Fiona Mwacharo, Suraj Bhandari, Ahmed Othman, Anne-Riikka Rautio

BIOGAS DRYING AND PURIFICATION METHODS

Fiona Mwacharo, Suraj Bhandari, Ahmed Othman, Anne-Riikka Rautio

BIOGAS DRYING AND PURIFICATION METHODS

CONTENTS

FIGURES

TABLES

PROLOGUE

In August 2020, *Biogas2030* statement was made, where the goal for national biogas production and use in 2030 was set to 4 TWh. The goal is approximately four times higher than the current production rate in Finland. In order to reach this not only political decisions must be made but also new technologies and business models have to be created. In Finland, there is large potential for biogas production in agriculture, especially in animal farms, that created suitable biomasses through the year.

Although the production of biogas in farms is growing all the time, the energy is often used in the farms as heat and power. The profit gained from the biogas would be better and also the availability of renewable fuels would increase in Finland if the biogas would be purified and sold as fuel. However, in a small scale with current technologies this is not profitable. HABITUS project (Decentralized Biogas Production and liquefaction in Finland, funded by Regional Council of Central Ostrobothnia, European Regional Development Fund) is answering this challenge by creating new technologies suitable for purification and liquefaction of biogas in the small scale. This report was written during summer 2020 for HABITUS project to review the current state and future trends of biogas purification and upgrading technologies.

1. INTRODUCTION

Biogas is a renewable energy source that is produced from the anaerobic digestion of organic matter such as sewage, sludge, manure, household and industry waste. It is also produced from the anaerobic degradation of landfills and is then referred to as landfill gas. (Petersson & Wellinger 2009, 4.) Biogas is primarily composed of 50-70 % methane (CH_4) and 30 – 50 % carbon-dioxide (CO_2). The amount of CH_4 and CO_2 varies depending on the type of organic substrate used and pH of the reactor. There are other compounds found in biogas in minor amounts such as nitrogen (N_2) in the range of 0 – 3 %, water vapour (H_2O) in the range of 5 – 10 % (this may be higher in thermophilic temperatures), oxygen (O_2) in the range of 0 – 1 %, hydrogen sulphide (H_2S) in the range of 0 – 1 %, ammonia (NH_3), hydrocarbons in the range of 0 – 200 mg m^{-3} and siloxanes in the range of 0 – 41 mg/m³. Other than CH_4 these other gasses are unwanted and considered contaminants. (Angelidaki, Treu, Tsapekos, Luo, Campanaro, Wenzel & Kougias 2018, 452.)

Biogas is used as a fuel for on-site heating, steam and electricity generation. It can also be used as a substrate in fuel cells and as a substitute of natural gas. In Europe, biogas production accounted for 13.4 million tons of oil equivalent (toe) in 2014, which represents 52.3 TWh of produced electricity. Additionally, the European supply of biogas is expected to increase up to 18 – 20 million m3 by 2030. (Muños, Meier, Diaz & Jeison 2015, 728.)

Biogas typically requires treatment prior to use. This treatment can be divided into two main parts: purification and upgrading. Purification involves the removal of impurities such as H_2S, siloxanes, H_2O, volatile organic compounds (VOCs) and NH_3. However, in practice it is typically H_2S that is targeted and there are H_2S removal units in many biogas plants nowadays. Upgrading aims to convert the biogas to a higher fuel standard by increasing its low calorific value. Biogas can be upgraded to biomethane, which is similar to natural gas. Natural gas primarily consists of methane. Before purification, natural gas can contain up to 85 % of methane. The remaining percentage consists of contaminants such as ethane, propane and carbon dioxide. After processing, natural gas is almost pure methane (up to 98 %). The composition of biomethane from biogas varies depending on national regulations, with some countries requiring >95 % methane content. (Angelidaki et al. 2018, 452; Mokhatab, Poe & Speight 2006, 3-4.)

The aim of this report is to review the current and future biogas purification and upgrading trends, and biogas transportation methods. This report will also review the current biogas trends in Finland.

2. BIOGAS PURIFICATION AND DRYING

There are numerous methods for biogas purification and drying. These methods will be discussed in this chapter.

2.1 Desulphurization

Biogas typically contains trace amounts of sulphur in the form of hydrogen sulphide. H_2S is undesirable in biogas as it has a negative effect on human health, can result in the formation of acid rain when the biogas is burned for heat and power generation, and can corrode engines and degrade engine lube oil. The European Committee of Standards stipulates that the H_2S concentrations in biogas used as a biofuel should be less than 20 mg/m³. (Okoro & Sun 2019, 3.)

The amount of sulphur in biogas varies based on the feed and process. In manure digestion, the typical sulphur concentration is between 500 and 3000 ppm but can reach up to 30 000 ppm depending on the manure quality and how it is processed. Biogas produced from municipal waste typically has smaller concentrations of sulphur, particularly when phosphor is removed during the water treatment process using iron salts such as ferrous sulphate because, in an anaerobic environment, the iron salts react with H_2S to form insoluble iron sulphide. The sulphur concentration in biogas produced from landfills in Finland varies between 20 and 600 ppm. (Arnold 2009, 25.)

Several major technologies are applied in the desulphurization of biogas. These technologies include in-situ microaeration, adsorption, absorption and biofiltration. These will be discussed in this subchapter.

2.1.1 In-situ microaeration

The simplest method of desulphurization is adding oxygen or air directly into a digester or storage tank where biogas from anaerobic digestion is produced, as shown in FIGURE 1. Bacteria such as *thiobacillus*, which are typically already present in the digester, uses the oxygen to break down the H_2S to S. 3-6 % of air is dosed using (for example) an air pump. (Allegue & Hinge 2014, 9.) The pumped air should not be in the range of 6 – 12 % as this can make the biogas explosive. (Wellinger & Lindberg 2000, 14.) In-situ microaeration is regarded as highly efficient, with up to 99 % of H_2S removed on laboratory scale. (Tang, Shigematsu, Morimura & Kida 2004.) It has also been successfully implemented in long-term, full-scale systems with up to 90 % of H_2S removed. (Chen, Wu, Qi, Ding & Zhao 2020, 6.)
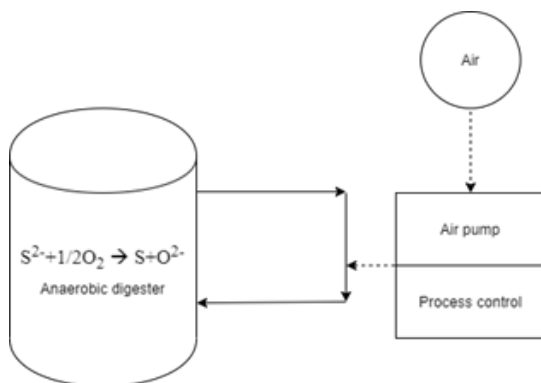

FIGURE 1. Microaeration of anaerobic digester (adapted from Jeniček, Horejš, Pokorná-Krayzelová, Bindzar & Bartáček 2017)

Besides its effectiveness and high efficiency, the main advantage of sulphide removal using microaeration is that it is done within the anaerobic digester without the need of creating a separate desulphurization unit or using additional chemicals. Also, while there is a surplus of nitrogen from using air rather than pure oxygen, its effect on the methane content in the biogas (it decreases the methane content) is lower than expected (maximum 2 %). (Jeniček et al. 2017, 44.) Additionally, the bacteria use carbon dioxide in the biogas as a carbon source which lowers the CO_2 concentrations (CO_2 is a contaminant in biogas). (Wellinger & Lindberg 2000, 14.)

However, this method does have its drawbacks. The elemental sulphur could be further oxidized to produce sulphates, which can inhibit the production of methane, and it can also clog the oxygen supply pipes. Sulphuric acid may also form from the oxidation of H_2S in the presence of water vapour which can lead to corrosion problems in the digester. (Okoro & Sun 2019, 11.) Recent studies have revealed the use of a membrane to overcome these drawbacks. A membrane allows for a precise amount of oxygen added without directly mixing the air and biogas. (Perera, Botheju & Bakke 2014.)

In-situ microaeration is recommended for use in small-scale, especially in agricultural (on-farm) use where further upgrading of the biogas is not needed. Thus, this method is used mainly to eradicate corrosion and odour problems. The biogas is then used in CHP engine units. (Allegue & Hinge 2014, 9.)

2.1.2 Adsorption techniques for desulphurization of biogas

Biogas desulphurization can also be done via adsorption. Adsorption occurs when a gas/liquid forms a bond and adheres to the surface of an adsorbent forming a film. Adsorbents are solids that are highly porous and have the ideal surface area for adsorption. They are typically used to separate liquid or gas mixtures and to remove air and water pollutants. The adsorbed material forms a film on the adsorbent. This film is multi-layered for gases and monolayered for liquids. (Králik 2014.)

The selected adsorbent material for biogas desulphurization should be economical and operational and fit the following criteria; it should have a high adsorption capacity for H_2S, the adsorption kinetics should be fast, be able to regenerate via a suitable pathway, and have multi-functionality regarding removing other contaminants such as ammonia. H_2S removal using an adsorption material has been reported as an effective sulphur removal method and can reduce the H_2S content to as low as <1 ppm. (Pourzolfaghar, Izhar, Esfahan & Ismail 2014, 22.) The most common adsorbent material used for desulphurization of biogas is activated carbon. (Cebula 2009, 9.)

Activated carbon is a highly porous material having a high adsorption capacity (Kwaśny & Balcerzak 2016, 39). It has been reported as being highly efficient in removing low concentrations of H_2S from biogas (Okoro & Sun 2019, 9). According to Arnold (2009, 41), one kilogram of activated carbon can remove 0.2 – 0.5 kg of H_2S. The surface of activated carbon catalyses the oxidation of H_2S to elemental sulphur and sulphate, when oxygen is present. The elemental sulphur and sulphate are adsorbed on the surface. Activated carbon can be further enhanced by "impregnating" it with a suitable chemical such as sodium hydroxide (NaOH) and potassium hydroxide (KOH). These caustic chemicals allow for additional sulphide oxidation by forming sulphide salts. (Okoro & Sun 2019, 9.) Impregnation can increase the removal capacity from 10 – 20 kg H_2S/m^3 (virgin activated carbon) to 120 – 140 kg H_2S/m^3 (impregnated activated carbon)

(Awe, Zhao, Nzihou, Minh & Lyczko 2016, 277). Other impregnating chemicals include potassium carbonate, sodium carbonate and potassium iodide. Research has shown that the removal capacity of impregnated activated carbon can be 40 – 60 times higher than virgin activated carbon. (Pourzolfaghar et al. 2014, 23.) The reaction best occurs at 7 – 8 bars and at temperatures of 50 – 60 °C. This temperature is easily achieved via the heat generated during compression (Wellinger & Lindberg 2000, 16).

However, while impregnated activated carbon is highly efficient, it does have its disadvantages. One disadvantage is the impregnation decreases the ignition temperature of the carbon which is hazardous as it can self-ignite. Furthermore, the elemental sulphur formed from the oxidation of H_2S cannot be washed off the carbon with water therefore it is difficult to regenerate it. To overcome these disadvantages, an alternative would be to use virgin activated carbon. Virgin activated carbon is cheaper than its impregnated alternative; regeneration can occur via cold/hot water washing or thermal treatment, though this process decreases the H_2S adsorption capacity remarkably, and the carbon surface can be incorporated with heteroatoms such as oxygen and nitrogen which allows the activated carbon to act as a catalyst for oxidation. (Pourzolfaghar et al. 2014, 23-24.)

Nevertheless, impregnated carbons are used more often in this industry than virgin carbons. This is due to the high complexity of the reactions on virgin carbons as they involve a wide spectrum of physical and chemical properties. Recent studies on virgin activated carbon are based on: the exploration of the effects of dynamic conditions (such as the concentration of H_2S, humidity and oxygen content) on the carbon, the identification of the surface features of the virgin activated carbon which is significant in understanding the performance of its H_2S adsorption, and the feasibility of regeneration by different methods. (Pourzolfaghar et al. 2014, 23-24.) Adsorption using activated carbon is the most widely used adsorption technology at industrial scale (Santos-Clotas, Cabrera-Codony, Castillo, Martín, Poch & Monclús 2019, 9). According to Arnold (2009, 57), the cost of using activated carbon for smaller installation (1000 m³/h ca) with no pre-treatment was estimated as 0.14 – 0.5 cents/m³ (Euros).

Oxide adsorbents are also used for H_2S removal. The most used oxide adsorbents for H_2S removal are metal oxides. H_2S adsorbs on metal oxides by the sulphur binding as a metal sulphide and the release of water vapour. (SevernWye 2017, 8.) Metal oxides have a removal capacity of 98 % (Wiheeb, Ahmad, Murat, Kim & Othman 2013, 456). The common metals in the metal oxides used for H_2S adsorption include aluminium (Al), iron (Fe), manganese (Mn), cobalt (Co), copper (Cu) and zinc (Zn). These oxides have high porosity surfaces, good mechanical strength and have a high resistance to temperature. (Kwaśny & Balcerzak 2016, 40.)

Out of the metal oxides, iron oxide is one of the most commonly used adsorbents for H_2S removal. It is often used in the form of steel wool, iron pellets, iron fillings and iron sponge. For everyone kg of iron oxide, 0.20 – 0.716 kg of H_2S is removed. (Magomnang & Villanueva 2014, 66.) Iron oxide can be regenerated but this reaction is highly exothermic. Regeneration occurs by injecting 1– 5 % of air into the reaction column forming elemental sulphur. Regeneration can only occur for a limited amount of time (until the iron oxide surface is covered with elemental sulphur). (Allegue & Hinge 2014, 12.) Regeneration results in the formation of the pollutant sulphur dioxide (SO_2), therefore limiting the use of this technique to large-scale (Wiheeb et al. 2013, 457). Silica can also be used as an adsorbent, typically after it has been impregnated with copper (II) oxide (CuO) and zinc (II) oxide (ZnO). Mesoporous silica is used in this way because its structure has pores with uniform size as well as a high surface area, which allows for selective adsorption of contaminants. (Kwaśny & Balcerzak 2016, 40.)

2.1.3 Absorption techniques for desulphurization of biogas

Desulphurization of biogas via absorption is the process where the biogas directly interacts with water or a suitable solvent via packed beds/columns and spray towers. Through this interaction the H_2S in the biogas is absorbed in the water or is chemically converted to elemental sulphur or a metal sulphide. The main desulphurization absorption techniques can be divided into four categories: physical absorption and chemical absorption. (Okoro & Sun 2019, 7.) Absorption methods have high efficiency removal (up to 99 %) and are suitable for flow rates between $100 - 10\,000$ m³/h. The absorption methods described in this subchapter are economically feasible for large scale biogas plants. (Allegue & Hinge 2012, 57.)

Water scrubbing is a physical absorption method for H_2S removal that can also be used for the removal of CO_2. Both H_2S and CO_2 are more soluble in water than CH_4. This method is implemented by feeding pressurized biogas into the bottom of a packed column while water is fed from the top, as displayed in FIGURE 2. Thus, the absorption process is counter current. The water leaves the bottom of the column with H_2S/CO_2 dissolved in it and can be regenerated and recirculated back to the absorption column. The regeneration is done by stripping with air or by de-pressurizing in a similar column. It is more cost effective to use cheap water such as the outlet water from a sewage treatment plant, rather than recirculate the water. (Wellinger & Lindberg 2000, 10.) H_2S levels can be reduced to as low as 5 mg/m³ by using the water scrubbing method. However, high levels of H_2S (>500 ppm) in the biogas can result in fouling and plugging the regenerative system, as well as the release of high H_2S emissions into the atmosphere from the exhaust gas. (Allegue & Hinge 2014, 18.) Therefore, the H_2S can be removed using a different method and water scrubbing used to remove the CO_2. Typically, methane purity of 80-99 % can be achieved from water scrubbing. (Sun, Li, Yan, Liu, Yu & Yu 2015, 524.) Further details of water scrubbing are discussed in chapter 3.1.2.
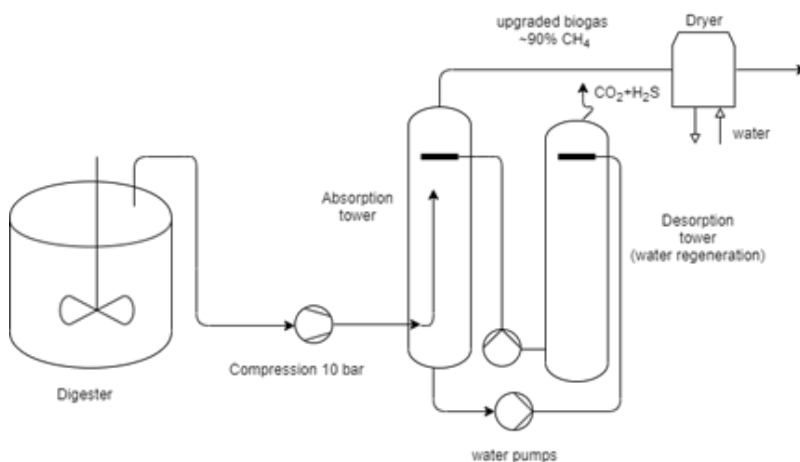
FIGURE 2. Schematic of water scrubbing absorption and regeneration for H_2S/CO_2 removal from biogas (adapted from Wellinger & Lindberg 2000, 11)

Other than water, another solvent that can be used for the physical absorption of H_2S and CO_2 is dimethyl ether of polyethylene glycol (DMPEG), known commercially as Selexol. Just as in water, both H_2S and CO_2 are more soluble in Selexol than CH_4. Furthermore, H_2S and CO_2 are more soluble in Selexol than in they are in water, meaning that less solvent and thus less pumping is needed to achieve the desired results. The other contaminants such as water and halogen-

ated hydrocarbons are also removed when biogas is scrubbed with Selexol. Selexol scrubbing is typically designed with regeneration and recirculation. Air-stripping is not recommended as it can react with the H_2S to form elemental sulphur which can cause operational problems. Instead steam or inert gas can be used. As a method to selectively remove H_2S, its costs have not shown to be competitive. It is likely to only be considered when simultaneously removing CO_2. (Wellinger & Lindberg 2000, 11 & 16.)

