Environmental and Economic Assessment of Carbon Mineralization for Biogas Upgrading

By

Katherine Starr

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Katherine Starr

under the supervision of Dr. Gara Villalba and Dr. Xavier Gabarrell, from the ICTA and the Department of Chemical Engineering at the UAB, and Dr. Laura Talens Peiró, a Marie Curie IEF research fellow at INSEAD and currently working at the Institute for Environment and Sustainability (JRC-IES)

Xavier Gabarrell Laura Talens Peiró Gara Villalba

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"If we could change ourselves, the tendencies in the world would also change ...
We need not wait to see what others do."
- Ghandi

For my family

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Abbreviations

A	annual capital cost
AD	anaerobic digestor
ADP E	abiotic depletion, elements
ADP F	abiotic depletion, fossil
aq	aqueous (phase)
AP	acidification potential
APC	air pollution control residues
AS	chemical scrubbing with amine solution/amine scrubbing
AwR	alkaline with regeneration
B	annual income
b_{ch}	standard chemical exergy of the compound
b_e	standard chemical exergy of the element
b_{ph}	physical exergy
BA	bottom ash
BABIU	bottom ash for biogas upgrading
C	annual costs (excluding capital)
$CaCO_3$	calcium carbonate
CaO	calcium oxide
Ca(OH)2	calcium hydroxide
CCS	carbon capture and storage
CED	cumulative energy demand
CExC	cumulative exergy consumption
CExD	cumulative exergy demand
CExM	cumulative exergy mix
CH_4	methane
CO_2	carbon dioxide
Cry	cryogenic separation
DEA	diethanolamine ($C_4H_{11}NO_2$)
e_2	exergy efficiency
EP	eutrophication potential
eq	equivalent
EU	European Union
Ex	exergy
FAETP	freshwater aquatic ecotoxicity potential
FU	functional unit
g	gram
g	gas (phase)
G	Gibbs free energy of formation
GHG	greenhouse gases
GWP	global warming potential

h	hour
H	enthalpy
H_2	hydrogen
H_2S	hydrogen sulfide
HPWS	high pressure water scrubbing
HTTP/HTP	human toxicity potential
i	indicator under study
I	investment (total capital cost)
KCl	potassium chloride
KOH	potassium hydroxide
kWe	kilowatt electric
kWh	kilowatt hour
l	liquid (phase)
L	lifetime
LCA	life cycle assessment
m	meter
m^3	cubic meter, volume
MAETP	marine aquatic ecotoxicity potential
MBT	mechanical biological treatment
MEA	monoethanolamine (C_2H_7NO)
MFA	material flow analysis
MS	membrane separation
MSW	municipal solid waste
MSWI	municipal solid waste incinerator
n_e	number of moles of element per unit of compound
NaCl	sodium chloride
NaOH	sodium hydroxide
NH_3	ammonia
Nm^3	normal meters cubed
O_2	oxygen
O&M	operation and maintenance
ODP	ozone layer depletion potential
OM	organic matter
OPS	organic physical scrubbing
POCP	Photochemical ozone creation potential
ppm	parts per million
PSA	pressure swing adsorption
r	discount rate
s	solid (phase)
S	entropy
SC	specific cost

SF	scaling factor
t	tonne (1000 kg)
T	temperature
TETP	terrestrial ecotoxicity potential
tkm	tonne kilometer
U	annual total of indicator under study
VOC	volatile organic compound
WMS	waste management scheme
ww	wastewater
x_0	initial scale
x_s	actual scale
y	year
z_0	initial cost
z_s	scaled cost

$CAD	Canadian dollar, currency
€	Euro, currency of the European Union

k	kilo (10^3)
M	mega (10^6)
G	giga (10^9)
T	tera (10^{12})
P	peta (10^{15})

Summary

Our world has been increasingly looking for solutions to reduce the greenhouse gas (GHG) emissions of our planet. Various solutions have been proposed, including carbon capture and storage (CCS). Focus for application of CCS has normally centered on large scale energy production that burns fossil fuel. Recently, developers have been working on applying CCS to biogas upgrading technology. This entails removing CO_2 from biogas emitted from anaerobic digestors and landfills while also increasing the CH_4 concentration to render the biogas suitable as natural gas substitute.

Two novel technologies under review also stores the removed CO_2 in a solid form, through a process called carbon mineralization. This process uses calcium oxides found in industrial waste to fix CO_2 by forming calcium carbonate. Ideally these novel upgrading technologies should have more environmental benefit over conventional ones based on the fact that they immediately store CO_2, while conventional ones do not. The first technology is called alkaline with regeneration (AwR) and consists of using an alkaline solution to strip the CO_2. The alkaline solution is then regenerated by exposing it to a waste rich in CaO. The second is called bottom ash for biogas upgrading (BABIU) which relies on a direct gas-solid phase interaction with bottom ash from municipal solid waste incinerators. This thesis examines whether or not these two novel technologies have an environmental benefit over conventional upgrading technologies, based on industrial ecology tools. Life cycle assessment, material flow analysis, and exergy analysis were applied for the environmental and resource assessments. The thesis also examines the long term feasibility of applying these technologies, both from a material and economic point of view.

Overall it was determined that the novel technologies generally do not have a better environmental performance over conventional technologies, especially AwR which was found to have a higher impact due to the use of the alkaline solution. Despite this, both novel technologies had significant CO_2 savings over conventional technologies. As well since both novel processes are in the pilot plant stage it is possible to pinpoint what can be improved in order to increase the all around environmental benefit, for example by increasing the regeneration rate of the alkaline solution in AwR. The economic assessment was conducted on AwR and it was found that improving its operational costs would help create a business case for potential application. The results not only help the developers of the novel technologies to improve their long term environmental and economic viability but also can be used by developers and manufactures of similar technologies, such as other biogas upgrading or CCS technologies.

Resumen en Castellano

Durante los últimos años, la investigación y el desarrollo de tecnologías para la reducción de las emisiones de gases de efecto invernadero (GEI) en nuestro planeta ha incrementado. Varias soluciones se han propuesto, incluyendo la captura y secuestro de carbono (CCS en inglés). La aplicación de CCS se ha focalizado en las tecnologías de producción de energía a gran escala que utilizan combustibles fósiles. Recientemente, se ha trabajado en el uso de CCS en tecnologías de enriquecimiento de biogás. Esta práctica consiste en la eliminación del CO_2 del biogás emitido por digestores anaeróbicos y vertederos con el fin de incrementar la concentración de CH_4 en el biogás, generando así un potencial sustituto de gas natural.

Dos innovadoras tecnologías en desarrollo almacén además el CO_2 eliminado en una forma sólida, a través de un proceso llamado mineralización de carbono. Este proceso utiliza óxido cálcico de los residuos industriales para fijar el CO_2 en forma de carbonato cálcico. Idealmente estas tecnologías innovadoras de enriquecimiento deberían mostrar mayores beneficios ambientales en comparación con las tecnologías convencionales ya que almacenan inmediatamente el CO_2. La primera tecnología analizada es la regeneración de alcalino (AwR) que consiste en el uso de una solución alcalina para eliminar el CO_2 y que es regenerada mediante su exposición a un residuo industrial rico en CaO. La segunda tecnología es enriquecimiento de biogás con cenizas (BABIU), basada en la interacción directa del biogás con las cenizas resultantes de incineradores de residuos municipales. Esta tesis pretende determinar si estas tecnologías innovadoras muestran beneficios ambientales respecto a las tecnologías convencionales de enriquecimiento de biogás, mediante la aplicación de herramientas de la ecología industrial. El análisis de ciclo de vida, el análisis de flujos materiales y el análisis de exergía son aplicadas para el análisis ambiental y de recursos. Asimismo, la viabilidad a largo plazo de las tecnologías es examinada desde el punto de vista económico y material.

En general, los resultados indican que las tecnologías innovadoras no muestran un perfil ambiental notablemente mejor que las convencionales, especialmente para AwR donde el uso de la solución alcalina da lugar a un elevado impacto ambiental. Aún así, ambas tecnologías consiguen un significante ahorro de CO2 respecto a las tecnologías convencionales. Asimismo, dado que las dos tecnologías analizadas se encuentran en un período de prueba piloto, se identifican las potenciales mejoras para optimizar el perfil ambiental y económico, como incrementar la eficiencia de la regeneración de la solución alcalina en la tecnología AwR. El análisis económico realizado para AwR resaltó que reducir sus costes operacionales incrementaría la oportunidad de su implementación como negocio. Los resultados pueden ser usados tanto por promotores de estas innovadoras tecnologías para mejorar su viabilidad económica y ambiental a largo plazo, como por promotores y fabricantes de tecnologías similares, como aplicaciones de CCS o enriquecimiento de biogás.

Preface

This doctoral thesis has been developed at the Department of Chemical Engineering as part of the "Environmental Science and Technology" PhD program of the Institut de Ciència i Tecnologia Ambientals (ICTA) within the research group Sostenipra (Sostenibilitat i Prevenció Ambiental) in the Universitat Autònoma de Barcelona (UAB) from April 2010 to September 2013. This period includes a three month research stay, from February 2013 to April 2013, with the Energy and Resources group of the Copernicus Institute of Sustainable Development, which is part of Utrecht University in Utrecht, Netherlands.

This thesis is divided into four parts with a total of 11 chapters.

Part I covers the introduction and is divided into four chapters. **Chapter 1** introduces the topic of biogas upgrading and the importance of running a sustainability assessment. **Chapter 2** defines the objectives and goal of the thesis. **Chapter 3** describes eight different biogas upgrading technologies that were assessed throughout the thesis. **Chapter 4** gives an overview of the methodologies used.

Part II is divided into five chapters which all cover the application of industrial ecology tools in order to asses the environmental impact of biogas upgrading technologies.

Chapter 5 applies three life cycle assessments (LCA) to upgrading technologies with varying system boundaries. The functional unit (FU) is based on the separation of one ton of CO_2 from biogas. The inventory data for the novel technologies is based on laboratory scale data that has been scaled up. This assessment looks at, among other things, how the impact categories are affected by each component of the novel upgrading technologies.

Chapter 6 builds on the previous chapter by exploring further the environmental impact, with LCA, through a system boundary that counts the methane that is diverted, as a benefit to each technology. This chapter also uses a more recent data set and defines the system boundary as the upgrading of 1 kWh of biomethane. It also begins to explore the availability of resources required to apply the novel technologies on a wide scale in Spain.

Chapter 7 uses the results from the previous two chapters and improved data from the developers to look at how one of the novel technologies can improve its environmental performance. This LCA uses final pilot plant data for both of the novel technologies and defines where further improvements should be focused.

Chapter 8 complements the previous chapters by exploring the use of resources of the novel technologies. The total consumption and the efficiency of the consumption is analyzed using exergy.

Chapter 9 finalizes the environmental assessment by analyzing how much natural gas extraction would be avoided by the upgrading of biogas from landfills and anaerobic

digesters and whether the application of such novel technologies be would feasible. As well, based on previous LCA data, it explores how much CO_2 emissions can actually be avoided if these technologies were applied in Spain, Italy and Austria.

Part III is made up of **Chapter 10** which broadens the sustainability assessment by examining the economic feasibility of applying a novel biogas upgrading technology to landfills in Spain. It applies three different future scenarios in which the total costs and benefits are determined.

Part IV is comprised of **Chapter 11** which discusses the overall summary, conclusion and future recommendations.

Chapters 5 to 10 each present an article that is either published, under review, submitted, or soon to be submitted in a peer-reviewed indexed scientific journal. Therefore these chapters follow the format of an article and include: abstract, introduction, methodology, results, discussion and conclusion. All chapters include the co-authors of the manuscripts and in the case of the chapters based on submitted or soon to be submitted manuscripts, the co-authors reflects those listed at the time of submission of the thesis.

Dissemination

This thesis is mainly based on the following papers that are either published or accepted:

> Starr K., Gabarrell X., Villalba G., Talens L., Lombardi L. (2012) Life cycle assessment of biogas upgrading technologies. *Waste Management*, 32, 991-999.
>
> Starr K., Gabarrell X., Villalba G., Talens L., Lombardi L. Potential CO_2 Savings through Biomethane Generation from Municipal Waste Biogas. Accepted with minor revisions in *Biomass and Bioenergy*, August 2013.

This thesis is also based on the manuscripts that have either been submitted and are under review or that will be submitted shortly for publication in peer reviewed indexed journals.

In addition, the work included in the thesis was presented in several oral communications and posters at international conferences:

> Starr K., Villalba G., Gabarrell X., Talens Peiro L., Blanquez Cano, F. (2013) LCA Study on the Variables of a Novel Biogas Upgrading Technology. *ISIE 2013, 7th International Conference of the International Society for Industrial Ecology*. Ulsan, Korea. Poster
>
> Starr K., Gabarrell X., Villalba G., Talens L., Lombardi L. (2012) Biogas Upgrading: Global Warming Potential of Conventional and Innovative

Technologies. *ECOS 2012, The 25th International Conference on Efficiency, Cost, Optimization and Simulation of Energy Conversion Systems and Processes.* Perugia, Italy. Oral Communication

Starr K., Gabarrell X., Villalba G., Talens Peiro L. (2011) Potential reduction of CO_2 emissions in Spain through the application of carbon capture technologies in anaerobic digestion units. *Ecotech and tools, Environmental & Integrated Assessment of Complex Systems: Biosystems - Water - Land Management.* Montpellier, France. Poster

Starr K., Gabarrell X., Villalba G., Talens L., Lombardi L. (2011) CO_2 Balance of Biogas Upgrading Technologies. *Thirteenth International Waste Management and Landfill Symposium.* Sardinia, Italy. Poster

Part I

Introduction and Framework

Chapter 1

Introduction

Chapter 1 - Introduction

In our modern society our world is rapidly developing. The creation of new inventions and improvement of technologies are leading the way of this growth. The goal when developing new technologies is first and foremost its capacity to complete the selected task. New technologies that are based on established technologies look to improve the efficiency or add new benefits. In many cases these improvements focus on efficiency which often signifies economic improvement, but increasingly the focus has also been on ensuring that there is also an environmental benefit. Currently, a lot of research has been centered on creating technologies that reduce the environmental impact of developed societies in a way that allows them to continue living their lives in the manner in which they are accustomed without having to make significant changes. One example of this custom in developed society is the so called "disposable" culture in which once something is used it is immediately thrown out. Apart from the burden on the environment and natural resources required to increasingly produce more products, this cultural shift also signifies an increase in the amount of waste created and that requires disposal.

Increasingly, countries and municipalities have been adapting waste management strategies in order to separate and recycle profitable materials. In some regions of the world the population is not sensitized enough to ensure proper separation of waste. One item that should be separated, though it may not be immediately profitable, is organic matter. Organic waste in landfills decomposes to biogas through anaerobic digestion. This biogas is mainly composed of methane (CH_4) and carbon dioxide (CO_2), which are both greenhouse gases (GHG), and has smaller levels of other contaminates such as hydrogen sulphide (H_2S), nitrogen (N_2) and siloxanes (table 1.1). The concentration of each gas depends on the composition of the waste that is degrading and its age.

Table 1.1. Components of biogas and natural gas

Compound	Unit	Landfill	AD plant	Sewage sludge	Natural Gas	
					Denmark Standards	Sweden Standards
CH_4	%	35-65	60-70	55-65	89	95 - 99
CO_2	%	15-50	30-40	35-45	0.67	
N_2	%	5-40	< 1	< 1	0.28	< 5
O_2	%	0-5	< 0.2	< 0.4	0	
H_2S	ppm	0-100	10 - 4000	10 - 500	2.9	

Adapted from:(Petersson and Wellinger, 2009,Dirkse, 2009)

This gas, in uncontrolled circumstances, dissipates from the landfill site and is released into the atmosphere. In 2009 the landfills emissions in Spain accounted for around 4% of the total reported CO_2 emissions (UNFCCC, 2013). In many countries regulations are in

place to capture the biogas. In Europe there is legislation to ensure that European countries capture the biogas that is emitted from landfill and at a minimum this gas must be flared off (European Commission, 1999). Flaring burns the methane to produce CO_2, which is a less potent GHG.

