286)

The system that used 95% O_2 was estimated to have the lowest operating costs. The reason for this was evaluated to be because even the capital costs were the largest, there was no power loss due to dilution of the biogas unlike when air was used. Another reason was the high price of concentrated O_2 in a case where pure oxygen was used. The system that used 95% O_2 was also found to be the most resistant against the variation in H_2S levels and electricity price in the sensitivity analysis conducted in the study. (Díaz et al., 2015, pp.285–286)

5 Biogas upgrading technologies

Biogas upgrading is not the same process as biogas purification although in practice these two processes are usually combined to reduce costs. The goal in biogas upgrading is to increase the calorific value of the gas and to reduce the need and costs of storing and transportation by removing inert gases such as CO_2 and N_2 that do not contain energy, whereas the goal in purification is to remove impurities such as H_2S (Ch. 4) that can be harmful to the process equipment and create emissions. (Kymäläinen, Pakarinen, 2015, pp 126–127)

Commercial technologies can roughly be divided into five main categories which are physical and chemical absorption, physical adsorption, cryogenic and membrane separation. It is also possible to combine these technologies in a hybrid system to increase the efficiency. (Hoyer et al., 2016, pp. 24–25)

5.1 Water scrubbing

Water scrubbing is the most common biogas upgrade technology (Ghaib, 2017, p.1822). It can be used to separate CO_2, H_2S, NH_3 and certain VOC compounds from biogas by absorbing them to the water phase from the gas phase (Hoyer et al., 2016, pp. 24–25). Separation of gasses is based on their different solubility to water (Vico, Artemio, 2017, pp.138–140). Carbon dioxide has a much greater solubility to water compared to CH_4 (Bauer, Hulteberg, 2013, pp.34–43). The solubility of gases depends on temperature and pressure conditions in the system (Hoyer et al., 2016, p.35).

Part of the H_2S is oxidized to elemental sulfur in the desorption column and the temperature and the pH of the process both have an effect on the rate of oxidation (Ryckebosch et al., 2011, p.1635). Increase in temperature and in the pH both favor the oxidation process (Bauer, Hulteberg, 2013, p.40).

The accepted H_2S level on the inlet gas to the water scrubbing upgrade unit depends on manufacturer and varies between 300–2500 ppm. If the H_2S level is exceeds the maximum level manufacturer has stated, there is a need for pre–treatment to lover the amount of H_2S to an acceptable level. (Bauer, Hulteberg, 2013, p.40)

5.1.1 Theoretical background

Absorption of gasses into liquid phase can be described with Henry's law which states that the concentration of gas dissolved to liquid depends on its partial pressure (Stumm, Morgan, 1995, pp.213–214). Henry's law can be expressed as following:

$$C_A = K_H p_A \tag{12}$$

where C_A is the concentration of A in the liquid phase, K_H is Henry's constant and p_A is the partial pressure of A in the gas phase. Henry's constant is only valid for a specific gas in a specific temperature and usually when the temperature decreases the solubility of the gas increases. (Stumm, Morgan, 1995, pp.213–214)

Henry's constant (K_H) is $1.29 * 10^{-3}$ M/atm for CH_4 and $3.39*10^{-2}$ M/atm for CO_2 at a temperature of 25 °C. This results that CO_2 has approximately 26 times greater solubility to water compared to CH_4. Henry's constant for H_2S 1,05*10–1 M/atm which means that it is even more soluble to water than CO_2 (Stumm, Morgan, 1995, pp.213–214). Therefore, H_2S is efficiently removed during adsorption and desorption processes (Bauer, Hulteberg, 2013, p.40).

The amount of process water needed for the separation of CO_2 depends on the process conditions, the required purity level of the biomethane and the design of the system. The solubility of CO_2 depends directly on the temperature and pressure used in the process. (Bauer, Hulteberg, 2013, pp.34–36)

The efficiency of the column depends on the number of theoretical plates, which are theoretical stages where the water and gas phases are in equilibrium with each other. The more theoretical plates the unit has, the more efficient it will be. The number of theoretical plates of the column is determined by the packing material inside the column and the height of the column itself. A high efficiency of the system decreases the needed water flow to remove a certain amount of CO_2 from the biogas. (Bauer, Hulteberg, 2013, pp.34–39)

When the amount of CO_2 in the gas mixture decreases, so does the partial pressure of it, making it harder to separate. When purification requirements are high and the allowed concentration of CO_2 in the biomethane is low, more water is needed to remove the remaining CO_2. (Bauer, Hulteberg, 2013, pp.34–39)

5.1.2 Process description

The water scrubbing system consists of two columns: a scrubber column (also known as adsorption column) and a stripper column (also known as desorption column) (Bauer, Hulteberg, 2013b, p.501). The CO_2 transfers to the water phase in the scrubber column and is released back to the gas phase in the stripper column. Columns can be either empty or filled with packing material, but it has been estimated that without packing material the efficiency of CO_2 separation can be almost 40 vol.% less. This is because the packing material increases the surface area available for the gas–liquid mass transfer. (Vico, Artemio, 2017, pp.138–140) Previously water scrubber systems without water circulation have been built and some of them are still operational. Systems without water recirculation are less stable and have more operational problems. (Bauer, Hulteberg, 2013, p.35)

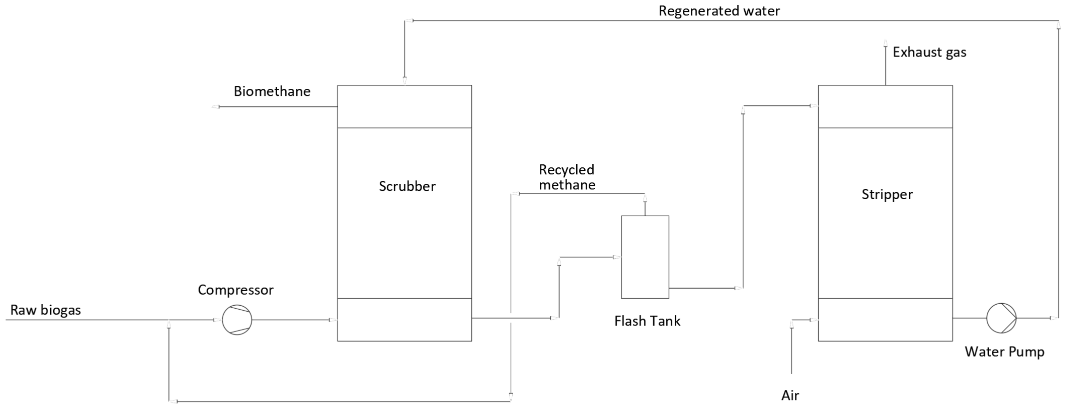

Figure 3 Simplified water scrubbing process diagram (Adapted from Adnan et al., 2019, p.4)

The temperature of the inlet gas led to the upgrade unit can usually be up to 40 ºC. The pressure of the raw biogas is then increased to 6–10 bar(a) and it is cooled to match the temperature of the process water in the scrubber. The change in the pressure and temperature causes most of the water vapor in the biogas to condensate prior to the absorption column. (Bauer, Hulteberg, 2013, pp.40–43)

Water is sprayed from the top of the adsorption column and the pressurized raw biogas is injected from the bottom of the column (Persson et al., 2006, p.18). To minimize CH_4 loss and the energy consumption of the process it is advised to use a counterflow system. (Bauer, Hulteberg, 2013, pp.40–43) Carbon dioxide and a small amount of methane are absorbed to water phase (Bauer, Hulteberg, 2013, p.501).

Operating parameters such as flow rate, temperature and pressure need to be considered when designing the columns (Vico, Artemio, 2017, pp.138–140). Increasing the height of the column and the packing material type determine the efficiency of the separation process. Increasing the diameter of the adsorption column increases the maximum volume flow of the biogas. Wider column also increases the minimum biogas flow required for the process to work. The water and biogas will be mixed in an unideal way if the flow to the system is too low. Depending on the design, minimum inlet flow is between 20–50% of the maximum flow. (Bauer, Hulteberg, 2013, pp.34–43)

To recover any CH_4 absorbed to the water, the water from the adsorption column is pumped to flash column where the pressure is decreased to 2.5–3.5 bar(a). The flash column holds no packing material. Its diameter should be wide enough, so the flow of the water decreases enough to let the gas bubbles be released in the column prior to desorption column. The column height needs to be sufficient to prevent any water to be sucked to the compressor. (Bauer, Hulteberg, 2013, pp.40–43)

In the flash tank most of the CH_4 and some of the CO_2 contained in the water, is released in the gas phase, and recycled back to the compressor prior to scrubber column (Bauer, Bauer et al. 2013, p. 501). The volume of the recycled gas is usually 20–30% of the inlet flow to the system. The composition of the gas released from the flash column is usually 80–90% CO_2 and 10–20% CH_4. (Hoyer et al., 2016, pp. 24–25)

The water from the flash column is pumped to the top of the desorption column and air is pumped to the bottom of the column. This column operates under atmospheric pressure and CO_2 and the remaining CH_4 are released, and the water is recirculated back to the top of the adsorber column. Depending on the design and the volume of the process it takes between 1–5 minutes to circulate the water once throughout the system. (Bauer, Hulteberg, 2013, pp.40–43)

The upgraded biomethane is saturated with water as it leaves the upgrade unit and needs to be dried to a required level depending on the end use (Hoyer et al., 2016, pp. 24–25). The exhaust gas contains mainly CO_2 and some CH_4, usually less than 1% of the total CH_4 content of the raw biogas. If the CH_4 content of the inlet gas increases, so does the CH_4 slip, unless the pressure of the flash column is decreased accordingly. (Bauer, Hulteberg, 2013, pp.40–43)

5.1.3 Investment cost and consumable

Water scrubbing is an older technology, and the capital investment and operating costs can be rather reliably evaluated. In a report made by Bauer et. al, it was concluded that the specific investment cost for basic water scrubbing system (excluding exhaust gas treatment, pre–treatment and heat recovery systems) decreased as the capacity on the biogas plant increased and it became constant in ~1500 €/Nm^3/h as the raw biogas flow exceeded 1000 Nm^3/h. (Bauer, Hulteberg, 2013, pp.40–43)

Water scrubbing technology doesn’t require large infrastructure and the process can be operated with a low biogas flowrate (Vico, Artemio, 2017, pp.138–140). A lot of consumables are not required in a water scrubbing system, besides from water that needs to be continuously replaced or treaded to prevent the drop in pH and increase of unwanted substances. Process might also need antifoaming agent. Chemical costs are usually low compared to the total capital and operating costs (Bauer, Hulteberg, 2013, pp.40–43) The main consumables for water scrubbing system are presented in table 9.

Table 9 Main consumable figures of a water scrubbing system (Bauer, Hulteberg, 2013, pp.40–43)

Consumable	
Water (m^3/day)	0.5-5
Electricity, total (kWh/m^3 raw biogas)	0.2-0.3
Electricity, compressors (kWh/m^3 raw biogas)	0.10-0.15
Electricity, pumps (kWh/m^3 raw biogas)	0.05-0.10
Electricity, cooling (kWh/m^3 raw biogas)	0.01-0.05

It can be seen from table 9 that there are three main components that use energy in the water scrubbing unit which are the compressor, water pump and the cooler. The total energy consumption of these units depends on the capacity and design of the unit, climate conditions as well as the properties of the inlet gas and the required purity level of the product. For example, the cooling unit consumes more energy when operating in hot climates. (Bauer, Hulteberg, 2013, pp.40–43)

Ghaib K. studied how different operating parameters affected the power consumption of a water scrubbing unit with Aspen Plus simulation software. The study concluded that the optimum temperature for the water used was 10 °C. The optimal operating pressure for scrubber was 6 bar and 0.25 bar for the stripper. (Ghaib, 2017, p.1822)

The total costs are evaluated to be 0,13 €/Nm^3 raw biogas (De Hullu et al., 2008, p.19). Operating time is usually guaranteed to be over 95% and maintenance costs are evaluated to be 2–3% of the total investment cost annually (Vico, Artemio, 2017, pp.138–140).

5.1.4 Operational challenges

H_2S forms sulfuric acid which lowers the pH of the process water. Acid conditions have been found to cause corrosion in the process equipment such as pumps and pipes. High chlorine concentration of water also increases the amount of corrosion. To avoid sulfuric acid from forming, thus minimizing the corrosion damage, the operating temperature of the process should be lowered as well as the H_2S level of the inlet gas. If corrosion causing substances have formed in the process, their amount and affects can be minimized by increasing the amount of makeup water or the alkalinity of the process. (Bauer, Hulteberg, 2013, pp.34–43)

Foaming inside the columns is a problem in many facilities and it lowers the CO_2 removal efficiency because it reduces the surface area between the gas and the liquid phase. Foaming can be caused by microbiological growth in the water scrubbing process or by some compounds that dissolve to water from the inlet gas. (Bauer, Hulteberg, 2013, pp.34–43) Foaming can be reduced or completely prevented by adding antifoaming agent to the process (Hoyer et al., 2016, pp. 24–25).

Some microorganisms are always present in the water scrubbing process but process parameters such as operating temperature, pH and the composition of the treated biogas have an effect of the rate of microbiological growth as well as which microbes thrive. (Bauer, Hulteberg, 2013, p.41) Microbiological growth can cause fouling or even clogging in the process (Persson et al., 2006, p.18).

Fouling decreases the CO_2 removal efficiency because it decreases the reaction surface area available. Frequent cleaning and use of biocides helps to minimize the problems caused by microorganisms. One way to prevent microbiological growth is treating the process water to minimize the amount of nutrients available for the microorganisms. (Hoyer et al., 2016, pp. 24–25) In severe cases there might be a need to replace the packing material entirely (Bauer, Hulteberg, 2013, p.41). Modern water scrubbers are operated in a lower temperature which has reduced the frequency of this problem (Hoyer et al., 2016, pp. 24–25).

5.2 Amine scrubbing

Amine scrubbing has the basic operating principle as water scrubbing with the exception that CO_2 is chemically bound to the amine process media instead of water. An amine scrubbing unit consists of a scrubber column where the CO_2 is absorbed and from a stripper column where the amine is regenerated. Both columns are filled with packing material to maximize the reaction area between gas and liquid phases. (Bauer, Hulteberg, 2013, pp.34–43) Amine scrubbing system can be used to obtain CO_2 as a side product from biogas upgrading (Sun et al., 2015, p.529).

Any possible O_2 and N_2 are not absorbed to the amine liquid, and they leave the process along the CH_4 and might need to be removed depending on the end use of the gas. Pre-removal of H_2S might be required depending on the amine used in the process, initial H_2S amount, and end use of the product gas. The main part of possible H_2S and NH_3 are removed from the process along with the CO_2 and there might be a need for post–treatment to avoid emission to atmosphere. (Hoyer et al., 2016, pp. 24–25)

There is a possibility some H_2S will not be removed during the absorption and need to be removed from the CH_4 stream with post-treatment. This depends on the H_2S level of the raw biogas and the amine used in the process. Post-treatment of the gas stream is simpler compared to the pre–treatment since there is no limitations for the amount of air that can be added to the gas mixture. (Hoyer et al., 2016, pp. 24–25)

5.2.1 Theoretical background

The theoretical background of an amine scrubbing system is similar to the background of a water scrubbing system which is covered in the chapter 5.1 of this thesis. The removal of CO_2 by absorption can be described with Henry's law (Eq. 12). The solubility of CO_2 to amine process media is higher compared to water (Persson et al., 2006, p.19). The solubility depends on the amine used in the process. (Bauer, Hulteberg, 2013, pp. 16–19) The CO_2 is absorbed to the amine liquid physically and chemically (Abdeen et al., 2016, p.694).

