

BIOGAS UPGRADING – TECHNICAL REVIEW

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TRANSPORTATION AND FUELS



Biogas Upgrading - Technical Review

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Foreword

This report has been written in corporation between the following authors from the companies Hulteberg Chemistry and Engineering and Energiforsk:

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Energiforsk, the Swedish Energy Research Centre, coordinates and conducts research and development in the field of energy. The research group Transportation and Fuels focuses on development within renewable transportation fuels and has long experience especially within biogas and other energy gases. Energiforsk was formed in the beginning of 2015 through the merger of four research organizations, among which the Swedish Gas Technology Centre, SGC, is the part which formed the research group behind this report.

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Previous co-workers of Energiforsk involved in the project have been Jonas Dahl and Tobias Persson.

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The following companies have been involved in the project and have contributed both directly and in-kind and given information and data which was used during the writing of the report. We would like to acknowledge the contribution from these companies, without whom the report would not have been possible to write. The project was carried out during 2015 and the beginning of 2016 with two meetings with the reference group.

The companies in the reference group and which have funded this project are listed below.

- Air Liquide
- Ammongas
- Biofrigas
- BMF Haase
- Carbotech
- DMT
- DVGW
- Envitec
- Greenlane Biogas
- Malmberg Water
- NeoZeo
- Pentair Haffman
- Purac Puregas
- Scandinavian Biogas
- Sysadvance

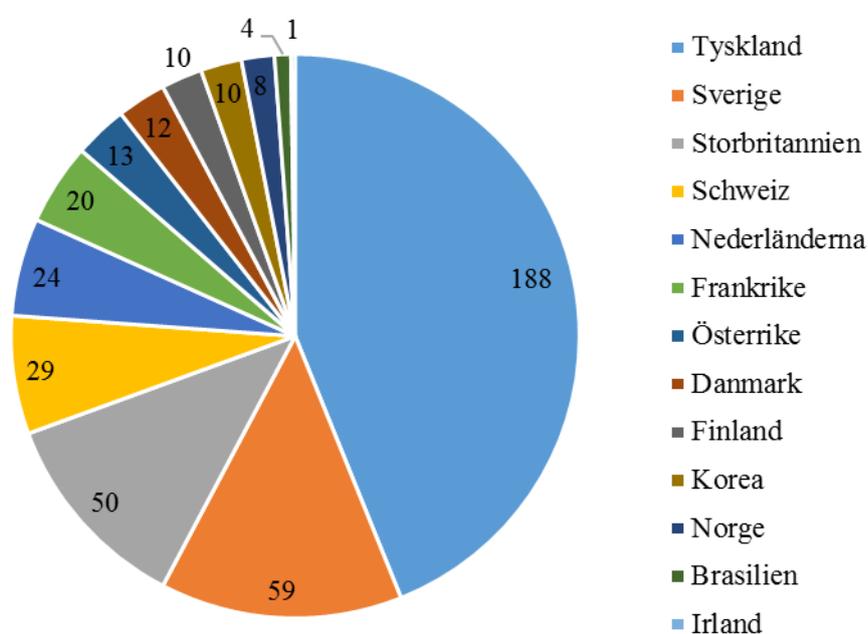
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A special thanks to:



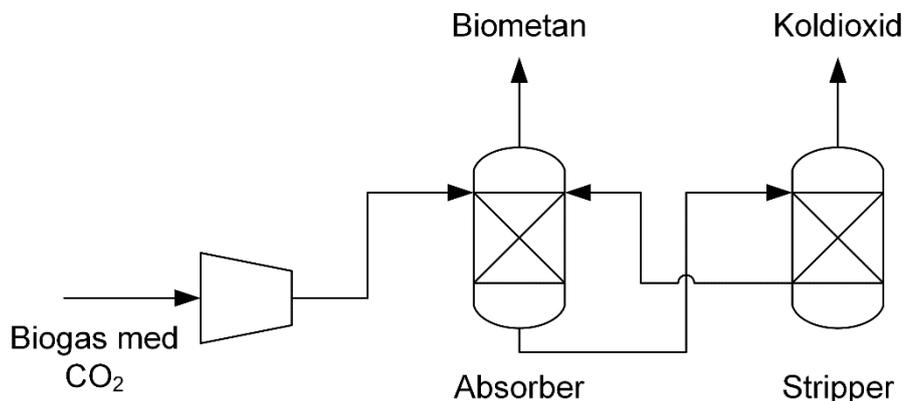
Utökad svensk sammanfattning

Den biogas som produceras världen över idag används primärt för att producera elektricitet i gasturbiner eller gasmotorer. Samtidigt finns det en drivkraft att minska koldioxidutsläppen från fossila bränslen, inom alla sektorer, men det är erkänt svårast att ersätta de som uppstår i transportsektorn. Det finns därför en drivkraft att uppgradera den biogas som produceras för att kunna använda den som en ersättning till naturgas, till exempel för transporter. Denna uppgradering görs genom att den koldioxid som också bildas vid produktionen frånges från metanen och en naturgasliknande produkt erhålls. Denna produkt kan antingen injiceras i ett naturgasnät eller, efter komprimering till högt tryck, användas för att driva gasfordon. Detta görs redan på ett antal platser i världen, figur 1.



Figur 1. Placering och antal biogasanläggningar med uppgradering inom IEA bioenergy task 37s medlemsländer för 2015.

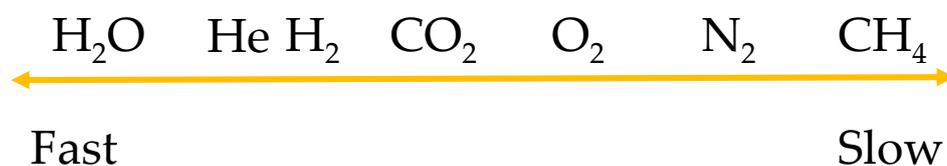
Som kan utläsas ur figuren är det Tyskland som är största land med Sverige och Storbritannien därefter. Uppgraderingen av gasen kan ske med ett par olika metoder. De bygger alla på skillnader mellan metan och koldioxid, skillnader som kan vara kemiska eller fysikaliska. Tre av de kommersiella metoderna bygger på att koldioxid och metan har olika löslighet i lösningsmedel. Dessa tre är vattenskrubbning, skrubbing med ett organiskt lösningsmedel (vanligtvis Genosorb®) och kemisk skrubbing med aminlösningar. I den sistnämnda metoden är det inte bara koldioxidens högre löslighet i vatten/aminlösningen, utan också en kemisk reaktion mellan aminen och koldioxid som ger avskiljningen. En generisk bild för dessa tre metoder återfinns i figur 2, de tre individuella teknikerna skiljer sig dock åt vad gäller design och värmeintegration och mer information om vardera teknik återfinns i huvudrapporten.



Figur 2. Generisk skrubberuppställning.

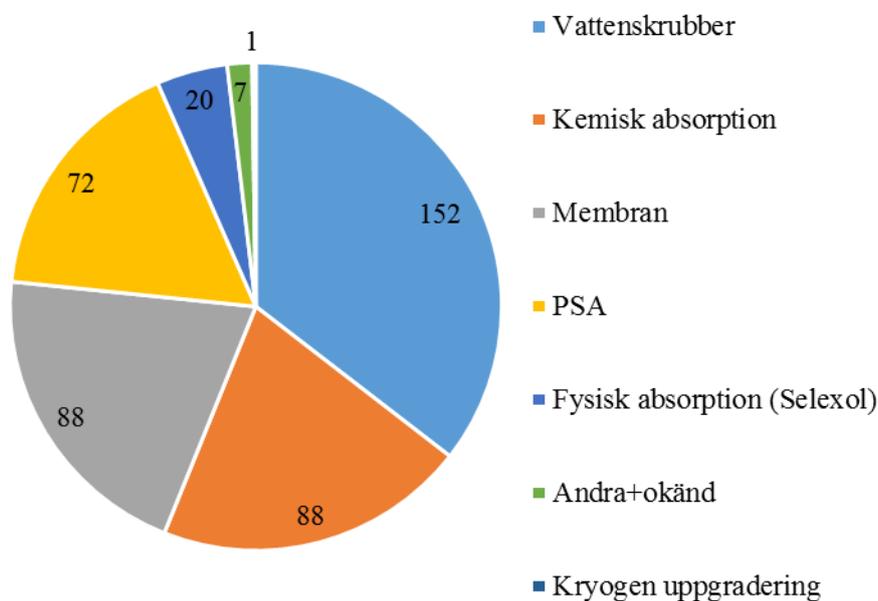
Utöver dessa tre metoder kan skillnaden mellan hur metan och koldioxid adsorberar på en yta användas. Denna teknik kallas för pressure swing adsorption och bygger på att koldioxid porkondenserar i små porer vid förhöjda tryck. Detta gör att det tar längre tid för koldioxid att bryta igenom en kolonn och det går därför att separera de två gaserna från varandra. För att regenerera kolonnen sänks trycket och koldioxiden drivs av, denna skillnad i tryck vid adsorption/desorption är vad som ger tekniken dess namn. För att tekniken ska kunna ge ett kontinuerligt flöde, kopplas ett antal kolonner ihop till ett system där olika kolonner befinner sig i olika faser, men i minst en kolonn adsorberas koldioxid och ren metan erhålls.

Det går också att använda olika molekylära egenskaper, storlek, affinitet med andra ämnen, för att separera koldioxid och metan med hjälp av semipermeabla membran. Genom att använda ett membran som har olika permeabilitet för olika gaser kan dessa separeras. De membran som används för separation av biogas har relativt långsam genomsläpplighet för metan jämfört med koldioxid. Då genomsläppligheten dessvärre inte är noll behövs flera membran seriekopplas för att erhålla god separation och hög återvinning av metan, figur 3 återger skillnaden i genomsläpplighet för en typ av membran.



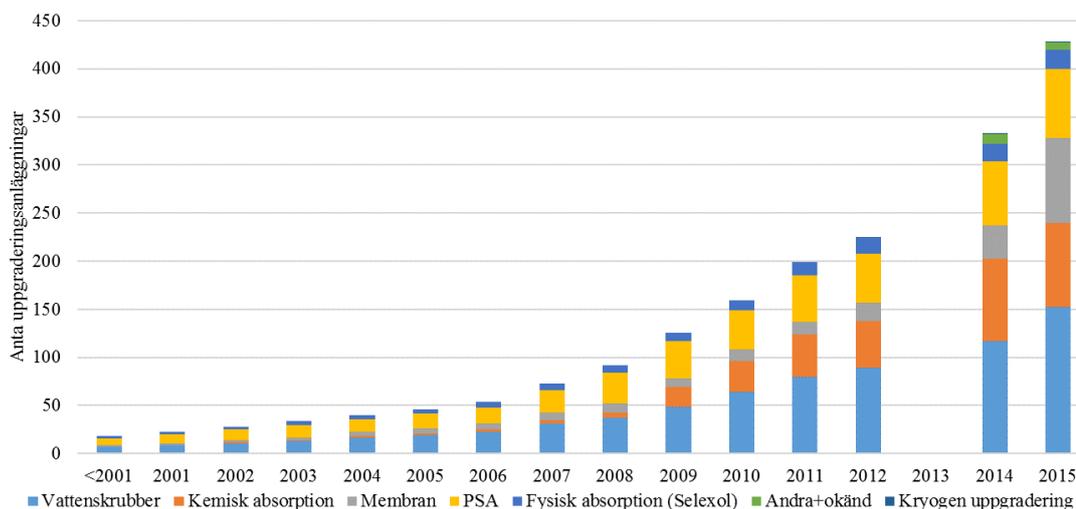
Figur 3. Membranpermeabilitet.

Slutligen kan den stora skillnaden i kokpunkt användas för att skilja de båda gaserna åt. Då kokpunkterna är långt under noll kallas denna metod kryogen separation eller kryogen destillering. Dessa metoder används i dag i stor utsträckning, med undantag för kryogenseparation. Av de lite drygt 400 uppgraderingsanläggningar som rapporterats inom IEA bioenergy task 37 under 2015 fördelade sig metoderna som i figur 4.



Figur 4. Fördelning av uppgraderingsanläggningar på olika tekniker

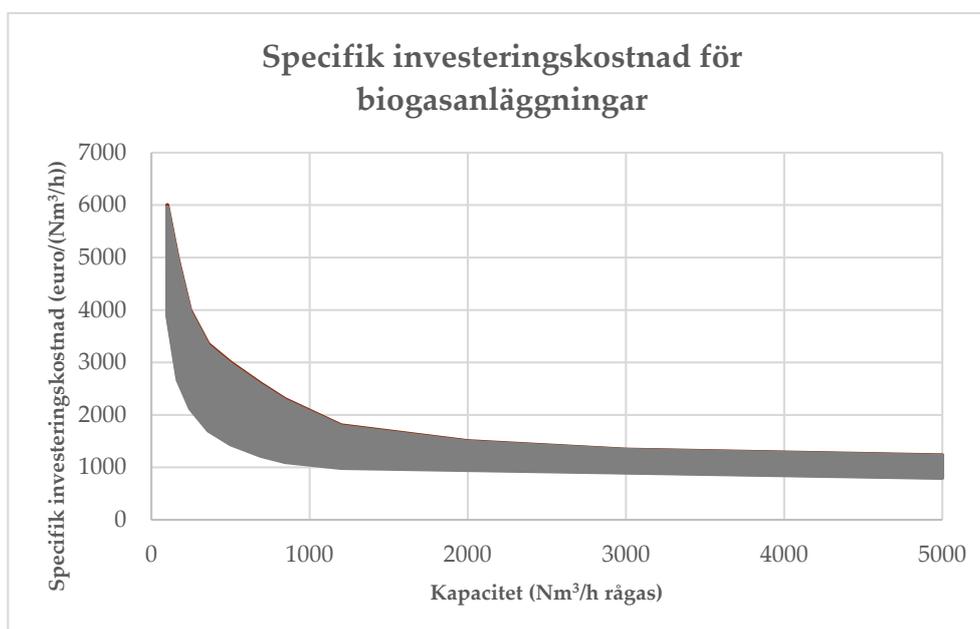
Då data för uppgraderingsteknik har samlats in under ett antal år går det att få intressant information kring hur de olika teknikerna utvecklas i förhållande till varandra, men också hur marknaden som helhet utvecklas. Det går att se att marknaden är i tydlig tillväxt, åtminstone för de länder som rapporterar till IEA bioenergy task 37, figur 5.



Figur 5. Antal uppgraderingsanläggningar och deras tekniker under sedan 2001 inom IEA Bioenergy task 37-länderna.

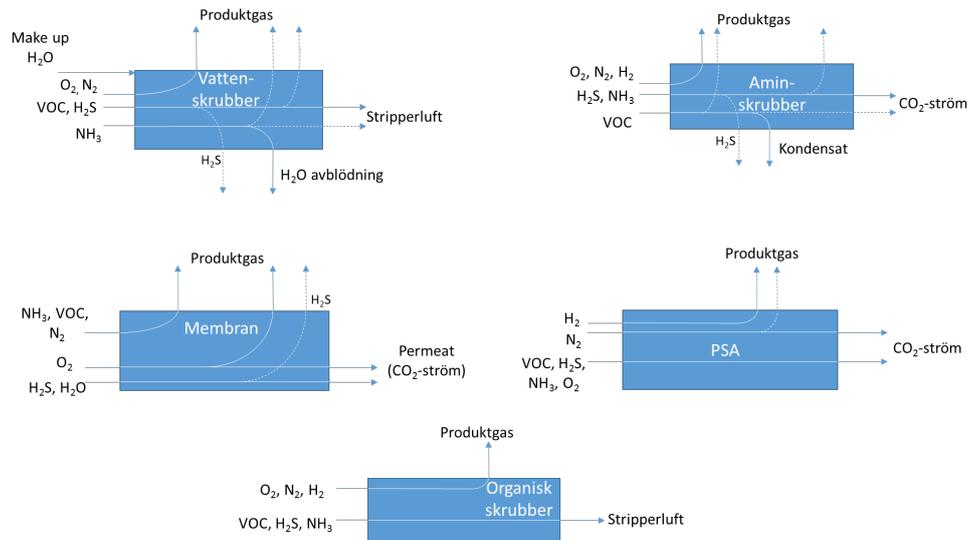
Den tydligaste tillväxten är för membrantekniken, men även kemisk absorption och vattenskrubbning samt PSA växer i absoluta tal; dessa tappar dock marknadsandelar till membrantekniken. I denna rapport har data för investering i de olika teknikerna

samlats in från ett antal leverantörer. Data visar ett spann i investeringskostnad som funktion av biogaskapacitet, men det går inte att påvisa en signifikant skillnad mellan de olika teknikerna; det kan vara större skillnad mellan två leverantörer med samma teknik än mellan olika tekniker, data sammanfattas i figur 6. Den ekonomiska informationen är för fall med en rågas som innehåller 60% metan, 200 ppm svavelväte, är mättad på vatten vid 40 °C, har max 0,1 % syre och 0,4 % kväve på volymbasis, innehåller mindre än 100 ppm ammoniak, inga siloxaner och håller ett tryck på 20 mbar(g). Produktgasen som genereras håller minst 97% metanhalt, ha mindre är 20 mg/Nm³ svavel innan odorisering, en daggpunkt på -10 °C vid 200 bar(g) och har ett tryck över 4 bar(g).



Figur 6. Den specifika investeringskostnaden för ett standardprojekt.

Som kan utläsas ur figur 5 finns det en tydlig effekt av att gå upp i skala när det gäller investeringskostnaden. Det kan också konstateras att det är relativt stor skillnad mellan olika tekniker och leverantörer vid lägre kapaciteter, då variansen mellan dessa blir större. Energiförbrukningen är en annan faktor som är relativt lik mellan de olika teknikerna. Det blir sålunda viktigt att inte bara stirra sig blind på investeringskostnaden, utan att också överväga andra aspekter. En sådan aspekt är den kvalitet som förväntas på den egna biogasen som ska uppgraderas. Beroende på vad den innehåller för föroreningar kan de olika uppgraderingsteknikerna falla olika väl ut. I figur 7 framgår hur de vanligaste spårämnena uppför sig när de passerar genom en uppgraderingsanläggning.



Figur 7. Blockschema över hur föroreningar uppför sig när de passerar genom de olika, vanligaste uppgraderingsteknikerna.

Det går att utläsa vissa skillnader mellan de olika teknikerna. Först och främst skiljer sig vatten- och organiskskrubber från de andra i det att ingen ren CO₂-ström erhålls då luft används i strippern. Vidare avskiljer PSA och membran syre helt eller delvis, medan PSA även avskiljer delar av kvävgasen. VOC följer helt med produktgasen i membranläggningar, medan VOC helt avskiljs i den organiska skrubbern och PSA samt delvis i vatten- och aminskrubbern. Vad gäller svavelväte skiljes den av helt i den organiska skrubbern och PSA-anläggningar och delvis i de andra teknikerna. Dock är det vanligast att denna förorening hanteras på olika sätt innan. Om det är mycket svavel i gasen kan det först doseras kemikalier i rötchambran för att minska bildningen, en biologisk avsvavling kan göras efter rötningen och den sista svavelmängden kan adsorberas i aktiv kol. I skrubberteknikerna (ej organisk skrubber) är det av intresse att se till att det inte bildas utfällning av salter om både svavel och ammoniak finns i gasen.

Andra saker som skiljer mellan teknikerna vad gäller förbrukningsvaror är sådant som skumdämpande kemikalier, pH justerande kemikalier etc. Men behovet av förbehandling av biogasen, d.v.s. hur mycket och vilka olika föroreningar som finns i den, är den faktor som påverkar kostnaden mest mellan olika projekt. På samma sätt kommer behovet av förbehandling att påverka investeringskostnaden för anläggningen och skilja sig från de siffror som presenteras i figur 5.

Vid produktion av biogas med membran, aminskrubber eller PSA erhålls en ren koldioxidström som kan användas. Den vanligaste tänkta tillämpningen för denna koldioxid är i växthus, i livsmedelsindustrin eller som kylmedia. Men en ny teknik som är under framväxt är att omvandla elektricitet till gas då elkostnaden är låg, t.ex. vid gynnsamma förhållanden för vindkraftsproduktion. Detta blir ett sätt att balansera elektricitetsutbudet mot övriga energikällor och gasnätet skulle kunna fungera som ett lager för överskottselektricitet.