Some landfill sites are taking advantage of the high calorific value of methane and are burning the gas directly to form electricity and sometimes heat as well. Another option exists that has been emerging in recent years, which is biogas upgrading. This technology isolates the methane contained in biogas in order to create a gas that has a similar composition to natural gas and can therefore be used as an alternative to it. The gas is often referred to as biomethane. This thesis focuses on technologies that remove CO_2 from the biogas, which is an important step in biogas upgrading (Petersson and Wellinger, 2009).

Landfills and other sources of biogas, such as wastewater treatment sites and farms (via anaerobic digestion (AD) units), have been slowly embracing the idea of upgrading biogas. There are currently six different types of biogas upgrading technologies that are on the market (see chapter 3) and interest has been growing to improve these technologies or to develop new methods. As these technologies remove CO_2, the processes that are used are similar to carbon capture and storage (CCS) technologies that are being studied for potential application for large scale industries such as electricity production and cement production (IPCC, 2005). One emerging CCS process that has been receiving great interest in the environmental community is carbon mineralization because it transforms CO_2 into an insoluble salt.

Two technologies that have been developed within the framework of the European Commission UPGAS-LOWCO2 project apply carbon mineralization in order to upgrade biogas. These technologies, known as alkaline with regeneration (AwR) and bottom ash for biogas upgrading (BABIU) (chapter 3) have an advantage over conventional technologies as they immediately store the CO_2 that is removed from the biogas, while conventional technologies often release the CO_2 back into the environment.

Biogas that comes from landfills contains a mixture of CO_2 and CH_4 that comes from biogenic and anthropogenic origins. While most of the gases are counted towards the GHG emissions, the biogenic CO_2 emissions are normally not included (see chapter 4) (IPCC, 2005). Regardless of whether the source of CO_2 is biogenic or anthropogenic it is important to note that reducing any amount of CO_2 from going into the atmosphere helps to mitigate climate change.

1.1 Sustainability and Industrial Ecology

Sustainability is a concept of maintaining the status quo over time. In terms of development of societies, it is best explained as “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs” (WCED, 1987).

There are three interrelated aspects to sustainability: social, economic and environmental. The concept of sustainability can also be applied to technologies. In this case sustainability refers to ensuring that the technology can exist for a long time. This would be ensured through: social understanding, acceptance, and equality; economic viability; and that the required environmental resources are not depleted.

Industrial ecology is a discipline that looks to understand how societies and industries interact with the environment. From this understanding it is then possible to not only quantify the interactions, but also to see how these interactions can be improved in order to reduce the environmental burden of an industry or society. Therefore it can also be used to explore how environmental sustainability can be achieved.

Environmental sustainability can be attained by mitigating the pollution of environmental resources and by reducing the extraction of non renewable resources. All of which will help ensure their future availability. An important concept that is applied to sustainability is the idea of closing the material cycle. Society tends to extract resources, create a product from said resources, use the product, and when the usefulness of the product is completed it is thrown away. Part of environmental sustainability looks to close this material cycle so that nothing is extracted and nothing is disposed of (Fig 1.1).

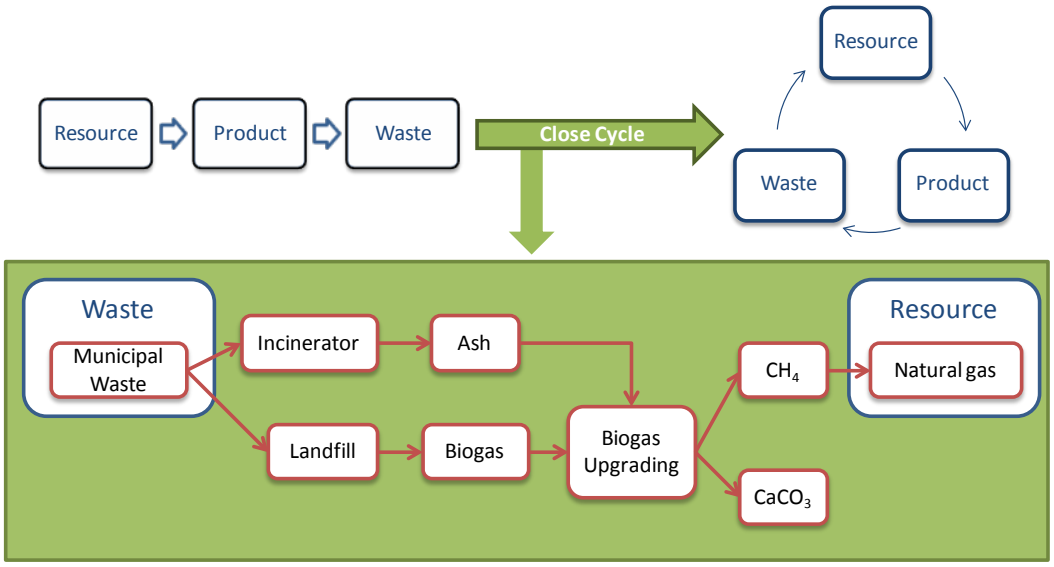


Figure 1.1 Closing the material cycle with novel biogas upgrading

The AwR and BABIU technologies are examples of how the material cycle can be closed. It takes a waste and creates a resource, an alternative to natural gas (Fig 1.1). Despite this promising aspect, it is important to ensure that other environmental resources are not being depleted. Not solely resources that they themselves use but also ones that other industries and society in general require.

This thesis has applied industrial ecology tools in order to better understand how a novel process, which is under development and which has supposed environmental benefits, truly impacts the environment and what changes can be made in order to improve its environmental footprint. As the economics of a technology often plays a more prominent role over environmental aspects, the environmental assessment was complemented by an economic study in order to better determine the potential sustainability of novel biogas upgrading technologies.

Chapter 2

Objectives

Chapter 2 - Objectives of Thesis

The main objectives of the thesis are described below. Table 2.1 describes which chapters address each of the objectives.

Objective I – To determine whether the environmental benefits of the novel biogas upgrading technologies outweigh the environmental impacts created.
Objective II – To determine whether the novel upgrading technologies consume natural resources in an efficient manner.
Objective III – To determine how much natural gas can be substituted by biomethane, upgraded from biogas, under different municipal waste management system scenarios
Objective IV – To determine whether there is enough carbon mineralization material available for wide scale application of the novel technologies.
Objective V – To determine whether the application of a novel biogas upgrading technology is economically feasible.

Table 2.1 Chapters that address each thesis objective

	Objective				
	I	II	III	IV	V
Chapter 5	•				
Chapter 6	•			•	
Chapter 7	•				
Chapter 8		•			
Chapter 9			•	•	
Chapter 10					•

Transversal questions that were also addressed throughout the thesis include:

- ***Question 1:*** How can different industrial ecology tools serve to assess technologies and how do they complement each other?
- ***Question 2:*** As the technologies are still in the development stage, what changes can be made in order to improve the environmental and economic performance? How can environmental assessment at the pilot scale be used at industrial scale? What are the limitations?

Chapter 3

Biogas Upgrading Technologies

Chapter 3 - Biogas Upgrading Technologies

Biogas can be upgraded by using six main technologies: cryogenic separation, membrane separation, organic physical scrubbing, chemical scrubbing, pressure swing adsorption, and high pressure water scrubbing. These technologies are based on four principle techniques: absorption, adsorption, membrane and cryogenic. In recent years there has been growing interest in the application of biogas upgrading technologies. While biogas upgrading technologies have been around since the 1990's (Bauer et al., 2013) Fig. 3.1 shows how the number of constructed facilities for each technology has increased almost 4 fold between 2006 and 2012.

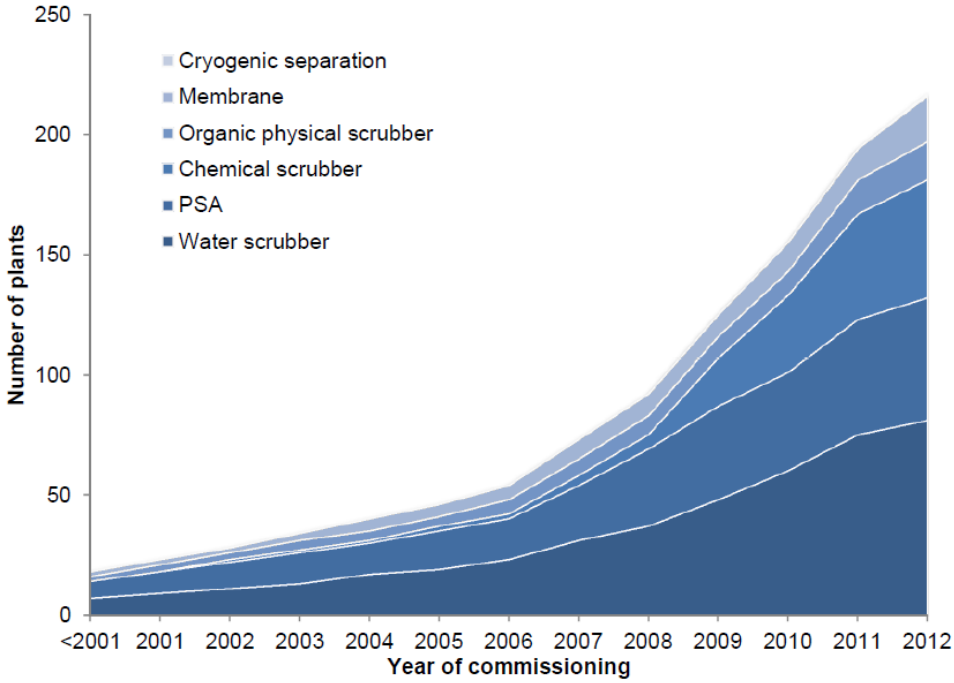


Figure 3.1. Application of biogas upgrading technologies over the years
Source: (Bauer et al., 2013)

While the application has been growing, so has the interest in developing different ways to separate the CH_4 from CO_2 (Bauer et al., 2013). One such novel technique that is gaining interest is carbon mineralization. The conventional technologies and the novel ones under review are found in table 3.1 (Petersson and Wellinger, 2009,Bauer et al., 2013). The description of each technology follows.

Table 3.1. List of conventional and novel biogas upgrading technologies.

Technique	Technology	Acronym
Conventional		
Absorption	High pressure water scrubbing	HPWS
	Chemical scrubbing	AS
	Organic physical scrubbing	OPS
Adsorption	Pressure swing adsorption	PSA

Membrane	Membrane separation	MS
Cryogenic	Cryogenic separation	Cry
Novel		
Carbon Mineralization	Alkaline with regeneration	AwR
	Bottom ash for biogas upgrading	BABIU

3.1 Conventional Technologies

This section explains the six main biogas upgrading technologies on the market. These include; the absorption technologies of high pressure water scrubbing, chemical scrubbing and organic physical scrubbing; pressure swing adsorption; membrane separation; and cryogenic separation.

3.1.1 High Pressure Water Scrubbing

High pressure water scrubbing (HPWS) consists of using water in order to remove CO_2. As methane has a lower solubility in water, it is possible to selectively absorb for CO_2. This technology can also remove other biogas impurities such as H_2S and ammonia (Persson, 2003).

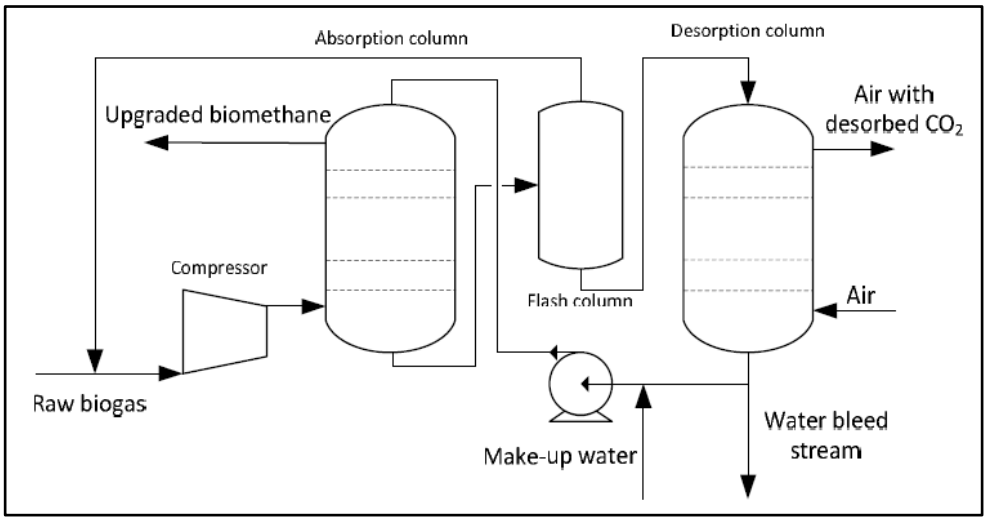


Figure 3.2. High Pressure Water Scrubbing Diagram
source:(Bauer et al., 2013)

Fig. 3.2 illustrates how the CO_2 is dissolved into water using high pressure in the absorption column. The solution is fed into a flash tank where the CO_2 is released. In the desorption column, the pressure is lowered in order to regenerate the water. The water is then re-circulated back into the absorption column with the necessary make-up water (Bauer et al., 2013). Some older models of the technology do not re-circulate the water, and thus the electrical consumption is lower (Persson, 2003).

3.1.2 Chemical Scrubbing

Chemical scrubbing (AS) uses an amine solution to form a reversible chemical reaction with CO_2. The most common chemicals used are diethanolamine (DEA) and monoethanolamine (MEA) (Bailey and Feron, 2005,Persson, 2003,Rao and Rubin, 2002a). Though recently more focus has been placed on methyldiethanolamine (MDEA) or a mixture of MDEA and piperazine (Bauer et al., 2013).

As seen in Fig. 3.3 the CO_2 reacts with the amine in the absorber column (Bauer et al., 2013) to create a water soluble salt (MacDowell et al., 2010). This solution is fed into the stripper column where steam is added in order to reverse the chemical reaction, thus releasing the CO_2 (Persson, 2003).

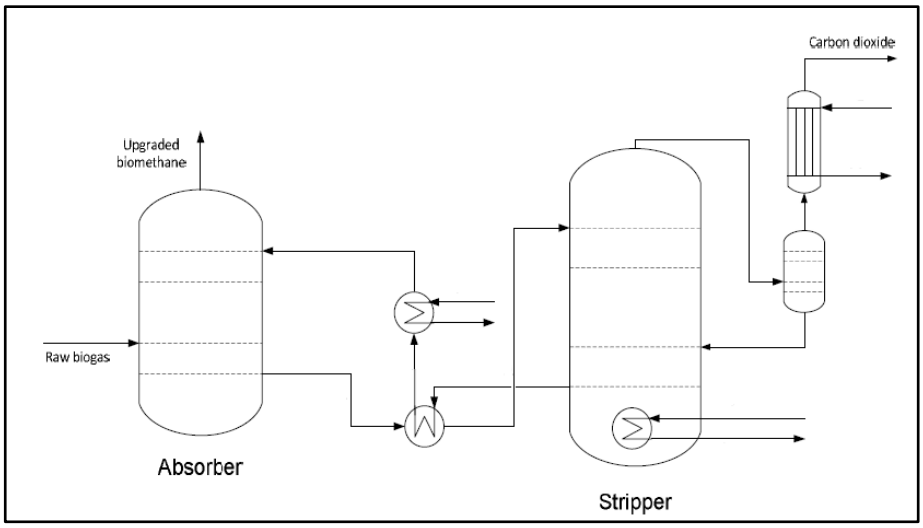


Figure 3.3. Amine Scrubbing diagram
adapted from:(Bauer et al., 2013)

3.1.3 Organic Physical Scrubbing

Organic physical scrubbing (OPS) uses a blend of polyethylene glycol dimethyl ethers in order to absorb the CO_2 (Bauer et al., 2013). The most common commercial blends are Selexol© by DOW chemical company or Gensorb© by ThyssenKrupp Uhde (Petersson and Wellinger, 2009).

