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Biogas upgrading - Review of commercial technologies

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SGC Rapport 2013:270

Biogas upgrading – Review of commercial technologies

(Biogasuppgradering – Granskning av kommersiella tekniker)

Fredric Bauer, Christian Hulteberg, Tobias Persson, Daniel Tamm

"Catalyzing energygas development
for sustainable solutions"

SGC
Svenskt
Gastekniskt
CenterAB

SGC Rapport 2013:270

Svenskt Gastekniskt Center AB, SGC

Om SGC

SGC är ett spjutspetsföretag inom hållbar utveckling med ett nationellt uppdrag. Vi arbetar under devisen *”Catalyzing energygas development for sustainable solutions”*. Vi samordnar branschgemensam utveckling kring framställning, distribution och användning av energigaser och sprider kunskap om energigaser. Fokus ligger på förnybara gaser från rötning och förgasning. Tillsammans med företag och med Energimyndigheten och dess kollektivforskningsprogram *Energigastekniskt utvecklingsprogram* utvecklar vi nya möjligheter för energigaserna att bidra till ett hållbart samhälle. Tillsammans med våra programråd inom *Rötning*, *Förgasning och bränslesyntes*, *Distribution och lagring*, *Kraft/Värme* och *Gasformiga drivmedel* identifierar vi frågeställningar av branschgemensamt intresse att genomföra forsknings-, utvecklings och/eller demonstrationsprojekt kring. Beslut om eventuell statlig medfinansiering från Energimyndigheten fattas av den externa Beslutsnämnden inom ramen för kollektivforskningsprogrammet som f.n. löper under tiden 090401–130331.

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Det här projektet har finansierats av Air Liquide, Avfall Sverige, Biosling, Bioprocess Control, Danish Gas Technology Centre, Econet Vatten och Miljöteknik, Greenlane Biogas, Lunds Energikoncernen, Läckeby Water, Malmberg Water, MemfoAct, Metener Oy, Stockholm Gas, Svenskt Vatten Utveckling, Vattenfall, och SGC via Energimyndigheten.

Malmö 2012

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About SGC

SGC is a leading-edge company within the field of sustainable development having a national Swedish assignment. We work under the vision of *“Catalyzing energygas development for sustainable solutions”*. We co-ordinate technical development including manufacture, distribution and utilization of energy gases and spread knowledge on energy gases. Focus is on renewable gases from anaerobic digestion and gasification. Together with private companies and the Swedish Energy Agency and its frame program *Development program for energy gas technology* we develop new solutions where the energygases could provide benefits for a sustainable society. Together with our program committees within *Anaerobic digestion*, *Gasification and fuel synthesis*, *Distribution and storage*, *Power/Heat* and *Gaseous fuels* we identify issues of joint interest for the industry to build common research, development and/or demonstrations projects around. Decisions on any financial support from the Swedish Energy Agency are made by the external Beslutsnämnden within the frame program that currently runs 090401–130331.

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SGC also publishes fact brochures and the results from our research projects in the report series *SGC Rapport*. Brochures could be purchase from the website.

SGC is since the start in 1990 located in Malmö. We are owned by Eon Gas Sverige AB, Energigas Sverige, Swedegas AB, Lunds Energikoncernen AB (publ) and Öresundskraft AB.

Financing of this project

This project has been financed by Air Liquide, Avfall Sverige, Bioprocess Control, Biosling, Danish Gas Technology Centre, Econet Vatten och Miljöteknik, Greenlane Biogas, Lunds Energikoncernen, Läckeby Water, Malmberg Water, MemfoAct, Metener Oy, Stockholm Gas, Svenskt Vatten Utveckling, Vattenfall, Göteborg Energi and SGC through the Swedish Energy Agency.

Malmö, Sweden 2012

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Preface

This report has been written in cooperation between four authors from three companies.

Christian Hulteberg and Fredric Bauer, Hulteberg Chemistry & Engineering
Hulteberg Chemistry & Engineering is a company active within development of new chemical engineering process, such as amine scrubbing of gas streams, and techno-economic evaluation of new technologies. Christian Hulteberg holds a PhD in chemical engineering and Fredric Bauer holds an MSc in Sustainable Energy Systems.

Tobias Persson, Svenskt Gastekniskt Center
Tobias Persson has a background as a process engineer at Malmberg Water and holds a PhD in the area of membrane technology. Through SGC he is responsible for the work focusing on biogas upgrading within IEA Bioenergy Task 37.

Daniel Tamm, BioMil
BioMil has been working with biogas projects for more than 30 years. Daniel Tamm has experience with fermentation plants as well as different gas upgrading techniques and has worked with gas upgrading in both the German and the Swedish biogas market.

Several companies have also contributed in-kind to the project and given information and data that has been used during the writing of the report. Without the contribution from these companies, the report would not have been possible to write. Thank you all very much.

The project has been carried out during 2012 with one reference group meeting in the beginning of the project to determine the content of the project and one meeting to discuss the first draft version and final changes.

A reference group has been attached to the project with the following participants. The members of the reference group are listed below.

Participant	**Company**
Andreas Dahlner	Econet Vatten och Miljö
Richard Faber	Vattenfall
Benjamin Fillion	Air Liquide
Håvard Fjeldvær	MemfoAct
Liisa Fransson	Lunds Energi
Gunnar Hagsköld	Vafab Miljö
Jürgen Jacoby	Vattenfall
Ulf Jonsson	Greenlane Biogas
Lars-Evert Karlsson	Purac Puregas
Lars Kjellstedt	Kjellstedt Consulting Boden
Torben Kvist	Dansk Gasteknisk Center
Jing Liu	Bioprocess Control
Juha Luostarinen	Metener Oy
Daniel Sandell	Malmberg Water
Max Strandberg	Purac Puregas

Summary

Biogas production is growing and there is an increasing demand for upgraded biogas, to be used as vehicle fuel or injected to the natural gas grid. To enable the efficient use of biogas in these applications the gas must be upgraded, i.e. the carbon dioxide, which constitutes a large part of the raw biogas from the digester, must be separated from the methane. This report aims to evaluate the biogas upgrading technologies that are commercially available and in operation today: amine scrubbers, water scrubbers, PSA units, organic scrubbers and membrane units. The technologies are described in detail by presenting the theory behind the separation mechanism, the upgrading process as a complete system, operational issues and how these are solved, and finally the most important financial data.

Furthermore, the best developed cryogenic technologies, which today are being used to purify landfill gas and biogas from some specific components and to liquefy biogas, are presented. Cryogenic upgrading is an interesting possibility, but as this report shows, the technology still has some important operational issues to resolve. Technologies which are especially focused on small-scale applications are finally presented, however not in as much detail as the other, more common technologies.

The report shows that for mid-scale applications, the most common options are all viable. The scrubbing technologies all perform well and have similar costs of investment and operation. The simplicity and reliability of the water scrubber has made this the preferred choice in many applications, but the high purity and very low methane slip from amine scrubbers are important characteristics. Regarding PSA and membrane units, the investment cost for these are about the same as for scrubbers. Furthermore, recent developments of the membrane units have also made it possible to reach low methane slips with this technology.

Biogas production is increasing, in Sweden and globally, and the interest for biogas upgrading to utilize the gas as vehicle fuel or in other traditional natural gas applications increases as well. The mature technologies will see a market with more and harder competition as new upgrading technologies such as cryogenic upgrading are established, and other technologies optimize the processes to decrease operation costs. Important issues for the future development of the biogas market relate to the implementation of new policy instruments. The work with the new European standard requirements for gas distributed through the existing gas grids is one issue that possibly can have a large effect on possibilities for distribution of upgraded biogas. However, the future will most probably be fuelled by an increasing amount of upgraded biogas.

Sammanfattning

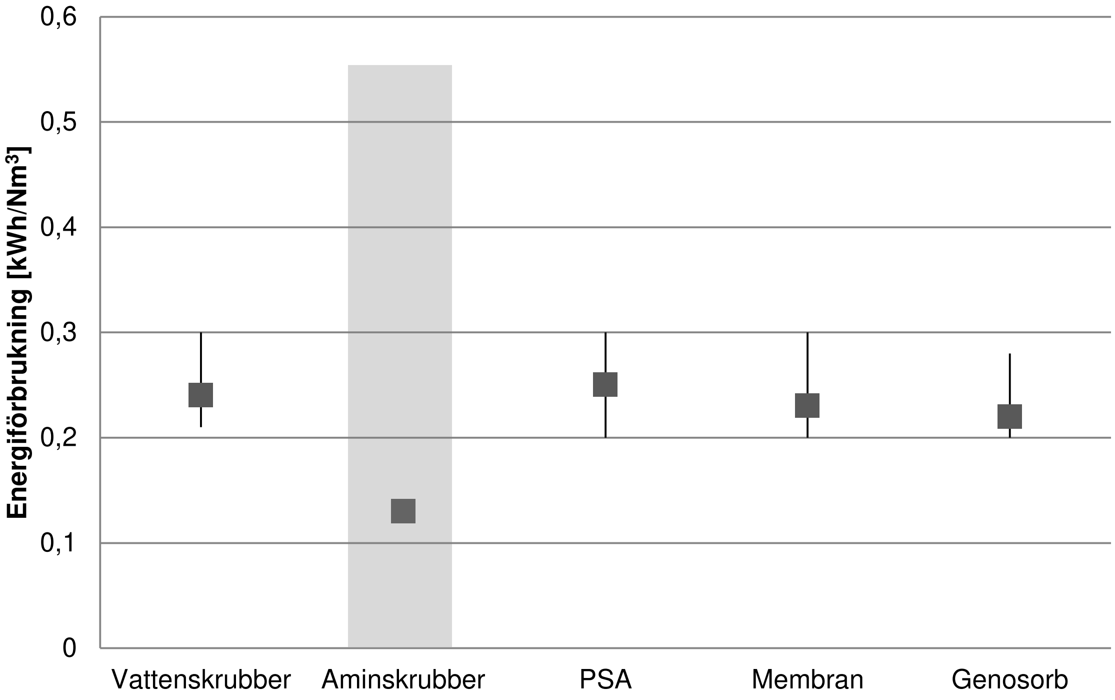
Intresset kring biogas liksom produktionen ökar ständigt, såväl i Sverige som globalt. För att kunna använda biogasen som fordonsbränsle eller för att distribuera den på naturgasnätet måste den råa biogasen uppgraderas, d.v.s. bl.a. koldioxiden måste tas bort för att öka gasens energiinnehåll. Att uppgradera biogas började man med redan på 1990-talet, men det är först under de senaste åren som den verkliga tillväxten inom detta område har tilltagit. Idag finns det mer än 220 biogasuppgraderingsanläggningar i världen varav ca 55 finns i Sverige.

Från början dominerade PSA och vattenskrubbern marknaden för biogasuppgraderingsanläggningar, men under senare tid har andra skrubbermetoder, som aminskrubbern, och membrananläggningar tagit en allt större del av marknaden. I denna rapport behandlas alla de större teknikerna som finns på marknaden idag och deras egenskaper jämförs mot varandra. De större existerande teknologierna är:

- Aminskrubbern - en kemisk skrubber som använder sig av aminer som binder in koldioxiden kemiskt. På detta sätt avlägsnas koldioxiden utan att biogasen behöver trycksättas. För att få koldioxiden att släppa från aminen igen måste värme tillföras för att driva reaktionen baklänges.
- PSA – Pressure Swing Adsorption är en metod som använder sig av en adsorbent som binder in koldioxid till dess yta. Vid ett högt tryck på biogasen binds koldioxiden in och genom att växla mellan högt och lågt tryck kan koldioxiden bindas in och avlägsnas i olika cykler.
- Membran - en fysisk barriär som är tillverkad på ett sådant sätt att koldioxiden kan passera igenom medan metanen inte kan. Genom att trycksätta biogasen kommer koldioxiden att pressas igenom membranfiltret medan metanen kommer att stanna kvar och på så vis uppgraderas biogasen.
- Vattenskrubbern - en fysisk skrubber som använder vatten för att separera koldioxiden från biogasen. Detta är möjligt eftersom koldioxid har mycket högre löslighet än metan i vatten. Genom att trycksätta biogasen kommer koldioxiden att lösa sig i vattnet och kunna transporteras bort.
- Organisk fysisk skrubber – en fysisk skrubber som fungerar som en vattenskrubber, men med den skillnaden att ett organiskt lösningsmedel används istället för vatten. I övrigt är dessa tekniker jämförbara.

I standardutförande är aminskrubbern effektivast för separation av koldioxid från biogasen då den kan ta bort hela 99.8% av koldioxiden i den inkommande biogasen. För övriga tekniker är denna siffra något lägre men inom samtliga tekniker finns möjlighet att nå 98% metan i den uppgraderade biogasen, dock beroende på den råa gasens egenskaper som t.ex. innehåll av syre och kväve.

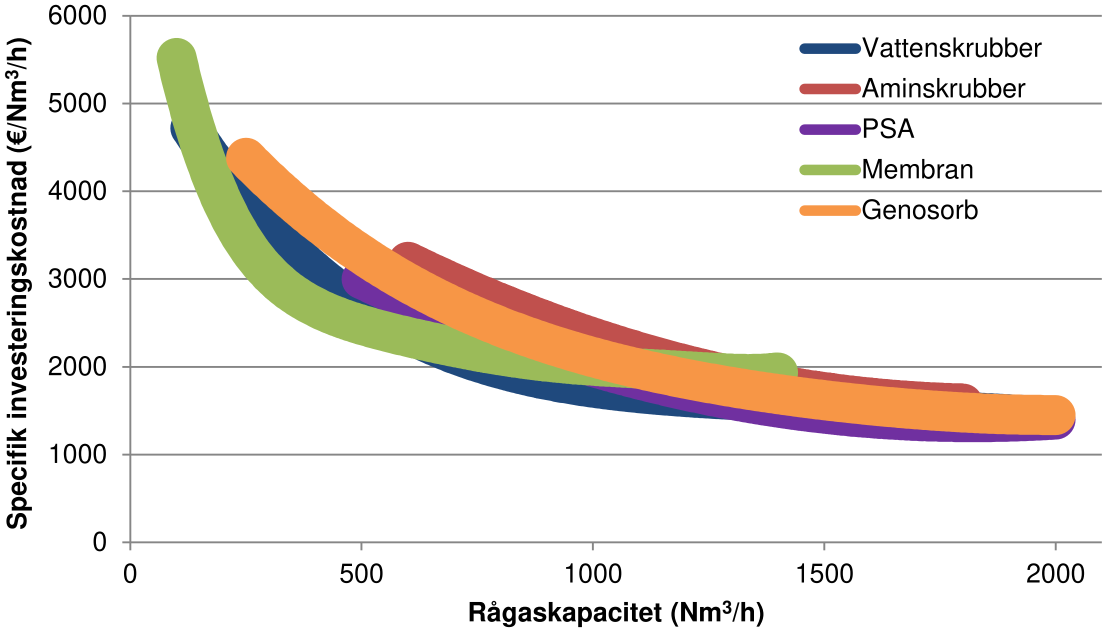
Energiförbrukningen för de olika teknikerna är liknande, med undantag för aminskrubbern, se figuren på nästa sida.



Som figuren ovan visar är elförbrukningen mellan 0.20 och 0.30 kWh/Nm^3 rå biogas för samtliga tekniker förutom för aminskrubbern. För aminskrubbern ligger elförbrukningen istället runt 0,13 kWh/Nm^3 men därtill kommer ett värmebehov på ca 0,55 kWh/Nm^3.

För att kunna jämföra den totala energiförbrukningen för en anläggning som injicerar biogasen på högtrycksnätet eller som säljer den som fordonsgas måste trycket på den uppgraderade biogasen tas med i den totala energiberäkningen. Trycket i den uppgraderade biogasen är i vattenskrubbern 6-10 bar(a), för aminskrubbern är ovan elförbrukning giltig för 5 bar(a), för PSA är trycket vanligtvis 6-10 bar(a), för membran 6-20 bar(a) och för genosorb 6-8 bar(a).

När det gäller investeringskostnaden är även den liknande för de olika teknikerna. I figuren på nästa sida ser man att kostnaden stiger kraftigt för anläggningar som är mindre än 300 Nm^3/h och man ser också att investeringskostnaden för de olika teknikerna närmar sig varandra när storleken överstiger 1000 Nm^3 rågas per timme. Denna jämförelse ska förstås ses som en indikation på att investeringskostnaderna är jämna om man jämför teknikerna med varandra, exakta investeringskostnader för ett givet projekt beror däremot på specifika förutsättningar och krav och de siffror som presenteras nedan ska således inte ses som givna kostnader vid investering i en ny uppgraderingsanläggning. Tekniker utvecklade specifikt för småskalig uppgradering av biogas är intressant och kunskap om detta har börjat spridas. Ännu är dock den specifika investeringskostnaden för små anläggningar för hög för att en storskalig spridning av teknikerna ska kunna anses trolig.



På senare tid har intresset för flytande biogas (LBG) ökat. Kondensering av biogasen öppnar för nya möjligheter tack vare den högre energidensiteten jämfört med komprimerad biogas, som leder till en större räckvidd av fordon och möjligheten till distribution av bränslet över längre sträckor. Under 2012 byggdes två nya anläggningar för flytande biogas i Europa, varav en i Sverige (Lidköping) med en kapacitet på drygt 60 GWh/år. Sedan tidigare finns det en anläggning i Storbritannien. Hittills använder LBG-anläggningar konventionell teknik för att uppgradera gasen, kompletterat med ett poleringssteg för att ta bort resterande koldioxid. Därefter kondenseras gasen med kryoteknik hämtad från LNG-branschen.

Kryotekniken kan även användas för själva gasuppgraderingen. Flera företag håller på att utveckla sådana teknologier som integrerar reningen och kondenseringen i en process. Förhoppningen är att få en billigare, mer effektiv process jämfört med de konventionella alternativen. Trots att verksamheten har pågått i flera år har dock ingen leverantör hittills kunnat visa upp en fullt fungerande fullskaleanläggning. Slutligen kan kryogena tekniker komma till gagn för att ta bort föroreningar som framförallt finns i deponigas som en förbehandling inför uppgradering med annan teknik. Grundtanken här är att många föroreningar har bra löslighet i flytande koldioxid som används som tvättmedel.

Intresset för produktion och uppgradering av biogas ökar och sprids, såväl i Sverige som i världen. Utformningen och tillämpningen av policyinstrument kan bli mycket betydelsefull för hur marknaden för biogas och uppgraderingsteknikerna utvecklas, ett exempel är arbetet med att ta fram en gemensam europeisk standard för den gas som distribueras via gasnätet. Högst troligen kommer framtiden dock att innehålla mer biogas.

Acronyms used in the report

AD	Anaerobic digester
CBG	Compressed biogas
CMS	Carbon molecular sieve
CNG	Compressed natural gas
DEA	Diethanolamine
IEA	International Energy Agency
LBG	Liquified biogas
LNG	Liquified natural gas
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MOF	Metal organic framework
PSA	Pressure swing adsorption
PZ	Piperazine
RTO	Regenerative thermal oxidation
WWTP	Waste water treatment plant

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1 Introduction

1.1 Earlier work

Biogas is often considered to be the best alternative vehicle fuel. In order to be used as a vehicle fuel, it is necessary to upgrade the raw biogas to the specifications defined in the Swedish standard for vehicle fuel gas (SS 15 54 38). Gas has been upgraded in Sweden since the late 1990's, however, the technologies used have evolved during this time and become more efficient. In addition, new technologies are being developed and new players have entered the market. Examples are cryogenic upgrading and new membrane solutions, which all now are represented by minor pilot plants or in full scale in Sweden and abroad. Also, the liquefaction of biogas to LBG (liquefied biogas) is getting increasing attention, with the first full scale plants being in operation.

In Sweden, there are by the time this report is published 55 biogas upgrading plants. The suppliers have grown considerably, leading to more sophisticated and optimized technologies. Furthermore, the biogas production inside and outside Sweden can be expected to increase rapidly in the coming years, which drives a further development of the technical solutions. As a consequence, the plants recently built are quite different from the ones built only five years ago. It is therefore desirable to collect updated information and compare it to data from the past. Another major change in the conditions is the implementation of new requirements for sustainability of fuels in order to receive tax reductions. In this context, the methane losses are very important for future gas upgrading plants. This issue will thus be specifically addressed in this report.

The first SGC report on the subject of biogas upgrading technologies was published ten years ago (Persson 2003). The report gave a comprehensive view on the gas upgrading situation at the time, including new technologies (membranes, cryogenic techniques), when only a limited number of plants were in operation. Since then, the market has developed considerably concerning both technology and number of plants in operation, and much new experience has been gained in the meantime.

During recent years, a number of similar reports treating the upgrading of biogas have been published. Among the scientific publications, a comprehensive review of biogas purification processes was published in 2009 (Abatzoglou & Boivin 2009). This paper does however mostly focus on the removal of contaminants such as hydrogen sulphide, ammonia and siloxanes, whereas the removal of carbon dioxide is only briefly mentioned. One article (Weiland 2010) gives an overview of the whole biogas chain including gas upgrading, but does not go into any details such as advantages and disadvantages or economical facts. Another scientific article (Ryckebosch et al. 2011) is confined to gas upgrading, but focuses on the removal of other compounds than carbon dioxide. Furthermore, no economical or environmental aspects are discussed in this paper, neither does it fit the specific situation in Sweden. Yet another report (Bekkering et al. 2010) focuses on the Netherlands and contains a compilation of energy usages and efficiency of different upgrading methods. However, the article is missing an economical evaluation of the different options and uses exogenous data which today can be considered outdated, which also is the reason that some newer approaches are not covered in this report.

In the non-scientific area, a large number of shorter and longer reports have been published recently. One of the most complete works was published by the institute Fraunhofer Umsicht (Urban et al. 2009). This report has a focus on the German market (and is thus only published in German), and emphasizes legislation and economy rather than technical details. It has a rather broad view on gas upgrading, including also methods for the removal of compounds such as sulphur, water and oxygen. However, the authors chose not to include some newer approaches such as membranes and cryogenic methods. Amine processes were also not considered a fully proven technology at the time, despite the fact that full scale plants were already in operation. Another aggregation of upgrading methods was published by IEA (Petersson & Wellinger 2009). This work covers a large number of technologies, but is rather short and does not go into technical details. As late as in 2012, an overview on current upgrading technologies has been published by Vienna University of Technology. However, it is very short and limited to mostly conventional approaches, excluding cryogenic methods.

Cryogenic technology has evolved considerably during the recent years, and has been examined in different publications some years ago (Benjaminsson 2006; N. Johansson 2008; Öhman 2009). Since then, no newer publications have been made in this area, so the most recent development with full scale plants and operational experience has not been documented yet. Other reports in the area of LBG have focused on logistics and economy rather than technology (Pettersson et al. 2006; Pettersson et al. 2007; Stenkvist et al. 2011). Finally, a shorter report focused exclusively on small scale solutions has been published recently (H. Blom et al. 2012).

1.2 Existing upgrading plants

According to the information published by IEA Bioenergy Task 37 more than 220 biogas upgrading units exist today. In Figure 1 it can be seen that most of the upgrading plants are situated in Germany and Sweden. Thereafter follows several countries with less than 20 upgrading units each. Although this is the most updated available list, information about some units may be missing (IEA Bioenergy Task 37 2012).