I sammanfattning går det att utläsa att intresset för att uppgradera biogas till biometan för användning som naturgasersättning eller för fordonsdrift ökar stadigt. Sedan den senaste rapporten publicerades har antalet anläggningar nästan fördubblats. Det är

tydligt att membranläggningar tar marknadsandelar i den växande marknaden. Tyskland är det land som har flest uppgraderingsanläggningar följt av Sverige. Dock är tillväxten störst på andra marknader, framförallt Storbritannien, Frankrike, Danmark, Finland och Korea.

Det visar sig också att det inte finns några större skillnader mellan teknikerna med avseende på investeringskostnad och energiåtgång, med undantag för aaminskrubbern som förbrukar mindre elektricitet men som istället kräver värme. Det blir därför viktigt att fokusera på andra aspekter så som för- och efterbehandling, beroende på vilka råvaror som används i processen och vilken produktgasstandard som ska mötas.

Summary

Biogas produced by anaerobic digestion is often used in gas turbines to produce electricity. In order to increase the value of the gas and to enable utilization of the gas in other applications, it may be advantageous to upgrade the biogas. In this way, the carbon dioxide as well as various impurities are removed and biomethane is produced. Biomethane is similar to natural gas and can be used in similar applications, e.g. fed into the natural gas grid, or as vehicle fuel.

Several different biogas upgrading techniques are on the market today. Some of them make use of the fact that carbon dioxide and methane have different solubility in different solvents. By choosing a solvent which has a high solubility for carbon dioxide but lets methane pass through unchanged, the carbon dioxide can be separated from the methane in biogas efficiently. Common solvents used for biogas upgrading are water, amines as well as organic solvents such as Genosorb[®]. The difference in adsorption behavior of carbon dioxide and methane on a surface at different pressures is used in pressure swing adsorption (PSA), which can be used to effectively separate carbon dioxide from methane. Another common biogas upgrading technique uses the fact that carbon dioxide is more likely to pass through a semi permeable barrier, e.g. a membrane, than methane. By letting biogas pass through such a membrane, the carbon dioxide can thus be removed from the gas, leaving concentrated methane in the product stream. Finally, the difference in boiling point between methane and carbon dioxide may be used to separate the gases in cryogenic distillation.

For this report, data on the specific investment cost was collected from companies supplying biogas upgrading plants using the above described processes. The data shows a span of investment costs, but it also shows that there is no significant general difference in investment cost between the different techniques when considering a given standard project. Also the energy consumption is rather similar for the different upgrading techniques. When deciding on a suitable biogas upgrading process, it is therefore important to rather consider other aspects. These may include the ability of the different processes to handle specific impurities present in the actual project or specific requirements in product gas quality. Also the need for consumables such as anti-foam, chemicals for pH regulation as well as operational costs for any needed pretreatment differs between biogas upgrading processes but is of course also dependent on the pretreatment needed in a project. It is important to remember that the conclusion regarding specific investment cost in this report is related to a standard case. In a real project, where more or less pre- and posttreatment will be needed depending on the choice of upgrading technique, the investment cost for different biogas upgrading techniques will most likely differ.

Biogas produced from various substrates such as agricultural residues, biological waste or sewage sludge contains low concentrations of unwanted substances, e.g. impurities, such as H₂S, siloxanes, ammonia, oxygen and volatile organic carbons (VOC). H₂S is separated from the methane in most biogas upgrading techniques. How efficient this removal is and thus whether it is enough to meet product gas requirements differs between the different techniques. Scrubbers using absorption in water, amines or organic solvent usually remove most of the H₂S, while polishing filters are needed for membrane upgrading and PSA. When separated from the methane gas, H₂S, however, ends up in a CO₂ rich side stream such as stripper air where it usually needs to be removed due to environmental legislation. If the CO₂ stream is utilized, the necessity to

remove H₂S depends on what the gas is used for. H₂S thus needs to be removed from the gas at some point in most cases, but depending on the biogas upgrading technique used, this may need to be done in the raw biogas or there may be a choice regarding where in the process to remove H₂S. Siloxanes may be harmful to process equipment when present at too high concentrations. In scrubber systems the produced biomethane usually needs further drying and the main part of siloxanes are removed in the dryers. Ammonia is soluble in water and the concentrations commonly found in biogas are usually removed in the condensation which is usually part of a biogas upgrading system in order to protect the upgrading system from liquid water. Ammonia is not usually a problem in biogas upgrading systems. However, when H₂S and ammonia are present simultaneously, it is important to prevent precipitation of compounds formed when these two react with each other. Since anaerobic digestion occurs under anaerobic conditions, e.g. with no oxygen present, the concentration of oxygen in biogas is usually low. Improper adjustment of oxygen injection systems used in order to biologically remove larger concentrations of H₂S may increase the oxygen levels of the raw biogas. However, the oxygen concentration is commonly monitored carefully in biogas systems in order to minimize the explosion risk. Biomethane quality requirements when the gas is fed into a natural gas grid are currently limiting the oxygen content in biomethane to almost zero, especially in gas grids which include gas storage systems. It may therefore be necessary to remove oxygen from the product gas, or raw biogas if preferred, if the oxygen present in the raw biogas is passed to the produced biomethane. This is valid for scrubber techniques except membrane and PSA systems which remove a significant amount of the oxygen.

The product gas leaving the plant must uphold certain gas quality criteria, either set as a bilateral agreement with the transporter and/or buyer of the biomethane, which currently are based on national specifications. A new CEN standard on biogas injection of H₂ gas quality has recently been sent to formal vote, regulating levels of minor impurities such as siloxanes and ammonia, and major ones such as hydrogen and oxygen. The minimum calorific content is specified, but the wobbe index is not. Allowed sulfur levels are still relatively high, and not including the contribution of odorization, which is still an issue handled nationally in Europe. Biomethane and compressed natural gas (CNG) delivered at the point of retail is also under standardization. There are efforts to introduce a second dedicated non-grid based grade, which will be beneficial to the sales of biomethane, since most of the parameters will easily be upheld by normal upgrading, with the exception of raw biogas containing larger amounts of siloxanes.

In biogas upgrading with membrane separation, amine scrubbers and PSA, very pure CO₂ can be produced. In biogas upgrading using these techniques, besides biomethane, CO₂ can be produced and utilized. The most common ways to use CO₂ are for the use in greenhouses, in the food and cooling industry or to utilize access electricity to let the CO₂ react with H₂ to produce methane, co-called power-to-gas. Power to gas constitutes a way to store access electricity in the form of gas which is gaining increased interest during recent years.

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1 Introduction

Biogas has a key role in the future market of renewable energy. It is considered to be a clean and environmentally friendly fuel unlike the non-renewable resources such as fossil fuels. The main components in biogas are methane and carbon dioxide. Besides the two main components there are some trace components present: ammonia, hydrogen sulphide, siloxanes, volatile organic carbons (VOC), oxygen and nitrogen. One of the possible futures for biogas is to be used as vehicle fuel, it is considered to be one of the best alternatives to replace fossil fuels and natural gas. In order to be used as vehicle fuel the biogas has to be upgraded and the purity of the biogas needs to match the standard for vehicle fuel [1]. During the upgrading process the carbon dioxide as well as the trace components are separated from the biogas.

Besides the possibility to be used as vehicle fuel biogas has other areas of use, such as functioning as a source for heat, steam and electricity production. In case the biogas is injected to the natural gas grid, it also needs to be upgraded. Here too is a requirement on the purity of the gas. Upgrading of biogas has been done since the late 1990's and from this point the technologies have evolved and become more efficient. New technologies have also made their way to the market.

1.1 BACKGROUND

In 2013, Bauer et al. made an evaluation of some of the available upgrading technologies, which were commercially available and in operation [2, 3]. The report by Bauer et al. was part of the publication series of the Swedish Gas Technology Centre (SGC report 270) and is the work which precedes this report. The evaluated technologies were amine scrubbers, water scrubbers, pressure swing adsorption (PSA), organic scrubbers and membrane units. In the reports, it was shown that the market has changed rapidly the recent years but is dominated by the first three technologies mentioned above. It also concluded that the investment costs, as well as the energy demand for the technologies were similar with one exception, the heat demand for the amine scrubber.

As mentioned by both Bauer et al. [2, 3] and Muñoz et al. [4] cryogenic separation is a technology that struggles with both technical and economical limitations but there is a large interest regarding this method and it has great potential of improvement compared to the other technologies evaluated by Bauer et al. [2, 3].

Also Adriani et al. [5] wrote a review on the upgrading of biogas. The report displays economic and environmental aspects and the concluding remark made was that there are several methods available and depending on the final product the implemented method should be chosen accordingly.

Muñoz et al. [4] highlights the possibility to use biotechnologies such as algal-bacterial photobioreactors. These technologies are some of the most recent developments and can provide simultaneous removal of carbon dioxide and trace components for example the hydrogen sulphides. Otherwise the paper focuses on the amounts of carbon dioxide and trace components, which can be separated through the different methods and in particular the biotechnologies.

Sun et al. [6] systematically reviewed biogas upgrading technologies and found that there are still large disagreements regarding the energy consumption and the methane

slip that occurs during the processes. They also highlight the importance of an increasing knowledge about how the novel technologies such as cryogenic separation and biological methods behave in large scale operations. Furthermore, the report presents different areas where the biogas can be utilized and some of the different requirements for the gas in these areas. Also the utilization of the separated carbon dioxide is discussed.

These publications all review the technology used for the upgrading of biogas, from types of technologies to methods for removing impurities and trace compounds. Despite this, there is still a lack of information from a plant owner and operator perspective on what other operating and maintenance costs can be expected, which trade-offs are possible in deciding between technologies etc. This report is striving to fill this void.

1.2 PURPOSE AND AIM

The purpose of this report is to complement and update the information on biogas upgrading previously collected and published by Bauer et al. [2]. The work presented in this report is an attempt to aid anyone interested in investing in a biogas upgrading unit. The ambition is that the contents of the report will aid in understanding the trade-offs between different upgrading technologies as well as in understanding the destiny of the potential impurities in the biogas, their origin and strategies for handling them depending on concentration. The report will also give updated information on investment costs as well as for operating and maintenance costs to further assist in writing suitable requests-for-quotations.

1.3 DISPOSITION

In chapter 2, the main techniques for biogas upgrading used on industrial scale are described. Chapter 3 focuses on methods to remove some of the main impurities present in biogas produced from various substrates by anaerobic digestion. In chapter 4, the requirements on biomethane gas quality for various applications in different countries are described. Possible uses of side streams rich on CO₂ are listed in chapter 5. Finally, the biogas upgrading techniques described in chapter 2 are compared to each other in different aspects in chapter 6.

1.4 EXISTING UPGRADING PLANTS

The amount of biomethane produced and the number of biogas upgrading plants is increasing. Since the last report was published, IEA Bioenergy Task 37 has restricted the comprehensive updating to its member countries. End of 2015, there were almost 430 biogas upgrading plants in the IEA Bioenergy Task 37 member countries, 100 more than last year. Their distribution among different member countries and the technology employed are shown in Figure 1. In Figure 2, the historical trend for the upgrading technology employed is shown. It is evident that the major expansion of the membrane technology is the result of last year's new builds. Water scrubber is the only other technology showing significant growth. Please note that the data for 2013 and 2014 only includes the IEA Bioenergy Task 37 member countries. Non-task 37 countries included in the dataset of 2012 are the USA (14), Japan (6), Canada (3), Spain (2) and Iceland (1). The USA have had significant growth in biomethane upgrading since then.

Other countries reported to have installed biogas upgrading units are Italy, Estonia, South Africa, India, New Zealand, Thailand, Indonesia.

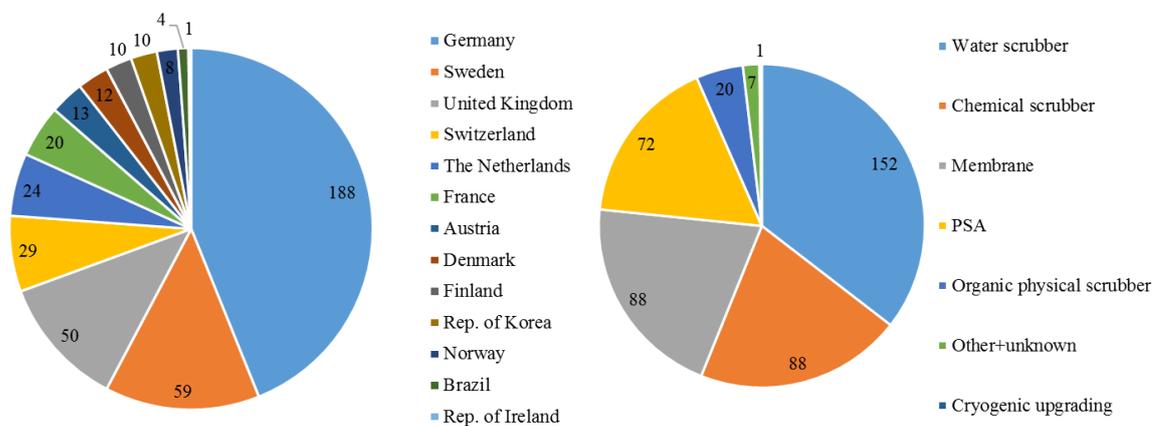


Figure 1. The distribution of operational biogas upgrading units among the IEA Bioenergy Task 37 member countries (data from 2015). The labels are in the order from the largest to the smallest.

1.5 MANUFACTURERS OF BIOGAS UPGRADING UNITS

The number of manufacturers of biogas upgrading plants is increasing every year (Figure 2) and the list shown in this report includes only those that were known by the authors at the time of publishing.

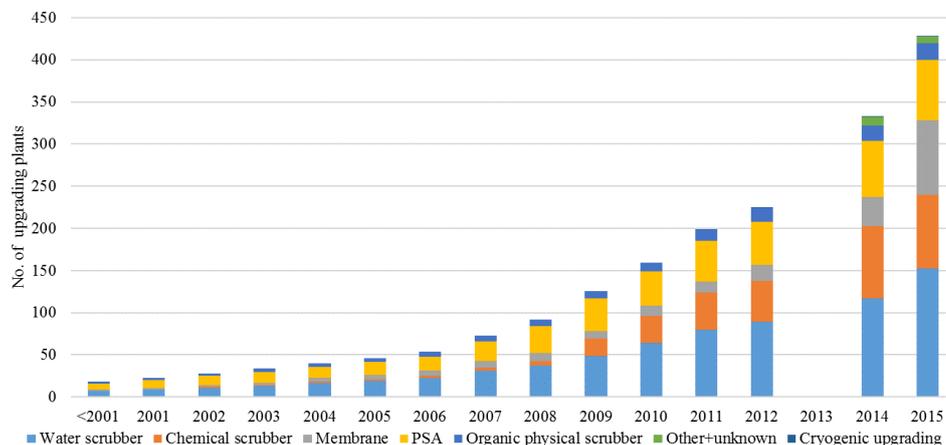


Figure 2. The historical trend of the growth in biogas upgrading units, distributed according to year and technology employed. Please note that the data for 2013 and 2014 only includes the IEA Bioenergy Task 37 member countries.

Tables 1 through 7 show manufacturers of upgrading units, sorted by technology type.

Table 1. Manufacturers of PSA units

Company	Homepage
Carbotech	www.carbotech.info
Cirmac	www.cirmac.com
ETW Energietechnik	www.etw-energy.com
Guild	www.moleculargate.com
Mahler	www.mahler-ags.com
NeoZeo	www.neo-zeo.com
Strabag	www.strabag-umweltanlagen.com
Sysadvance	www.sysadvance.com
Xebec	www.xebecinc.com

Table 2. Manufacturers of water scrubbing units

Company	Homepage
DMT	www.dmt-et.nl
Econet	www.econetgroup.se
Greenlane Biogas	www.greenlanebiogas.com
Malmberg Water	www.malmberg.se

Table 3. Manufacturers of chemical scrubbing units

Company	Homepage
Ammongas A/S	www.ammongas.dk
Arol Energy	www.arol-energy.com
Bilfinger EMS	www.ems.bilfinger.com
Cirmac	www.cirmac.com
Energy & waste technologies	www.ewtech-ing.com
Hera	www.heracleantech.com
Hitachi Zosen INOVA	www.hz-inova.com
MT-Biomethan	www.mt-biomethan.com
Purac Puregas	www.lackebywater.se
Strabag	www.strabag-umweltanlagen.com

Table 4. Manufacturers of organic physical scrubbing units

Company	Homepage
BMF HAASE Energietechnik	www.bmf-haase.de
Schwelm Anlagentechnik	www.schwelm-at.de

Table 5. Manufacturers of membrane units

Company	Homepage
Air Liquide	www.airliquide.com
Arol Energy	www.arol-energy.com
Axiom Angewandte Prozesstechnik	www.axiom.at
BebraBiogas	www.bebra-biogas.com
Cirmac	www.cirmac.com
DMT	www.dmt-et.nl
Eisenmann	www.eisenmann.com
EnviTec Biogas	www.envitec-biogas.com
Gastechnik Himmel	www.gt-himmel.com
Hitachi Zosen INOVA	www.hz-inova.com
Pentair Haffmans	www.haffmans.nl
Prodeval	www.prodeval.eu

Table 6. Manufacturers of cryogenic units

Company	Homepage
Acrion Technologies	www.acrion.com
Air Liquide	www.airliquideadvancedtechnologies.com
Cryostar	www.cryostar.com
FirmGreen	www.firmgreen.com
Gas treatment Services	www.gastreatmentservices.com
Gasrec	www.gasrec.co.uk

Table 7. Manufacturers with special focus on small scale biogas upgrading

Company	Homepage
BioGTS	www.biogts.com
Biosling	www.biosling.se
Biofrigas	www.biofrigas.se
BMF Haase Energietechnik	www.bmf-haase.de
Metener	www.metener.fi
NeoZeo	www.neo-zeo.com
Sysadvance	www.sysadvance.com

Table 8. Gas entry unit system Integrators

Company	Homepage
Orbital	www.orbital-uk.com
Itron Nederland (Bio2Net)	www.itron.com

2 Description of the available upgrading technologies

The basic concept of biogas upgrading is to concentrate the CH₄ in the raw biogas stream (~65%) by separating CO₂ (~35 %) and other minor gases (H₂S, H₂O, H₂, N₂, O₂ and VOC) from the inlet gas. This process can be carried out by applying different kind of separation technologies which utilize the different chemical and physical behavior of these gases. Accordingly, these technologies can also be grouped depending on which type of chemo-physical mechanisms they mainly utilize for the separation. These mechanisms are:

1. Adsorption
2. Absorption (physical and chemical)
3. Gas permeation
4. Cryogenic distillation

In the first group (1) the selective affinity of CO₂ onto a surface of a media (adsorption) at different pressures is used for controlling the separation. The technology is thus also called pressure swing adsorption (PSA) (see chapter 2.1).

The second group (2) is using the difference in selective affinity of solving gas into a liquid media (absorption). In this group, several different technologies have been developed based on different liquid absorption medias in which the CO₂ is dissolved and the CH₄ is not, depending on pressure and temperature. The temperatures and pressures utilized for controlling the absorption and desorption (stripping) process are subject to which media is used. Examples of medias are water, different kind of amines, as well as organic solvent and thus the main biogas upgrading techniques using absorption for separation are water scrubbing (see chapter 2.2), amine scrubbing (see chapter 2.3) and organic physical scrubbing (see chapter 2.4).

The third group (3), gas permeation, is using the fact that CO₂ and CH₄ gas molecules travel with different ease (permeates) through membranes. The permeability is higher for CO₂ than for CH₄, and membranes can thus separate this mixture. Biogas upgrading with membrane technology is further described in chapter 2.5.

The last group (4) is using the fact that CO₂ and CH₄ have different boiling points (-164 °C for CH₄ and -78 °C for CO₂ at 1 atm(a)). When biogas is cooled to these low temperatures, cryogenic distillation is possible and thus allows for separation of CH₄ and CO₂. Cryogenic distillation is further described in chapter 2.6.

In the following section the technologies available on the market, with brief notes on their benefits and limitations, are briefly described. Details on the theoretical background and processes are described in the previous report [2]. The below chapters have been written in collaboration with the suppliers of biogas upgrading systems which were part of the reference group on this project: Air Liquide, Ammongas, Biofrigas, BMF Haase Energietechnik, Carbotech, DMT, EnvTec, Greenlane, Malmberg Water, NeoZeo, Pentair, Purac and Sysadvance. These have all contributed, but none of them is alone responsible of any particular content of this report.