In this process, the biogas is first fed into an absorption column where the biomethane is released once the CO_2 is absorbed into the polyethylene glycol. The solvent is then heated and depressurized before entering the desorption column. The regenerated solution is then cooled before it re-enters the absorption column (Bauer et al., 2013,Petersson and Wellinger, 2009).

As seen in Fig 3.4 the OPS is quite similar to the HPWS process. The solubility of CO_2 in polyethylene glycol is much higher than that of water which means that less reagent is required in OPS than HPWS (Bauer et al., 2013). However, it is more difficult to regenerate the polyethylene glycol as opposed to water (Persson, 2003).

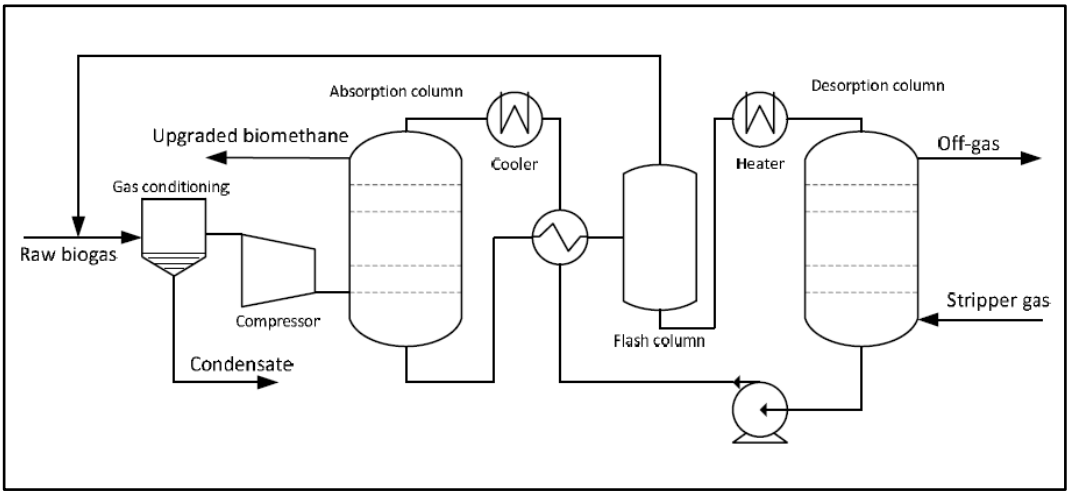


Figure 3.4. Organic Physical Scrubbing diagram
source:(Bauer et al., 2013)

3.1.4 Pressure Swing Adsorption

Pressure swing adsorption (PSA) uses a porous material to selectively adsorb CO_2 by focusing on the size of molecules and physical forces (Persson, 2003). Materials include silica gel and alumina (de Hullu et al., 2008), though the most common are activated carbon, and zeolite (Petersson and Wellinger, 2009). These materials can also selectively capture nitrogen, oxygen and H_2S, the later of which is irreversibly adsorbed and therefore must be removed beforehand.

This process consists of four steps, which in turn require four columns packed with adsorption material to ensure continuous operation (Persson, 2003). As seen in Fig. 3.5, the entering biogas is brought to a high pressure and fed into the adsorption column whereby the CO_2 is adsorbed and the biomethane leaves the reactor. The pressure in the column is reduced to near vacuum in two steps. In the first the gas normally contains methane so it is fed back into the system. In the second depressurizing step the CO_2 is fully released from the adsorption material into the environment. The adsorption material is then re-pressurized in order to prepare it to accept the biogas (de Hullu et al., 2008,Petersson and Wellinger, 2009).

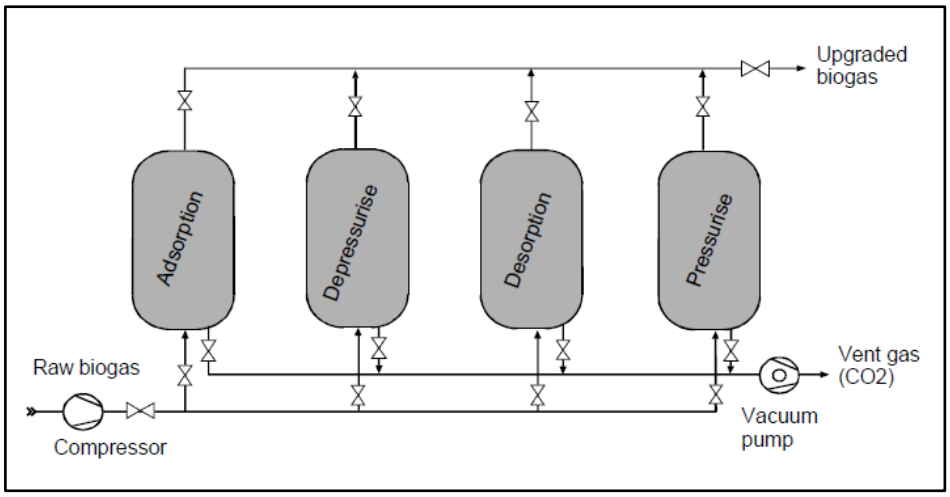


Figure 3.5. Pressure Swing Adsorption diagram
source: (Persson, 2003)

3.1.5 Cryogenic Separation

Cryogenic separation (Cry) relies on the different sublimation points of CH_4 (-161.5 °C) and CO_2 (-78.5 °C) (CRC, 2013). In this process, as seen in Fig. 3.6, the biogas is cooled and compressed until the CO_2 becomes liquid (-78.5). As the methane has a lower sublimation point the two gases can be separated in a distillation column. This technology can also selectively remove other gases such as H_2S, nitrogen, water, and siloxanes (Petersson and Wellinger, 2009).

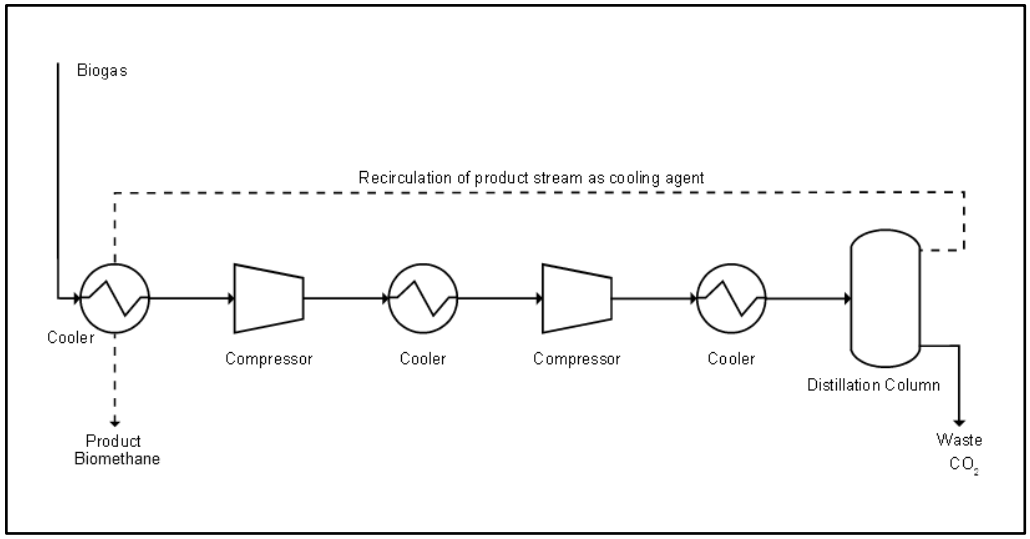


Figure 3.6. Cryogenic Separation diagram
adapted from:(de Hullu et al., 2008)

While there are companies that manufacture this technology and facilities that exist, there is a lot of interest in further improving and refining it. Therefore, one can consider that this technology is still under development (Bauer et al., 2013).

3.1.6 Membrane Separation

This process, membrane separation (MS), uses a dense filter membrane to selectively remove CO_2 from CH_4 using a membrane filter. The membrane used is continually being improved upon and new materials are constantly developed, though currently the most widely used membranes include carbon membrane and glassy polymer / polymeric hollow fibre. For most filters, water, hydrogen and oxygen can also be removed, though in this technology it is favourable to remove water beforehand in order to avoid condensation when the biogas is compressed (Bauer et al., 2013).

As seen in Fig. 3.7, the biogas is compressed and fed through a membrane. As methane is less permeable than the CO_2, the biomethane is separated while the CO_2 passes through the filter. There are three different configurations for membrane separation that have recently come on to the market. In the first one biogas is not internally circulated. This results in lower energy consumption, though there is a greater methane loss. The second system relies on using membranes in parallel to re-circulate biogas. The second setup takes the CO_2 rich gas that has permeated the filter, and passes it through another filter in order to lower methane slip. The third setup passes the gas that did not pass through the filter, the biomethane, and sends it through another filter to increase the methane concentration (Bauer et al., 2013).

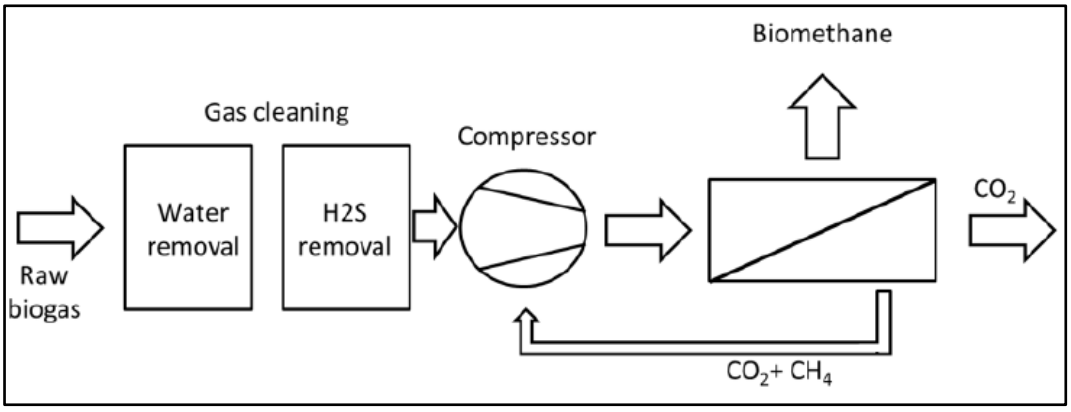


Figure 3.7. Membrane Separation,
source:(Bauer et al., 2013)

3.2 Carbon Mineralization

Carbon mineralization, also known as carbon looping and mineral carbonation, is a carbon sequestration process that consists of using a mineral that contains a metal oxide to react with CO_2 in order to form a non water soluble compound (IPCC, 2005)). Rocks such as silicate and minerals such as serpentine and olivine are natural sources of these oxides. However, industrial wastes such as steel slag, bottom ash and air pollution control residues from municipal solid waste incinerators are alternative sources. These wastes, rich in calcium oxides (CaO), generate calcium carbonate ($CaCO_3$) when they are put in contact with CO_2, according to equation 3.1.

(3.1) $$CaO_{(s)} + CO_{2(g)} \rightleftharpoons CaCO_{3(s)} + heat$$

Two technologies using this method are alkaline with regeneration (AwR) and bottom ash for biogas upgrading (BABIU) and are described below. Both technologies have been developed as part of the UPGAS-LOWCO2 project, financed by the European Commission Life+ programme, which had the following partners: Università degli Studi di Firenze (Florence Italy), Centro Servizi Ambiente Impanti S.p.A. (Terranuova Bracciolini, Italy), Università di Roma "Tor Vergata" (Rome, Italy), University of Natural Resources and Life Sciences (Vienna, Austria), and Universitat Autonoma de Barcelona (Barcelona, Spain).

3.2.1 Alkaline with Regeneration

Figure 3.8 shows the process of Alkaline with regeneration (AwR).

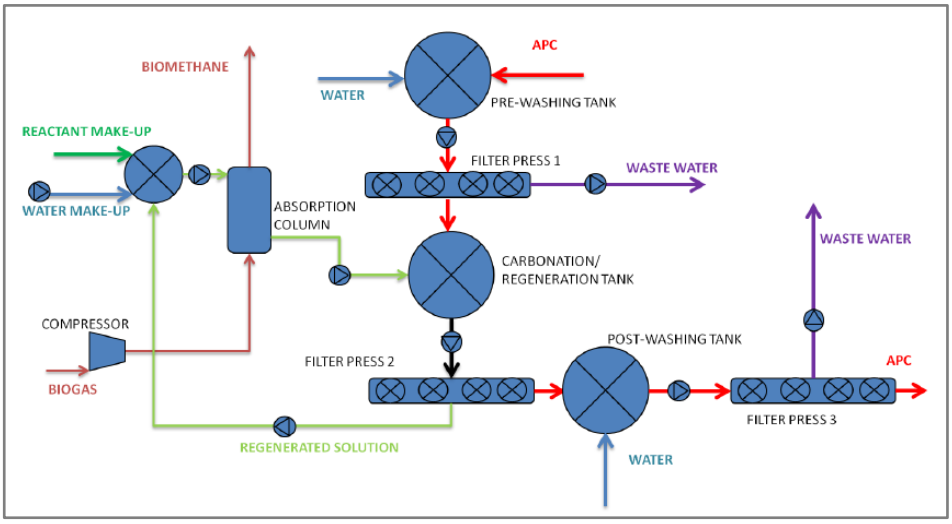


Figure 3.8. Alkaline with Regeneration diagram
source (Lombardi, 2012c)

AwR uses an alkaline solution to remove CO_2 from biogas. The alkaline solution used is either potassium hydroxide (KOH) or sodium hydroxide (NaOH) as they have a high affinity for CO_2. Once the biogas is stripped of CO_2, following equation 3.2 and 3.3, the biomethane exits the system and is dried and compressed.

(3.2) $2\ KOH_{(aq)} + CO_{2(g)} \rightarrow\ K_2CO_{3\ (aq)} + H_2O_{(l)}$

(3.3) $2\ NaOH_{(aq)} + CO_{2(g)} \rightarrow\ Na_2CO_{3\ (aq)} + H_2O_{(l)}$

The alkaline solution is then regenerated by passing it through a column packed with air pollution control residues (APC), which are rich in CaO. APC has been previously pre-washed to remove heavy metals and chlorine. After pre-washing, the APC is filtered and then placed into a stirred tank to react with the loaded solution. The carbonate solution then reacts with the CaO in the APC to form $CaCO_3$, following equations 3.4 and 3.5.

(3.4) $K_2CO_{3(aq)} + CaO_{(s)} + H_2O_{(l)} \rightarrow CaCO_{3(s)} + 2\ KOH_{(aq)} + heat$

(3.5) $Na_2CO_{3(aq)} + CaO_{(s)} + H_2O_{(l)} \rightarrow CaCO_{3(s)} + 2\ NaOH_{(aq)} + heat$

The slurry of APC residues and solution are filtered to separate the two and the regenerated alkaline solution is then placed back into the system. Any make-up water and base is added before entering the absorption column. The APC is then washed again to remove any remaining alkaline solution and then filtered again. It is possible to re-use this wastewater to pre-wash the APC (Lombardi, 2012c).

Throughout the development of this thesis, the AwR process was modified as the technology was scaled up from laboratory to pilot plant. The most notable change was that the APC was not washed before or after its use. Thus the process required two filters less and wastewater was not generated. Also, the regeneration levels changed from 70% to 50%. All the changes occurred during the scaling up are discussed in further detail in chapter 7.