Chemical absorption is yet another technique that can be used for H_2S removal. According to Petersson and Wellinger (2009, 7), the use of sodium hydroxide (NaOH) in chemical absorption is one of the oldest techniques of H_2S removal. NaOH washing occurs in the same way as water and Selexol scrubbing. The NaOH is an aqueous solution that improves the absorption capacity of water. Since NaOH reacts with H_2S to form either Na_2S or NaHS, it is now a chemical absorption processes rather than a purely physical one. The salts formed are insoluble, therefore this technique is non-regenerative. (Wellinger & Lindberg 2000, 16.) This method also has a high technical requirement and is hardly applied in biogas purification processes unless to treat extremely large gas volumes or where very large H_2S amounts are present. (Petersson & Wellinger 2009, 7.)

The in-situ chemical precipitation is a process where the conversion of dissolved sulphides into H_2S is limited by dosing the digester. This is done with chemicals that convert the dissolved sulphides into either insoluble metallic sulphide compounds or elemental sulphur (S). The most commonly used chemicals are divalent (Fe^{2+}) and trivalent (Fe^{3+}) iron salts including their chlorides, iron (III) oxide-hydroxide (FeOOH) and iron (III) hydroxide ($Fe(OH)_3$). The chemical reactions that occur in the precipitation of sulphides are as follows (Okoro & Sun 2019, 3-4):

$$FeCl_2 + HS^- + H^+ \rightarrow FeS + 2HCl \tag{1}$$
$$FeCl_3 + 2HS^- + H^+ \rightarrow FeS + 3HCl + S \tag{2}$$
$$2FeOOH + 3HS^- + 3H^+ \rightarrow 2FeS + S + 4H_2O \tag{3}$$
$$2Fe(OH)_3 + 3HS^- + 3H^+ \rightarrow 2FeS + S + 6H_2O \tag{4}$$
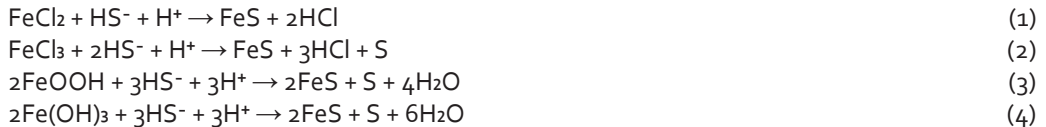
In-situ chemical precipitation is relatively cheap and requires minimal investment. It can be easily operated, monitored and handled as well as implemented in existing biogas plants. However, additional equipment, such as pumps, are necessary to maintain the chemical dosing, resulting in an increase in the number of unit operations. Furthermore, it is difficult to control the degree of desulphurization as iron ions can also react with phosphates in the sludge, which reduces the effectiveness of this method. This technique is typically utilized as the first stage of desulphurization in digesters with high H_2S concentrations or in situations where high H_2S concentrations in the biogas are allowed. (SevernWye 2017, 6.)

Furthermore, in-situ chemical precipitation is typically applied in small-scale operations, though a few studies (such as NYSERDA 2012) have explored its use on a large scale. However, recent studies have shown that dosing substrates with iron salts can hinder the availability of useful phosphates, which in turn impedes microorganisms from metabolising organic substrates for the formation of biomethane. (Smith & Carliell-Marquet 2008; Al-Imarah, Lafta, Jabr & Mohammad 2017.) For example, the studies by Al-Imarah et al. (2017) demonstrated that sludge dosed with iron chloride resulted in 20 % less biogas produced.

2.1.4 Biofiltration

Biofiltration is a method of removing the impurities from the biogas using microorganisms. There are two principal stages of biofiltration used to eliminate harmful gases from the raw biogas from the anaerobic digestion. (Molina & Aroca G, 2007, 115-112.) In the first stage, the impurities are removed from the gas stream to the liquid film, followed by solid support adsorption. In the second principle stage, impurities are biodegraded by the microorganisms present in the filtration bed's liquid and solid phases. The biofilter operation involves various processes, as it is believed that the contaminants have been transferable directly from the gas phase to the biofilm without dissolution. (Syed & Soreanu, 2006, 1-11.)

Biofilters are used to remove a wide variety of organic and inorganic compounds, such as ammonia and hydrogen sulfide. Several studies have shown that biofilters can achieve efficiency in removing H_2S by more than 99 %. (Baber & Shareefdeen, 2013, 69-77.) Low operating costs, low energy and equipment requirements, high productivity in removing contaminants, and no additional chemicals required are the key advantages of using biofilters for biogas treatment. On the other hand, this technique also carries some problems, such as accumulation of biomass on the surface, fouling, creation of preferential pathways, excessive pressure drops, and difficulty regulating the operational parameters. (Krishna Kalfe & Chen, 2015, 164-174.)

2.1.4.1 Bio scrubbers

Bio scrubber is a unit which purifies H_2S from biogas. It has two reactors in its unit that is an absorption tower and the activated sludge unit. The absorption tower absorbs all the impurities changing into the liquid phase which then passes into the second reactor that is activated sludge unit. Most of the reaction takes place in the second unit where the growth of microbes (Thiobacillus Bacteria) takes place and the addition of oxygen, nutrients for microorganisms, and maintenance of pH takes place. Along with these, the rotation of effluent from the second chamber takes place to the first one which is absorption tower, and the removal of excess waste takes place from the second unit. (Allegue & Hinge, 2014, 26).

Among the various types of scrubbers used in the different places, the most common type of bio scrubber system which is used for the removal of hydrogen sulfide from biogas is THIO-PAQ^{TM} Process. This system works in a principle that the solution of sodium hydroxide is introduced in a crosscurrent way to the biogas containing H_2S, where the hydrogen sulfide is absorbed in the water phase. The pH of the caustic solution in the bioreactor chamber from the microbe's ranges between 8.2 - 9 on which the process works on its best level. The reaction for the absorption of H_2S in the absorption tower with a caustic solution is shown below (Cline, Hoksberg, Abry, & Janssen, 2003, 3-8.)

$$H_2S \text{ (g)} + NaOH \text{ (aq)} \rightarrow NaHS \text{ (aq)} + 2H_2O \text{ (l)} \qquad (5)$$

After the reaction with the caustic solution, sodium hydrosulfide ($NaHS + H_2O$) solution passes through the bioreactor. The bioreactor is a chamber where the oxygen (air) is continuously introduced where the reaction between the sulfur bacteria and the scrubber mixture takes place. Bioreactor operating very close to the atmospheric pressure, where the conversion of sodium hydrosulfide ($NaHS + H_2O$) to elemental sulfur takes place (equation 6). (Cline et.al. 2003.)

$$NaHS + 0.5O_2 \rightarrow S_0 + NaOH \qquad (6)$$

However, not all the dissolved sulfide changes into elemental sulfur, as some portion less than six percent gets oxidized to form sulfate which can increase the basicity of the solution. To maintain the pH level basic (over 8.2), around 5 % of sodium hydroxide is added to the chamber. (Cline et.al. 2003.)

$$2NaHS + 4O_2 \rightarrow NaHSO_2 \rightarrow Na_2SO_4 + H_2SO_4 \tag{7}$$

During the continuous phase of conversion of dissolved sulfur to elemental sulfur, there is the accumulation of sulfate and elemental sulfur which can decrease the removal efficiency of the system. The continuous bleed stream is needed to lower this accumulation and the waste product from the system is very useful as a raw in the production of H_2SO_4. This system can have the H_2S capacity up to 99 %, depending on the environment of operation. (Allegue & Hinge, December 2014, 26.)

Typically, the flow ranges between 50 to 3000 cubic meters per hour, with the H_2S inlet of 3 000 to 30 000 ppm and out less than 100 to 150 ppm, which gives this system the best removal efficiency. (Biogas Utilization Systems and H_2S Bio-Scrubber Units, 2017). The system has the removal capacity of around 45 kilograms to 20 tons of sulfur per day depending on the amount of H_2S present on raw biogas and the operating environment. (Arnold, 2009). Differences between advantages and disadvantages of bio scrubbers as compared to biofilters is presented below. (Kennes, C., & Veiga, M. C. 2013, 133-162.)

TABLE 1. Advantages and disadvantages of bioscrubbers. (Kennes, C., & Veiga, M. C. 2013, 133-162.)

Advantages	Disadvantages
Smaller system volume with better pH control.	More than 98 % of elimination efficiency is more difficult to achieve
More efficient and reliable, with less clogging problem	Possibility to wash off the slowest growing microorganisms and difficulty with sludge management
Lower presence of toxic concentrations in the liquid phase	More complex to begin the process and higher operating costs

2.1.4.2 Biofilters

The biofilter is one of the techniques which comprise of immobilized microorganisms in the form of a biofilm that is fixed to a packed bed consisting of, or combinations of, materials such as peat, soil, manure, and synthetic substances. The FIGURE 3 shows the schematic representation of a biofilter and the hydrogen sulfide biofiltration which involves the following mechanisms: (1) transfer of H_2S from the gas phase to the aqueous phase (2) biofilm diffusion (3) adsorption by the biofilm and the packing material and (4) biodegradation by biofilm. In the presence of oxygen, hydrogen sulfide in the biogas with the help of microbes in the biofilter process is transformed into biomass, carbon dioxide, water, metabolic byproducts, and sulfur monoxide. (Devinny, Deshusses, & Webster, 1998, 22-318.)
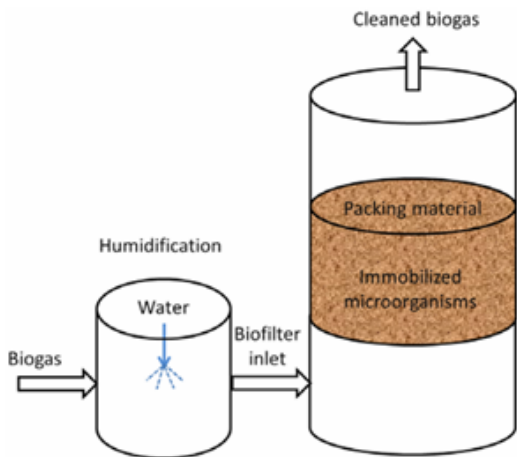
FIGURE 3. Schematic diagram of a biofilter (Devinny, Deshusses, & Webster, 1998, 22-318.)

Biofilter efficiency is influenced by several parameters such as temperature, moisture, pH, nutrients, oxygen levels, gas velocity, and pressure drops. The difference in the temperature governs the temperature of packed buds. The optimal bed temperature is around 35 to 37 Regional Council of Central Ostrobothnia whereas the packed bed's optimum moisture is about 40 to 60 %. An increase in pressure drop can be seen due to the excessive moisture however, while at low moisture rates substantial drop removal efficiency is observed. Hydrogen sulfide can be oxidized under the acidic conditions but the optimum value for pH conditions is between 6 and 8. (Devinny, Deshusses, & Webster, 1998, 22-318.)

Organic packaging materials such as compost have the advantage of providing the nutrients that are needed for microbial growth such as nitrogen, potassium, phosphorous and trace elements, and carbon as well as energy. Nevertheless, inorganic and synthetic materials need an extra supply of nutrients. Due to the excess biomass and bed compaction, decreases in biofilter efficiency, and increases in pressure drop are observed in long-term bioreactor activity. Since the nutrients are slowly reduced over time, which is the major downside of biofiltration, the large footprint needed for biofiltration is also considered a problem for practical applications. (Kennes, Rene, & Veiga, 2009, 1419-1436).

2.1.4.3 Bio trickling filters

A bio trickling filter is another technique for the removal of impurities from the raw biogas. It's working principle is that this system allows biogas to pass through the chemically inert gas, where the growth of microorganisms occurs on the material surface. Specific gases which are used as the source of energy will be consumed depending on the microorganism. This procedure has been applied successfully to separate hydrogen sulfides from the biogas, but this technique has not been implemented at a broad industrial level and is expected to be the potential technique for biogas upgrading. (Fernández et al., 2014, 484.)

An article published in 2017 showed an experimental design using hydrogenotrophic methanogens to reduce the concentration of carbon dioxide by injecting hydrogen to enrich the biogas. However, the projected goal of upgrading 90 % of biogas methane content at a rate of 90 m³ of biogas per reactor m³ per day was not achieved as a result. The following hydrogenotrophic

methanogens working stoichiometry (equation 7) demonstrates the bio tracking filter operating technology. (Dupnock & Deshusses, 2017, 488-502.)

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad\qquad (8)$$

As the purity of biogas is not as high as for natural gas it will need additional processing, and the system will not simultaneously remove carbon dioxide and hydrogen sulfide. To achieve more purity, the use of different microorganisms will be needed, so pre- or post-cleaning of H_2S is necessary. (Jensen, 2019 Spring, 28-37). Using proper microorganisms, however, can remove the hydrogen sulfide. To upgrade the biogas to its natural condition it will be necessary to use other upgrading technology, such as a chemical absorber that removes the remaining hydrogen sulfide. To reach the purity of 99.9 % of methane, the biogas will be pumped into the bio-trickling filter first, where it will be introduced to the hydrogen and then to the chemical absorber afterward. Where to obtain the quality of natural gas the hydrogen sulfide along with the remaining carbon dioxide will be eliminated. After the chemical absorber, the residual carbon dioxide can also be eliminated, by running it through the bio-trickling filter again instead of dumping it into waste. (Cano et al. 2018, 663-674.)

In the same report published in 2017, the construction of the plant is expected to begin in Denmark in 2020 and will be finished by 2021, "although the report does not provide any concrete details on the current situation." The plant will run for at least twenty years between 2021 and 2040 and is scheduled to be deconstructed by the end of 2040. The plant's operating costs are considered along with anaerobic digestion, "since the actual cost of biogas upgrading is not stated." Biogas plants can receive gross biomass of 360 000 tons per annum from local farmers. Biogas will be converted to biomethane by using various upgrading technologies and transmitted via the gas network. (Dupnock & Deshusses, 2017, 488-502). The benefits and drawbacks of biotrickling filters are listed below (TABLE 2). (Jensen, 2019, 28-37.)

TABLE 2. Advantages and disadvantages of biotrickling filter. (Jensen, 2019 Spring, 28-37)

Advantages	Disadvantages
No depletion of methane	Low methane purity (90 %) has already been shown to be consistent, requiring secondary methods to achieve natural gas purity.
It is a biological process that does not require the use of chemical substances and the use of hydrogen enables Power to Gas.	Removal of H_2S is not feasible, and chemicals must be used anyway if chemical absorption is used as the secondary upgrading technology.
Biogas enrichment would increase the yield of methane, allowing for larger CH_4 output and as CO_2 is converted to CH_4 rather than released after upgrade, the technology has very good potential for low carbon footprint per m³ of biomethane.	The process is highly dependent on electrolysis hydrogen, which means it's just as inexpensive and environmentally sustainable as the energy market is at a given time.

2.2 Removal of other contaminants

Other contaminants that need to be removed from biogas include halogens, oxygen, nitrogen and siloxanes. Industrial landfills (chemical) typically have high concentrations of halogens.

In Finland, these concentrations are relatively low and thus additional measures are not necessary regarding gas purification. It is typically when biogas is used in fuel-cells that damage caused from the presence of halogens needs to be taken into consideration. (Arnold 2009, 25.)

Halogenated hydrocarbons (especially chloro- and fluoro- hydrocarbons) together with longer hydrocarbons can cause corrosion in combined heat and power (CHP) engines. To remove them from biogas, the gas is passed through pressurized tube exchangers filled with activated carbon where they are adsorbed. The exchangers are typically designed to purify the gas for more than 10 hours. They are parallel to each other, and while one treats the gas the other is desorbed. To regenerate the activated carbon, it is heated to 200 °C. At this temperature, the adsorbed compounds are evaporated and carried away by inert gas. (Wellinger & Lindberg 2000, 17.)

Oxygen and nitrogen may be present in the biogas if air gets leaked into or excess air was added during desulphurisation via in-situ microaeration. The air can also leak in when the gas is being collected in landfills via permeable tubes when small under pressure is applied. Low amounts of oxygen are typically not a problem. At higher concentrations however, there is a risk of explosion. (Wellinger & Lindberg 2000, 17.) Oxygen and nitrogen can be removed from the biogas by adsorption with activated carbon, membranes or molecular sieves. It is, however, better to avoid their presence in biogas as they are both difficult and costly to remove. (Petersson & Wellinger 2009, 9.)