2.1 PRESSURE SWING ADSORPTION

Pressure swing adsorption (PSA) is a dry method used to separate gases via their physical properties. The basic principle is that raw biogas is compressed to an elevated pressure and then fed into an adsorption column, which retains the carbon dioxide but not the methane. When the column material is saturated with carbon dioxide the pressure is released and the carbon dioxide can be desorbed and led into an off-gas stream. For a continuous production, several columns are needed as they will be closed and opened consecutively. The typical set-up contains 4 adsorption columns (see process diagram in Figure 3) which are operated in parallel in 4 step cycles (the Skarstrom cycle) and thereby allows for a continuous operation. Adding even more columns and also optimising more advanced flow between the columns is way to increase separation efficiency and potentially also energy efficiency, but has to be balanced against acceptable complexity and investment costs. More details on the PSA process and operation is thoroughly described in the previous report [2].

The choice of adsorbent, the bed material, which selectively adsorbs CO₂ from the raw gas stream, is crucial for the function of the PSA unit. Common adsorbents materials are activated carbon, natural and synthetic zeolites, silica gels and carbon molecular sieves (CMS), but investigations into new adsorbents such as metal-organic frameworks are under development. Research and development of PSA technology is currently focusing on minimizing PSA units, optimizing the technology for small-scale applications and reducing energy use. Work is done also in combining different adsorbents to combine adsorbent characteristics and integrating separation of H₂S and CO₂ in a single column, which otherwise has to be separated in pre-treatment unit prior to the PSA columns. The same issues are as with free water in the raw gas which also has to be removed upstream of the PSA.

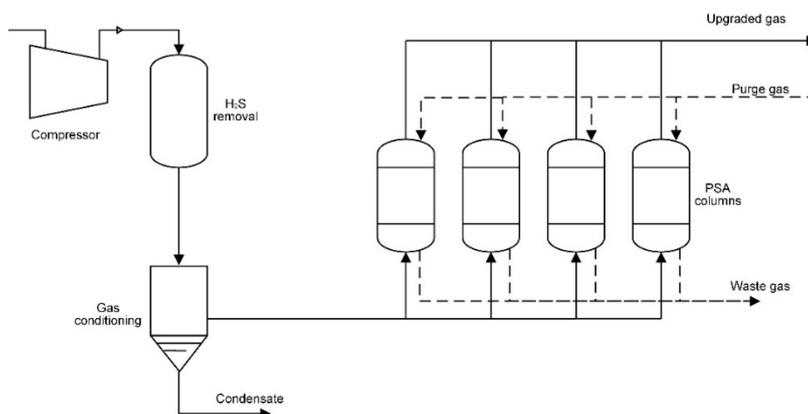


Figure 3. Process diagram for biogas upgrading with pressure swing adsorption (PSA)

H₂S will irreversibly bind to the adsorption media in a PSA process and therefore needs to be removed in the pretreatment. This is commonly done using a carbon filter, which is economically feasible for low and moderate concentrations of H₂S. Also NH₃ as well as VOC present in the raw biogas needs to be removed, which is done within the upgrading process in an adsorption column after the compression stage.

The biomethane leaving a PSA upgrading process has a dew point below $-50\text{ }^{\circ}\text{C}$ and is dry enough to be used without additional drying. O_2 and N_2 are removed efficiently from the biogas.

2.2 WATER SCRUBBING

In biogas upgrading using water scrubbing technology, water is used to separate the carbon dioxide from biogas. The process is based on the difference in solubility of carbon dioxide and methane in water and process parameters such as pressure and temperature in the water scrubber are chosen to maximize this difference in solubility. Today, most water scrubbers are operated at a pressure around 6-8 bar(a).

Often, the process water is recirculated in the biogas upgrading plant, which requires a desorption of the carbon dioxide from the process water. Carbon dioxide is desorbed from water in an air stripper at ambient pressure and temperature. To recover as much as possible of the methane dissolved in the process water in the absorption column, the water is lead through a flash column with lower pressure before desorption. The flashed gas is recirculated in the water scrubber and lead back to a point before compression and absorption. Waste gas treatment may be needed mostly to reduce the concentration of methane or H_2S . The process diagram of a water scrubber is presented in Figure 4.

The waste gas, e.g. the stripper air, from a water scrubber contains traces of methane. The water scrubber is a robust technology for biogas upgrading, which is able to handle various impurities in the raw biogas. Compounds such as H_2S , ammonia and certain VOC are dissolved in the process water and released with the stripper air. In many cases, post treatment of the stripper air is needed to fulfil environmental legislation. Alternatively, to remove e.g. H_2S in the stripper air it may be interesting to consider removing it in the raw gas before the upgrading process.

The upgraded gas is saturated with water and needs to be dried to the required dew point. Compounds such as H_2S , ammonia and VOC present in the raw biogas are usually removed by the water scrubber to a necessary extent and no further post treatment is needed.

For stable operation, the pH needs to be kept stable and a base is needed to increase the pH and to compensate the pH drop in the process water, which is a result of oxidation of mostly H_2S in the raw biogas. An antifoam agent may also be needed to improve mass transfer in the absorption column and increase the separation between carbon dioxide and methane. Growth of microorganisms in the columns in a water scrubber may be a problem. This is reduced in recent water scrubbers operating at a lower temperature and may be further minimized by the addition of biocides or treatment of the fresh water to the upgrading plant to minimize the amount of nutrients in the process water.

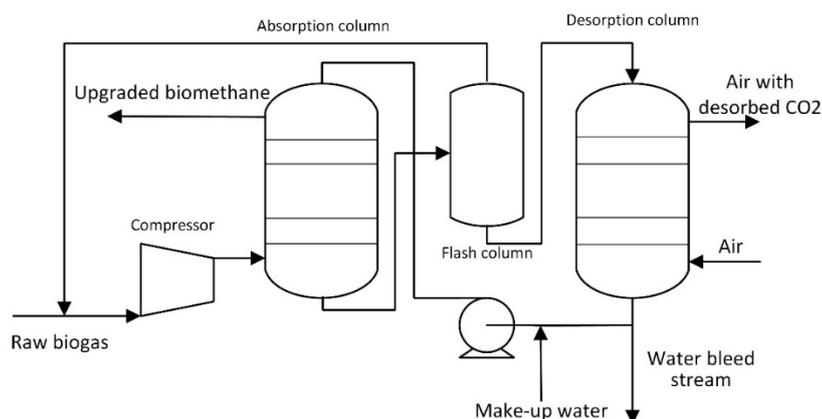


Figure 4. Process diagram for biogas upgrading with a water scrubber

This report focuses on the main biogas upgrading techniques, but these are also able to mix with each other to achieve positive synergies. One example of this is the recent study by [7] who investigated the theoretical potential to improve the performance of a water scrubber by adding a membrane unit. In this study, a membrane unit is placed in the gas from the flash column, which usually is recycled in the water scrubber. By bulk removal with membranes, the volumetric gas flow can be reduced and in this way, capacity in the compressor is freed. This hybrid solution leads to significant increase in capacity as well as a significant reduction in energy demand compared to a pure water scrubber.

2.3 AMINE SCRUBBING

The features of amine scrubbing are to use a reagent that chemically binds to the CO₂ molecule, removing it from the gas. This is most commonly performed using a water solution of amines (molecules with carbon and nitrogen), with the reaction product being either in the molecular or ion form. The most common amines used historically are methyldiethanolamine (MDEA), diethanolamine (DEA), monoethanolamine (MEA) [8] and primarily activated MDEEA (aMDEA) which is a mixture of MDEA and piperazine.

The inlet raw biogas enters the absorber from the bottom and is set in contact with the amine solution. The CO₂ content of the biogas reacts with the amine and is transferred to the solution. The spent amine solution is then led to the stripper where the CO₂ desorbs by regeneration with heat, Figure 5.

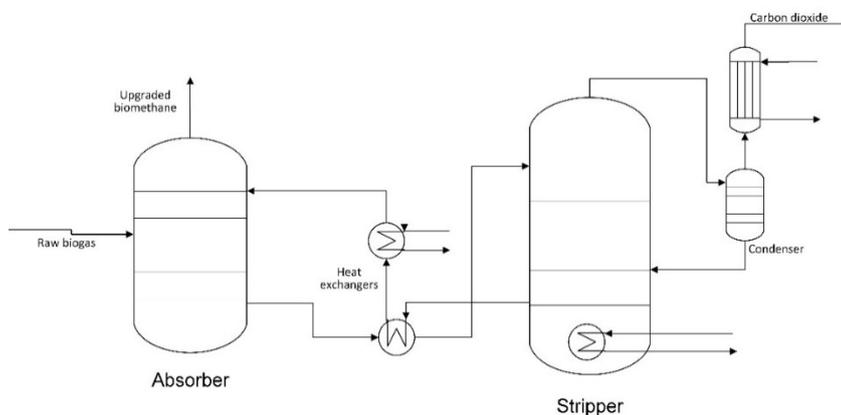


Figure 5. Process diagram for biogas upgrading with an amine scrubber

The amine scrubber process is able to handle gas without pretreatment as long as there are no liquid or solid impurities present. Most of the H_2S and NH_3 present in the raw gas is passed on to the CO_2 rich stream and may need removal there due to environmental legislation. It is, however, often an advantage to be able to remove these compounds in the CO_2 rich stream instead of the raw gas because there are no restrictions in the amount of air that may be introduced in this gas stream. When the heat needed for an amine scrubber biogas upgrading process is produced in a steam boiler, the CO_2 stream can be lead through this boiler and H_2S will be removed. In an amine scrubber, very pure CO_2 may be produced, which makes this process suitable to combine with the utilization of CO_2 , chapter 5.

O_2 and N_2 are passed through the absorption column together with the upgraded biomethane. Whether removal is needed there depends in gas quality requirements. For more details, see chapter 4. When H_2S is present in the raw gas in high concentration, a polish filter for H_2S may be needed in the product gas since not all H_2S is removed in the absorption column. Whether this is needed, depends on the requirements on product gas quality as well, but also on the amine used in the process, since the solubility of H_2S in the amine solution differs between different amines used. Furthermore, the biomethane leaving the absorption column is saturated with water and the produced biomethane needs to be dried to lower the dew point.

The amine scrubber differs from the other techniques described in this report in electrical energy required for the biogas upgrading. The demand for electricity in this process is lower than that required in the other techniques. However, in an amine scrubber, energy in the form of heat is required for the regeneration. An amine scrubber works at low pressure (100-200 mbar) compared to the other techniques described in this report. This gives a flexibility depending on the need of pressure in the product gas. When low pressure in the biomethane stream is sufficient, this biogas upgrading technique has lower energy consumption for compression compared to the other techniques. When higher pressure is needed, the produced biomethane is compressed to the desired pressure, with the result of an increased energy consumption. In this way, compression is only needed for the CH_4 stream and no energy is needed to compress CO_2 .



Figure 6. Amine scrubber from Ammongas in Freva, Norway

There are four major areas of operating issues that are commonly identified in operating amine systems. These are failure to meet specifications, foaming, amine loss and corrosion [9]. The first operating issue is as worrying as it is multifaceted. It should be dealt with by assuring the right design specifications, e.g. inlet CO₂-concentration, inlet temperature of CO₂, gas and liquid flow rates and inlet temperature of the amine solution to the absorber. Another issue may be the change in amine concentration due to reasons such as leakage, degraded solvent and foaming among others. Difficulties to meet specifications is of course not a problem related specifically to amine scrubbers, but is valid for all biogas upgrading techniques. The difference lies rather in the ways to solve the problem.

Foaming may occur at any point of operation. This is, however, most common during start-up and not usually needed continuously as in a water scrubber. Several reasons are possible but the most recurring reason is hydrocarbons (from oil-rests from manufacturing pipes and vessels). This can usually be prevented by good hygiene, insuring no contaminants in the feed and to foam test the make-up water.

Amine loss can arise from obvious leakage in joints, gauges etc. but may also be due to entrainment of liquid to the gas streams. A more sudden amine loss is most likely to be derived from failure of demister components. Only minor amounts of amine are lost in an amine scrubber during normal operation.

Corrosion is a broad topic and may cause serious issues in operation and result in downtime. It is therefore important to use appropriate materials and design the plant properly. More information on troubleshooting this type of problem may be found elsewhere [10].

2.4 ORGANIC PHYSICAL SCRUBBING

Among organic physical scrubbers, Genosorb® is the most used solvent for biogas upgrading processes. The solvent consists of a mixture of dimethyl ethers and polyethylene glycol. The absorption occurring in these organic physical scrubbers can be explained similar to the absorption in a water scrubber, by Henry's law. The solubility of CO₂ in the organic solvent compared to water is however much higher. This results in the recirculating volume of the solvent being much lower when using the organic solvent and thus the required column diameter is much smaller.

The process flow and operating much resembles the one for a water or amine scrubber. The biogas is compressed to a pressure of 7-8 bar(a) and cooled and then fed to the bottom of an absorption column. Here CO₂ is absorbed to the liquid phase. The spent solvent is then primarily led to a flash drum where some of the CO₂ and CH₄ is desorbed and then further on to the desorption column where the rest of the solvent is regenerated by adding heat.

The heat needed is supplied from waste heat within the process. This makes the energy consumption for an organic physical absorber resemble the consumption for a water scrubber, only requiring electricity for mainly the compressor, the cooler and the feed pump. The process diagram for an organic physical scrubber is presented in Figure 7.

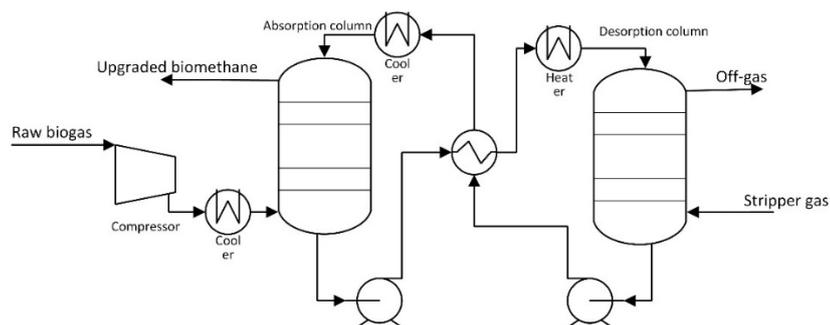


Figure 7. Process diagram for biogas upgrading with an organic physical scrubber

The corroding effect seen in the amine scrubber is not present in the Genosorb® scrubber as the solvent is anti-corroding. This results in piping not being necessarily made in stainless steel. The foaming issue seen in amine scrubbers can also be neglected, however the addition of organic solvent make-up may be necessary to compensate for minor evaporation losses.



Figure 8. Organic physical scrubber from BMF Haase in Wolfshagen, Germany

The organic physical scrubber is a robust technology being able to handle various impurities in similarity to the water scrubber. Most other impurities such as H_2S , NH_3 and VOCs are dissolved in the organic solvent and in this way passed on to the stripper air. Therefore, post treatment of the stripper air for mostly H_2S may be needed in many cases due to environmental legislation. In these cases, it may be a good idea to remove the H_2S already in the raw gas instead of the stripper air. However, the process itself is not harmed or compromised by high concentrations of H_2S or NH_3 in the raw gas. Only the combination of these two will be a problem when present at high concentrations resulting in precipitation of ammonium sulphate. In this case, one of them needs to be removed in the raw gas.

The water soluble fraction of the VOCs present in the raw gas are mostly removed with the condensate during compression of the gas prior to the actual organic scrubber. The solvent soluble VOCs such as limonene will dissolve in the organic solvent used in the scrubbing process and will thus be concentrated. However, this problem may be solved relatively simple through the addition of a cleaning step of the solvent, e.g. by solvent distillation, to remove these VOCs. This constitutes a more economical alternative to the often used active carbon filter otherwise used to remove VOCs from the raw gas, especially for biogas with high concentrations of VOCs, where the cost for activated carbon would be relatively high.

O_2 and N_2 present in the raw gas pass through the absorption in a physical organic scrubber and will be present in the product biomethane. The product gas also contains small amounts of water. For dew point standards lower than $-20\text{ }^\circ\text{C}$ at 1 bar(a), further drying of the product gas is needed.

2.5 MEMBRANE SEPARATION

Biogas upgrading using membrane technology uses the fact that gases have different permeability through a membrane fiber. During separation of carbon dioxide and methane in biogas upgrading, polymeric hollow fiber membranes are used. The membrane separation commonly occurs at pressures in the range of 10 to 20 bar(a). This results in higher pressure in the produced biomethane than that for other upgrading techniques. When using the biomethane in high pressure applications, this is an advantage, but it is important to consider that the pressure in the biomethane needs to be reduced for certain applications. The membrane fibers on the market are continuously improved to gain better selectivity and higher permeability to achieve better separation and lower methane slip. Also, to increase the methane concentration in the product gas, several membrane stages are usually used in sequence (see Figure 9(ii)). To acquire lower methane slip, a third membrane stage may be added in the permeate, e.g. the waste gas, from the first membrane step (see Figure 9(iii)). More details on the 2 and 3 stage membrane process for biogas upgrading are given in the previous report [2]. Process configurations within membrane separation for biogas upgrading are constantly developed further with the latest development of a four stage process, which further reduces the recycle rate. The process design with several membrane stages in biogas upgrading results in a flexible process, where parameters such as methane slip, energy consumption, etc. can be optimized. In this way, a good trade-off can be found in order to optimize the economics of each project depending on its constraints (energy cost, biomethane price, environmental requirements, etc).

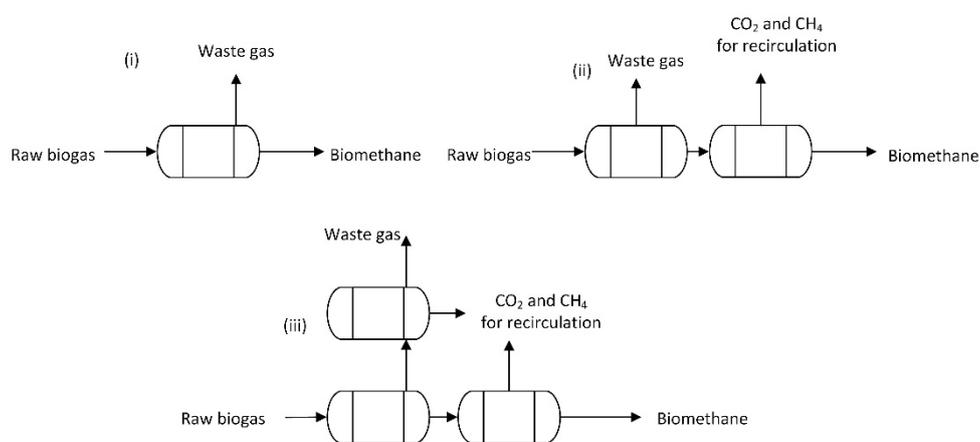


Figure 9. Different process configurations in biogas upgrading with membranes: (i) one stage, (ii) two stages, (iii) three stages

Most membranes are sensitive to liquid water, oil and particles and these need to be removed in condensate filters, coalescence filters or even activated carbon filters for extra security. Also condensation on the membrane surface should be avoided especially if compounds such as H₂S or NH₃ are present in the gas, which would result in the formation of acid on the membrane surface. Therefore, it is important that the gas remains above the dew point through the separation process.

Part of the H₂S in the biogas is also removed with the CO₂ stream, but separation is not sufficient to handle high concentrations of H₂S in the raw biogas and separation of H₂S prior to the membrane upgrading is common. It is, however, important to remember that moderate concentrations of H₂S do not damage the membrane surface as long as

no condensation of water occurs there. Also NH_3 is harmful to the membranes if it is dissolved in condensed water on the membrane surface. NH_3 present in the raw gas is, however, removed efficiently in the biogas drying steps which are common practice in biogas upgrading with membranes, and it is unusual to find NH_3 in the gas in the membrane separation step. Certain VOCs may be harmful to the membrane fiber and damage these irreversibly and VOCs are therefore commonly removed prior to the membrane separation step.