There are a few amine solutions commonly used in the process, such as monoethanolamide (MEA), methyl diethanolamine (MDEA) or diethanolamine (DEA). (Hoyer et al., 2016, p.25). Most commonly used amine is activated methyl diethanolamine (aMDEA) which is a mixture of MDEA and piperazine (PZ). Compared to MDEA, aMDEA has a considerably higher absorption capacity for CO_2. (Bauer, Hulteberg, 2013, pp.502–503)

The CO_2 is bonded to the amine with covalent bonds (Abdeen et al., 2016, p.694). The possible reactions between MEA and CO_2 are the following:

$$2RNH_2 + CO_2 \rightleftharpoons RNH_3^+ + RNHCOO^- \tag{13}$$

$$RNH_2 + CO_2 + H_2O \rightleftharpoons RNH_3^+ + HCO_3^- \tag{14}$$

(Abdeen et al., 2016, p.694)

There is a need for 4–7 times more amine in the process compared to the amount of CO_2 in the raw biogas to prevent equilibrium limitations in the absorption. There are equilibrium restrictions in the desorption rection but the increase in temperature strongly favors the regeneration of the amine. (Bauer, Hulteberg, 2013, pp. 16–19)

5.2.2 Process description

The process diagram of the amine scrubbing system is shown on figure 4. Raw biogas is led to the scrubber from the bottom of the scrubber column, while the amine solution is sprayed from the top of the column (Hoyer et al., 2016, pp. 25–26). The pressure in the absorber column is ambient or slightly elevated, 1–2 bar(a), depending on the specific system. The CH_4 flows up to the top part of the column and is removed from the process, while the CO_2 is retained to the liquid phase. The reaction between the amine solution and CO_2 is exothermic and the solutions temperature rises from the 20–40°C inlet temperature to 45–65°C. The absorption process is more efficient in high temperatures from a kinetic standpoint but less efficient from a thermodynamic standpoint. (Bauer, Hulteberg, 2013, pp.502–503)

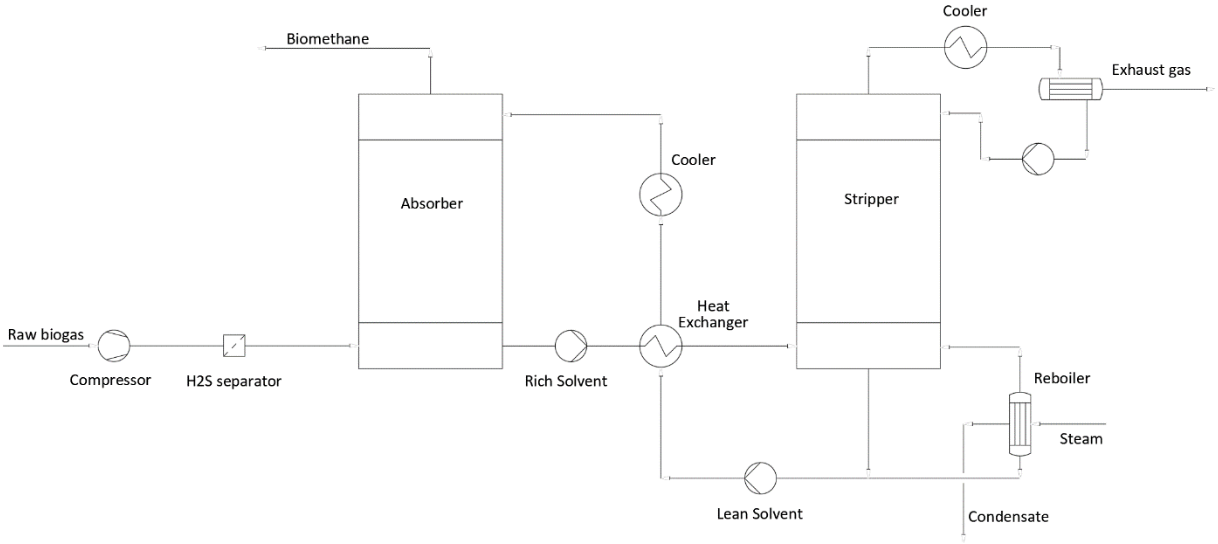

Figure 4 Simplified process diagram of amine scrubbing unit (Adapted from Adnan et al., 2019, p.4)

The CO_2-rich amine solution is pumped from the bottom of the scrubber unit to the top of the stripper unit through a heat exchanger unit to increase its temperature (Fig. 4). The pressure of the stripper unit is 1,5–3 bar(a). In the stripper unit the amine liquid is sprayed from the top and a steam flow is fed from the bottom of the column. There is a reboiler located on the bottom of the stripper unit where a part of the amine solution is boiled. This releases the remaining CO_2 from the amine liquid and creates the steam which heats the amine solution entering the stripper column. The amount of heat applied to the reboiler is 120–150°C which can be achieves with oil or steam. If stripper is operated in a vacuum the applied heat can be as low as 90°C. (Bauer, Hulteberg, 2013, pp.502–503)

Steam decreases the partial pressure of the CO_2 which improves the kinetics of the desorption. Any H_2S bound to the amine is released at the stripper column along with the CO_2. The gas stream from the stripper unit, containing CO_2, H_2S and steam, is cooled and the condensate which has a small amount of amine is recirculated bac to the stripper. Cooled gas mixture is released to the atmosphere. The upgraded CH_4 needs to be dried before possible liquefaction of grid injection. (Bauer, Hulteberg, 2013, pp.34–43)

5.2.3 Investment and consumables

The initial investment costs vary depending on the capacity of the system. In report written by Hoyer et al. the specific investment cost gradually decreased from over 3000 €/Nm^3/h to 1500 €/Nm^3/h as the capacity of the raw biogas increased from 600 Nm^3/h to 1800 Nm^3/h. (Bauer, Hulteberg, 2013, pp.21–22) The investment cost is not constant for capacity of 1800 Nm^3/h and increasing the capacity would further decrease the specific investment cost. The total costs without H_2S removal are evaluated to be 0,17 €/Nm^3 raw biogas. (De Hullu et al., 2008, p.19)

When high end pressure is needed for grid injection, additional compression of the biomethane increases the electricity consumption (Bauer, Hulteberg, 2013, pp.21–22). The main consumables of the amine scrubbing system are presented in table 10.

Table 10 Main consumable figures of an amine scrubbing system (Bauer, Hulteberg, 2013, pp.21–22)

Consumable	
Heat (kWh/m^3 raw biogas)	0.55
Electricity, total (kWh/m^3 raw biogas)	0.12-0.14
Electricity, total when under vacuum (kWh/m^3 raw biogas)	0.17-0.19
Chemicals, like antifoaming agent (kg/Nm^3 raw biogas)	$3*10^{-5}$
Water (l/Nm^3 raw biogas)	$3*10^{-5}$

If district heating is used in the reboiler unit, the stripper system needs to be under vacuum since the temperature of the reboiler is lower, only about 90°C. It can be seen from table 10 that the system uses about 0.05 kWh/ m^3 raw biogas more electricity in this case. (Bauer, Hulteberg, 2013, pp.21–22)

The amine scrubbing unit can be equipped with heat recovery system that can yield 85°C and 55°C water streams. Methane slip is usually less than 0.1% and the methane purity over 99%. The annual downtime of the system is about 4%. (Bauer, Hulteberg, 2013, pp.21–22)

5.2.4 Operational challenges

Foaming in the columns is most frequent during start–up phase and is usually caused by hydrocarbons. Foaming can be prevented by minimizing the number of contaminants in the feed and make–up water. (Hoyer et al., 2016, p.27) Antifoaming agent can be used temporarily, or amine solution can also be continuously partially filtered to remove particles and contaminants that cause foaming. (Bauer, Hulteberg, 2013, pp.21–22)

Only small amount of amine is lost in normal operating conditions and sudden loss of amine in the process can be caused by leakage, problem in a demister unit or entrainment of fluid to the CH_4 or CO_2 gas streams. (Hoyer et al., 2016, p.27) Amine loss can also be caused by amine reacting with possible contaminants. Thermal degradation of the amine occurs if the temperature surpasses 175°C (Bauer, Hulteberg, 2013, pp.21–22)

Corrosion caused by the amine, can result in premature wearing of the process equipment and the piping, and increase the downtime and maintenance costs. Problems caused by corrosion can be minimized by material and design choices. (Hoyer et al., 2016, p.27)

5.3 Pressure swing adsorption (PSA)

In pressure swing adsorption (PSA) gasses are separated by absorbing them to an absorbent material in an elevated pressure. The method is based on the difference in physical properties of the gasses which causes them to be absorbed in different rates and amounts. PSA can be used to remove CO_2, N_2 and O_2 from raw biogas. (Hoyer et al., 2016, pp. 23–24). PSA system can be used to produce high purity CO_2 as a side product (Sun et al., 2015, p.529).

Desulfurization prior to PSA unit is crucial because H_2S can cause irreversible damage to the bed material inside the columns. Raw biogas should also be dried to remove any excess water before it’s led to the upgrade process. (Vico, Artemio, 2017, pp.142–145)

5.3.1 Theoretical background

The absorbent materials work on two principles in separating CO_2 from CH_4; either the equilibrium type where the amount of CO_2 absorbed is greater than the amount of CH_4

absorbed, or the kinetic type where CO_2 is absorbed faster than CH_4. (Bauer, Hulteberg, 2013, p.25)

To ensure an acceptable gas separation efficiency, it is crucial to choose a bed material that selectively absorbs CO_2 from the raw biogas stream (Hoyer et al., 2016, pp. 23–24). Absorbent materials used are porous solid materials that have a large surface area which increases the separation efficiency of the CO_2 since gas–absorbent contact area is maximized (Bauer, Hulteberg, 2013, p.25).

Common absorber materials to use in a PSA unit are for example activated carbon, silica gel, zeolites, and carbon molecular sieves (CMS). Zeolites and activated carbon are examples of equilibrium adsorbents and CMS is an example of kinetic adsorbents. (Bauer, Hulteberg, 2013, p.25) New types of absorbent materials are continuously developed to increase the process efficiency and to minimize the costs (Hoyer et al., 2016, pp. 23–24).

5.3.2 Process description

When upgrading biogas, the CH_4 flows freely throughout the system while CO_2 is retained to the absorbent material (Bauer, Hulteberg, 2013, pp.23–27). Any possible N_2 and O_2 contained in the raw biogas are adsorbed into the porous bed material due to their smaller molecular size compared to CH_4 (Vilardi, Bassano, Deiana, Verdone, 2020, p.2). When absorbent material becomes saturated with CO_2 the pressure inside the column is lowered and CO_2 is desorbed. There are several columns in the system working in parallel alternating the different steps to ensure continuous operation. (Bauer, Hulteberg, 2013, pp.23–27)

In a PSA system each parallel column goes through a 4–step cycle of pressurization, feed, blowdown and purge. This cycle is also known as the Skarstrom cycle. (Hoyer et al., 2016, pp. 23–24).

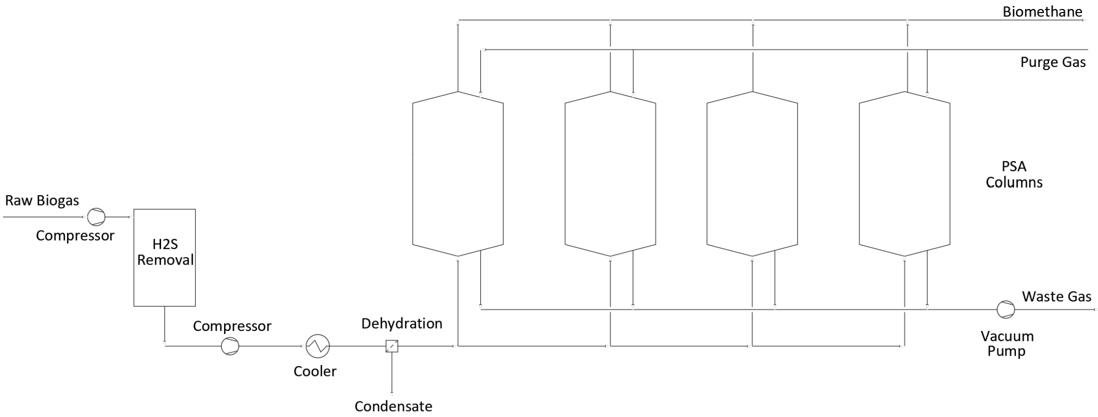

Figure 5 Simplified PSA process diagram (Adapted from Adnan et al., 2019, p.6)

During the first two steps the raw biogas is fed to the column, and it is pressurized to 4–10 bar depending on the system design. The column is filled with absorbent material and the CO_2 of the raw biogas is retained while the CH_4 flows through the column. When this process continues the bed material will slowly become saturated with CO_2 after which the feed of the raw biogas is stopped, and blowdown step is initiated. Pressure of the column is lowered gradually which causes the CO_2 to be released from the bed material. Some CH_4 is also absorbed during the process because the column was initially filled with raw biogas, and it is released from the bed material with the CO_2 during pressure decrease. (Vico, Artemio, 2017, pp.142–145)

CO_2 is released from the system to the atmosphere when the pressure reaches its lowest point (Bauer, Hulteberg, 2013, p.24). This exhaust gas contains a small amount of CH_4, about 2%, and should be oxidized or otherwise removed to avoid any CH_4 emissions (Vico, Artemio, 2017, pp.142–145). Purity of the upgraded biomethane varies between 95–98% and when leaving the unit is in high pressure (Vilardi et al., 2020, p.2).

To remove all the remaining CO_2 left on the surface of the bed material, the column is flushed with biomethane or raw biogas. Once the column is completely regenerated, completing the cycle, it is repressurized and the feed is initiated again. One cycles duration varies between 2–10 minutes depending on the design of the system. (Bauer, Hulteberg, 2013, pp.23–27)

Typical system configuration consists of 4 columns as there are 4 steps on the cycle. These columns are usually connected so that the gas exiting from the column during blowdown is used to pressurize another column (Hoyer et al., 2016, pp. 23–24). This decreases the power consumption of the compressors as well as the CH_4 slip of the upgrade process (Bauer, Hulteberg, 2013, pp.23–27).