Siloxanes are compounds that have a silicone-oxygen bond. They are typically used in products such as shampoos and deodorants, and thus can be found in the biogas produced in sewage sludge treatment plants as well as landfill gas. When burned, siloxanes form silicon oxide, a white powder, which can cause issues in gas engines. It causes abrasion on the surfaces of spark plugs, valves and cylinder heads. (Petersson & Wellinger 2009, 9; Wellinger & Lindberg 2000, 17.)

There are several techniques for removing siloxanes from biogas. These techniques are typically used for the combined removal of siloxanes and other harmful compounds. They include adsorption on activated carbon, cooling the gas, absorption in hydrocarbon liquid mixtures, and activated aluminium and silica gel. (Petersson & Wellinger 2009, 9.)

2.3 Water removal

Most of the time discarding biogas from desulphurization unit contains saturated water. Where total amount of water that consist biogas count on temperature which roughly at 35 °C biogas contains 5 % of water content. (Ryckebosch 2011, 1634.) Physical and chemical technologies such as adsorption, absorption or condensation are current methods to eliminate H_2O. (Rutledge 2005, 38.) To begin with pressurized columns (600–1000 kPa) which filled with silica, alumina, magnesium oxide or active carbon. Where, water adsorption can reduce biomethane's dewpoint to -40 °C. To apply this technology, two respectively adsorption towers are needed; First one is starting the operation until saturation and the second one is start regeneration at low pressure. (Persson 2006.)

Before water enters to the water adsorption, it should eliminate dust and oil particles first, also it necessitates high investment cost but lower operation cost. Similar to carbon dioxide removal in organic solvent, water absorption can reduce biomethane's dewpoint down to –15 °C which requires regeneration of the solvent at 200 °C. Must be remembered, this process

is removing oil and dust particles at the same time with absorption of water. Although, the high operation pressure necessitates high operation and investment cost, where a low biomethane flow rate of 500 m3/h is requires assuring the economic sustainability of glycol-based absorption. (Ryckebosch, 2011, 1643.) All things considered, the subsequent separation of the condensed water droplets by demisters, cyclones or water traps consider the easiest but less efficient H_2O isolation method because of the fact that it can reduce biomethane dewpoint to 0.5 °C which is cause by water freezing at the surface of the heat exchanger. with this in mind, the process works in atmospheric pressure. However, reducing dewpoint further to −18 °C in need to compress the biomethane before the cooling (Ryckebosch, 2011, 1643). At the present time, electric cooling or underground pipelines provided with water traps as an exchanger is used to cool down the biogas. (Peterson and Wellinger 2009, 10.)

The raw biogas typically contains some water vapor and the amount of it depends on the temperature, for instance, 5 % of water concentration is possibly at 35 °C (Rutledge 2005; Persson M. 2003, 1634). Hence, the water concentration decreases when the temperature decreases, and vice versa. With this intention, the automobile fuels design at the dew point of the minimum of 10 °C at 1 atm. (Rutledge 2005, 1634.) There is two-stage to remove moisture, physical and chemical separation.

2.3.1 Condensation

The main reason for using physical drying processes is to avoid the water be in touch with equipment such as compressors, pipes, activated carbon bend, and other parts of the processes, that are sensitive to corrosion. The refrigeration, however, considers as the easiest way of water vapor removal, wherein can drop the dew point to 0.5 °C because of freezing issues on the shell of the heat exchanger (Ryckebosch, 2011, 1634). Under those circumstances, and improve the dewpoint to its lower point, it should compress the gas right before cooling it. Then, it is possible to expand to preferred pressure, because when dewpoint is decreasing the higher pressure is required to be used. (Ryckebosch, 2011, 1634.)

   The Methods which use condensed water physically isolated by biogas are;
   - Demister: in this step wired mesh (micropores 0.5–2 nm) is used to detach liquid particles, where 2–20 °C of dewpoint can reach in 1 atm.
   - Cyclone: in this step centrifugal force is used to detach water droplets.
   - Moisture traps: in this step the temperature decreases by expansion which causes condensation. Therefore, the condensed water can be removed from the water tap in the biogas pipe. (Ryckebosch, 2011, 1634.)

2.4 Purification summary

Estimation of purification technologies costs is difficult because many essential parameters are strongly dependent on local circumstances. Additionally, the technical possibilities of a particular technology (such as H_2S removal efficiencies) do not often correspond with the most economic operation. An overview of the purification technologies discussed in this chapter are presented in TABLE 3 together with their cost estimations. (SevernWye 2017, 12; Allegue & Hinge 2014, 26.)

TABLE 3. Summary of biogas purification and drying technology (adapted from Allegue & Hinge 2014, 26; Erler 2009, 71; Okoro & Sun 2019, 19)

Method	H_2S removal efficiency	Approximate annual operating cost (€/ [1000 Nm^3/h])	Advantages	Disadvantages
In-situ microaeration	90 – 99 %	20 300	• No additional costs for separate unit • No additional chemicals	• Elemental sulphur can be oxidized to sulphates which limits CH_4 content • Suphuric acid can form causing corrosion in the digester
Impregnated activated carbon	95 – 99 %	(overall adsorption cost) 60 000	• 40 – 60 times more efficient than activated carbon • Can remove multiple contaminants (H_2S, siloxanes, water)	• Decreases ignition temperature of carbon which can cause it to self-ignite • Difficult to regenerate
Iron oxide	99.98 %		• Highly effective and efficient method	• High operation costs • Highly chemical intensive
In-situ chemical precipitation (iron salts)	N.A	70 000	• Easy to monitor, handle and implement	• Difficult to control degree of H_2S removal • Can impede formation of CH_4
Bio scrubber	98 %	130 000	• Can be used for biogas with up to 30 000 mg/m^3 H_2S • Highly efficient with little clogging issue	• High operation costs • Difficult to achieve efficiencies >98 % • Can wash off slow growing microorganisms
Biofilter	90 – 99 %	560 000	• Low energy and equipment requirements • No additional chemicals	• Accumulation of biomass on surface • Large carbon footprint
Bio-trickling filter	100 – 200 ppm	100 000	• No CH_4 depletion • No additional chemicals • Methane enrichment (conversion of CO_2 to CH_4)	• High amount of air bubbles in the biogas

3. BIOGAS UPGRADING

All the impurities mentioned in the chapter above need to be removed to upgrade biogas to biomethane with the quality of natural gas quality. When H_2O vapor, H_2S, siloxanes, carbon hydrates and NH_3 are removed, the carbon dioxide is essential impurity to be eliminated from biogas to match Wobbe Index as in the FIGURE 4. Furthermore, the declining in the relative density is relay on CO_2 removal, where that display's in incline in the Wobbe index. (Hagen, M 2001.)
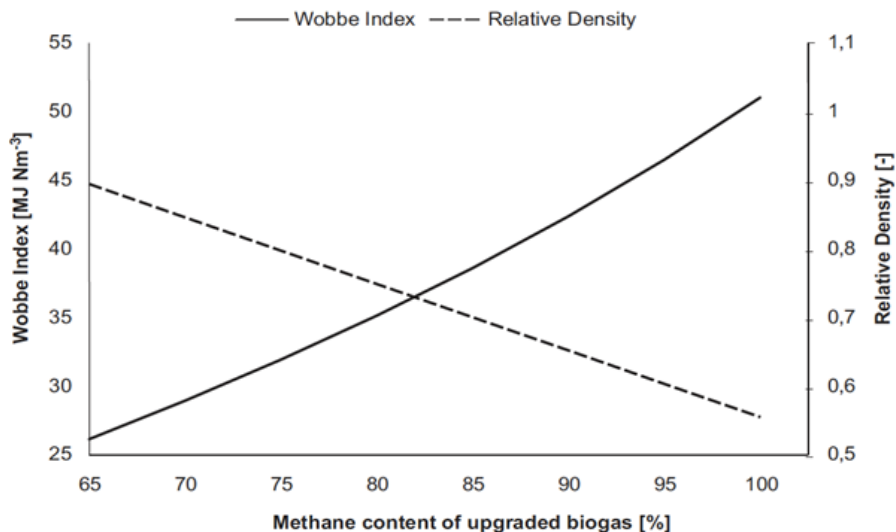
FIGURE 4. Wobbe index and relative density as function of methane content of the upgraded gas. (Hagen, M 2001.)

Biomethane usually consists 97-99 % of methane and 1-3 % of carbon dioxide despite the it's intentional use, where usually, vehicle fuel qualification demands a combined CO_2 and N_2 substance of 1.5–4.5 %, on the other hand the pipeline qualifications demand CO_2 substance less than 3 %. (Rutledge 2005.) Any of the following methods can be used to remove CO_2 from the biogas:
(1) physical and chemical CO_2 absorption, (2) membrane separation, (3) cryogenic separation, (4) adsorption techniques (e.g. pressure swing adsorption (PSA), vacuum swing adsorption (VSA)) and (6) biological methane enrichment. (Ryckebosch, 2011.)
In the following subchapters some of these methods are described in more detailed.

3.1 Physical and chemical absorption of CO_2

This section of the report describes the technologies used to upgrade biogas to biomethane. Organic physical scrubbing, water scrubbing, and amine scrubbing are discussed with their working process and operating costs which differ depending on the geographic location and operating environment.

3.1.1 Organic physical scrubbing

Among the different types of technologies used for upgrading biogas, organic physical scrubbing is a technique where organic solvents are used as an absorption medium to remove carbon

dioxide from unpurified biogas. The report presented here is based on organic physical scrubbers which use Genosorb® 1753 as an organic solvent that is the most widely used in industrial applications. The working theory of organic physical scrubber is alike as that of water scrubber which is that the solubility of carbon dioxide in water is much greater than that of methane. A combination of dimethyl ethers with polyethylene glycol makes the organic solvent of Genosorb used in the technology for CO_2 removal. (Bauer, Fredric, Hulteberg, Persson, & Tamm, 2013, 23-24.)

When compared between the organic solvent and water, from many studies it is found that the solubility rate of carbon dioxide in an organic solvent is greater by five times than the latter which is about 0.18 M/atm (Maréchal, Laurence, & Gassner, 2010). In Selexol and water the solubility of CO_2 is higher by 17 and 26 times respectively than that of methane. As the solubility is already higher which lowers the recirculation of Selexol in an organic physical scrubber. (Barry & Lyddon, 2008, 7.) The simplified schematic illustration of the organic physical scrubber is shown below. (Fredric et al. 2013, 45-49.)
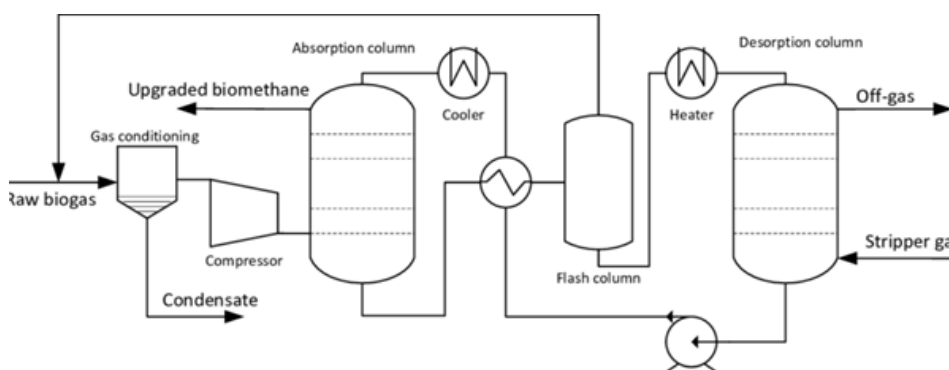
FIGURE 5. Flow diagram of physical scrubber for biogas upgrading. (Fredric et.al.2013, 46.)

Both raw biogas and organic solvents are cooled before introducing them in a crosscurrent moment in the absorption tower. Organic solvent cooled to 20 °C, and raw biogas compressed to $7-8$ atm pressure in the absorption tower helps to maintain the optimal environment for optimal operation. Temperature plays a significant role in the column were to expand the interaction between the reactants. After the absorption of carbon dioxide with Selexol and before delivering, upgraded biogas is dried to absorb the extra moisture. After lowering the pressure and increasing the temperature, the organic solvent is inserted from the top of the flash chamber after leaving through the absorption chamber base. Through the flash column, some portion of dissolved methane along with CO_2 can pass again through the compressor, as shown in FIGURE 5. Certain phenomena such as the amount of methane in unpurified biogas, compression in the absorption chamber, and needed methane slip determine the accurate pressure used in the flash chamber. After increasing the organic solvent's temperature to around 40 °C, the air is introduced from the base, and random packing material is packed to raise the surface of the interaction between the air and solvent in the desorption chamber. The pressure is lowered to one bar, and no external heating system is used as heat is obtained from the compressor and regenerative thermal oxidation (RTO) unit. (Fredric et al. 2013,45-49.)

The operation of scrubbing begins with removing hydrogen sulphide with activated charcoal, and elimination of moisture should be done before upgrading biogas through organic physical scrubbing to achieve higher purity of methane. Also, the presence of elements like siloxanes

should be removed before upgrading biogas. Present organic physical scrubber technology provides methane recovery up to 98.5 %; however, the recovery rate depends on the quality of impurified biogas and working conditions. The cost to start a physical organic scrubber is high initially, but it decreases in increasing size and capacity. The investment cost for organic physical scrubbing is shown in FIGURE 6. (Fredric et al. 2013, 48.)
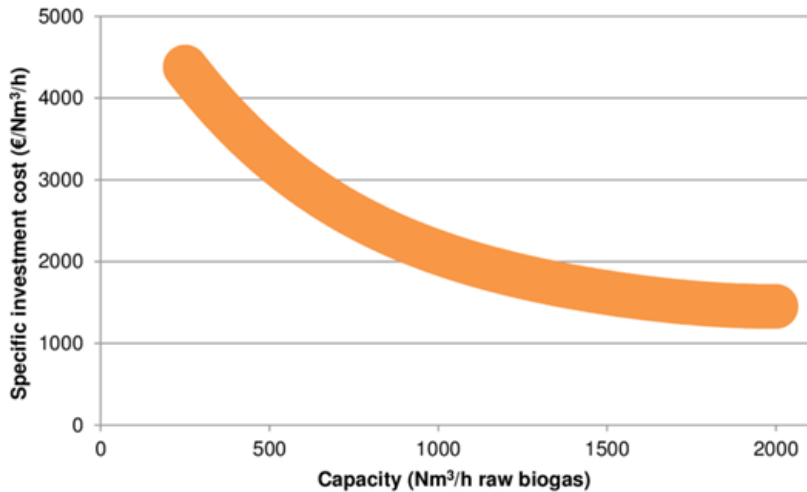
FIGURE 6. Investment cost for organic physical scrubbing including RTO and biomethane dryer. (Fredric et al. 2013, 48.)

Average electricity consumption in the organic physical scrubber is shown in the FIGURE 7. The removal efficiency is mostly ensured to be 96 to 98 % and the annual cost of maintenance is around 2 to 3 % of investing cost. (Fredric et al. 2013, 49.)
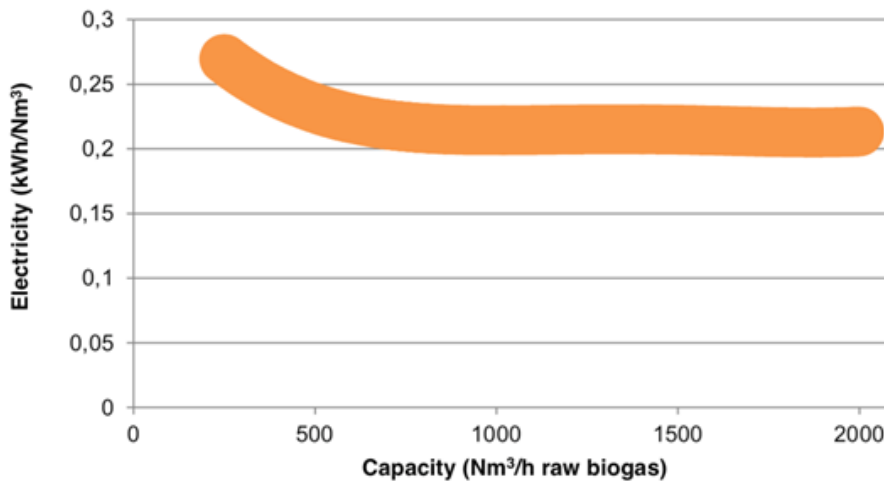
FIGURE 7. Average electricity consumption in the organic physical scrubber. (Fredric et al. 2013, 49.)