3.2.2 Bottom Ash for Biogas Upgrading

Bottom ash for biogas upgrading (BABIU) focuses on a direct solid-gas interaction. This process uses bottom ash (BA) from a municipal solid waste incinerator rich in CaO to adsorb CO_2. This is a batch process which requires two reactors with a total of four sub-units in order to assure continual upgrading (as showed in Fig. 3.9). BA is first weathered and large pieces of BA are removed using a grate. Then it is loaded into a reactor by a small truck. The air is removed by pumping nitrogen into the reactor. This is important to ensure that air and CH_4 are not combined, as they are an explosive combination at high concentrations. Once the air is purged the biogas can enter. It must remain in the reactor for six hours after which the biomethane is removed from the top and the BA is removed from the reactor to be filled again. The filling, purging, upgrading and emptying are run in tandem with the second reactor in order to ensure a continuous process (Mostbauer and Lenz, 2007b,Lombardi, 2012c). This is shown in Fig 3.9 where the solid lines denote that reactor 2 is prepared while reactor 1 is running, then with the dotted lines one can see that the reactor 1 is then prepared while rector 2 is running.

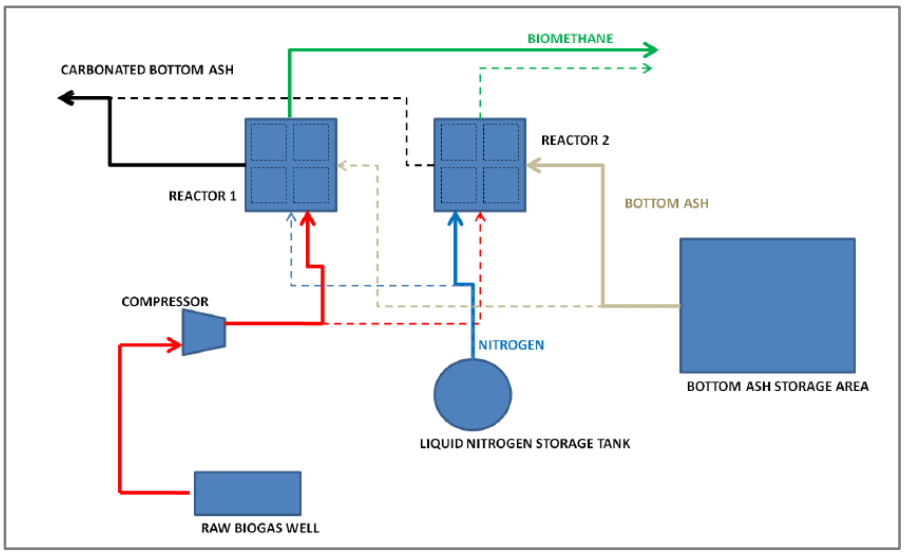
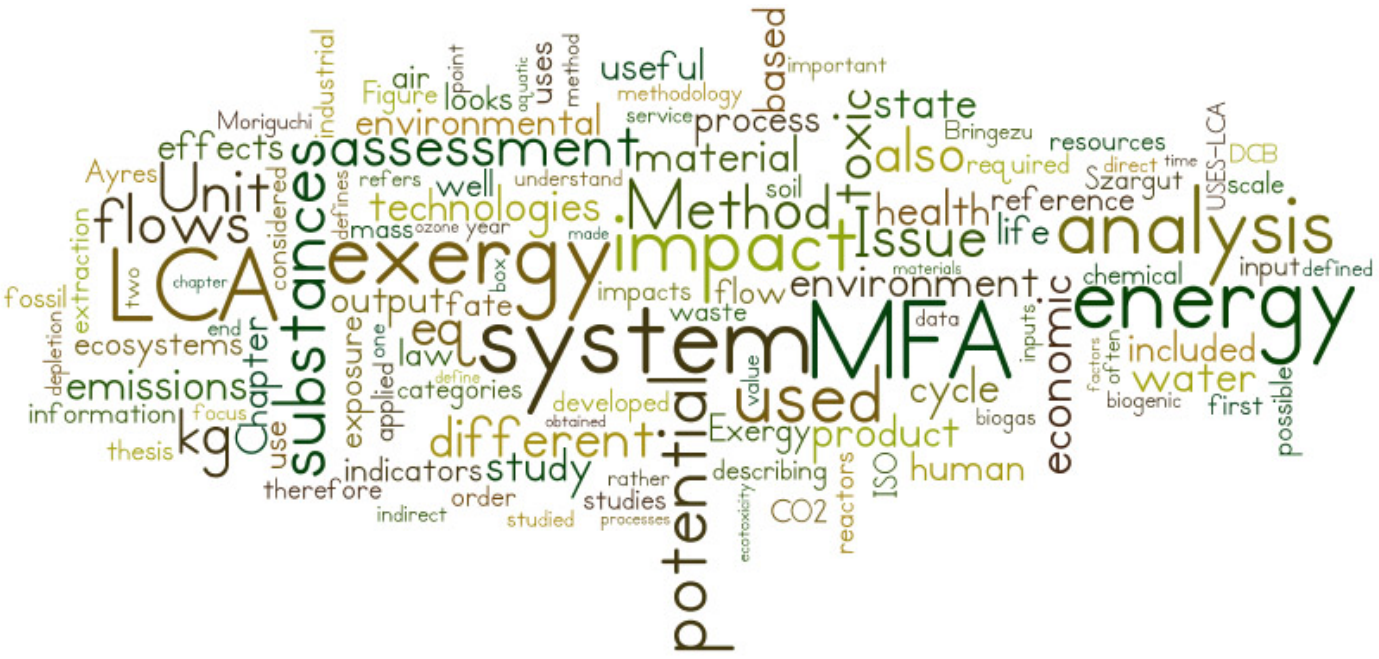


Figure 3.9. Bottom Ash for Biogas Upgrading diagram
source: (Lombardi, 2012c)

3.3 Pre-cleaning of biogas

Depending on the composition, the upgrading technology, and the final use of biomethane, it may be necessary to pre-clean the biogas before removing CO_2. Some of the compounds that would need to be removed include: water, ammonia, siloxanes, oxygen, nitrogen, particulates and hydrogen sulphide (H_2S) (Petersson and Wellinger, 2009). Hydrogen sulphide is the most common problem because if H_2S levels are too high then they must be removed in order to avoid the production of sulphur which can cause damage to the upgrading equipment (de Hullu et al., 2008). This can be eliminated in some CO_2 removal technologies such as HPWS and in this case would not have to be removed beforehand (Persson, 2003). Siloxanes can cause engine corrosion when combusted because it creates a fine powder called silicon oxide. Though siloxanes are only generated in landfill and wastewater treatment facilities and not anaerobic digestion units as this compound is found in personal care items such as shampoos and deodorants (Petersson and Wellinger, 2009). The impurities contained in biogas required for removal prior to biogas upgrading are selected on a case by case basis.


Chapter 4
Methodology

Chapter 4 - Methodology

This section defines the different methodologies used for the assessment of biogas upgrading technologies. For Part II the tools used are material flow analysis (MFA), life cycle assessment (LCA), and exergy analysis, all used by the research field of Industrial Ecology. The economic assessment, in Part III, uses techno-economic tools. An overview of each methodology used is described below. More detailed explanation can be found in the chapters in which the methodologies are applied (table 4.1).

Table 4.1 Methodology used in each chapter

	Methodology			
	MFA	LCA	Exergy	Economic
Chapter 5		•		
Chapter 6		•		
Chapter 7	•	•		
Chapter 8		•	•	
Chapter 9	•			
Chapter 10				•

4.1 Material Flow Analysis

Material flow analysis (MFA) is a methodology that looks at quantifying the flows and stocks of a system in a defined area and period of time (Brunner and Rechberger, 2004). It is used to understand and quantify the interaction between the environment and a society and/or economy. In other words, it is used to define the metabolism of a region, economic sector, substance, or product (Villalba Méndez and Talens Peiró, 2013,Bringezu and Moriguchi, 2002).

MFA is one of the first tools developed in the field of industrial ecology. It stared out in the 1960s as a way to quantify and understand the metabolism of societies both on a city and nation wide scale (Wolman, 1965,Ayres and Kneese, 1969). Despite its early start it only began obtaining momentum in the 1990s which then helped create the foundations for the field of industrial ecology (Sendra Sala, 2008).

It is based on the mass conservation law which states that energy, matter and mass are conserved and therefore cannot be destroyed or created, but only rearranged or metamorphosed (Ayres and Ayres, 1999). This conversation means that the inputs to a system are equal to the outputs and any accumulation in the system. Therefore by running a mass balance it is possible to identify missing flows and accumulations in the system.

In order to run an MFA it is necessary to follow the following steps: 1) Definition of the process along with the system boundaries, both physical and temporal. 2) Label all of the input and output flows, as well as any accumulations in the system. 3) Identify the known values of each flow. 4) List all the mass balances, and if necessary make

assumptions if there is incomplete data. 5) Solve for unknown variables (Villalba Méndez and Talens Peiró, 2013,Bringezu and Moriguchi, 2002).

There are two ways in which a material flow analysis (MFA) study can be conducted. The focus can be on the flow of a particular item such as a chemical substance, material or product; or the focus can also have a larger scope such as a company, industrial sector or geographic region (Bringezu and Moriguchi, 2002). Within the same context, MFA can be run on various scales: global, national, regional, based on a functional unit, service, or product (Fischer-Kowalski and Hüttler, 1998,Sendra et al., 2007).

MFA is based on a black box idea, whereby the inputs and outputs are studied but not what occurs 'within the box'. These are classified as either direct or indirect flows. Direct refers to the flows that cross the system boundary, or rather the black box. The indirect flows refer to those that are required for a product or economic service but do not cross into the system boundary, or into the black box (Bringezu and Moriguchi, 2002,Sendra Sala, 2008). The MFA based study in chapters 7 and 9 deal solely with the direct flows of waste on a national scale in one year.

MFA is the basis for any life cycle assessment and exergy assessment as it provides the necessary quantification of the direct and indirect flows (Villalba Méndez and Talens Peiró, 2013).

4.2 Life Cycle Assessment

Life cycle assessment (LCA) studies the environmental impact of a process or product during its entire life cycle. Every resource that is required (input) and any pollutants generated (output) are inventoried and its impact is determined through a set of parameters. In most cases LCA looks at the following points related to a product, service or process: extraction, manufacturing, transport, use and disposal. This entire scope is called cradle to grave as it goes from beginning to end, though there are various different scopes that can be selected in an LCA. In this thesis most of the LCAs focused on cradle to gate, which means that it was studied from extraction up to the use phase. The principal reason for this selection was that the carbonated wastes have not been fully studied and therefore their end use is not well-established as it may have commercial value which may be preferred over disposal in a landfill. The requirements for treatment prior to disposal may vary depending on the original source of the waste. For example, air pollution control residues are considered as hazardous waste, but studies by the developers of the novel biogas upgrading technologies indicate that they are considered non-hazardous after use because the carbonation helps reduce the leaching of heavy metals. However, this warrants further study.

The study of LCA emerged in the 1970s as a response to energy and waste management problems. In the 1990s, efforts were made to harmonize and develop the methodology with the Society of Environmental Toxicology and Chemistry (SETAC) leading the way (Udo de Haes, 2002). The International Standards Organization started working on standardizing the LCA methodology in 1994 and created the ISO 14040 (ISO, 2006).

The ISO 14040 guideline identifies three main stages: 1) Definition of the system under study through the establishment of the goal and scope; 2) The inventory analysis where all of the information needed is compiled; 3) The impact assessment stage where the environment impact of the system is determined. All of these stages are important for the assessment and are interrelated for the interpretation of results (fig 4.1).

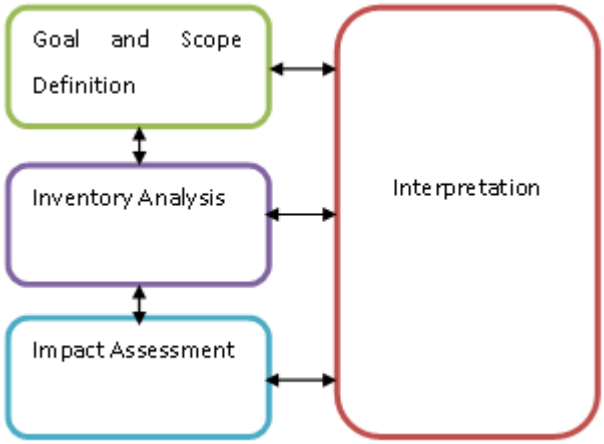


Figure 4.1 Phases of life cycle assessment according to ISO 14040
Source:(ISO, 2006)

In LCA, it is important to establish the focus of the study and what systems and flows are included. This is defined by the functional unit (FU), which sets the point of comparison of the study, and is also defined by the system boundary. The definition chosen for the FU, as well as the system boundaries can affect the results obtained. In this thesis three LCAs were performed with two different functional units and multiple system boundaries. The differences and similarities between these will be discussed in the chapter 11.

Once the data is collected, often through literature review or in collaboration with industries, it is possible to run the environmental analysis. In LCA, the input and output flows of the processes are examined for their impacts. Impact categories are divided into midpoint and endpoint categories. Midpoint indicators are points in the cause and effect chain where a characterization factor is applied in order to understand the environmental significance of an emission or extraction. Endpoint indicators are applied at the end of the casue effect chain and are divided into encompassing categories, which include human health, natural resources and ecosystem quality. Both are complementary to each other and have their own strengths and weaknesses (Bare et al., 2000,Curran et al., 2011).

This thesis, which started in 2010, applied the CML 2001 impact assessment method developed by Guinee et al. (Guinée et al., 2002). This is a method that uses the mid-point impact factors and was selected as it provides more certainty and clarity than endpoint impact factors. The cumulative energy demand was also applied. The definition of all of these impact categories can be found in table 4.2.

Table 4.2 Environmental impact categories

Impact category	*Description*
ADP *Abiotic depletion potential*	*Issue:* It is concerned with the protection of human welfare, human health and ecosystem health. It is related to the extraction of minerals and fossil fuels due to inputs into the system. It can be divided into fossil and elements. *Method:* Determined for each extraction of minerals and fossil fuels based on concentration reserves and the rate of de-accumulation. *Unit*: kg Sb eq. for ADP elements and MJ for ADP fossil
AP *Acidification potential*	*Issue:* Acidifying substances cause a wide range of impacts on soil, groundwater, surface water, organisms, ecosystems and materials (buildings). *Method:* Calculated with the adapted RAINS 10 model, describing the fate and deposition of acidifying substances. *Unit:* kg SO_2 eq.
EP *Eutrophication potential*	*Issue:* Impact due to excessive levels of macro-nutrients in the environment caused by emissions of nutrients into the air, water and soil. *Method:* Based on the stoichiometric procedure of Heijungs *et al.* (1992). Fate and exposure is not included. *Unit:* kg phosphate(PO_4^{3-}) eq.
GWP *Global warming potential*	*Issue:* Adverse effects upon ecosystem health, human health and material welfare. Climate change is related to emissions of greenhouse gases into air. *Method:* The characterisation model as developed by the Intergovernmental Panel on Climate Change (IPCC). Factors are expressed as for time horizon of 100 years. *Unit:* kg CO_2 eq.
ODP *Ozone layer depletion potential*	*Issue:* Because of stratospheric ozone depletion, a larger fraction of UV-B radiation reaches the earth's surface. This can have harmful effects upon human health, animal health, terrestrial and aquatic ecosystems, biochemical cycles and on materials. This category is output-related and at global scale. *Method:* Developed by the World Meteorological Organisation (WMO) and defines ozone depletion potential of different gasses. *Unit:* kg R11 eq.
POCP *Photochemical oxidation potential*	*Issue:* Photo-oxidant formation is the formation of reactive substances (mainly ozone) which are injurious to human health and ecosystems and which also may damage crops. *Method:* Calculated with the UNECE Trajectory model (including fate), and expressed in kg ethylene equivalents. *Unit:* kg Ethene (C_2H_4) eq.
HTP/HTTP *Human toxicity potential*	*Issue:* It concerns the effects of toxic substances on the human environment. Health risks of exposure in the working environment are not included. *Method:* Calculated with USES-LCA, describing fate, exposure and effects of toxic substances for an infinite time horizon. *Unit:* kg DCB eq.
TETP *Terrestrial ecotoxicity potential*	*Issue:* It refers to impacts of toxic substances on terrestrial ecosystems, as a result of emissions of toxic substances into the air, water and soil. *Method:* It is calculated with USES-LCA, describing fate, exposure and effects of toxic substances. *Unit:* kg DCB eq.
FAETP *Fresh water aquatic ecotoxicity*	*Issue:* It refers to impact on fresh water ecosystems, as a result of emissions of toxic substances into to the air, water and soil. *Method:* It is calculated with USES-LCA, describing fate, exposure and

potential	effects of toxic substances. *Unit:* kg DCB eq.
MAETP *Marine aquatic ecotoxicity potential*	*Issue:* It refers to impacts of toxic substances on marine ecosystems, as a result of emissions of toxic substances into the air, water and soil. *Method:* It is calculated with USES-LCA, describing fate, exposure and effects of toxic substances. *Unit:* kg DCB eq.
CED *Cumulative energy demand*	*Issue:* It aims to investigate the energy use throughout the life cycle of a good or a service. This includes the direct as well as the indirect uses. *Method:* Characterization factors were given for the energy resources divided in: non renewable, fossil and nuclear, renewable, biomass, wind, solar, geothermal and water. *Unit:* MJ

Table adapted from: (Rives Boschmonart, 2011,Martínez Blanco, 2012). Source: (Guinée et al., 2001,Garrett and Collins, 2009)

LCA is a useful tool as is doesn't simply focus on the environmental impact of running a system, but rather looks at the impact it can have for its creation and disposal. While LCA is useful and is widely used in the scientific community it is important to integrate other types of environmental analysis in order to ensure that all aspects are covered.