It is possible to add more than 4 columns into the system to increase the CH_4 yield and to decrease CH_4 loss of the separation process. Alternatively, increasing the complexity of the system increases the initial investment and operation costs. (Hoyer et al., 2016, p.23)

5.3.3 Investment cost and consumables

The PSA upgrade unit doesn't require any heat and it can be operated regardless of the surrounding climate temperature (Vico, Artemio, 2017, pp.142–145). PSA is a dry process which means no water is either consumed and no wastewater is generated in the process. Since the PSA unit requires relatively high pressure it does however consume a significant amount of electricity. There might also be a need for a cooling unit to dry the incoming raw biogas and to cool the compressor unit. (Bauer, Hulteberg, 2013, pp.27–28)

In the report of Hoyer et al. the specific investment cost decreased from approximately 3000 €/Nm^3/h to 1500 €/Nm^3/h as the capacity of the raw biogas increased from 500 Nm^3/h to 2000 Nm^3/h. It is noteworthy that investment cost is not constant for capacity of 2000 Nm^3/h and increasing the capacity will further decrease the specific investment cost. (Bauer, Hulteberg, 2013, pp.27–28)

It has been evaluated that power requirement for PSA unit varies between 0.15–0.3 kWh/Nm^3 raw biogas. Sweden has over 50 biogas upgrading plants, 8 of which are PSA units. Power consumption in these facilities is estimated to be 0.25–0.3 kWh/Nm^3 raw biogas. Variation can be explained with that the cooling unit and possible catalytic oxidizer to prevent CH_4 emission increase the power consumption. (Bauer, Hulteberg, 2013, pp.27–28) The total costs are evaluated to be 0.25 €/Nm^3 raw biogas (De Hullu et al., 2008, p.19).

5.4 Membrane technology

The basic principle in separating CO_2 from CH_4 with membrane technology is that as CO_2 has a smaller molecule size, it passes through the membrane material as the CH_4 is retained (Hoyer et al., 2016, pp. 30–31). Membrane technology is an alternative for conventional biogas upgrading systems although it has been applied to natural gas in the past. Membranes have been used for biogas upgrading for few decades and more selective membranes and processes with higher methane yield are being developed which has increased the interest in membranes as an alternative for conventional technologies. (Bauer, Hulteberg, 2013, pp.28–32)

Most membranes used in biogas upgrade units are sensitive to many impurities present in the raw biogas such as particles, water, H_2S and NH_3 (Hoyer et al., 2016, pp. 30–31). The raw biogas is usually desulfurized, and excess water vapor is removed before it enters the upgrade unit. NH_3 is effectively removed with the water vapor. H_2S is removed before the upgrading process also because it can't be separated to a sufficient extent with typical membranes. It is noteworthy that H_2S and NH_3 are corrosive in the presence of water on the membranes surface damaging it, but moderate concentrations oppose no threat to the membrane if the dew point of the gas is not reached. (Bauer, Hulteberg, 2013, pp.28–32)

Water vapour is removed usually by a cooling unit to prevent condensation during the gas compression. If the raw biogas contains high levels of siloxanes or VOCs, they need to be removed with pre–treatment as well. (Hoyer et al., 2016, pp. 30–31) The pre–treatment unit can also contain a filter to prevent any particles in the feed as they can damage compressors and the membranes (Bauer, Hulteberg, 2013, pp.28–32).

5.4.1 Theoretical background

There are two options for separating CH_4 and CO_2 with membranes, either with gas permeation membrane or with membrane contactors. The permeation membrane system is commonly used, and it is based on the molecular size of the separated gasses. (Scholz, Melin, Wessling, 2013)

Typical membrane material for biogas upgrading is a glassy polymer. The permeation rate of different gas components mainly depends on their molecular size but also the hydrophilicity of the molecules. (Bauer, Hulteberg, 2013, pp.28–32)

There are three types of modules used for gas permeation membranes: hollow fiber, spiral wound, and envelope type modules. Hollow fiber and spiral wound modules have a high packing density and that's why they are most commonly used. (Scholz et al., 2013)

The feed gas stream is separated into two streams in the membrane. The CO_2 stream is the permeate that passes the membrane and the CH_4 stream is the retentate that remains on the original side of the feed. (Bauer, Hulteberg, 2013, p.31) The passing of gas molecules through a dense polymer membrane can be expressed with the equation 15:

$$J_i = \frac{D_i K_i^G (p_{i_0} - p_{i_l})}{l} \tag{15}$$

where J_i is the gas flux, D_i is the permeate diffusion coefficient, K_i^G is the sorption coefficient, p_{i0} is the pressure prior to the membrane and the p_{il} is the pressure after the membrane and l is the thickness of the membrane. (Bauer, Hulteberg, 2013, pp.31–32)

Membrane's ability to separate two gasses from each other is the ratio between their permeabilities over the membrane and is called the membrane selectivity (Baker, 1983, pp.304–305). Membrane selectivity can be calculated with the equation 16:

$$\alpha_{ab} = \frac{P_a}{P_b} \tag{16}$$

where α_{ab} is the membrane selectivity for gas a and b, P_a and P_b is the permeability of gas a and b. (Baker, 1983, pp.304–305)

Permeability of the gas a can be expressed as the product of diffusion coefficient D_a and the sorption coefficient K_a. Diffusion coefficient expresses the movement of individual molecule through the membrane material whereas the sorption coefficient expresses the number of molecules dissolved in the membrane material. (Baker, 1983, pp.304–305) The equation 16 can therefore be written in the following form

$$\alpha_{ab} = \left(\frac{D_a}{D_b}\right)\left(\frac{K_a}{K_b}\right) \tag{17}$$

(Baker, 1983, pp.304–305)

The diffusion coefficient decreases as the size of the molecules increase regardless of the membrane material. Which means that the selectivity of the membrane always favors the movement of smaller particles through the membrane material. (Baker, 1983, pp.304–305)

The partial pressure of the CO_2 between each side of the membrane, shown in the equation 16, is the driving force for the separation process. To achieve a suitable separation efficiency, vacuum is usually used on the permeate side of the membrane. (Bauer, Hulteberg, 2013, p.32)

5.4.2 Process description

There are a lot of different options regarding the process design, depending on type and number of membranes used, as well as manufacturer of the membrane unit (Scholz et al., 2013). After the pre–treatment the purified biogas is pressurized to 5–20 bar and then fed to the membrane unit (Bauer, Hulteberg, 2013, pp.31–32).

The first design option, presented in figure 6, includes no internal circulation of the biogas and therefore has a lower electricity consumption of the compressor, but alternatively increases the CH_4 slip. Membranes with high selectivity are used in systems like these to minimize the CH_4 loss. In addition to CO_2 also water vapor, H_2 and O_2 are removed to some extent from CH_4 stream. Since there is some CH_4 present in the CO_2 stream it is beneficial to use this gas in a CHP or a boiler. To avoid emission the exhaust gas should be oxidized, torched, or otherwise treaded if it’s not utilized (Bauer, Hulteberg, 2013, pp.31–32). Since most of the water vapor is removed prior to the upgrade unit and the significant portion of the remaining vapor leaves the system in the CO_2 gas stream. There is no need for post-treating the biomethane and it can be directly injected to the gas grid or used as a vehicle fuel (Bauer, Hulteberg, 2013, pp.31–32).

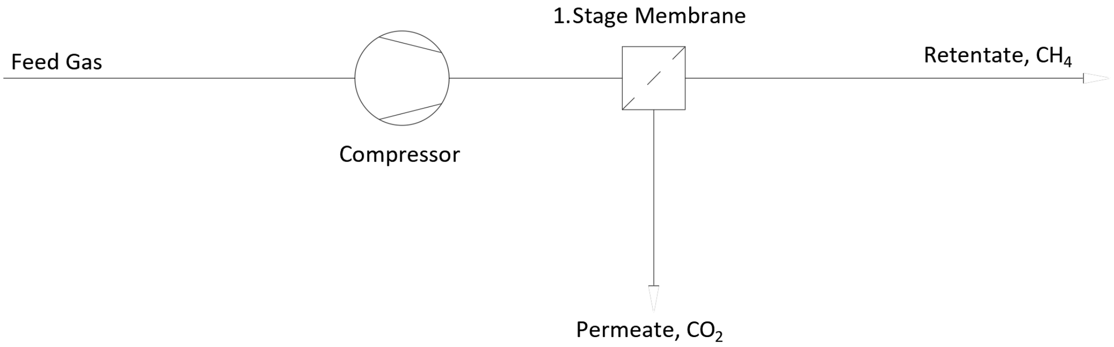

Figure 6 Simplified 1. Stage membrane separation process diagram (Adapted from, Haider, Lindbråthen, Hägg, 2016, p.225)

The two–stage membrane system presented in figure 7, uses dual membranes, and recirculates the retentate from the second membrane back to the compressor unit while the permeate is led out from the system as exhaust gas. This process design increases the methane yield compared to the single state process. The circulation system increases the compressor units' electricity consumption. Recovery of CH_4 of this kind of systems varies between 98–99%. (Bauer, Hulteberg, 2013, pp.31–32)

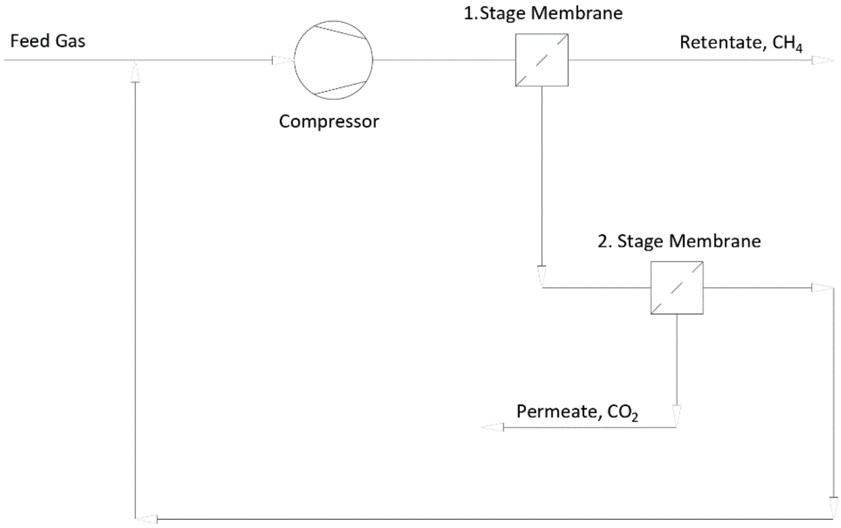

Figure 7 Simplified 2. stage membrane separation process diagram (Adapted from, Haider et al., 2016, p.225)

In three state membrane process design presented in figure 8, the permeate from the first membrane is treated again just like in two stage process. The difference is that also the permeate from the first membrane is polished with a third membrane. The permeate from the second membrane and the retentate from the third membrane are mixed and the gas blend is recirculated back to the compressor. CH_4 recovery of this kind of systems varies between 99–99,5%. (Bauer, Hulteberg, 2013, pp.31–32) Four stage processes are currently being developed to further increase the CH_4 yield (Hoyer et al., 2016, pp. 30–31).

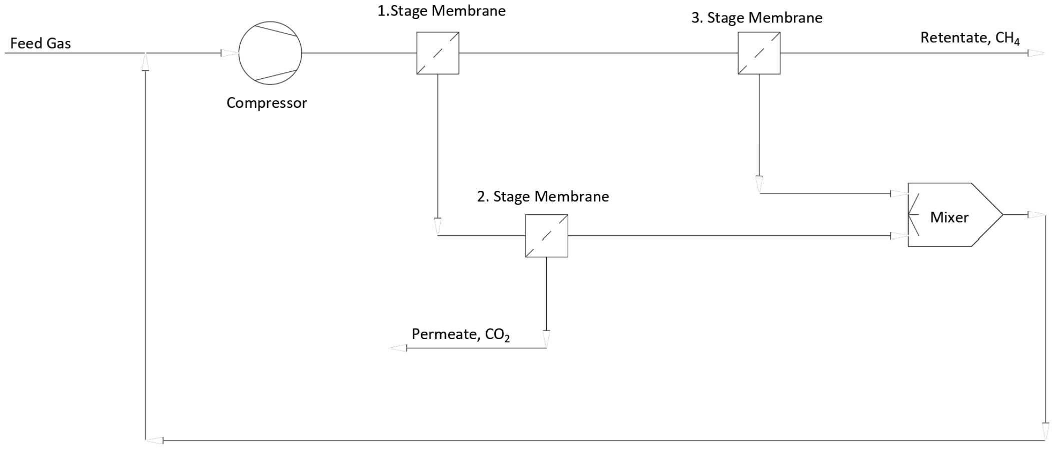

Figure 8 Simplified 3. stage membrane separation process diagram (Adapted from, Haider et al., 2016, p.226)

The most common options are the two stage, and three stage process designs. They provide a higher methane yield compared to the simpler one stage process. (Bauer, Hulteberg, 2013, pp.31–32)

5.4.3 Investment cost and consumables

Selective membranes combined with suitable design are required to be able to obtain high purity biomethane with minimal CH_4 slip. Process design of the membrane unit is flexible and can be tailored according to the plant's specific needs and energy consumption and purification grade can be optimized. (Bauer, Hulteberg, 2013, p.33) Membranes are continuously improved to increase the efficiency by gaining higher permeability ad better selectivity and to reduce production costs.

The investment cost of a membrane upgrading unit depends strongly on the design and requirements of the system. In the report of Bauer and Hultenberg the estimated specific investment cost became constant around 2000 €/Nm^3/h when the feed flow of the raw biogas exceeded 800 Nm^3/h. (Bauer, Hulteberg, 2013, p.33)

The electricity consumption of the membrane upgrade unit depends on the electricity used by the compression unit which in turn depends on the total feed flow as well as the complexity of the system. Complexity of the system, with the number of membranes and recirculation systems used, increases along with the purification requirements and when the CH_4 slip is minimized. The electricity consumption can be estimated to vary between 0.2–0.3 kWh/Nm^3 of raw biogas. (Bauer, Hulteberg, 2013, p.33) The total costs without H_2S removal are evaluated to be 0.12 €/Nm^3 raw biogas (De Hullu et al., 2008, p.31).

Biomethane upgraded with membranes fulfills the purity requirements of the gas grid and can be directly injected without any post–treatment. The purity of the biomethane obtained with the membrane upgrade unit can be over 98% and many suppliers guarantee this grade for the product. (Bauer, Hulteberg, 2013, p.33)

The downtime of the unit is usually under 5% and there are existing plants with just 2% downtime annually. Costs of service agreements usually vary between 3–4% of the total investment cost. The membrane upgrade unit doesn’t use any consumables part from the oil used in the compressor unit (Bauer, Hulteberg, 2013, p.33).

The lifetime of the membranes depends on the quality of the feed gas and presence of impurities can lower the lifetime of the membranes significantly. Lifetime of the membranes is estimated to be 5–10 years but there are existing biogas upgrading plants that have been using the same membranes over 10 years. (Bauer, Hulteberg, 2013, p.33)

5.5 Cryogenic technology

Cryogenic separation is based on different boiling points of gasses. CH_4 has a lower boiling point, –161.5°C, compared to CO_2. –78.2°C, thus CO_2 can be removed from the raw biogas by condensation. (Vico, Artemio, 2017, pp.145–148) It is possible to separate O_2 and N_2 from the raw biogas with cryogenic separation if the CH_4 is condensed. (Sun et al., 2015)

An extremely pure CO_2 can be obtained from the cryogenic separation process as a side product (Sun et al., 2015, p.529).

The purity of the biomethane obtained from the process is 95–99% (Bragança et al., 2020) The methane slip is during the process is usually under 1% (Allegue, Hinge, 2020, pp.40–42).

The cryogenic separation process is considered a new technology and it is still under development even though there are a few small–scale operational plants (Ullah Khan et al., 2017, pp.283–284). The existing cryogenic upgrade plants are small scale (280–400 Nm^3/h raw biogas) facilities, and they are reported to have severe operational issues (Bauer, Hulteberg, 2013, p.60) Cryogenic separation can be a noteworthy option when the end goal is to produce liquefied biomethane (LBG) (Ullah Khan et al., 2017, pp.283–284).