3.1.2 Water scrubbing

Water scrubbing is a technology used widely for biogas upgrading (FIGURE 8. Khan et al. 2017, 281.) CO_2 is discharged along with the water from the absorption column after the separation of carbon dioxide from the impurified biogas. Absorption is operated at the pressure between 6 to 10 bar, after which the pressure is lowered to normal atmospheric pressure just before releasing the water to the desorption chamber. (Fredric et al. 2013, 34).
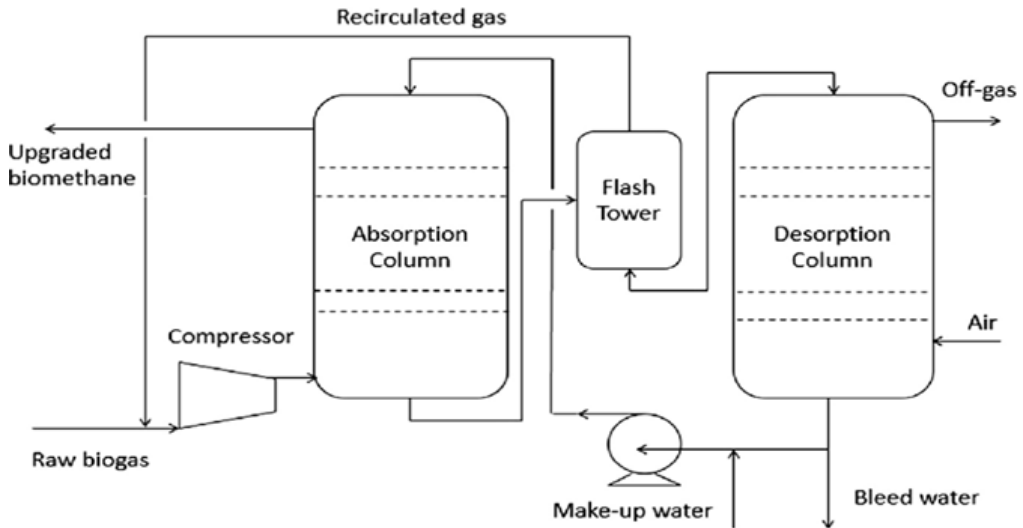
FIGURE 8. Flow diagram of water scrubber. (Khan et al. 2017, 281.)

Since the rate of dissolvability of methane is lower by almost 26 times than that of carbon dioxide, in an ideal condition, the concentration of methane dissolving in water will be 4 % when 100 % of CO_2 is dissolved in water. (Persson 2003, 188.)

Pressure and temperature play a major role in the operating procedure, as they decide the volume of carbon dioxide that will remain in the methane. The amount of water required to absorb a certain volume of carbon dioxide from the raw biogas is determined by the way the column is installed and constructed. The water flow rate needed to absorb CO_2 is indirectly proportional to the volume of carbon dioxide present in raw biogas and directly proportional to the solubility of carbon dioxide at a certain temperature. A decrease in temperature leads to an increase in solubility of carbon dioxide and vice versa and there is no effect of pH on the flow of water on biogas upgrading (Petersson & Wellinger, 2009, 7.)

Before injecting the raw biogas to the absorption chamber, the pressure is increased to around 6 to 10 bar, which initially may have the temperature up to 40 °C. For instance, by raising the pressure up to 6 bar and decreasing the temperature of the biogas from the original 40 °C to around 15 °C, 95 % of the water vapor in the biogas gets condensed and can be removed before introducing the gas into the absorption column. Also, ammonia and volatile compounds can be removed through the condensation process along with water. Water and biogas are introduced into the absorption chamber (FIGURE 8) in a counter-current direction so that the heavy loss of methane and energy consumption could be reduced. To make sure the wastewater leaving the absorption column takes away a large volume of carbon dioxide and less possible volume of methane, water is equilibrated with the smallest and greatest partial pressure of methane and carbon dioxide respectively. (Fredric et al. 2013, 38-39.)

The column's packaging material plays a significant role in yielding higher purity methane by extending the biogas and water interaction. The packing material quality and bed height ensure absorption efficiency, and the diameter determines the amount of gas throughput. (Ralph & Jr, 1994.) In the flash chamber, the water containing carbon dioxide and trace methane is injected from the top. The pressure is lowered to 2.3 to 3.5 bars so that the small portion of carbon dioxide and methane is driven away from the water, which is then recirculated to the compressor. The ratio of methane to carbon dioxide in the flash column, on average, is around 3 to 17, as the major volume is occupied by carbon dioxide in water. After that, the water having the composition of less than 1 % of methane is injected into the desorption column. Through the flash column, the volume of gas returning to the compressor on average is from 20 to 30 % of total gas entering into the chamber. Water containing a large amount of CO_2 from the flash column is transferred into the column of desorption, where air from the bottom and water from the top of the chamber is inserted. The column is filled with random packing to make the concentration of carbon dioxide in water very small. When the air with the lowered pressure meets the carbon dioxide in water, it leads to a partial carbon dioxide pressure very close to zero. Therefore, the concentration of carbon dioxide in water is very small, almost nil, and recirculated back to the absorption chamber to reduce water consumption in the system. (Fredric et al. 2013, 38-39.)

In the system, temperature determines the required rate of flow of water to clean a certain volume of biogas. Water used can be either increased or decreased by changing the temperature of the water, as an increase in temperature leads to higher water consumption and vice versa. Based on the several temperature and pressure, the required volume of water needed to upgrade 1000 normal cubic meters of biogas with less than 2 % of CO_2 on it is given in the TABLE 4.

TABLE 4. Required volume of water to upgrade 1000 cubic meters of biogas at different pressure and temperature. (Fredric et al. 2013, 39.)

Pressure in bar	Water temperature in °C	Water flow in m³ per hour
8	20	210-230
8	14	180-200
6.5	14	210-230

Generally, biogas which is obtained from anaerobic digestion is directly introduced into the system. In the adsorption chamber, H_2S having the concentration usually between 300 to 2 500 ppm is absorbed in water with CO_2. However, hydrogen sulfide is released in the desorption process and needs to be cleaned before it is released in the atmosphere to lower the harm caused to humans and the environment. Cleaning of H_2S is mostly done by activated charcoal. Hydrogen sulphide on the addition of oxygen in the desorption chamber gets oxidize to change into sulphuric acid and elementary sulphur (Ryckebosch, Drouillon, & Vervaerenc, 2011, 1633-1645.) The temperature and pH of the water affect the rate of oxidation of hydrogen sulphide. In the experiment performed, raising the temperature by 20 degrees and pH from 4 to 8 rose the oxidation rate by three and four times respectively for hydrogen sulphide. (Garnett, Hubinger, & Fernandez, 1987, 439–443.) Rusting which is caused by formation of H_2S causes problems in the operation of the plant. Concentration of hydrogen sulfide can be lowered by reducing the temperature and pH during the operation. Sometimes the growth of microbes causes clogging and creates problems in the normal operation of the system. (Håkansson, 2006, 55.)

Being well-developed technology with a high percentage of purifying capacity, the operational cost of water scrubber is high in the initial stage with less raw biogas purifying capacity. But the cost decreases with increasing the capacity of the system. The investment cost excluding the gas cleaning, heat recovery, and off-gas recovery is shown in the FIGURE 9 (Fredric et al. 2013, 41-42.)
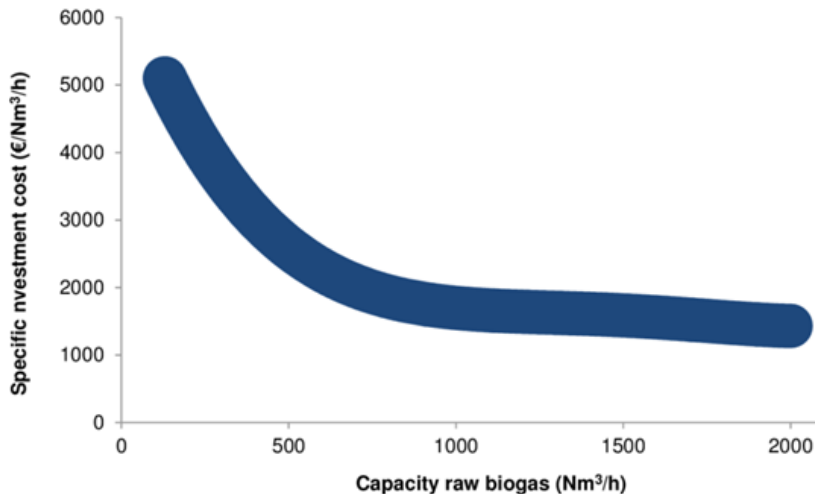
FIGURE 9. Investment cost of water scrubbing excluding the gas cleaning, heat recovery, and off-gas recovery. (Fredric et al. 2013, 42.)

In the water scrubber, water used to absorb carbon dioxide is contaminated with different impurities from raw biogas and therefore needs to be replaced. When the same water is used for a long period, there is a high possibility that the equipment gets rusted due to sulphuric acid from the oxidation of hydrogen sulphide. Usually, the volume of water consumed in a day is around 0.5 to 5 m³, but it differs between the working environment and the plant's size. Energy consumed by the major sources of water scrubber, which are compressors, cooling mechanisms, and water pump, largely depends on the manufacturing of plant, close environment, and characters of the incoming raw biogas. (Fredric et al. 2013, 42-43).

Consumption of energy increases when water pump operates at lower loads and energy depends on several factors such as the amount of water pumping in a certain period, the capacity of the pump, and pressure at entrance and exit points. When operating on a full load the average energy consumed by pumps in water scrubber is about 0.05 to 0.10 kWh/m³. However, for the compressor working at a pressure of about 6 to 8 bars, energy consumption is around 0.10 to 0.15 kWh/m³ of compressed raw biogas. Categorized into two sections "warm" and "cold", different energy is required by cooler depending on the place of situation and design of water scrubber. When comparing the energy consumption, less energy is needed for a warm system which cools the biogas of temperature around 30 to 50 °C by using a dry cooler. Ordinarily, 200 kW of heat can be eliminated using 1 to 5 kW of electricity by a dry cooler. On the other hand, operating at the temperature of 5 to 15 °C, energy consumption is quite high for cooling machines around 20 to 50 kW of electrical energy to cool 100 kW of heat. In the modern water scrubbers, energy consumed by cooler to cool the compressed biogas is about 0.01 to 0.05 kWh/m³ of incoming raw biogas. (Fredric et al. 2013, 42-43.)

The FIGURE 10 shows the range of electricity consumption by water scrubber. The figure might not be true for every plant since numerous factors are affecting the electricity used for biogas upgrading by water scrubber as described above. This data provided by the biogas upgrading companies in Sweden and Germany can be taken as an example of the range between the size of the operational plant. However, described in water scrubber above, there is no effect of different concentrations of gases mostly methane in the raw biogas for the consumption of electricity. (Fredric et al. 2013, 43-44.)
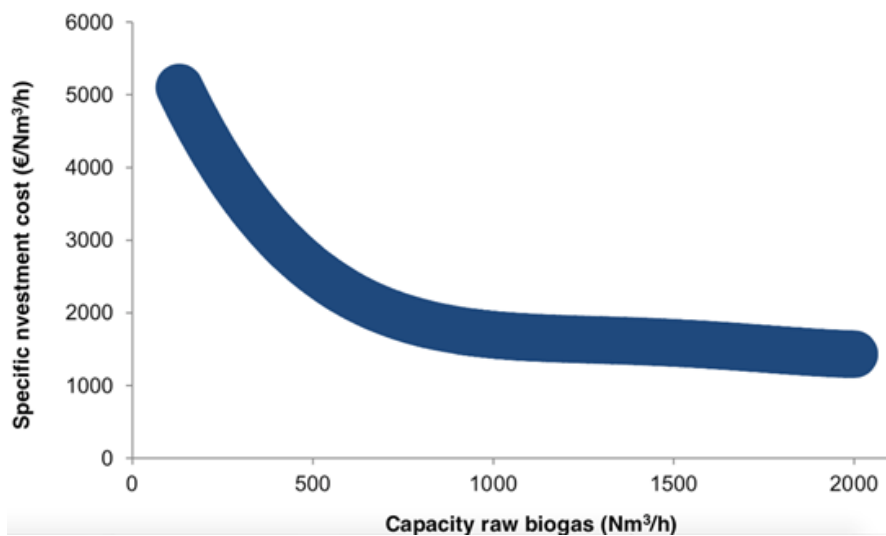
FIGURE 10. Consumption of electricity based on various size of water scrubbers. (Fredric et al. 2013, 44.)

Water scrubber can upgrade the raw biogas up to 98 % methane content. As water scrubber fails to remove the oxygen and nitrogen so the concertation of these should be taken into consideration and can be removed by using other techniques discussed in this report. The concentration of nitrogen and oxygen in the upgraded biogas will be doubled if the raw biogas contains the methane about 50 % of total gas and additional oxygen and nitrogen is also transported from the desorption column when water meets the air. Thus, the volume of nitrogen and oxygen from the unpurified biogas plays a significant role in determining the final purity of methane after biogas upgrading. (Holmgren et al. 2010, 1-8.)

3.1.3 Amine scrubbing

Amine scrubbing is a technology used for biogas upgrading like other upgrading technologies as water and physical organic scrubbing are described in the above sections. The working principle of amine scrubbing is that the amine mixture attaches the carbon dioxide from raw biogas. Amine solutions contain the chemicals having molecules with carbon and nitrogen, some of which are monoethanolomine (MEA), methyldiethanolamine (MDEA), diethnolamine (DEA). (L. Kohl & B. Nielsen, 1997, 900). However, aMDEA which is a combination of methyldiethanolamine and piperazine is mostly used at an industrial level. This system is not broadly used as water, physical organic, and PSA scrubbing. (Fredric et al.2013, 16.)

As mentioned earlier, most of the industries use aMDEA to purify biogas from amine scrubber which generally contains two main chambers an absorber and a striper. An absorption chamber

where the amine is introduced in a countercurrent way to raw biogas removes the carbon dioxide from the biogas (Huertas; Giraldo & Izquierdo). The FIGURE 11 demonstrates the schematic diagram of an amine scrubber. (Fredric et.al. 2013, 16-17.)
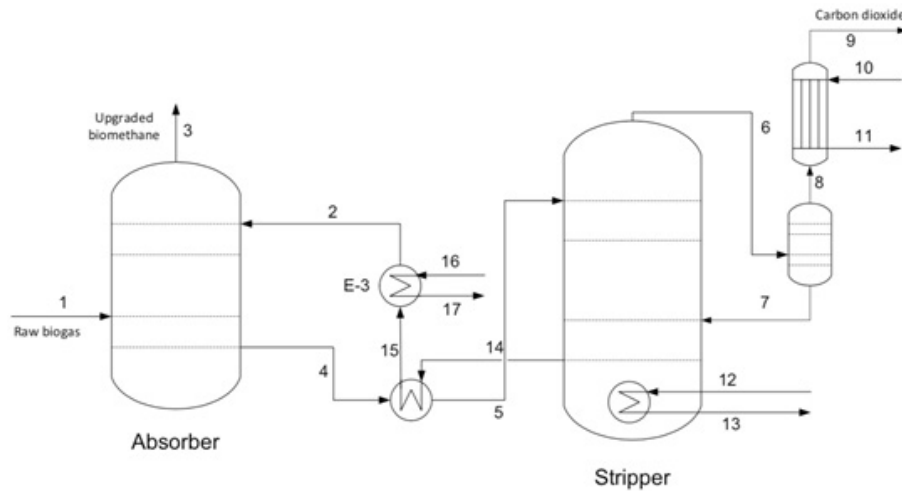
FIGURE 11. Flow diagram of amine scrubber. (Fredric et al.2013, 17.)

Raw biogas commonly having a temperature of about 20 to 40 °C enters through the bottom of the absorber column. Amine solution is introduced into the absorber where due to the exothermic reaction the temperature increases to 45 to 65 °C and pressure is kept one to two bars to make the reaction happen. The CO_2 and H_2S rich liquid passes through the bottom of the absorber chamber which is preheated with the stream from stripper as represented by number 14 in the diagram. After the reaction the stream mainly consisting of methane passes through the top of the absorption chamber. To acquire the required final concentration of upgraded biogas, an absorption chamber is made with typical length and design of diameter in a way in which at the specified gas flow rate to have the lowest pressure drop. (Fredric et al. 2013, 17.)

The liquid which is heated in HX1 (known as lean/rich heat exchanger) after passing through the absorber is introduced to the kind of flash box inside the stripper. Lean and rich denotes the liquid amine with and without CO_2, respectively. In the flash box, carbon dioxide contained in HX1 is removed and liquid is further passed to the packing material. Steam is introduced to the liquid in the packing column and liquid is passed further to the reboiler. Having a temperature of around 120 to 150 °C and pressure from 1.5 to 3 bar, reboiler has two principal uses. It creates an environment for releasing of CO_2 and H_2S from amine solution and releasing of vapor from the boiler helps to increase the kinetics of the desorption by decreasing the partial pressure of carbon dioxide in the column. (Kohl & Nielsen, 2005, 155-163.)

When the liquid is introduced to the reboiler which is heated through either steam, water, or oil, the evaporated vapor containing carbon dioxide, hydrogen sulfide and steam is passed via the top of the stripper chamber represented by number 6 in the FIGURE 11. The vapor is condensed where the condensed steam is again brought back to the stripper which contains a small portion of amine; however, the carbon dioxide (and H_2S) does not pass into the stripper. After the amine scrubbing the purified gas contains moisture that needs to be removed with other methods.