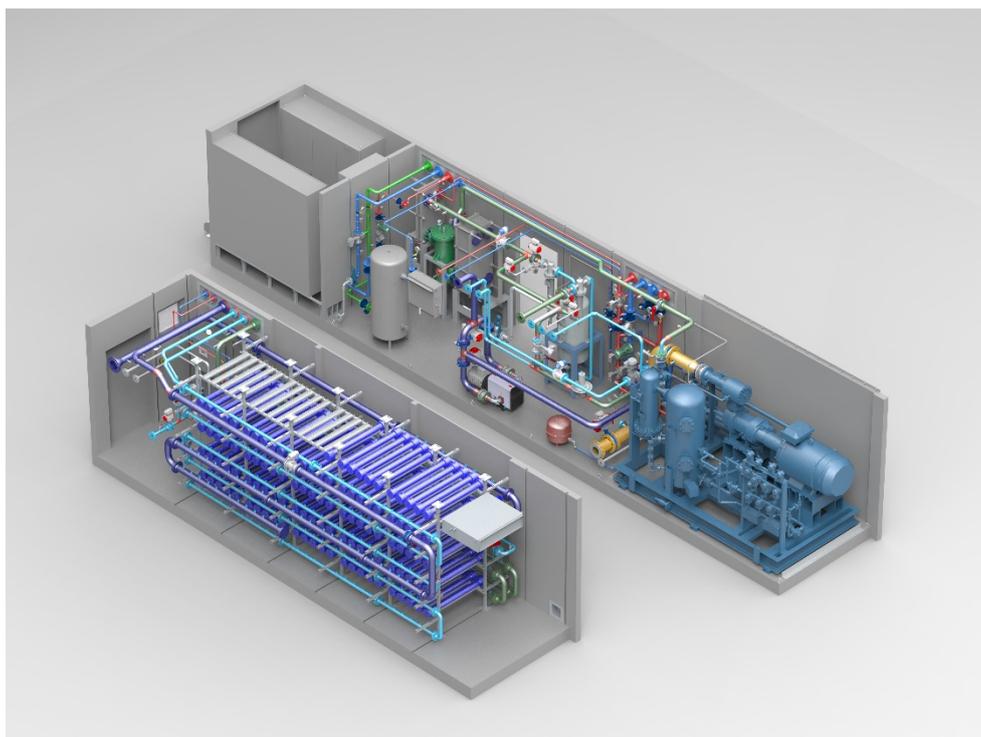


Figure 10. Typical layout of a membrane upgrading plant from EnviTec.

In membranes used for biogas upgrading, water vapor is removed from the biogas together with the carbon dioxide and drying of the product gas is usually not necessary. O_2 is partly removed with a membrane process. Whether additional separation is necessary depends on the concentrations in the raw biogas and requirements in the upgraded biomethane (see chapter 4).

Few consumables are used in a membrane upgrading plant. The lifetime of membranes for biogas upgrading is dependent on the biogas quality, the quality of pretreatment as well as the quality of operation. There are, however, membrane upgrading plants on the market which have been running successfully with their initial membranes for more than 10 years.

2.6 CRYOGENIC UPGRADING

When biogas is cooled under pressure, the CO_2 turns to its liquid state, while methane remains in a gaseous state. In this way, these two gases can be separated from each other. This simple transition however only happens under elevated pressure. At atmospheric pressure the CO_2 will sublime, going directly from the gaseous to the solid state. For details on this, please refer to the phase diagram in [2]. Cryogenic

distillation is, however, to our knowledge not used commercially for biogas upgrading in any larger scale. In [2] the technology of the Dutch company Gas Treatment Services was described in depth. The commercial ventures described failed, and to our knowledge there is only one smaller demonstration plant, situated close to the headquarters of the company. Biofrigas in Sweden sells small scale (ca. 35 Nm³/h raw gas) biogas upgrading and liquefaction with cryogenic distillation. The French clean tech company Cryo Pur has built a pilot plant with a capacity of 120 Nm³/h raw gas at the site of Valenton waste water treatment plant in Paris (see Figure 11) and are planning their first larger scale project during this and next year.



Figure 11 Cryogenic biogas upgrading and liquefaction, pilot plant from Cryo Pur, Valetton, France

The raw biogas needs to be pretreated to remove H₂S before the cryogenic upgrading, as the H₂S otherwise may damage the heat exchangers. VOC and siloxanes are efficiently removed during the cooling and condensation process which is a natural part of the cryogenic upgrading process.

Biogas upgrading with cryogenic distillation can be used to remove trace contaminants from landfill gas. In this way, O₂ and N₂ can be removed from the methane, which is otherwise only possible with biogas upgrading using pressure swing adsorption. This is described in more detail in the previous report [2].

Cryogenic distillation is used for several other purposes, such as methane removal from CO₂ streams (see chapter 3.7.4) and liquefaction of CO₂ to produce bio-LNG or LBG (see chapter 4.5).

3 Handling of impurities

3.1 IMPURITIES BALANCE OVER UPGRADING SYSTEMS

Raw biogas contains non-wanted compounds often referred to as impurities or contaminants. These compounds include H_2S , NH_3 , VOC, siloxanes, O_2 , N_2 and H_2 . For each biogas upgrading technique, some of these compounds may be harmful to the process and therefore need to be removed before the upgrading process. There may also be limitations on these compounds in the upgraded biomethane (see Chapter 4). In this case, the impurities may need to be removed depending on whether they are separated in the biogas upgrading together with the CO_2 or whether they will be present in the product gas. In this case, it needs to be considered whether it is advantageous to remove the impurities in the raw gas or in the upgraded biomethane. Impurities may also end up in another stream than the upgraded biomethane. In this case, there are often waste gas limitations or, when this stream is used as a byproduct, other kind of regulations. Also, it needs to be considered where the process to best remove these substances in the process. An indicative overview over the path of different impurities through the biogas upgrading step with different upgrading techniques can be found in Figure 12.

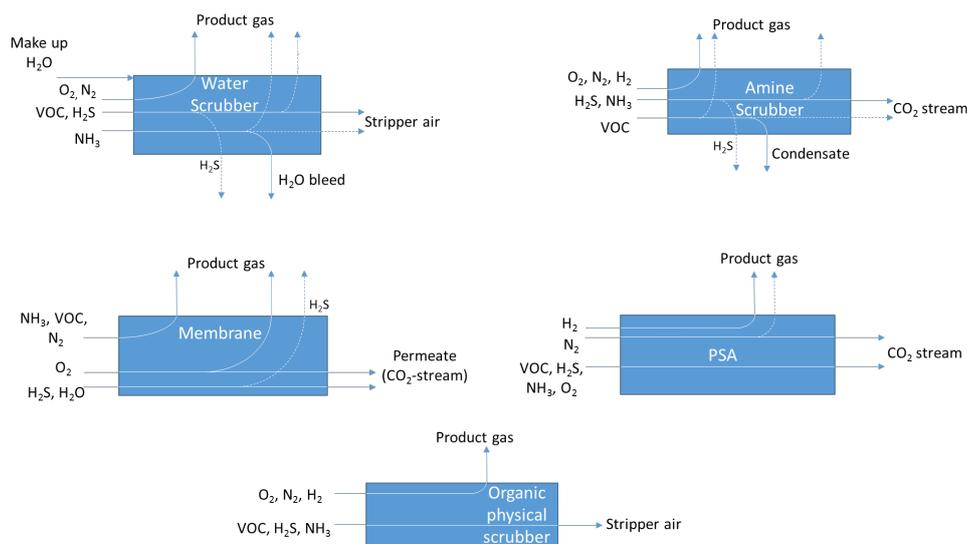


Figure 12. Path of impurities in biogas through different biogas upgrading processes

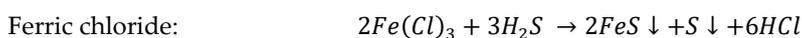
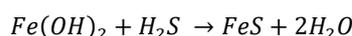
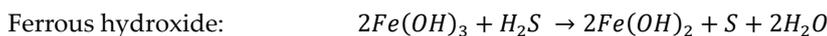
3.2 H_2S REMOVAL

At some conditions relatively large amounts of hydrogen sulfide is being produced in the digester. This results in an increased amount of hydrogen sulfide in the primary raw biogas feed stream. This increase in sulfur content would make the moderate sulfur removal (from ca 200-300 ppm) by adsorption in an active carbon filter insubstantial. This summary has been made to identify possible methods to reduce the initial sulfur content ranging from 2,000-10,000 ppm down to moderate levels below 300 ppm as well as from 200-300 ppm to very low values. The screened methods can be divided into removal steps ranging from primary to tertiary steps.

3.2.1 Primary removal

Iron salt addition

The mechanism of the addition of iron salts is simply as follows from the reactions below, where the iron salt reacts with the hydrogen sulfide to produce insoluble salts.



The precipitation then prevents the hydrogen sulfide to transport further downstream. Reductions can be made to reach levels of 50-200 ppmv, and is thus regarded as a primary step of hydrogen sulfide removal. To acquire lower concentrations of hydrogen sulfide the iron salts need to be added in large excess, which is one reason this method most often is combined with further processing [11]; albeit the addition of iron has other benefits than just sulphur removal.

3.2.2 Secondary removal

Biological sulphur removal

This method is conducted by inoculate a strain of bacteria, that feed on sulfur, on a carrier. The carrier may be in the form of e.g. filling plates or bark. This method is commonly used when considering smaller emissions from for example larger farms or slaughterhouses. Companies distributing this process are e.g. Thiopaq, Bioskrub, CSO and H+S Systemtechnik. In principle the gas is scrubbed by a mild alkali-solution where after it is led to a digester. In the digester the hydrogen sulphide is converted into organic sulfur, which precipitate and is removed with the digestate. The downside of this method is that air or oxygen is required in the digester. Since the rate of reaction is relatively low a large reactor volume is required to be able to handle the large amounts of sulfur as previously described, which will imply high costs, however doing this in-situ in the digester lowers the cost.

3.2.3 Tertiary removal

Activated carbon

This method is based on interactions between the hydrogen sulfide and the activated carbon pore surface in presence of oxygen to form sulfides and hydrogen and is the most common method used at the moment. The process is done in gas phase at low temperatures and pressures. It is, however, necessary to prevent condensation of liquid water in the activated carbon filter and the gas is therefore usually heated before it enters the activated carbon filter. Both physical and chemical adsorptions occur in activated carbon filters. [12]

To improve the H₂S removal capacity different impregnating with suitable chemicals can be made on the activated carbon, such as Zn, HNO₃, K₂CO₃, NaOH and Alkaline chemicals etc. The hydrogen sulfide removal capacity of an activated carbon depends on many operating conditions such as relative humidity, operating temperature and

filter pore volume. [13] Regeneration needs to be performed periodically (or indeed continuously in some cases) with oxygen to keep the impregnants to the metal oxide form [14].

There are mainly three types of activated carbon used for desulfurization, granular activated carbon (GAC), extruded activated carbon (EAC) and activated carbon filter (ACF). The activated carbon filter has shorter fiber diameters which creates a large contact area and it fits well for the desulfurization in regard to its lower volume density, lower filtration resistance and lower pressure drop compare to granular activated carbon [15]. The process is normally operated with a lead-lag control system with two adsorber beds and continuously measuring of sulfur content in gas stream and/or with an indicator in between the vessels, see Figure 13. Depending on the requirements in the project, also simpler arrangements are possible. These may, however, result in lower removal reliability or require the plant to be shut off during change of carbon.

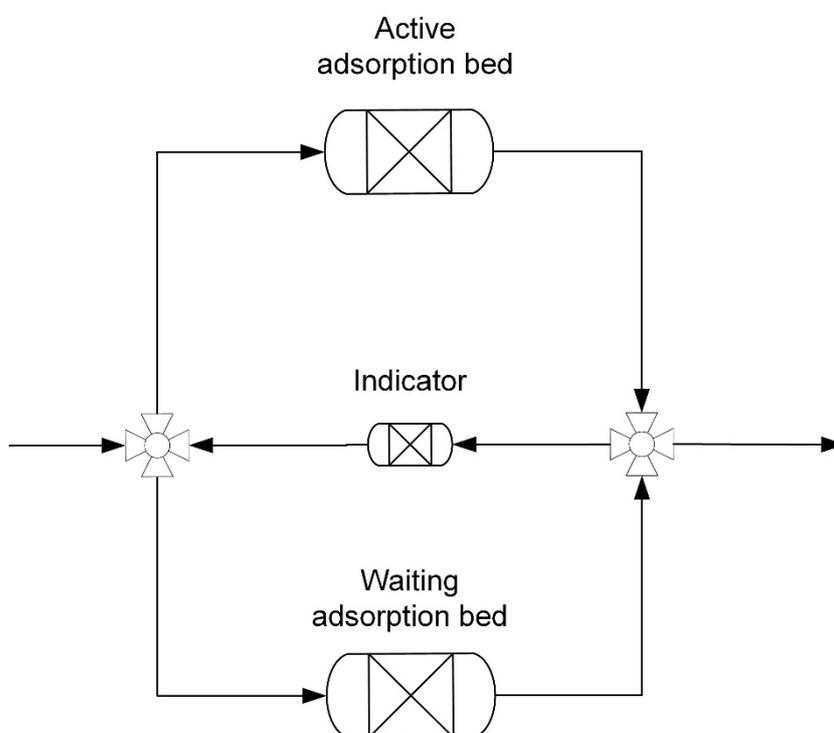


Figure 13. Lead-lag desulfurization system with activated carbon

Scrubber-/adsorption methods

To separate sulfur before entering the amine scrubber this pretreatment should be relatively selective towards sulfur. This means that the method should preferably not cause any change in the carbon dioxide content.

Among available methods [8] the most probably applicable are Gatechnik, Sulfiban, Purisol and Ferrox/Manchester. The Purisol process is based on absorption of hydrogen sulphide in an adsorption column at low temperature and pressure. The process utilizes a n-methyl-2-pyrrolidone (NMP) as solvent, which dissolves sulfur more than 10 times better than carbon dioxide and substantially better than water.

The Ferrox/Manchester processes are based on adsorption of sulfur onto solid iron based adsorbents. These may either be regenerated (requires high temperature) or be exchanged. One commercial adsorbent suitable for this application is SulfaTreat [16].

3.2.4 Unconventional methods

Scavengers

By injecting a chemical into the gas mixture the gas may be moved from gas phase to liquid phase. This is recommended for levels close to 1,000 ppm or less. In Figure 14, a general process flow diagram is shown. The process results in a reacted sulphur-triazine solution, which has to be taken care of separately. Usually it is possible to send it to waste water treatment.

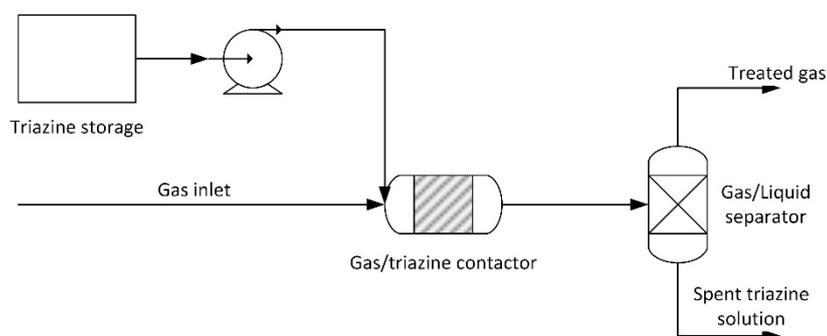


Figure 14. Process flow diagram for sulfur removal through triazine injection

Refrigeration

Another possible method to decrease the sulfur content in the gas stream is to cool it down to a temperature where the hydrogen sulphide condenses. This method is economical when large amounts of sulfur have to be separated, but does not lower the sulfur content to the lowest degree. Tentatively the gas would first be cooled down before being compressed to separate the main content followed by a second cooling after compression to remove as much as sulfur as possible. This method is based on only physical phenomena and is because of this very reliable.

3.3 SILOXANE REMOVAL

In raw landfill gas but also to some extent in other biogas, there is a strong possibility to find volatile siloxanes such as hexamethyldisiloxane, see Figure 15. Siloxanes are used in different consumer products such as cosmetics, deodorants, soaps, food additives, defoamers and as a replacement for tetrachloroethylene, used for dry cleaning. This wide usage results in concentrations up to 50 mg/Nm³ can be found in biogas, which is far beyond the limit set by several engine manufacturers of 15 mg/Nm³. Siloxanes are water-insoluble and have a surprisingly high vapor pressure.

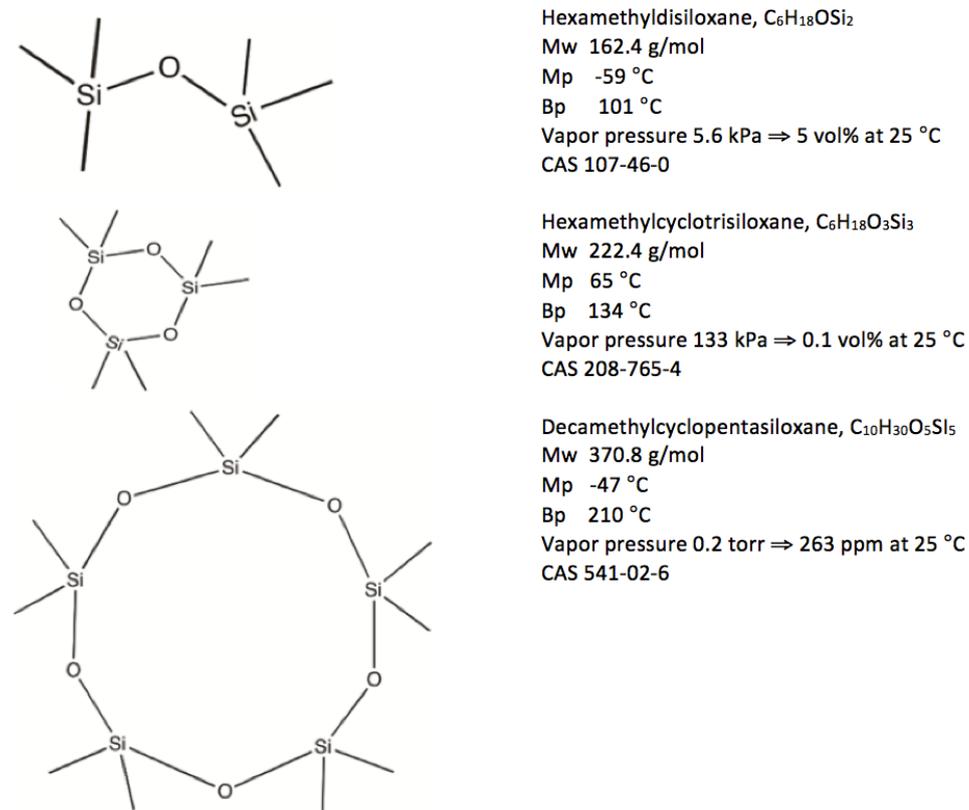


Figure 15. Chemical structure and properties of some common siloxanes

When the siloxanes reach the dryer they adsorb on to the zeolite surface situated in the dryer, used as desiccant. The main question is what might occur with the siloxanes when the dryer is being regenerated. The most probable outcome is that the siloxanes decompose upon heating and will precipitate as silicone, leading to fouling through pore blockage in the long term and thus lowering the effective rate of the desiccant.

The traditional routes of siloxane removal are either by water scrubbing, removing the most volatile component trimethylsilanol [11], or by scrubbing with hot sulfuric acid. Hot sulfuric acid may though be regarded as problematic to handle due to its corrosive ability. A preferred method for removal of high levels of siloxane is now probably by first chilling the gas to $-30\text{ }^\circ\text{C}$ and then by adsorption to a guard bed of either activated carbon or a molecular sieve such as silica gel. Both alternatives have proven good adsorption efficiency and may be thermally regenerated, though the desorption efficiency is slightly higher for the silica gel.

If the gas is relatively free of VOC, the removal can be performed using a vacuum swing adsorber (VSA) where a vacuum is applied to regenerate the adsorption bed. In the case with both VOC and siloxanes, a temperature swing adsorption (TSA) process may be used. [17]

3.4 AMMONIA REMOVAL

The amount of ammonia present in biogas is dependent on the substrate used in the anaerobic digestion. Biogas produced from slaughterhouse waste has been shown to

contain more ammonia (approx. 100 ppm) than biogas produced from household waste and industrial waste, where no or very little ammonia was detected [18]. Also other substrates rich in nitrous compounds, such as chicken manure and fresh grass, results in biogas with high ammonia concentrations [19].