5.5.1 Process description

Cryogenic separation process can be divided into 4 steps which are pre–treatment of the raw biogas, gas compression, gas cleaning and CO_2 removal (Ullah Khan et al., 2017, pp.283–284). The simplified process diagram of the cryogenic upgrade system is presented in figure 9.

There are several process designs options, but typically during the process the pressure is elevated to approximately 40 bars and temperature reduced to approximately –90 °C (Allegue, Hinge, 2020, pp.40–42). During the first step major impurities like H_2S, water, siloxanes and other undesirable components of the raw biogas are removed. (Ullah Khan et al., 2017, pp.283–284) Possible siloxanes and VOC are removed during the cooling and condensation processes (Ullah Khan et al., 2017, pp.283–284). To remove any remaining impurities the gas can be filtered before the distillation process (Allegue, Hinge, 2020, pp.40–42).

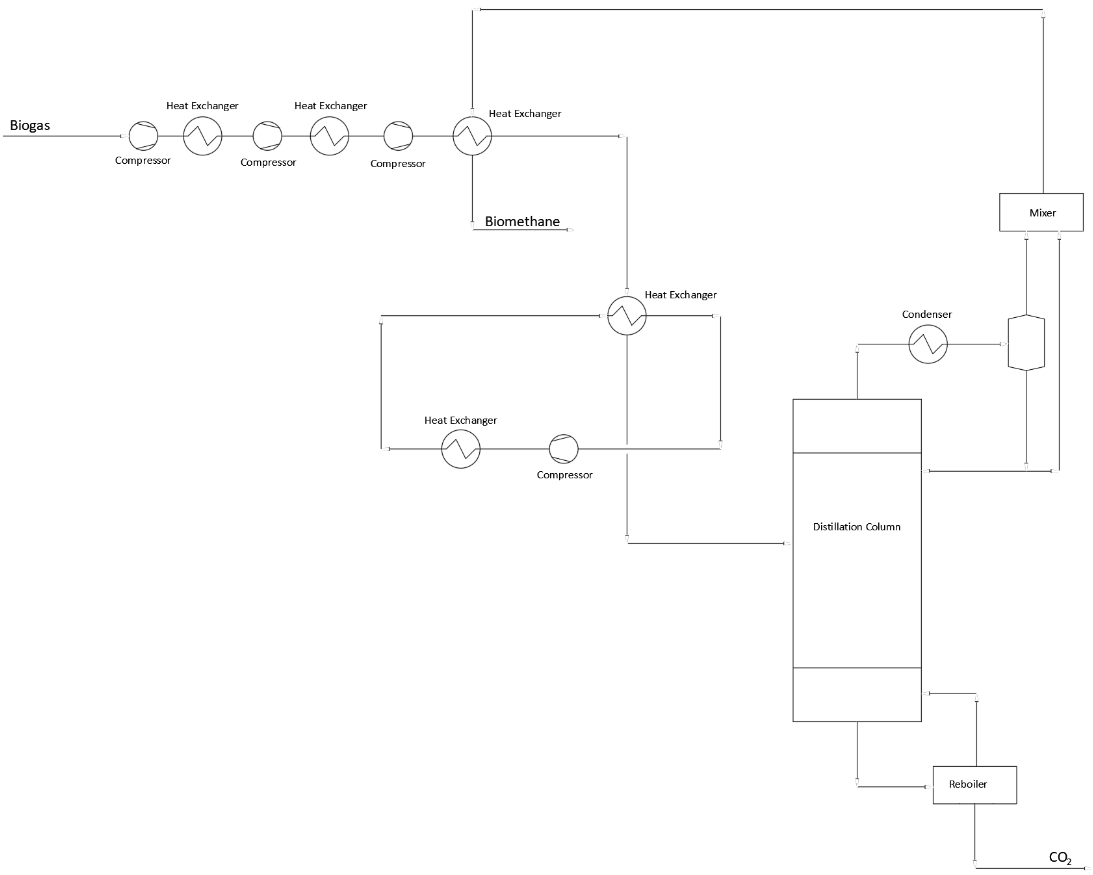

Figure 9 Simplified Cryogenic upgrade unit process diagram (Adapted from, Esfandiyar, Alireza, Hossein, 2022, p.4)

According to the simplified diagram, presented in figure 9, the pressure of the biogas is elevated in a 3-stage process to over 40 bar pressure. The temperature of the gas is lowered to −70 ◦C with a series of heat exchangers prior to the distillation column. The low temperature of the biomethane leaving the distillation column is used to cool the compressed biogas entering the column. The final cooling before the distillation is done with a refrigerant loop. (Esfandiyar et al., 2022, p.3)

The temperature is the lowered to –85 °C to liquefy the CO_2. When raw biogas is cooled under elevated pressure the CO_2 can be liquefied while the CH_4 remains in a gaseous form which makes it possible to separate them from each other. In ambient pressure CO_2 sublimates directly to solid form, creating dry ice. (Bauer, Hulteberg, 2013, p.60)

The solubility of CH_4 is higher to liquid CO_2 and to minimize the CH_4 slip, freezing or sublimation of the CO_2 can be used. This kind of system is usually a batch process where there are two parallel process lines where CO_2 is allowed to freeze in a heat exchanger until the capacity of the equipment is reached after which the line is changed, and the heat exchanger is defrosted, and the CO_2 removed in a liquid or gaseous stage. (Ullah Khan et al., 2017, pp.283–284)

The obtained biomethane is extremely pure and can be either injected to the gas grid or further cooled to create LBG (Allegue, Hinge, 2020, pp.40–42). When producing LBG the pressure of approximately 80 bar and a low temperature −170 °C is needed (Vico, Artemio, 2017, pp.145–148).

5.5.2 Investment cost and consumables

In a study made by Esfandiyar et al. the costs for cryogenic separation process for biogas were evaluated with a simulated process (Esfandiyar et al., 2022, p14). The main costs evaluated are presented in table 11.

Table 11 The main costs of the cryogenic upgrade unit from a simulated process (Esfandiyar et al., 2022, p14)

	USD	€
Energy costs	252 407	234 739
Investment cost	10 303 200	9 581 976
Equipment costs	3 471 800	3 228 774
Installation costs	1 111 600	4 262 562
Total annual costs	3 686 807	3 428 731

Table 11 shows that the total investment cost for cryogenic system was almost 10 million € of which the share of the equipment was over 3 million. The raw biogas flow for simulation was 600 m^3/h and the payback period for the equipment 5 years (Esfandiyar et al., 2022, p.14). The total costs for upgrade process are evaluated to be 0.44 €/Nm^3 raw biogas (De Hullu et al., 2008, p.27).

The electricity consumption of the process including the upgrading and the liquefaction is estimated to vary between 1.4–.8 kWh/kg LBG which equals 1.7–2.10 kWh/Nm^3 raw biogas (Spoof-Tuomi, 2020, p.22). It has been estimated that energy equivalent of 5–10% of the produced biomethane is consumed by the process (Sun et al., 2015, p.524).

5.6 Summary of upgrade technologies

According to the report made by Allegue & Hinge the dominating processes used in the industry today are water scrubbing, PSA and amine scrubbing and lists the membrane separation still as developing technology along with cryogenic technique. (Allegue, Hinge, 2020, pp.40–42) The report made by Hoyer et al. supports this view but also mentions that membrane separation technology is slowly increasing its popularity due to development of the high selective low-cost membrane materials whereas cryogenic separation technology is still struggling with operational issues even though there is a large interest towards it. (Hoyer et al., 2016)

5.6.1 Advantages and disadvantages

The advantages and disadvantages of different upgrade technologies are presented in table 12. It is possible to achieve a high CH_4 purity and low CH_4 slip with all the technologies reviewed (Table 12)

Table 12 Advantages and disadvantages of upgrade technologies (Adapted from 1)Adnan et al., 2019, p.4–8; 2) De Hullu et al., 2008, p.34; 3) Ryckebosch et al., 2011, p.1640; 4) Vico, Artemio, 2017, p.144)

Technology	Advantages	Disadvantages
Water scrubbing	• Low methane loss (3 • High methane purity (1 • No use of chemicals (2 • Can be used to remove small amounts of H_2S (2,3 • Low operating and maintenance costs (1 • Well known and simple process (1,2	• High water consumption (1,2 • High operating costs (3 • Risk of clogging due microbiological fouling (1,3 • Risk of foaming (3
Amine scrubbing	• Low methane loss (1,3 • High methane purity (1,3 • Faster and more CO_2 dissolved per unit of volume compared to water scrubbing (1	• High heat consumption (1 • Requires pre–treatment (1 • Risk of foaming (1 • Corrosion (3 • Possible problems from handling the amine (1
Pressure swing adsorption	• Low methane loss (1 • High methane purity (1 • No use of chemicals (1 • Possibility to remove N_2 and O_2 (2 • High pressure product (4	• Complex process (1 • Pretreatment required depending on the system (1 • Energy consumption increases to obtain higher purity of the product gas (1
Membrane	• Low energy consumption depending on the simplicity of the system (3 • Low cost (1 • No use of chemicals • Simple process (1,2 • Low maintenance (2 • High reliability	• Pretreatment is required (1 • Energy consumption increases to obtain higher purity of the product gas (3 • New process compared to other commercial techniques (3
Cryogenic	• Low methane loss (1 • High methane purity ((1 • No use of chemicals (1 • Lower energy consumption compared to other methods when producing LBG (1 • High purity CO_2 can be obtained (3	• Technology is still under development (1 • High investment and operating costs (1 • Pretreatment is required (1 • High energy demand (1

Water scrubber is the only system that has a high water consumption. Water scrubbing is usually found to be the simplest and cheapest option of all the commercial upgrade technologies. (Table 12) Water scrubbing is the least sensitive to impurities withing the raw biogas of all the upgrade methods currently in commercial use and usually biogas can be directed directly to the upgrade unit from the digester. (Bauer, Hulteberg, 2013, pp.34–43)

Compared to chemical adsorption using water as a solvent is a more environmentally friendly and operating the process is simpler. Water as a solvent is also economically more appealing and usually there is an unlimited supply and easy access to water with high enough quality to use in the process. The process is also less energy intensive compared to chemical adsorption regarding the CO_2 recovery process. (Vico, Artemio, 2017, pp.138–140)

Amine scrubbing isn't a new technology, but it is not as old and common as water scrubbing or PSA. Amine scrubbing is considered a mature technology, but it is still under constant development to increase the efficiency. (Hoyer et al., 2016, pp. 24–25) Amine scrubbing is the only technology that uses chemicals and requires heat to regenerate the amine (Table 12).

The amount of electricity used in the process is lower compared to many other upgrade technologies, but the heat requirement of the amine regeneration is high. Since the systems usually operates at a low pressure, the total energy consumption is lower compared to the other technologies when the required CH_4 stream has no pressure requirement. (Table 12) When high end pressure is needed, additional compression of the biomethane increases the electricity consumption. (Hoyer et al., 2016, pp. 24–25)

Due to the higher solubility of CO_2 to amine compared to water, the amount of process media that needs to be circulated through the process is smaller compared to water scrubbing (Table 12). This also decreases the column sizes needed for the process compared to water scrubbing. (Bauer, Hulteberg, 2013, pp. 24–25)

Both water scrubbing and amine scrubbing systems have a risk of foaming (Table 12). Because the pH of the process media is high, there is only a minimal risk for microbiological fouling unlike in water scrubbing systems. (Bauer, Hulteberg, 2013, pp.34–43)

PSA can be used to remove possible N_2 and O_2 from the biogas but the process itself is complex (Table 12). The capital costs of the PSA unit are regarded to be high as well as the operating costs (Vico, Artemio, 2017, pp.142–145). One disadvantage of PSA technology is the complex process control. Also need for pre–treatment of the raw biogas and the possible post-treatment of the exhaust gas increase the operating costs. (Vico, Artemio, 2017, pp.142–145)

The main advantages of membranes in biogas upgrading are that they require no chemicals or water and can be scaled easily without significant efficiency losses. (Pettersson, Wellinger 2009, p.11) Compared to the other upgrade technologies membranes also have other advantages like low capital and operational costs, easy installation, operation and maintenance as well as compact modular design that decreases the area requirement. (Haider, Lindbråthen et al. 2016, p. 223) To achieve a high purity methane product multiple stage membrane system is required which increases the electricity consumption of the process (Table 12).

Cryogenic upgrading technology is expected to have several benefits compared to conventional upgrading methods. There is no contact between the chemicals and the treated gas. (Hoyer et al., 2016, pp. pp.58–66) Cryogenic separation is the only upgrade technology that can be used to produce CO_2 that meets the quality demands of the pipeline transportation without post-treatment (Sun et al., 2015, p.529). When producing vehicle fuel, cryogenic separation may be considered as a superior technology compared to other upgrading methods because it is possible to produce LBG directly without additional liquefaction unit (Hoyer et al., 2016, pp. pp.58–66; Sun et al., 2015, p.529).

The main drawback of the cryogenic upgrade process, beside the fact that it is still under development, is that it requires a lot of different process equipment, such as compressors and heat exchangers, as well as a lot of energy to maintain these conditions. The operating as well as the capital costs of the system are considered to be high compared to the costs of other upgrade technologies. (Vico, Artemio, 2017, pp.145–148)

Even though CO_2 can be obtained from the process the production costs are high. Other disadvantage is that the efficiency of the process depends on the surrounding temperature and operating in a hot environment decreases the efficiency of the process. (Baena-Moreno et al., 2019, p.1256)

5.6.2 Economical comparison

The purity of the produced biomethane, operating costs and the specific investment costs vary between different technologies. The key figures for different upgrade systems are presented in table 13.

Table 13 Key technical figures of different upgrade technologies (Adapted from 1) Allegue, Hinge, 2020, p.45; 2) De Hullu et al., 2008, p.34; 3) Deng et al., 2020, p.241; 4) Sun et al., 2015, p.523; 5) Wellinger, Murphy, Baxter, 2013, p.369)

Technology	**CH_4 purity (%)**	**CH_4 slip (%)**	**H_2S removal prior to the unit**	**Electricity consumption (kWh/m^3 raw biogas)**	**Heat consumption (€/m^3 raw biogas)**	**Total costs (€/m^3 raw biogas)**	**Specific investment costs (€/m^3 raw biogas/h)**
Water scrubbing	98–99.5 (1,4	1–2 (1,4	No, if concentration is moderate (3	0.25–0.3 (1	– (1	0.15 (2	1500 (5
Amine scrubbing	95–99.9 (1,4	0.1–0.2 (1,4	Yes (3	0.1–0.25 (1	0,5–0,75 (1	0.17 (2	1500 (5
Pressure swing adsorption	90–98.5 (1,4	1–10 (1,4	Yes (3	0.25–0.3 (1	– (1	0.25 (2	1500 (5
Membrane	85–99 (1,4	1–15 (1,4	Yes (3	0.18–0.21 (1	– (1	0.12 (2	2000 (5
Cryogenic	98–99.9 (1,4	0.1–2 (1,4	Yes (3	0.2–1.05 (1	– (1	0.44 (2	Data not available (5

The table 13 shows that CH_4 purity is over 95% for all units but for PSA and membrane separation processes there is a need for a multi–stage process to be able to produce high purity product which increases the power consumption of the unit (Hoyer et al., 2016, pp. 23–32). The CH_4 slip for these units also depends on the complexity of the system. For other units the CH_4 slip is less than 2%.