4.2.1 Accounting for CO_2 and CH_4 emissions from landfills

There is a lot of debate in the LCA community on how emissions from the degradation of biogenic and anthropogenic carbon in waste should be accounted. For general accounting of CO_2 emissions, the IPCC guidelines state all but biogenic CO_2 should be included (IPCC, 2005). Despite these guidelines, this issue is still debated amongst LCA practitioners. The issue comes down to the allocation of the gas itself, and who bears the impact of the gas.

This thesis took into account both anthropogenic and biogenic carbon as it was felt that biogenic carbon still contributes to the overall GHG. How the CH_4 and CO_2 emission and savings can be attributed in biogas can be interpreted in different ways. Therefore chapters 5, 6, and 7 accounted for CO_2 and CH_4 in different ways and thus making it possible to explore the difference in results.

4.2.2 Accounting for Infrastructure in LCA

For this study the infrastructure (housing unit and each component required such as conveyer belt, compressors, pumps, etc) of the biogas upgrading technologies was generally not included. Since the infrastructure often results in a minimal contribution and is often not included in LCA studies, it was generally not included as well. The novel technologies are in the pilot plant stage, therefore the information on the final mass of certain components are currently not available (For example, the total amount of metal used in the pipe system for AwR). As well, information for the conventional technologies was not readily available. The only information that was included was for the main reactors of AwR, BABIU and HPWS. Even though the first two are at the pilot plant stage it was possible to estimate the material requirements at the industrial scale as reactors.

Estimations were possible as laboratory and then pilot plant scale information was known, and reactors tend to increase relative to the volume of the contents. The potential lifetime of the reactors was taken into account when determining the impact of the reactors, therefore further reducing its impact.

4.3 Exergy Analysis

Exergy analysis is used in Industrial Ecology in order to quantify resource consumption, wastes and losses, and the efficiency of a process or system. Going one step further than material flow analysis, exergy analysis not only accounts for material but also energy flows. Exergy is based on the thermodynamic laws of energy conservation (first law) and energy degradation (second law). By applying these two laws, we can identify which part of the energy output is useful. This useful energy is regarded as exergy, while the rest is considered as energy of a lower quality also known as an exergy loss. Exergy analysis helps investigate how the energy is degraded through a process as it does not apply the law of conservation (Szargut, 2005).

Figure 4.2 illustrates further the definition of exergy. The red line defines that the energy input is equal to the energy output (first law). Though one can see that the energy output also includes heat, waste and energy that is no longer useful for work. Therefore the blue line defines that the exergy output does not equal the input because it does not include degraded forms of energy.

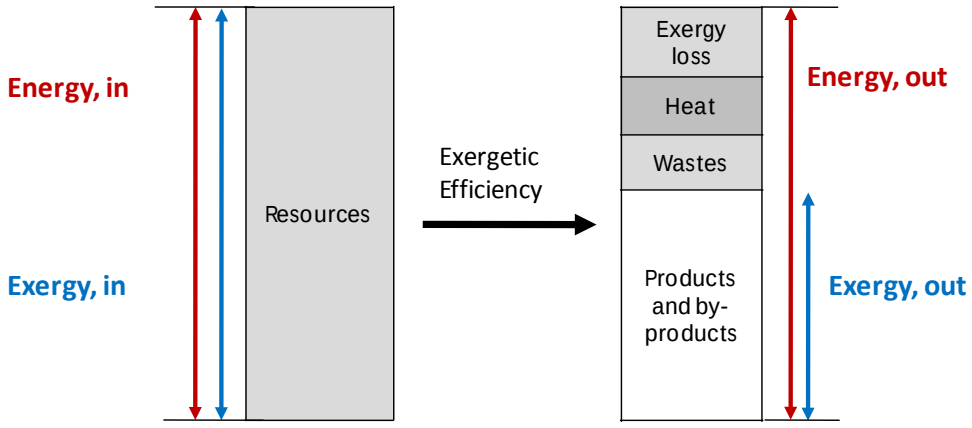


Figure 4.2 First and Second law analysis of real process.
Source: (Talens, 2009). Modified from (Dewulf et al., 2008)

Exergy can also be defined as the amount of useful energy (work) that can be obtained when a resources such as energy or material, is brought into equilibrium with its surroundings through reversible processes (Dewulf et al., 2008,Brunner and Rechberger, 2004,Szargut, 2005). This surrounding environment is considered as a reference state. There are four different types of exergy: physical, kinetic, potential and chemical. As the reference state is considered as the surrounding environment, it is easy to define for the first three exergies. The reference state for chemical exergy needs further clarification as

the environment is a non equilibrium system (Talens, 2009). The reference state for chemicals is determined as the likely state in which a chemical species will end up as after it has gone through all of its reactions. From this analysis it is possible to determine the standard reference reaction and equation, which are used to calculate the exergy of a chemical compound (Szargut et al., 1988,Talens, 2009). This thesis uses the reference state defined by Szargut (2005). Figure 4.3 demonstrates this concept with iron.

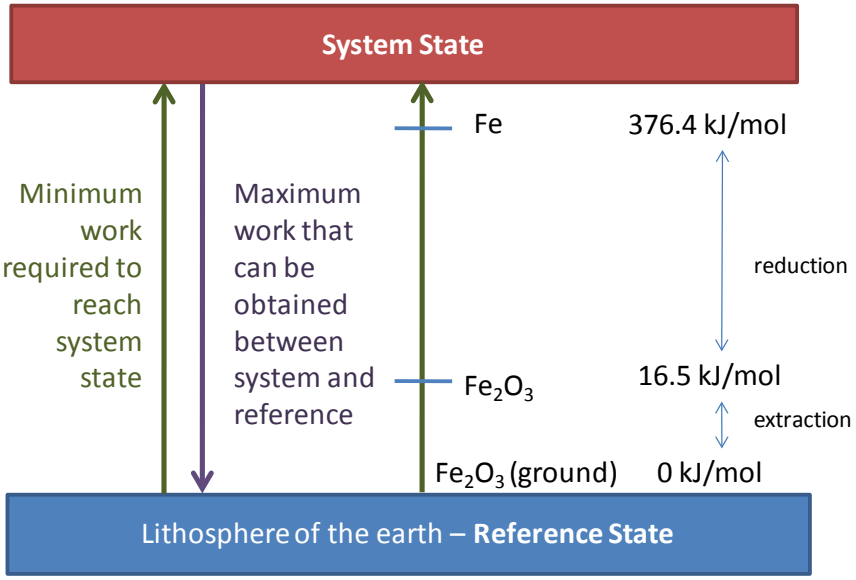


Figure 4.3. Reference state and exergy of iron
Source/adapted from: (Gutowski, 2008)

Various exergy indicators have been developed over the year. Two of the most widely used methods are exergy efficiency (e_2) and cumulative exergy consumption (CExC) (Szargut et al., 1988). The e_2 looks at the ratio between the exergy of the useful product and the exergy of the inputs of the system under study. A high value signifies that there is a lower loss of exergy. CExC looks at the exergetic sum of the natural resources required to produce a product. The higher the value, the more resources are required. This value is dependent on the raw materials and the processes used. Further details can be found in chapter 8.

4.4 Economic Assessment

In order to help ensure long term sustainability of a technology it is important to determine whether it is economically feasible. There are various different economic models that can be applied, some of which are often favoured in Industrial Ecology, which all have their benefits and limitaions. One such method is life cycle costing which uses the same life cycle thinking as environmental LCA, in other words, it looks at the costs from cradle to grave (Carlsson Reich, 2005). While it is often defined as the economic counterpart to LCA it lacks a standardized methodlogy which can lead to confusion in how it is applied (Carlsson Reich, 2005,Jeswani et al., 2010). Another is cost benefit analysis which, apart from the economic costs, applies costs to environmental and social indicators. It therefore includes a lot of direct and indirect flows, which can lead to uncertainty (Jeswani et al., 2010).

As the technology under review is still in the development phase it was decided to use techno-economic assessment. This is a widely used economic method, especially for the assessment of carbon capture technologies (Kuramochi et al., 2011,Berghout et al., 2013,Gibbins et al., 2011). It that applies a bottom up approach that allows for a detailed understanding of the costs involved in the process and where improvements can be made (Blok, 2007). Applying this more traditional approach also allows for comparison with other technologies and sets up the foundation for further economic studies.

As the name suggests it combines technical assessments, such as scaling up equipment, with traditional economic assessments such as net present value and annuity factor (all explained further in chapter 10).

For this assessment, preliminary data was obtained from the developers and was further expanded upon through literature search and consultations with experts and manufacturers. As some data was either private, or not yet available for Spain, assumptions had to be made based on literature reviews. As the novel technologies are in their developmental phase, the cost analysis was projected to the year 2025, which is a potential year when the technologies could be ready for marketing.

Part II

Environmental Assessment


Chapter 5
Life Cycle Assessment of Biogas Upgrading Technologies

Chapter 5 - **Life Cycle Assessment of Biogas Upgrading Technologies**

based on the following paper: Katherine Starr, Xavier Gabarrell, Gara Villalba, Laura Talens, and Lidia Lombardi (2012) Life cycle assessment of biogas upgrading technologies. Waste Management, 32, 991-999.

Abstract

This article evaluates the life cycle assessment (LCA) of three biogas upgrading technologies. An in-depth study and evaluation was conducted on High Pressure Water Scrubbing (HPWS), as well as Alkaline with Regeneration (AwR) and Bottom Ash Upgrading (BABIU), which additionally offer carbon storage. AwR and BABIU are two novel technologies that utilize waste from municipal solid waste incinerators - namely Bottom Ash (BA) and Air Pollution Control residues (APC) - and are able to store CO_2 from biogas through accelerated carbonation processes. These are compared to High Pressure Water Scrubbing (HPWS) which is a widely used technology in Europe. The AwR uses an alkaline solution to remove the CO_2 and then the solution – rich in carbonate and bicarbonate ions - is regenerated through carbonation of APC. The BABIU process directly exposes the gas to the BA to remove and immediately store the CO_2, again by carbonation. It was determined that the AwR process had an 84% higher impact in all LCA categories largely due to the energy intensive production of the alkaline reactants. The BABIU process had the lowest impact in most categories even when compared to five other CO_2 capture technologies on the market. AwR and BABIU have a particularly low impact in the global warming potential category as a result of the immediate storage of the CO_2. For AwR, it was determined that using NaOH instead of KOH improves its environmental performance by 34%. For the BABIU process the use of renewable energies would improve its impact since it accounts for 55% of the impact.

5.1 Introduction

Carbon capture technologies help to not only reduce the CO_2 emitted into the atmosphere but it can also be applied to the biogas upgrading process. Biogas upgrading technologies, also known as biomethane purification technologies, are being installed more frequently in waste management facilities such as landfills, anaerobic digesters and waste water treatment facilities. These technologies remove impurities from biogas and convert it into biomethane which may be used as a source of vehicle fuel or injected into the natural gas grid (Persson et al., 2006,Petersson and Wellinger, 2009). Apart from the economic profitability, these technologies also have an important positive environmental impact as it prevents the emission of methane, a powerful greenhouse gas 25 times more powerful than CO_2, and in some cases prevents CO_2 from being released as well. These technologies can also be used to help waste management facilities fulfil the European Commission Directive EC 31/1999 (European Commission, 1999) which mandates that all landfill gas must be captured and flared, though it is encouraged to use the gas in energy recovery. Despite the increasing interest in these technologies, there is very little research about its environmental impact.

Biogas from anaerobic biodegradation processes is mainly composed of methane (CH_4), (35-65%) and carbon dioxide (CO_2) (15-50%). It has also smaller levels of other contaminates such as hydrogen sulphide, nitrogen, water, oxygen, ammonia and siloxanes. The concentration of each compound varies depending on the source of the gas and its composition. For example, waste containing higher organic concentration leads to a biogas with higher methane gas content (de Hullu et al., 2008,Petersson and Wellinger, 2009). When CO_2 and other impurities are removed during the upgrading process, the methane concentration increases and thus the resulting biomethane can be utilized as an alternative to natural gas. This article focuses on the carbon capture technologies that upgrade biogas by removing its CO_2 content.

There are quite a few different technologies on the market today. The main unit operations used are absorption, adsorption, membrane separation and cryogenic separation. Further information about these unit operations and their associated technologies can be found in Table 5.1. A common factor of all of these techniques is that the removed CO_2 is normally released back into the atmosphere. In some cases, if its quality is high enough, it can be used for industrial purposes such as increasing the CO_2 concentration for photosynthesis in greenhouses or for carbonation in food production (Lems and Dirkse, 2009).

Table 5.1. Current biogas upgrading technologies

Unit operation	Technology	Acronym	Description of process[a]
Absorption	High Pressure water scrubbing	HPWS	Water absorbs CO_2 under high pressure conditions. Regenerated by depressurizing.
	Chemical Scrubbing	AS	Amine solution absorbs CO_2. The amine solution is regenerated by heating.

	Organic Physical Scrubbing	OPS	Polyethylene glycol absorbs CO_2. It is regenerated by heating or depressurizing.
Adsorption	Pressure Swing Adsorption	PSA	Highly pressurized gas is passed through a medium such as activated carbon. Once the pressure is reduced the CO_2 is released from the carbon, regenerating it.
Membrane	Membrane Separation	MS	Pressurized biogas is passed through a membrane which is selective for CO_2.
Cryogenic	Cryogenic Separation	Cry	Biogas is cooled until the CO_2 changes to a liquid or solid phase while the methane remains a gas. This allows for easy separation.

[a] (Petersson and Wellinger, 2009,Rao and Rubin, 2002b,Persson, 2003,de Hullu et al., 2008)

Two new technologies assessed in this article are: Alkaline with Regeneration - from here on referred to as AwR - developed jointly by the Università degli Studi di Firenze and the Università di Roma "Tor Vergata" in Italy (Baciocchi et al., 2011b) and Bottom Ash for Biogas Upgrading - from here on referred to as BABIU- developed by the University of Natural Resources and Life Sciences in Austria (Mostbauer and Lenz, 2007b). They both utilize a different upgrading unit operation called carbon mineralization (or carbonate looping). This technique is gaining ground as a viable method for biogas upgrading (IPCC, 2005,MacDowell et al., 2010). This process uses calcium oxide (CaO) to fix CO_2 and produces solid calcium carbonate ($CaCO_3$) as demonstrated in equation 5.1.

(5.1) $$CaO_{(s)} + CO_{2(g)} \rightleftharpoons CaCO_{3(s)} + heat$$

This process not only selectively removes CO_2 from the biogas but it also stores it. The Life Cycle Assessment (LCA) of the process was assessed and compared with other technologies that are currently on the market.