Ammonia can be removed from biogas through drying by condensation. In this way, excess water is condensed and removed together with part of the ammonia, which is water-soluble.

Additional ammonia can be removed in a gas wash dryer such as the Siloxa GKW which combines drying with absorption of NH_3 and H_2S in water [20]. In this process the gas flows through a packed column in opposite direction of a cold stream of condensed water. This way, NH_3 and H_2S are removed both through condensation and further absorption of gaseous NH_3 and H_2S in water.

Ammonia can also be removed from biogas using molecular sieves which separate gas compounds on the basis of their difference in molecular size. In this way, both NH_3 and H_2S can be removed from concentrations around 2 vol% to less than 1 ppmv [21]. Once the molecular sieves are saturated with NH_3 and H_2S , they need to be regenerated, which increases both investment and operational costs.

3.5 OXYGEN REMOVAL

There are several methods for removing oxygen and there are some of the main upgrading methods already handling this in without modifications (e.g. PSA or membranes). This chapter deals with dedicated technologies or polishing methods should they be required.

3.5.1 Catalytic oxidation

Oxygen can be removed from raw or upgraded biogas, e.g. biomethane, through chemical adsorption. When biogas or methane is led through a reactor containing platinum and palladium catalysts, the oxygen content can be reduced to below 1 ppmv [21]. In this process, hydrogen is oxidized to water, carbon monoxide is oxidized to carbon dioxide and higher hydrocarbons are oxidized to carbon dioxide and water. It is thus important to keep in mind that the reduction of oxygen in biogas or biomethane will consume hydrocarbons, which may lead to a reduction of the methane content in the gas. The amount of methane consumed depends on the oxygen reduction which usually is a question of low concentrations as well as the concentration of other hydrocarbons which may be oxidized instead of methane to reduce the methane consumption in the process.

This solution gives a simple set-up which uses only one reactor and is very easy to regulate. Since water is produced in this process, the gas needs to be dried after the oxygen removal. This is usually no problem if the catalytic oxidation can be placed before an already existing drying step, but it may constitute extra investment and operational cost when a drying step needs to be added only due to the addition of an oxygen removal step.

The catalytic oxidation process operates at high temperatures (up to 500 °C depending on process conditions), which requires adequate selection of materials for piping and the reactor, but also results in the need to cool the gas after the oxygen removal. With smart heat integration, where the incoming gas to the catalytic reactor is pre-heated by

heat exchanging with the outgoing gas, the catalytic process will operate on an auto-thermal basis without the need of extra heating during continuous operation and the cooling requirement will decrease significantly.

The platinum and palladium catalysts are sensitive to substances such as sulphur containing compounds, chlorine, arsenic, phosphor, oil or mists of alkali and acid and these need to be removed from the gas if present. Without these catalyst poisons present in the gas, the catalyst is assumed to operate without the need of change for several years.

3.5.2 Chemisorption

Another process to reduce oxygen in biogas or methane is chemisorption using a copper surface where copper is oxidized to copper oxide. In this process, no extra humidity is added to the gas and no gas drying is therefore necessary. However, the copper surface needs to be regenerated once it is saturated with oxygen. The copper surface is regenerated using hydrogen or carbon monoxide before it can be used again for the reduction of oxygen. The need for regeneration increases the investment cost and complicates the regulation of the oxygen removal compared to the catalytic oxidation with platinum and palladium catalysts. For continuous operation, at least two reactors are needed so that the second reactor is in operation during the time where the first one is regenerated.

Chemisorption with copper for the removal of oxygen from biogas requires lower temperatures than the above mentioned process with palladium and platinum catalysts (usually around 200 °C). This makes material selection slightly easier. Heat recovery in the same way as in the catalytic oxidation process is interesting also in this process to reduce operational cost.

The copper surface is sensitive to sulphur containing compounds as well as oil and salts.

3.6 VOC/BTX REMOVAL

The amount of VOC present in the biogas varies widely from what source is being digested, where the general trend is that much lower quantities can be seen in biogases produced from farm based plants rather than from those produced from landfill sites. In Table 9 below, a span of a rather high difference of 690 mg VOC/m³ biogas has been seen in the averaged value of raw biogas coming from the digester when different raw materials are being digested [18].

	Waste plant	Treatment plant	Waste plant + treatment plant	Energy crop and byproduct from food industry	Manure
No. of clean gases (n=)	2	2	3	3	1
Average VOC in biogas, mg/m ³	700 mg/m ³	200 mg/m ³	400 mg/m ³	10-30 mg/m ³	20 mg/m ³

Table 9. Comparison of VOC content in biogases digested from different raw materials [18]

VOC is often sufficiently reduced by the different biogas upgrading processes but can also exclusively be removed further. For further polishing of biogas the most common application used is by passing through a filter of activated carbon. Two beds are then operated in parallel to be able to regenerate one bed while the other is running. The carbons can be recovered using thermal regeneration. [22]

In the case with both VOC and siloxanes, as mentioned before, a temperature swing adsorption (TSA) process may be used [17]. Alternative methods include membrane filtration and catalytic removal, where catalytic removal has suited well for many applications with high efficiency and good economy.

3.7 METHANE REMOVAL IN SIDE STREAMS

3.7.1 RTO - Regenerative Thermal oxidation

Regenerative thermal oxidation (RTO) is an energy-efficient and flexible solution that combines gas-phase thermal oxidation with regenerative heat exchange to remove contaminants from biogas. It can almost cover about 97% of the heat from the purified gas and reuse it for preheating inlet gas. By using refractory material with high heat transfer ability, such as ceramic media. The operation temperatures are between 750 and 1,000 °C.

The simplest RTO arrangement consists of one horizontal combustion chamber with one burner for oxidizer startup and this chamber is connected with two vertical heat recovery chambers, which are packed with ceramic media. Both chambers contain one inlet and one outlet valve that switch the flow direction every 1-3 min depending on the cycle time. The cold inlet contaminated gas is preheated in the first heat-exchange chamber and then enter the combustion chamber to oxidize. Then the purified gas leaves the second heat-exchange chamber where heat is recovered from the ceramic media. A typical process diagram of an RTO is presented in Figure 16.

In the commercial market there are mainly two kinds of RTO, two chambers and three chambers while the switching-valve techniques can vary.

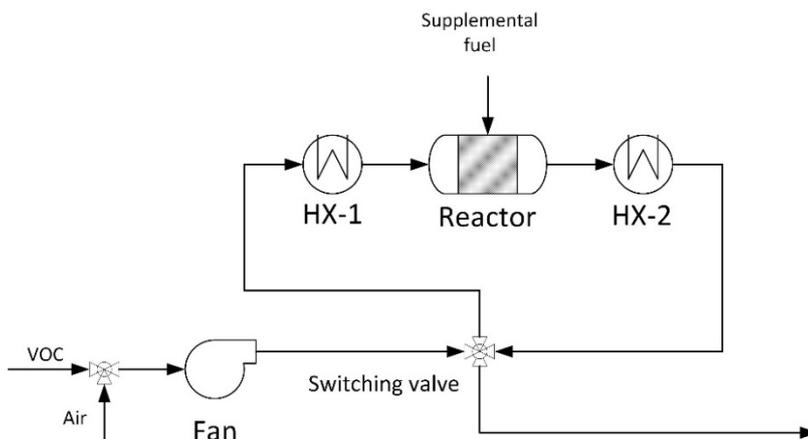


Figure 16. A typical process diagram of an RTO

3.7.2 Regenerative catalytic oxidation (RCO)

As an alternative to RTO the RCO can run at much lower temperatures between 250-500 °C which is more energy saving. It is possible to retrofit the RTO with RCO in many situations which is shown to be profitable. The overall principle for RCO is the same compared with RTO and the only difference is a small layer of catalyst bed is added above the ceramic media in the chambers.

The selection of catalyst should satisfy requirements like high activity in oxidation of specific substances in the biogas, high thermal stability and high mechanical strength etc.

Company name	Website
Alliance corporation	http://www.alliancecorp.com
ANGUIL	http://www.anguil.com/oxidizers/
B&W MEGTEC	http://www.megtec.com
BMF Haase	http://www.bmf-haase.de/en
Catalytic Combustion	http://www.catalyticcombustion.com
CECO Environmental	http://www.cecoenviro.com
CHIMICAN	http://www.chimican.com
CMM Custom Machin Manufacturing	http://www.thecmmgroup.com
Condorchem envitech	http://blog-en.condorchem.com
CTP	http://www.ctp-airpollutioncontrol.com
DURR	http://www.durr.com/en/
EISENMANN	http://www.eisenmann.com/en.html

Company name	Website
EnviTec Biogas	http://www.envitec-biogas.com/en/home.html
EPCON	http://www.epconlp.com
Krantz	http://www.krantz.de/en/Pages/default.aspx
LESNI	http://www.lesni.co.uk/index.php
PRODESA	http://www.prodesa.net/index.php/en/

Table 10. Companies that provide RTO and RCO

3.7.3 Genset

An electricity generating set in lean burn mode, driven by off gases, is a way to recover energy and reduce emissions when handling the off-gases from the different types of upgrading processes. Operating an internal combustion engine, producing energy from the expansion of combustible fluids by ignition, can be done also on lean gas. Force applied on a piston can be subtracted as mechanical energy, which is converted to electrical energy.

In the off-gases small partitions of both methane and VOCs are present, which are possible to combust. The normal methane content varies from upgrading technology to upgrading technology, but even the highest values of approximately 1-5% in the off-gas is not sufficient to achieve a heating value high enough to operate the engines. Yet a higher heating-value can be obtained by by-passing parts of the raw biogas or, in the PSA case, altering operation modus such that the effective heating value of the off-gas is at least 5 MJ/m³ [23], before being mixed with air to combust.

The drawbacks with this method is the appearance of NO_x-gases and particulate matter formed in the combustion, which has to be handled by filters, catalytic reduction or other suitable methods. The investment in this type of technology, as well as the loss of upgraded methane will have to be traded-off vs. the sale of renewable energy.

3.7.4 Cryogenic distillation

In membrane upgrading which produce a relatively pure CO₂ stream, cryogenic distillation can be used to separate the methane from the CO₂ to reduce methane emissions to below 10 ppm (cryogenic distillation is described further in chapter 2.6) [24]. Pentair Haffmans has supplied several systems where membrane upgrading is complemented with a cryogenic distillation step to reduce the methane concentration in the CO₂ stream and return the separated methane to the membrane feed. In this way, the methane slip of the system is eliminated completely. The cryogenic distillation is performed at 18 bar and -24 °C and the liquefied CO₂ is used for the liquefaction of further CO₂. A second cryogenic step can be added to produce liquid CO₂ which can be used for further applications (chapter 5). The compression and cooling of CO₂ is energy demanding, but this is an economical viable option when the price of methane is high and there are strict limitations of methane emissions

3.8 POSSIBLE PURIFICATION SEQUENCES DEPENDING ON GAS QUALITY

Various aspects are important to consider when designing the sequence of purification steps in biogas upgrading. The first issue concerns whether to remove impurities in the raw biogas, in the produced biomethane or in any other available stream (Chapter 3.1).

The different purification methods described above have different requirements regarding heat and pressure. As an example, a carbon filter requires super-heat to avoid condensation in the carbon bed and thus heating is required to implement in the wet gas before the carbon filter. If a fan or compressor which increases the gas temperature is installed directly downstream, further heating may not be needed.

When installing several purification steps in the same gas stream, it is important to consider competition of different compounds to make sure that the desired compound is removed in the actual step designed for it. It is for example not wise to install a purification step where H₂S competes with VOC in a gas stream containing a high concentration of H₂S and only traces of VOC. In this case, most likely, only H₂S will be removed. It would then be better to first remove the bulk of H₂S before the gas enters the purification step intended for VOC removal.

4 Product gas treatment and conditioning

4.1 PRODUCT GAS QUALITY

The product gas leaving the plant must uphold certain gas quality criteria, either set as a bilateral agreement with the transporter and/or buyer of the biomethane, which currently are based on national specifications. Limits on minor and major impurities are set, in order to safeguard the integrity and proper functioning of the gas transport system and the end-user's gas consuming installations, and most importantly the health and safety of people.

4.1.1 Current standards

There are a number of standards for the automotive use of compressed natural gas (CNG). SAE J1616, "Surface Vehicle Recommended Practice - Recommended Practice for Compressed Natural Gas Vehicle Fuel", published by SAE (Society of Automotive Engineering) in 1994, is one of the oldest standards on CNG quality [25]. In its first part, the focus is on gas quality parameters that have a bearing on the corrosion of gas cylinders and tank systems, including sections on water, hydrogen sulphide (23 mg/m³), carbon dioxide (3%), methanol (poisonous), oxygen, particles (5 µm filter), oil and higher hydrocarbons. Properties of engine performance are discussed in the second section, with quantitative values on energy content specified (Wobbe index). Comments on the relationship between water content and drivability are also made.

The current international standard for CNG, issued in 2006, "ISO 15403 Natural gas – Natural gas for use as a compressed fuel for vehicles", is based largely on the SAE J1616 [26]. It is divided in two parts, where the first one is normative, but with no quantitative limits. Part 2, an informative technical report, was issued on request from the OEM's (Original Equipment Manufacturer, i.e. vehicle manufacturers), which wanted more information published on suggestions for suitable limits for parameters such as water, sulfur compounds, particles, higher hydrocarbons, carbon dioxide, oxygen, glycol/methanol and compressor oil content.

The German national standard for CNG, "DIN 51624:2008-02 Kraftstoffe für Kraftfahrzeuge – Erdgas – Anforderungen und Prüfverfahren (Automotive fuels – Compressed natural gas – Requirements and test methods)" is one of the most strict standards issued to date [27]. The limits of total sulfur, methane content and methane number exclude a large portion of the European grid-gas qualities. The limit of sulfur, 10 mg/kg, is identical to the one imposed for diesel and petrol. Oil and particles on the other hand, because of no test methods being available, are only described qualitatively. Outside of Europe, the standard issued by the state of California (California Code of Regulations, 13 CCR § 2292.5 Specifications for Compressed Natural Gas) is used by several states in the US [28].

Regarding biomethane, there is a range of national standards in Europe for the injection of upgraded and purified biogas to the natural gas grid. An overview was published by Marcogaz in 2006 [29]. A number of other countries have since then introduced standards, e.g. Belgium and the Czech Republic. In most cases, the demands on heating value correspond to the ones of natural gas quality specifications issued. Outside Europe there is the "Rule 30" standard issued by Southern California Gas Company [30]. It is for many parameters much more stringent than several of its European counterparts. The Swedish standard SS 155438 "Motor fuels - Biogas as fuel for high-

speed Otto engines” is to date the only standard regulating the direct utilization of biomethane as automotive fuel [1]. Another alternative outside the EU can be found in the Republic of Korea with similar conditions as in Sweden [31].

4.1.2 Ongoing standardization

Work on the international standardization of biomethane injection into the natural gas system has been ongoing since the Marcogaz report was issued. In Europe, work is organized by CEN in a joint technical committee (TC408) “for transport applications and injection in natural gas pipelines”. The work started late 2011. In addition to biomethane, natural gas used as an automotive fuel has also been included to the scope of the work. Early 2014, working drafts of the standard were issued. As seen in Figure 17, there are two parts. The one for injection of biomethane into the grid, FprEN 16723-1 [32], relies heavily upon the parallel standardization work in CEN/TC234/WG11 on natural gas quality, which resulted in the publication of EN 16726 “Gas infrastructure – Quality of gas - Group H” [33]. Mandate M/475 from the European Commission stipulates that the parameters and limits adopted by EN 16726 should be taken over and referred to by TC408. FprEN 16723-1 has been sent to formal vote. If accepted, it will be published late 2016.

The second part for automotive fuel, prEN 16723-2, is a stand-alone document [34]. As seen in Figure 17, there will be two gaseous fuel grades defined, reflecting the current market situation with non-grid based sourcing solutions of CNG and LNG complementing the one of the grid, both renewable and fossil. In addition, natural gas specifications of a few national markets would also be compliant with such a second grade. Current work is focused on finding consensus for limits of parameters such as MN¹, sulfur, compressor oil and siloxanes. A limit range for calorific content will also be specified, while one for Wobbe index maybe will not be included, since that parameter is excluded from EN 16726. If consensus is not reached during 2016, the FPrEN 16723-2 will have to be deleted.

¹ Methane number (MN) is by definition dimensionless. It is calculated by comparing the composition of the actual fuel used with data from testing of different ternary mixes of reference fuels made by AVL back in the 70's. There's no analytical solution, so dedicated software is needed to estimate the MN, with several commercial alternatives available on the market.

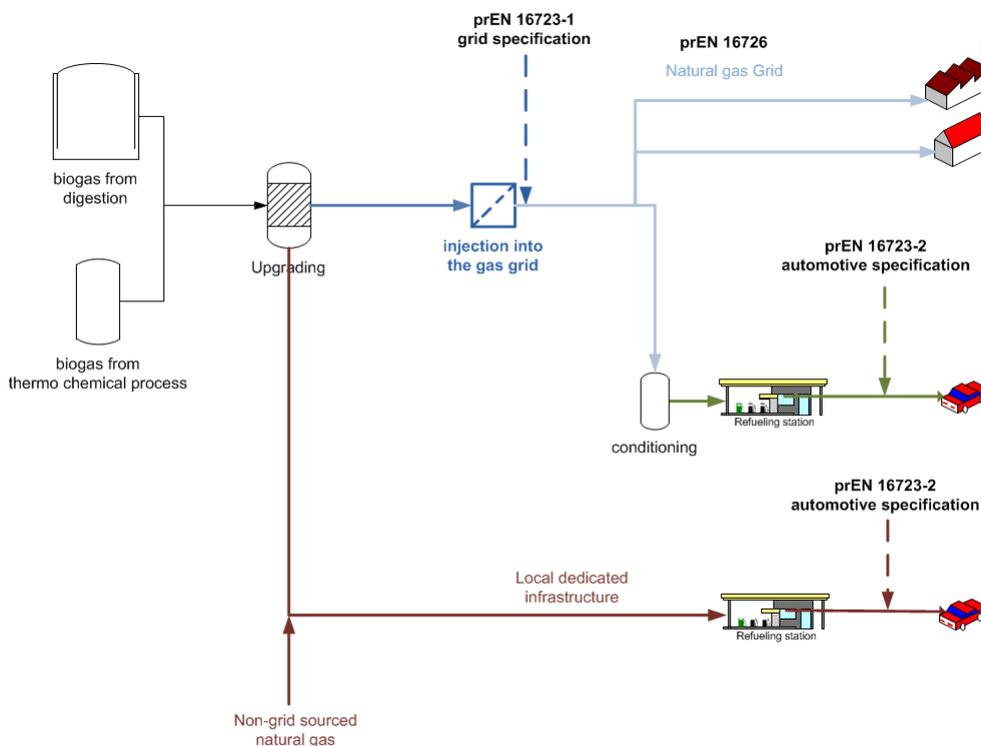


Figure 17. Schematic of the biomethane and natural gas transport system, showing in which points of the gas network the different standards of CEN/TC408 will apply; the point of entry for injection, and the point of use as automotive fuel. Source: CEN/TC408 working group.

4.1.3 Parameters of interest

Sulfur is the most discussed parameter in FprEN 16723-2 [34]. The automotive industry has a need for quite low levels of sulfur in order to achieve durability in their exhaust after-treatment systems (EATS). Currently, natural gas is not supplying fuel at the 10 ppmM level, normal for other fuels such as diesel and petrol. EN 16726 puts a maximum limit of 20 mg/m³, odorization excluded since it is a national issue (see chapter 4.3). In FprEN 16723-2, it is suggested that the normal grade (grid based) has a level of 30 mg/m³, while the second dedicated grade limit value will be 10 mg/m³, in both cases inclusive of odorization. A competing proposal is to have no value at all, and let it instead be covered in a national foreword. In most cases, biomethane and LNG readily meet the 10 ppmV requirement.