The water scrubbing is the least sensitive system for H_2S but also needs pre–treatment step if the concentrations are high (Deng et al., 2020, p.241).

Table 13 shows that the electricity consumption of different types of upgrade units is quite similar varying between 0.2–0.3 kWh/m^3 apart from amine scrubbing which consumes about half of that electricity amount than other technologies. However, amine scrubbing is the only technology that also consumes heat in addition to electricity to regenerate the amine (Allegue, Hinge, 2020, p.45).

Total costs for the upgrade units vary between 0.12–0.44 €/m^3 raw biogas (Table 13). The capacity of the systems was se to be 250 m^3/h raw biogas, with 60% methane content, interest rate of the investment to 6% and the payback period to 3 years for these evaluations. (De Hullu et al., 2008, pp.8–43). The cryogenic system has the highest operating costs, but it is not directly comparable to other systems because it is usually used to produce LBG (Ullah Khan et al., 2017, pp.283–284). The PSA has the highest and membrane separation the lowest operating costs of the conventional biogas upgrade technologies. The operating costs of these systems depend on the complexity (Hoyer et al., 2016, pp. 23–32). The operating costs for water and amine scrubbing systems are roughly the same.

The specific investment costs vary between 1500–2000 €/m^3 raw biogas/h for all technologies according to the study by Wellinger & Murphy in 2013. It was also discovered that the cost regression was marginal after the upgrade capacity of the system surpassed 1000 m^3 raw biogas/h. The study concluded that the costs were comparable for all the technologies between upgrade capacities of 700–1400 m^3 raw biogas/h. (Wellinger et al., 2013, p.369)

6 Materials and methods

As mentioned in the chapter 2 of this thesis, using feedstock with high protein content, such as slaughterhouse waste, chicken manure or fishery waste, may lead to higher H_2S levels than normally found in the raw biogas. The biogas composition was studied to determine the average level of H_2S produced during the fermentation process to better evaluate a suitable desulfurization method.

Different commercial biogas upgrade and liquefaction units were compared from an economical perspective based on received quotes. Comparison was done based on capital expenditures (CAPEX), operating expenses (OPEX) and heat and electricity sensitivity of these systems.

6.1 Method of producing and measuring the composition of H2S-rich biogas

H_2S-rich biogas formation has been studied in the laboratory scale reactors presented in figure 10. The effects of different feedstocks and process conditions to the gas production and composition can be studied with these tests.

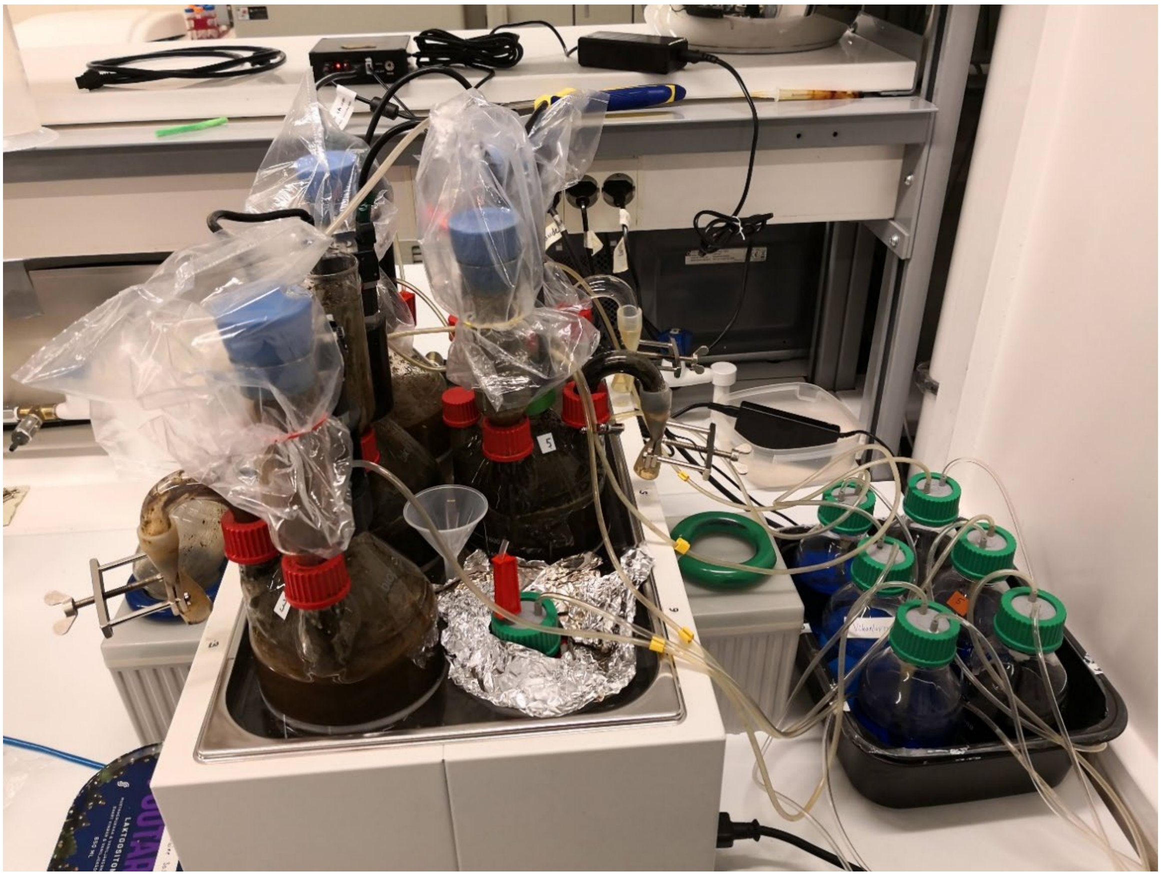

Figure 10 Ongoing laboratory scale bioreactors

The laboratory scale bioreactor setup can be seen in figure 10. Reactors were kept in a steady temperature with a water bath and constantly stirred with mixers. Biogas data from an experiment that best reflected the normal process conditions during the anaerobic digestion process was selected to obtain reliable information of the biogas composition during normal operation. (Koskenniemi, 2019) The main process conditions and operating parameters of BioReactor Simulators (BRS) are shown in table 14.

Table 14 Conditions and process parameters used in BRS3, BRS4 and BRS5 (Koskenniemi, 2019)

	BRS5	BRS3-4
Volume (l)	2	2
Temperature	50	50
TS (%)	8	8
HRT (days)	7	25

It can be seen in table 14 that the reactors had the same operating conditions. Only the hydraulic retention time (HRT) was longer in the BRS3 and BRS4 compared to BRS5. (Table 14)

The experiment set up is presented in figure 11. Bioreactor BRS5 was fed with chicken manure and liquid obtained from decanting the sludge from parallel bioreactors BRS3 and BRS4.

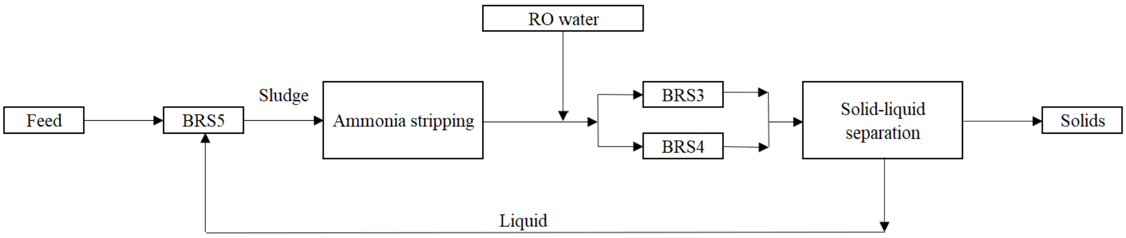

Figure 11 Block diagram of the experiment system (Koskenniemi, 2019)

Separate ammonification process reactor was represented by the BRS5. Separated ammonification is a pre-treatment process for the actual biogas fermentation (Virkajärvi, 2022). The main biogas fermenter was represented by the parallel reactors BRS3 and BRS4. The ammonia stripped sludge was fed to the bioreactor BRS3 and BRS4 along with reverse osmosis (RO) purified water as seen in figure 11.

Biogas composition from BRS3 was measured between 8.4.2019–17.12.2019. Dataset of these measurements was obtained from an internal report by Koskenniemi (2019). The unreliable measurement results, due to short measurement time (<150 s) were filtered out from the data set. The raw unfiltered data is presented in appendix 1.

6.2 Method of economical comparison

The capacity of the upgrading and liquefaction systems was chosen to be approximately 1700 m^3 raw biogas/h. The annual CAPEX was calculated with a 10 year payback period with an interest rate of 5%. The price for the heat and electricity was chosen to be 0.1 €/kWh.

The CAPEX included the necessary equipment as well as installation and commissioning of the system. The needed equipment depends on the technology and the specific system design, but mainly include pumps, heat exchangers, coolers, columns, instruments, valves, and piping. The main equipment for each system is covered in chapter 5 of this thesis. The total investment costs are confidential and are expressed as X for the cheapest unit and the cost for the other units as the multiplier of X.

The OPEX included electricity, heat, and maintenance costs. There are also other expenses for these systems such as water, chemical and waste disposal costs but their share of total costs was evaluated to be insignificant and therefore not included.

Not all quotations included maintenance costs, and these were evaluated as an average based on other quotations to make the quotations comparable with each other. According to the quotations, 70–80% of the applied heat in the amine scrubbing systems could be recovered to use in other processes in the biogas plant. However, it was evaluated that a majority of the heat available from these systems is low grade and only 20–30% of the total heat applied could be recovered. These heat recoveries were deducted from the total heat consumption of these units. The 10% difference between amine scrubbing systems heat recovery potential is based on the supplier's evaluation of the of the distribution of the low and high grade heat streams available.

7 Results

In this chapter results of biogas data analysis and the commercial data obtained from received system quotations are presented.

7.1 Hydrogen sulfide-rich biogas

The results of biogas composition measurements from BRS3 between 8.4.2019–17.12.2019 are shown in figure 12. Amount of O_2 stayed below 4% for the entire measurement period and was left out from the graphical presentation because it is not relevant for this study.

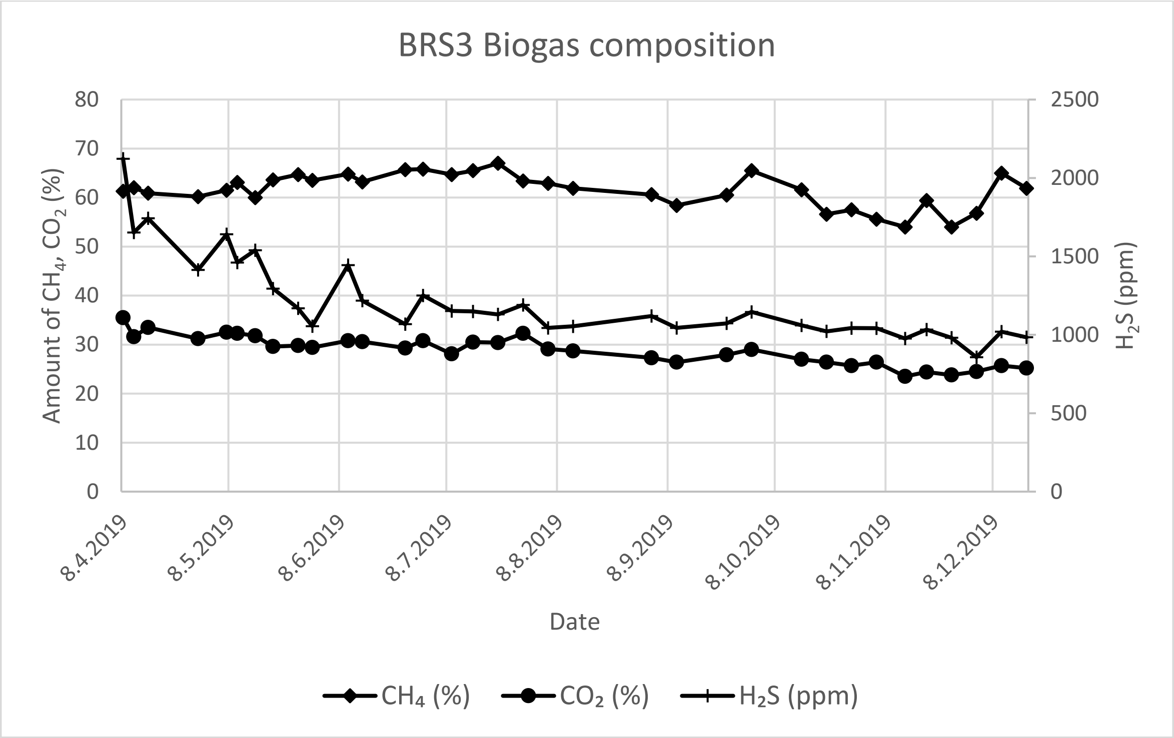

Figure 12 Biogas composition of the test reactor BRS3 during 8.4.2019–17.12.2019 (Adapted from, Koskenniemi, 2019)

The H_2S concentration fluctuated at the beginning of the test period and values over 2000 ppm can be seen in figure 12. The H_2S level gradually dropped but the concentration mainly stayed above 1000 ppm till the end of the experiment. The average values of the gas components during the measurement period are presented in table 15.

Table 15 Average biogas component values in test reactor BRS3 between 8.4.2019–17.12.2019 (Adapted from, Koskenniemi, 2019)

Reactor	**CH_4 (%)**	**CO_2 (%)**	**O_2 (%)**	**H_2S (ppm)**
BRS3	61	29	1	1200

It can be seen in table 15 that during the test period average amount of H_2S was 1200 ppm. The amount of H_2S produced during the test period was greater compared to a traditional biogas production process. (Table 15)

7.2 Economical comparison

The results for economical evaluation of biogas upgrade systems for grid injection and liquefaction systems are presented in this chapter. Results include the distribution of the CAPEX and OPEX, key consumption figures as well as the electricity and the sensitivity analysis.

7.2.1 Systems for grid injection

Quotations for two different amine scrubbing, two water scrubbing and one membrane separation unit to produce biomethane for grid injection were compared. The total costs per one cubic meter of treated biogas for these units can be separated to operating and capital costs shown on figure 13.