Depending on the type of amine solution used different reactions may happen, however as mentioned previously mostly used amine mixture is aMDEA. The reaction shown below occurs with the amine used (aMDEA). (Fredric et al.2013, 18.)

$$CO_2 + PZ - \rightarrow PZH^+ + HCO_3^- \tag{9}$$
$$CO_2 + MDEA <-> MDEAH^+ + HCO_3^- \tag{10}$$

The rate of CO_2 absorption of the combination of MDEA and PZ is quite high comparing to that of MDEA alone since the absorption capacity of secondary amines (PZ) is higher. Moreover, secondary amines increase the capacity for the reaction with tertiary amine which is economical due to low heat required for the reaction. (Fredric et al.2013, 19-20.)

There are mainly three types of standard sizes of amine-based upgrading technology used in Sweden with the raw biogas inlet capacity with 600, 900, and 1800 m³/h. However, technology with two different inlet capacity of 700 and 1400 m³ of raw biogas in Germany. In Sweden raw biogas up to 60 % is carbon dioxide concentration can be upgraded and hydrogen sulfide concentration up to 300 ppm with the available technology. When installing the system, there are certain agreements done regarding the usages of water in the absorption chamber, energy (electricity) consumption, and the use of chemicals. Electricity consumption in amine scrubber is mostly dependent on the inlet rate of biogas, the highest load usually leads to lower electricity utilization and vice versa. Also, depending on the geographical location of operation, mostly 0.14 kWh of electricity is needed to upgrade one cubic meter of biogas with the lowest load whereas, 0.12 kWh for the same volume of biogas with higher load. When compared to the consumption of energy at the stripper column for the regeneration of amine which is around 0.55 kWh is much higher than that of the absorption column. The typical investment cost of an amine scrubbing unit which decreases with an increase in capacity of raw biogas is presented in the FIGURE 12, which varies with the size and flow rate. (Fredric et al.2013, 20-21.)
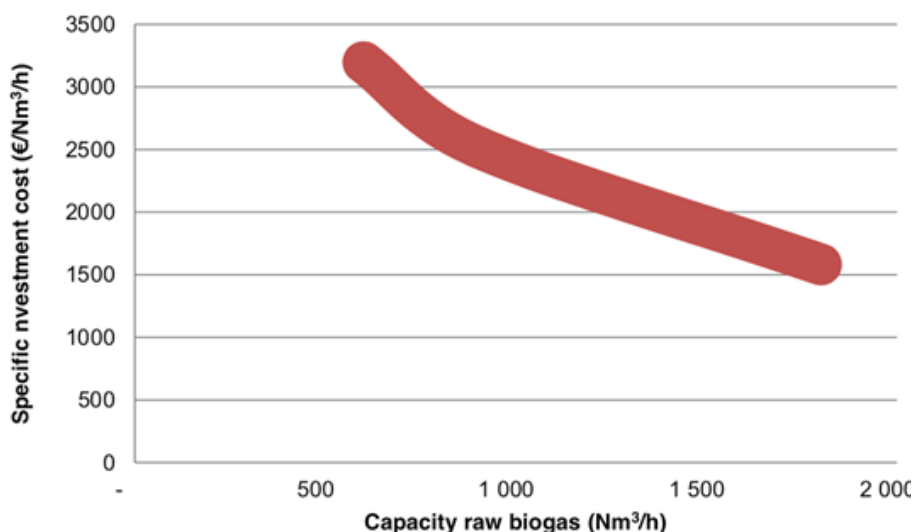

FIGURE 12. Investment cost of amine scrubbing depending on the raw biogas capacity. (Fredric et al. 2013, 21.)

During the operation of amine scrubber, there is a high probability of arising from several problems such as loss of amine, foaming, rusting of different types of equipment, and difficulty in

meeting the requirements. (Abry & DuPart 1995, 41-50.) The problem may also arise in the stripper column which function is to absorb the carbon dioxide from the amine solution. However, there may be some default in the operation of the stripper column which leads to the passing of solution with a high concentration of carbon dioxide with it. Some of the factors causing operational issues could be due to the leakage from the lean/rich heat exchanger, an impurity of the solvent, lack of well-functioning of reboiler. In some cases, mechanical defect leads to the unequal supply of amine solution in the absorption chamber because of plugging. The presence of oxygen and carboxylic acids in the inlet gas leads to the contamination of the solvent. (Fredric et al. 2013, 21-22.)

Loss of amine is not too high in the amine scrubber but can cause several operational problems. Losses are mostly experienced from joints, heat exchangers, pressure gauges, and loss in the form of vapor through the gas streams. In addition to that, reactions caused by the contaminants also leads to a decrease of amine (Ralph & Strigle 1994, 354). Corrosion of different parts of the machines causes different interruption in the operation. However, proper manufacturing of plant can control the corrosion to some extent. As amine scrubber fails to remove hydrogen sulfide completely the removal should be done beforehand e.g. by using activated carbon. Also, the situation is similar to the oxygen as it should be removed before amine scrubbing. As oxygen reacts with the compounds of amine leading to the different operational problems. (Fredric et al. 2013, 21-22.)

3.2 Membrane separation

Two essential processes have applied in membrane separation, both of which rely on selective permeability characteristics of the membranes. These processes are gas-gas separation and gas-liquid absorption separation. However, sometimes it is necessary to divide these processes into several phases respectively because of imperfection in separation. (Wellinger, 2011, 3.) As a result, it is possible to observe a remarkable loss in CH_4 but that can be solved by recirculation. (Ryckebosch, 2011, 1642.)

3.2.1 Gas–gas separation

The first stage of cleaning biogas from hydrocarbons, hydrogen sulfide, and oil vaper is to pass them via compressors, where the gas pressure goes from 2 000 to 3 600 kPa. Smaller polar molecules such as CO_2, H_2S, and oil vapers are isolated via an acetate-cellulose membrane. However, this type of membranes is not efficient for isolating nitrogen gas from methane, in which the highest isolation can get up to 92 % in this particular process. To solve these issues the extra phases are added to get up to 96 % of methane (Ryckebosch, 2011, 1642). Furthermore, the off-gas either uses in a steam boiler or it goes to flare which depends on the consideration of methane, for fear that the off-gas may consist of 10-25 % of methane. In reality, some membranes are particular for specific molecules such as H_2S. In this case, CO_2 can be isolated in different stage, hence, hollow fiber membranes are a built-in cross-flow system to ensure the high effectivity of the isolation. (Ryckebosch, 2011, 1642; Wellinger, 2011, 3.)

The review paper displays interesting excrement that has been conducted by Kim et al (2004). In their experiments, they manage to discriminate methane from carbon dioxide by the permanent carrier membranes of polyvinyl amine (PVA) and put it correspondingly to other layers, resulting in a greater carbon dioxide isolation. Moreover, the correspondingly linked layers of ammonium fluoride gave the greatest isolation of CO_2 to CH_4 (>1:1000). (Ryckebosch, 2011, 1642.)

A high-pressure membrane prosses is used to reach 10 % per m³ reduction comparable to natural gas by a small test. In their experiments, they used low pressure (800 kPa) membrane isolation process which requires getting rid of all trace elements before the membrane-unit by active carbon. Although this may be true, the membrane was not examined for a long time, hence new experimental studies needed to display the long turn efficiency for this prosses. (Ryckebosch, 2011, 1642.)

3.2.2 Gas–liquid absorption separation

Although this technique is new, it is very efficient and can upgrade biogas with 55 % methane to 96 % in one step. Since the absorption membrane works in at 1 atm, the process can be constructed in low-cost meanwhile sufficiently upgrading the biogas. The separation of the gaseous phase from the liquid phase done by a micro porous hydrophobic membrane. When the particles differentiate through the membrane the gas steam should be absorbed on the other side by the liquid flowing with the opposite direction of the flow. To avoid the liquid flowing to the gas side, trivial pressurization of the gas is applied. Furthermore, the heat is should renew which discharges pure carbon dioxide, where it can be utilized for industrial applications. (Ryckebosch, 2011, 1642; Wellinger A, 2005, 12.)

In 1992, Guha et al. conducted a study to show the potentiality of hollow fiber contained liquid membrane (HFCLM). As an illustration, the study used aqueous solution or water as a slim layer which was held in between two independent sets of hydrophobic microporous hollow fibers. The newer process, however, has challenges in the regeneration of the liquid membrane as well as critical issues of humidity control. However, it is possible to solve them by adding a dryer to moistened gas which recently all of HFCLM excludes these shortcomings (Ryckebosch, 2011, 1642; Guha 1992, 593-604).

The review paper of Esteves and Mota (2002), displays an interesting study for the new collective membrane and Pressure Swing Adsorption (PSA) process for gas isolation. In high purity region the Pressure Swing Adsorption (PSA) has high benefits, whereas, the membrane as advantage in speed concerning matter. The system consists of module and a dual-bed PSA-units. The most of the size separation are carried out in membrane, because of maximizing the average driving force. For higher purity of methane and carbon dioxide, both gas flow and residual gas are fed to the PSA process at a deferent stage. Resulting from the enhancement of the isolation performance; which can be obtained by using standalone PSA, while the purity drops when carbon dioxide gets to 60 % because of the low selectivity CH_4 to CO_2 on active carbon. (Ryckebosch, 2011, 1642; Esteves 2002, 275-80.)

Using various set-ups and both water and an aqueous DEA solution (20 %) as a liquid membrane, mixtures of 40 % CO_2 and 60 % CH_4 can be isolated. With a single short length permeator using the DEA aqueous solution, a purification rate of biogas (> 92 % CO_2) and a high recovery rate of CH_4 (as high as 98 %) were possible. Water as a liquid membrane supported much lower levels of purification. (Ryckebosch, 2011, 1642; Guha 1992, 593-604.)

3.3 Cryogenic separation

Producing biomethane by cooling and compressing the biogas is possible due to the fact that methane and carbon dioxide (and other impurities) deliquesce in different temperatures and pressures. One of the isolated remaining impurities from the gas is liquid carbon dioxide. Up to

8 000 kPa of raw biogas is compressed. Compression is carried out with interim cooling at various levels. It is necessary to dry the compressed gas in order to avoid freezing in the following cooling stages. Ultimately, the dried and compressed biogas is cooled until ~45 °C. In the next step, to recover the remaining CH_4, the condensed CO_2 is extracted and treated. The biogas is further cooled to 55 °C and then extended to 800-1 000 kPa in a Tank for expansion, reaching a temperature of approximately 110 °C. There is a gas-solid phase equilibrium in these situations, with CO_2 being the solid phase and more than 97 % CH_4 containing the gaseous phase. Prior to leaving the plant, the CH_4 gas stream is collected and heated. (Ryckebosch, 2011, 1643; Persson 2003, 88; Hagen 2001, 188.)

When the desired product is liquid biomethane (LBM), that has purity comparable to liquid natural gas (LNG), this method is specific for purification. According to Hagen et al. (2001) the cost of this technique is equivalent to the absorption technique. As an illustration, in Netherlands a four-step cryogenic system is used to upgrade biogas to the purity comparable to natural gas

1. Biogas is compresses to 100 bars, followed by cooling to -25 °C.
2. All the impurities and other undesired components are isolated from biogas, and biogas further cooled to -55 °C.
3. In order to raise the calorific value, CO_2 is isolated from the mixture gas. Therefore, the gas is further cooled to -85 °C where the carbon dioxide solidifies. This step is done by using three different vessels:
    — first vessel, for upgrading biogas (-85 °C)
    — second one, for intermediate temperature (-85 °C to – 60 °C)
    — and the third vessel, to liquefy carbon dioxide (-60 °C)
4. This gaseous phase can be injected odours into the natural gas grid before depressurized (Ryckebosch, 2011, 1643).

3.4 Adsorption

There are currently various adsorption techniques that are commercially available for biogas upgrading. These techniques include pressure swing adsorption (PSA)/vacuum swing adsorption (VSA), temperature swing adsorption (TSA) and electric swing adsorption (ESA). (Allegue & Hinge 2012, 32.)

3.4.1 Pressure swing adsorption (PSA)/Vacuum swing adsorption (VSA)

Pressure swing adsorption is the most used adsorption technique in biogas upgrading. At higher pressures and lower temperatures, adsorption is, in principle, expected to be higher. In PSA, pressure differences are used to achieve separation. (Wilken et al. 2017, 15.) The separation is done in columns containing highly porous adsorbents such as activated carbon, zeolite, silica-gel, activated alumina and polymeric sorbents. Other than CO_2, other impurities such as H_2S and water can be removed using this technique. The diameter of the adsorbents' pores should be such that CO_2 is adsorbed while CH_4 is not. CO_2 has a kinetic diameter of 3.4 Å and that of CH_4 is 3.8 Å. Molecular sieve adsorbents that has an average pore size of 3.7 Å can adsorb CO_2 molecules while excluding CH_4 molecules. (Muños et al. 2015, 735.)

The adsorption process begins by compressing pre-purified biogas to 4 – 10 bars. The compression results in an increase in temperature of the gas. It must be cooled down to approximately 70 °C before flowing into the adsorption column, in order to improve adsorption. (Wilken et al.

2017, 15.) A PSA column cycle, so called Skarstrom cycle, is made of four phases: pressurization, feed, blowdown and purge. The compression of the biogas is the pressurization phase. During the feed phase, the raw biogas is fed into the bottom of an adsorption column. As the gas flows upwards, CO_2 is adsorbed while CH_4 flows through the column. However, a small percentage of CH_4 is also adsorbed. When the column is saturated, the feed is shut, and the blowdown phase begins. The pressure in the column is decreased to desorb the CO_2, and the CO_2-rich gas is pumped out the column. When the column pressure is at its lowest, the purge is initiated. Upgraded gas is blown through the column to remove all desorbed CO_2 and possible CH_4. As the column is now regenerated, it can be repressurized with either raw biogas or upgraded gas. The cycle is now complete. (Bauer et al. 2013, 23 – 24.)

A PSA plant typically has four to six adsorption columns to allow for continuous operation (as shown in FIGURE 13). This is done such that one of the columns is used for adsorption while the others are in different regeneration phases. To reduce methane loss, the columns are interconnected such that gas flow exiting one column during blowdown is used to pressurize the adjacent column. This also reduces energy consumption (Bauer et al. 2013, 23.) It is important to ensure that there is no H_2S in the raw gas as it is permanently adsorbed onto the adsorbent which subsequently destroys the structure of the adsorbing material (Petterson & Welinger 2009, 9.)
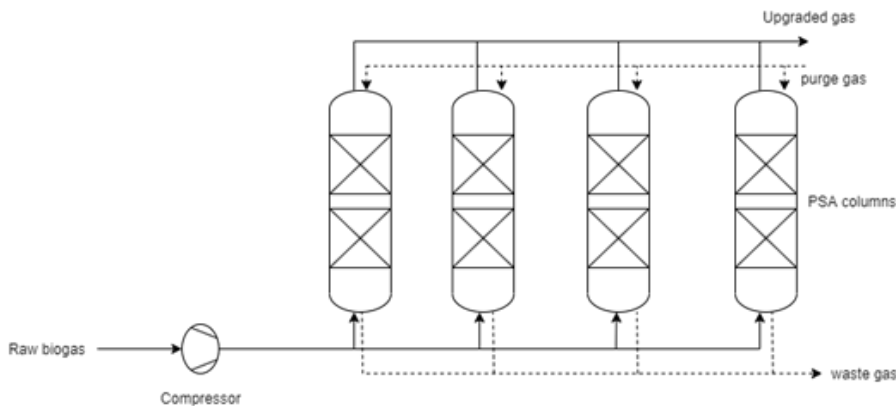
FIGURE 13. Process diagram of biogas upgrading by pressure swing adsorption (adapted from Muños et al. 2015, 735; Bauer et al. 2013, 23).

PSA is suitable for small to medium scale plants. The capital costs of PSA units decrease linearly from 2700 €/(Nm³/h) for flow rates designs of 600 Nm³/h to 1500 €/(Nm³/h) for flow rates designs of 2000 Nm³/h. Solvents are not used in PSA nor is heat needed for regeneration which are both good advantages for using it over other processes. Up to 98 % of methane with a purity of 96 – 98 % is recovered using PSA. (Muños et al. 2015, 736.) PSA does, however, have its disadvantages. The power requirement for PSA units is between 0.15 and 0.35 kWhel/m³ of gas. There is also a methane loss of approximately 1.5 – 2.5 vol.%, and lastly the mechanical stress on the equipment is relatively high as there is high speed loading, pressure retention and the columns need an extremely finely tuned valve clearance. (Wilken et al. 2017, 15.)

Vacuum swing adsorption (VSA) is similar to PSA. The main difference is that the adsorption process in VSA occurs at near atmospheric pressure. This negates the high compression costs of PSA. The CO_2 is regenerated by using a vacuum. (Arya et al. 2015, 404.)

3.4.2 Temperature swing adsorption (TSA) and electric swing adsorption (ESA)

Just as pressure variations are used for CO_2 capture in PSA, temperature variations can also be used to remove CO_2 from biogas. Temperature swing adsorption (TSA) operates by heating the adsorption column using a hot medium such as hot water or steam and is cooled using a cool medium such as cold water, before the next adsorption cycle. (Jiang, Roskilly & Wang 2018, 398.) Since adsorption is exothermic, the amount of CO_2 adsorbed is increased when the temperature is lowered. To regenerate the column, the temperature is increased. (Hedin, Andersson, Bergström & Yan 2013, 420.) Heating and cooling the adsorbent is time consuming resulting in long TSA cycles (several hours), and continual heating of the adsorbent can result in its deterioration, otherwise known as thermal aging. (Ribeiro, Grande & Rodrigues 2014, 1986.)