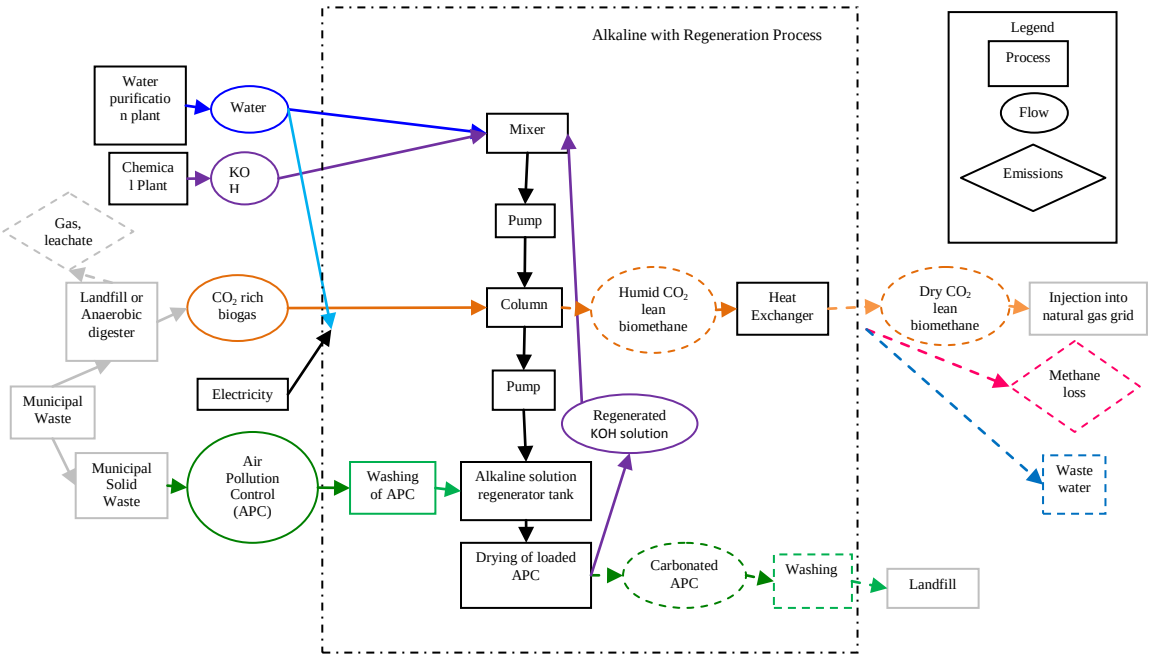


Figure 5.1. AwR process

The AwR process as seen in figure 5.1 is a continuous process that utilizes an aqueous alkaline solution, which is composed of potassium hydroxide (KOH), to absorb the CO_2 out of the biogas (equation 5.2). The exiting biomethane is dried and cooled so that it may be used. Once the CO_2 is absorbed the loaded solution is pumped through a regeneration reactor containing an industrial waste rich in CaO upon which the CO_2 from the solution becomes adsorbed into the waste (equation 5.3). In this case the waste used is an air pollution control (APC) residues from municipal solid waste incinerators. The regenerated solution is fed back into the system. Due to losses only 70% of the solution is regenerated. The carbonated APC residue is then dried and can be disposed of in a landfill.

(5.2) $2\ KOH_{(aq)} + CO_{2(g)} \rightarrow\ K_2CO_{3\ (aq)} + H_2O_{(l)}$

(5.3) $K_2CO_{3(aq)} +\ CaO_{(s)} +\ H_2O_{(l)}\ \rightarrow\ CaCO_{3(s)} + 2\ KOH_{(aq)} +\ heat$

The BABIU technology, as can be seen in figure 5.2, is a batch process that bypasses the solvent stage and directly removes the CO_2 from the biogas through direct adsorption onto the CaO rich waste as described in equation 5.1. In this case, the waste used is bottom ash (BA) from municipal solid waste incineration. Before the BA is placed into the reactor it needs to be weathered and filtered for size via a grate. The reactors are filled with BA and the air contained in the reactor is purged with Nitrogen to create an inert atmosphere. The CO_2 rich biogas is pumped through the BA. The upgraded biomethane is then dried and cooled so that it can be used. Once the BA is fully carbonated it is removed and sent to the landfill. The process then begins again. As this is a batch process 4 reactors would run in tandem to ensure that there is a continuous flow of gas (Mostbauer and Lenz, 2007b).

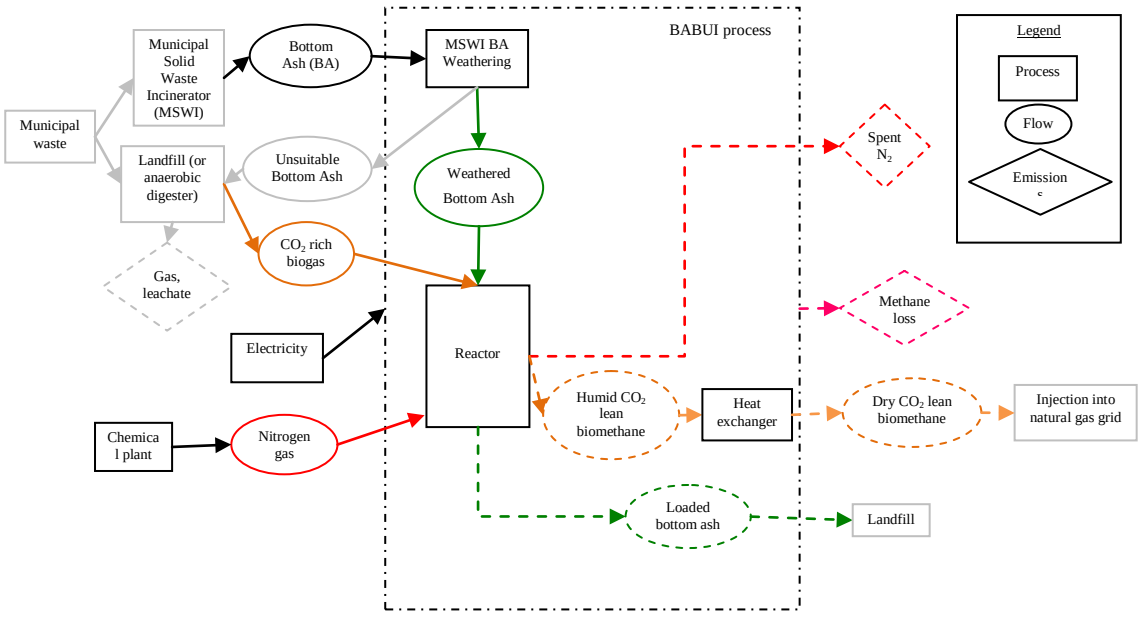


Figure 5.2. BABIU process

These two novel technologies were compared to High Pressure Water Scrubbing (HPWS). HPWS absorbs CO_2 into water under high pressure conditions and is a continuous process. Biogas is pumped into the system and compressed. It is then passed through a water scrubber where the CO_2 is absorbed. The biomethane is dried and is ready to be sent on to be used. The loaded water is then passed through a flash tank to be depressurized and it is passed through an air stripper which removes the CO_2 from the water. The regenerated water is then re-circulated and due to minimal losses only a small amount of water needs to be replaced. (Flotech Greenlane, 2010,Petersson and Wellinger, 2009,DMT Environmental Technologies,)

Upgrading technologies have various advantages; most notably the production of an alternative source for methane which may help contribute to the reduction of the dependence on natural gas, which over the long run may result in a monetary profit. They also have a positive effect on the environment by offering a renewable source of energy and reducing greenhouse gas emissions. Furthermore, the AwR and BABIU technologies help close the material cycle by using waste as inputs to the process. This waste immediately stores the CO_2 and there is an added environmental benefit in that these wastes which leach heavy metals are now stabilized through the carbonation process (Mostbauer and Lenz, 2007b). It is important to quantify the environmental impacts of these technologies from a life cycle approach in order to assess and compare them.

This study compared the environmental impact of the AwR and BABIU processes to the currently used technologies, found in table 5.1. A full scale comparison was done with HPWS, one of the most widely used techniques (Petersson and Wellinger, 2009). Comparing novel technologies to ones that are established helps to determine if and what improvements need to be made so that the technology is truly beneficial to the environment and is therefore a reasonable technological system to pursue.

5.2 Methodology

For this study a Life Cycle Assessment (LCA) was conducted following the ISO 14040 (ISO, 2006). The LCA has 4 major steps: goal and scope, inventory analysis phase, impact assessment phase and an interpretation of the results phase.

5.2.1 Goal and Scope

The objective of this study is to determine the environmental impact of different biogas upgrading systems. More specifically we examine the impact of carbon mineralization, using AwR and BABIU, in comparison to technologies currently on the market. Three LCAs were conducted: a full scale LCA comparing AwR and BABIU with HPWS; a simplified LCA comparing AwR, BABIU and the six technologies listed in table 5.1; and an LCA that also compares the eight technologies but focuses on methane recovery.

5.2.1.1 System Boundaries

All of the LCAs included the total amount of reagent and energy used to process the biogas. The full scale study of AwR, BABIU and HPWS included as well the transport of reagents to the up-grading plant and the amount and material used for the main infrastructure component (i.e. the reactor or the column). A third LCA study, called methane recovery, which focuses on the impact of the quality of biomethane takes into account the reagent, energy, the amount of biogas processed and the methane slip. The system boundaries of these assessments can be found in figure 5.3.

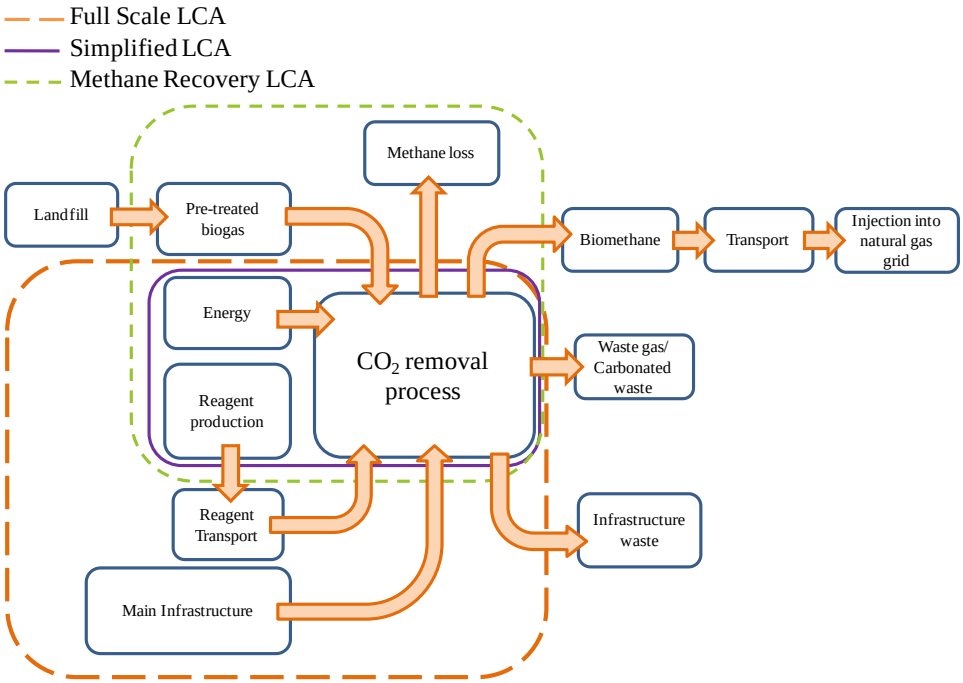


Figure 5.3. System boundary of the life cycle assessment

The processes associated with the biogas generation (landfilling, anaerobic digesters, wastewater treatment facilities), the pre-treatment of biogas, the housing unit for the entire system, the material used for the creation of the smaller parts of the system (i.e. pump, pipes, etc), the production of all of the infrastructure, and transportation of biomethane to the natural gas grid were all excluded in the evaluation because they are all common characteristics to all technologies under review.

5.2.1.2 Functional Unit

The functional unit (FU) is the removal of 1 tonne of CO_2 from biogas, which has a theoretical composition of 50% CO_2 and 50% CH_4 (by volume). Impurities such as H_2S, are neglected since in most cases they would be removed beforehand via filters (Persson, 2003,Petersson and Wellinger, 2009).

The quality of the biomethane produced can differ amongst the technologies, but in general it can be assumed that its composition is fit to substitute natural gas (Persson et al., 2006). Thus, it was decided that the final concentration of methane contained in the biomethane would not be included as part of the functional unit.

5.2.2 Inventory Analysis

A state of the art review was undertaken to determine which upgrading technologies to include in the study. Upgrading technologies were selected based on the data available for the electricity used, the quality of the biomethane and the methane slip. Data were collected from different sources: forms and questionnaires, interviews and literature surveys. Forms and questionnaires were prepared and sent to the institutions that are developing these technologies. Information for the AwR and BABIU technologies was obtained directly from the developers at the Università degli Studi di Firenze and the Università di Roma "Tor Vergata" in Italy and University of Natural Resources and Life Sciences in Austria. The HPWS data was obtained through email communications and questionnaires sent to the representatives from the following manufacturers: Greenlane Biogas (part of the Flotech Group) and DMT Environmental Technologies. The information for all the other technologies was obtained through literature review. All the information obtained and its source can be found in table 5.2. Out of the 8 technologies that were reviewed 7 use a compound to isolate the CH_4. Despite this, it was only possible to find sufficient information about the amount and composition of reagent used in HPWS and AS processes. It was decided to include the reagent in the LCA and after reviewing and analysing the results, with a focus on the role the reagent plays in the overall impact, it was decided that this information would remain in the analysis.

Table 5.2. Inventory list per 1 ton of CO_2 removed (functional unit)

	AwR	BABIU	HPWS	PSA	AS MEA	AS DEA	OPS	Cry	MS	reference
Inputs										
Electricity (MJ)[a]	160	314	770	915	433	433	1069	1275	1264	c, d, e, f, g, h, i, j, k, l, m, n
Potassium hydroxide (kg)[a]	430									k
Air pollution control residue (kg)	5000									k
Tap water (kg)[a]	7210		129							k,m,n
Nitrogen (kg)[b]		76								l
Bottom ash (kg)		45455								l
DEA (kg)[a]						1.2				o
MEA (kg)[a]					1.5					p
Transport via lorry	50 (KOH)	50	n/a							k, l

(km)[a]	135 (APC)									
Diesel (kg)[a]		11								l
Stainless steel (kg)[b]	0.05	0.2	0.03							k,l,m,n
Gravel (kg)[a]		17.5								l
Mastic asphalt (kg)[a]		12.5								l
Concrete (kg)[b]		4.7								l
Outputs										
Biomethane (m3)[r]	511	518	522	513	516	516	516	523	607	
Methane purity (%)	96.7	90.3	98	97.5	99	99	97	98	85	c, e, g, h, i, j, k, l, m, n, q,
Methane loss (%)	2.3	0.78	1	3.5	0.1	0.1	4	0.65	13.5	c, d, e, f, g, i, j, k, l, m, n, q

[a] (Swiss Center for Life Cycle Inventories., 2009), [b] (PE International, 2010), [c] (Petersson and Wellinger, 2009), [d] (MT- BIOMETHAN, 2010), [e] (Dachs and Zach, 2008), [f] (Pertl et al., 2010), [g] (Urban, 2007), [h] (Bekkering et al., 2010), [i] (Lems and Dirkse, 2009), [j] (de Arespacochaga et al., 2010), [k] (Olivieri et al., 2010), [l](Mostbauer, 2010), [m] (Rowntree, 2010), [n] (Kruit, 2010), [o] (Bailey and Feron, 2005), [p](Rao and Rubin, 2002b), [q] (de Hullu et al., 2008) , [r] Inherent to each technology (see 5.2.1.2 for more details)

5.2.3 Impact Assessment phase

The LCA was run on GaBi 4.4 using inventory from both the PE international (PE International, 2010) and the Ecoinvent 2.1 (Swiss Center for Life Cycle Inventories., 2009) database as can be seen in table 5.2. The LCA was conducted using the CML 2001 impact assessment method (Guinée et al., 2002), which includes the following environmental impact categories: Abiotic Depletion, elements (ADP E) [kg Sb-Equiv.]; Abiotic Depletion, fossil (ADP F) [MJ]; Acidification Potential (AP) [kg SO2-Equiv.], Eutrophication Potential (EP) [kg Phosphate-Equiv.]; Freshwater Aquatic Ecotoxicity Potential (FAETP) [kg DCB-Equiv.]; Human Toxicity Potential (HTP) [kg DCB-Equiv.]; Marine Aquatic Ecotoxicity Potential (MAETP) [kg DCB-Equiv.]; Ozone Layer Depletion Potential, steady state (ODP) [kg R11-Equiv.]; Terrestrial Ecotoxicity Potential (TETP) [kg DCB-Equiv.]; Global Warming Potential, 100 years (GWP) [kg CO_2-Equiv.]; Photochemical Ozone Creation Potential (POCP) [kg Ethene-Equiv.]. The Primary Energy demand from renewable and non-renewable resources, regarded by Ecoinvent as Cumulative Energy Demand (CED) (Swiss Center for Life Cycle Inventories., 2009), was determined using the same databases.