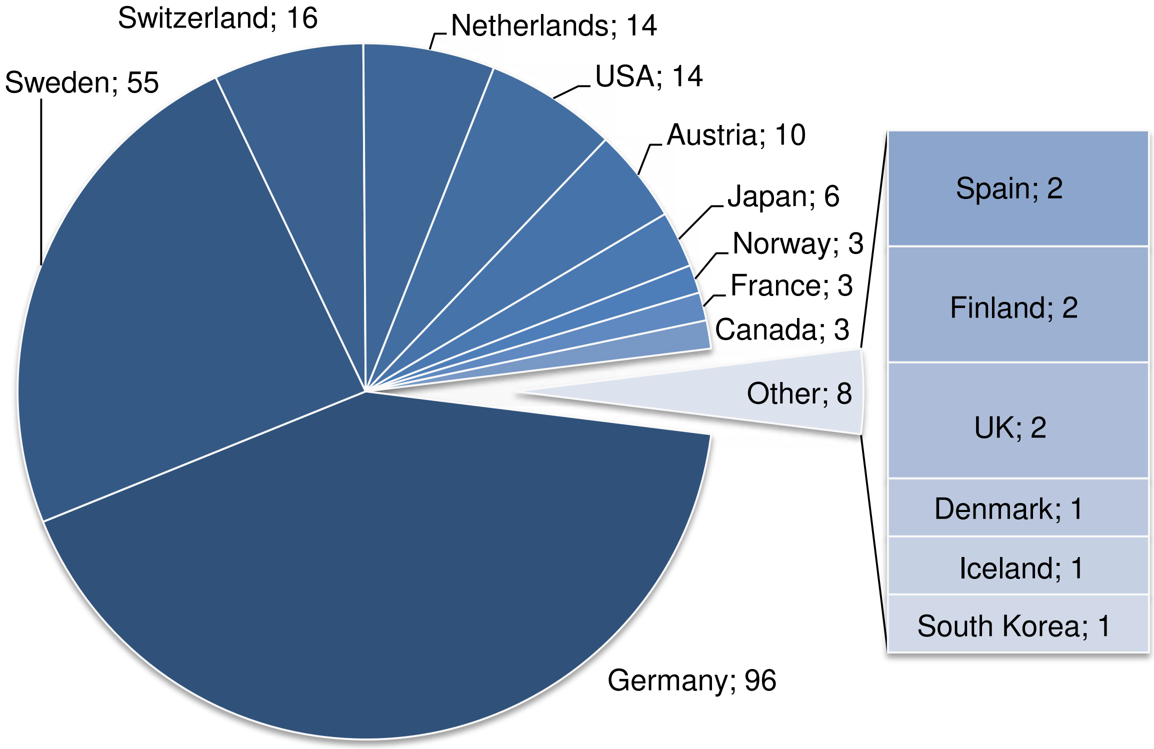

Figure 1 The geographical location of the 221 biogas upgrading plants that has been identified by IEA Bioenergy Task 37

Figure 2 shows the technologies that are used by the upgrading plants that are in operation today and which year they were commissioned. Until 2008 it was mainly the water scrubbing and PSA technology that dominated the market, but lately chemical scrubbers, and to a minor extent also membrane separation units, have increased their market share. The main part of the chemical scrubbers is amine scrubbers, but other chemical scrubbers are also included in this category.

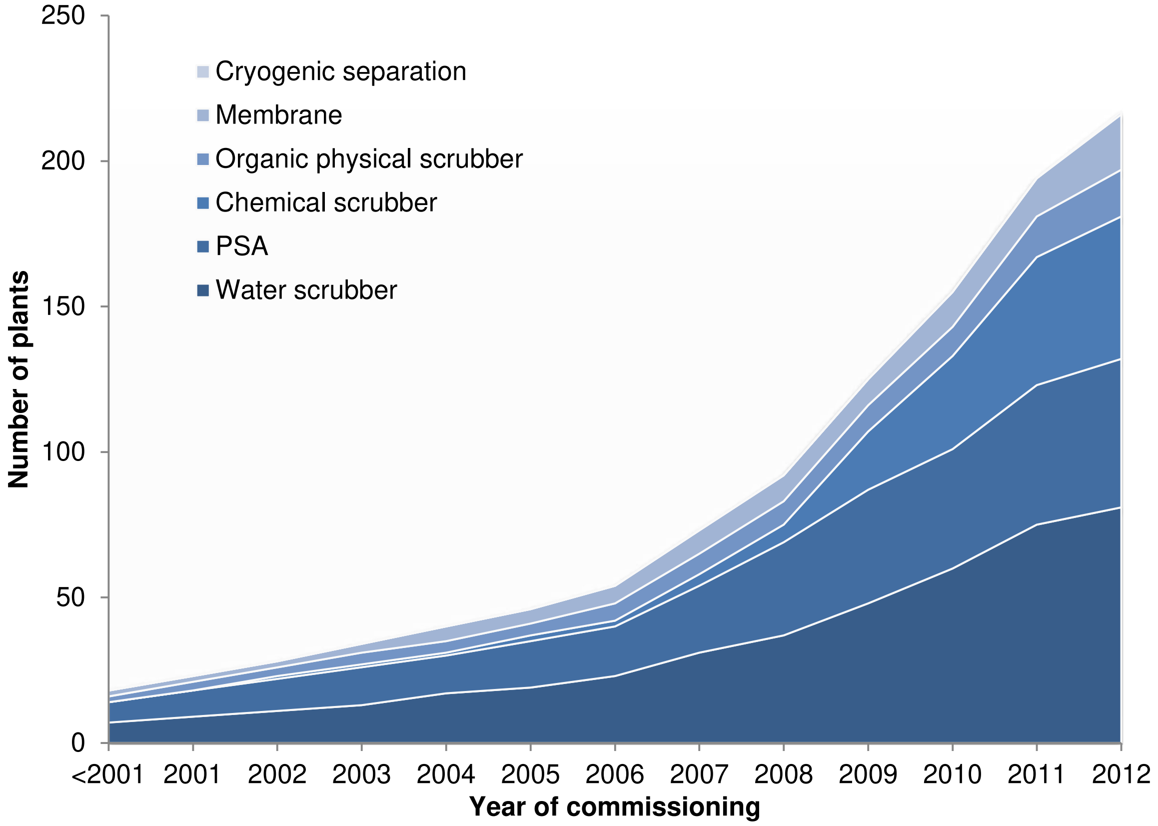

Figure 2 Visualisation of the technologies that are used in the biogas upgrading plants manufactured in different years. Only plants that are in operation today are included. Data from IEA Task 37

1.3 Manufacturers of biogas upgrading units

The number of manufacturer of biogas upgrading plants is increasing every year and the list shown in this report includes only those that were known by the authors at the time of publishing. Tables 1 through 7 show manufacturers of upgrading units, sorted by technology type.

Table 1 Manufacturers of PSA units

Company	Homepage
Acrona-systems	www.acrona-systems.com
CarboTech	www.carbotech.de
Cirmac	www.cirmac.com
ETW Energietechnik	www.etw-energy.com
Guild	www.moleculargate.com
Strabag	www.strabag-umweltanlagen.com
Xebec	www.xebecinc.com
Mahler	www.mahler-ags.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
RosRoca	www.rosroca.com

Table 3 Manufacturers of chemical scrubbing units

Company	Homepage
BIS E.M.S. GmbH	www.ems-clp.de
Cirmac	www.cirmac.com
Hera	www.heracleantech.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
HAASE Energietechnik	www.haase.de

Table 5 Manufacturers of membrane units

Company	Homepage
Air Liquide	www.airliquide.com
BebraBiogas	www.bebra-biogas.com
Biogast	www.biogast.nl
Cirmac	www.cirmac.com
DMT	www.dmt-et.nl
Eisenmann	www.eisenmann.com
EnviTec Biogas	www.envitec-biogas.com
Haffmans	www.haffmans.nl
Gastechnik Himmel	www.gt-himmel.com
Mainsite Technologies	www.mainsite-technologies.de
Memfoact	www.memfoact.no
MT-Biomethan	www.mt-biomethan.com

Table 6 Manufacturers of cryogenic units

Company	Homepage
Gas treatment Services	www.gastreatmentservices.com
Acrion Technologies	www.acrion.com
Terracastus Technologies	www.terracastus.com
FirmGreen	www.firmgreen.com

Prometheus Energy	www.prometheusenergy.com
Cryostar	www.cryostar.com
Hamworthy	www.hamworthy.com
Gasrec	www.gasrec.co.uk
Air Liquide	www.airliquideadvancedtechnologies.com

Table 7 Manufacturers with special focus on small scale biogas upgrading

Company	Homepage
Biosling	www.biosling.se
Metener	www.metener.fi

1.4 Aims, scope and report disposition

The present report aims at presenting a review of biogas upgrading today, taking into account and comparing relevant upgrading methods by presenting their advantages and shortcomings. Each technology is described in detail, including a technical walk-through, a description of different conditions influencing energy consumption, methane loss, investment costs, etc. The report focuses on the upgrading technologies which are commonly used today, i.e. pressure swing adsorption, amine scrubbing, water scrubbing, physical scrubbing with organic solvents and membrane separation. The report intentionally also includes even less-proven methods such as cryogenic technology as well as small scale approaches, albeit on a less detailed level, because this is where the strongest development can be observed.

The aim is to provide a reference for existing biogas upgrading plants in order to evaluate their technology, place themselves in the right context and identify optimization possibilities. It shall also be a reference for those planning to build a gas upgrading plant, and give the underlying knowledge and holistic view necessary for choosing the most suitable solution.

The report has been prepared in cooperation with several manufacturers of biogas upgrading units to ensure that reliable and updated data is presented. Not all technologies are represented by a manufacturer in the reference group. Also to ensure reliable data in these chapters, the authors have contacted industry representatives to review the data presented about these technologies. The data collected during this project have also been compared to data from the research literature, to see if recent developments have meant any drastic changes.

Chapter 2 presents the technologies that are available for biogas upgrading. This chapter presents technological details and is intended for the reader who wants a proper understanding of the technologies, the driving forces behind them and their limitations. The reader not interested in these details may jump directly to Chapter 3 which presents a comparison between the upgrading technologies, with respect to investment costs, energy demand, consumables and gas purity. Chapter 4 presents the developments within cryogenic separation and liquefaction, a quickly developing topic. In Chapter 5 two new technologies especially designed for small scale upgrading applications are described. Finally, some concluding remarks and visions about future developments are presented in Chapter 6. In Appendix I-III some specific theoretic considerations are presented.

2 Description of the available upgrading technologies

This chapter, which constitutes the main part of this report, aims to thoroughly describe the five commercially available upgrading technologies, amine scrubbing, water scrubbing, pressure swing adsorption, membrane separation and physical scrubbing with organic solvents. This chapter has been written in cooperation with several manufacturers of upgrading plants. Significant parts of the data have been supplied by the manufacturers, and compared with data from the literature. The investment costs are presented as intervals of specific investment cost, as it may vary with several factors, e.g. location, integration with existing equipment and other site specific information.

2.1 Amine scrubbing

This chapter has been written in cooperation between the authors and the company Purac Puregas which is active within the area of biogas upgrading.

The use of reactive systems for removing CO_2 from biogas is not a brand new notion, but it is less common compared to other technologies such as PSA and water scrubbing. The synopsis of features of the technology is to use a reagent that chemically binds to the CO_2 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 for the purpose of sour gas removal (carbon dioxide and hydrogen sulphide) are methyldiethanolamine (MDEA), diethnolamine (DEA) and monoethanolamine (MEA) (Kohl & Nielsen 1997). Some of these are still used, however, to the authors' knowledge, the most common amine system used industrially today is a mixture of MDEA and piperazine (PZ) often termed activated MDEA (aMDEA). This system was introduced by BASF (Appl et al. 1982), but is today supplied by several major suppliers of chemical such as BASF, DOW chemicals and Taminco.

This chapter will deal with the purification of biogas with water solutions of amines, the general process layout, operation and the effect of contaminants as well as vendor information on costs and consumables.

2.1.1 Process description

Absorption of CO_2 from biogas using amines in today's biogas industry is mainly performed using aMDEA. The process may be described generically but actual vendors each have their variations of the process. In general terms the technology consists of an absorber, in which the CO_2 is removed from the biogas, and a stripper in which the CO_2 is removed from the amine solution. A general process overview is shown in Figure 3.

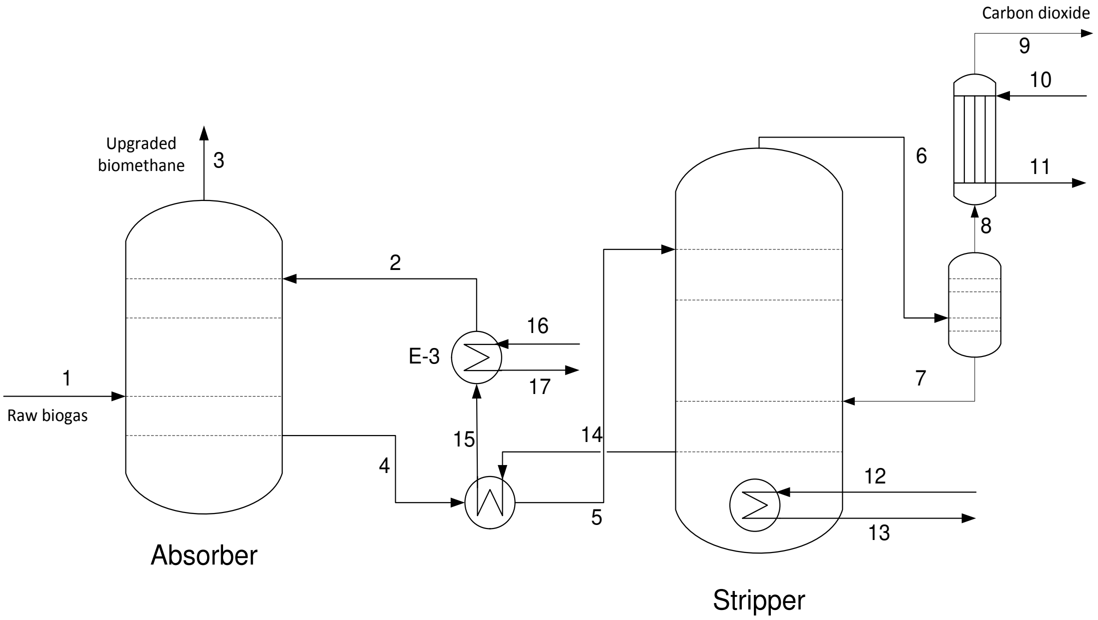

Figure 3 Simplified process flow diagram of an amine scrubber for biogas upgrading.

As seen in the figure, the inlet stream (1), using the numbers as per Figure 3, enters the absorber from the bottom, in which it is contacted with the amine solution (2). The CO_2 (and H_2S) part of the biogas is reacted with the amine and transferred from the gas to the liquid phase. This is an exothermic reaction, heating the solution from the inlet 20-40°C to 45-65°C. The absorption is favored by low temperatures from a thermodynamic standpoint but at higher temperatures from a kinetic standpoint. The amine is fed in significant excess to the expected CO_2 content (4-7 times more on a molecular basis) to avoid equilibrium constraints of the reaction. The product stream (3) exits in the top and contains mainly methane. The operating pressure of the absorber is 1-2 bar(a).

The liquid exiting the absorber (4) is preheated using the stripper exit stream (14) in HX 1, normally termed lean/rich heat exchanger where lean refers to amine solution without CO_2 and rich to amine solution with CO_2. The liquid is then passed to the top of the stripper column (5). Inside the stripper column, the liquid enters a flash box (or similar) where any CO_2 released in HX1 is removed. The liquid is then distributed and passed through a packing material where it is contacted with steam and CO_2 released further down in the stripper column. The bottom part of the stripper column is equipped with a reboiler in which heat is added (120-150°C) and part of the amine solution boiled. The purpose of the reboiler is twofold; first of all it provides the required heat of reaction for the release of CO_2 (and H_2S) from the amine, secondly it generates steam to lower the partial pressure of the CO_2 in the column which improves the kinetics of the desorption. The reaction is limited by equilibrium but at the elevated temperatures used the reaction is pushed strongly towards the lean amine. The stripper pressure is slightly higher than the absorber pressure, usually 1.5-3 bar(a).

The heat supplied to the reboiler (12) may be hot water/oil or steam; there are also examples when district heat is used at 90°C which require a stripper column operating under vacuum. The mixture of the released CO_2 (and H_2S) and steam exit the stripper column in the top (6) and is cooled in a condenser. The condensate (mainly steam but with traces of amine) is returned to the stripper (7). The cooled gas stream will consist mainly of CO_2 and if H_2S is entered into the system it will leave it here. In the simplified flowsheet, there is no integration but the cooling loops may naturally be integrated. As the pH of the solution is quite high with the basic amines in solution, there is little to no risk of bacterial growth. Therefore any contactor may be used; trays, structured or random packing alike.

As per the figure the generic amine system may be represented for systems ranging from small scale, such as biogas applications, to applications in the oil, gas and chemical industry with units several meters in diameter. The pressure is however most likely higher in the large industrial applications. More specific to the biogas case, there is usually gas sweetening (H_2S removal) upstream of the system to avoid smell and material issues downstream. The product gas will also have to be dried before being used in an automotive or indeed any other application. This is done using temperature swing adsorption, pressure swing adsorption or freeze drying.

2.1.2 Theoretical background

The degree of purification of the amine-based systems may be viewed as follows. Under normal operating conditions, the system is operating close to what may be described as an ideal plug flow, with little or no back-mixing (at least for the purpose of describing an actual system). This means that one gas segment which is entered in the bottom of the column will pass through the column and shrink in size as the CO_2 is removed from the gas segment, but it does not mix with other gas segments. The driving force of the absorption may be mainly ascribed to the level of CO_2 in the gas as there is a surplus of amine in the system. Using this line of thinking it may be realized that, as there is no back-mixing, the purity of the exiting gas is based on the column height alone. It also explains why much temperature increase is seen in the bottom part of the column.

With respect to throughput this is limited in the lower end by enabling contact between the gas and liquid through distributers etc. In the upper end, the throughput is limited by the lifting force of the flowing gas compared to the weight of the flowing liquid. This point is called the flooding point and may be expressed as

$$F = \frac{L}{G} * \sqrt{\left(\frac{\rho_G}{\rho_L}\right)} \qquad \textit{Eq. 1}$$

G is packing specific but is a function of the gas velocity, L is the liquid flow and it is weighted using the square root of the gas density divided by the liquid density. Using the flooding point of the packing, the gas velocity of flooding may be determined for the intended liquid flow rates. This maximum gas velocity is then used for setting the design gas velocity, usually 50-80% of the flooding gas velocity.

Looking at a molecular level, there are several reactions that may take place (X. Zhang et al. 2001), they may however be summarized using the following equilibrium reactions

$$CO_2 + PZ \cdot H_2O \leftrightarrow PZH^+ + HCO_3^- \qquad \textit{Eq. 2}$$

$$CO_2 + MDEA \cdot H_2O \leftrightarrow MDEAH^+ + HCO_3^- \qquad \textit{Eq. 3}$$

The reason for the simplification is the pH at which the reaction is taking place. There is a significant difference between the absorption capacity of the MDEA alone and the mixture of MDEA and PZ. The reason is that the secondary or primary amines (PZ) have very high reaction rates with CO_2 and the ability of the system to react the CO_2 further with the tertiary amine. The tertiary amine on the other hand has relatively low heat of reaction, making the regeneration affordable from an energy standpoint (Bishnoi & Rochelle 2000).

Amine scrubbing for biogas upgrading is today a mature technology, but the technology is still developing. New process designs have been suggested in which double absorption columns are used, one of which is pressurized to increase the solubility of carbon dioxide in the solvent and thus increase the separation of the gases (Dreyer & Bosse Kraftwerke GmbH n.d.). These systems are not yet commercialised and it is, at the time of writing this report, difficult to estimate the potential impact of these new process designs. An amine scrubber used for biogas upgrading today is shown in Figure 4.

Figure 4 An amine scrubber used for biogas upgrading in Sweden. Image from Purac Puregas.

2.1.3 Investment and consumables

To be able to get up-to-date information regarding consumables, investment cost and supplier interface with customers a supplier of amine-based biogas purification systems has been interviewed. The supplier has three standard sizes that they offer to the Swedish market and two that they offer to the German market. The differences between the markets are mainly on the feed used for the fermentation, resulting in a significantly higher CO_2 level in the German digester gas. But there are also differences with respect to supply pressure requirements etc.

The systems have a nameplate capacity of 600, 900 and 1 800 Nm^3/h of inlet raw biogas for the Swedish market and 700 and 1 400 Nm^3/h of inlet raw biogas for the German market. The design value with respect to CO_2 concentration in the inlet gas is 60% in the Swedish case and 50% in the German case. The systems are designed to have a certain turndown as per Table 8. These values are of course dependent on the inlet conditions such that they depend on the inlet level of CO_2, as an example the Swedish systems accept a methane content ranging from 55% to 70%. The systems are designed to handle a maximum 300 ppm H_2S in the incoming gas.

Table 8 Turndown ratio of standard amine scrubbing units for biogas upgrading available at the Swedish market.

Capacity raw biogas (Nm^3/h)	**Lowest flow rate (Nm^3/h)**	**Highest flow rate (Nm^3/h)**
600	100	700
900	300	1 000
1 800	800	2 000

In the delivery, there are certain guarantee values with respect to water consumption, electricity, methane slip and chemicals. The water consumption is specified to 0.00003 m^3/Nm^3 raw biogas. Electricity is slightly dependent on where in the operating window the units are operating, with the lowest consumption at the highest load (0.12 kWh/Nm^3 raw biogas) and the highest at the lowest load (0.14 kWh/Nm^3 raw biogas). Further, the stripper column requires heat to regenerate the amine, this heat demand is approximately 0.55 $kwh//Nm^3$ raw biogas. The methane slip based on third party measurements is 0.06% (99.94% of the inlet methane exit as product) and the guarantee value is set to 0.1%. With respect to chemicals (antifoam, amine make-up) the consumption is guaranteed at 0.00003 kg/Nm^3 raw biogas

With respect to the investment cost, the systems vary with size and there is an 8 MSEK difference between the smallest and the largest system. In the investment cost the gas purification unit including transport, commissioning, heat recovery system, analysis equipment and a guaranteed 96% availability is included. Service contracts are offered, but at an additional cost (annually around 3% of the investment cost). The specific investment costs may be viewed in Figure 5. In 2008 the purification systems were redesigned to modular construction and the investment cost has not increased since.

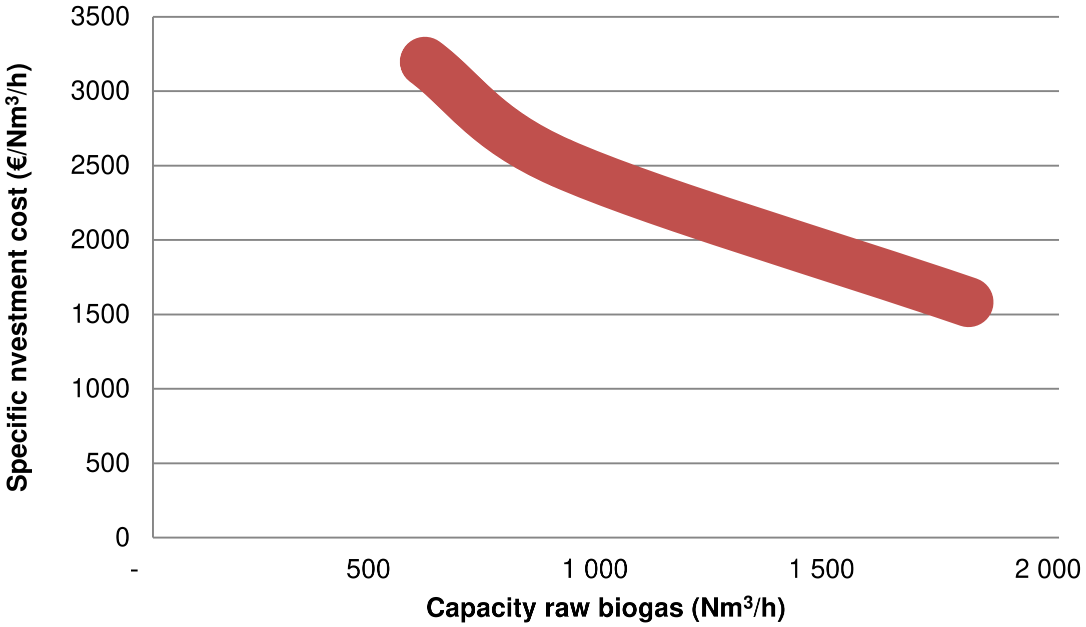

Figure 5 Specific investment cost for amine scrubbing upgrading units.