Electric swing adsorption (ESA) also uses temperature variations for CO_2 adsorption and column regeneration, but whereas in TSA the temperature variations are due to a medium such as water or steam, ESA uses electricity passed through a conductor. ESA therefore has an advantage in unit productivity as electric heating is faster. ESA also has larger differences in temperature than TSA therefore there are significant differences in loading at high and low temperatures. (Grande, Ribeiro, Oliveira & Rodrigues 2009, 1220.) Currently, ESA use is at its early stages. There is ongoing research on the cycle design and cycle scale-up. (Ribeiro et al. 2014, 1997.)

3.5 Biogas upgrading summary

When choosing a biogas upgrading technology, the cheapest one is not always the best one. It is important to consider whether the technology is economically viable. Moreover, just like with purification technologies, local conditions such as water supply, emission limits and available heat affect which upgrading technology is best suited for a biogas plant. (Allegue & Hinge 2012, 44.) TABLE 5 displays the costs and significant parameters of various biogas upgrading technologies.

TABLE 5. Summary of biogas upgrading technologies. (adapted from Sahota et al. 2018, 86; Severn-Wye 2017, 13; Allegue & Hinge 2012, 45.)

Method	CH₄ purity (%)	CH₄ loss (%)	H₂S co-removal	Energy consumption (kWh/Nm³)	Typical investment cost [€/(m³/h)] for 500 m³/h CH₄
Physical scrubbing	93 – 98	<4	Possible	0.10 – 0.33	3 500
Water scrubbing	95 – 98	<2	Yes	0.2 – 0.5	3 500
Amine scrubbing	95 – 98	<0.5	No	0.05 – 0.18	3 500
Pressure swing adsorption	96 – 98	<3	Possible	0.16 – 0.43	3 700
Membrane	90 –99	<5	Possible	0.18 – 0.35	3 500 - 3700
Cryogenic separation	99	<0.1	No	0.18 – 0.25	-

4. BIOMETHANE PRESSURIZATION AND TRANSPORTATION

4.1 Biomethane pressurization

The existing gas network determines the design of the compressor and thus the pressure of biomethane (delivery pressure) and the gas upgrading process (inlet pressure). The work and cost of compressor rise by the power of the pressure differences, where, as greater the pressure differences the greater of power consumption. It is also essential to avoid oil lubricate compressors due the fact that they could possible contaminate the biogas, correspondingly to DVGW G 206 (DVDW, 2008a) that biomethane should be industrially free of oil vaper and dust. While oil free compressors are ideal for the pressurization, more methane are exhibited to lost, thus higher the maintenance for equipment. However, the loss of gas is solved by return feed to the facility. On another hand, load-running compressors have also lower efficiency. Moreover, steam-saturated compressors are more likely to produce water which need extra effort to remove. (Bachmann 2013, 385-387.)

End pressure, flow rate and initial pressure are the factors that to be consider when choosing the compressor, beside the one-stage or two-stage compression factor. Because, the greater pressure differentials are need, the compressors need to be cooled. Hence, volume flow, pressure after compression (grid pressure) are the critical parameters for the selection of the compressor. While screw compressors have higher expenses for maintenance and operating cost, it necessitates less maintenance and are less vulnerable to technical struggle than piston compressors. Hence, it is essential to consider the price and operating cost of screw compressor versus the benefit of higher availability. As an illustration, when transport network of biogas fed is high-pressure then two-stage compression is needed. For this reason, the first stage should be the screw compressor and the second stage, would be preferred piston compressor. The reason behand that is the endurance of screw compressor. (Bachmann 2013, 385-387.)

Gas pressure regulation is required when biomethane is fed into low pressure natural gas network. Hence, limit the fluctuating inlet is regulated by gas pressure regulation facilities. Gas meters monitor the flow of gas in working condition. The gas volume can be converted to a normal state according to the calibration system (Nm³ or m³ STP) along with the pressure and temperature probes and the determination of the gas composition. Furthermore, flow meters or displacement meters are used counting on the safety need, accuracy and cost effectiveness. (Bachmann 2013, 385-387.)

4.2 Biomethane distribution

After production, biomethane is distributed to the end user by either using the natural gas grid or transported by trucks to the filling station as compressed biomethane gas (CBM) or as liquified biomethane (LBM). The most common and typically cost-efficient distribution method is injecting the biomethane into a natural gas grid. (IRENA 2018, 32.)

The injection of biomethane into the natural gas transmission grid has a lot of legal, commercial, technical and regulatory issues that should be considered. The gas quality and energy quantity need to be determined accurately and should be set to the parameters of the grid. Different countries have different parameters. In Germany, the energy supplied should not deviate by over 2 % of the energy quantity that was originally calculated. The gas grid is operated at pressures in the range of 50 to 100 bar and it can even be higher in some cases. Industrial large-

scale consumers, storage facilities underground and gas filling stations are typically connected directly to the transmission grid. Regional grids transport gas connected to the main gas transmission grids and transport gas to a region or city. They typically operate in the pressure range of 4 to 40 bar. Commercial consumers, industrial users and many natural gas refuelling stations are connected to regional grids. Distribution grids are located downstream of regional grids. They are used for transporting gas to residential areas. They typically operate in the pressure range of 20 mbar to 1.0 bar. Biomethane grids can also be operated independent of natural gas grids to allow regional transport from the biomethane plant to the end-consumer. (Wilken et al. 2017, 18.)

The alternative for biomethane transportation is to compress it and put it in pressurized steel gas cylinders. It is typically compressed to 200–250 bar. The pressurised cylinders can have a capacity as small as 2 kg and as large as several hundred kgs. One kg of biomethane has the energy equivalent of roughly 13.3 kWh. In many countries throughout the world, households are supplied with biomethane via compressed gas cylinders as an alternative to fossil fuels and the depletion of trees for fuel. (Wilken et al. 2017, 21.)

5. BIOGAS PRODUCTION COSTS

Biogas production costs highly depend on the kind of substrate used. Substrates such as energy crops, which are easily digestible, are costlier but offer less investment costs since such substrates have high energy density and high rate of biogas production and thus need smaller biogas reactors. Substrates such as industrial and agricultural waste may be cheaper but require more investment costs. (Kampman et al. 2016, 30.) The most common feedstock used is manure, though its biogas yield is significantly lower than the biogas produced from crop residues. The feedstock with the highest yield is industrial waste, which can provide approximately 0.4 toe (tonne of oil equivalent) of energy per tonne. Other than yields, the costs and effort needed for the collection of different volumes of feedstock varies. Technologies used also vary. (IEA 2020.)

Biogas systems used at household scale are typically used in developing countries to provide heating and cooking fuel. These units typically have an output of about 1 m3 per day, which provides two to three hours of stove cooking time from about 20 to 30 kg of animal manure. These basic technologies cost about USD 10 – 30/MWh (approximately 7 – 25 €/MWh). They typically have shorter lifetimes and production yields that vary. Locally available feedstock is typically at zero cost. (IEA 2020.)

When scaling up the biodigesters, a more structured system is needed for continuous flow of feedstock in large quantities. (IEA 2020.) Investment in the digester constitutes the largest percentage of total investment for anaerobic digestion (this is approximately 40 – 45 % for energy crops and 55 – 60 % for industrial or agricultural waste). Additionally, investment is needed for feedstock storage (especially for energy crops), pre-treatment and feeding equipment, electrical and control systems and buildings. (IRENA 2018, 26 – 27.)

In order to reach the optimal temperature for digestion, heat is required. Relatively dry substrates such as energy crops require less heat requirements since less water is heated compared to manure or industrial wastewater. The heat demand also depends on the climate in which the biogas plant is located. Approximately 5 – 10 % of the total energy used in producing biogas is used in heating the digesters. Additionally, electricity is needed for pumps to operate, for process-monitoring and other essential tasks. The electricity demand varies between 20 kWhe - 30 kWhe per MWh of produced biogas. (IRENA 2018, 28.)

For production capacities ranging from 500 m³/h to 2000 m³/h of raw biogas production, the costs range between USD 0.55/m³ (~0.50 €/m³) and USD 0.81/m³ (~0.70 €/ m³) of methane where energy crops were the substrates, USD 0.23/ m³ (~0.20 €/m³) and USD 0.41/m³ (~0.30 €/ m³) of methane where manure was the substrate, and USD 0.12/m³ (~0.10 €/m³) and USD 0.52 (~0.40 €/m³) where industrial waste products were the substrates. (IRENA 2018, 28.)

5.1 Costs of upgrading

To produce biomethane, upgrade systems are needed to meet the quality requirements for the gas. The total cost of upgrading depends on the plant capacity, the technology and equipment used and the project-specific requirements (these include the quality of biomethane needed, the raw biogas quality and environmental regulations). The larger the installed capacities, the lower the capital and operating costs. The most commonly used technologies for biogas upgrading are water or amine scrubbers, pressure swing adsorption and membrane separation. In a survey conducted in 2012 on companies producing and upgrading biogas to biomethane, the cost of upgrading in a 500 m³/h raw biogas upgrading capacity plant was between USD 0.17/m³ (~0.15 €/m³) and USD 2.50/m³ (~2.00 €/m³), for 1000 m³/h raw biogas upgrading capacity the costs were between USD 0.14/m³ (~0.10 €/m³) and USD 0.18/m³ (~0.15 €/m³), and for 2000 m³/h raw biogas upgrading capacity the costs were between USD 0.09/m³ (~0.7 €/m³) and USD 0.16/ m³ (~0.10 €/m³). (IRENA 2018, 30.)

6. FUTURE TRENDS

The key determining factor that affects the development of biogas production is economics. The increasing use of biogas in various aspects such as heat and fuel-use, has increased the profitability of biogas plants. There also continues to be technological improvement in biogas upgrading technologies to biomethane, which could lead to improved cost performance and eventually biomethane could become cost competitive with fossil fuel use in transport. (Scarlat, Dallemand & Fahl 2018, 471.)

Biogas purification and upgrading technologies have recently experienced rapid development, where many techniques have been revisited, modified and strengthened, and novel technologies have been proposed. The main technologies used presently are ex-situ approaches, and extensive effort has been made over the years to improve the efficiency and promote the economic viability of these technologies. (Sarker, Lamb, Hjelme & Lien 2018, 686.) There are various novel ex-situ techniques for desulphurization of biogas and upgrading of biogas.

However, in-situ purification and upgrading techniques have been gaining significant attention recently. Studies comparing in-situ and ex-situ techniques have shown that in-situ techniques have an increased economic performance for small to medium-scale biogas plants, having above 85 v/v% of biomethane from upgraded biogas. There are different technologies currently being studied for in-situ methane enrichment. (Sarker et al. 2018, 686.)

6.1 Novel desulphurization technologies

One innovative desulphurization technique is adsorption on red soil made from red rock. Red soil is the product of intensive chemical weathering which affects rocks by leaching and oxidizing processes. It can contain a large amount of iron in the form of goethite [$FeO(OH)$], magnetite (Fe_3O_4) and hematite (Fe_2O_3). The iron oxides in red soil enables it to adsorb H_2S from biogas where it is oxidized by the iron oxide to elemental sulphur. A lab-scale study conducted by Mrosso, Machunda & Pogrebnaya (2020) explored the efficiency of H_2S removal using red rock collected from a village in Tanzania. The red rock was crushed and sieved into diverse particle sizes ranging from 0.32 μm to 1 mm. The samples were divided and calcinated at 500 °C, 750 °C and 1000 °C for approximately two hours. They were then placed on a small plastic bed reactor (5*1 cm) where both ends of the reactor were supported with cotton wool and the biogas flowed through. The study found that the sample with particle size 0.32 – 250 μm calcined at 1000 °C had a H_2S removal rate of 95 % at a low flow rate of 0.006 m³/h. The red rock was regenerated by being exposed to ambient air for a week. The regenerated material had 93 % removal efficiency. The suggestion was made to enhance red rock potential for H_2S removal by using the material in pellet form or adding some pore-forming material. (Mrosso et al. 2020, 2-3, 8.)

A second innovative biogas desulphurization technology is FlasH2S. This technology makes use of scrubbing and caustic solutions which, as previously discussed, is one of the oldest methods of effective H_2S removal from biogas. The aim of this technology is to improve the separation selectivity of H_2S over CO_2, since extensive CO_2 absorption can greatly increase chemical consumption in scrubbing. In FlasH2S, water is used as the main scrubbing liquid and NaOH is used as a caustic. The caustic feed ratio is adjusted carefully to maintain a particular pH of the scrubbing liquid to increase separation selectivity. Secondly, as H_2S and CO_2 have different absorption kinetics in caustic solutions, this difference can be used advantageously for the selective removal of H_2S. CO_2 absorption is remarkable slower than H_2S therefore contact time

between gas and liquid can be kept very short so that H_2S is absorbed while CO_2 is not. The dissolved H_2S is then removed in a separate oxidation chamber where it is oxidized by hydrogen peroxide (H_2O_2) to elemental sulphur (minor), sulphite and sulphate (major). This technique was successfully implemented in a single-staged biogas plant with a capacity of 200 m^3_{STP}/h at an existing biogas/biomethane plant in Austria. The results at the pilot plant suggested that a multi-staged concept could result in higher desulphurization efficiency with lower consumption of chemicals and water. (Miltner, Makaruk & Harasek 2017, 1333.)

6.2 Recent advances in biogas upgrading

One recent innovation in biogas upgrading is an industrial lung. This is a biotechnologically hybridized process that uses carbonic anhydrase enzymes for the removal of CO_2 from biogas. These enzymes enhance and catalyse CO_2 breakdown in cell metabolism. They can be similarly used in an absorbing column to remove CO_2. The enzymes pull CO_2 into the aqueous phase where it is selected by the absorbent in the absorbing tower. After absorption, the absorbent is regenerated by heat in a stripper column and releases a stream of over 90 % CO_2. Laboratory-scale research has shown that using carbonic anhydrase enzymes for CO_2 removal can purify the biogas to up to 95 – 99 % methane content with a CO_2 content of <1 %. However, production costs of the enzyme are high, and the process is limited by the enzyme's lifetime. (Sahota et al. 2018, 85.)

6.3 In-situ methane enrichment

Biogas can be upgraded in-situ to methane (>85 %) by increasing the pressure within the reactor. The pressure in an anaerobic reactor can potentially reach close to 1000 bar though this depends on the type of microorganisms used. However, existing technologies have thus far only successfully operated in the pressure range of 1 – 90 bar. High pressure causes the CO_2 in the reactor to dissolve into the liquid phase which then directly exists as effluent. The gas-phase biogas is then enriched in methane content. The solubility of a gas in liquid phase is directly correlated to Henry's gas constant, which for NH_3, H_2S, CO_2, CH_4, H_2, and is 62, 0.115, 0.0318, 0.0016 and 0.00078 mol/L/bar, respectively (at standard temperature and pressure). The higher Henry's gas constant is, the more gas can dissolve into the liquid phase. Thus NH_3, H_2S, CO_2 and H_2 are more soluble than CH_4 at standard temperature and pressure and will dissolve in high-pressure reactors reducing the amount of unwanted compounds in the biogas. This also reduces the need for compression for natural gas grid injection. (Sarker et al. 2018, 692.) An investigation on the effects of pressure on microbial ability for biogas production have been done. This investigation showed that the level of methane production was unaffected by the digester's pressures at 1, 50 and 100 bar. (Merkle, Baer, Haag, Zielonka, Ortloff, Graf & Lemmer 2017.) As other investigations have had similar results, research on the development of pressurized reactors in anaerobic digestion plants has been slowly increasing. (Sarker et al. 2018, 692).

In-situ methane enrichment can also be conducted without pressurizing the digester. Since CO_2 is soluble in water (to some extent) there will always be some CO_2 dissolved in the liquid phase in the digester. Thus, the sludge from the digester can be circulated to a desorption column, where the CO_2 by pumping air through the sludge, and the sludge is directed back to the digester where more CO_2 is dissolved. By continuously recirculating the sludge, more CO_2 is removed and the methane in the digester is enriched. (Allegue & Hinge 2012, 42.) In the study conducted by Boontawee and Koonaphapdeelert (2016), in-situ methane enrichment in a biogas digester was examined by continuously stripping CO_2 from the effluent before recirculating

it back to the digester. This study was conducted in lab-scale, where a 1 000 L working volume digester was coupled with a 110 L stripping column. Chicken manure was used as the substrate. They varied the recirculation rate from 200 %– 400 % of the digester volume and found that the higher the recirculation rate, the higher the methane enrichment. The maximum methane concentration (70.2 %) was from a 400 % recirculation flow rate, and at this rate the CO_2 had reduced by more than 31.6 %. H_2S was also removed, and at 400 % recirculation rate, more than 60 % was removed. However, this method also resulted in methane loss in the desorption process (between 3.7 % and 10.3 % loss). Further studies are required to reduce methane loss and increase the rate of methane enrichment. (Boontawee & Koonaphapdeelert 2016, 82.)