The origin of silicon containing siloxanes in biogas is man-made silicon products and additives. Landfill gas and biogas from wastewater treatment plants thus have the highest silicon levels, with raw biogas levels of 10-20 mg/m³, and peak levels above 100 mg/m³ reported. The effect of siloxanes on appliances is cumulative, hinging on its precipitation during combustion as silica (silicon dioxide). The silica builds up on valves, cylinder walls and liners, causing abrasion and blockages. Downstream of the engine, switch-type oxygen sensors may withstand less than 0.1 mg Si/m³ if wanting to avoid replacement during the lifetime of the car. Silica build-up in the after-treatment system catalysts lead to cumulative and irreversible loss of degrading activity. Rather than a strict limit value, FprEN 16723-1 adopts a limit value range (0.3 – 1 mg/m³). The actual limit is to be decided in bilateral agreements between gas grid operators and biomethane producers, taking into account current test method accuracy and dilution

effects. The lower level would be used when there are no dilution effects. The level in FprEN 16723-2 is yet to be decided. The newly revised Swedish standard has a limit value of 0.7 mg/kg (comparable to 0.5 mg/m³). The limit will be lowered to safer levels as soon as reliable and economically viable online measurement methods are available. No standardized test method is available, but SP Technical Research Institute of Sweden has published their validated analytical test method [35].

For the injection standard, health related parameters such as PAHs, HCN and chlorinated and fluorinated compounds are not included in the standard, with reference to national assessments and regulations. An example of an appropriate methodology will be issued in the form of a Technical Report (CEN/TR)², based on a special deterministic exposure model devised by the French safety authority AFFSET (Agence française de sécurité sanitaire de l'environnement et du travail).

After health, the second most important criteria is the integrity of the pipelines. Besides levels for water, hydrogen sulphide, ammonia and oxygen, which are set to avoid corrosion, there is also a special need for stringent levels of oxygen and hydrogen if the gas is not conveyed in a dry system and if the gas is conveyed in proximity to underground storage systems. In EN16726, oxygen is therefore stated with two levels, 0.0001 % and 1 % (mole/mole). The latter figure is also stipulated by the automotive fuel standard. Hydrogen, on the other hand, is not regulated in EN 16726, because of the difficulty to find one or even two values which satisfy the large array of possible limits for different parts of the European gas grid. The automotive fuel standard FprEN 16723-2 has stipulated a maximum limit of 2 %v(mole/mole), in order to protect the high-pressure storage cylinders from corrosion. This limit originates from SAE J1616, and according to information from one of the persons involved it is a precautionary level with no scientific basis.

Avoiding liquid water at all temperatures and pressures gives protection from corrosion. The -8°C limit on the water dew temperature at maximum operating pressure stipulated by EN 16726 is in most cases more than satisfactory. However, when decompression chilling takes place in natural gas vehicles, there is a risk for hydrocarbon hydrate formation in the fuel system, impairing drivability. Therefore, in the automotive fuel standard there are three classes of water dew points, -10°C, -20°C and -30°C at 200 bars, in order to allow for climate dependent adoption at national level. The risk of precipitation of higher hydrocarbons has been regulated by setting a hydrocarbon dew temperature limit of maximum -2°C for all pressures. Drivability is also affected by entrained compressor oil, mostly originating from the refuelling station compressors. Just like with water, complete engine failure is not the result, but rather different degrees of reduced drivability, including engine stalling, and increased maintenance costs. Also, combustion of the oil in the engine leads to more particle formation, which invariably increases the carcinogenicity of the emissions. Presently, there is no standardized test method available for measuring compressor oil, but a method has recently been developed by SP Technical Research Institute of Sweden [36]. The current draft of FprEN 16723-2 includes reference to compressor oil, but with no stated limit. An informative annex is included on the issue of compressor oil and solid particulates, inclusive of biogenic material such as microorganisms, describing the type and setup of filters for their removal.

² "Proposed limit values for contaminants in biomethane based on health assessment criteria"

4.2 GRID INJECTION

This section presents an overview of the status of grid injection, including rules and regulations, market drivers and market actor interplay, of the countries of France, Germany, Sweden and the Netherlands. Other countries with significant grid injection markets are the UK, Switzerland, Austria and Denmark, see section 1.4. An upcoming IEA task 37 publication that covers grid injection is scheduled to 2018.

4.2.1 France

In France, the distribution grid is managed by GrDF (the main national distribution grid operator - regulated industry), or by a local distribution company. If the localization of the injection project is served by the distribution gas network and if the quantities of biomethane produced is compatible with the grid capacity, then the project can inject into the distribution grid. Two contracts, one for connection and the other for injection, are then established. They define the regulatory framework of the project.

If not injected into the distribution grid, the biomethane can be injected into the transport grid if it serves the localization of the project. The two operators managing the transport grid in France are GRTgaz and TIGF. The connection to the transport grid is done after the connection and injection contracts are established, provided that the construction and operation contracts have been awarded to the transport grid operator.

In France, a Grid Entry Unit (GEU) is connected to the biogas upgrading unit outlet. The GEU is owned and operated by the grid operator. The latter is responsible for pressure delivery, gas quality control & metering (which is around 4 bars for distribution grid and 16 to 70 bars for transport grid) and its odourisation. The cost of operating the injection station by the grid operator is around 22 k€ for distribution grid.

Overview on status

In December 2015, the French market had 17 biogas upgrading units injecting in the grid, and a prototype for non-grid based use of biomethane as automotive fuel, a growth of 11 units compared to 2014. Those new units convert more than 3,600 m³/h of biogas to biomethane and inject it to the natural gas grid.

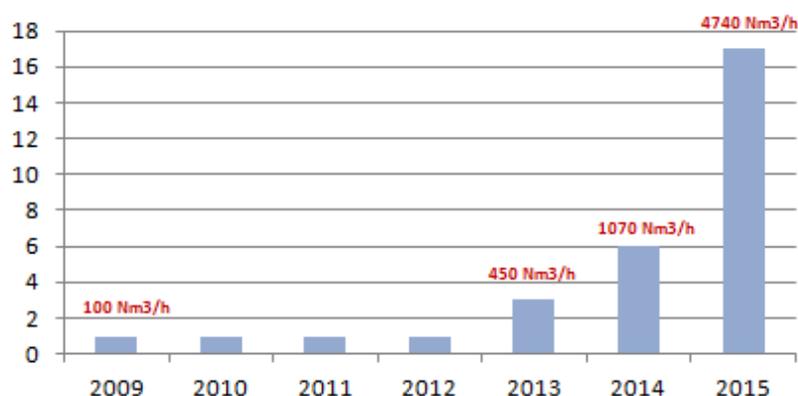


Figure 18. Evolution of the number of plants injecting biomethane in the French natural gas grid, and the accumulated biomethane injection capacity. Source: Air Liquide.

The tendency in France is to install membrane technology. Amongst the 17 plants installed, 12 are based on membrane technology. The second technology used is water scrubbing with 3 plants installed. PSA is not widely used in France, only one plant has been installed so far. The membrane technology is developed in France mainly for historical reasons: In France, the biogas upgrading market is relatively new, and its emergence coincided with the development of membrane technology. The first references injecting in France are using membrane technology.

Market drivers

In France, the market is driven by the subsidies that the government gives to the development of biogas upgrading projects including grants for construction, feed-in tariffs (covering 15 years' operation periods from initial start-up, introduced in November 2011) & a Green Gas Certification scheme. In 2015, the biogas upgrading market has seen a significant increase compared to previous years, and is expected to continue increasing in the upcoming years, in order to get closer to meeting the government renewable energy objectives. Bio CNG powered NGV's are becoming a reality in France: Around 30 public CNG refueling stations have opened, and about 10 of them will start offering bio CNG during 2016.

Rules, regulations and standards

In France, the "gas to grid" market is well regulated, and the decrees and laws are developing to suite the new research findings and engineering developments.

The regulations cover:

- The financial aspect:
 - × determining a fixed and guaranteed price, which varies depending on the type and balance of feedstock used for the biomethane injected. tariff are provided for 15 years to the biomethane producer
 - × Biomethane Producers are entitle to access to the Biomethane FiT through "approved" Biomethane Offtakers, which are subsequently compensated by the Deposits and Consignments Fund.
 - × They define a legal frame for the green gas certificate scheme, that push for the development of the biomethane production throughout financial remuneration, and throughout public awareness of the origin of the gas consumed
- The risk, contractual & technical aspects:
 - × Via the definition of contractual conditions between the biomethane producer, the gas network operator and the gas offtaker. Those conditions concern the technical aspects of the project, and the scope that should be handled by each stakeholder.
 - × Via the definition of a "last resort offtaker" who has the obligation to buy biomethane from the producer at the guaranteed and fixed price defined by the government if no other supplier agrees to purchase the biomethane.
 - × Via feedstock definition. Since June 2014, amended regulations allow biomethane injection processed from landfill gas or from biogas produced from the AD of sewage sludges.

The technical specifications/standards imposed by the gas network operator are highlighted in Table 11.

Table 11. Biomethane quality restrictions in France

Description	Specification
Higher Calorific Value	For a Gas H zone injection : 10.7 to 12.8 kWh/m ³ (n)
	For a Gaz B zone injection: 9.5 to 10.5 kWh/m ³ (n)
Wobbe index	H Gas : 13.64 to 15.70 kWh/ m ³ (n) (combustion 25°C : 13.6 to 15.66)
	L Gas (gas B type) : 12.01 to 13.06 kWh/m ³ (n) (combustion 25°C : 11.97 to 12.97)
Density	From 0.555 to 0.70
Dew point	Less than -5°C under the maximal pressure conditions before the grid connection
Hydrocarbons dew point	less than -2°C from 1 to 70 bar
Total sulphur	Less than 30 mgS/ m ³ (n)
Sulphur in mercaptanes	Less than 6 mgS/m ³ (n)
Sulphur content in H₂S + COS	Less than 5 mgS/m ³ (n)
CO₂ content	For H Gas zone injection : less than 3.5% mol.
	For L Gaz zone injection: less than 11.7% mol.
THT content (for odourisation)	From 15 to 40 mg/m ³ (n)
O₂ content	For a Gas H zone injection : less than 0.75% mol.
	For a Gaz B zone injection: less than 3% mol.
Hg	Less than 1 µg/m ³ (n)
Cl	Less than 1 mg/m ³ (n)
F	Less than 10 mg/m ³ (n)
H₂	Less than 6 %
NH₃	Less than 3 mg/m ³ (n)
CO	Less than 2 %
Biomethane temperature	Between 5°C & 35°C
Higher Calorific Value	For a Gas H zone injection : 10.7 to 12.8 kWh/ m ³ (n)
	For a Gaz B zone injection: 9.5 to 10.5 kWh/ m ³ (n)
Wobbe index	H Gas : 13.64 to 15.70 kWh/ m ³ (n) (combustion 25°C : 13.6 to 15.66)
	L Gas (gas B type) : 12.01 to 13.06 kWh/ m ³ (n) (combustion 25°C : 11.97 to 12.97)
Density	From 0.555 to 0.70
Dew point	Less than -5°C under the maximal pressure conditions before the grid connection
Hydrocarbons dew point	less than -2°C from 1 to 70 bar
Total sulphur	Less than 30 mgS/ m ³ (n)
Sulphure in mercaptanes	Less than 6 mgS/m ³ (n)
Sulphure content in H₂S + COS	Less than to 5 mgS/m ³ (n)
CO₂ content	For H Gas zone injection : less than 3.5% mol.
	For L Gaz zone injection: less than 11.7% mol.
THT content (for odourisation)	From 15 to 40 mg/m ³ (n)
O₂ content	For a Gas H zone injection : less than 0.75% mol.
	For a Gaz B zone injection: less than 3% mol.
Hg	Less than 1 µg/m ³ (n)
Cl	Less than 1 mg/m ³ (n)
F	Less than 10 mg/m ³ (n)

Description	Specification
H₂	Less than 6 %
NH₃	Less than 3 mg/m ³ (n)
CO	Less than 2 %
Biomethane temperature	Between 5°C and 35°C

Interplay between grid owners and biogas producers

The biomethane producer has the duty to bring the upgraded biogas to the gas quality defined by the grid operator. The grid operator is in charge of supervising this quality and odorizing the biogas via the injection station.

4.2.2 Germany

Overview on status

In Germany, 195 injection plants are prognosticated for 2015 (see Figure 19). This is an increase of 44 plants by 2014. They will inject approximately 122,000 m³/h biomethane into the natural gas grid. This equates circa 1.1 % of the demand of natural gas in Germany.

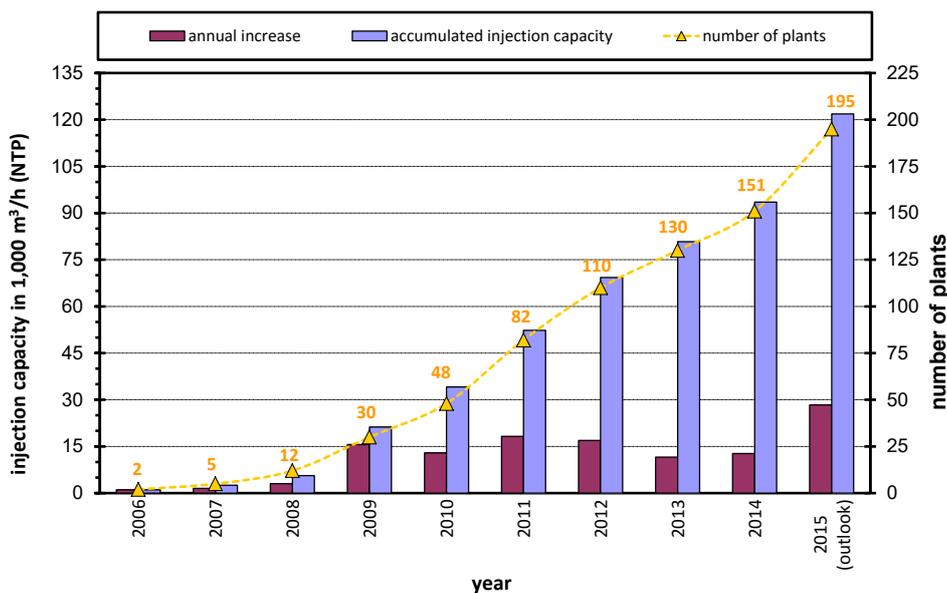


Figure 19. Development of injection plants in Germany [37].

The distribution by percentage of the upgrading technology 2015 is nearly analog to 2014 (Figure 20). The most plants use chemical and water scrubber technology. But the tendency to install membrane technology is visible. [37]

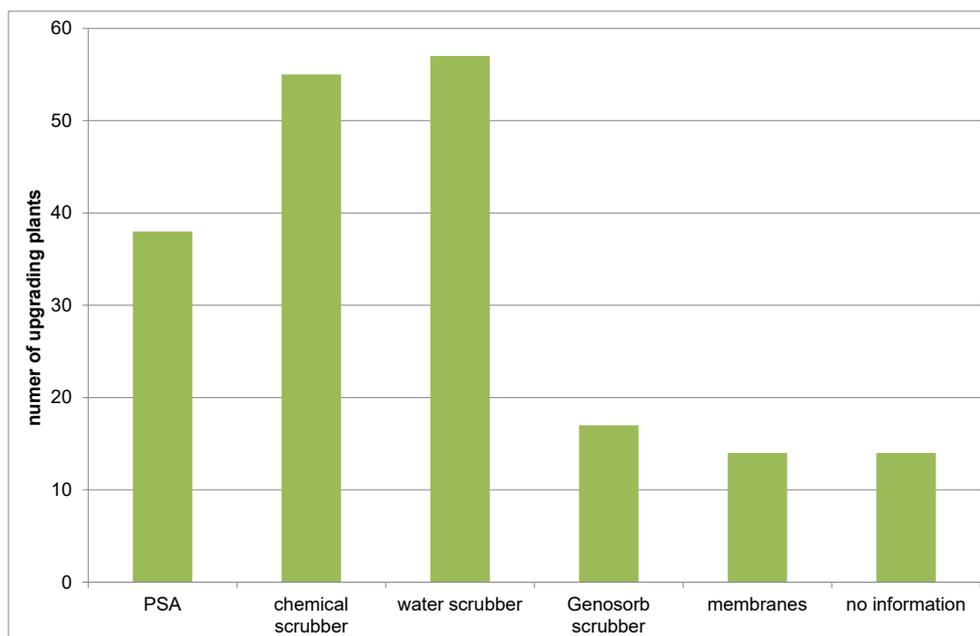


Figure 20. Number of used upgrading technology [37]

Market drivers

In Germany the market for biogas is a problematic market. The motivation to produce biogas is the funding by renewable energy law. The benchmarks without funding are much lower than the production costs of biogas. The German Renewable Energies Heat Act (EEWärmeG) forces the use of biogas in the private heat generation of new buildings, but the use of biogas is only one of many possibilities to save fossil energy. There are e.g. possibilities to install PV, a heat pump or to insulate the buildings much better than required instead of the use of biogas. Only in Baden-Württemberg the law was enlarged also to apply on old buildings. In this case the owner has the possibility to use 15 % (energy equivalent) biogas for heating if a change of the heater system or a big renovation has to be made. Due to this the gas supplier can force the biogas injection.

Rules, regulations and standards

Legislative for public gas supply in Germany

The statutory rule basis is the "Energy Industry Act" (EnWG). This law resulted in the "Gas Network Access Ordinance" (GasNZV) and the "Gas Grid Fee Ordinance" (GasNEV) were changed. The EnWG gives the framework for all questions related to energy supply. The ordinances define the declarations of the EnWG. In the GasNZV the conditions for the grid access are regulated. The GasNZV ensures for the quality of the injected gas according to the DVGW standards G 260 "gas properties" and G 262 "Use of gases from renewable sources in the public gas supply" with status 2007. This fixing of the technical rules in 2007 is regrettable as meanwhile the technical rules were developed further the actual standard of technology was not depicted in the GasNZV anymore. In the GasNEV the method to calculate the charges to access the gas transportation grid are defined. The legislative process for the public gas supply in Germany is outlined in Figure 21.

By starting the biogas injection the renewable energy law (EEG) was applied to the power generation with biogas. In this law the funding and the funded substrates are regulated. The renewable energy law will be monitored every year and will be adapted every 4 to 6 years.

Parallel to the development of biogas injection a lot of legal questions surfaced which need to be regulated. Thus, the institution "Clearingstelle EEG" was founded by the Federal Ministry for the Environment, Nature Conservation and Nuclear Power to clarify disputes and issues of application that arise.

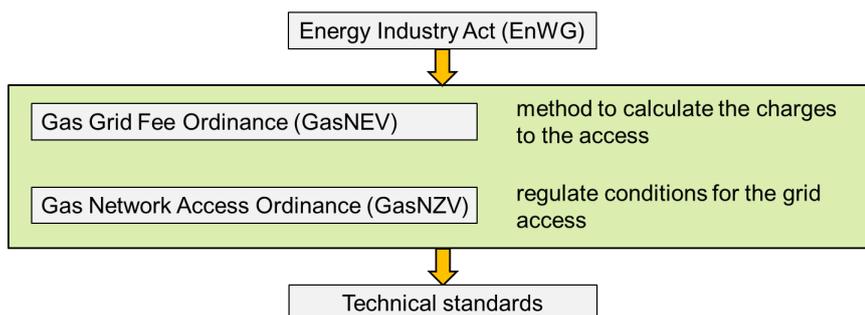


Figure 21. Overview of the legislative process for the public gas supply in Germany

Technical standards for public natural gas supply in Germany

Since 2006 biogas plants in Germany have injected upgraded biogas into the gas grid. At this time the discussion was started about gas quality needs for grid injection and what consequences the fluctuating values would have on the gas grid. Neither the gas transmission companies nor the administration knew much about quality requirements, cleaning, conditioning, injection, material behavior, regulation and the use of biogas. No special technical standards for biogas injection existed and the existing rules were not sufficient because the rules are designed for natural gas and not for renewable gases which contain impurities which do not exist in natural gases. To get a safe standard for these questions the DVGW started a R&D program to define biogas and to create rules. The most important technical standards of the DVGW are shown in Table 12. The most important standards are the G 260 and the G 262 which regulate the gas quality which will be injected respectively transported.