The standard systems aside, there are additional features that may be included in the delivery, such as additional sulphur removal, should this be required by the customer. Should the system be used for export to the natural gas grid, propane dosing may be included. For the vehicle sector, a bypass control may be included to meet the 97%±1% specification and final compression. With respect to heat integration there are two add-ons offered, namely a cooler for the incoming raw biogas and/or a double heat recovery system yielding one hot water stream at 85°C and one a 55°C instead of one single hot water stream with an intermediate temperature. Other options include control line for export to low pressure gas grid and air compressor for instrumentation. Finally there is a vacuum option for the stripper column. This option allows for operation of the reboiler at 90°C and thus district heat may be used; the vacuum option adds another 0.05 kWh/Nm^3 raw biogas in electricity consumption.

2.1.4 Operation

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 (Abry & R. S. DuPart 1995). The first operating issue is as worrying as it is multifaceted. There are many reasons why specifications are not met, some of which will be mentioned here. First of all, the compliance with design specifications should be checked, e.g. the inlet concentration of CO_2 may have changed significantly or the temperature may be too low in the inlet section. Furthermore, the other flow rates, i.e. gas and liquid, should also be verified and matched with operating specifications. Another explanation could be that the inlet temperature of the amine to the absorber is too high e.g. due to fouled lean/rich or cooling heat exchangers or indeed high ambient temperatures. Another change may be in the amine concentration, rendering it too low or too high; low amine levels may be caused by amine loss. There may also be an upset in the stripping section, resulting in the returning amine solution having too high CO_2 concentrations. Such an upset may be due to foaming, lacking or inadequate reboiler function, contaminated or degraded solvent, plugged packing or leakage in the lean/rich heat exchanger. Degradation of the solvent is mainly due to either oxygen or carboxylic acids in the feed gas. There may also be a misdistribution in the absorber due to plugging, which may be caused e.g. by mechanical failure.

Foaming is most likely to occur on start-up but may also occur at other points in time during operation. Foaming symptoms are high delta pressure over the absorber or stripper, amine carryover from absorber or stripper, swinging liquid levels in any vessel, off-specification of treated gas or poorly stripped solvent. The most common causes are hydrocarbons (foaming at start-up is primarily caused by oil-rests from manufacturing present in piping and vessels), suspended solids (FeS, carbon fines, filter rests) and in rare cases bacteria. For preventing foaming process hygiene is key; it is important to ensure that the inlet gas is free of contaminants and that any make-up water added is foam tested. Foaming should also be temporarily treated by antifoaming agents while the true reason of foaming is investigated. However, it should be noted that excess use of antifoam will have inverse effect and lead to additional foam formation. One preventive measure is to filter a part of the amine flow continuously to remove any particles fed or created in the system.

Amine loss in itself is a much investigated topic (Stewart & Lanning 1994), there are obvious potential losses in all mechanical joints, flanges, pressure gauges, sample line purges, heat exchangers etc. Another potential point of loss is the entrainment of liquid drops in the gas streams, which may be counteracted by demister or washer sections in the gas flow. A sudden increase in losses may be due to the failure of such demister components. An unusually high operating temperature in the stripper exit (leading to higher cooler exit gas temperature) will also increase losses as the exit gas is saturated with amines; the vapor pressure of amines are low but there is still a vapor pressure. The loss of amine may also be due to side reactions caused by contaminants or indeed thermal degradation should any surface in contact with the amine surpass 175°C. Operating experience of biogas plants reveals that no or very little amine make-up is required.

Corrosion is a broad topic and will not be covered in its entirety in this context. The takeaway point is that corrosion may cause serious issues in operation and result in downtime but that it may be controlled and minimized with proper plant design. More information on troubleshooting this type of problem may be found elsewhere (M. S. DuPart et al. 1993).

There are a few types of containments in this kind of systems. They range from traces of organic and inorganic compounds (including bacteria and virus) to oxygen, nitrogen and hydrogen. With respect to oxygen, this is mainly found in landfill gas and will have to be removed prior to the amine stage as the oxygen reacts irreversibly with the active amine components. Raw biogas from an AD does however normally not contain any significant volumes of air, i.e. nitrogen and oxygen. The most important contaminant is H_2S, which is commonly removed before the amine scrubber using activated carbon.

2.2 Pressure swing adsorption

Pressure swing adsorption (PSA) is a dry method used to separate gases via physical properties. Explaining PSA on a macro level, the 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. PSA unit characteristics include feeding pressure, purging pressure, adsorbent, cycle time and column interconnectedness among other things. In Figure 6 a simplified process diagram for a PSA upgrading unit is shown.

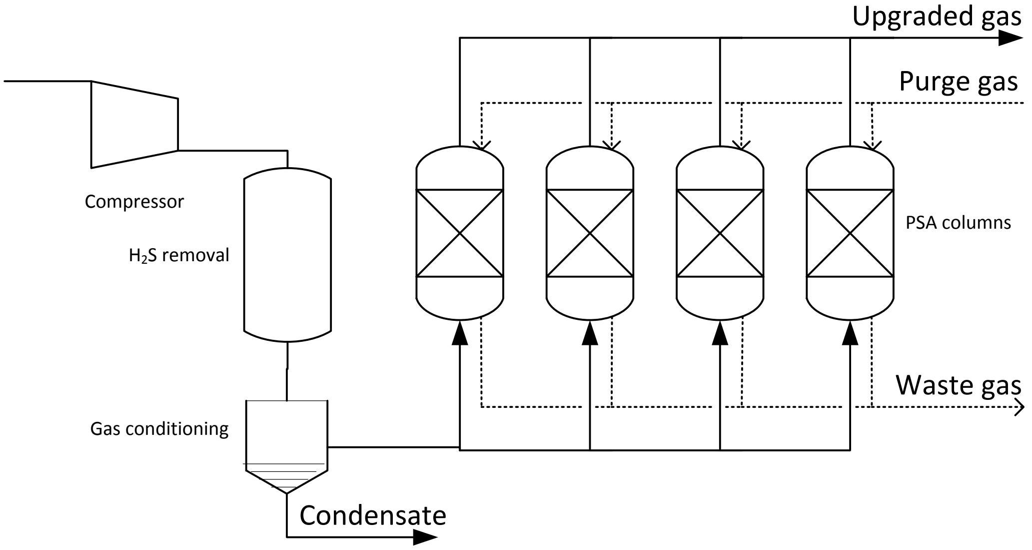

Figure 6 Process diagram for upgrading of biogas with PSA. H2S and water vapour is separated from the raw biogas before it is fed to the adsorption column. Multiple columns work in parallel cycles for a continuous process. Figure adapted from (De Hullu et al. 2008)

In Sweden there are today 55 biogas upgrading units, 8 of which are using PSA technology. The upgraded biogas from these units are used as vehicle fuel and injected to the gas grid, and the feedstocks for the biogas production in these units are sewage sludge, biowaste and manure, according to IEA (IEA Bioenergy Task 37 2012).

2.2.1 Process description

A PSA column cycle principally consists of four phases; a so called Skarstrom cycle is pressurization (1), feed (2), blowdown (3) and purge (4), which is shown below in Figure 7 together with a pressure profile of the cycle phases. During the feed phase the column is fed with raw biogas. The carbon dioxide is adsorbed on the bed material while the methane flows through the column. When the bed is saturated with carbon dioxide the feed is closed and the blowdown phase is initiated. The pressure is decreased considerably to desorb the carbon dioxide from the adsorbent and the carbon dioxide rich gas is pumped out of the column. As the column in the beginning of this phase was filled with raw biogas, some methane is lost with the desorbed carbon dioxide. At the lowest column pressure the purge is initiated. Upgraded gas is blown through the column to empty it from all the carbon dioxide that has desorbed from the column bed. The column is now regenerated and can be repressurized, either with raw biogas or with upgraded gas, and the cycle is complete (Grande 2011).

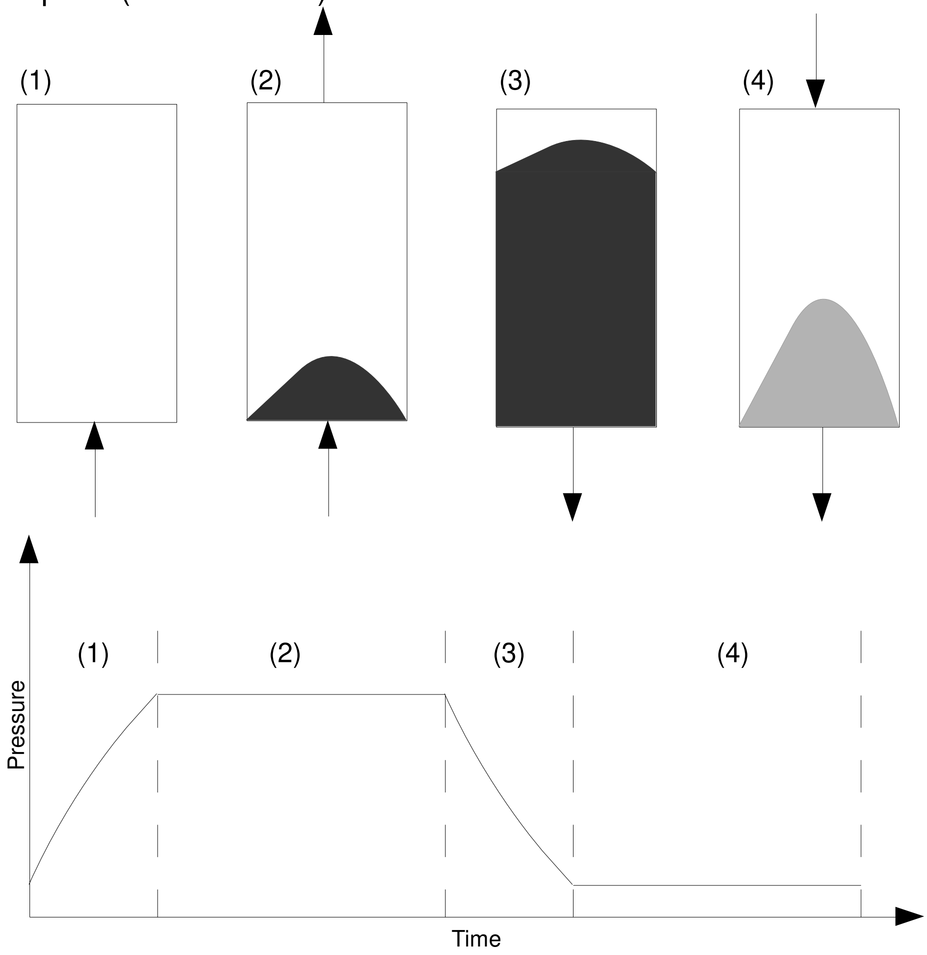

Figure 7 Schematics of the four phases in the Skarstrom cycle and a pressure profile of the cycle. Figure adapted from (Rege et al. 2001)

As this cycle consists of four phases, a common design for PSA units includes four columns. Thus one of the columns is always engaged in adsorption while the other three are in different phases of regeneration. To reduce the loss of methane from the process the columns are usually interconnected so that the exiting gasflow from one column during blowdown is used to pressurize another column in a pressure equalization phase, which also reduces the energy consumption of the process. A PSA column cycle is typically 2-10 min long (Spoorthi et al. 2010; Grande 2011).

Using several columns there are many ways of modifying the process cycle to increase the yield of methane from raw biogas to upgraded gas, reduce the methane loss and increase the energy efficiency of the process. The gas flow from the blowdown phase can be recirculated together with the raw biogas, which can increase the yield with up to five per cent. New advanced process cycles with nine cycle phases have been proposed. According to simulations, a four column PSA unit using this new cycle would be able to produce upgraded gas with 98% methane purity with a higher yield and lower energy consumption (Santos et al. 2011). Increasing the number of columns can also give new opportunities for design of new cycles, as this enables a more advanced flow of gases between columns to optimize energy use. However, the complexity and installation cost will inevitably increase which means that there is a trade-off between system efficiency and cost. Research and development of PSA technology focusing on minimizing PSA units, optimizing the technology for small scale applications, reducing energy use and combining different adsorbents to combine adsorbent characteristics and integrating separation of H_2S and CO_2 in a single column (Grande 2011; Spoorthi et al. 2010; Maheshwary & Ambriano 2012).

Figure 8 PSA upgrading unit in Sweden. The exterior view (left) shows, from the left, the catalytic oxidizer, active carbon filters, pressure levelization tank (white) and a container with the PSA columns. The interior view (right) shows valves and PSA columns. Images from E.ON Gas Sweden.

2.2.2 Theoretical background

The choice of absorbent, the bed material which selectively adsorbs carbon dioxide from the raw gas stream, is crucial for the function of the PSA unit. The adsorbent is a porous solid with a high specific area in order to maximize the contact with the gas. Common adsorbent materials are activated carbons, natural and synthetic zeolites, silica gels and carbon molecular sieves (CMS) (Grande 2011; Alonso-Vicario et al. 2010). A new type of adsorbent material is the metal-organic frameworks (MOFs). These materials have previously been used to store gases such as hydrogen, but also show a large potential for use in PSA. At the time of writing, there are no commercial systems using MOFs available; the application is still in research. For these new materials to be implemented in PSA applications successfully they not only have to have a activity and selectivity for carbon dioxide but also be non-hazardous, readily available and stable for a long time (Cavenati et al. 2008; Pirngruber et al. 2012). Generally, adsorbents are one of two types; equilibrium adsorbents (activated carbons, zeolites) which have the capacity to adsorb much more carbon dioxide than methane, while kinetic adsorbents (CMS) have micropores which the small carbon dioxide molecules can penetrate faster than the hydrocarbons which thus pass the column bed unretained (Grande 2011).

The correlation between gas adsorption and pressure for a specific adsorbent is shown in adsorption isotherm diagrams. In Figure 9, the adsorption isotherms for two generic adsorbents, (1) and (2), are shown. The isotherms show the equilibrium level of adsorption at a given pressure. During a PSA operation the raw biogas is fed into the column at the pressure P_{feed}, at which the adsorbents can retain a given amount of carbon dioxide, $q_{feed,1}$ and $q_{feed,2}$. When equilibrium is reached, i.e. when the adsorbent is saturated with carbon dioxide, the pressure is decreased to P_r to regenerate the adsorbent. The carbon dioxide desorbs from the surface and a new equilibrium will be reached, $q_{reg,1}$ and $q_{reg,2}$. Δq thus equals the amount of carbon dioxide that has been separated from the raw gas stream during this process cycle. Although the adsorbent (2) has the capacity to adsorb much more carbon dioxide at P_f, it is obvious that adsorbent (1) is a better choice for this process as Δq_1 is much larger than Δq_2. Thus, a good adsorbent has a nearly linear isotherm, as a curve with a very steep first part makes it necessary to desorb the carbon dioxide at very low pressures to ensure an efficient separation which increases the power consumption of the process (Grande 2011).

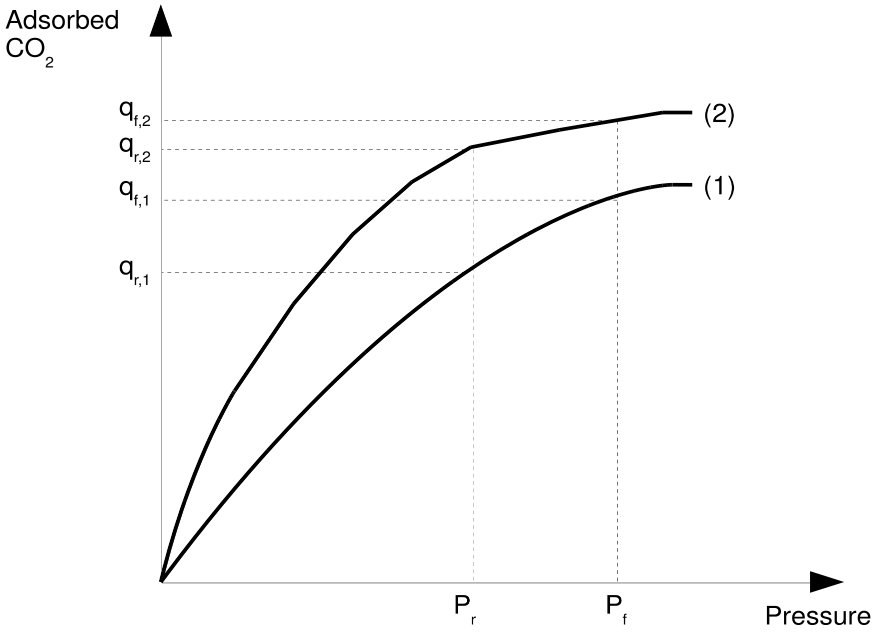

Figure 9 Two generic adsorbant isotherms showing the partial pressure of CO2 in the gas streams at feed pressure (high) and regeneration pressure (low). Δq equals the separating capacity for one column cycle. Image adapted from (Grande 2011).

2.2.3 Operation

Emissions from a PSA unit is the carbon dioxide rich gas which is let out from the column during blowdown and purge. As previously mentioned the gas from the purge phase is usually recirculated to enhance the yield of methane from the upgrading process. The gas from the blowdown step does however also contain some methane which can be dealt with in several ways.

The vent gas from the process can be torched, if the methane content of the gas is high enough, or it can be catalytically oxidized in a special unit to prevent methane leakage. The vent gas stream can also be combusted together with an addition of raw biogas from the digester to produce heat which can be used locally, e.g. to heat the digester or supply heat to a local heat demand. Burning methane does however decrease the yield of upgraded biomethane (Arnold 2011; Arnold & Vetter 2010). In lack of a local heat demand the most important issue is to ensure a minimal leakage of methane to the atmosphere. Many units do not have system to oxidize the methane in the vent gas stream. According to PSA suppliers the loss of methane to the atmosphere should in these cases however be below 2% of total methane production. Measurements conducted within the Swedish programme Voluntary Agreement, set up by the Swedish Waste Management Society in 2007 to study losses and emissions from biogas production, show low emissions of methane. Losses from the PSA upgrading units measured within this programme were 1.8% in median, whereas the average value was 2.5% due to a single unit with relatively high losses. Units with end-of-pipe treatment, i.e. combustion or catalytic oxidation of methane, showed even lower methane losses with a median of 0.7% and an average value of 1.0% (Holmgren et al. 2010).

2.2.4 Investment cost and consumables

As no manufucturer of PSA units have participated as full partner in this project, the accessible information on investment costs are limited. Earlier studies have shown that the investment for a PSA unit with a capacity of 500 Nm3/h is around 1.1-1.4 M€ (Urban et al. 2009), adjusted for inflation since 2009. The specific investment cost decreases with increasing throughput capacity according to this and other studies, but the investment cost is also heavily influenced by design factors such as raw gas composition, product gas quality specification and quality of pressure vessel materials according to a manufacturer. The estimated investment cost curve, based on data from (Urban et al. 2009) is shown in Figure 10.

PSA technology does not demand a lot of resources, which makes it suitable for many applications. The technology is dry; it does not consume any water and also does not create contaminated waste water. The process also does not require any heat. However, the electricity demand of the process is significant due to the relatively high pressures used in the process. Further, a cooling machine may be needed for the demoisturisation of the gas and the cooling of the main compressor if no external cooling water is available.

According to producers of PSA systems electricity consumption for upgrading with PSA is 0.15-0.3 kWh/Nm^3 raw biogas Research literature suggests similar levels of electricity consumption, 0.2 kWh/Nm^3 raw biogas for the upgrading plus an additional 0,17 kWh/Nm3 product gas for drying and final compression (Pertl et al. 2010). Process values from Swedish PSA units show an energy demand of 0.25-0.3 kWh/Nm^3. The electric energy demand for PSA units is thus well verified. The lowest values are probably reachable in a system which can utilize external cooling water whereas the somewhat higher values are probable for a system with a cooling machine. The use of a catalytic oxidizer also adds to the energy demand, which in that case probably will be close 0.3 kWh/Nm^3.

Using a filter with activated carbon to separate H_2S before the PSA columns will include a consumption of activated carbon for this separation. This demand is however rather limited. Maintenance of a PSA-unit is usually planned to twice a year, according to system producers.

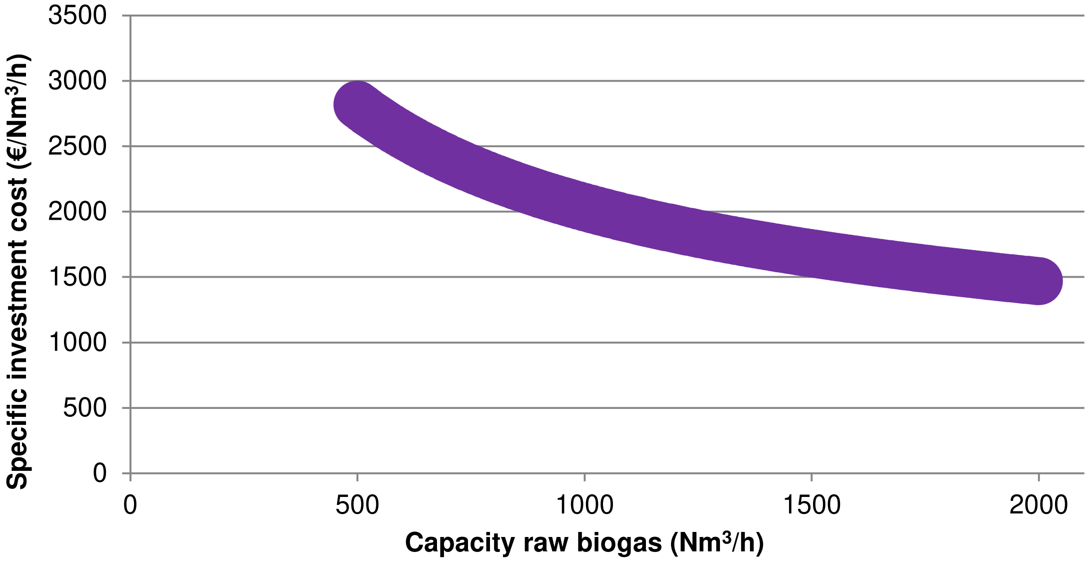

Figure 10 Specific investment cost for PSA upgrading units.

2.3 Membrane separation

This chapter has been written in cooperation between the authors and the companies Air Liquide Medal, EnviTec Biogas, Evonik Fibres, MemfoACT AS and DMT Environmental Technology that all are active within the area of biogas upgrading.

A membrane is a dense filter that can separate the components in a gas or a liquid down to the molecular level. Membranes were used for landfill gas upgrading already in the beginning of the 1990s in the USA (Petersson & Wellinger 2009). These units were built with less selective membranes and a much lower recovery demand for the methane. In most applications on the European market today, the biomethane needs to have a methane concentration around 97-98% and the upgrading process needs to have a methane recovery above 98%. Exceptions exist in countries, e.g. the Netherlands and Germany, were L gas grids exist with lower Wobbe index limitations.

To be able to combine high methane recovery with high methane concentration requires, selective membranes and suitable design. One of the first unit of this type was built in Bruck in Austria 2007 with membranes from Air Liquide Medal^{TM} and since then several more units with similar properties have been built in e.g. Austria, Germany and France. In 2012, at least seven new units have been built with membranes from various manufacturers such as Air Liquide Medal^{TM}, Evonik Sepuran® and MemfoACT AS.

The membranes used for biogas upgrading retain most of the methane while most of the carbon dioxide permeate through the membrane, see Figure 11. This results in biomethane that can be injected into the gas grid or used as vehicle fuel.

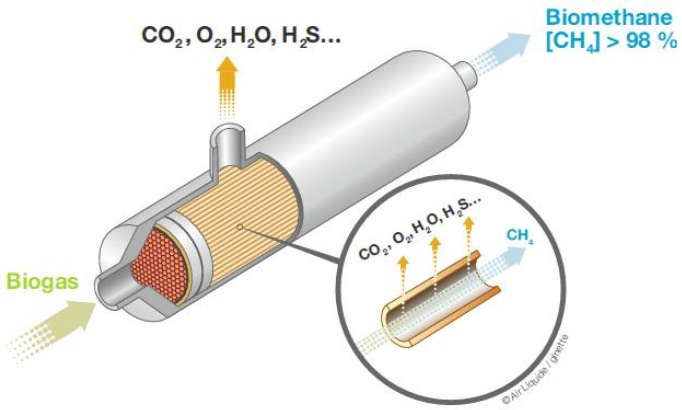

Figure 11 Illustration showing the separation involved during upgrading of biogas with membranes. Image from Air Liquide.