Electromethanogenesis is yet another novel technique for upgrading biogas in-situ. This technology uses methanogens (collectively known as hydrogenotrophic methanogens) to convert CO_2 in to CH_4. Hydrogenotrophic methanogens are biocatalysts capable of methane production and they include methanobacteriales, methanococcales, methanomicrobials and methanosarcenaceae. These microbes can reduce carbon dioxide to methane using molecular hydrogen as shown in equation 11. (Hara, Onaka, Kobayashi, Fu, Kawaguchi, Vilcaez, Sato 2013, 7022.)

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O \tag{11}$$

The methane can also be produced electrochemically (electromethanogenesis) by reducing the CO_2 at a voltage of 0.169 V under standard condition or -0.244 V at a pH of 7 via the following reaction (Cheng, Xing, Call & Logan 2009, 3953.):

$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O \tag{12}$$

In electromethanogenesis, a microbially-catalysed electrode (biocathode) is used such that the microbial consortia on the cathode's surface use protons and electrons to reduce the CO_2, rather than using molecular hydrogen. (Hara et al. 2013, 7022.) The electrons come from an anode. In a typical bioelectrochemical reactor, the anode and cathode chambers are generally separated by a membrane such as proton exchange, anion exchange, charge mosaic or bipolar, which allows only protons (H^+) to pass through from the anode to the cathode. Studies on electromethanogenesis have only been on lab-scale so far. There is no solid proof of full-scale application therefore further research is needed in this field. (Sarker et al. 2018, 695.)

7. BIOGAS PLANTS IN FINLAND

Many biogas plants are operating in Finland which is either own by public or private companies. Biogas plants in Finland take the raw material mainly from municipal waste, wastewater treatment plants, biowaste from industries, and animal farms. This report reviews some of the biogas plants operating in Finland and compares the different biogas plants based on their size, biogas production capacity, and cost.

7.1 Gasum Oy

Gasum is a company that owns different biogas plants in Finland and Sweden. Currently, 12 biogas plants working in Finland and Sweden. (Gasum acquires Mäkikylä biogas plant in Finland from Kouvolan Vesi, 2019.) The company provides biogas production along with the distribution of produced recycled fertilizers and services related to biodegradable waste processing. It is the largest producer of biogas in the Nordic countries. Currently, Gasum produces around 650 GWh of biogas per annum and by 2024, Gasum is planning to produce around 4 TWh of biogas. (Gasum biogas plant, 2020.) On June 2019 Mäkikylä biogas plant has been transferred to the Gasum, which aims to increase the production of biogas in the new plant whose initial processing capacity is about 20 thousand tons of biomass per year. Gasum aims to increase the production of biogas which can be used as fuel in vehicles which will ultimately reduce the emission from traffic. For this Gasum is building new biogas plants in Lohja (Finland) and Sweden. (Gasum acquires Mäkikylä biogas plant in Finland from Kouvolan Vesi, 2019.) Biogas plants of Gasum in Finland with their location, established date, raw material used, processing capacity and biogas production per year is given in the TABLE 6 below. (Gasum biogas plant, 2020.)

TABLE 6. Comparison between the different biogas plants of Gasum based on the raw material used, waste processing capacity and biogas production capacity per year.

Name of biogas plant and location	Established date	Raw material used	Processing capacity per year	Biogas production per year
Huittinen biogas plant/ Huittinen	2010	Sewage from the town, pig farm and waste products from factories.	60 000 tons	35 GWh/year
Honkajoki biogas plant/ Honkajoki	2014	Waste from food industries and separately collected biowaste.	60 000 tons	35 GWh/year
Riihimäki biogas plant / Riihimäki	2016 (Gasum's largest biogas plant in Finland)	Sewage sludge, waste from industries and biowaste collected from other places.	75 000 tons	45 GWH/year
Turku biogas plant/ Turku	2009	Mainly sewage sludge	130 000 tons	61 GWh/year
Vehmaa biogas palnt/ Vehmaa	2005 (Finland oldest industrial-biogas plant)	Side streams from enzyme and food industries, sludge from pig farm.	90 000 tons	30 GWh/year
Kuopio biogas plant / Kuopio	2014	Sludge from wastewater plant, biodegradable waste from food industries.	60 000 tons	35 GWh/year

7.2 Other biogas plants

The TABLE 7 below shows the six biogas plants in Finland in the order of small to larger in size with their location, investment cost, waste capacity, biogas production capacity along with the size of the reactor used to produce biogas. Annual waste capacity depends on the investment cost and the size of the plant, bigger the plant will be higher will be the waste processing capacity. However, the biogas produced from anaerobic digestion is independent of the waste processing capacity of the plant, as different biowaste has different methane production capacity. Higher methane can be yield from Grease residues, byproducts from food industries, bio waste, and gutting waste than cattle manure, sewage sludge, and animal solid manure. Moreover, the digestion process is quite faster in dry anaerobic digestion which helps to increase the waste processing capacity than the plant with the wet anaerobic digestion process. The size of the reactor used is directly proportional to the type of anaerobic digestion (wet or dry) used in the plant and due to the higher content of water in the wet anaerobic digestion process, it requires bigger reactor than dry anaerobic digestion. (Rannaste, 2016.)

TABLE 7. Comparison of different biogas plants in Finland based on the Investment, annual waste processing capacity, biogas production capacity and size of reactors. (Rannaste, 2016.)

Plant's name/Location	Investment (euros)	Annual Waste capacity (Tons/year).	Biogas production capacity (GWh/year)	Size of reactor used
Joutsan Ekokaasu Ltd / Joutsa	1 600 000 €	4 750	2.0	700 cubic meters
Satakierto Ltd / Köyliö	4 00 000 €	19 000	4.6	2300 cubic meters
BioKymppi Ltd / Kitee	5 500 000 €	19 000	13.1	3000 + 1000 cubic meters (Reactor 1+2)
Biotehdas Oulu / Rusko	8 000 000 €	19 000	16.2	2700 cubic meters
Lakeuden Etappi Ltd / Pojanluoma	17 000 000 €	55 000	23.6	2* 3200 cubic meters
Ämmässuo Waste Treatment Center / Espoo	40 300 000 €	60 000	129.0	2*2400 cubic meters

Mustankorkea Oy
Mustankorkea Oy is a waste management company located in Jyväskylä and was established in 1998. This company gets its raw material form the household from a resident of around 200 000 living in the region and waste from industries and process the waste of 150 to 200 thousand tons per year. The company made a profit of 17.1 million euros in the year 2017 operated by 32 permanent and 10 temporary employees. The waste generated is used to produce biogas and its upgrading and finally used as a vehicle fuel. Raw materials used to produce biogas are food waste and undigested sewage sludge. The biogas plant has a production capacity of 19 thousand tons of biogas per annum. Raw gas from the anaerobic digestion is upgraded to around 97 % methane which is then used in vehicles. Moreover, this company produces compost from the biowaste and sewage sludge and has a total capacity of 34 thousand tons per annum. The compost is used in the fields to provide nutrients to the crops. Moreover, the soil from the com-

post is used for various places for example gardens, parks, and so on. Only in 2017 company almost 48 thousand tons of compost soil which was higher than the previous years. (Martika-inen, 2018.)

For the process of biological process total of 13 thousand tons of biowaste is obtained from municipalities, residents and industries, 5 thousand tons of undigested sewage sludge from municipalities, and one thousand tons of manure from farms per annum. This makes a total of 19 thousand tons of waste from which 15 GWh of biogas is obtained. The biogas is upgraded to biomethane and is sold back to the companies, residents, and municipalities. The digester in an anaerobic digester is separated in two different sections dry and wet fraction which are used to produce soil from compost and liquid fertilizer or sewer, respectively. From the digester around 10 thousand cubic meters of liquid is obtained which is used as a liquid fertilizer in the agricul-tural process and wastewater is sent to the treatment plant. The solid waste from the digester is sent to a composting plant which is about 21 thousand tons per year. From composting plant 8 to 12 thousand cubic meters of cured compost is generated which is either sold to costumers or cured compost is further processed to make soil which is about 50 to 60 thousand cubic me-ters per annum which are finally sold for the consumers. About 15 thousand kilograms of gas was sold from the station and 5 thousand kg gas sold to other stations. (Martikainen, 2018.)

Joutsa biogas plant
Joutsa biogas plant (Joutsan Ekokaasu Ltd) located in Joutsa Finland was established by local waste management and biogas entrepreneur in 2014 with an investment of 1.6 million euros. (Biojätteestä polttoainetta 200 henkilöautolle., 2013). The raw material used to produce biogas in the Joutsa biogas plant is mainly organic waste which is taken from the waste management plants and the municipalities in the nearby area. The plant has the capacity of processing the raw material (organic waste) up to 6 175 tons per year, the average raw material from the differ-ent sources used in the plant is shown in the TABLE 8. (Joutsan seudun biokaasulaitos, 2012.)

TABLE 8. Raw materials from different sources used in Joutsa biogas plants. (Joutsan seudun biokaasulaitos, 2012.)

Feed	Amount [tons/year]	Gate fee [€/ton]
Biowaste	1000	60
Sludge	2000	40
Grease pit sludge	750	70
Septic tank and cesspit sludge	1000	10

Organic waste from the municipality is introduced into the hygienization chamber where any harmful microorganisms are killed by heating the thermally insulated tank at around 70 °C. Biogas produced in the plant is used to heat the chamber after which the organic waste from the hygienization unit is ready to feed into the two reactors having an area of 750 and 1 000 m3. Around 85 % of total produced biogas is from the small reactor (750 m3) and the rest of the biogas production takes place in a big reactor (100 m3). (Rannaste, 2016.) Raw biogas from the reactor is purified by the purification unit and compressed which is then used as a vehicle fuel for more than 200 cars yearly. (Biojätteestä polttoainetta 200 henkilöautolle., 2013.)

Change in temperature affects the volume of biogas, however, the mass remains the same. Therefore, biogas is sold in kilograms and the unit cost per kilogram from the plant is around

1.37 euros when this report was written. Besides selling biogas the major income of the plant is from the collection of gate fees from waste transports, gate fees depend on the waste materials, and the fee for different waste is given in the TABLE 8. Despite being the small plant, the Joutsa biogas plant can produce 100 thousand cubic meters of biogas and 4 400 tons of digestate every year if 5 thousand tons of organic waste is processed annually. The plant produces around 2 GWh net worth of biogas, however, up to 25 % is only used for the operation process. The rest of the biogas is burned due to the lower demand for bio-gas fuel used in vehicles. Out of 1.6 GWh of total biogas energy, only 0.5 GWh is used as the fuel in the vehicles. (Rannaste, 2016.)

8. CLOSING MARKS

Transport climate Policy of Finland" in the long run is doing several types of research to reduce the emission of GHG (greenhouse gases). For this, biogas is listed on the top list and to eliminate the release greenhouse gas to a high level for which the current biogas production which is around 1 TWh should be increased by ten times by 2045. (Biogas has a significant role in Finland's goal of carbon-free transport by 2045, 2018.) To increase the production of biogas in Finland, Gasum Oy has received support from Finland's Ministry of Economic Affairs and Employment of 7.83 million euros. (Gasum receives Government funding to increase Finnish biogas production, 2018.) Besides increasing the production of biogas, the use of electric cars, and an increase in gas-fueled vehicles would contribute to the reduction of GHG to more than 85 percent caused by current road transport. (Biogas has a significant role in Finland's goal of carbon-free transport by 2045, 2018.)

REFERENCES

1. Abry, R.G., & DuPart, R.S., 1995. Amine plant troubleshooting and optimization. Hydro-carbon Processing, 41–50.

2. Al-Imarah, K.A., Lafta, T.M., Jabr, A.K. & Mohammad, A.N. 2017. Desulphurization for Biogas Gen-erated by Lab Anaerobic Digestion Unit. IOSR Journal of Agriculture and Veterinary Science, 10(8), 66–73.

3. Allegue, L. B. & Hinge, J. 2012. Biogas and Bio-syngas upgrading. Danish Technological Institute.

4. Allegue, L. B. & Hinge, J. 2014. Biogas Upgrading: Evaluation of Methods for H2S Removal. Danish Technological Institute and biological technologies for biogas upgrading. Rev. Environ. Sci. Biotechnol., 14, 727–759.

5. Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H. & Kougias, P.G. 2018. Biogas upgrading and utilization: Current status and perspectives. Biotechnology Advances 36, 452–466.

6. Håkansson, A. 2006. Preventing Microbial Growth on pall-rings when upgrading biogas using absorption with water wash. SGC Rapport, The Tema Institute, Department of Water and Environmental Studies, 55.

7. Arnold, M. 2009. Reduction and monitoring of biogas trace compounds. VTT Technical Research Cen-tre: Espoo.

8. Arya, A., Divekar, S., Rawat, R., Gupta, P., Garg, M.O., Dasgupta, S., Nanoti, A., Singh, R., Xiao, P. & Webley, P.A. 2015. Upgrading Biogas at Low Pressure by Vacuum Swing Adsorption. Industrial and Engineering Chemistry Research, 54(1), 404–413.

9. Awe, O.W., Zhao, Y., Nzihou, A., Minh, D.P. & Lyczko, N. 2017. A review of biogas utilization, purification and upgrading technologies. Waste and Biomass Valorization, 8, 267–283.

10. Baber, Z., & Shareefdeen, Z. 2013. Management and control of air emissions from electronic industries. Clean Techn. Environ. Policy, 69–77.

11. Bachmann, E.S.N. (2013). Design and engineering of biogas plants. In The biogas handbook (pp. 385-387). Woodhead Publishing.

12. Barry, B., & Lyddon, L. 2008. A COMPARISON OF PHYSICAL SOLVENTS FOR ACID GAS REMOVAL. Bryan Research & Engineering, Inc., Bryan, Texas, U.S.A.

13. Bauer, F., Hulteberg, C., Persson, T., & Tamm, D. (2013). Biogas upgrading - Review of commercial technologies. SGC Rapport; Svenskt Gastek. 270, 23–24.

14. Biogas has a significant role in Finland's goal of carbon-free transport by 2045. 2018. Bioenergy International. Available: https://bioenergyinternational.com/opinion-commentary/biogas-has-a-significant-role-in-finlands-goal-of-carbon-free-transport-by-2045. Accessed 23 August 2020.

15. Biogas Utilization Systems and H2S Bio-Scrubber Units. 2016. (Green Energy Network, Thailand). Green Energy Network Co., Ltd. Available: http://www.greenenergynet.net/biogas-utilization-systems-and-h2s-bio-scrubber-units/. Accessed 10 August 2020.

16. Biogas Utilization Systems and H2S Bio-Scrubber Units. 2017. (Green Energy Network Co., Ltd.) Green Energy Network. Available: http://www.greenenergynet.net/biogas-utilization-systems-and-h2s-bio-scrubber-units/. Accessed 15 August 2020.

17. Biojätteestä polttoainetta 200 henkilöautolle. 2013. Available: https://asiakas.kotisivukone.com/files/joutsanekokaasu.kotisivukone.com/joutsa_lehdistotiedote2.pdf. Accessed 25 August 2020.

18. Boontawee, S. & Koonaphapdeelert, S. 2016. In-situ Biomethane Enrichment by Recirculation of Biogas Channel Digester Effluent Using Gas Stripping Column. Energy Procedia, 89, 78–84.

19. Cebula, J. 2009. Biogas Purification by Sorption Techniques. Architecture Civil Engineering Environment, 2, 95–104.

20. Chen, Q., Wu, W., Qi, D., Ding, Y. & Zao, Z. 2020. Review on microaeration-based anaerobic digestion: State of the art, challenges, and prospectives. Science of the Total Science, 710.

21. Cline, C., Hoksberg, A., Abry, R., & Janssen, A. 2003. BIOLOGICAL PROCESS FOR H2S REMOVAL FROM GAS STREAMS THE SHELL-PAQUES/THIOPAQTM GAS DESULFURIZATION PROCESS. Paper for the LRGCC, Norman (Oklahoma), USA, 3–8.

22. Davis, W.T., & Buonicore, A.J. (Eds.). 2000. Air pollution engineering manual (Vol. 2). New York: Wiley.

23. De Arespacochaga, N., Valderrama, C., Mesa, C., Bouchy, L., & Cortina, J.L. (2014). Biogas deep clean-up based on adsorption technologies for Solid Oxide Fuel Cell applications. Chemical Engineer-ing Journal, 255, 593–603.

24. Devinny, J., Deshusses, M., & Webster, T. 1998. Biofiltration For Air Pollution Control. New York , London: CRC Press, 22–318.

25. DuPart, M.S., Bacon, T.R., & Edwards, D.J. 1993. Understanding corrosion in alkanolamine gas treating plants: Part 1 and 2. Hydrocarbon Processing; (United States), 72(4).

26. Dupnock, T., & Deshusses, M. 2017. High-Performance Biogas Upgrading Using a Biotrickling Filter and Hydrogenotrophic Methanogens. Applied Biochemistry and Biotechnology, 183, 488–502.