DVGW standard	Description
G 100 – B1 [38]	qualification requirements for experts for biogas injection plants
G 260 [39]	gas quality
G 262 [40]	usage of gases from renewable sources in the public gas supply
G 265-1 [41]	design, construction, and start-up of biogas upgrading and injection plants
G 265-2 [42]	operation, service, and maintenance of biogas upgrading and injection plants
G 290 [43]	reinjection of biogas into upstream transportations pipelines
G 291 [44]	guideline for interpretation of technical questions on the topic of biogas injection
G 292 [45]	monitoring and control of biogas injection from dispatching point of view
G 415 [46]	guideline for planning, design, and operation of raw biogas pipelines
G 493-1 [47, 48]	qualification criteria for designers and manufacturers of gas pressure regulating and metering stations and biogas feed-in systems
G 685 [48]	gas billing
G 1000 [49]	qualification of operators of gas supply installations
G 1030 [50]	qualification of operators for production, transmission, upgrading, conditioning, or injection of biogas

Table 12. Important technical standards of the DVGW [51]

Description	Unit	G 260, 2 nd gas family, G 262
Calorific value $H_{S,n}$	MJ/m ³	30.2 – 47.2
Relative density $d = \rho_{Gas} / \rho_{air}$	-	0.55 – 0.75
Minimum methane content	mol.-%	90 (L-gas) 95 (H-gas)
Hydrogen	mol.-%	< 10 (DIN 51624: ≤ 2)
Siloxanes (reference value)	mg/m ³	5
Ammonia	ppm	technically free
Dew point of hydrocarbons	°C	- 2 (1 bar ≤ p ≤ 70 bar)
Dew point of water	mg/m ³	200 (≤ 10 bar) 50 (> 10 bar)
Dust, liquids, Amines	-	technically free
Oxygen content	mol.-%	3 0.001*
Oxygen content in HP-grids (> 16 bar)	ppm	10
Total sulphur (including odorants)	mg/m ³	8 (DIN 51624: < 10 mg/kg)
Sulphur in mercaptanes	mg/m ³	6
Organic sulphur	mg/m ³	-
Hydrogen sulphide content	ppm	3.3

* underground storage and international transfer point

Table 13. Gas quality restrictions in Germany [27, 39, 40]

Interplay between grid owners and biogas producers

When the biogas injection started in Germany the legislature reacted and forced the injection of biogas into the gas grid by laws which regulate the relationship between the injector and the grid operator and also regulate the feed of injected biogas. The injected biogas quality must be similar to the described gas quality in the G 260. The grid operator has the duty to upgrade the biomethane to the transported gas quality. That means that LPG and/or air are added to the upgraded biogas until the combustion specific values are nearly similar to the transported natural gas in front of the injection. The limits of impurities, flow and main components are regulated in contracts between the injector and the grid operator. The grid operator is then responsible that the Weights and Measure Act will be fulfilled.

4.2.3 Sweden

In Sweden grid injection of biomethane to the natural gas grid is marginal compared to the larger distribution of biomethane through smaller local gas grids and non-grid based logistics solutions [52].

Overview on status

There are currently 59 upgrading units in operation in Sweden, inclusive of the complementary liquefaction operation in Lidköping. Water scrubbing is the dominating technology (42), with chemical scrubbing (11) as second choice. Recently the first membrane unit was taken into operation. The dominance of the two technologies can be explained by the location in Sweden of two of their major technology suppliers: Malmberg Water and Purac Puregas. The company Greenlane has also Swedish history, even though it now have foreign owners.

Not included is the new upgrading unit of the thermal gasification plant in Gothenburg (Gothenburg Biomass Gasification). Still being a pilot plant primarily used for research and development purposes, it produced and injected approximately 30 GWh during 2015. The target is to run the 20 MW_{methane} plant for 8,000 hours a year, producing 160 GWh biomethane with a cold gas efficiency of 65% (biomass to biomethane) and a total energy efficiency of 90% (biomass to useful energy, biomethane + district heating). The substrate up to now has been wood pellets, but from 2016 tests will be conducted with the target fuel, wood chips.

Only 10 upgrading plants (including GoBiGas) are injecting the biomethane into the natural gas grid, a natural consequence of the restricted coverage of it, merely spanning the west coast of Sweden and a smaller part of the inland to the east. Stockholm is the only capital in Europe, except Malta, with no natural gas grid connection. Since 2013, the local Stockholm gas grid is supplied through the LNG import terminal in Nynäshamn. This grid have three biomethane injection points. 286 GWh was injected to the two grids during 2014. The potential capacity however was 673 GWh, significantly increased by the addition of the GoBiGas plant.

Market drivers

Due to the uncertainties regarding extension of current policies (the tax exemption, which finally was extended and accepted by the European union until the end of 2020), paired with the lower prices of energy carriers in general, the market growth slumped markedly during 2015, with only one new upgrading unit erected.

Sweden has a governmental vision to have a fossil free transportation sector by 2050. The results of a Swedish Government Official Report on the subject were published in 2013, adding a softer goal of a fossil independent transport sector by 2030. The Swedish Energy Agency have recently been given the task to suggest a strategy to implement them, but with no set deadline and with no additional resources. The gas business in Sweden has in 2015 launched their own vision and strategy work, envisioning that 15 TWh of biogas could be produced by 2030, thereof 12 TWh to be used as automotive fuel. Biomethane from gasification of forestry residues constitutes a major share of the envisioned potential. The development of the market hinges upon how the government choose to answer to the proposals of the Official Report, especially regarding the new policy situation post 2020. There is uncertainty about if gaseous fuels are still viewed as an important player in the future transport fuel mix. It stands clear that the future electrification of public transport in urban areas will decrease the current market of

CNG powered buses, right now consuming half of the CNG volume, and the largest long-term contractor of biomethane.

Rules, regulations and standards

There are no specific government regulations in Sweden for the grid injection. The only official documents are issued by the TSO Swedegas.

From 2000 and onwards, many actors used as reference the Swedish biogas standard SS155438:1999, and grid owners used it as reference for the parameters specific to biogas, even though it was not intended to set specification for grid injection. Siloxane was not specified, but the restriction on inerts such as N₂ made it impossible for landfill gas to be upgraded to specs, since until the introduction of membranes and more efficient cryogenic liquefaction, there was no commercially available economic alternative for N₂ removal. The levels of siloxane have proven to be quite low in Sweden, even in the biogas of wastewater treatment plants [18]. When Denmark started grid injection, their authorities issued biomethane gas quality specifications (“Gasreglementet”, section C-12, 10.3-6 [53]), which the Swedish TSO Swedegas have incorporated in their specification³ [54]. The level of ammonia is set at 3 mg/m³, and siloxanes at 1 mg/m³. If the grid injection standard FprEN 16723-1 from CEN is confirmed in the formal vote during 2016, it will become the new natural reference point. All conflicting documents issued by national standard bodies must be withdrawn. However, in most countries the standard will not be made law, and bilateral agreements and specifications of DSO’s and TSO’s can be different. The Netherlands and Denmark have stricter national levels for siloxanes, and they have therefore applied for deviations.

The national regulations for odorisation in Sweden simply state that the gas needs to be sufficiently odorised to be detectable by a significant proportion of the population. THT (see section 4.3) dominates the market, but market actors may choose to use any odorant they want. The normal level is 15 mg THT/m³, corresponding to 5.5 mg S/m³. The transmission grid is odorised through dosing at the entry point from Denmark. (Quality rules, special safety rules or other important, odorisation, etc.)

Interplay between grid owners and biogas producers

In Sweden there are no specific regulations ruling how the market actors should interact. Bilateral agreements are used, with reference to the above mentioned specifications. The retail sister companies of the DSO’s have historically also invested in biogas production, sometimes filling up the whole value chain. That trend is now diminishing in strength, driven by the downturn in the economy of the energy sector. Municipal actors are still important players in the biogas production, e.g. wastewater treatment plants contributing roughly 40 % of the biomethane produced. There are two major private actors, Swedish Biogas International and Scandinavian Biogas. The Swedish TSO Swedegas is despite the market downturn still very interested in supporting the growth of biomethane grid injection. They are involved in the “Green Gas Commitment” platform, where six European TSO’s have vowed to have fossil free supply in their transmission grids by 2050 [54].

³ “Kvalitetsspecifikation” https://www.swedegas.se/vara_tjanster/tjanster/anslutning. They have also issued conditions that need to be met in order to accommodate biomethane grid injection projects: “Villkor för överföring av biogas”.

4.2.4 The Netherlands

In The Netherlands, the distribution grid is managed by the Gas-unie, or by a local distribution company. There are two different types of natural gas standards in the Netherlands: H-gas and G-gas. Historically the main type of gas that has been used in the Netherlands is G-gas. G-gas is “Groningen” gas and refers to the gas quality that was produced over the last decades from local sources, mainly from Groningen, in the Netherlands. H-gas is a standard that is compatible with the natural gas coming from the off shore field in the Nord sea, and is comparable with the Natural gas that is imported. The Netherlands import large amounts of natural gas through and LNG terminal in “Rotterdam” and a direct pipeline from Russia. The main gas standard in the Netherlands is G-gas, although the gas standard is under debate and is being changed slowly towards H-gas.

Biomethane is delivered in the Netherlands mainly to the G-gas network. In the Netherlands, a Grid Entry Unit (GEU) is connected to the biogas upgrading unit outlet. The GEU is owned by the Biogas producer, but operated through cooperation between the gas grid operator and producer of Biomethane. The quality control and measurement has to be done by a Notified body (“meetbedrijf”), that secures quality protocol and control and amount gas delivered by the Biomethane producer.

Overview on status

In December 2015, the NL market had 20 biogas upgrading units injecting G-gas in the grid. The main technologies in the Netherlands are membrane technology (8), water scrubbing (3), PSA (3) and (2) Amin wash. There are 4 membrane systems operating with CO₂-recovery units that also produce CO₂. The CO₂ is mainly sold to the greenhouses in the Netherlands. PSA is not widely used in The Netherlands, only three plant has been installed and two are old: (Installed before 1990).

Market drivers

In The Netherlands, the market is driven by the subsidies (SDE) that the government gives to the development of biogas upgrading projects, feed-in tariffs (covering 12 year operation periods from initial start-up), and a Green Gas Certification scheme. The feed-in tariffs are being changed every year and being constantly compared with other sources of green energy. Biogas to electricity is currently declining in the Netherlands, Biogas to biomethane is a more economical solution. The Dutch market is progressing slowly with 3-5 new installations per year. The Netherlands is currently struggling to meet the renewable energy objectives issued by the European Union.

Bio CNG is available in The Netherlands in a number of public CNG stations, and biomethane is available with “green tickets”

- The financial aspect:
 - × SDE gives a fixed and guaranteed price, which varies depending on the type and balance of feedstock used for the biomethane injected. tariff are provided for 12 years to the biomethane producer and are different every year.
 - × Biomethane Producers have to choose between SDE or green gas tickets (transport fuel).
 - × The use of Bio-tickets is allowed for installations without SDE.

Rules, regulations and standards

The technical specifications/standards imposed by the gas network operator are issued in cooperation with the authorities [55]. A significant trait of the Dutch gas grid is the low limit of silica from siloxanes, 0.1 mg Si/m³.

Interplay between grid owners and biogas producers

In The Netherlands, the “gas to grid” market is dominated by the “Bio2net” station. However, the application of this device is not mandatory and several gas grid units have developed their own gas to grid device.

4.3 ODORISATION

The most prevalent source of sulfur is added for safety reasons; most of the odorization compounds used contains sulfur. In some countries, the odorant is added well above the by the OEM’s wished for 10 ppmM sulfur level. Upcoming standardization for automotive CNG/biomethane (FPrEN 16723-2 (chapter 4.1.2) suggests a limit in the normal grade (grid based) of 30 mg/m³ [34]. However, DG Energy has asked the gas business to voluntarily prepare for a lowering of the total sulfur limit in future specifications.

Odorization is still a national issue, with a large variation in types of regulations and the level of odorization required. With some exceptions such as Sweden, odorization is not required in the high-pressure transmission grids of Europe. An overview of the types and levels of odorization in different European countries has been issued by Marcogaz, see Table 14. The market is dominated by the odorant tetrahydrothiophene (THT), due to its chemical stability and competitive cost. Mixtures of mercaptans are also used, such as the mixture Scentinel E comprising of 75 % tert-butylmercaptan (TBM), 16 % iso-propylmercaptan (IPM), 8 % n-butylmercaptan and 1 % sulfides. They represent a sulfur poor odorization alternative, since their greater olfactory power makes it possible to get the same odorizing effect with only a third of the level of THT. In Germany a sulfur free alternative has been introduced, a mixture of methyl acrylate (MA), ethyl acrylate (EA) and 2-ethyl-3-methyl pyrazine, and since more than 10 years it is used in a large part of the German natural gas network. Acrylates have a smell different from the one of sulfur containing ones, thus making information campaigns a necessity. A minor concern is that EA is placed on the watch list of potential carcinogens (suspected but not proven). It is also an allergen. Regarding biomethane, a recent concern is the potential masking effect some trace compounds, such as terpenes, may have on the perceived smell of the added odorants. A recent Dutch study explored the subject but is unfortunately not in the public domain [56].

Country	Odorant	Consumption pattern (%)	Min. Conc.	Max. Conc.	Typical Conc.
AT	THT	93	9	End point requirement	12-14
	Other	5	-		-
	Sulfur free	2	8		10
BE	THT	-	17	34	20
	TBM+IPM+NPM		5.4	7.1	6
CH	THT		10	30	15-30
CZ	THT	10	10	30	12
	TBM+DMS	89	5	30	10
	Sulfur free	1	8.8	8.8	8.8
DE	THT	55-70	10	20	15-18
	Other		-	-	-
	THT+EA	2	8		11-15
	Sulfur free	25	8.8	16	11-15
DK	THT		10.5 (consumer location)	-	11-17
EL (GR)	THT		15	35	20
ES	THT		15-trans. 18-dist.	-	22
FR	THT		15	40	25
HU	THT+TBM		13	25	16
IE ⁴	TBM+DMS		3	10	6
IT ⁴	THT	50	32	-	-
	TBM+IPM+NPM	50	8	-	-
NL	THT		10	36	18
NO	THT		12	15	-
PL ⁴	THT		-	-	25
PT	THT		8	40	24
RO	EM		3	30	8
SK	THT	99	8	40	18
	THT+TBM	1	2,1	15	7
UK ⁴	TBM+DMS		5	8	6

Table 14. Typical odorant concentrations in Europe. tetrahydrothiophene (THT), tert-butylmercaptan (TBM), iso-propylmercaptan (IPM), n-butylmercaptan (NBM); dimethyl sulfide (DMS); ethyl acrylate (EA) [57].

4.4 CALORIFIC ADJUSTMENT AND BILLING

In most countries it is necessary to add propane to the injected biomethane in order to meet the specification of the natural gas grid, up to 20 % of the calorific content might stem from the propane addition. Not only does it constitute a large cost both regarding OPEX and CAPEX, it is also diminishing the renewable value of the biomethane by forcing the addition of a fossil component. From the grid owners perspective however it facilitates interoperability and customer billing issues. There are examples of dedicated biomethane grids, e.g. in Denmark, where a complete section of the natural gas grid is turned into dedicated biomethane grids. However, since consumption and production may not always be in perfect balance, it will be tempting to let there be a

⁴ These countries express the concentration unit in reference to standard conditions, rather than normal conditions as the others do. The difference is related to the temperature to which the volume is expressed. (see EN ISO 1443)

flow and interchange of fossil and renewable gas between different sectors. From an end-user technical perspective, this has turned out to work quite fine, appliances being able to accommodate a pretty wide range of gas qualities. From a billing point of view it is however less straight forward. Unless the energy utility is willing to let their customers pay only for the lesser quality, and get energy for free occasionally, it has to come up with a measuring solution. For large volume users that is no problem, a dedicated gas chromatograph is easily afforded. But for residential customers there is no economically feasible solution to solve it with the implementation of gas analysis.

By using modeling and computer algorithms in “gas quality tracking” systems, it is possible to within reasonable error extrapolate the calorific value delivered to each customer, no matter how small. The model needs to be adapted and validated in order to work. Typically the data of already installed gas measurement devices is used, plus a number of test campaign units, only necessary for the testing and validation period. Further reading [58-60].

4.5 BIO-LNG

Biogas can be liquefied using cryogenic distillation (see chapter 2.6). In order to liquefy biogas with cryogenic distillation, the CO₂ content first needs to be reduced to 50-125 ppm [2]. This can be achieved directly in some biogas upgrading processes while others may need a polishing filter in the produced biomethane. In Lidköping, Sweden, biogas is upgraded using a water scrubber. The produced biomethane is treated in a polishing filter to remove further CO₂ and then led into a liquefaction unit from Air Liquide. In Oslo, Norway a similar process is supplied by Wärtsilä (former Hamworhty). In another recently introduced technology setup, DMT is connecting biogas upgrading using membrane separation with cryogenic liquefaction, which benefits from the high output pressure of the membrane upgrading. By liquefying at increased pressure (60 bar and -120 °C), it is possible to allow the carbon dioxide level to be as high as 0.5%, which is easily reached by normal membrane upgrading operation. In a flash unit the product LBG goes down to -160 C, and most of the carbon dioxide together with some of the methane is recirculated back to the inlet of the upgrading unit.

4.6 BIO- CNG

Non-grid distribution and utilization of biomethane as automotive fuel require compression to at least 200 bar, the minimum required for CNG refueling stations. Often the mobile CNG storages used to replenish these non-grid stations have design pressures of up to 350 bar, to increase transport and refuelling efficiency. Read more in the IEA Bioenergy task 37 case study [52].

Since a large share of the needed compression work is exerted in the first compression stages, it is possible to make full use of the elevated product gas pressure that some biogas upgrading technologies provide. However, the amount of work needed to compress the gas stands in proportion to the volume, making post-upgrading compression roughly half as energy consuming as raw gas compression. The energy cost of compressing biomethane from 1 to 200 bar is equivalent to 2-3 % of its energy content. For more information on the science of compression [2]

Oil and water impurities are the two most common sources of drivability issues in natural gas vehicles (NGVs). Oil and water are rarely the cause of major breakdowns or engine failures, but only at elevated levels a source of increased maintenance costs and decreased vehicle availability. Efficient drying down to less than 10 mg/m^3 , and lower than 1 mg/m^3 in cooler climates, will effectively take away all water related drivability issues. More information on standardization of water and compressor oil content in section 4.1.3. Compressors may have oil slips, which need to be controlled in order to secure proper functioning of vehicles. A recommendation is to have at least two coalescing filters in series installed, one directly adjacent to the compressor, and one just before the storage, in order to allow cooling and precipitation as aerosol of the dissolved oil. With proper maintenance, oil slips lower than $5\text{-}10 \text{ mg/m}^3$ are possible to achieve. Also the choice of oil type affects the amount of oil being entrained in the gas. Mineral oil based lubricants have a greater tendency to dissolve at elevated pressures and temperatures than synthetic ones. Certain additives have been shown to be the source of oil related engine problems. Read more about best practice of control of oil, water and sulfur in CNG at refueling station level [61] Details on the development of the referenced compressor oil test method [62, 63].

Gas quality is in the business often interpreted as the calorific value of the gas. In the natural gas business Wobbe index is used to define the specific calorific content of gas, by using the density ratio between the gas and air for normalization. For transiently operated internal combustion engines in NGVs another important measure is the methane number, the gaseous correspondent to octane number, defined as MN 100 for pure methane and MN 0 for pure hydrogen. Naturally, biomethane is in itself a high MN fuel, while the propane addition of grid injection makes the biomethane to become on par with the natural gas of the grid. The higher the content of higher hydrocarbons, the lower the MN. Especially heavy-duty NGV's with dual fuel engines (methane diesel) may not work properly (drastic decrease in fuel efficiency) if MN is lower than 80, because of the onset of knocking at higher loads. Most of the distributed natural gas has an MN over 70, but the recently adopted natural gas standard has a minimum level of MN 65. More information on MN and its standardisation in section 4.1.2.

5 Utilization of carbon dioxide separated through biogas upgrading

There are several areas of application for the CO₂ produced as a byproduct from biogas upgrading. Some of these applications will be investigated in the following chapter. The quality of the gas is most often technical grade or food grade, which do not differ very much more than the requirement to analyze every batch to fulfill food grade quality [64].

5.1 GREENHOUSES

Photosynthesis is a chemical process, which uses energy from light to convert carbon dioxide and water. In green plants the carbon dioxide and water are converted into sugars that enables growth. Carbon dioxide is therefore an important element when it comes to plant growth. The aim with most greenhouses is to increase the growth rate of the plants, in order to increase the productivity, and one way to do this is to enhance the carbon dioxide levels. Different plants experience various enhancements of the growth rate; some of these have been studied by Kirschbaum and can be seen in Table 15 [64].