During the separation of carbon dioxide, also water vapor, hydrogen and parts of the oxygen are removed from the biomethane. The permeation rate through a typical membrane (made of a glassy polymer) used in biogas applications, is mainly depending on the size of the molecules (Baker 2004) but also on the hydrophilicity. The relative permeation rates shown in Figure 12 are based on experiences from the membrane manufacturer.

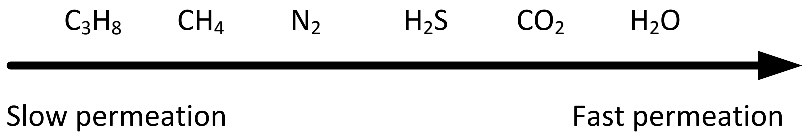

Figure 12 Relative permeation rate of different molecules through a membrane produced from a glassy polymer.

On the market today, membranes produced by several manufacturer are used for biogas upgrading, e.g. two types of polymeric (glassy polymers) hollow fibre membranes (Air Liquide Medal^{TM} and Evonik Sepuran®) and one carbon membrane (manufactured by MemfoACT AS), see Figure 13. The membranes are continuously improved to get higher selectivity, higher permeability and cheaper manufacturing.

Figure 13 Hollow fibre membrane from Evonik Sepuran to the left, from Air Liquide Medal in the middle and carbon membrane from Memfoact to the right. Images from Evonik Fibres, Air Liquide and Memfoact.

2.3.1 Process description

A typical and simplified design of a biogas upgrading unit based with membranes is shown in Figure 14.

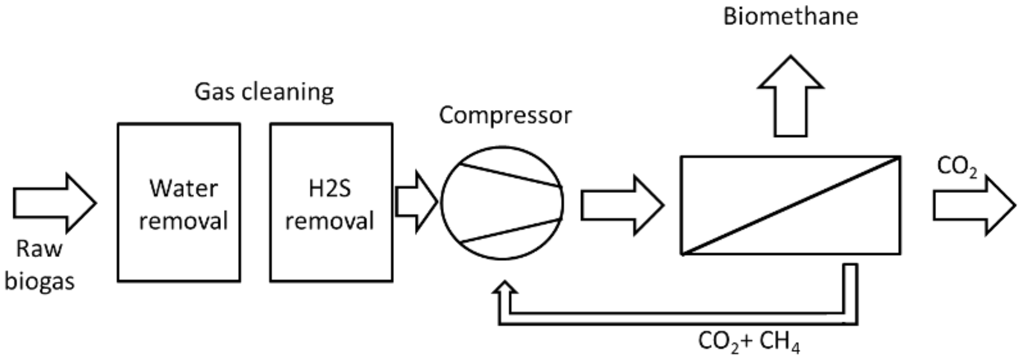

Figure 14 Typical design of a biogas upgrading unit with membranes

The raw biogas is normally cleaned before compression to remove water and hydrogen sulfide. In cases where ammonia, siloxanes and volatile organic carbons are expected in significant concentrations, these components are also commonly removed before the biogas upgrading. The water is removed to prevent condensation during compression and hydrogen sulfide is removed since it will not be sufficiently separated by the membranes. The water is commonly removed by cooling and condensation while hydrogen sulfide commonly is removed with activated carbon. Additional to this cleaning, it is also common to have a particle filter to protect the compressor and the membranes.

After gas cleaning, the biogas is compressed to 6-20 bar(a). The pressure that is used depends on requirements on the specific site as well as the design and manufacturer of the upgrading unit. Since oil lubricated compressors are commonly used, it is important to have an efficient oil separation after compression. This oil separation is important not only for the oil residues from the compressor but also for removing oil naturally occurring in the biogas. The oil will otherwise foul the membrane and decrease its lifetime.

The membrane separation stage is designed differently depending on the manufacturer of the system and the membranes they are using. Three of the most common designs on the market today are shown in Figure 15.

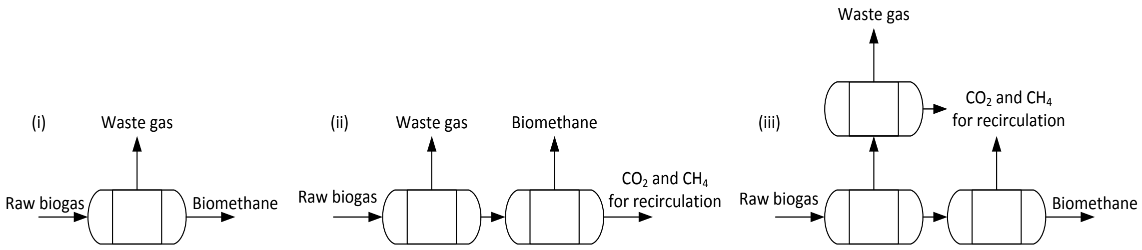

Figure 15 Three different designs of the membrane stage, that are available on the market today.

The first design (i) includes no internal circulation of the biogas and therefore lower energy consumption for the compression. However, the methane loss will be higher and it is important to use membranes with high selectivity, i.e. large difference between the permeation rate of methane and carbon dioxide, to minimize the methane loss. It is also beneficial if methane in the off-gas can be used in an efficient way by e.g. cogeneration in a boiler or CHP. The second design (ii) is used in most biogas upgrading units built with membranes from Air Liquide Medal^{TM}. This design increases the methane recovery compared to design (i). In this case the permeate (the gas passing through the membrane) from the first membrane stage is removed from the system while the permeate from the second membrane stage is recirculated back to the compressor to minimize the methane slip, which will increase the energy consumption. The third design (iii) is used with membranes from Evonik Sepuran®. The retentate (the gas not passing through the membrane) from the first stage is polished in the second membrane stage, in a similar way as in design (ii) to obtain a product gas of with a purity of more than 97% methane. Additional to design (ii), also the permeate of the first stage is polished in a third membrane stage, to minimize the CH_4 concentration in the off-gas and the volume of gas circulated back to the compressor. The permeate stream of the second stage and the retentate of the third stage are combined and recycled to the compressor.

In a membrane unit, the main part of the remaining water after compression is separated from the biomethane together with the carbon dioxide. Therefore, a gas dryer is commonly not needed to further decrease the dew point. Figure 16 shows the biogas upgrading plant in Poundbury in UK based on membrane technology.

Figure 16 The membrane biogas upgrading plant in Poundbury with a capacity of 650 Nm^3/h raw biogas. Images from DMT.

2.3.2 Theoretical background

The gas stream going into a membrane is called the feed stream. The feed is separated into permeate and retentate inside the membrane module. Retentate is the gas stream that does not pass through the membrane while permeate is the gas stream that passes through the membrane.

The transport of a gas molecule through a dense polymeric membrane can be expressed by Eq. 3 (Baker 2004).

$$j_i = \frac{D_i K_i \Delta p_i}{l} \qquad \text{Eq. 3}$$

In the equation j_i denotes the molar flux for gas i, D_i is the permeate diffusion coefficient, K_i is the sorption coefficient, Δp_i is the difference in partial pressure between the feed and permeate side and l is the membrane thickness.

The permeability of a membrane is defined as the product of the diffusion and sorption coefficient and the membrane selectivity for gas “a” and “b” is defined as the permeability of gas “a” divided by the permeability of gas “b”. Which coefficient, sorption or diffusion, that dominates Eq. 3 depends on the type of material that is used in the membrane. According to Baker (2004), the permeability decreases with increasing size of the molecule in a glassy polymer (commonly used in the membranes for biogas upgrading), since the diffusion coefficient is dominating.

The driving force for the separation of gases throughout the membrane is the difference between the partial pressure of carbon dioxide in the retentate and the permeate, see Eq. 3. The permeate mainly consists of carbon dioxide and at atmospheric pressure this yields a partial pressure of carbon dioxide close to 1 bar(a). If the operating pressure in the system is 10 bar(a), the difference in partial pressure, and thus the driving force, would be zero when 10% carbon dioxide remains in the retentate. Since such upgrading is commonly not sufficient for the market, vacuum is frequently used on the permeate side to decrease the partial pressure in the permeate to facilitate methane concentrations above 97% and less than 3% carbon dioxide in the produced biomethane. The need of vacuum is minimised by the fact that the membrane stage is commonly split into two stages, where the removal of the main part of the carbon dioxide takes place without vacuum in the first stage.

2.3.3 Investment cost and consumables

Figure 17 shows the approximate range of the investment costs for biogas upgrading units on the market today. These values have been discussed with several companies that are selling membrane upgrading units. The investment cost is highly dependent on the design of the plant. The values in the figure are referring to plants designed for a specific capacity that are not prepared for future expansion or redundancy on key components. Neither gas cleaning nor off-gas treatment is included in the price.

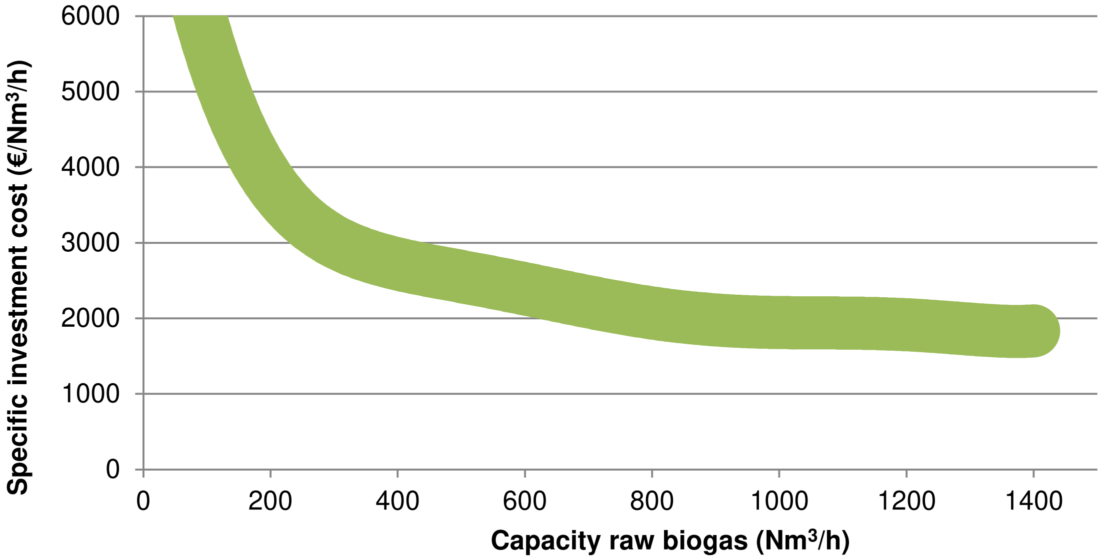

Figure 17 Specific investment costs of membrane based biogas upgrading units available on the market 2012.

The availability of a biogas upgrading unit is commonly guaranteed to be above 95%. Some existing membrane plants are operating with availabilities above 98%. The availability can always be increased by redundancy of key components which of course will increase the investment costs.

Service contracts are offered by most manufacturers for an additional cost of 3-4% of the investment cost, which includes membrane replacement. Few consumables are used in a membrane upgrading unit. It is commonly oil for the compressor and activated carbon for the removal of hydrogen sulfide that is needed. Additional maintenance costs for other pretreatment steps could also be of importance. The estimated life time for the membranes is around 5-10 years.

The energy consumption for a membrane upgrading plant is mainly determined by the energy consumption of the compressor. As will be discussed in the chapter 3, the energy consumption of a compressor depends very little on the methane concentration in the raw biogas. Therefore, the energy consumption will be independent of raw gas composition as long as it is expressed as kWh/Nm^3 raw biogas. According to the manufacturers, an electricity in the interval 0.20-0.30 kWh/Nm^3 can be guaranteed. This demand is valid for most applications and independent of size.

The energy consumption for a specific application will depend on several parameters such as the methane slip, the required carbon dioxide removal (i.e. methane concentration of the produced biomethane), the installed membrane area and the applied pressure. If high concentration of methane is required in the biomethane, a larger membrane area and/or higher pressure is needed. Furthermore, if a larger methane slip is allowed, less biogas needs to be recirculated to the compressor which in turn will decrease the energy consumption. Finally, the installed membrane area will determine which pressure that is needed to upgrade a specified volume of biogas. If the membrane area is large, a lower pressure is needed since lower flux (permeate flow per membrane area) can be accepted, see Eq. 3.

2.3.4 Operation

Several actors on the market today can guarantee a methane concentration above 98%. As discussed before, a higher energy consumption and possibly also a larger membrane area is required to increase the methane concentration in the upgraded biogas.

The methane recovery varies between the different applications and designs, as presented in Figure 15. Recoveries between 98% and 99% are possible for units with design (ii) whereas recoveries around 99-99.5% are expected for units with design (iii). If the methane in the off-gas needs to be removed it is today either oxidized in a regenerative thermal oxidizer or used in combined heat and power plants together with raw biogas. Another possibility that exist on the market is liquefaction of the carbon dioxide and thereby recovering 100% of the methane in the waste gas by cryogenic separation. The carbon dioxide can then be delivered either as a liquid or a gas depending on the request from the costumer.

2.4 Water scrubbing

This chapter has been written in cooperation between the authors and the companies Econet Vatten & Miljöteknik AB, Greenlane Biogas AB and Malmberg Water AB, which all are active in the biogas upgrading business as water scrubber manufacturers.

A water scrubber is a physical scrubber that uses the fact that carbon dioxide has much higher solubility than methane in water. In a water scrubber, carbon dioxide is separated from the raw biogas and dissolved into the water in the absorption column by using high pressure, normally 6-10 bar(a). The carbon dioxide is then released from the water again in the desorption column, by addition of air at atmospheric pressure, see Figure 18.

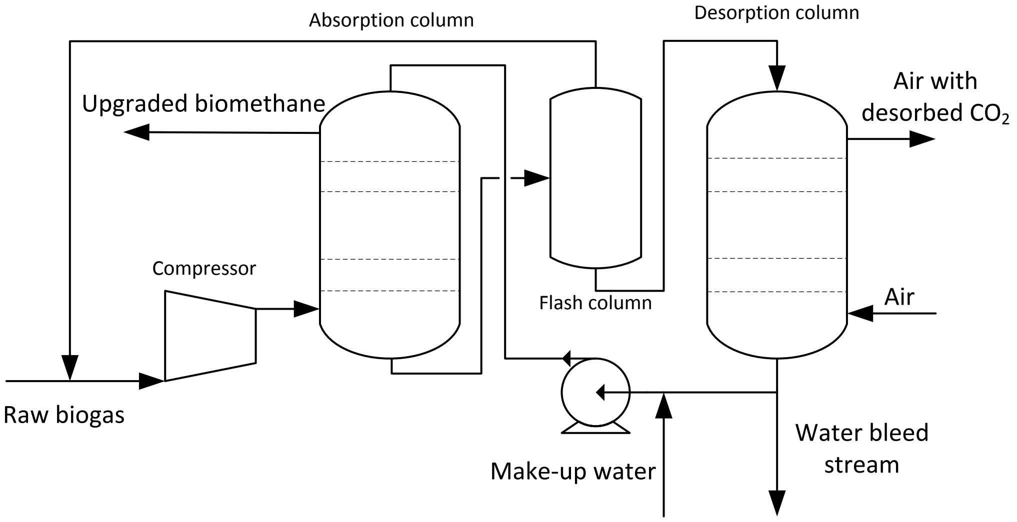

Figure 18 Schematic illustration of a water scrubber.

Ten years ago, units without circulation of the water were built (Persson 2003). Some of them still exist today, but all new plants have a recirculating system for the water, as shown in Figure 18. The units with the circulating water system have more stable operation and less operational problems.

2.4.1 Theoretical background

The absorption of carbon dioxide and methane into water is described by Henry's law (Eq. 4), which describes the relation between the partial pressure of a gas and the concentration of the gas in a liquid in contact with the gas (Stumm & Morgan 1996).

$$C_A\ (M) = K_H\ (M/atm) * p_A\ (atm) \qquad \text{Eq. 4}$$

In Eq. 4, C_A is the concentration of A in the liquid-phase, K_H is Henry's constant and p_A is the partial pressure of A. The Henry constant at 25°C (K_H) for carbon dioxide is $3.4*10^{-2}$ M/atm and for methane $1.3 * 10^{-3}$ M/atm (Stumm & Morgan 1996), resulting in a solubility for carbon dioxide that is approximately 26 times higher than for methane. If the raw biogas consists of 50% of methane and carbon dioxide respectively, the partial pressures of these gases will be equal in the bottom of the absorption column. Furthermore, if 100% of the carbon dioxide is dissolved in the water, at least 4% of the methane will also be dissolved in the water – in an ideal system.

The amount of water needed to remove a certain amount of carbon dioxide depends on the design of the column, the required carbon dioxide concentration in the upgraded biogas and the solubility of carbon dioxide in a certain volume of water (determined by the pressure and the temperature). The height of the column and the type of packing will determine the number of theoretical plates, which is a hypothetical stage where two phases establish equilibrium with each other. A column with more theoretical plates will be more efficient and require a lower water flow to treat a certain volume of biogas.

The removal of the last molecules of carbon dioxide from the biogas is the most difficult separation, due to the low partial pressure of the remaining carbon dioxide. Therefore, a higher water flow will be required to reach very low carbon dioxide concentrations (Swanson 2011). How much the water flow needs to be increased will depend on the number of theoretical plates in the column.

With a specific design and a specified carbon dioxide concentration in the upgraded biogas, the water flow will be determined by the solubility of carbon dioxide. This is the case in most units and the water flow can then be described as Eq. 5.

$$Q_{water}(l/h) = \frac{Q_{CO_2}(g)(mol/h)}{C_{CO_2}(aq)(M)} \qquad \text{Eq. 5}$$

where Q_{water} is the required water flow, Q_{CO2} is the molar flow of carbon dioxide that shall be removed and C_{CO2} is the solubility of carbon dioxide described as the maximum concentration possible to reach in water.

The amount of carbon dioxide that needs to be removed is described by the total flow rate and the gas composition, while the solubility is determined by Henry's law (Eq. 4). This gives the following expression

$$Q_{water}(l/h) = \frac{Q_{biogas} * \%CO_2(mol/h)}{K_H * p_{tot} * \%CO_2(M)} \qquad \text{Eq. 6}$$

where Q_{biogas} is the total biogas flow, $\%CO_2$ is the percentage of carbon dioxide in the raw biogas and P_{tot} is the pressure in the absorption column. The percentage of carbon dioxide in the incoming biogas can be removed from this expression, showing that the needed water flow is independent of the percentage CO_2 in the incoming biogas.

The value of Henry's constant for a specific gas is only valid at one specific temperature. When the temperature is increased, the solubility usually decreases and vice versa. The following example of the van't Hoff equation is one example that can be used to get an approximation of how the solubility varies with the temperature (Sander 2011).

$$K_H(T_2) = K_H(T_1)\exp\left[C\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] \qquad \text{Eq. 7}$$

In Eq. 7, T_1 and T_2 are the absolute temperatures for which the constant is known and searched respectively, while C is a specific coefficient which is defined as $C=d\ln(kH))/d(1/T)$. For CO_2 in water, the value of this constant is 2400.Figure 19 shows how the solubility of CO_2 changes between 10°C and 25°C according to Eq. 7. As can be seen in the figure, the solubility is more than 50% higher at 10°C than at 25°C. A similar graph has also been published earlier (Petersson & Wellinger 2009).

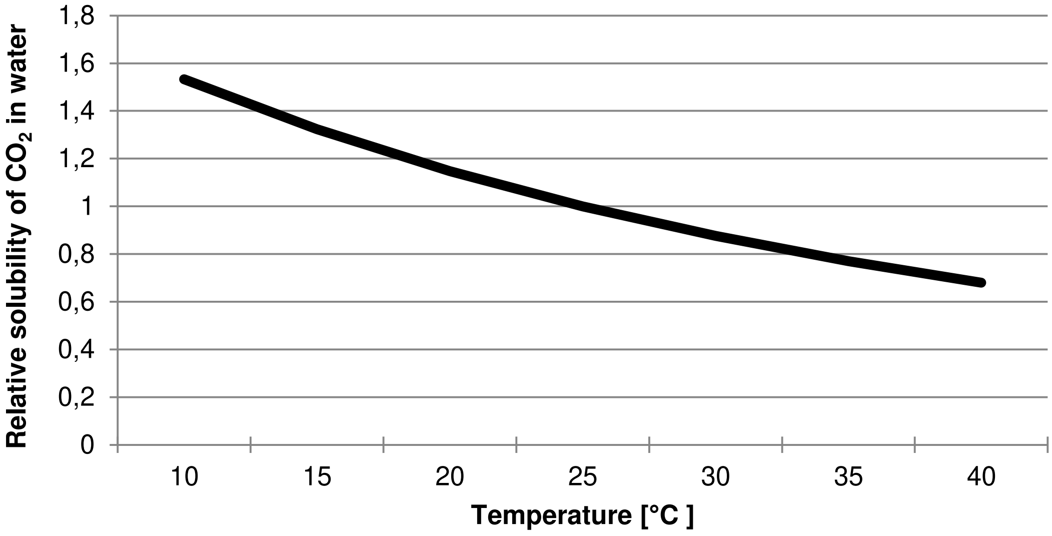

Figure 19 Relative solubility of CO2 in water in the temperature interval between 10°C and 40°C. Solubility normalized to the value at 25°C.

The importance of pH for the water flow is discussed in detail in Appendix I which shows that pH has no effect on the water flow needed to remove a certain amount of carbon dioxide from the biogas.

2.4.2 Process description

A typical and simplified design of a biogas upgrading unit is shown in Figure 18. A photograph of a water scrubber with a unit for regenerative thermal oxidation (RTO) is shown in Figure 20 .The raw biogas is usually allowed to have a temperature up to 40 ºC when it arrives to the upgrading plant. The pressure of the raw biogas is increased to around 6-10 bar(a) (depending on the manufacturer and application) before it enters the absorption column. By increasing the pressure and lowering the temperature (to the temperature of the water in the scrubber), most of the water in the biogas is condensed and separated from the gas before it enters the absorption column. If the raw biogas is saturated with water at 40 ºC when it enters the upgrading unit, only around 5% of the water content will remain in the gas phase if the pressure is increased to 6 bar(a) and the temperature is lowered to 15 ºC (calculated with Antoine equation). Also, volatile organic substances and ammonia have been identified in this condensate.

Figure 20 A water scrubber for biogas upgrading. The two towers are the absorption and desorption columns. The scrubber is equipped with an RTO unit which is shown to the right in the photograph. Image from Malmberg Water

The pressurized biogas is injected into the bottom of the absorption column and water is injected to the top of the column. It is important that the water and the gas have a counterflow to minimize the energy consumption as well as the methane loss. The water leaving the absorption column has been equilibrated with the highest partial pressure of carbon dioxide and the lowest partial pressure of methane. This results in that the water contains as much carbon dioxide as possible and as little methane as possible, see Eq. 4.

The absorption column is filled with random packing, a typical design of this packing is shown in

Figure 21, to increase the contact surface between the water and the biogas to make sure that the carbon dioxide is absorbed as efficiently as possible in the water. The height of the bed and the type of packing determines the efficiency of separation in the column, whereas the diameter determines the gas throughput capacity (Strigle 1994). Thus, a higher bed can clean biogas with lower incoming methane concentration and a wider column can treat a larger volume of biogas. It is also important to know that the diameter does not only increase the maximum capacity but also the minimum raw gas flow that is possible to treat. If the load is too low, the water will not be evenly distributed over the cross section area and the biogas will be mixed with the water in a suboptimal way. The minimum load varies between 20% and 50% of the maximum capacity, depending on the design.

Figure 21 A typical design of random packing which is used in water scrubber absorption columns. Image from Malmberg Water.

To avoid releasing the methane that is absorbed by the water in the absorption column, the water is transported into a flash column. In the flash column, the pressure is decreased to around 2.5 – 3.5 bar(a). Some of the carbon dioxide as well as the main part of the methane is released from the water and circulated back to the compressor. Since much more carbon dioxide than methane is dissolved in the water, the composition of the released gas in the flash column will normally be 80-90% carbon dioxide and 10-20% methane. Thereby, the partial pressure of the methane will only be 10-20% of the pressure in the flash column, resulting in a low solubility of methane according to Eq. 4. The water that is transported to the desorption column will contain the main part of the carbon dioxide but less than 1% of the methane in the raw biogas.