27. Electrical Current into Methane by Electromethanogenesis. Environmental Science and Technology, 43, 3953–3958.

28. Erler, R. 2009. Brochure on "biogas utilization chains". Leipzig: DBI Gas- und Umwelttechnik GmbH.

29. Esteves, I.A.A.C., & Mota, J.P.B. (2002). Simulation of a new hybrid membrane/pressure swing adsorption process for gas separation. Desalination, 148(1-3), 275–280.

30. Fernández, M., Ramírez, M., Manuel, D.J., & Cantero, G. 2014. Biogas biodesulfurization in an anoxic biotrickling filter packed with open-pore polyurethane foam. Journal of Hazarous material, 264, 529–535.

31. Garnett, S., Hubinger, S., & Fernandez, M. May 1987. Oxidation of H2S in seawater as a function of temperature, pH, and ionic strength. Environmental science and technology, 21(5), 439–443.

32. Gasum acquires Mäkikylä biogas plant in Finland from Kouvolan Vesi. 2019. NS ENERGY. Available: https://www.nsenergybusiness.com/news/gasum-makikyla-kouvolan-vesi/. Accessed 15 August 2020.

33. Gasum biogas plant. 2020. Available: https://www.gasum.com/en/our-operations/biogas-production/biogas-plants/. Accessed 17 August 2020.

34. Gasum receives Government funding to increase Finnish biogas production. 2018. Bioenergy International. Available: https://bioenergyinternational.com/biogas/gasum-receives-government-funding-increase-finnish-biogas-production. Accessed 25 August 2020.

35. Grande, C.A., Ribeiro, R.P.L., Oliveira, E.L.G. & Rodrigues, A.E. 2009. Electric swing adsorption as emerging CO2 capture technique. Energy procedia, 1, 1219–1225.

36. Guha, A.K., Majumdar, S., & Sirkar, K.K. (1992). Gas separation modes in a hollow fiber contained liquid membrane permeator. Industrial & engineering chemistry research, 31(2), 593–604.

37. Hagen, M., Polman, E., Jensen, J., Myken, A., Joensson, O., & Dahl, A. 2001. Adding gas from bio-mass to the gas grid. Contract No: XVII/4.1030, 99–412.

38. Hara, M., Onaka, Y., Kobayashi, H., Fu, Q., Kawaguchi, H., Vilcaez, J. & Sato, K. 2013. Mechanism of Electromethanogenic Reduction of CO2 by a Thermophilic Methanogen. Energy Procedia, 37, 7021–7028.

39. Hedin, N., Andersson, L., Bergström, L. & Yan, J. 2013. Adsorbents for the post-combustion capture of CO2 using rapid temperature swing or vacuum swing adsorption. Applied Energy, 104, 418–433.

40. Holmgren , M., Hellström , H., & Petersson, A. 2010. The Swedish voluntary agreement for control of methane emissions from biogas plants. SP Technical Research Institute Of Sweden , Sweden.

41. Holmgren, M.A., Hellström, H., Petersson, A., & Blom, A. 2012. The Swedish voluntary agreement for control of methane emissions from biogas plants. SP Technical Research Institute of Sweden.

42. Huertas, J.I.,Giraldo, N., & Izquierdo, S. 2016. Removal of H2S and CO2 from Biogas by Amine Absorption. Mass Transfer in Chemical Engineering Processes (142). DOI: 10.5772/20039.

43. Cano, P. I., Colon, J., Ramírez, M., Lafuente, J., Gabriel, D., & Cantero, D. 2018. Life cycle assessment of different physical-chemical and biological technologies for biogas desulfurization in sewage treatment plants. Journal of cleaner production, 181, 663–674.

44. IEA. 2020. Outlook for biogas and biomethane: Prospects for organic growth. Available: https://www.iea.org/reports/outlook-for-biogas-and-biomethane-prospects-for-organic-growth/sustainable-supply-potential-and-costs. Accessed 23 July 2020

45. IRENA. 2018. Biogas for road vehicles: Technology brief. International Renewable Energy Agency: Abu Dhabi.

46. Jeniček, P., Horejš, J., Pokorná-Krayzelová, L., Bindzar, J. & Bartáček, J. 2017. Simple biogas desulphurization by microaeration – Full scale experience. Anaerobe, 46, 41–45.

47. Jenne, C., & Noche, B. 2011. Biogas as a partial solution for energy shortages within a European gas grid infrastructure.

48. Jensen, L. 2019 Spring. Life Cycle Cost Analysis of Biogas Upgrading via a Bio Trickling Filter. University of Southern Denmark, 28–37.

49. Jiang, L., Roskilly, A. P. & Wang, R. Z. 2018. Performance exploration of temperature swing adsorp-tion technology for carbon dioxide capture. Energy Conversion and Management, 165, 396–404.

50. Joutsan seudun biokaasulaitos. 2012. Available: https://www.kaasuyhdistys.fi/sites/default/files/pdf/esitykset/20120510_kevatkokous/kalmari.pdf. Ac-cessed 20 August 2020

51. Kampman, B., Leguijt, C., Scholten, T., Tallat-Kelpsaite, J. Brückmann, R., Maroulis, G., Lesschen, J. P., Meesters, K., Sikirica, N., & Elbersen, B. 2016. Optimal use of biogas from waste streams: An as-sessment of the potential of biogas from digestion in the EU beyond 2020. European Commission.

52. Kennes, C., Rene, E., & Veiga, M. 2009. Bioprocesses for air pollution control. Chemical Technology and Biotechnology, 84(10), 1419–1436.

53. Kennes, C., & Veiga, M.C. (Eds.). 2013. Bioreactors for waste gas treatment (Vol. 4). Springer Science & Business Media, 133–162.

54. Khan, I., Hafiz, M., Hashim, H., & Othman , M. 2017. Biogas as a renewable energy fuel – A review of biogas upgrading, utilisation and storage. Energy Conversion and Management, 281.

55. Kim, T.J., Li, B., & Hägg, M. B. (2004). Novel fixed-site–carrier polyvinylamine membrane for carbon dioxide capture. Journal of Polymer Science Part B: Polymer Physics, 42(23), 4326–4336.

56. Kohl , A. L., & Nielsen, R. B. 1997. Gas Purification. Gulf Publishing Company.

57. Králik, M. 2014. Adsorption, chemisorption and catalyst. Chemical Papers, 68(12), 1625–1638.

58. Krich, K., Augenstein, D., & Batmale, J. 2005. Biomethane from Dairy Waste. Western United Dairymen. http://www.suscon.org/pdfs/news/biomethane_report/Full_Report.pdf

59. Krishna Kalfe, G., & Chen, L. 2015. Field evaluation of wood bark-based down-flow bio-filters for mitigation of odor, ammonia, and hydrogen sulfide emissions from confined swine nursery barns. Journal of Environmental Management, 147, 164-174.

60. Kulkarni, M.B. & Ghanegaonkar, P.M. 2019. Hydrogen sulphide removal from biogas using chemical absorption technique in packed column reactors. Global Journal of Environmental Science and Management, 5(1), 155 – 166.

61. Kwaśny, J. & Balcerzak, W. 2016. Sorbents Used for Biogas Desulphurization in the Adsorption Process. Polish Journal of Environmental Studies, 25(1), 37–43.

62. L Kohl, A., & B Nielsen, R. 1997. Gas Purification fifth edition. Houston, Tex. : Gulf Pub.

63. Magomnang, A.S.M., & Villanueva, E.P. 2014. Removal of Hydrogen Sulphide from Biogas using Dry Desulphurization Systems. International Conference on Agricultural, Environmental and Biologi-cal Science: Phuket, Thailand, 65 – 68.

64. Maréchal, F., Laurence , T., & Gassner, M. 2010. Thermochemical production of liquid fuels from biomass: Thermo-economic modeling, process design and process integration analysis. Biomass and Bioenergy, 34(12), 1838–1854.

65. Martikainen, E. 2018. Mustankorkea Oy – Biological waste treatment and making products (and profit?) out of it. Mustankorkea Oy, Jyväskylä.

66. Merkle, W., Baer, K., Haag, N. L., Zielonka, S., Ortloff, F., Graf., F. & Lemmer, A. 2017. High-pressure anaerobic digestion up to 100 bar: Influence of initial pressure on production kinetics and spe-cific methane yields. Environmental Technology, 38(3), 337–44.

67. Miltner, M., Makaruk, A. & Harasek, M. 2017. Review on available biogas upgrading technologies and innovations towards advanced solutions. Journal of Cleaner Production, 161, 1329–1337.

68. Mokhatab, S., Poe, W. A. & Speight, J. G. 2006. Handbook of Natural Gas Transmission and Pro-cessing. Elsevier, Inc: Massachusetts.

69. Molina, L., & Aroca, G. 2007. Effects of gas flow rate, inlet concentration and temperature on the biofiltration of toluene vapors. Journal of Environmental Management, 84(2), 115–122.

70. Mrosso, R., Machunda, R. & Pogrebnaya, T. 2020. Removal of Hydrogen Sulphide from Biogas Using a Red Rock. Hindawi Journal of Energy. 2309378.

71. Muños, R., Meier, L., Diaz, I. & Jeison, D. 2015. A review on the state-of-the-art of physical/chemical and biological technologies for biogas upgrading. Reviews in Environmental Science and Bio/Technology, 14, 727–759.

72. NYSERDA. 2012. Assessment of Biochemical Process Controls for Reduction of Hydrogen Sulphide Concentrations in Biogas from Farm Digesters. New York State Energy Research and Development Authority: New York, USA.

73. Okoro, O. & Sun, Z. 2019. Desulphurisation of Biogas: A Systematic Qualitative and Economic-Based Quantitative Review of Alternative Strategies. Chem engineering, 3, 76.

74. Perera, W., Botheju, D., & Bakke, R. 2014. Biogas purification using membrane micro-aeration: A mass transfer analysis. INTERNATIONAL JOURNAL OF ENERGY AND ENVIRONMENT 5(4), 431–446.

75. Persson, M. 2003. Utvärdering av uppgraderingstekniker för biogas, Malmö: Swedish Gas Center, Report SGC 142.

76. Persson, M., Jönsson, O., & Wellinger, A. 2006, December. Biogas upgrading to vehicle fuel standards and grid injection. In IEA Bioenergy task (Vol. 37, pp. 1-34).

77. Petersson , A., & WeLLInGer, A. 2009 . Biogas upgrading technologies – developments and innovations. IEA Bioenergy Task 37 - Energy from biogas and landfill gas.

78. Petersson, A & Wellinger, A. 2009. Biogas upgrading technologies – developments and innovations. Available: https://task37.ieabioenergy.com/files/daten-redaktion/download/publi-task37/upgrading_rz_low_final.pdf. Accessed 20 July 2020.

79. Pourzolfaghar, H., Izhar, S., Esfahan, Z.M. & Ismail, M.H.S. 2014. Review of H2S Sorbents at Low-Temperature Desulphurization of Biogas. International Journal of Chemical and Environmental Engi-neering, 5(1), 22 – 28.

80. Ralph, F., & Strigle, Jr. 1994. Packed tower design and applications: random and structured packings. Gulf Pub. Co.

81. Rannaste, E. 2016 April . COMPARISON OF JOUTSA BIOGAS PLANT WITH OTHER FINNISH BIOGAS PLANTS. Bachelors Thesis, Oulu University of Applied Sciences.

82. Ribeiro, R.P.P.L., Grande, C.A. & Rodrigues, A.E. 2014. Electric Swing Adsorption for Gas Separa-tion and Purification: A Review. Separation Science and Technology, 49(13), 1985 – 2002.

83. Roberts, C.A., Gibbins, J., Panesar, R., & Kelsall, G. 2005. Potential for improvement in power genera-tion with post-combustion capture of CO2. In Greenhouse Gas Control Technologies 7 (pp. 155-163). Elsevier Science Ltd.

84. Roks, M. F. M., Luning, L., & Coops, O. Feasibility of applying new membrane for processing landfill gas to natural gas quality at low pressure (8 bar).[Haalbaarheid toepassing nieuw membraan voor opwerking stortgas naar aardgaskwaliteit bij lage druk (8 bar)] Nederland: Aquilo Gas Separation bv; 1997. 57.

85. Rutledge, B. 2005. California biogas industry assessment white paper. WestStart-Calstart, Pasadena, USA.

86. Ryckebosch, E., Drouillon, M., & Vervaeren, H. 2011. Techniques for transformation of biogas to bi-omethane. Biomass and bioenergy, 35(5), 1633–1645.

87. Sahota, S., Shah, G., Ghosh, P., Kapoor, R., Sengupta, S., Sing, P., Vijay, V., Sahay, A., Vijay, V. K. & Thakur, I. S. 2018. Bioresource Technology Reports, 1, 79 – 88.

88. Santos-Clotas, E., Cabrera-Codony, A., Castillo, A., Martín, M. J., Poch, M. & Monclús, H. 2019. En-vironmental decision support system for biogas upgrading to feasible fuel. Energies, 12, 1546.

89. Sarker, S., Lamb, J.J., Hjelme, D.R. & Lien, K.M. 2018. Overview of Recent Progress Towards In-situ Biogas Upgrading Techniques. Fuel, 226, 686 – 697.

90. Scarlat, N., Dallemand, J. & Fahl, F. Biogas: Development and perspectives in Europe. Renewable Energy, 129, 457 – 472.

91. Schomaker, A.H.H.M., Boerboom, A.A.M., Visser, A., & Pfeifer, A.E. 2000. Anaerobic digestion of agro-industrial wastes: information networks technical summary on gas treatment. AD_NETT Project FAIR-CT96-2083 (DG12-SSMI).

92. Severn Wye. 2017. Introduction to Production of Biomethane from Biogas: A Guide for England and Wales. Severn Wye Agency: Bangor, Wales.

93. Shareefdeen, Z. (2005). Biotechnology for odor and air pollution control. Springer Science & Business Media.

94. Smith, J.A. & Carliell-Marquet, C.M. The digestibility of iron-dosed activated sludge. Bioresource Technology, 99(18), 8585 – 8592.

95. Stewart, E. J., & Lanning, R. A. 1994. Reduce amine plant solvent losses; Part 1. Hydrocarbon Processing;(United States), 73(5), 354.

96. Strigle, R.F., 1994. Packed tower design and applications: random and structured packings 2nd ed., Houston, TX: Gulf Pub. Co.

97. Sun, Q., Li, H., Yan, J., Liu, L., Yu, Z. & Yu, X. 2015. Selection of appropriate biogas upgrading technology-a review of biogas cleaning, upgrading and utilisation. Renewable and Sustainable Energy Reviews 51, 521 – 532.

98. Syed, M. & Soreanu, G. 2006. Removal of hydrogen sulfide from gas streams using biological processes - A review. (ss. 1-14). Canada: Wastewater Technology Centre, 1–11.

99. Tang, Y., Shigematsu, T., Morimura, S.I., Kida, K. 2004. The effects of micro-aeration on the phylogenetic diversity of microorganisms in a thermophilic anaerobic municipal solid-waste digester. Water Res., 38, 2537–2550.

100. Terrigeol, A. 2012. Molecular sieves contaminants: Effects, consequences and mitigation. In Annual Gas Processors Association Europe Conference, Berlin.

101. Wellinger, A & Lindberg, A. 2000. Biogas Upgrading and Utilization. Available: http://www.iea-biogas.net/files/daten-redaktion/download/publi-task37/Biogas%20upgrading.pdf. Accessed 16 July 2020

102. Wiheeb, A. D., Shamsudin, I. K., Ahmad, M. A., Murat, M. N., Kim, J. & Othman, M. R. 2013. Pre-sent technologies for hydrogen sulphide removal from gaseous mixtures. Rev Chem Eng, 29(6), 449–470.

103. Wilken, D., Strippel, F., Hofmann, F., Maciejczyk, M., Klinkmüller, L., Wagner, L., Bontempo, G., Münch, J., Scheidl, S., Conton, M., Deremince, B., René, W., Zetsche, N. & Findeisen, C. 2017. Bio-gas to Biomethane. Fachverband Biogas e. V: Germany.

104. Zicari, S. M. 2003. Removal of hydrogen sulfide from biogas using cow-manure compost (Doctoral dissertation, Cornell University).

BIOGAS DRYING AND PURIFICATION METHODS

In August 2020, Biogas2030 statement was made, where the goal for national biogas production and use in 2030 was set to 4 TWh. The goal is approximately four times higher than the current production rate in Finland. In order to reach this not only political decisions must be made but also new technologies and business models have to be created. In Finland, there is large potential for biogas production in agriculture, especially in animal farms, that created suitable biomasses through the year.

Although the production of biogas in farms is growing all the time, the energy is often used in the farms as heat and power. The profit gained from the biogas would be better and also the availability of renewable fuels would increase in Finland if the biogas would be purified and sold as fuel. However, in a small scale with current technologies this is not profitable. HABITUS project (Decentralized Biogas Production and liquefaction in Finland, funded by Regional Council of Central Ostrobothnia, European Regional Development Fund) is answering this challenge by creating new technologies suitable for purification and liquefaction of biogas in the small scale. This report was written during summer 2020 for HABITUS project to review the current state and future trends of biogas purification and upgrading technologies.

Centria
UNIVERSITY OF APPLIED SCIENCES

Leverage from
the EU
2014−2020

European Union
European Regional
Development Fund