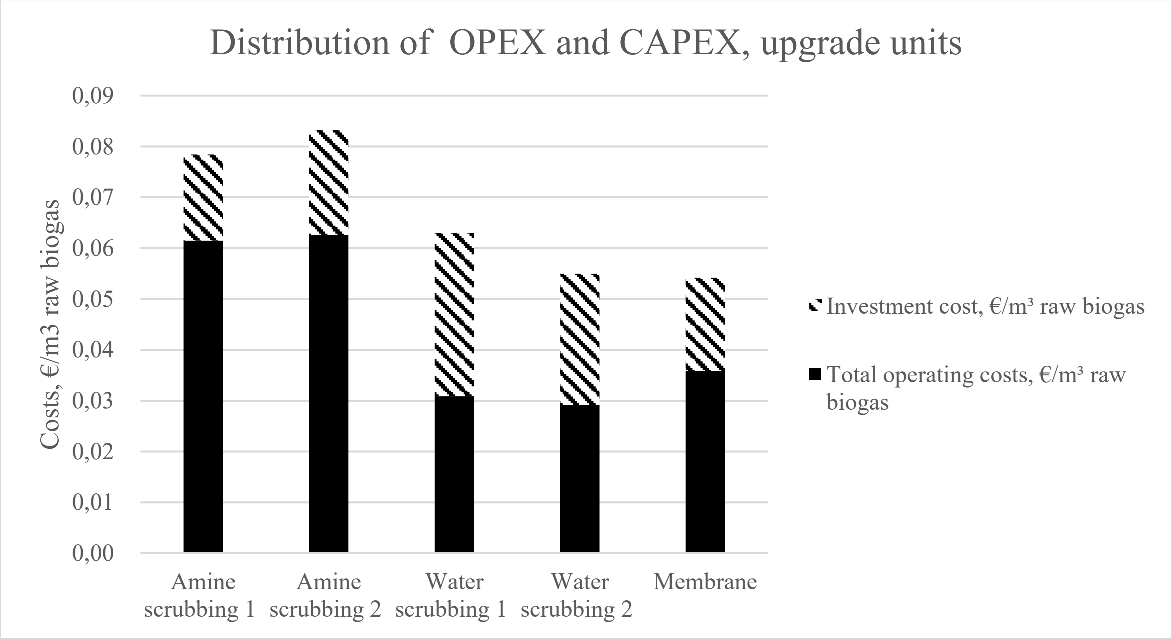

Figure 13 Operating and investment costs for biogas upgrade units

The two amine scrubbing systems have the highest total costs of 0.079–0.082 €/m^3 raw biogas with the majority of the price consisting of operating costs. The total costs for the two water scrubbing units vary between 0.055–0.063 €/m^3 raw biogas and approximately half of the expenses come from the investment costs. The total costs for the membrane unit are roughly the same as for the water scrubbing systems but a smaller portion consists of initial investment cost. (Fig 13)

The electricity and heat consumption as well as from the investment payback of the upgrade systems vary. The key figures obtained from upgrade unit quotations are presented in table 16.

Table 16 Key figures from the upgrade unit quotations

Technology	Amine Scrubbing 1	Amine scrubbing 2	Water Scrubbing 1	Water Scrubbing 2	Membrane
Investment cost, €	X	1.21 X	1.85 X	1.51 X	1.07 X
Electricity consumption, kWh/m^3 raw biogas	0.07	0.11	0.25	0.23	0.30
Heat consumption, kWh/m^3 raw biogas	0.49*	0.46**	–	–	–

* 30% of used heat is evaluated to be recovered to other processes
** 20% of used heat is evaluated to be recovered to other processes

The amine scrubbing systems and the membrane system have the lowest initial investment costs compared to the two water scrubbing systems. Amine scrubbing systems have the lowest electricity consumptions varying between 0.7–0.11 kWh/m^3 raw biogas depending on the supplier. The water scrubbing units consume over twice as much electricity compared to the amine scrubbing systems and membrane unit has the highest electricity consumption of all the options. (Table 16)

The distribution of CAPEX and OPEX for each case are represented on figure 14. The share of the OPEX is divided to heat, electricity, and maintenance costs.

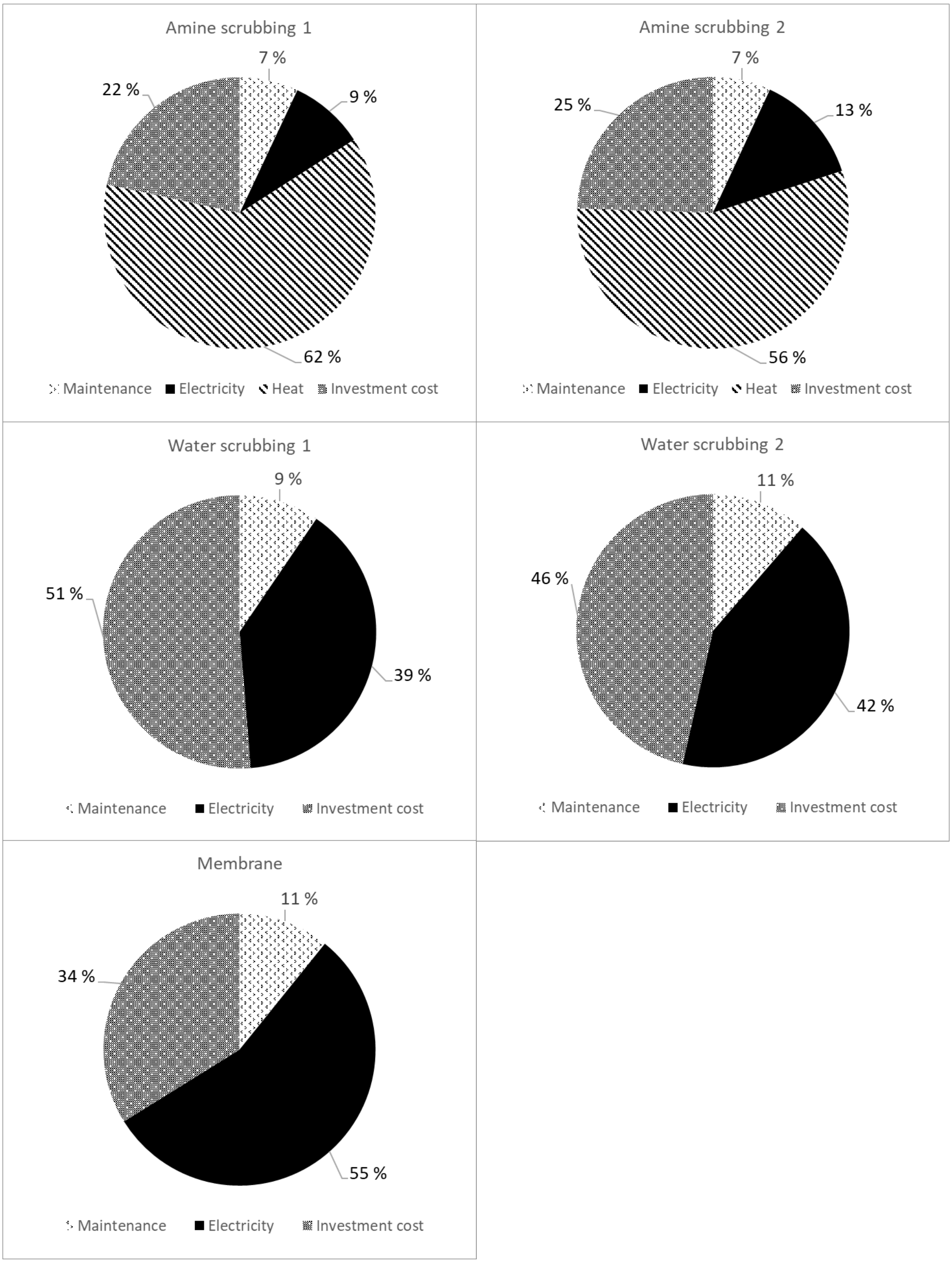

Figure 14 Cost distribution of the upgrade systems

The main share of the costs for amine scrubbing systems 56–62% consists of heat costs and 22–25% of investment costs. Share of electricity costs are 9–13% and maintenance costs are 7% for both units. The largest share of total costs for both water scrubbing systems consists of investment costs. The electricity costs vary between 39–42% and the maintenance costs are between 9–11%. The main share of 55% of total expenses for the membrane unit consists of the electricity consumption, investment costs are 34% and the maintenance costs 11%. (Fig. 14)

7.2.2 Systems for liquefaction

There are three quotations for upgrade units paired with liquefaction units, two of which use membrane separation and the third one amine scrubbing to upgrade the biogas. Liquefaction is done with a cryogenic unit. There are also two separate quotations for cryogenic upgrade units that produce LBG. The total expenses per one cubic meter of treated biogas for these units can be separated to OPEX and CAPEX presented on figure 15.

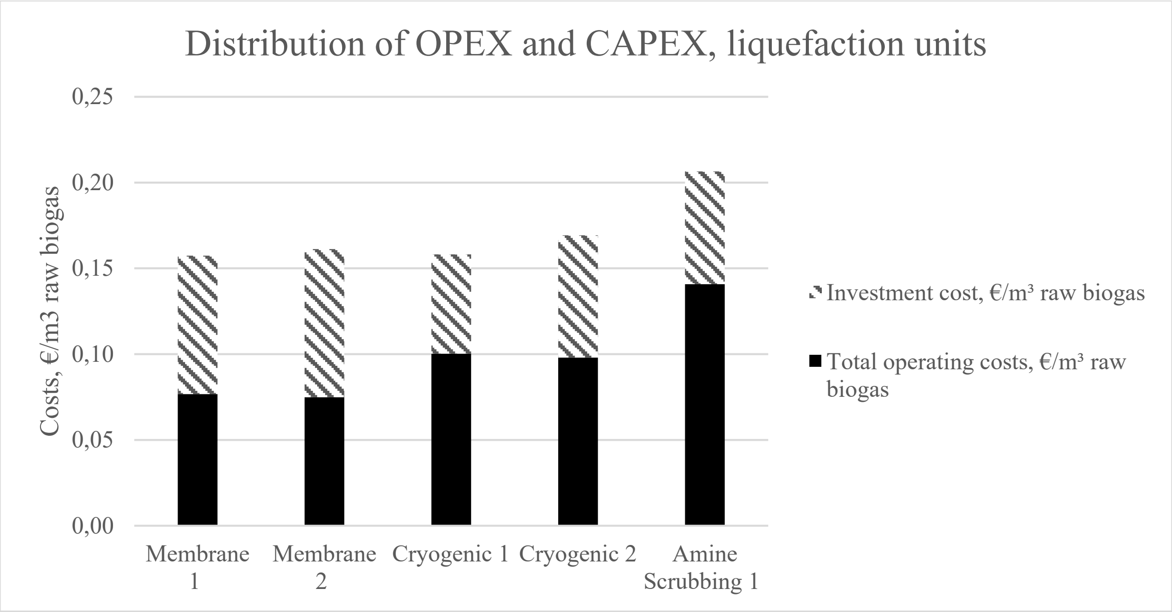

Figure 15 Operating and investment costs for biogas liquefaction units

Total costs of membrane units are approximately 0.16€/m^3 raw biogas. Over half of the total costs consist of CAPEX for both membrane systems. Both cryogenic separation units have a roughly the same total costs of which over half consists of OPEX. The amine scrubbing system has the highest total expenses of 0.21 €/m^3 raw biogas out of the five units. The majority of almost 70% of the price consists of operating costs. (Fig. 15)

Power and heat demand of the liquefaction systems vary. The key figures from upgrade unit quotations are presented in table 17.

Table 17 Key figures from upgrade and liquefaction quotations

Technology	**Membrane 1**	**Membrane 2**	**Cryogenic 1**	**Cryogenic 2**	**Amine Scrubbing**
Investment cost, €	1.42 X	1.51 X	X	1.24 X	1.12 X
Electricity consumption, kWh/m^3 raw biogas	0.70	0.64	0.83	0.86	0.77
Heat consumption, kWh/m^3 raw biogas	–	–	–	–	0.56*

* 20% of used heat is evaluated to be recovered to other processes

It can be seen in table 17 that the capital investment cost for the cryogenic unit 1 is the lowest following closely by amine scrubbing system and the cryogenic system 2. The investment costs for the membrane units are the highest.

The electricity consumption of the units varies between 0.64–0.86 kWh/m^3 raw biogas. The two membrane units have the lowest electricity consumption figures and the cryogenic units the highest. The amine scrubbing system ranks between these four systems. Amine scrubbing unit is the only one that consumes heat in addition to electricity. It was evaluated that 20% of the heat applied to the system could be recovered as useable heat for other processes of the biogas plant.

The more precise composition of the totals costs for each unit are represented on figure 16. There are also other expenses such as water, chemical and waste disposal costs but their share of total costs was evaluated to be insignificant.

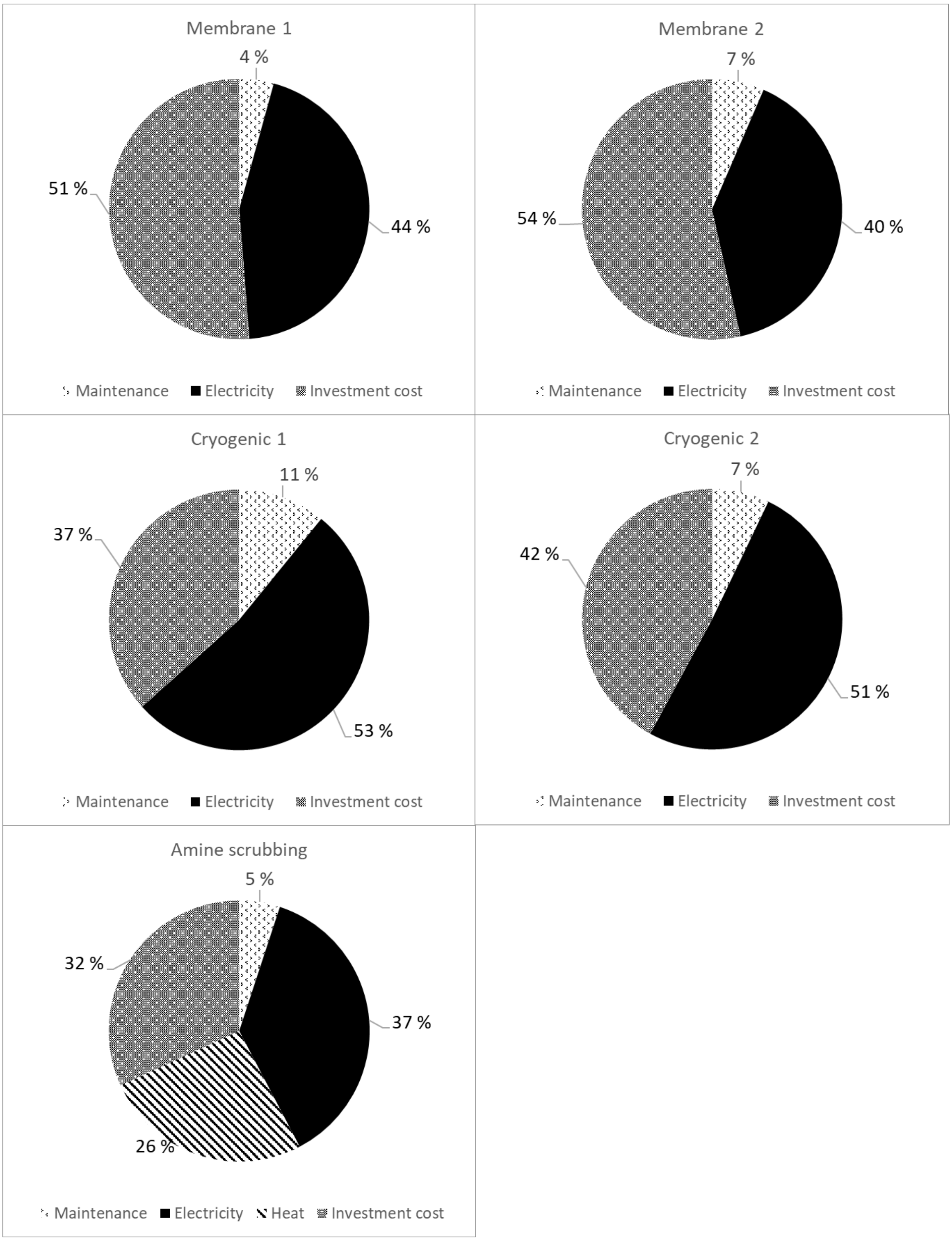

Figure 16 Cost distribution of the liquefaction systems

The distribution of the total costs of the two membrane units are roughly the same with 40–44% of the total expenses coming from electricity consumption and 51–54% coming from investment cost. Maintenance costs are evaluated to be 4–7%. The electricity consumption shares for cryogenic units varies between 51–53% and the share of investment costs varies between 37–42%. The maintenance costs for the cryogenic units vary between 7–11%. The maintenance cost for amine scrubbing system is 5% of the total costs. The share of initial investment costs is 27% and the electricity consumptions share is 37%. Amine scrubbing unit is the only system that uses heat, and its share of the total expenses is 26%. (Fig.16)

7.2.3 Electricity price sensitivity analysis

The electricity price fluctuation causes changes to the OPEX of the biogas upgrade and liquefaction systems. Some units can be more sensitive to electricity price increasing and it is important factor when choosing a propriate biogas upgrade or liquefaction system for a project.