The pressure in the flash column has to be decreased to maintain the same methane slip if the methane concentration in the raw biogas increases. The reason is that more methane and less carbon dioxide is transported with the water into the flash column, resulting in a changed composition – more CH_4 and less CO_2 – in the flash column gas volume. If the pressure is kept constant, the partial pressure of methane will increase significantly resulting in higher solubility in the water according to Eq. 4. For a system working at 8 bar(a), the flash pressure has to be decreased from about 3 bar(a) to about 2 bar(a) when the methane concentration is increased from 50% to 80% in the incoming raw biogas.

The flash column has no packing and is designed with a diameter wide enough to decrease the vertical speed of the water to such an extent that even small gas bubbles are able to rise instead of being dragged into the desorption column. The top of the flash column should be designed so that water is not sucked into the gas going back to the compressor. The volume of this gas stream going back to the compressor is usually 20-30% of the incoming raw gas flow.

After removing most of the methane from the water in the flash column, the carbon dioxide is released from the water in the desorption column. The water enters the top of the desorption column, while air is entering at the bottom. This column is also filled with random packing to increase the contact surface between the air and the water. The low percentage of carbon dioxide in the air in combination with decreased pressure results in a partial pressure of carbon dioxide close to zero and thus a very low solubility of carbon dioxide in the water. The water leaving the desorption column is virtually free from carbon dioxide and is pumped back into the top of the absorption column. The time it takes to circulate a specific volume of water one time in a water scrubbing system is around 1-5 minutes depending on design and current load.

Table 9 shows how much water is needed to upgrade 1000 Nm^3 of biogas per hour to less than 2% CO_2 in the upgraded biogas. Values are given for various temperatures and pressures. The methane concentration in the raw biogas has no influence on the water flow, as described previously. The pressure is directly proportional to the needed water flow, as shown in Eq. 4 and a water flow corresponding to another pressure can therefore easily be calculated. The required water flow depends also on the temperature of the water. A few degrees lower temperature will decrease the required water volume several percentage units. This relation is shown in Eq. 7 and Figure 19.

Table 9 Typical water flow needed to upgrade 1000 NM^3/h raw biogas.

Pressure [bar(a)]	**Water temperature [°C]**	**Water flow [m^3/h]**
8	20	210-230
8	14	180-200
6.5	14	210-230

2.4.3 Operation

The water scrubber is the upgrading method on the market today that is the least sensitive to impurities. Commonly, the biogas is injected directly from the digester.

The allowed concentration of hydrogen sulphide varies between different manufacturers and is commonly between 300 and 2500 ppm. Hydrogen sulphide is efficiently absorbed by the water during the absorption and released during the desorption process. Exiting air streams with high concentrations of hydrogen sulphide must be treated before they are vented to the atmosphere to avoid environmental and health problems. This is commonly performed by an activated carbon filter or some type of regenerative thermal oxidation (RTO).

In the desorption column, where air is added, the hydrogen sulphide will be partly oxidized to elementary sulfur (Ryckebosch et al. 2011) and sulfuric acid. The rate of oxidation of H_2S in air-saturated water has been studied and a clear correlation with both the temperature and the pH of the water has been shown (Millero et al. 1987). The rate of oxidation was increased around 3 times when the temperature was increased with 20 degrees and around 4 times when the pH was increased from 4 to 8 at the investigated conditions.

If hydrogen sulphide is oxidized to sulphuric acid, the alkalinity will decrease and the pH will drop. This has been experienced in several plants and could cause corrosion on various components, such as water pumps and pipes, especially if these are made of cast iron. The corrosion rate also depends on the chlorine concentration in the water. A higher chlorine concentration results in a more severe corrosion. This problem can be avoided by adding alkalinity during the operation or exchanging a larger volume of water in the system. Furthermore, by decreasing the hydrogen sulphide concentration in the biogas, decreasing the process water temperature and by operating at lower pH in the water, the produced amount of sulphuric acid can be minimized.

In several plants that are in operation in Sweden today, no antifoaming agent is needed. In contrast, in other plants the operation is impossible if the antifoaming agent is not added, especially in Germany. The reason for this is, as of today, not properly understood. The antifoaming agents that are used are based on silica as well as on organic degradable compounds. The cost for antifoaming agents is marginal when compared to the total operation and capital cost.

Foam can be created in the water scrubber both by molecules excreted from microorganisms, such as carbohydrates, or by compounds transported with the biogas that are dissolved in the water. It has been experienced in some plants that the antifoaming agent has been needed from day one, suggesting that something was coming with the biogas into the system, while severe foaming has been observed in clear correlation with microbiological growth in other units. It is not clear if the positive effect from the antifoaming agent only originate from removing foam or if the decreased surface tension also is of importance (Strigle 1994). The need of antifoaming agent is usually indicated by difficulties to reach low carbon dioxide concentration (0-2%) in the upgraded biogas. This is due to the decreased contact between the water and the biogas that decreases the efficiency of absorption in the column.

There will always be living microorganisms in a water scrubber and depending on various parameters such as water temperature, pH in the water, composition of the raw gas, existing microorganisms in the surrounding air and addition of chemicals, e.g. biocides, this situation will vary between different sites. Occasionally, some water scrubbers are clogged by fungi and other type of microorganisms (Håkansson 2006). The random packing then has to be removed from the column and replaced by cleaned packing before the unit can be started again. Figure 22 shows how pall rings are clogged by microbial growth.

Figure 22 Microbial growth on pall rings used in water scrubber columns. Image from (Tynell 2005)*.*

Historically, microbial growth in the water scrubber columns used to be a larger problem as the water temperature in the scrubbers used to be higher – especially in the summer – and in units where treated sewage water was used as process water. This water contained more nutrients and COD than drinking water does, which is the normal quality used today. Some old units are still in operation, but no new systems of this type are built today. Even though the problem used to be more severe, it still exists today and is treated by addition of biocides and/or frequent cleaning of the scrubber columns. However, the manufacturers are aware of this possible problem and claim to know what to do if it occurs, in order to minimize lost process availability.

2.4.4 Investment cost and consumables

The investment cost for a water scrubber has been rather stable during the last years, which in turn indicates that the technology is mature. Today, the value of the currency and exchange rates are probably as important as the development of the technique for changes in the investment cost. Figure 23 shows the approximate range of the investment costs for water scrubbers on the market today. The values have been discussed and accepted by the companies participating in this study. The values in the figure are referring to plants designed for a specific capacity and not prepared for future expansion or redundancy on key components. Neither gas cleaning, heat recovery systems nor off-gas treatment is included in the price.

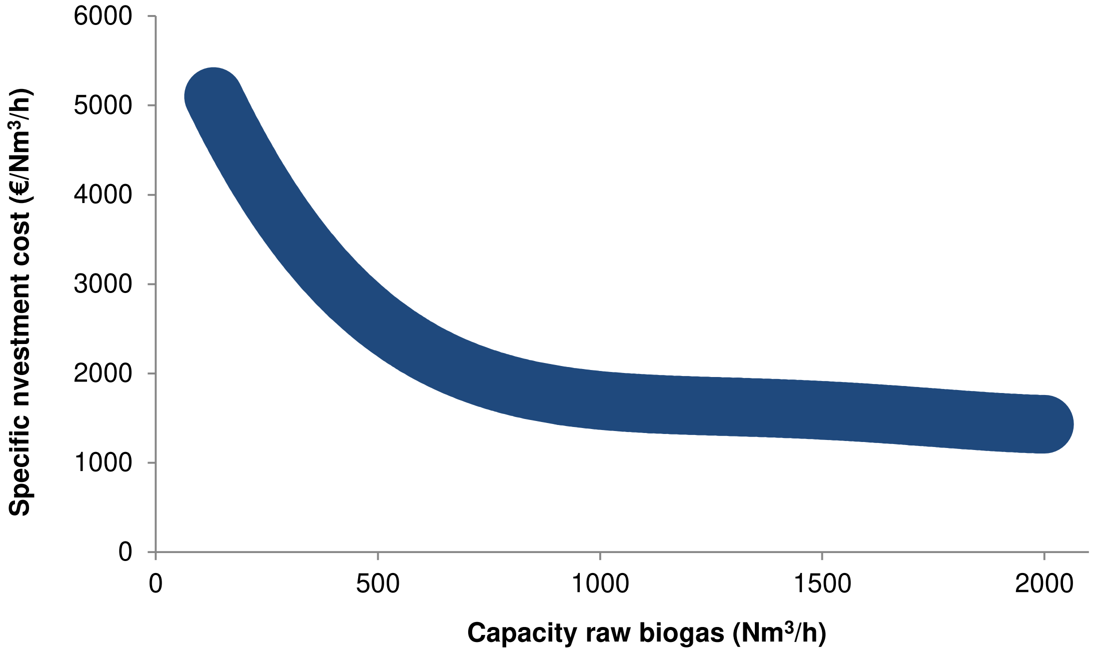

Figure 23 Specific investment costs for water scrubbers without optional equipment.

The availability of a plant is commonly guaranteed to be 95-96%, but higher availabilities are possible to get if additional investment costs are added to get redundancy of key components such as compressors and water pump.

Very low amounts of consumables are used in a water scrubber. The most important is water that needs to be replaced to prevent accumulation of undesired substances from the raw biogas and also to avoid decreased pH originating from oxidized hydrogen sulphide, if this is not solved using other methods. The volume of water needed varies between different plants and sizes and their operating conditions, however common water consumption is around 0.5-5 m^3/day. Except for water, also oil for the compressors – depending on compressor type – and smaller volumes of antifoaming agent could be required.

The maintenance cost for a water scrubber is annually around 2-3% of the investment cost and service contracts can be signed with some of the producers. The energy consumption to upgrade biogas with a water scrubber has three main sources; the compressor, the water pump and the cooling machine all have significant energy demands. The amount of energy that is consumed by these units depends on the properties of the “raw” biogas, the design of the water scrubber and the surrounding climate. All energy consumptions that are discussed in this chapter are referred to Nm^3 of raw biogas entering the unit.

The energy needed for compression is usually quite constant around 0.10-0.15 kWh/Nm^3 in modern applications operating at pressures around 6-8 bar(a). A thorough discussion on compression energy is presented in Chapter 3. In existing water scrubbers, the water pump is commonly a centrifugal pump. The energy demand of the pump depends on the volume of water, the inlet and outlet pressure and the efficiency of the pump. The pump is commonly chosen to have a high efficiency at full load. The efficiency of the pump could be around 80% at the design point and 10-30% lower at half load, which increases the specific energy consumption significantly when operating at lower loads. The volume of the water that is needed to remove the carbon dioxide depends on the temperature of the water and the pressure in the system but not the methane concentration in the raw biogas, as discussed before. The energy needed for the water pump is usually around 0.05-0.10 kWh/Nm^3 in modern applications at design conditions (full load).

The energy needed for cooling the process water and the compressed gas depends on several factors such as the climate of the location and the design of the water scrubber. The cooling system is usually divided into two systems, one "warm" and one "cold". The warm system is used to cool the compressed biogas to a temperature between 30°C and 50°C by using a dry cooler to remove the absorbed heat from the refrigerant. The temperature of the refrigerant in the "cold" system is commonly 5-15°C. Therefore, a dry cooler can only be used during the winter to cool this system while a cooling machine is needed during the rest of the year. The energy consumption of a dry cooler can be very low (1-5 kW) even for applications when more than 200 kW of heat is removed, while the energy consumption of a cooling machine is much higher. A cooling machine normally operates with a coefficient of performance (COP) between 2 and 5, depending on the design and the outdoor temperature, which corresponds to 20-50 kW electricity to cool 100 kW heat. The energy consumed by the cooling system is usually around 0.01-0.05 kWh/Nm^3 in modern applications.

Some water scrubbers are equipped with a heat recovery system that can be used to heat the digester. This can be designed in different ways, either by connecting a heat exchanger directly to the warm system, as described above, or by also using a cooling machine that is transferring the heat from the cold cooling system to the warm system. The second alternative increases the energy consumption of the water scrubber, especially during the winter, but it makes it possible to use up to 80% or even more of the electricity consumed by the water scrubber as heat. In this report this alternative is not discussed further.

Figure 24 shows the electricity consumption in water scrubbers manufactured with the latest technology. The data has been given by leading manufacturers and data from a few plants in operation in Germany has been used to verify the data. These values are the annual average and valid for systems without additional options. As discussed above, the energy consumption will change depending on several factors, therefore this figure should not be seen as the absolute truth but instead an indication of what range to expect for different sizes in most cases. Please note that the energy consumption will be identical for raw biogas with different concentrations of methane since this will not affect the volume of water that is needed to be circulated in the system.

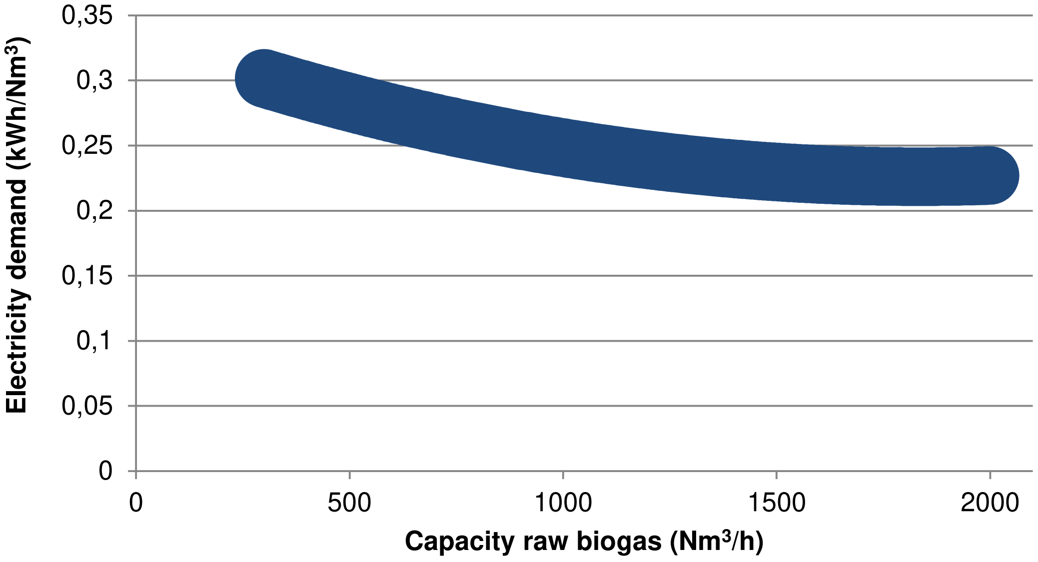

Figure 24 Average electricity consumption for water scrubbers with different size and the latest design.

2.4.5 Biomethane recovery and quality

The methane recovery in a modern water scrubber is above 99% by guarantee of the manufacturers. The methane slip from several water scrubbers in Sweden has been studied during the last years (Holmgren et al. 2010) and the results shows that the average methane recovery has below 99%. The reason for this is that many of the units in this study have an older design and different guarantee values. It is also probable that some plants are operating with a flash pressure that is too high and possibly also a water flow rate that is higher than needed. Both these parameters will increase the methane slip and decrease the recovery.

The quality of the produced biomethane fulfills the demands on the European market today. Lately some countries, e.g. Denmark, are demanding a methane concentration close to 98% in the produced biogas to ensure a stable and reliable heating value and overall quality on the gas in the natural gas grid. Work is ongoing to establish a common European standard for injection of biomethane into the natural gas grid systems and for use as vehicle fuel. This work is performed within the CEN project committee CEN/TC 408.

98% methane content is possible to reach with a water scrubber but there are a few important circumstances that need to be addressed. The oxygen and nitrogen in the raw biogas will not be separated in the water scrubber and the concentration of these will therefore be important to consider when discussing this matter. With a methane concentration around 50% in the raw biogas, the concentration of oxygen and nitrogen will be doubled in the biomethane due to the removal of carbon dioxide. Furthermore, some additional oxygen and nitrogen will be transported with the water from the aerated desorption column to the absorption column. Therefore the accepted level of oxygen and nitrogen in the raw biogas is very important when discussing how high methane concentration can be reached with stable operation.

Also important to consider is that the water scrubber is commonly regulated against the carbon dioxide concentration in the biomethane and if this concentration is close to zero, the regulation could be instable.

Another important parameter to discuss is if the required concentration of biomethane is an instant value, hourly average or daily average. In all systems a disturbance can occur that results in changed properties of the produced biogas. This is normal when downstream conditioning such as drying is used. For the system to have time to react and adjust these disturbances, it would be beneficial if the required levels are daily averages and not instant values. If the limits will be valid for instant values there is a risk for a decrease of the availability of the plant, at least with current design and regulation. Figure 25 below shows the instant values of the methane concentration from four plants in Germany during seven days in October 2012. These plants already today operate with a methane concentration in the area of 98%. The sudden changes in the methane concentration are from the change of dryers. It is important to consider that these plants are not optimized to operate above 98% at all times, therefore further improvements are probable when this is the aim.

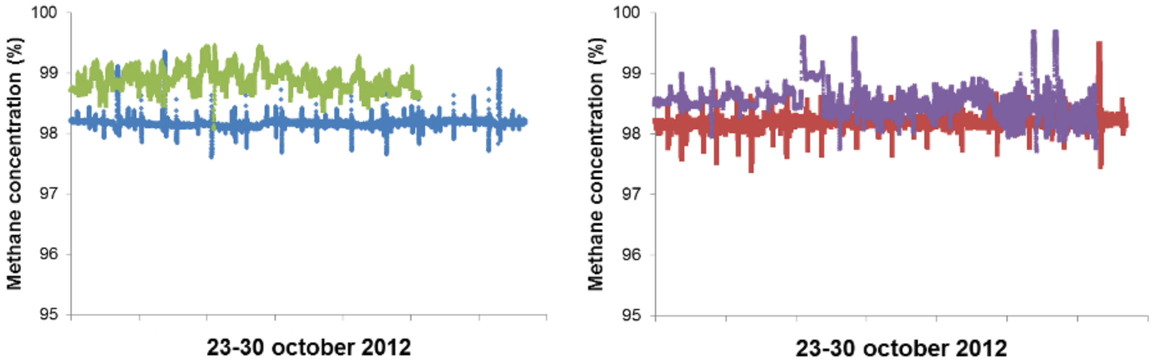

Figure 25 Variations in methane concentration in four water scrubber upgrading units in Germany during seven days in October 2012.

The carbon dioxide content in the product gas from the plants shown in Figure 25 was close to 1.5% for two plants, between 1 and 1.5% for one plant and between 0.5 and 1.0% for the last one. The additional energy consumption to decrease the carbon dioxide from 2.5% to 1.5% - corresponding to 98% methane instead of 97% - was evaluated at a water scrubber in operation in Germany during this project with support from one of the manufacturer. The results show that the energy consumption increased with approximately 2%.

2.5 Organic physical scrubbing

This chapter has been written in cooperation between the authors and the company HAASE Energietechnik GmbH that is a manufacturer of organic physical scrubbers. The description in this chapter is valid for scrubbers that are using Genosorb® 1753 as the organic solvent. This is the most common solvent today and used in most organic physical scrubbers on the market for biogas upgrading processes.

2.5.1 Process description

In organic physical scrubbing, the carbon dioxide in the biogas is absorbed in an organic solvent. The solvent in Genosorb plants is a mix of dimethyl ethers of polyethylene glycol. The theoretical background for absorption in an organic physical scrubber is similar as for a water scrubber. The absorption of carbon dioxide and methane into the organic solvent is described by Henry's law (Eq. 4). However, the solubility of carbon dioxide is much higher in the organic solvent than in water, i.e. the value of Henry's constant for carbon dioxide is higher. Carbon dioxide has a solubility of 0.18 M/atm in Selexol which is about five times higher than in water (Tock et al. 2010). Carbon dioxide is about 17 times more soluble than methane in the Genosorb solvent (Burr & Lyddon 2008) which is actually a smaller difference than for water, in which carbon dioxide is 26 times more soluble than methane. Due to the higher solubility of carbon dioxide in the solvent, the volume of solvent that must be recirculated in the system decreases significantly compared to a water scrubber.

The process is deigned in a similar way as a water scrubber with the following two main differences:

- the diameters of the columns is smaller since lower flow of the organic solvent is required
- the organic solvent has to be heated before desorption and cooled before absorption

A schematic illustration of the process is shown in Figure 26.

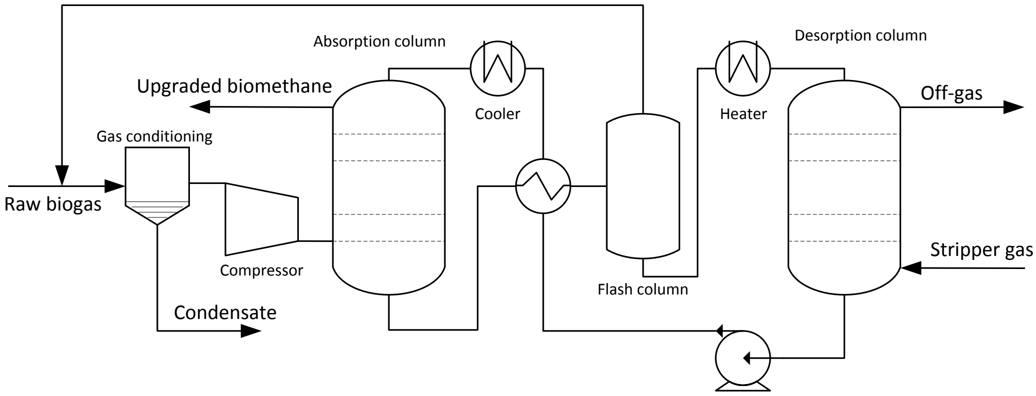

Figure 26 A simplified process flow diagram of a typical organic physical scrubbing process.

The biogas is compressed to 7-8 bar(a) and thereafter cooled before it is injected into the bottom of the absorption column. The organic solvent is added to the top of the column so that the gas and the liquid have a counter current flow. The organic solvent is cooled before being injected into the column to keep the absorption column around 20 °C. The temperature is important since it affects the value of Henry's constant, as described in Eq. 7 in the water scrubber section. The column is filled with random packing to increase the contact surface between the solvent and the biogas. The carbon dioxide is absorbed to the organic solvent and the upgraded biogas is dried before it is delivered to the gas grid or the fuelling station.

The organic solvent that is leaving the bottom of the absorption column is heat exchanged with the organic solvent that will be injected to the top of the column. Thereafter, the organic solvent is injected into the flash column, where the pressure is decreased. The main part of the dissolved methane, as well as some carbon dioxide, is released and circulated back to the compressor. The exact pressure that is used in the flash column depends on the required methane slip, pressure in the absorption column and the concentration of methane in the raw biogas.

To regenerate the organic solvent, it is further heated to reach around 40 °C before entering the desorption column. It is injected into the top of the column and the pressure is decreased to 1 bar(a). This column is also filled with random packing to increase the contact surface between the solvent and the air that is injected into the bottom of the desorption column. All heat that is required in the process is waste heat, which is generated by the compressor and the regenerative thermal oxidation (RTO) unit that oxidizes the methane slip from the exhaust air.

Due to the anticorroding feature of the organic solvent, the pipework does not have to be made of stainless steel and the low freezing point of the organic solvent makes it possible for the system to run up to a temperature of -20°C without the need of extra heat or an electrical radiator. In Figure 27 an organic physical scrubber installed in Germany is shown.

Figure 27 An organic physical scrubber with a capacity of 1100 Nm^3/h of raw biogas. Image from Haase Energietechnik.

2.5.2 Operation

Hydrogen sulphide is commonly removed before the upgrading unit to protect the components in the system and to fulfill requirements in air pollution control regulations. This is done with an activated carbon filter after the main part of the water in the raw biogas has been removed. The water is removed by increasing the pressure and cooling the gas. If ammonia and siloxanes exist in significant concentration, they are removed from the raw biogas before the biogas upgrading process.

The methane recovery in a modern organic physical scrubber is above 98.5% and this is guaranteed by the manufacturer. A methane content of 98% in the upgraded biogas is reached in some plants today. However, the value that can be guaranteed depends on the raw biogas quality and other project-specific conditions.

2.5.3 Investment cost and consumables

This technology was developed in 2004 and is today a mature technology and large changes in the investment costs should not be expected within a near future. The investment costs decrease with increasing size in a similar way as for the other technologies discussed in this chapter, see Figure 28.