Table 15. Growth enhancement in response to increased levels of carbon dioxide [64].

Observation	CO ₂ enhancement
All herbaceous plants	+ 45 %
Woody plants	+ 48 %
Grassland biomass	+ 12 %
Forest growth	+ 23 %

A common way to increase the carbon dioxide level in the greenhouse is by using a burner that runs on carbon-based fuels. However, contaminants in the fuels and incomplete combustion can be a problem. Another possibility is to use liquid carbon dioxide. The liquid carbon dioxide is then stored in special tanks outside and a vaporization unit is required to be able and distribute the carbon dioxide inside the greenhouse.

Enhancement of carbon dioxide levels in greenhouses is a possible usage area for the carbon dioxide separated through biogas upgrading. Something that needs to be taken into account is the purity of the carbon dioxide. Depending on upgrading technique different amounts of contaminants may still be present in the outgoing stream of carbon dioxide. Contaminants can be a problem to both the plants and the humans working inside the greenhouse. For example sulphur levels needs to be lower than 0.02 wt% [65].

In the Netherlands, the greenhouse sector and the government agreed on a goal of 20% renewable energy in the greenhouse sector in 2020, which includes a need for renewable CO₂ [66]. This could come from large scale energy producers, process

industry and biomass after fermentation, composting or incineration. In a study by Smit [66], a need of more CO₂ in greenhouses in the future, as a result of better isolated greenhouses resulting in decreased lighting, is identified. As well, the benefits of better CO₂ dosing are mentioned. As a result of these, CO₂ sources which facilitate this compared to the system today, will be needed.

5.2 FOOD INDUSTRY

Carbon dioxide is widely used in the food industry and is for example a key component in modified atmospheric packaging (MAP). The MAP process lowers the oxygen content in food packages, mainly packages for meat, fruit and vegetables, which contributes to a slower oxidation rate [67]. Another common way to utilize carbon dioxide in the food industry is to produce carbonated soft drinks and soda water.

Similar to the utilization in greenhouses the purity needs to be considered. For the food industry it is of high importance that the purity of the carbon dioxide is high. The requirements are higher in this branch and for beverages and food the purity needs to be 99.9 %. In order to reach these high levels of purity it is possible to use cryogenic distillation [68, 69]. This is, however, a process with high costs associated to it.

The food industry is probably not the most interesting utilization area for the carbon dioxide separated through biogas upgrading. This due to the high costs associated to the high quality of carbon dioxide, which is required.

5.3 COOLING INDUSTRY

Solid carbon dioxide, also called “dry ice”, can be used as a cooling medium during transportation of frozen food products but the more common one is liquid carbon dioxide used as a refrigerant. R744 is a carbon dioxide based refrigerant with many advantages. It is a non-toxic, non-flammable and environmentally friendly refrigerant but not completely without drawbacks. Complex thermodynamics of the carbon dioxide and high pressures needed to be able and use it in a heat pump are two of them [70].

R744 as a refrigerant has many applications such as water heat pumps, air conditioning systems and commercial refrigeration. A future possibility for the refrigerant would be to use it in an industrial heat pump. It would allow for waste heat recovery while at the same time providing low temperature heat [70, 71].

Carbon dioxide used as a refrigerant has, similar to the food industry, a high requirement on quality. Typical specifications on purity from one retailer of R744 displays a purity >99.99 % [71]. Based on the same conclusion as mentioned above, the separated carbon dioxide might not be of interest for the cooling industry.

5.4 POWER-TO-GAS

Carbon dioxide could be used as an energy carrier. Through electrolysis of water using non-expensive (excess) electric power from volatile sources e.g. wind and solar, hydrogen and oxygen can be obtained. The hydrogen could be used as such as a fuel or chemical. However, the infrastructure for hydrogen is limited today and there are still technical issues with storage, transport and safety to handle hydrogen. But hydrogen

could also be reacted with carbon dioxide to form methane and for methane there is an extensive infrastructure and well-known practices on how to store and handle the gas. Using electrolysis to produce hydrogen and letting it react with carbon dioxide to form methane is commonly referred to as the “Power-to-gas” concept. In relation to an anaerobic digestion unit, an interesting perspective is reasonably to add the hydrogen into the biogas reactor as such to treat the carbon dioxide in situ, thus increasing the overall methane yield from the reactor. Using the hydrogen this way the Power-to-gas concept could also be regarded as an upgrading process. In Europe today there are some 40 demonstration plants in operation and/or being built. Of course the hydrogen could also be used to produce other goods, e.g. methanol or synthesis gas for materials’ production. A precondition for the Power-to-gas concept to be of interest is usually the availability of non-expensive electric power. This is also the greatest challenge of the concept – in particular to secure a steady availability over time. On the contrary the Power-to-gas concept is often discussed as a means to control the power system, which does not fit with a steady operation of the concept as such.

6 Comparison between the different upgrading technologies

6.1 INVESTMENT COSTS

In order to compare the specific investment cost for biogas upgrading using the different techniques described in chapter 2, data was collected from the suppliers of biogas upgrading equipment which were part of the reference group in this study. The data is valid for biogas upgrading with the specifications presented in Table 16 and is presented in Figure 22.

	Raw gas specifications	Product gas requirements
Pressure:	20 mbar(g)	> 4 bar(g)
Methane concentration	60 vol%	> 97 vol%
Sulphur concentration	200 ppm H ₂ S	< 20 mg/Nm ³ (excl. odourisation)
Water concentration	Saturated with water at 40 °C	Dew point -10 °C at 200 bar(g)
Other requirements	Max. 0.1 vol% O ₂ and 0.4 vol% N ₂ , no siloxanes, max. 100 ppm NH ₃	

Table 16. Requirements for biogas upgrading for the collection of data for the specific investment cost. Furthermore, the requirement was a methane slip under 1%, no heat recovery, costs for an annual average as well as a container based scope or similar.

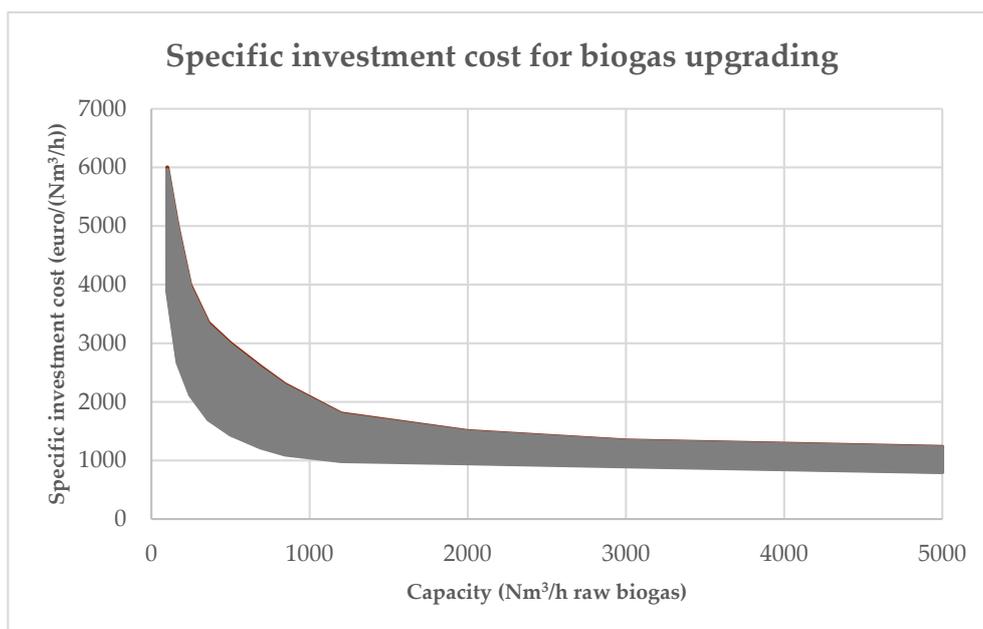


Figure 22. Specific investment cost for biogas upgrading, data collected from different suppliers of biogas upgrading equipment.

The specific investment cost for biogas upgrading decreases with increased capacity. Furthermore, the variation of investment cost figures from different suppliers is greater in smaller upgrading plants. There is a certain spread between specific investment costs, but from the data given by the biogas upgrading suppliers which were part of this study, no general trend could be seen regarding the difference in investment cost between techniques. The spread between investment costs of different suppliers for the same biogas upgrading technique was as wide as between different techniques. The data, however, shows that the economy of scale, e.g. lower specific investment cost for larger capacities, is more pronounced for membrane upgrading in the lower capacity range and for the other techniques in the upper capacity range.

It is important to remember that the investment costs presented in Figure 21 are valid for a certain base case. For specific projects there may of course be a more or less economic choice regarding upgrading technique depending on the circumstances in the project. Our conclusion from the data reported by the biogas upgrading suppliers is first of all that biogas upgrading techniques need to be compared in particular projects in which also other aspects such as operational cost, need of pretreatment, etc. are considered (see chapter 6.2 to 6.5).

6.2 ENERGY CONSUMPTION

The energy required to upgrade one Nm³ biogas is usually around 0.2-0.3 kWh electricity [2]. Biogas upgrading with amine scrubber requires less electricity but has a heat demand which none of the other technologies have. Plant data was collected for this report from operators of biogas upgrading plants using various upgrading techniques. 6 plants were visited; 2 membrane plants, 1 amine scrubber, 1 organic physical scrubber, 1 water scrubber and 1 PSA plant. The collected data confirms the picture given in Bauer et. al. [2]. The amount of data is, however, not sufficient to draw any more detailed conclusions than those given in Bauer et al, and the difference between two plants using the same upgrading technique is not generally smaller than the difference between different techniques. Interestingly enough, at least from an academic standpoint, the amount of useful energy (exergy) required for performing the upgrading is exactly the same independent of technology. If translated into electricity equivalents using the method suggested in [72] all of the upgrading technologies are in the 0.2-0.3 kWh_{electricity equivalents}/Nm³ of biogas range.

6.3 ADDITIONAL FACTORS AFFECTING SPECIFIC PRODUCTION COST

There are many factors that affect the specific production cost for a biogas upgrading unit. As already mentioned in the chapters above, the different techniques differ in need of consumables as energy and chemicals such as absorption agent, anti-foam, pH regulation, etc. (chapter 2). Also other consumables such as replacement oil for compressors and other equipment need to be taken into account. Biogas upgrading units may be equipped with more or less heat recovery which influences the investment cost. Logically, a biogas upgrading plant with more heat recovery will have a lower operational cost than one without heat recovery, but this is usually a trade-off with slightly higher investment cost.

One more important factor resulting in a price difference between different upgrading plants is the variety of service agreements available on the market. These are closely related to guarantees given on availability, which often require a certain service level or redundancy package regarding equipment. It is therefore important to look at a certain

project and compare prices. This report can only give a rough overview of price levels and the exact price for a biogas upgrading plant will depend on local circumstances as well as customer needs and will best be asked for directly from the suppliers of biogas upgrading plants.

6.4 METHANE SLIP

The methane slip of a biogas upgrading plant is a measure of the methane lost in the process and thus not present in the upgraded product gas. It is, however, important to keep in mind that there are different definitions used to present the methane slip. In this report, we refer to methane slip as a measure of product loss. The methane slip is thus reported as the amount of methane in the product gas in relation to the amount of methane in the raw gas:

$$\text{methane slip (\%)} = 100 - \frac{\text{methane content in product gas } \left(\frac{\text{Nm}^3}{\text{h}}\right)}{\text{methane content in raw gas } \left(\frac{\text{Nm}^3}{\text{h}}\right)} \cdot 100$$

The methane slip can be influenced through both process optimization and process design. Therefore, it may vary between plants using the same upgrading technique and in some cases, the methane slip can be decreased by altering the process design with more membrane steps or changed operational parameters such as pressure levels. There is therefore in some case a tradeoff between methane slip and investment or operational cost. The methane slip for the biogas upgrading techniques discussed in this report are summarized in Table 17. The numbers presented in this table reflect on what is achievable with the different techniques. However, in some cases, extra investment packages are needed to reach the lowest reported methane slip.

	Methane slip
Pressure swing adsorption (PSA)	1-1.5%
Water scrubber	1%
Amine scrubber	<0.1%
Membrane separation	0.5%
Organic physical scrubber	0.5-2%
Cryogenic upgrading	No data ⁵

Table 17. Methane slip for different biogas upgrading techniques

As already mentioned above, it is important not to confuse the methane slip reported in Table 17 with the methane concentration in a stream released to the atmosphere such as the stripper air in a water or organic physical scrubber. This concentration is dependent on the stripper air flow and the methane concentration can be decreased as described in chapter 0. The numbers presented in Table 17 do neither reflect any concentrations of methane in side streams in other upgrading techniques such as membrane separation or cryogenic upgrading.

⁵ For pilot plant data, reference [21]

6.5 REQUIREMENTS GAS QUALITY – INLET AND OUTLET

The composition of biogas produced in anaerobic digestion depends on the substrate used in the digester [18]. When choosing a suitable technique for biogas upgrading, it is therefore important to also consider how different compounds present in the biogas affect the process, the product gas as well as possible need for treatment of other streams such as waste gas or process water.

Scrubber techniques using water, amine or organic solvents to dissolve CO₂ and in this way separate it from CH₄ are robust technologies able to handle moderate concentrations of various impurities such as H₂S and NH₃. These are mostly dissolved in the solvent together with CO₂ and in this way removed with the CO₂ rich stream or, in the case of NH₃ in the water scrubber, with the process water. In an amine scrubber, the separation of H₂S from the gas is not as efficient as for the other techniques and significant amounts can be passed to the product gas, resulting in the need of a polishing filter to reduce H₂S to gas quality requirements. These technologies are also able to handle some VOC, which is removed with the condensate water or the CO₂ rich stream. Biogas upgrading using membrane separation requires more pretreatment as impurities such as VOC may damage the membranes.

Inert gases such as O₂, N₂ and H₂ take different paths in the different biogas upgrading processes, where they are passed to the product gas stream in water, amine and organic solvent scrubbers while they are only partly passed to the product gas in membrane separation. In biogas upgrading with PSA, these inert gases are passed to the CO₂ stream and thus removed from the biogas.

Gaseous water is removed in biogas upgrading with membrane separation and PSA together with the CO₂. In a water scrubber, the product gas is saturated with water and needs to be dried. Also the produced biomethane from an amine and organic physical scrubber contains some water which in most cases needs to be dried before grid injection. In pure cryogenic upgrading, where the biogas is directly refrigerated, low-concentration impurities such as water, hydrogen sulfide and siloxanes will be removed in the first stage, when the gas is chilled down to approximately -25 °C.

The produced biomethane leaves the upgrading process with various pressures. The amine scrubber process occurs at almost ambient pressure and the biomethane is usually compressed after the scrubber. This gives the flexibility to produce gas with any desired pressure. The water, amine and organic physical scrubber produce biomethane with moderate pressures in the range of 5-8 bar(a), whereas biomethane produced by membrane separation usually hold a higher pressure around 10-20 bar(a). When used in a low pressure application, some of the pressure is thus lost from the compression in membrane upgrading. On the other hand, when compressing the biomethane to even higher pressures after the biogas upgrading process, the compression needed after upgrading is smaller in biomethane produced with membrane separation than the other techniques available.

The aspects regarding requirements of biogas quality are summarized in Table 18. We have chosen not to include water in this table due to the fact that biomethane drying is a standard operation in biogas upgrading with techniques which do not produce dry biomethane and this is therefore in our opinion not considered a post treatment but rather a part of biogas upgrading. It is, however, important to remember that biomethane drying is required after upgrading with water scrubbers, amine scrubbers

and in some cases organic physical scrubbers, while the biomethane produced with membrane separation and PSA is dry enough to be used directly.

	H ₂ S	O ₂ , N ₂ , H ₂	VOC	NH ₃
PSA	Low concentrations	Passed to CO ₂ stream, H ₂ passed to product gas	Removal in raw gas needed.	Removal in raw gas needed.
Water scrubber	Moderate concentrations; main part passed to the stripper air	Passed to the product gas	Moderate concentrations; main part removed with the condensate and stripper air	Moderate concentrations; main part removed with process water
Amine scrubber	Moderate concentrations; main part passed to CO ₂ stream; polish filter may be needed in product gas	Passed to the product gas	Moderate concentrations; main part removed with the condensate and CO ₂ stream	Moderate concentrations; main part passed to the CO ₂ stream
Organic physical scrubber	Moderate concentrations; main part passed to the stripper air	Passed to the product gas	Moderate concentrations; main part passed to the stripper air	Moderate concentrations; main part passed to the stripper air
Membrane upgrading	Low concentrations; in part passed to product gas	Passed to the product gas and CO ₂ stream	Removal in raw gas needed.	Usually removed with condensate during raw gas drying
Pure cryogenic upgrading ⁶	Moderate concentrations; removed during first stage refrigeration	Passed to the product gas	Moderate to high concentrations; removed during first stage refrigeration	Moderate to high concentrations; removed during first stage refrigeration

Table 18. Summary of the effect of different contaminants in the raw gas on the various biogas upgrading techniques and their pass through the process.

⁶ Only based on pilot scale data, reference [21]

7 Concluding remarks

Biogas upgrading, e.g. the removal of carbon dioxide to produce biomethane for the use in natural gas grids and as vehicle fuel, is continuing to gain interest around the world. Compared to 2013 when our last report was published [2], there are today roughly twice as many biogas upgrading plants. In Germany we see increased interest in building new biogas upgrading plants and Sweden is continuing to have a large market share, although not growing as fast during the recent years. During the last years, also England, France, Denmark, Finland and Korea have experienced a significant increase of the number of biogas upgrading plants.

Three years ago, we saw that water scrubbers and PSA were the main biogas upgrading techniques on the market and that amine scrubbers had started to take significant market shares. Membrane technology, organic scrubbers and cryogenic biogas upgrading were then described as upcoming technologies [2]. In the present report, we can see that there now are more membrane than PSA biogas upgrading plants and also organic scrubbers are present with a significant amount of upgrading plants. The development of cryogenic biogas upgrading appears to be somewhat slower and this is still a marginal biogas upgrading technique.

In the present report, we show that there is no general significant difference in neither investment cost nor energy demand between the different biogas upgrading techniques other than the amine scrubber requiring less electricity but more heat than the other techniques. It is therefore more important to consider other aspects such as necessity to pre- or posttreat depending on the raw material quality and product gas standards. During recent years, product gas standards have been more and more well defined. Also, the use of a larger variety of substrates for biogas production results in a larger heterogeneity of biogas compositions.

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BIOGAS UPGRADING – TECHNICAL REVIEW

Biogas som produceras genom rötning används ofta för att framställa elektricitet. För att höja värdet av gasen och möjliggöra att använda det för andra applikationer kan det vara fördelaktigt att uppgradera biogasen till biometan genom att separera metanet från koldioxiden och andra eventuella föroreningar. Biometan liknar fossilt metan, naturgas, och kan användas i liknande applikationer, t.ex. för inmatning i naturgasnät eller som fordonsbränsle. Detta görs idag i över 400 biogasuppgraderings-anläggningar runt om i världen.

Denna rapport beskriver de vanligaste teknikerna för uppgradering av biogas och jämför dem med varandra med avseende på investerings- och driftkostnad och potentialen att hantera olika föroreningar som kan finnas i biogasen. Dessutom diskuteras reningsmetoder för att ta bort dessa föroreningar som H₂S, siloxaner, ammoniak, syre och VOC samt rening av sidoströmmar från restmetan. Dessa diskuteras utifrån förbehandling, dvs rening av biogasen, och rening av produktgasen eller sidoströmmar. Potentialen att hantera de olika föroreningarna och vad som händer med dessa i uppgraderingsprocessen diskuteras i rapporten.

Förutom biometan kan även andra produkter fås i en biogasuppgradering. Några exempel på användande av koldioxiden i olika tillämpningar nämns.

Den senaste tidens ökade marknadsaktivitet för inmatning av uppgraderad biogas i naturgasnätet, men även för användning som fordonsbränsle, har åtföljts av mer arbete inom standardisering både på nationell och internationell nivå. I rapporten ges en överblick.

Another step forward in Swedish energy research

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