The capture and upgrading technologies (BABIU and AwR) were compared to HPWS by performing a more detailed and full scale LCA. For all the technologies, including those in table 5.2, it was only possible to perform a simplified LCA due to limitations of data. For chemical scrubbing two separate solutions were considered: Amine Scrubbing with monoethanolamine (AS MEA) and amine scrubbing with diethanolamine (AS DEA). An analysis was run to determine if impacts differ depending on the solution used. A further analysis was run on all of these technologies to examine if the quality of the outgoing biomethane affects the overall environmental impact.

5.3 Results and Discussion

5.3.1 Full Scale LCA for BABIU, AwR and HPWS

Figure 5.4 shows the results for each impact category analysed by LCA for the AwR, BABIU and HPWS technologies. Overall the AwR process had the largest impact in all of the categories except for the global warming potential (GWP) due to its ability to store CO_2. The BABIU process had the lowest environmental impact in all but the ozone layer depletion potential (OPD) category where the diesel used in transport caused it to have a higher impact. The HPWS was found to be in the mid-range though its impact values follow more closely to those of the BABIU process while the values of the AwR are often 84% higher than the other two. The negative percentage numbers for AwR and BABIU represent that they store more CO_2 than they produce.

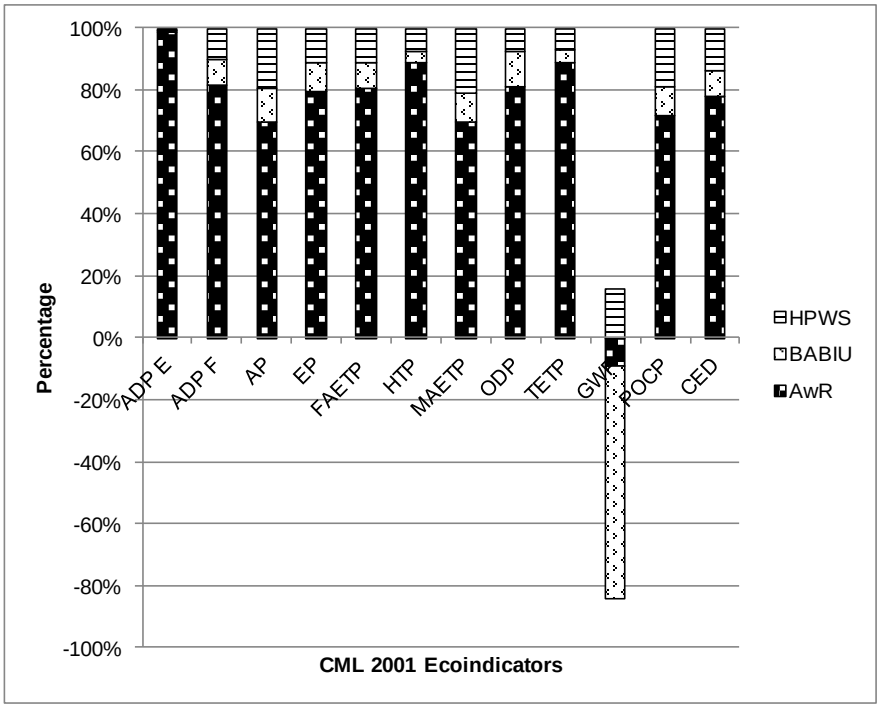


Figure 5.4. Impact comparison of biogas upgrading technologies

A breakdown of the impacts for each technology is provided in the next section as a way to obtain a clearer understanding as of the impact of each component in the processes

5.3.1.1 AwR breakdown

The KOH solution used in the process has the largest impact in the 11 out of the 12 evaluated environmental impact categories, accounting for an average of 92% of the overall impact. After the reagent, the electricity used has a noticeable impact though in comparison to the reagent its impact is quite minimal accounting for about 7-0.2% of the total impact. Meanwhile in GWP its impact is compensated by the 1 ton of CO_2 stored.

The alkaline solution used in this process is a mix of potassium hydroxide (KOH) and water. Its high impact can be attributed to the fact that 30% of the solution needs to be replaced and also that the production of the KOH in itself has a high impact due to the high energy consumption for its production by electrolysis. Sodium Hydroxide (NaOH) is a possible replacement for KOH in this technology. If the same volume as KOH is used, the environmental impact is reduced in 8 out of the 12 categories. The highest savings found was an impact reduced by 44% and the lowest reduction was at 18% with an average of a 34% lower impact. In order for the AwR to be reduced to levels comparable with HPWS and BABIU the overall impacts would need to be reduced by about 84%, which is not achieved by switching to NaOH. Therefore in order to improve this technology and thus decrease the environmental impact of this process then both a different base and a higher rate of regeneration would need to be developed.

5.3.1.2 BABIU breakdown

The life cycle assessment of the BABIU process, as can be seen in figure 5.5, shows that for 10 out of the 12 categories the electricity used has the highest impact, at around 55%, which can be attributed to the drying and preparation of the biomethane. After that it can be seen that at 23% the transportation has a significant impact in most categories and plays the largest role in the ODP at 49% of the total impact, of which, the largest impact for transportation was the transport of Bottom Ash. The infrastructure and the production of reagents had a significant impact on the abiotic depletion of elements (ADP E). The largest factor for the impact of the infrastructure was the cement used for the reactor. For the GWP, it is quite clear that the CO_2 produced in by this process is significantly compensated by the amount of CO_2 separated and stored by the process.

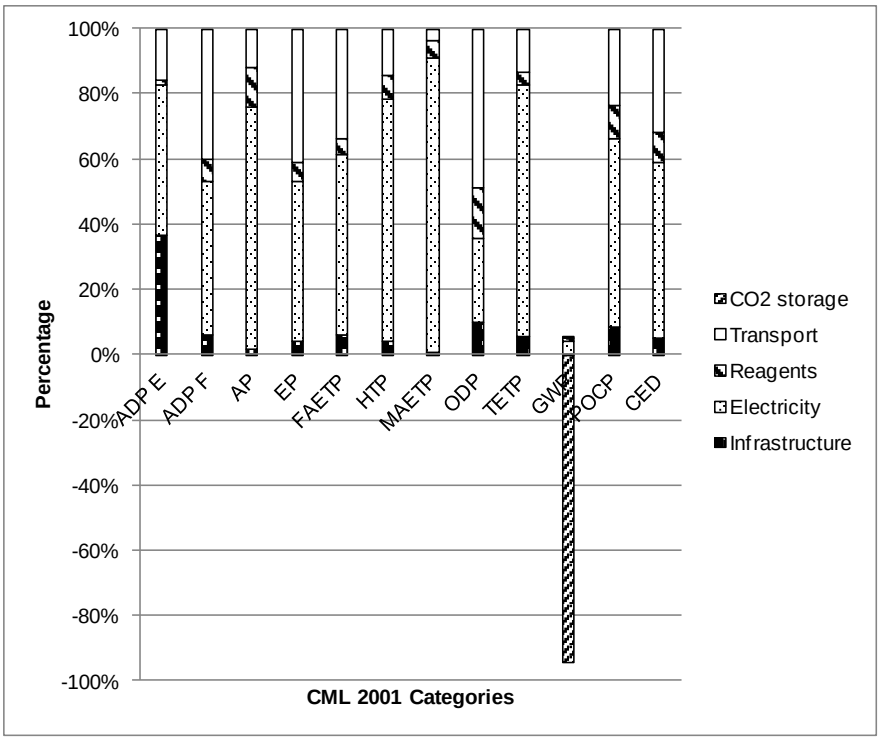


Figure 5.5. Disaggregated impact of BABIU

Results show that improving the transport by truck could help reduce the overall impact. For the analysis a distance of 50 km was chosen therefore one option would be to find a closer source or a different mode of transport. A requirement for this technology could be that a source of BA must be within a certain distance of the installation, thus ensuring a minimal impact due to transportation.

5.3.1.3 HPWS breakdown

In the HPWS the electricity used in this system, with an average overall impact of 97%, outweighs any other input having the highest effect on all of the 12 categories. Apart from that the only other impact of significance is that of the 29% impact of the infrastructure in the abiotic depletion potential of elements, which in this case was solely made up of steel. As the main components of this process involve water and electricity (high pressure), and the water had a negligible impact of between 0.09 and 0.02%, it can be concluded that if the pressure is lowered then the impact would reduce as well. Though to compensate for the loss of efficiency larger amounts of water would be required resulting in a larger vessel and equipment, which could cause a larger rather than smaller impact. This is most likely not an easy nor very feasible task, therefore another way to reduce the impact would be to use electricity from renewables, though this would not necessarily be able to be applied to all installations.

To summarize, AwR has the highest impact followed by the HPWS and BABIU is a close third. Due to carbon mineralization AwR and BABIU have an advantage over the HPWS in reducing the effect of these technologies on climate change.

5.3.2 Simplified LCA

In order to understand how these technologies compare to others on the market another analysis was conducted using more processes with a smaller set of parameters, this time focusing mainly on the electricity use and reagents.

Figure 5.6 shows that the HPWS and BABIU processes are relatively on par for the least impact, along with amine scrubbing. Meanwhile the AwR has the greatest impact in 5 categories: ADP E, ADP F, HTP, ODP and TETP. In the other categories, AwR has similarly large impacts as OPS, MS, Cry and PSA, in which the latter two are heavily reliant on electricity for the separation process. As was seen in the other analysis, the BABIU and AwR processes have the best performance in the GWP due to their capacity to store CO_2. Meanwhile out of the other technologies on the market the amine scrubbing produces the least amount of CO_2 followed by the HPWS process.

For the GWP the electricity played the largest impact in this category in all of the technologies apart from AwR, which as was mentioned beforehand is highly affected by the reagent used.

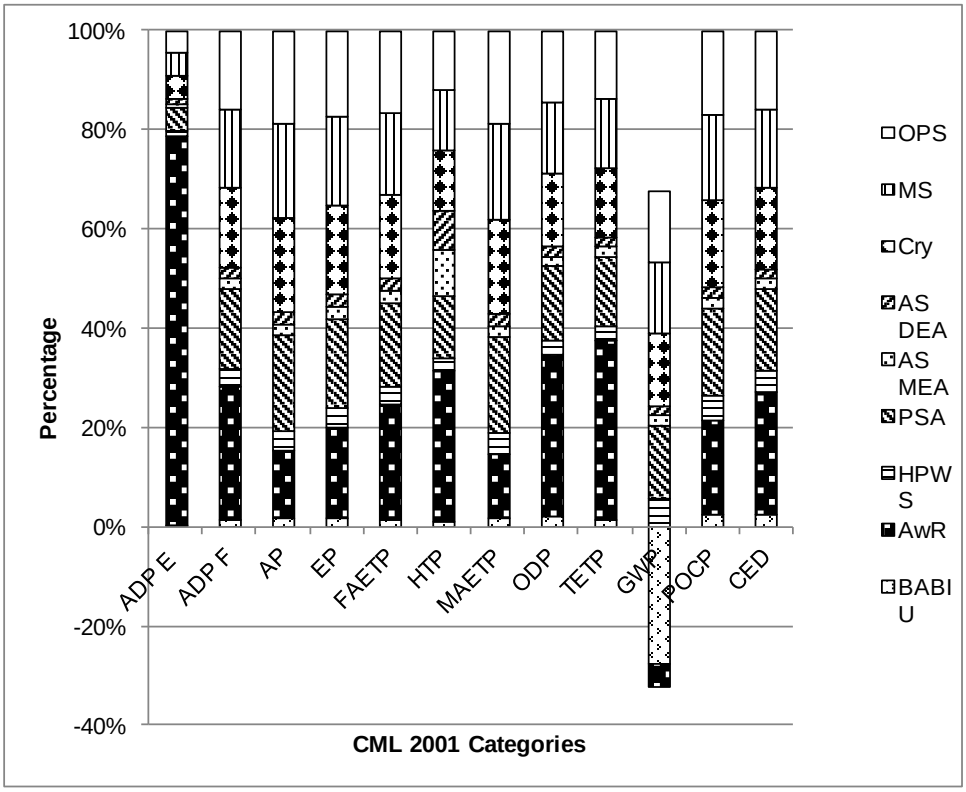


Figure 5.6. Simplified LCA of biogas upgrading technologies

It should be noted that for some of these technologies, such as HPWS and Cry, there exists the possibility to isolate the CO_2 and store it or if it is of a high enough quality it can be used for industrial purposes (Lems and Dirkse, 2009,Kruit, 2010). If this is included in the system analyzed the impacts of the technologies would be reduced by 1 ton of CO_2. However, after taking into account the transport of CO_2, the energy needed to store the CO_2 and the way in which the CO_2 is stored, then the benefits of 1 ton "saving" would be reduced or even end up with a greater impact.

5.3.2.1 Methane Recovery

Methane recovery is an important variable to consider as the goal of biogas upgrading is to obtain a high concentration of methane. Therefore the amount that each technology is able to isolate as well as its efficiency in doing so should be factored in. To explore this variable further the boundaries of the system can be expanded to include the biogas that was processed as described in figure 5.1. For such a study the following assumptions were taken into consideration: the methane that is processed and in the long run used is considered as a positive impact; the CO_2 that is processed is either considered neutral if it is captured, or it is considered as a negative impact if it is released back into the atmosphere; and the methane lost within each process was also considered as a negative impact. Applying these parameters to the LCA modifies significantly the GWP. The following changes were encountered when this method was applied: The BABIU and HPWS are tied for the highest savings at 9.1 tonnes of CO_2 equivalent per 1 ton of CO_2 removed. These systems are then followed closely by MS

which saved 8.7 t/FU, and PSA which saved 8.5 t/FU. The novel AwR process can be found in the bottom half at 8.0 t/FU. While being slightly surpassed by AS at 8.1t/FU it has a higher savings than Cry and OPS which had savings of 7.7 t/FU and 7.5 t/FU respectively. Applying these system boundaries, after the compensation obtained from the biogas, the electricity once again had the largest impact on most of the processes, though for some such as membrane separation, the methane lost in the process contributed greatly to the impact of the process.

As mentioned in the methodology section, the final quality of the biomethane was not taken into account as it pertains specifically to each technology. A sensitivity analysis was performed relating methane content of the biogas and the GWP impact factor. The results showed that there is no correlation between the two.