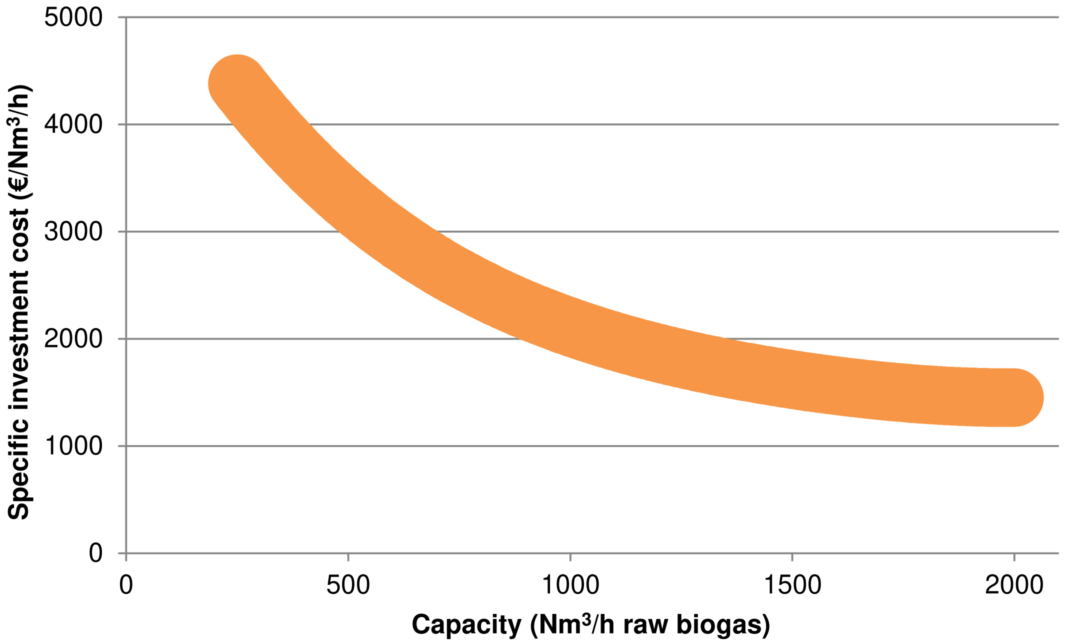

Figure 28 Specific investment cost for organic physical scrubbers for biogas upgrading, including RTO and biomethane dryer.

Few consumables are required in the process. Activated carbon is required for the removal of hydrogen sulphide and test gas for the analyses equipment (as for all upgrading technologies). No consumption of antifoaming agent or water is needed, however a minor addition (once a year) of organic solvent to compensate for losses caused by vaporization is required.

The entire energy consumption is electricity since no additional heat is needed when a RTO with heat recovery is used to oxidise the methane in the waste gas.

The energy consumption to upgrade biogas with an organic physical scrubber is similar to that of a water scrubber and the same components (compressor, cooler and feed pump) are the main energy consumers. Compared to the water scrubber, the feed pump consumes less energy in an organic physical scrubber due to the lower flow rate. Just as for the water scrubber, the energy consumption will depend on the size of the unit, see Figure 29, but not on the methane concentration in the raw biogas.

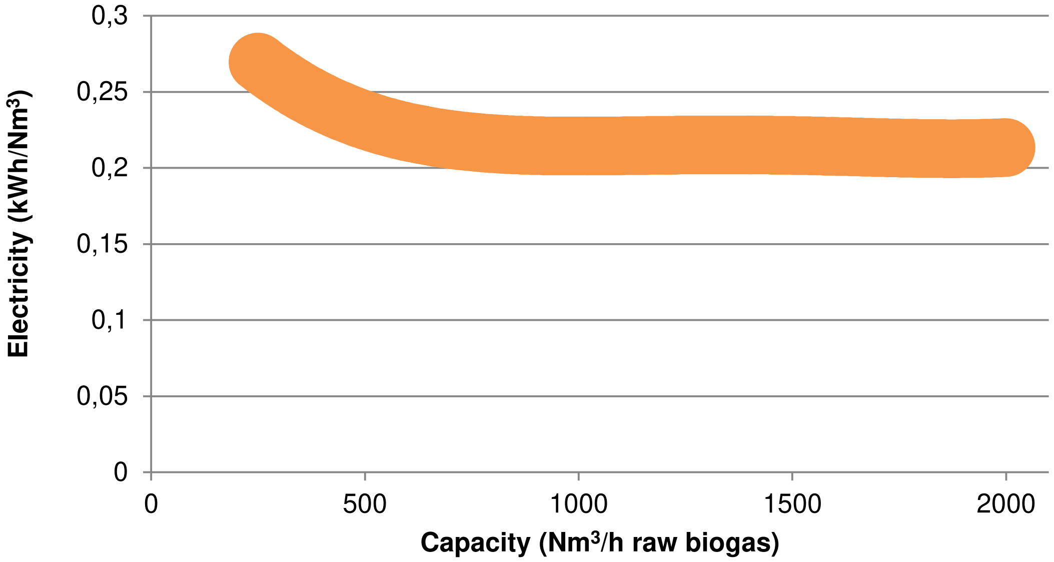

Figure 29 Average electricity consumption in an organic physical scrubber.

The availability is commonly guaranteed to be 96-98 % and the maintenance cost is annually around 2-3% of the investment cost. Agreements to take care of the maintenance costs can be signed with the manufacturer.

3 Comparison between the different technologies

In this section, the technologies that are considered mature enough will be compared. During the work with compiling information and contacting suppliers, it has become apparent that water scrubbing, organic physical scrubbing, amine wash, membranes and PSA are the technologies mature enough to warrant a detailed comparison. Cryogenic upgrading is a technology under development and demonstration and it would not be fair to use the data as is today in a comparison to the mature technologies.

3.1 Gas purity

The relevant measure of comparison between the technologies is their ability to remove CO_2 from the inlet biogas (assuming a typical composition of 60% CH_4 and 40% CO_2). The PSA is capable of removing 98-99% of the inlet CO_2. Most membrane manufacturers can guarantee a 98% CH_4 purity, which is also possible for the physical scrubbers in most applications. The amine scrubber has the best performance in this regard with a 99.8% CO_2 removal in the standard configuration.

In comparing the technologies with respect to product purity, it has to be mentioned that none of the mature technologies will separate nitrogen in their standard configurations. PSA and physical scrubbers will not remove oxygen, while amine scrubbers will be irreversibly damaged by oxygen as the amines are oxidized and no longer react with the carbon dioxide. Membranes have the ability to partly separate oxygen, but not nitrogen as the permeation rate of nitrogen is similar to that of methane. That indicates that all nitrogen in the inlet gas will end up in the product gas and the product purity will therefore be a function of the nitrogen content of the inlet biogas. PSA has the ability to remove both nitrogen and oxygen using more complex adsorbent bed configurations but it is a costly extra investment for a minor purification issue. Oxygen and nitrogen is only an issue if biological sulphur removal is used by introducing air to the final step of the AD or when upgrading landfill gas. Nitrogen and oxygen is hence normally not considered an issue in upgraded biogas purity. With regards to other contaminants, all technologies except the water scrubber require pre-treatment of the raw biogas to remove H_2S which will otherwise damage the adsorber bed, the amines and the membranes. A thorough investigation of the presence of other contaminants in the raw gas, the effect on upgrading equipment and the presence in the upgraded biomethane was published in 2012 by SGC (Arrhenius & U. Johansson 2012).

If considering CO_2 as an alternative product, in the PSA and water scrubber technologies it will be diluted by the balance methane (PSA) and the stripper air and hydrogen sulphided (water scrubber). The hydrogen sulphided may be removed upstream but this is currently only being done in the amine scrubber case, resulting in a concentrated and sulphur free CO_2. The CO_2 stream in the case of the scrubbing technologies will have to be dried prior to use, this is however not necessary in the PSA case.

3.2 Consumables

There are three major consumables to consider when discussing biogas upgrading: water, power and chemicals. Aside from these three, the amine scrubber has a heat demand that none of the other technologies have.

The water consumption of the water scrubber is quite varying depending on load and mode of operation, but may be narrowed down to 0.00004-0.0004 m^3/Nm^3. This figure is quite similar to the reported water consumption of the amine scrubber which is 0.00003 m^3/Nm^3. In the case of the other upgrading methods, the water requirement is zero.

From the supplier information, it may be concluded that the specific power consumption varies rather much with the scale of the upgrading unit. In the water scrubber case, the specific power consumption is approximately 0.3 kWh/Nm^3 at the lower end of the capacity spectrum (400 Nm^3/h) but decreases towards 0.23 kWh/Nm^3 with the throughput being increased towards 2 000 Nm^3/h. There is also a significant winter/summer difference in the electricity consumption due to the need of cooling the water during the summer. In the case of the amine system, it has an electric power requirement of 0.14 kWh/Nm^3 when operating in the lower part of a plant capacity and 0.12 kWh/Nm^3 when operating in the higher part of plant capacity. The PSA span is rather large with a consumption of 0.2-0.3 kWh/Nm^3, which is the same reported span as in the membrane case. All of the considered technologies are depicted in Figure 30.

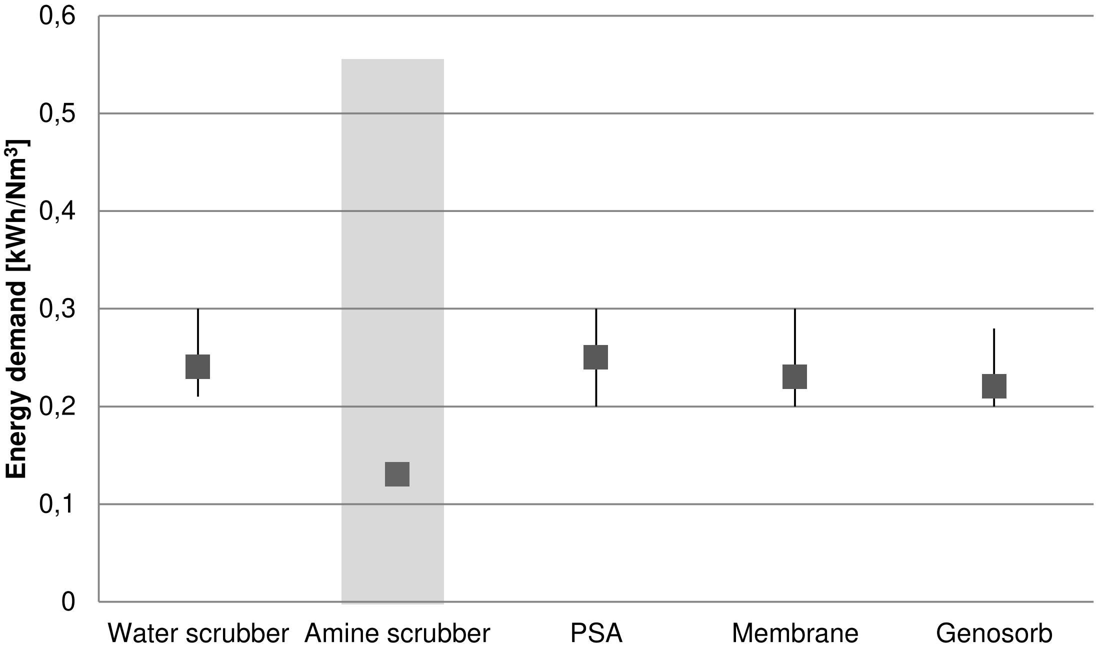

Figure 30 The energy demand of the different biogas upgrading technologies. All technologies have an electric power demand, which is shown as an interval, but amine scrubbers also have a heat demand, which is shown by the grey bar. The pressure levels of the upgraded gas streams are not equal and a higher inherent energy in the gas streams is available at higher pressures. For more details on the value of the inherent energy, see Figure 32.

Only the amine scrubber system has a heat requirement. The heat is required for reversing the chemical reaction and liberating the CO_2. The amount of heat depends to some extent on the inlet methane concentration, but since system heat loss is constant this effect is to some extent buffered. A typical value for the heat demand is 0.55 kWh/Nm^3, which is required in heating the stripper. The heat is added at 150-120°C and 80% of the heat may be reused in low-temperature (65°C) applications such as substrate pre-heating or AD heating. Catalytic or thermal oxidation of methane in the off-gas from both physical scrubbers, membrane and PSA can also be used to heat the AD or the substrate as well as the excess heat from the compressors.

The chemical consumption of the water scrubber and amine scrubber is mainly anti-foaming agents and, in the amine scrubber case, make-up of amine. The requirement is small, with the highest reported by the amine scrubber system (0.00003 kg/Nm^3) with the water scrubber being in the same vicinity. Hydrogen sulphide removal requires activated charcoal, both for PSA, genosorb, membranes and amines; there is also an option in the case of water scrubbers to use sulphur removal on the off-gas to meet environmental permits. All of the technologies have approximately the same need for lubricant oil for the compressors.

3.3 Methane slip

The methane slip is quite high in the PSA case with 1.8-2% reported as mean and median values. Higher values are most probably due to temporary technical problems. The water scrubber has a slip of about 1% in modern plants. Values much higher than this are not probable in a well-functioning plant. Both these technologies require tail-end solutions to decrease the methane slip to meet stricter regulations. This may be done by thermal or catalytic oxidation of the methane slip. The amine scrubber system has a much lower amine slip with 0.1% guaranteed. Organic physical scrubbers have a higher slip than the other technologies, but the methane is oxidized to supply heat to the process to enable the desorption and thus it is utilized internally. Membranes also seem to enable operation with a very low methane slip, about 0.5%, with design (iii) in Figure 15. In some membrane applications on the market, liquefaction of the carbon dioxide in the waste gas is used to recover 100% of the methane in the waste gas by cryogenic separation.

3.4 Investment costs

The investment cost of the various technologies has been reported earlier in the text, but in summary the different upgrading methods does not differ much; especially not at higher throughputs. The specific investment costs are shown together in Figure 31.

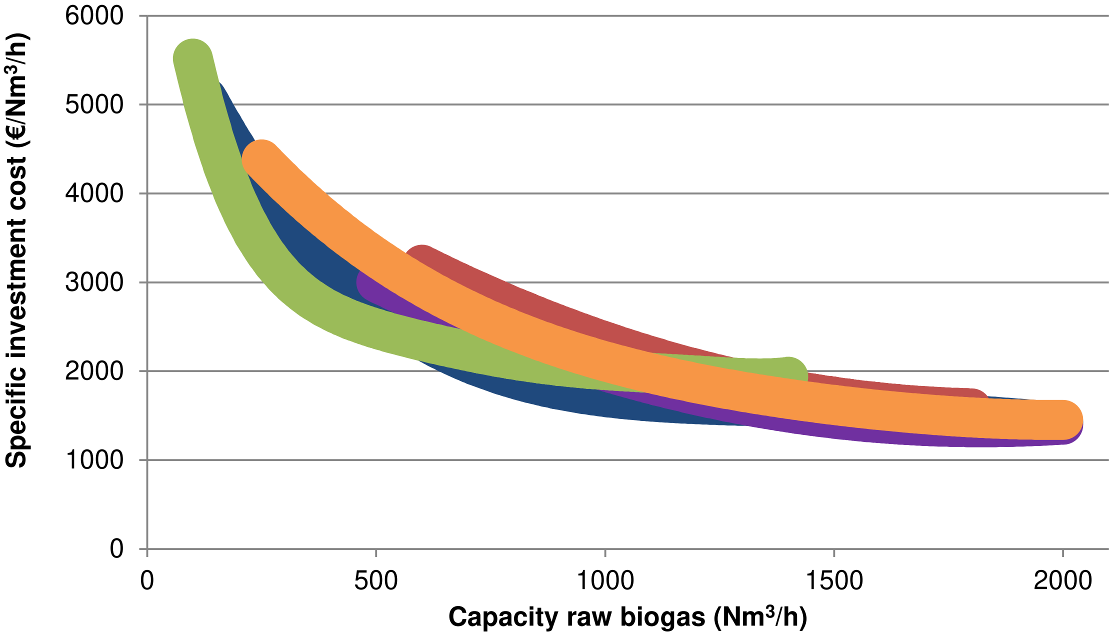

Figure 31 The specific investment cost of water scrubbers, amine scrubbers, PSA units and membrane units as a function of raw biogas throughput. Investment cost for organic physical scrubber includes RTO.

As seen in the figure, the amine scrubber is slightly higher in investment cost in the lower end of the spectra and the membrane technology is slightly lower in investment cost in the lower to mid-scale range. The investment costs start to converge at the higher throughputs. There is little difference from an investment point of view between the PSA and the physical scrubber technologies.

3.5 Recent developments

When the different technologies for biogas upgrading were compared by Urban et al, it was obvious that operating costs were not a deciding issue at that time. As can be seen in this chapter, the specific investment costs for the different technologies are approximately equal. One difference is that membrane units are available at lower throughput capacities than the other options. Further, the energy required for upgrading is also about the same, where the lower electricity demand for amine systems is compensated for by the heating demand. The operating costs will thus be roughly the same for the technologies. Hence, it can be said that the development of these technologies over the last years has not led to any drastic decrease in either energy demand or capital costs.

However, when comparing the market situation today with the one just a few years back, it is obvious that amine systems have taken a great leap forward. In 2009, amine scrubbers were still only used at demonstration plants, whereas today the systems are constructed and sold in different standardized sizes. There was also a concern regarding the amines themselves, e.g. their corrosive impact on process equipment. These concerns were mainly regarding DEA and MEA, whereas today MDEA is the most commonly used amine in amine scrubbing systems. The technology has thus matured significantly in these few years. Water scrubbing and PSA are mature technologies since many years, and the development of these systems is mainly incremental. For instance, water scrubber systems have been optimized to reduce the fresh water demand and PSA systems have been developed to reduce the number of expensive pressure valves and to decrease the process cycle time.

3.6 Gas compression

The upgraded biomethane can be used for different applications, requiring different gas pressure. The upgrading technologies operate at different pressure, making a proper comparison of the energy demand for specific applications difficult. Feeding upgraded biomethane into the gas distribution grid at 5 bar(a) can be done directly from the pressurized upgrading systems such as water scrubbers and PSA units, whereas the gas from an amine scrubber must be pressurized after the upgrading. The natural gas transmission grid is operated at 60 bar(a) and vehicle fuel is handled at about 250 bar(a) which requires further compression of the gas from all technologies. The energy needed for this compression does however differ significantly as the first compression steps (1-10 bar) are the most expensive, in terms of energy. To enable the reader to compare the energy needed for compression of the upgraded gas for applications at the most common pressure levels, the energy demand needed for compression between different pressure levels is shown in Figure 32. Here, the gas has been regarded as cool (0 ºC) in the beginning of each compression step, which is also shown in the figure. Figure 33 shows the energy demand needed for compression of a gas to a specific pressure ratio, which is independent of absolute pressure, i.e. the energy needed for compression from 1 to 10 bar is equal to the energy needed for compression from 10 to 100 bar. The figure also shows the temperature of the gas after compression by a specific pressure ratio.

The energy needed to compress a gas depends on the volume of gas that shall be compressed, the inlet temperature of the gas, the ratio of specific heats (c_p/c_v) for the gas, inlet and outlet pressure and the efficiency of the compressor (McCabe et al. 2005). The ratio of specific heats is the only parameter that depends on the composition of the biogas and since methane and carbon dioxide have similar ratios of specific heats (c_p/c_v equals 1.307 for methane and 1.304 for carbon dioxide at 15ºC and 1 atm(a) (Compressed Gas Association 1999)) minor differences in the composition of the biogas will not be of importance for the energy consumption of the compressor. The efficiency of the compressor is usually rather constant for various loads and, furthermore, variations of inlet pressure and inlet temperature are usually rather small and not affecting the overall energy consumption significantly. Thus, the values presented below are also valid for the raw biogas compression.

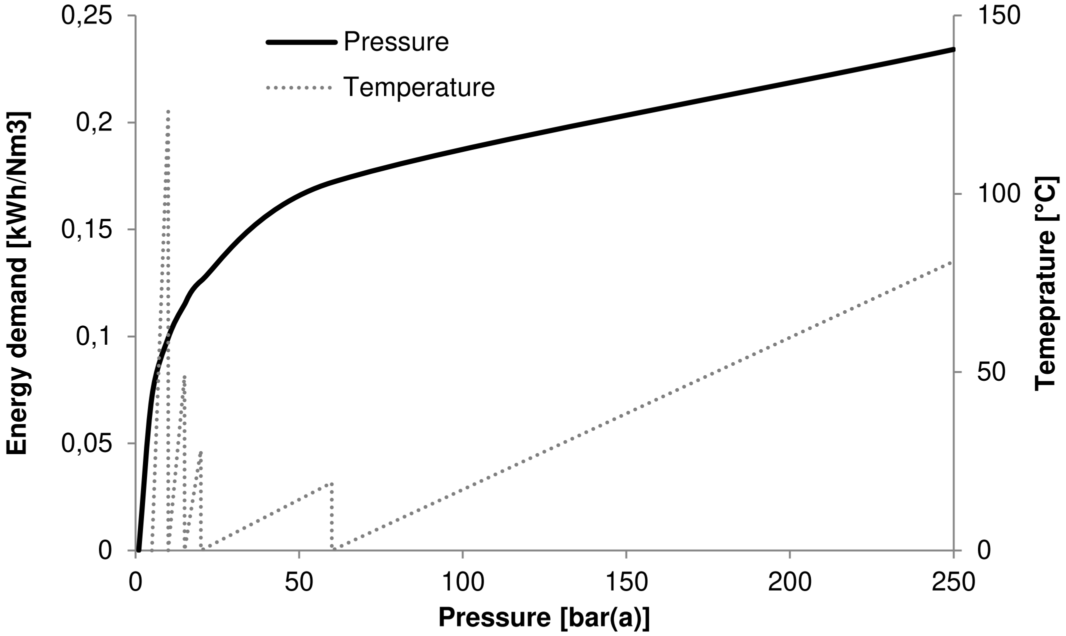

Figure 32 Energy demand for compression of biomethane between different pressure levels. The inlet gas is considered to be cool before each compression.

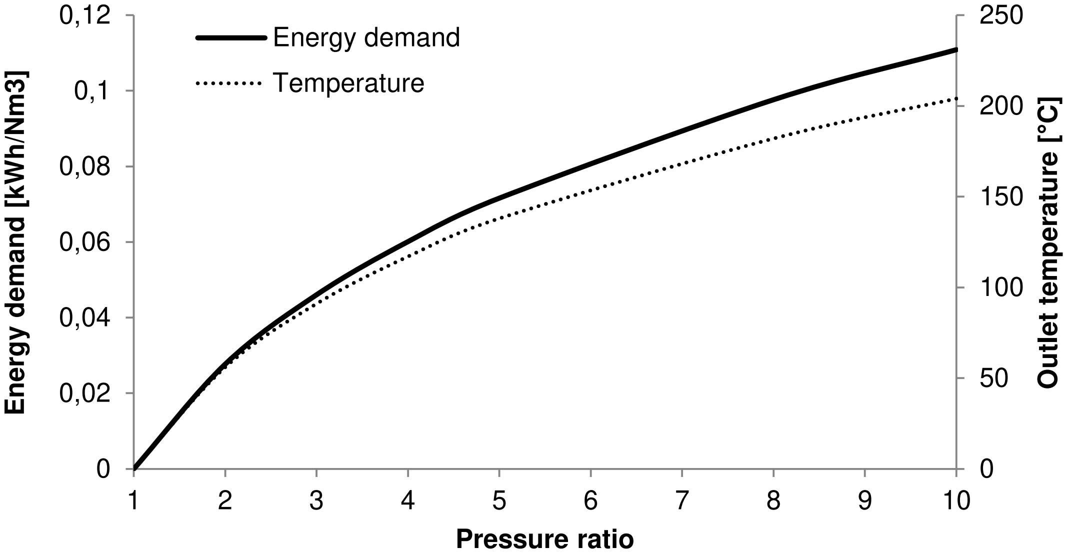

Figure 33 Energy demand for compression of biogas by a specific pressure ratio and outlet temperature of the gas after compression. The gas is considered to be cool before compression.