7.2.3.1 Systems for grid injection

Some of the upgrade units are more energy intensive regarding the electricity consumption. The electricity sensitivity for the biogas upgrade systems total costs is shown on figure 17.

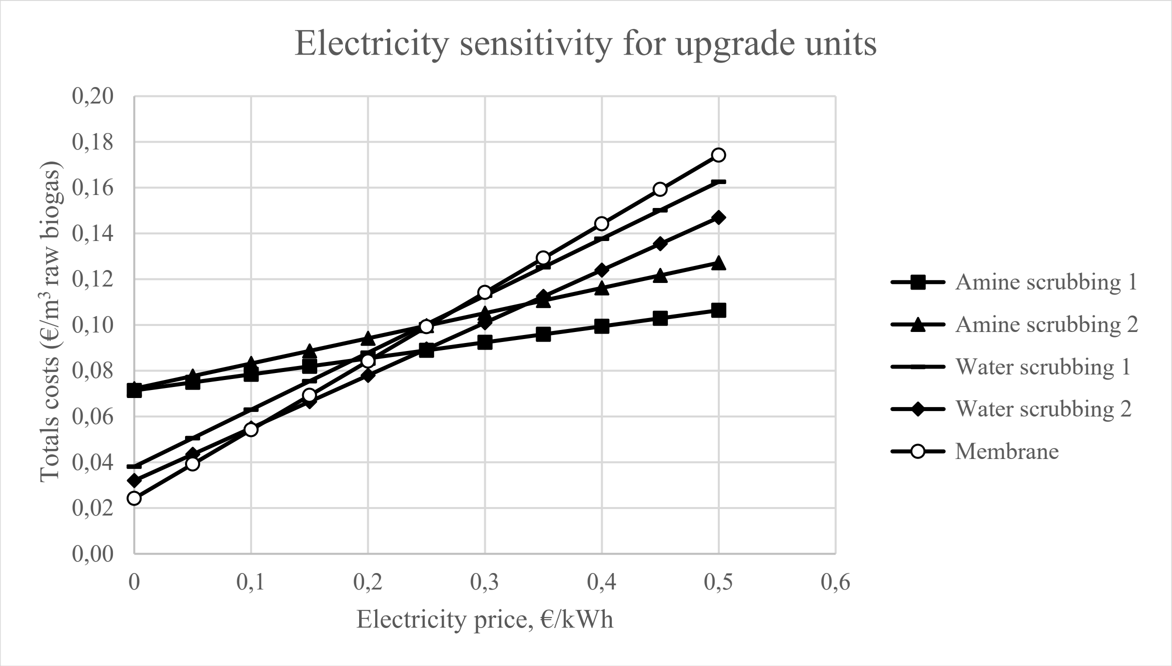

Figure 17 Total costs of the biogas upgrade units as a function of electricity price

The two amine scrubbing systems have the highest total costs when electricity price varies between 0–0.2 €/kWh. After the electricity price increases above 0.2 €/kWh the amine scrubbing system 1 becomes more economically appealing option compared to the water scrubbing system 1 and the membrane system. When electricity price further increases to 0.25 €/kWh the second amine scrubbing system becomes more viable option than the water scrubbing system 1 and the membrane system. At this point the amine scrubbing system 1 also surpasses the profitability of the water scrubbing system 2. After the electricity price has surpassed 0.35 €/kWh both of the amine scrubbing upgrade systems have lower total costs compared to other units. (Fig. 17)

7.2.3.2 Systems for liquefaction

All the biogas liquefaction systems use roughly 40–53% share of electricity of the total costs apart from the amine scrubbing system that has an electricity consumption share of 37% shown on figure 16. The electricity sensitivity for the liquefaction units is shown on figure 18.

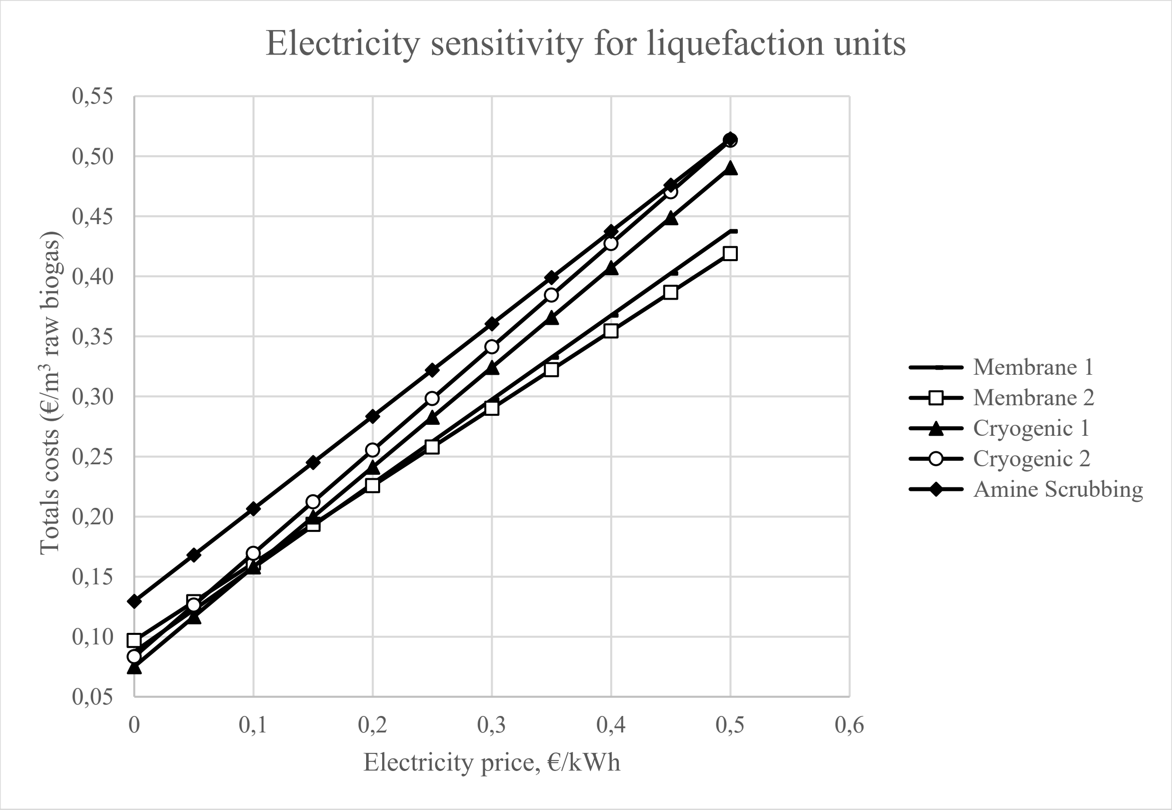

Figure 18 Total costs of the biogas liquefaction units as a function of electricity price

When electricity price is close to 0 there is little to no difference between different liquefaction systems, apart from the amine scrubbing system, but the two membrane units have the lowest total costs as the electricity price increases past 0.15 €/kWh. Initially the amine scrubbing system has the highest total costs, but as the electricity price increases to 0,5 €/kWh, it becomes as profitable as the cryogenic system 2. The membrane unit 2 has the lowest total expenses when the electricity price surpasses 0.25 €/kWh. (Fig. 18)

7.2.4 Heat price sensitivity analysis

The amine scrubbing systems are very energy intensive regarding heat consumption and the price of the heat greatly affects the OPEX of amine scrubbing units. Therefore, it is essential to evaluate how the heat price fluctuation will affect the total costs for these units compared to the other upgrade and liquefaction systems.

7.2.4.1 Systems for grid injection

The heat sensitivity analysis is shown in figure 19. As only the amine scrubbing systems use heat the total costs for water scrubbing units and the membrane unit do not change as the heat price increases.

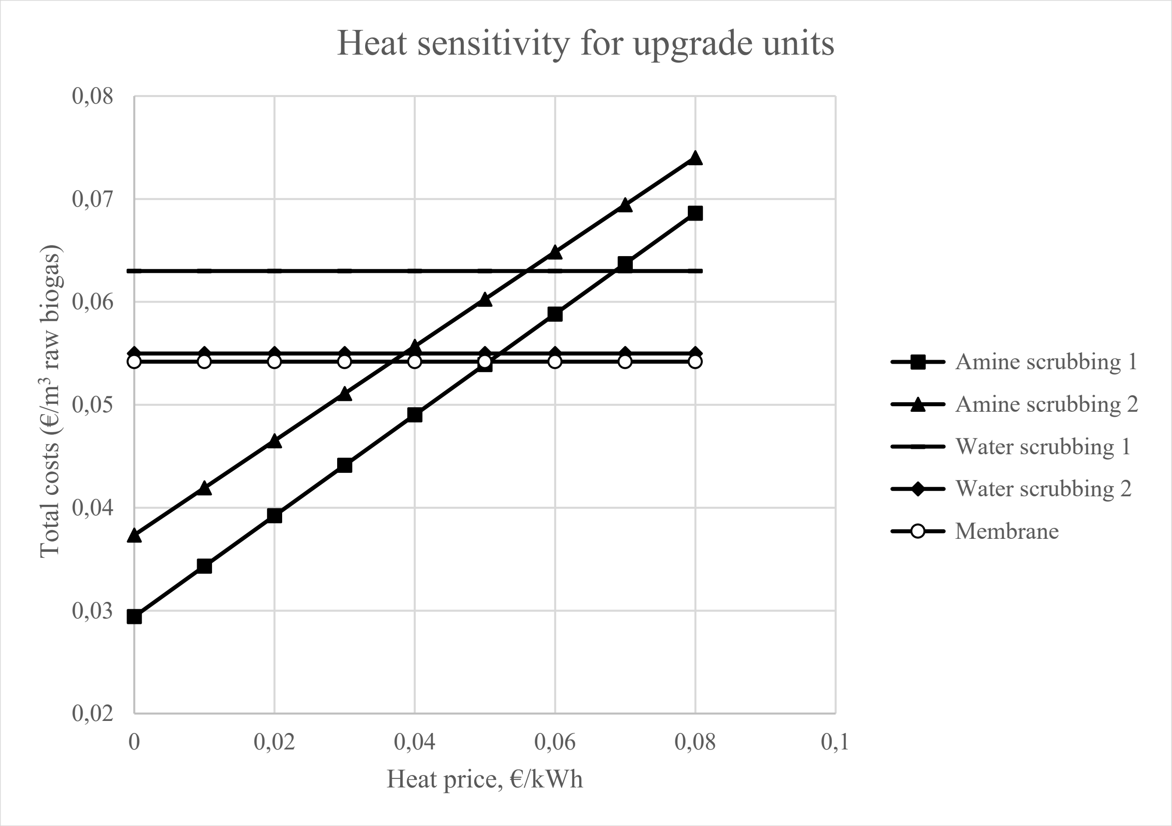

Figure 19 Total costs of the biogas upgrade units as a function of heat price

Figure 19 shows that the water scrubbing system 1 has the highest operating costs when the price for the heat is zero. The costs for the membrane system and the water scrubbing system 2 are approximately the same. Initially the amine scrubbing systems have the lowest total costs. After the price for the heat increases to 0.04 €/kWh the amine scrubbing system 1 has higher total costs compared to the membrane system and the water scrubbing system 2. When the price increases further to 0.05 €/kWh amine scrubbing system 2 also becomes more expensive compared to the membrane system and the water scrubbing system 2. After the heat price increases past 0.07 €/kWh both amine scrubbing units have higher total costs compared to other options.

7.2.4.2 Systems for liquefaction

The amine scrubbing unit combined with the liquefaction unit is the only system that uses heat. Thus, it is the only system that's costs are affected by the heat price fluctuation. The heat sensitivity analysis is illustrated on figure 20.

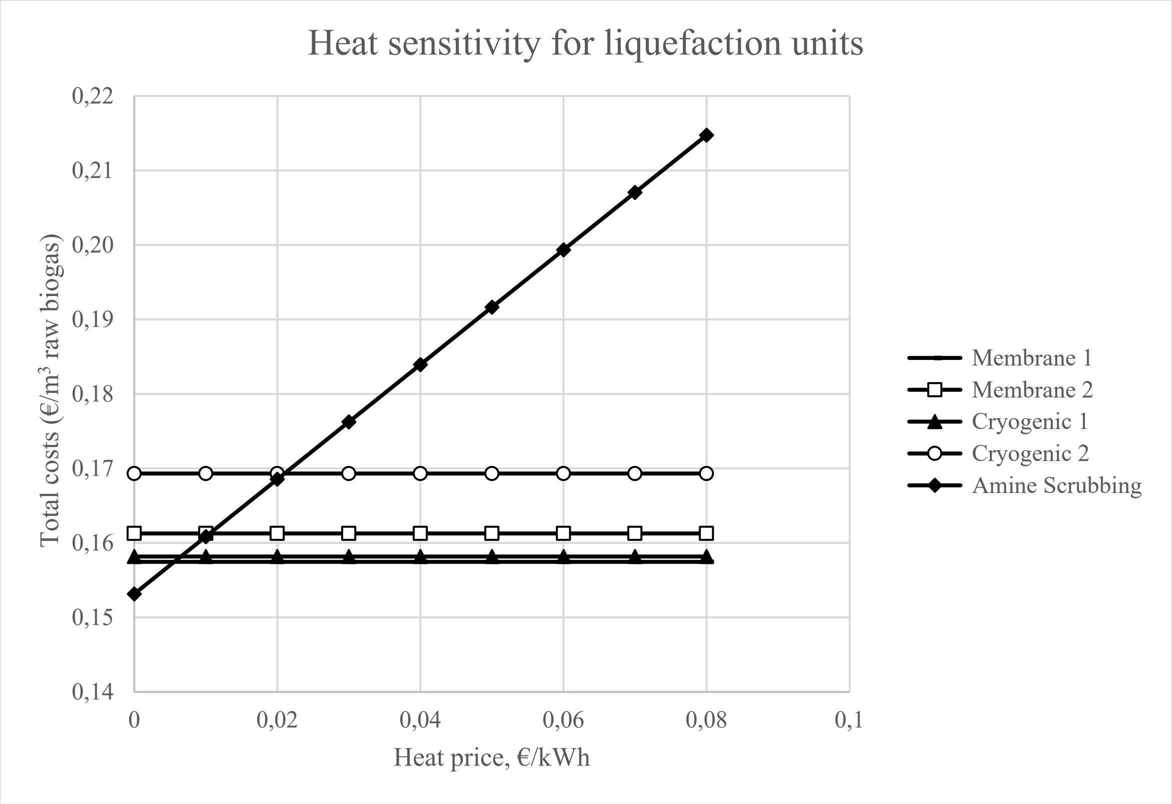

Figure 20 Total costs of the biogas liquefaction units as a function of heat price

The graph 20 shows that the amine scrubbing system has initially lowest total costs and the cryogenic system 2 the highest. After the price of the heat surpasses 0.01 €/kWh the costs of amine scrubbing system become greater than all the other option apart from cryogenic system 2. The costs for the amine scrubbing system become the largest of all the options after the heat price increases past 0.02 €/kWh.