These values have been calculated for a single step isentropic compressor, using the process simulation software Aspen Plus, assuming an isentropic efficiency of 0.85 and an engine efficiency of 0.9.

4 Cryogenic separation and liquefaction

The technical field of cryogenic gas treatment comprises a lot of different processes and have been used for the following three tasks for biogas:

- Removal of trace contaminants, mainly in the landfill gas context
- Removal of main components such as CO_2, N_2 etc (gas upgrading)
- Condensation of upgraded biomethane to bio-LNG (LBG)

As a consequence, cryogenic processes cannot be treated as a homogeneous family of gas upgrading techniques. Furthermore, most processes currently available are under development, so little sound data is available.

4.1 Technical background

Cryogenic processes make use of low temperatures in order to achieve the wanted results. There is no fixed temperature level below which processes are considered "cryogenic". However, the processes described here operate at temperatures well below -50 °C (approx 220 K), i.e. in an area where common gases become a liquid. Figure 34 illustrates the condensation point of some common gases in the area of biogas.

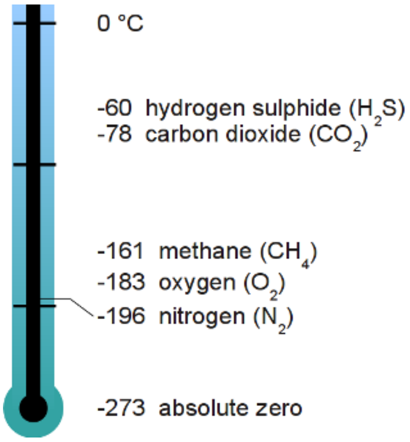

Figure 34 Boiling (condensation) point at atmospheric pressure for some pure gases. Pure CO_2 sublimates under these conditions at -78 °C while it condensates at elevated pressure. For diluted gases, other temperatures may be valid.

4.1.1 Cooling options

Common to cryogenic processes is the need to generate low temperatures. Cooling of a stream can be achieved either indirectly (by heat exchangers with colder media) or directly. For the indirect option, one possibility is the usage of liquid nitrogen in order to liquefy another gas (biomethane), thereby consuming the liquid nitrogen. This is evidently the most basic setup for a liquefaction process and has been used in some pilot plants for a proof of concept since very little technique is needed for the supply of cooling energy. However, this is not viable in a larger scale because the running costs get too high.

For the direct cooling alternative, a lot of different processes have been developed, all consisting of a combination of compressors, heat exchangers and expansion devices forming a cooling cycle. Direct cooling is also the method used to lower the temperature of the refrigerants in chillers. Therefore, a combination of direct cooling (of the refrigerant) and indirect cooling (heat transport from the biogas to the refrigerant) is often used in the case of biogas cooling. Details on cooling cycles can be found in Appendix II.

4.2 Purification of landfill gas

Landfill gas is very similar to digester gas, being composed mainly of methane and carbon dioxide. The main challenge in the use of landfill gas as a fuel is the varying and elevated content of trace contaminants such as siloxanes and halogen compounds, some of them being known and others not even being identified. Furthermore, landfill gas can contain elevated amounts of nitrogen which cannot be removed by most conventional gas upgrading techniques. Techniques capable of removing nitrogen from biogas/landfill gas include PSA and cryogenic upgrading to liquefied methane (see further on in this chapter).

One cryogenic technique specifically developed for the removal of trace contaminants is the CO_2 Wash® process developed by US based Acrion Technologies. In this process, the raw gas stream is cleaned by liquid carbon dioxide, even called “CO_2 Wash”. The idea is that many impurities such as halogenated hydrocarbons or siloxanes have a much higher solubility in carbon dioxide than methane. The process is mostly interesting for the treatment of landfill gas with its high and varying contents of impurities.

Usually, the CO_2 Wash® process is combined with other gas treatment steps in order to produce CBG (compressed biogas) or LBG. A possible setup for LBG production is shown in Figure 35. After compression, H_2S removal and drying, the gas stream enters a cryogenic column at the bottom and is then led upwards, meeting a stream of liquid CO_2. Impurities are dissolved in the liquid CO_2 and bled off the system at the sump. The gas stream leaving the head of the column contains methane, a part of the carbon dioxide of the raw biogas as well as the oxygen and nitrogen from the raw gas. The rest of the carbon dioxide leaves the system in the upper half of the column as a liquid, food grade CO_2 stream.

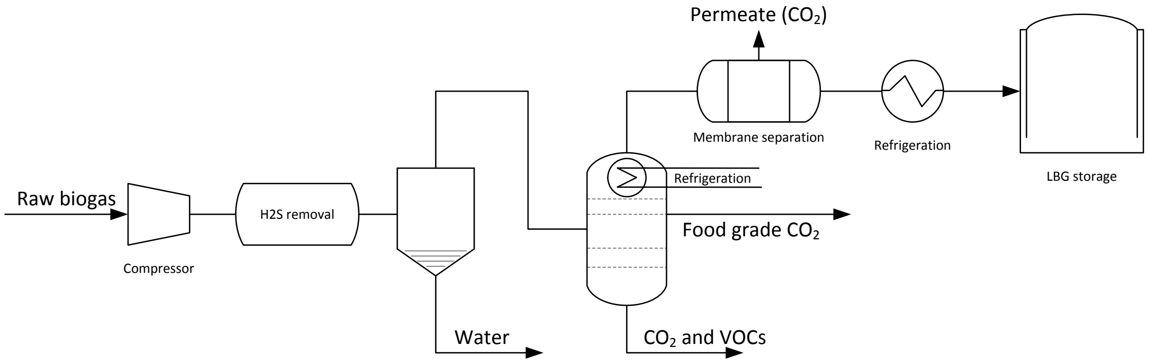

Figure 35 Schematic overview of LBG production with the CO_2 Wash process.

The purified gas can be directly used in boilers and CHP engines; in this case, the CO_2 Wash® system leads to less wearing of the installation and a longer lifetime.

Alternatively, the gas can be further upgraded to vehicle quality and liquefied by other upgrading techniques as shown in Figure 35.

The CO_2 Wash technology has previously been licensed separately for the production of compressed biomethane and liquefied biogas. Originally, the CBG license was held by Firmgreen Inc. Today, Terracastus has the global rights to the CO_2 Wash technology for both CBG and LBG production.

4.2.1 Existing liquefaction plants

Before the CBG license was passed to Terracastus, Firmgreen Inc. had initiated some projects involving the CO_2 Wash technology. These projects are to be completed by Firmgreen. None of these projects have been completed yet, so no operation experience is available by now. One of the projects nearest to completion is located at the Novo Gramacho landfill near Rio de Janeiro, Brazil, which should have gone into operation in the autumn of 2012 but has been delayed and not finished at the time of publishing. The plant will have a capacity for 20 000 Nm^3/h landfill gas and will be owned by Gás Verde, SA, who sell the cleaned gas to Petrobras' nearby refinery.

Terracastus was planning a biogas upgrading plant at a NSR waste treatment plant in Helsingborg in Sweden where LBG was to be produced from landfill and digester gas. However, this project was cancelled because Volvo is looking for a new stakeholder for Terracastus. The Helsingborg project was planned with the process steps shown in Figure 35. In addition, a molecular sieve polishing step was planned after the membrane unit, according to Terracastus.

The CO_2 Wash® technology is considered economical for gas flows exceeding 500 Nm^3/h.

Table 10 Process properties for the CO_2 Wash process. Properties are theoretical or from pilot plant operation as no data from full-scale operation are available yet.

Methane slip	0.037 % (less than 0.5 %) [Andersson 2009]
Methane loss in CO_2 Wash	1.8 %
Energy demand	0.76 kWh/Nm^3 raw gas (approx. 15 % of produced LNG energy) [Andersson 2009]
Food grade CO_2 recovery	25 % of incoming CO_2 [Andersson 2009]

4.3 Upgrading of biogas

Compared to other upgrading techniques, cryogenic approaches have the following potential or expected benefits:

- Hope for low energy demand during upgrading
- No contact between gas and chemicals
- Production of pure CO_2 as a side product
- Possibility to produce LBG
- Possibility to remove nitrogen from the gas stream

Since the condensation temperatures of the different compounds of biogas are quite different as shown in Figure 34, it is principally easy to separate methane and carbon dioxide by gradually cooling down the mixture and thereby liquefying the carbon dioxide. Other compounds with higher condensation temperature than methane such as water and hydrogen sulphide are removed simultaneously. It is also possible to lower the temperature in several steps, each of them removing certain compounds. This way it is possible to minimize the irreversibilities of heat exchangers and optimize the refrigerant cycle. An example for this is the GPP® process of GtS, which is explained in detail in Appendix III.

When cooling common digester gases, the first compounds to be removed are low-concentration impurities such as water, hydrogen sulphide, siloxanes and halogens at a temperature down to approx. -25 °C. These compounds can be removed mostly in their liquid state.

When continuing to decrease the temperature, the next compound being condensed is carbon dioxide. However, carbon dioxide will directly shift from the gaseous to the solid phase unless the cooling unit is operated at elevated pressure, which can be seen in the phase diagram in Figure 36. Because of the high concentration solid carbon dioxide can be a problem in the process by plugging pipes and devices such as heat exchangers. Therefore it can be an advantage to operate the process at a higher pressure where cold CO_2 is a liquid rather than a solid. However, since the solubility of methane in solid CO_2 is very low whereas more methane dissolves in liquid CO_2, the sublimation or freezing of CO_2 can be used for a more efficient separation of these two compounds in order to minimize methane losses. In this case, this step is designed as a batch process where operating conditions in the cooling step (normally a heat exchanger) are chosen such that the carbon dioxide is permitted to freeze or sublimate as a solid until the capacity of the heat exchanger is reached. Then, production is shifted to a parallel line while the heat exchanger in the first line is defrosted. Carbon dioxide is recovered in either gaseous or liquid state.

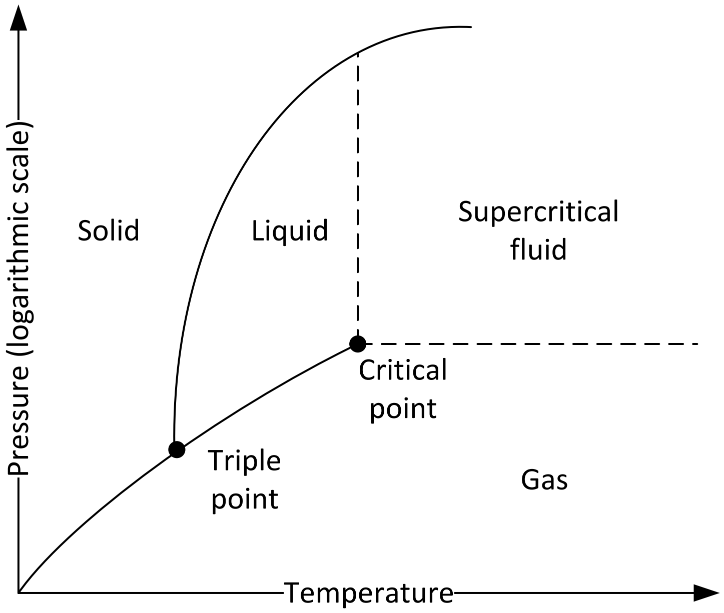

Figure 36 Phase diagram of carbon dioxide. The triple point is at -56.6°C and 5.2 bar(a). Sublimation occurs at -78.5°C at a pressure of 1 bar(a).

Since nitrogen has a boiling point which is lower than the one of methane, nitrogen will not be removed from the gas stream in a mere cryogenic gas upgrading plant. For the removal of nitrogen, a further cooling step for the liquefaction of methane is needed as explained in the following chapter.

4.3.1 Existing plants

In the early 1990s, Prometheus Energy developed a cryogenic process for the upgrading of landfill gas. First, a pilot plant in Canada was build in 2000; later, in 2006, a larger plant with a capacity of 280 Nm^3/h (4 800 kg/day) was erected at the Bowerman Landfill in the USA. The energy consumption of the process is 1.54 kWh/Nm^3 product gas (N. Johansson 2008).Since then and until today, there have been no updates or other news whatsoever on the plans of Prometheus Energy to further develop the technology.

At the moment, Gastreatment Services (GtS) from The Netherlands is the only supplier of cryogenic upgrading technology. GtS have a pilot plant in the Netherlands, consisting of a unit for CGB production and another unit with higher capacity for liquefaction. Therefore, the two units are linked via a buffer and the liquefaction unit must be operated semi-batchwise. Apart from the pilot plant, GtS have built commercial cryogenic upgrading plants in Loudden and Sundsvall in Sweden. Another plant was originally planned in Varberg but will not be built. GtS does not give any statements on the state of the existing plants. Therefore, the following information is collected from different persons involved in the operation of the plants.

The Loudden plant at Tivoliverket is owned by Scandinavian Biogas Fuels AB and has been built since 2009 with a planned capacity of 400 Nm^3/h of raw biogas. Since then, the plant has had several severe operational problems ranging from programming issues to leakages and design flaws for heat exchangers and cooling machines. Also, the gas entering the liquefaction step contained too high concentrations of carbon dioxide, c.f. Table 11. This should have been corrected by the addition of a polishing step using a molecular sieve, which never has been implemented. In late 2011, the first LBG was produced, however, the production never exceeded very limited flows. Most of the problems have been solved in the meantime, but there is no more activity from GtS at the moment. After having cancelled all contracts with GtS, Scandinavian Biogas Fuels will require the removal of the plant and is looking at other, conventional solutions for upgrading and distribution.

The situation in Sundsvall is similar. According to Mittsverige Vatten, the supplier of the raw gas, the plant is almost finished but is not able to produce noteworthy amounts of liquid biogas on a continuous basis. The gas supply contract as well as the building license have expired in autumn 2012.

In the meantime, GtS have announced the delivery of a new plant for LBG production to the Schoteroog landfill in Haarlem in the northern part of the Netherlands. This is near the headquarter of GtS, which should give much better conditions to work with the plant optimization and handle and solve practical problems. The plant is to treat gas from the nearby WWTP with a total raw gas flow of 280 Nm^3/h equivalent to approx. 122 kg/h of LBG. The upgrading part of the plant is in operation since mid 2012 and is reported to work as expected. The liquefaction step has been commissioned in autumn 2012, but without any information on its operability at the hour of writing.

Methane losses are specified by GtS to be less than 2 %, and can be expected to be below 0.5 % in an optimized plant (K. Andersson et al. 2009). Electricity consumption is expected by GtS to be approx. 0.45 kWh/Nm^3 raw gas for LBG production. Almost 100 % of the CO_2 can be recovered as LCO2; however, this will increase the energy demand of the process.

The LBG is normally produced at an elevated pressure of 17 bar(a), which implies that it can be stored at temperatures much higher than -160 °C. This can be an inconvenience for distribution purposes since the margin to the pressure where the boil-off of the LBG must be released to the atmosphere becomes quite small. If the LBG was produced at lower pressure (and hence lower temperature), it could be stored for a longer time without the need to release boiled-off gas.

Apart from GtS, a small startup company in Gothenburg called BioFriGas is aiming at developing a small scale, low budget cryogenic biogas upgrading and liquefaction process. Work has begun and a first pilot plant has been built at Sobacken, the waste treatment plant in Borås in Sweden. At the moment, the only information available on the planned process available is that it is supposed to be based on standard equipment and shall have a capacity of 25 Nm^3/h.

4.4 Liquefaction of upgraded biomethane

The third application of cryogenic techniques in the biogas context is the production of liquefied biomethane from conventionally upgraded gas streams, often called LBG or bio-LNG. LBG has a number of advantages compared to CBG which are mostly related to the higher energy density. 1 Nm^3 gaseous methane is equal to 1.7 litres of liquid methane. LBG has more than double the volumetric energy density of gaseous biomethane compressed to 250 bar(a).

- More efficient transport, bigger geographical marketing range
- Lower energy consumption and investment costs at filling stations
- Opening up of new markets such as LNG backups, trucks and ships

4.4.1 The liquefaction process

Because of the low boiling point of methane, very low temperatures are needed to produce LBG. At these temperatures, common compounds such as water, carbon dioxide or hydrogen sulphide are in their solid state and have a very limited solubility in the liquid methane. In order to avoid plugging and freezing problems, some stringent purity requirements are valid for the gas entering a liquefaction step Table 11.

Table 11 Purity requirements for the liquefaction of biomethane (Flynn 2005).

Compound	**Limit for liquefaction**
Water, H_2O	0.5 ppm
Hydrogen sulphide, H_2S	3.5 ppm
Carbon dioxide, CO_2	50 – 125 ppm

Normally, the limiting purity requirement is the 50 ppm(v) constraint for carbon dioxide because it precipitates in the liquefaction unit at higher concentrations. This level is difficult to achieve with most upgrading technologies. At the moment, only optimized amine scrubbers and possibly cryogenic upgrading units are able to comply to the CO_2 constraint out of the box. Other upgrading plants such as water scrubbers, PSA units and membrane separation plants must be completed with a polishing step to reduce the CO_2 concentration in the upgraded gas.

Currently, the standard method used in this polishing step is a molecular sieve working with temperature and pressure swing adsorption. Here, the difference in molecule size between methane and carbon dioxide is used to trap the CO_2 molecules, while methane molecules can more or less freely pass the columns. The purge gas from the polishing step typically contains between 60 and 70 % methane (or 5-10 % of the total incoming methane) and can be returned to the raw gas inlet of the upgrading plant. The polishing step uses essentially the same technology as PSA upgrading plants. However, due to the low amounts of CO_2 in the treated gas stream, the cycle time is much longer, typically several hours, so the valve wearing is not as critical as in PSA upgrading plants.

When upgraded biogas is directly cooled down in an expansion valve, the stream leaves the valve in a two phase regime where a part of the stream is in the liquid phase, whereas the other part still is gaseous. In this case, the cycle is constructed so that the gaseous fraction is recycled back to the compression step while the liquid fraction is removed from the process as a product stream. As a side effect, the liquefaction process may be deployed to remove nitrogen impurities from the methane stream (nitrogen has a slightly lower boiling point than methane), which is especially interesting in the treatment of landfill gas.

An alternative is to cool down the upgraded biogas in a heat exchanger with external cooling. In this case, the entire gas stream can be liquefied in one step.

4.4.2 Existing plants

Air Liquide Advanced Technologies has in 2012 commissioned their first plant for the liquefaction of biogas in Lidköping where it is part of a system for the production of liquid biogas. After a conventional fermentation and gas upgrading using a water scrubber plant owned by Swedish Biogas International, where gas with vehicle fuel quality is produced, the gas enters the liquefaction unit consisting of a temperature pressure swing adsorption unit polishing step followed by the liquefaction process. The plant is shown in Figure 37.

Figure 37 The Lidköping Biogas plant. In front the filling station is shown, and behind that the liquefaction unit is situated.

The technology for methane liquefaction is based on a reverse nitrogen Brayton cycle. This process extracts heat from methane, liquefying it in a plate-fin heat exchanger. The reverse nitrogen Brayton cycle is shown in Figure 38. The process can be divided into the following steps, which are also shown in Figure 38 .

1. Nitrogen is compressed inside a centrifugal compressor.
2. Compressed nitrogen is then over-pressurised in a turbo-booster before entering the heat exchanger to be cooled down
3. The nitrogen stream is expanded, generating the cold power for the system at a temperature of 110 K (-163 °C),
4. The low pressure stream flows back in the plate heat exchanger and cools down both methane and the high pressure nitrogen stream,
5. Biomethane is liquefied at 110 K and is released at a pressure of 3.5 bar(a). The outlet pressure can be adjusted depending on the customer requirements.

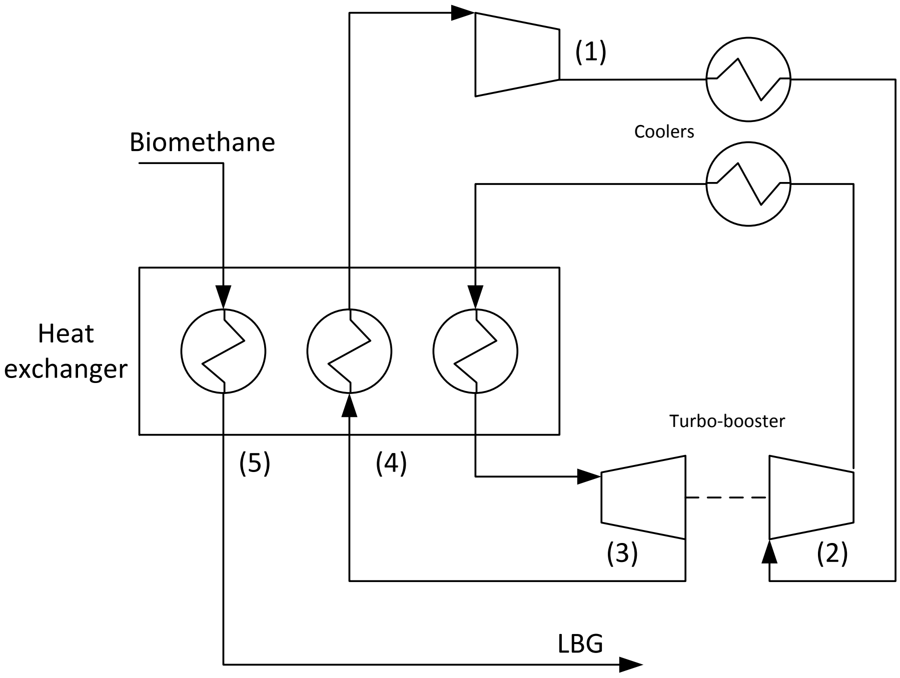

Figure 38 Simplified process flow diagram of the liquefaction process used by Air Liquide.

According to Air Liquide and Göteborg Energi, the Lidköping plant was in partial load in summer 2012 when it delivered the first LBG to Gothenburg, and the plant has undergone a performance test during the autumn of 2012. The liquefaction plant is now completed and has been successfully commissioned. Its performance meets the requirements set up. However, a number of adjustments and optimization changes have been done and will have to be done.

Table 12 Contractual requirements for the Lidköping LBG plant including the polishing step. Data from Air Liquide and Göteborg Energi.

Electricity demand	max 1.56 kWh/kg LBG (1.12 kWh/Nm³ CH_4)
Process capacity	550 kg/h (765 Nm³/h)
LBG temperature from plant	-163°C
LBG pressure from plant	1.5 bar(a)
LBG pressure from tank	4-5 bar(a)
Raw gas constraints	Swedish standard for vehicle fuel plus extra requirements
Heat recovery	Possible, approx. 1 MW at 45 °C
Investment costs	83.6 MSEK

Another plant for liquefaction of biogas is currently being built at the Esval landfill near Oslo, Norway. The supplier of the polishing and liquefaction equipment is Wärtsilä who recently have acquired Hamworthy, a supplier of cryogenic gas processes. After some years of cooperation with Sintef, Wärtsilä have developed small scale solutions for gas liquefaction. The only existing plant using this technology by the time of publishing is a pilot plant situated in Moss, Norway. It has been operating since October 2012 and has a capacity of 3 ton LBG/day equal to 170 Nm³/h.

The Esval plant is a full-scale plant with a capacity of 610 Nm³/h and will be delivered during 2013. It will receive AD gas from household waste which has been upgraded to vehicle quality by a water scrubber unit. After compression to 20-30 bar(a) in an oil free piston compressor the gas is polished in order to further remove carbon dioxide and hydrogen sulphide. This polishing step is done by PTSA in a molecular sieve. The reject from the polishing step contains up to 40 % CO_2 and is recycled to the raw biogas stream.