8 Discussion

In this chapter different desulfurization, upgrade and liquefaction systems are compared. Comparison was based on literature review, data available from received quotations and studied biogas composition.

8.1 Desulfurization technologies

In table 7 it can be seen that all desulfurization systems based on biotechnology were unstable and unable to handle peak levels of H_2S (Bailon Allegue, Hinge, 2014, p.21). Also, oxygen injection for these systems was required which leads to dilution of the gas due to N_2 if air is used for oxygen feed. Bioscrubber was the only biotechnology-based option where the oxygen feed wasn't in direct contact with the gas stream meaning there is no dilution problem unlike in biofilter and biotrickling filter. (Bailon Allegue, Hinge, 2014, p.21) The cost estimations for biotechnology-based desulfurization methods varied (Table 8). Biotrickling filter was the most expensive option of all systems reviewed with operation costs of 1.427 €/m^3 raw biogas. Out of all biobased systems the biofilter had the lowest operation costs of 0.114 €/m^3 raw biogas. (Table 8)

Dosing of iron salts was mentioned to be a low costing process (Table 7) but that depends on the initial and the required end concentration of the H_2S. According to the cost evaluation by Okoro & Sun, the total costs for iron salts are the lowest for all the systems compared with costs of 0.009 €/m^3 raw biogas (Table 8). Iron sponge as well as iron salts is listed to have low costs and the process stated to be simple (Table 7). It however has over 7 times larger operating costs compared to iron salts (Table 8). Problems with handling and disposing the bed material are mentioned as disadvantages for this system (Bailon Allegue, Hinge, 2014, pp.13–14).

Activated carbon filter is the only desulfurization system that can provide a reliable low concentration H_2S outlet gas, but it is listed to be expensive especially when the concentration of the inlet gas was high (Table 7). Also, the unit had the smallest removal capacity. According to the evaluation by Okoro & Sun the activated carbon filter has operating costs of 1.158 €/m^3 raw biogas which is the second largest after the biotrickling filter system (Table 8).

Microaeration is also mentioned to be low costing process but has several disadvantages regarding the process. Oxygen needs to be injected to the system which creates an explosion hazard and dilutes the biogas if air is used in the process. Possible clogging of the oxygen injection system was also mentioned as one of disadvantages. (Table 7) Total costs for microaeration are the smallest after iron salts with operating costs of 0.069 €/m^3 raw biogas (Table 8).

The analysis of the biogas data showed an average value of 1200 ppm of H_2S (Table 15). With a gas flow of 1700 m^3/h raw biogas this equals approximately 55 kg S/day. Addition of iron salts or iron sponge would provide a sufficient removal capacity for evaluated sulfur amount. Activated carbon had the lowest removal capacity of 9 kg S/day compared to other methods. This would mean that multiple units are required to achieve a sufficient removal capacity which would increase the costs of the desulfurization unit.

8.2 Systems for grid injection

On the CAPEX and OPEX comparison (Fig.13) amine scrubbing systems were found to have the highest totals costs that mostly consisted of operating costs. Operating costs for these systems were higher than with any other technology. As amine scrubbing systems require a vast amount of heat the OPEX is directly proportional to the heat costs. In the heat sensitivity analysis, it was found that amine scrubbing systems are the most economic option when the price of the heat was under 0.04–0.05 €/kWh (Fig.13).

Electricity consumption figures of upgrade systems presented in table 16 match the values found from literature (Table 13) quite accurately although the electricity consumption for amine scrubbing system 1 is bellow and for amine scrubbing system 2 on the lower range. Amine scrubbing units are the only ones that require heat for the amine regeneration process (Allegue, Hinge, 2020, p.45). The evaluated heat amounts for these systems are similar with the evaluations found in literature review (Table 13) when the recovered heat of 20–30% is not included. (Table 16) Amine scrubbing system could be a good option to locations where a steady heat supply with a low cost is available. The possible corrosion and handling problems due to amine used in the process should be considered. (Table 12.)

The water scrubbing systems had the lowest OPEX of all the upgrade systems included in the review (Fig.13). This could be due to a fact that the costs for water consumption and disposal were not included in the review as they were considered to be insignificant compared to the electricity and maintenance costs. As there was little difference between the total costs of water scrubbing and membrane systems including the water costs could have turned the evaluation to favor the membrane unit. Water scrubbing could be a viable option for locations where water price, availability and disposal are feasible (Table 12.). Also, the average temperature in the operating location should be considered when making evaluations of the operating costs. A high surrounding temperature increases the cooling need and thus power consumption of the cooling unit. (Bauer, Hulteberg, 2013, pp.40–43) The water scrubbing upgrade system is the most commonly used technology (Ghaib, 2017, p.1822) even though it has possible operational problems such as foaming and clogging (Table 12.).

The electricity consumption of the membrane unit was close to the higher range value presented in table 13. In figure 14 it can be seen that 55% of the membrane units' total costs consist of electricity consumption which is the highest share compared to the other systems reviewed, thus the membrane system was found to be the most sensitive to the electricity price increase. The membrane unit reviewed uses a 3–stage system, illustrated in figure 8, which explains the higher range consumption figure compared to the literature value (Allegue, Hinge, 2020, p.45). Membrane upgrade unit could be a good option for a location where electricity price is low or where amine or water scrubbing systems aren't feasible. The process is described to be reliable and low maintenance (Table 12.).

There was only a 4% difference between the maintenance costs (Fig.14). This could have been due to a fact that not all quotations included an estimate for maintenance as it was valued as an average based on information found from other quotations.

The evaluated total costs were significantly smaller to the evaluation made by De Hullu et al. (Table 13) The differences could be explained by different methodology used in the calculations. For example, De Hullu et al. used a 3 year payback period with a 6% interest rate, when a 10 year period with a 5% interest rate was used in this thesis. The total costs presented in table 13 are still comparable with each other as they are all evaluated by the same means and provide an overview of the total costs of each unit.

8.3 Systems for liquefaction

On the CAPEX and OPEX comparison of liquefaction systems, it was found that amine scrubbing system had the highest total costs of 0.21 €/m^3 raw biogas with the highest operating costs (Fig.15) Operating costs of this unit are depended on the heat price used in the evaluation. In the heat sensitivity analysis (Fig.20) it was found that when the heat price exceeded 0.02 €/kWh the amine scrubbing systems total costs become the highest.

Cryogenic units had higher operating costs than the membrane units. There was little difference between the total costs which varied between 0.16–0.17 €/m^3 raw biogas depending on the system. Reliable estimations for total costs of different upgrade systems combined with liquefaction units were not found in literature review.

There was little to no difference between the electricity sensitivity of liquefaction units as all systems are electricity intensive. The total costs of all units increased 0.06–0.08 € as the electricity price increased with 0.1 €/kWh. The membrane systems were found to be the least sensitive to energy price fluctuation and became the cheapest option after electricity price surpassed 0.1 €/kWh. (Fig. 18)

As mentioned above, cryogenic systems had similar total costs compared to membrane units. Cryogenic units could be used to produce high purity CO_2 (Sun et al., 2015, p.529) which could possibly create revenue for the facility. Although, cryogenic upgrade systems are mentioned to suffer from severe operational problems (table 12.) which could increase the actual total costs by increasing the down time of the facility and the maintenance costs of the unit. It could also be possible that due to operation issues the process works in a suboptimal way which might lead to product losses or increase the operating costs.

9 Conclusions

In this thesis different biogas upgrade and desulfurization technologies were reviewed to find optimal solutions for desulfurization and biomethane production for grid injection or vehicle use. Commercially available desulfurization technologies were evaluated based on literature review. In addition, data of biogas composition from a laboratory scale test bioreactor was analyzed, to determine an average concentration of H_2S in the produced biogas, to better evaluate the suitable desulfurization method for the company's process. The comparison between available biogas upgrade and liquefaction systems was based on the literature review and quotations received from equipment suppliers.

Based on the literature review the addition of ferric salt directly to the fermenter or with the feed material was the economically best option for desulfurization. The process was concluded to be simple and well known. Another possible option from the economical point of view was microaeration with pure oxygen generated on site, but this desulfurization method however has a lot of know operational challenges. Both methods require a secondary H_2S removal system prior to the upgrade unit to maintain a steady and efficient desulfurization.

Activated carbon filter was found to be the best option as a secondary desulfurization system. According to the literature review it has stable desulfurization efficiency, and it is possible to achieve low concentration levels of H_2S with this method. Because the average H_2S concentration was found to be high based on laboratory scale test reactors, activated carbon filter cannot be advised to be used as a primary desulfurization method, due to the high costs of the system resulting from high H_2S levels of the raw biogas.

Total costs of the upgrade system were found to be very case sensitive depending on electricity and heat prices. Amine scrubbing systems had the highest total and operating costs out of all upgrade and liquefaction units reviewed. This resulted directly from the set price of the heat, but electricity and heat sensitivity analysis showed how the fluctuation in the utility prices affected the operating costs for these units compared to other technologies. Amine scrubbing upgrade system was found to be the most cost efficient when the price of the heat was below 0.04–0.05 €/kWh or when the electricity price was higher than 0.25-0.35

€/kWh. For liquefaction systems, amine scrubbing units had the highest total costs even when the electricity price was 0.05 €/kWh and became the most expensive option when heat price was greater than 0.02 €/kWh.

The best solution for biogas liquefaction based on the cost evaluation of the supplier quotations evaluated would be the membrane upgrade unit combined with the separate liquefaction unit. This solution was found to be the most resistant to electricity price fluctuation and had the lowest total costs of the reviewed liquefaction quotations. Literature review also suggest that membrane systems are simple, reliable, and low maintenance.

The weakest option for liquefaction based on the electricity sensitivity evaluation, was the cryogenic separation. Literature review also suggested that this technology is not mature enough to be applied in a commercial scale facility and has several operational issues even though a high purity CO_2 could be obtained as a side product.

As there was no quotation received for a PSA upgrade system a reliable evaluation for this technology could not be conducted and was left out from the review. The fact that not all vendors supplied equally accurate information about the utility consumptions, maintenance, and specifications of the initial investment costs, which resulted that some base assumption for some technologies needed to be evaluated based on the information found in other quotations. This made it challenging to compare the data from the received quotations. As newer upgrade systems are constantly being developed to achieve higher efficiency and lower production costs the findings in this thesis need to be revised accordingly.

Based on this thesis, a two-stage desulfurization unit of iron salt or microaeration paired with active carbon filtration can be recommended for desulfurization of the H_2S-rich biogas. For producing LBG a membrane based upgrade system paired with a liquefaction unit can be recommended. Cryogenic separation cannot be recommended for producing biomethane for grid injection or vehicle use.

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Appendix 1. Raw unfiltered biogas data for BRS3 between 8.4.2019–17.12.2019

BRS3							measurement	
start date	end date	CH4 (%)	CO2 (%)	O2 (%)	H2S (ppm)	Bal (%)	time (s)	pvm
8.4.2019	11.4.2019	61,3	35,5	0,3	2123	3	295	11.4.2019
11.4.2019	15.4.2019	62	31,6	0,7	1652	5,6	150	15.4.2019
15.4.2019	18.4.2019	60,9	33,5	0,5	1743	5	150	18.4.2019
29.4.2019	2.5.2019	60,2	31,2	1	1414	7,5	186	2.5.2019
7.5.2019	10.5.2019	61,5	32,5	0,6	1641	5,4	150	10.5.2019
10.5.2019	15.5.2019	63,1	32,3	0,2	1461	4,4	150	14.5.2019
15.5.2019	20.5.2019	60	31,8	0,4	1539	3,8	151	20.5.2019
20.5.2019	27.5.2019	63,6	29,6	0,7	1295	6,2	312	27.5.2019
27.5.2019	31.5.2019	64,7	29,8	0,5	1169	4,9	160	31.5.2019
31.5.2019	7.6.2019	63,5	29,4	0,8	1055	6,3	150	7.1.1900
10.6.2019	14.6.2019	64,8	30,8	0,4	1444	4	150	14.6.2019
14.6.2019	20.6.2019	63,2	30,6	0,7	1218	5,5	310	20.6.2019
26.6.2019	1.7.2019	65,7	29,3	0,8	1068	4,3	150	1.7.2019
1.7.2019	9.7.2019	65,8	30,8	0,4	1251	3,1	357	9.7.2019
9.7.2019	15.7.2019	64,7	28,1	1,1	1152	6	150	15.7.2019
15.7.2019	22.7.2019	65,5	30,5	0,6	1149	3,5	150	22.7.2019
22.7.2019	29.7.2019	67	30,4	0,3	1130	2,3	364	29.7.2019
29.7.2019	5.8.2019	63,4	32,3	0,8	1191	3,5	235	5.8.2019
5.8.2019	12.8.2019	62,9	29,1	0,9	1044	7,1	164	12.8.2019
12.8.2019	16.8.2019	61,9	28,7	1	1054	8,4	151	16.8.2019
27.8.2019	28.8.2019	59	25,9	2,1	830	13	118	
3.9.2019	5.9.2019	60,6	27,3	2,2	1120	10,1	244	5.9.2019
10.9.2019	12.9.2019	58,4	26,4	2,6	1044	12,7	243	12.9.2019
24.9.2019	26.9.2019	60,5	27,9	1,3	1073	10,2	251	26.9.2019
1.10.2019	8.10.2019	65,5	29	0,7	1146	4,7	221	3.10.2019
15.10.2019	17.10.2019	61,6	27	1,6	1060	9,8	214	17.10.2019
22.10.2019	24.10.2019	56,6	26,4	2,5	1022	14,6	203	24.10.2019
29.10.2019	31.10.2019	57,5	25,7	2,7	1043	14,2	232	31.10.2019
5.11.2019	7.11.2019	55,6	26,4	2,6	1042	15,5	204	7.11.2019
13.11.2019	15.11.2019	54	23,5	2,6	976	20	240	15.11.2019
19.11.2019	21.11.2019	59,4	24,4	2,1	1033	14,1	261	21.11.2019
26.11.2019	28.11.2019	54	23,8	3,3	981	19	284	28.11.2019
3.12.2019	5.12.2019	56,8	24,5	2,3	857	16,4	238	5.12.2019
10.12.2019	12.12.2019	65	25,7	1	1020	8,4	221	12.12.2019
17.12.2019	19.12.2019	61,9	25,2	1,3	984	11,6	243	19.12.2019
14.1.2020	15.1.2020	52,1	38,2	0,6	426	9	207	15.1.2020