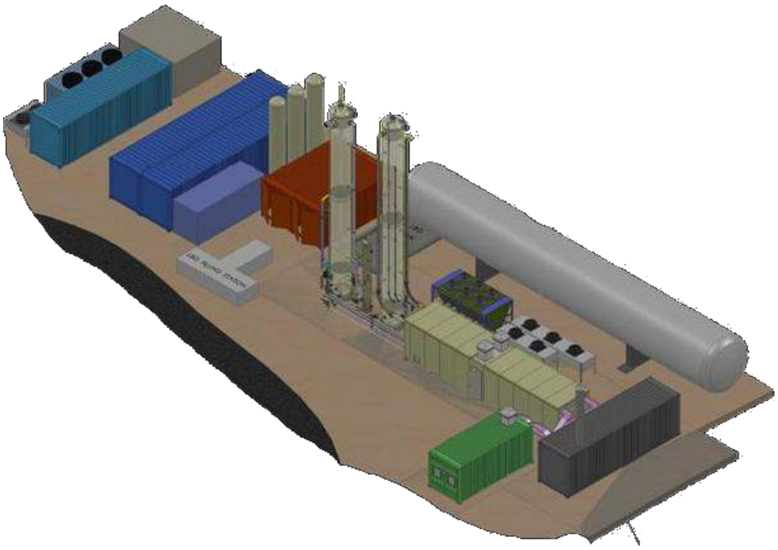

Figure 39 Layout of the plant under construction in Esval/Oslo, Norway. Image from Wärtsilä.

The cooling process is divided into a pre-cooling step, followed by a closed-loop mixed refrigerant cycle. All heat exchangers are assembled in one multi-pass unit where the gas is cooled and liquefied in one step. After the heat exchangers, the LBG is released into the storage tank via a throttle valve.

The mixed refrigerant process was chosen by Hamworthy because of the higher efficiency and a relatively simple plant layout with only one standard, off-the shelf cooling compressor, which limits the investment costs. The process works at 50 - 100 % of design capacity at a constant efficiency. The mixed refrigerant is optimized during the commissioning phase, then the system is sealed thus keeping a constant composition of the refrigerant.

Table 13 Properties of the Wärtsilä liquefaction process.

Electricity demand	0.5-0.6 kWh/kg LBG (estimated)
Process capacity	3 – 25 ton/d (170 – 1 440 Nm^3/h)
LBG temperature	-160 °C
LBG pressure	2.0 bar(a)

Also, London-based Gasrec is operating two plants where biogas is upgraded, liquefied and marketed as Bio-LNG. Apart the above mentioned current plants, several other biogas liquefaction plants have been built some years ago. One of them is a plant at Guildford, UK, taken into operation in 2008. The plant has a capacity of 16 ton/d of LNG (925 Nm^3/h LNG) and uses an mixed refrigerant cooling cycle developed by GTI (Gas Technology Institute) (Källgren 2011).

In 2009, Linde Gas in a joint venture with Waste Management has delivered their first plant using the GTI process to the Altamont Landfill near Livermore, California, USA. The plant has a capacity of 1200 Nm^3/h and started operation in October 2009. Apart the liquefaction unit, the Livermore plant incorporates units for compression and removal of contaminants such as H_2S, CO_2 and N_2 (Luftglass 2010).

The same year, a liquefaction unit was constructed at the Albury landfill in Surrey, Great Britain. This plant has a capacity of 2200 Nm^3/h raw landfill gas (K. Andersson et al. 2009). According to Linde, the GTI process is a reasonable choice down to a capacity of 30 tons/day (1700 Nm^3/h) of LBG. Smaller units are not economically interesting because the GTI process deploys the relatively expensive mixed refrigerant configuration in order to obtain high efficiencies. Hence, the Linde technology is applicable only for the biggest biogas and landfill plants with a raw gas production of around 3000 Nm^3/h. The properties of the process developed by Linde Gas/GTI is shown in Table 14.

Table 14 Properties for the Linde Gas/GTI process. Data from pilot plant operation

Process capacity	> 30 ton/d (1700 Nm^3/h CH_4)
Electricity demand	29.3 kWh/MMBtu (1.0 kWh/Nm^3 CH_4) [GTI 2004]
Availability	86 % (Altamont, July 2010)

5 Small scale biogas upgrading

To upgrade biogas in a small scale (0-100 Nm^3/h) is commonly very expensive due to high specific investment costs of the upgrading equipment. For a plant with low capacity, more or less the same number of valves, analysis equipment and pipes are needed as for a plant with much larger capacity. The dimensions of the pipes and valves will be smaller, but the investment cost will still be high compared to the capacity.

This chapter will not cover the global market for small scale biogas upgrading, but instead describe two new techniques available on the market today. Conventional water scrubbing, PSA and biogas upgrading with membranes are all available in small scale on the market today (H. Blom et al. 2012), and also small scale cryogenic approaches are being developed. These technologies have already been described and are therefore not further discussed here.

5.1 High pressure batchwise water scrubbing

In Kalmari farm in Finland a special type of water scrubbing is used to upgrade the biogas. The main difference to conventional water scrubbing is the very high pressure that is used in the system (150 bar(g)) and that the system is operated batchwise with two absorption columns. Gas is driven from the absorption column with water, so at the end the column is completely filled with water. Thereafter it is emptied and the cycle starts again. The water is thereafter treated as in a conventional water scrubber with a flash tank to minimize the methane slip and a desorption column to remove the carbon dioxide.

The first unit was built in 2005 and two more units have been built since, one at the University of Jyväskylä in Finland and one in northern China. A photograph of the unit can be seen in Figure 40.

Figure 40 The columns performing the separation of carbon dioxide from the biogas in the Metener biogas upgrading system. Image from Metener Oy.

The electricity consumption in these units is higher than in a conventional water scrubber, due to the high pressure used. However, the produced biomethane has a very high pressure and can be used in a vehicle fuel filling station with only minor additional compression. The electricity consumption of the plant, including the electricity needed for the filling station and further pressurizing to 270 bar(a), is around 0.4-0.5 kWh/Nm^3 of raw biogas, and the system operates with a methane slip of 1-3%, all according to the manufacturer.

Due to the high pressure, the components in the system such as absorption and desorption columns can be built much smaller than in a conventional water scrubber. However, they need to withstand the high pressure. The footprint of the system will be smaller as well as the investment cost. The investment cost of a plant (including dispenser and basic storage) with a capacity of 60 Nm^3/h is around 380.000 €.

5.2 Rotary coil water scrubber

A method to upgrade biogas in small scale that is similar to a conventional water scrubber, is to use a rotating coil in which the compression and scrubbing occurs. This technology is being developed by the Swedish company Biosling. Today, no commercial units have been sold and delivered to customers, but the product is available on the market.

The compression of water and biogas is unique for the Biosling unit. Biogas and water with a pressure of 2 bar(a) are alternately fed into coils of plastic hoses that are rotating. The rotation increases the pressure up to around 10 bar(g) and most of the carbon dioxide will be dissolved into the water inside these coils.

As described in Chapter 2, it is beneficial for any type of physical scrubbing to have a counter current flow of the fluid and the gas, which is not possible for the coil pump used in the Biosling process. Thus, a product gas with 97% CH_4, which is commonly requested on the market today, cannot be reached by just using the coils for upgrading. Instead, a conventional water scrubber is used for the final removal of carbon dioxide. Using only the rotating coil unit, a product purity of 94% can be reached, according to the manufacturer. Hence, the technology may be more suited for applications in which a lower product purity is sufficient, as the unit without the final polishing scrubber would have a lower investment cost. The coil pump and the columns of the water scrubber can be seen in
Figure 41.

Figure 41 3D image of the Biosling upgrading unit with two rotating coils and a small water scrubber unit. Image from Biosling.

The investment cost is depending on the model but is about 360 000 to 460 000 € for a unit with a capacity of up to 72 Nm^3/h and the electricity demand for this unit is around 0.15 – 0.25 kWh/Nm^3 raw biogas depending on the size of the upgrading unit, according to the manufacturer. The biogas is upgraded to a product purity of more than 97% methane. The methane slip is expected to be around 1% according to the manufacturer.

6 Concluding remarks

Biogas upgrading, i.e. removal of CO_2 and other impurities from the biomethane, is becoming an increasingly popular and important process. Upgrading the raw biogas to biomethane enables the use of biogas in vehicles as fuel or for injection into the natural gas grid for use in any application connected to the grid. Since SGC performed a first review of upgrading technologies in 2003 (Persson 2003) the technologies have matured significantly and new technologies have reached the market. There are also significant developments over the last few years, i.e. since the publishing of the thorough report on biogas upgrading by the institute Fraunhofer IWES (Urban et al. 2009).

The technologies which are dominating the market today are water scrubbing, PSA and amine scrubbing. This is an important difference compared to a few years ago when amine scrubbing was still a rather unestablished technology. Today membrane separation is a technology trying to get established in the field of biogas upgrading. Organic physical scrubbers, such as Genosorb scrubbers, still have a minor share of the biogas upgrading market. The market share of this technology does however not seem to increase, but remains at about 10%. Cryogenic upgrading technologies, which have sometimes been stated to be the best choice for combination with liquefaction of biomethane, are still struggling with operational problems, but the large interest in these technologies by many different stakeholders shows that the technology may break through within a short period of time, if the problems are properly resolved.

As has been shown in this project, the specific investment costs for all the presented upgrading technologies are similar. The specific investment costs are about 1500-2000 €/Nm^3/h for upgrading units with raw gas capacities larger than 800-1000 Nm^3/h. For smaller units, the specific investment costs increase significantly. There are thus important economies of scale to consider when planning for new biogas plants and/or new upgrading capacity. The energy demand of the technologies are also similar, the electricity demand is about 0.2-0.3 kWh/Nm^3 raw biogas, except for the amine scrubber which has an electric power demand of about half. The amine scrubber must however also be supplied with about 0.55 kWh/Nm^3 of raw biogas to regenerate the amine. Gas compressors, liquid pumps and cooling machines are the main reasons for the electricity demand. Optimization of flow rates and temperatures are thus important tasks for the efficient operation of the upgrading units. Depending on the intended end application, the pressurization of the raw biogas in some technologies may be valuable as it decreases the need for later compression, an aspect which is also important to consider. Small scale upgrading is also an interesting topic, but will most likely not become too common due to the high specific investment costs for small upgrading plants.

LBG is today produced at full scale, the process does however use traditional upgrading with a subsequent cryogenic liquefaction step. This was the projected path for LBG a few years ago (Öhman 2009) and will probably remain the most viable process path in the near future. A large-scale production of LBG in Europe is however still most probably several years - maybe a decade - away. Although LNG on a global scale is increasing in traded volumes, the small-scale LNG distribution and storage technology used for maritime and road transport applications is advanced and still relatively rare, albeit these emergent markets are growing quite rapidly driven by customer demand and supporting government policies. Compared to the CNG business, the infrastructure is less disperse, with each terminal handling larger volumes distributed to fewer customers. The use of LBG for heavy road transports is an interesting future application, considering the gas quality requirements that many current and future engine technologies demand in order to reach performance on par with diesel. But as concluded before, the production will for several more years continue to be only marginal.

Biogas production is increasing, in Sweden and globally, and the interest for biogas upgrading to utilize the gas as vehicle fuel or in other traditional natural gas applications increases as well. The mature technologies will see a market with more and harder competition as new upgrading technologies such as membrane separation are established, and other technologies optimize the processes to decrease operation costs. Important issues for the future development of the biogas market relate to the implementation of new policy instruments. The work with the new European standard requirements for gas distributed through the existing gas grids is one issue that possibly can have a large effect on possibilities for distribution of upgraded biogas. However, the future will most probably be fuelled by an increasing amount of upgraded biogas.

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Appendix I Importance of pH for a water scrubber

Even if pH can affect the solubility of carbon dioxide, the influence of pH on the solubility of carbon dioxide in a water scrubber is rather small. This can be explained by studying two cases, process waters with low and high alkalinity. The alkalinity is assumed to be constant in the system during the few minutes it takes for the water to circulate through all columns. The alkalinity can be expressed as in Eq. 1 (Stumm & Morgan 1996).

$$[Alk] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] - [H^+] \qquad \text{Eq. 1}$$

$$C_A\ (M) = K_H\ (M/atm) * p_A\ (atm) \qquad \text{Eq. 2}$$

If the water has low alkalinity, the contribution to the solubility from hydrogen carbonate and carbonate will be insignificant due to their low concentration, see Eq. 1. This implies that the total solubility can be described by Eq. 2. This can be explained by that in a system with low alkalinity (without acid) pH will drop to 3.5-4 in the bottom of the absorption column while the pH in the bottom of the desorption column will be increased to around 6. The pH in the absorption column will be much lower than 6.4 which is the first acidity constant (pK_{a1}) for the carbonate system, which is the pH when the concentration of dissolved amount of carbon dioxide is equal to the concentration of HCO_3^- (Stumm and Morgan 1996), see Figure 1. Since the pH in the bottom of the absorption column is more than two pH units lower than pK_{a1}, less than one percent of the total dissolved carbon dioxide will be dissolved as ions in the water. Therefore the solubility of carbon dioxide will only be depending on Henry's constant and not the ionic forms in the carbonate system.

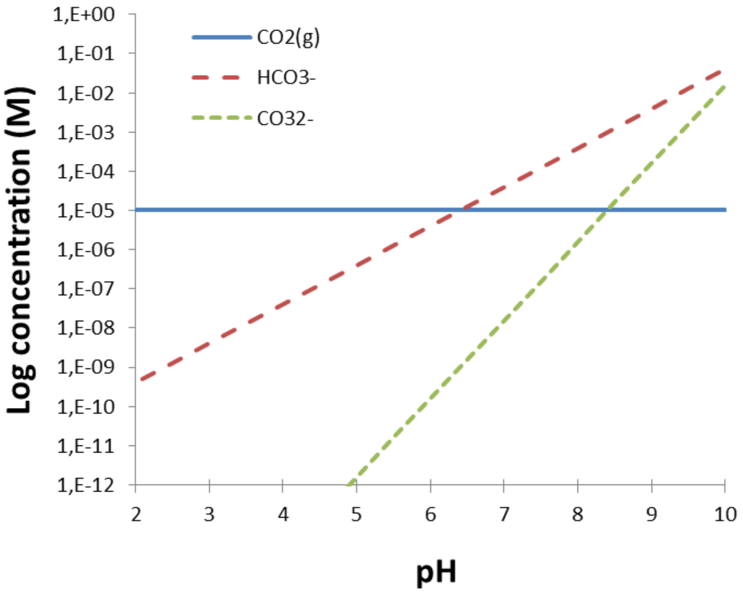

Figure 1 The calculated pH diagram for the carbonate system in the liquid-phase in the desorption column. Water was assumed to be equilibrated with the atmosphere ($p_{CO2} = 10^{-3.5}$ atm) and the constants $pK_H = 1.5$, $pK_{a1} = 6.4$ and $pK_{a2} = 10.4$ were used (all valid at 25°C). In the absorption column p_{CO2} is around $10^{0.5}$ atm which will increase all concentration approximately 10^4 times.

The maximum alkalinity that can be used without operational problems in a conventional water scrubber is determined by the solubility of lime. If $[CO_3^{2-}]*[Ca^{2+}] >$ 10^-8.3, lime will precipitate (Stumm and Morgan 1996). If pH in the bottom of the desorption column is above 8, there is a risk of precipitation of lime on different surfaces due to the high concentration of carbonate.

If pH is 8 in the bottom of the desorption column, pH will theoretically be 5-5.5 in the bottom of the absorption column if the alkalinity is constant due to increased partial pressure of carbon dioxide. This is at least one unit below pK_{a1} which means that maximum 10% of the dissolved carbon dioxide is in the form of hydrogen carbonate. However, the carbonate dissolved as hydrogen carbonate will not be released in the desorption column. The reason for this is that the alkalinity is constant and that the concentration of all ions included in Eq. 1 is very low in comparison to that of hydrogen carbonate if pH is equal to 8 ($[CO_3^{2-}]$ will be around 1% of $[HCO_3^-]$). Therefore, almost the same concentration of carbon dioxide will be in ionic form in both the absorption and desorption column and these ions will not affect the solubility of the carbon dioxide, but instead only be circulated between the different columns.

If the alkalinity is very high in the water that is used in the water scrubber it is recommended to install a softener to keep pH below 8 in the desorption column to prevent precipitation of lime. However, it is important to avoid removing more hardness than needed, since a water with higher hardness is more resistant to foam and will buffer sulphuric acid produced from oxidized hydrogen sulphide.

Appendix II Theory on refrigeration cycles

In the context of liquefied methane, quantities are often specified in units other than standard cubic meters, e.g. kg or gallons. In order to facilitate the comparison of the different technologies, the conversion coefficients for the most common units are shown in Table 1 below.

Table 1: Conversion coefficients between different units for gas quantities.

	Nm³	**kg**	**US liq. gallon**	**litre**
Nm³	1.00	0.72	0.45	1.71
kg	1.39	1.00	0.63	2.38
US liq. gallon	2.21	1.59	1.00	3.79
litre	0.58	0.42	0.26	1.00

The Joule Thomson effect and inversion temperature

When compressing and expanding real, non-ideal gases, temperature will change if the pressure is changed adiabatically (i.e. without the exchange of thermal energy, e.g. in an insulated valve). This effect is called the Joule Thomson effect. The sign and magnitude of the temperature change is normally expressed by the Joule Thomson coefficient which is defined as

$$\mu_{JT} = \left(\frac{\partial T}{\partial p} \right)_H$$

The coefficient depends on the type of gas as well as its pressure and temperature before expansion. At a certain temperature, the so-called inversion temperature, μ_{JT} is zero, so the temperature does not change upon a pressure change. Above the inversion temperature, μ_{JT} is negative, so the gas gets warmer on expansion, while the coefficient is positive at temperatures below the inversion temperature. At room temperature, almost all gases have a positive coefficient and will be cooled down by expansion, the only exceptions being hydrogen, helium and neon. The existence of the inversion temperature implies that it is not possible to cool a gas beyond this temperature by expansion valves. An additional cooling effect can be achieved by replacing the throttle valve by a turbine which additionally extracts work from the gas.

Standard cooling cycles

The elemental steps in direct cooling cycles are as follows:

1. Compression: As gases are compressed, the temperature rises.
2. Cooling: The compressed hot gas is cooled against some other medium. This may be at room temperature or against another stream at low temperature.

3. Expansion: Analogue to compression, temperature will decrease when gases are expanded. This is the step where cold is generated. The expansion may take place in an expansion (throttle) valve or in a motor or turbine. In the latter case, mechanical energy is removed from the system.
4. Warming (optional, only in closed-loop): The cold stream may be used as is, or used to cool down another stream (see step 2). Then, the stream is recycled to the compression step.

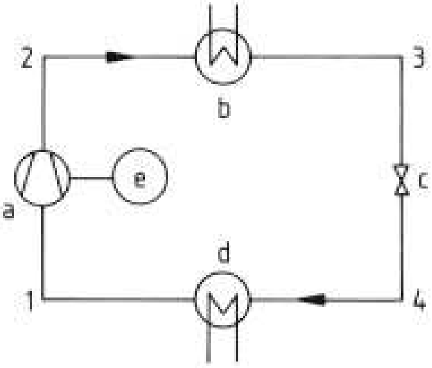

Figure 1: Simplest setup for a cooling cycle including a) compressor b) condensor c) expansion valve d) evaporator

Since this cooling cycle works near the boiling point of the refrigerant, the partial pressure of the liquids is usually low, so the potential to draw the liquid into pumps is very limited (low NPSH – Net Positive Suction Head). Therefore, pumps in such systems usually are submersed in order to avoid cavitation at the suction side.

Advanced cooling cycles

The cooling cycle in Figure is the simplest possible alternative. The investment costs for it are moderate and the technique requires relatively little engineering know-how. Often, nitrogen is used as the refrigerant medium in the loop, so the process is also referred to as the nitrogen expansion process. However, this setup has some limitations, e.g. a limited possible temperature drop per cooling step and a low energy efficiency.

In order to increase the possible temperature drop, several loops can be combined into a cascade, where the cold side of one loop is used to cool the warm side of the next loop. It is also possible to extend the loop with more compressors and/or valves; then the process is called a multi stage cycle.

The low efficiency is partly due to the fact that the different components in biogas have different cooling curves, and partly to high temperature gradients in heat exchangers and therefore high irreversibility losses. In order to obtain a higher efficiency, the single refrigerant nitrogen can be replaced by a mixture of substances with different boiling points in a so-called mixed refrigerant cycle. By this means, the properties of the refrigerants can be fine-tuned to the requirements of the application, so the refrigerant has a boiling range corresponding to the desired temperature range for cooling. This way, the heat exchangers can be operated at the refrigerant's boiling temperature at any point, leading to a highly efficient heat transfer as compared to a heat exchange with a pure liquid or gaseous phase.

With a suitable refrigerant mix, very high temperature drops can be realised which otherwise would require a cascade cycle with multiple steps. Furthermore, it is possible to use only one refrigerant pump for the whole process, as opposed to a cascade process where each step needs its own pump. However, MRC processes require much more know-how and are more sophisticated than single refrigerant cycles, so the development costs are higher too. This makes it difficult to deploy MRC processes for the relatively small-scale biogas applications.

Appendix III The GtS cryogenic upgrading process

The Dutch company Gastreatment Services bv (GtS) is the supplier of a modular cryogenic system for the cleaning, upgrading and liquefaction of biogas. A process scheme showing the modules can be found on web site of GtS.

In two of the modules (GTP – Gas Treatment Package, and TCR – Total Contaminant Removal), the gas is essentially compressed to 17-26 bar(a) and then cooled down for the removal of moisture. Both modules integrate energy recovery by reheating the dried gas. Because of the low temperature of -25 °C in the TCR module, also a number of contaminants are removed with the condensate. The modules can be completed with a SOXIA catalyst to further remove remaining contaminants.

Following the drying modules, the gas is liquefied in the GPP module (Gastreatment Power Package). The module consists of two stages which are illustrated in Figure 1. In the first stage, the gas is further cooled to -50 °C where liquid CO_2 is separated. In the second stage, the temperature is further lowered below the freezing point of CO_2 in two parallel columns. Since CO_2 becomes solid at this temperature, the heat exchangers must be operated batch-wise where one unit is in operation (online) while the other is defrosted, so the accumulated CO_2 becomes a liquid again and is collected together with the CO_2 from the first stage. The liquid CO_2 can either be used for cooling the incoming gas and thereby lowering the total energy consumption, or be sold as a product. In the case of the production of compressed biomethane, the upgraded, cold biomethane can also be used to cool down incoming streams in order to reduce the energy consumption.

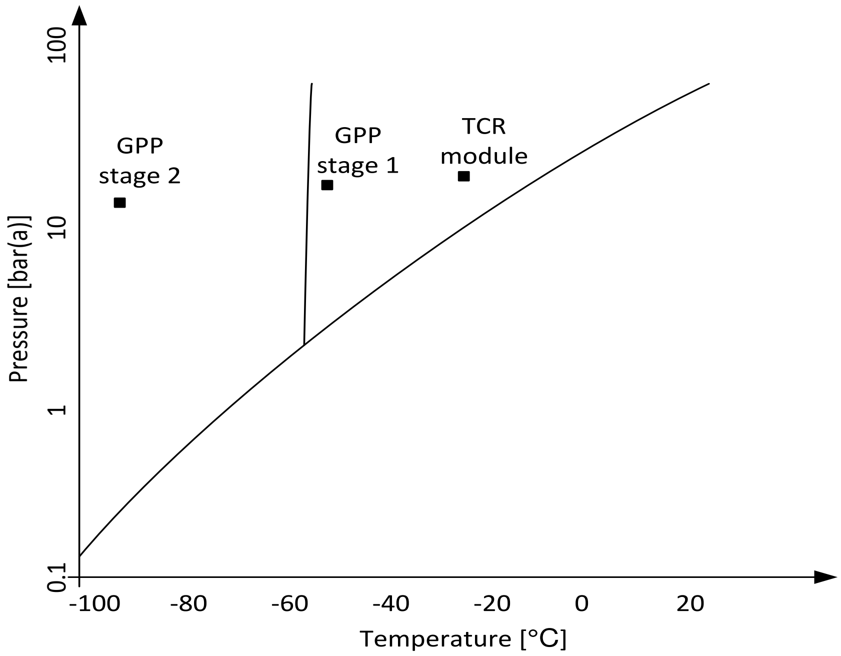

Figure 1 The GtS gas upgrading process GPP in the phase diagram for pure CO_2.

If LBG is to be produced, the GPP module can be extended by a supplementary cooling step called GPP+ where the methane is liquefied. This is done by compressing and subsequently flashing the biomethane. According to GtS, this step also finally adjusts the LBG quality, without further specification as to how. Additionally, nitrogen can be separated from the methane; also this is not further explained in the information from GtS. The available block diagram does not show any stream where nitrogen may leave the system.