5.3.2.2 Solvent for Amine Scrubbing

For amine scrubbing a number of different compounds can be used whereby the number and position of the amines vary. In this study two different compounds were used in order to see if there was a difference between the solutions. The solutions that were chosen were Monoethanolamine (MEA) and Diethanolamine (DEA) as they are widely used (Persson, 2003,Petersson and Wellinger, 2009,Urban, 2007). The production processes of both compounds are quite similar in that MEA and DEA are both produced from ammonia and ethylene oxide. DEA requires a higher amount of ethylene oxide and therefore one would think therefore that the DEA would have a greater impact, though higher amounts of MEA is required to remove the same amount of CO_2 (Weissermel and Arpe, 2003). By viewing figure 5.6, it is clear that overall there is no difference in impact between the two solutions. Though through an analysis it was determined that MEA overall has a 20% greater impact than DEA. Therefore one can conclude that, while not significant, the amount of solvent used is more relevant than the solvent chosen for the upgrading

5.4 Conclusion

The use of carbon mineralization technology, used by the AwR and BABIU processes, is a viable option for biogas upgrading. Under certain conditions, such as minimized used of additional reagents, it can be considered as better for the environment in comparison to the other technologies currently on the market. Data for the novel technologies is based on laboratory values scaled up to industrial production and therefore values may change.

Overall the BABIU process was found to have the least environmental impact of all the biogas upgrading technologies. This process is then followed by AS and HPWS which have the best performance out of the technologies currently used and presented in table 5.1. The energy intensive PSA and Cry technologies have some of the highest impacts out of those found in table 5.1. For most of the technologies the electricity use had the highest impact, but it can be reduced by increasing the supply from renewable. The impact of the climate change category can be minimized if the removed CO_2 is stored or used in industry.

The AwR system showed to have one of the highest impacts compared to all of the other technologies. The amount of reagent needed for the system was the greatest factor even though 70% of the solvent is regenerated. The other technologies that do use reagents had some of the lowest environmental impacts and their reagent production had a very small effect on their overall impact. Therefore if the AwR process increases its regeneration rate and/or changes its solution then their environmental performance may be improved, though further studies are underway. It is important to be aware of the fact that even if these technologies are shown to have a lower environmental impact it would only be possible to introduce them to the market if an economic analysis shows them to be better or comparable to conventional technologies.

The results not only provide an insight into which technology is the most beneficial to the environment, in terms of greenhouse gas releases, but it also gives interested parties better knowledge as to what factors should be reviewed when implementing, developing and/or improving upgrading technologies.

Chapter 6

Potential CO_2 Savings through Biomethane Generation from Municipal Waste Biogas

Chapter 6 - **Potential CO_2 Savings through Biomethane Generation from Municipal Waste Biogas**

based on the following paper: Katherine Starr , Xavier Gabarrell, Gara Villalba, Laura Talens and Lidia Lombardi. Potential CO_2 Savings through Biomethane Generation from Municipal Waste Biogas. *Accepted with minor revision in Biomass and Bioenergy*.

Abstract

An alternative source of methane that can also reduce the greenhouse gas effect is one that comes from the upgrading of biogas. This section studies eight technologies through life cycle assessment (LCA). Six of the technologies are ones that are already on the market and the two others are novel technologies that use carbon mineralization to store CO_2 upon their removal. The two novel technologies include alkaline with regeneration (AwR) and bottom ash upgrading (BABIU). These technologies use waste rich in calcium, from municipal solid waste incinerators (MSWI), to store the CO_2 from biogas. Among all conventional technologies, high pressure water scrubbing and chemical scrubbing with amine had the lowest CO_2 impacts. Of the novel technologies BABIU saves 10% more CO_2 than AwR. An uncertainty analysis and a material flow analysis demonstrated that proximity to a MSWI is an important factor to consider. As well, it was seen that while the technology is promising it cannot be applied to an entire country if the proper infrastructure is not in place.

6.1 Introduction

Among the renewables, the biogas industry in the EU is growing, reaching about 8.3 Mtoe in 2009 with more than 6000 biogas plants. The main source is agriculture (52%), then landfills (36%) and sewage plants (12%) (Eurobserv'er, 2010).

Biogas can be fed with a variety of bio-materials which can be waste or energy crops. Biogas produced in anaerobic digestion plants (AD-plants) or landfill sites is primarily composed of methane (CH_4) and carbon dioxide (CO_2) with smaller amounts of hydrogen sulphide (H_2S) and ammonia (NH_3). Trace amounts of hydrogen (H_2), saturated or halogenated carbohydrates and oxygen (O_2) are occasionally present in the biogas. Usually the gas is saturated with water vapour and may contain dust particles and organic silicon compounds (e.g. siloxanes).

Biogas from anaerobic digestion plants (AD-plants) or landfill sites can be directly used for the production of heat and steam, electricity, vehicle fuels and chemicals. Alternatively, it can be further upgraded to increase the methane concentration, by removing CO_2 and other impurities, in order to be suitable as a substitute for natural gas in the already established distribution grid. This gas can now be regarded as biomethane and is of a quality where it can fed into the natural gas distribution grid or be used as a vehicle fuel. This option is gaining more interest throughout Europe and there are currently several different commercial technologies for reducing the concentration of CO_2 in biogas.

There are four different types of upgrading technologies which removes CO_2 and they include absorption, adsorption, membrane separation and cryogenic separation. For the absorption processes a reagent is used to absorb CO_2. Within absorption one can find high pressure water scrubbing (HPWS) which uses water, chemical scrubbing (AS) which uses an amine based solvent such as diethanolamine (DEA), and organic physical scrubbing (OPS) which uses a commercial blend of polyethylene glycol. Under adsorption CO_2 is normally adsorbed onto a medium such as activated carbon and then removed through changes in pressure, as in the case of pressure swing adsorption (PSA). For membrane separation (MS) a selective membrane is used to separate CO_2 from the biogas. Cryogenic separation (Cry) separates CH_4 and CO_2 through a decrease in temperature which causes a change in the physical state of the gases (Petersson and Wellinger, 2009). The marketed technologies use varying techniques to process the gas but what they do have in common is that they do not permanently store the CO_2, instead it is sent back into the atmosphere or used for industrial purposes if it meets quality requirements (Lems and Dirkse, 2009).

Currently, there are two novel upgrading technologies under development which additionally store the separated CO_2 through carbon mineralization. These technologies use wastes from municipal solid waste incinerators (MSWI) rich in calcium compounds to fix CO_2 and thus form calcium carbonate ($CaCO_3$). The two technologies that are being developed, and are currently in the pilot plant stage, are alkaline with regeneration (AwR) – developed jointly by the Universita degli Studi di Firenze and the Universita di

Roma "Tor Vergata" in Italy (Baciocchi et al., 2011a,Baciocchi et al., 2011b) - and the bottom ash for biogas upgrading (BABIU) – developed by the University of Natural Resources and Life Sciences in Austria (Mostbauer and Lenz, 2007a,Olivieri et al., 2011). The AwR process, which is a continuous process, absorbs the CO_2 using an alkaline solution of potassium hydroxide (KOH). This solution is regenerated at a rate of 70% when put into contact with air pollution control residues (APC) which is rich in calcium. Once the CO_2 is adsorbed into the APC the biogas (from here referred to as biomethane) is free of impurities. BABIU, which is a batch process, uses a direct solid-gas phase interaction. Biogas is pumped through a column containing bottom ash (BA) rich in calcium, CO_2 is absorbed in the BA and thus the resulting biomethane has a high concentration of CH_4.

In this study the amount of greenhouse gases created and saved by implementing these technologies is analyzed through a life cycle assessment (LCA). Previous studies (Starr et al., 2012b,Starr et al., 2012a) focused on the removal of one ton of CO_2 while this study focuses on the potential energy that can be generated. Eight technologies that were described above are examined and they include AwR, BABIU, PSA, HPWS, OPS, Cry, MS, and AS. LCA is a useful tool to determine the environmental impact of technologies. While it is often applied to technologies that are on the market, it is often used during the development phase in order to help create a more environmentally sound process (Gabarrell et al., 2012). While LCAs have various indicators that can be selected, the Global Warming Potential was chosen as the focus of the study as one of the roles of biogas upgrading technologies could be considered to be reducing CO_2 emissions from anaerobic digesters or landfills.

These results are then compared with a Material Flow Analysis (MFA), which quantifies the flows and stocks of a system, in order to determine the applicability of the novel technologies.

6.2 Methodology

A life cycle assessment (LCA) was run according to the ISO 14040 (ISO, 2006). A material flow analysis (MFA) was conducted for the waste flow of Spain as a complement to the LCA.

6.2.1 Life Cycle Assessment

6.2.1.1 Goal and Scope

The goal of this study is to determine the global warming potential (GWP) of biogas upgrading technologies. By accounting the GWP, we can identify the process that diverts the highest amount of greenhouse gases from being emitted into the atmosphere.

6.2.1.2 Functional Unit

The functional unit used for this study is 1 kWh of biomethane upgraded from biogas which is composed of 50% CH_4 and 50% CO_2. This hypothetical composition is applied as it allows one to disregard any prior gas treatment.

6.2.1.3 System Boundaries

The system boundaries include the electricity used to treat the gas, the production of any reagents used, the amount of biogas that is upgraded, the amount of methane lost during the process either through the treatment (know as methane slip) or lost within the waste gas. Fig. 6.1 demonstrates the boundaries for the LCA and the uncertainty analysis.

The processes excluded for the LCA and the uncertainty analyses are the generation of the biogas in landfills and its pre-treatment, and the infrastructure for the CO_2 removal process and to manage the waste generated. The transport of the reagents was excluded from the LCA study, but it was included in an uncertainty analysis discussed in section 3.3.2.

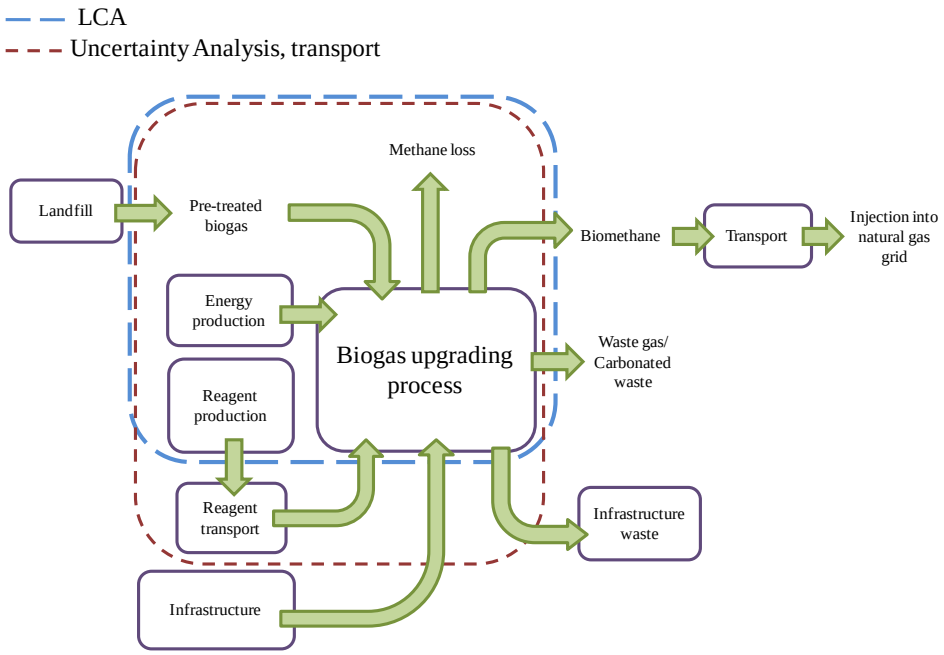


Figure 6.1. System boundaries
Based on figure 5.3

6.2.1.4 Literature Review

The technologies that were chosen for the study are: AwR, BABIU, HPWS, PSA, AS, Cry, MS and OPS (Starr et al., 2012b).

6.2.2 Life Cycle Inventory

A life cycle inventory was conducted on the eight chosen technologies. Information on the AwR and BABIU process was obtained through direct email communication and information request forms sent to the Universities developing these technologies. Actually, the information for the AwR and BABIU have to be considered preliminary as it is the results of the laboratory analysis phase of the project and has been upscaled to industry size.

Information for the HPWS was obtained through email communications and questionnaires received from representatives of two manufacturers, Greenlane Biogas (part of the Flotech Group) and DMT Environmental Technologies. Information for the other technologies was obtained through literature review. The median point was chosen for information that had more than one value.

Information for reagents used in certain processes was not obtainable and therefore was not included in the study, as in these cases their impact could be considered negligible (Starr et al., 2012b).

Data for the LCA was complemented by the Ecoinvent 2.2 (Swiss Center for Life Cycle Inventories., 2010) and GaBi PE databases (PE International, 2010) and inventory data for Spain was used. The inventory data used can be found in Table 6.1.

Table 6.1. Life cycle inventory data for biogas upgrading technologies per 1 kWh of biomethane (functional unit)

		BABIU	AwR	HPWS	PSA	OPS	AS	MS	Cry	reference
Inputs	Electricity (kWh) [a]	0.017	0.009	0.042	0.051	0.060	0.024	0.068	0.070	[c,d,e-n]
	KOH (kg) [a]		0.087							[k]
	H_2O (kg) [a]		1.468	0.025						[k,m,n]
	N_2 (kg) [b]	0.015								[l]
	DEA (kg) [a]						0.0002			[o]
	BA (kg)	8.890								[l]
	APC (kg)		1.018							[k]
	Diesel (kg) [a]	0.002								[l]
	Biogas (m3)	0.203	0.206	0.203	0.209	0.210	0.202	0.233	0.203	
	Heat (kWh) [a]					0.031	0.109			[f,i,p]
Properties	Biomethane purity (%)	90.3	96.7	98	97.5	97	99	85	98	[c,d,f,h-n,q]
	Methane loss (%)	0.78	2.3	1	3.5	4	0.1	13.5	0.65	[c,d,e-h,j-n,q]

[a] (Swiss Center for Life Cycle Inventories., 2010) [b] (PE International, 2010) [c] (Petersson and Wellinger, 2009) [d] (Lems and Dirkse, 2009) [e] (MT- BIOMETHAN, 2010) [f] (Dachs and Zach, 2008) [g] (Pertl et al., 2010) [h] (Urban, 2007) [i] (Bekkering et al., 2010) [j] (de Arespacochaga et al., 2010) [k] (Olivieri et al., 2010) [l] (Mostbauer, 2010) [m] (Rowntree, 2010) [n] (Kruit, 2010) [o] (Bailey and Feron, 2005) [p] (Beil et al., 2012) [q] (de Hullu et al., 2008)

6.2.3 Life Cycle Impact Assessment

The LCA was run using the program GaBi 4.4. The impact indicator selected for this study is the Global Warming Potential, 100 years [g CO_2 equiv.] from the CML 2001 method (Guinée et al., 2002). For this impact indicator positive values mean that CO_2 is being emitted and therefore is considered as a negative impact on the environment. Meanwhile negative values mean that CO_2 is removed from the environment and therefore is seen as a positive impact to the environment, or as a CO_2 savings.

The following assumptions were taken into consideration. The methane that is upgraded (also referred to as biomethane) and used as a substitute for natural gas down the line is

considered as a CO_2 savings. The CO_2 originally contained in the biogas can either be considered CO_2 neutral if it is released back into the environment or as a savings if it is stored. The methane slip (methane loss) of each process is considered as a CO_2 emission.

As the methane slip and the final biomethane concentration is a property that is inherent to each technology, a sensitivity analysis was performed to ensure that the end results were independent of these factors. A sensitivity analysis was also preformed to evaluate possible changes once the novel technologies reach industrial scale. As well, two uncertainty analyses were also performed to explore the effects on CO_2 emissions in: the regeneration rate in AwR, the distance between a municipal solid waste incinerator and AwR and BABIU facilities, and the effect of the country where the upgrading plant is located.

6.2.4 Material Flow Analysis

BABIU and AwR are currently being developed with the goal of applying it to waste treatment processes (Anaerobic Digesters (AD) and landfills) while using waste from another waste treatment process (MSWI). Therefore it is important to study the flows of waste to see whether there would be enough Bottom ash (BA) and air pollution control (APC) residues from MSWI for BABIU and AwR, respectively.

Therefore a MFA was conducted on the municipal waste flows of Spain in 2008. This data was obtained through literature reviews and personal communications with people in the field (Farreny, 2011,MARM, 2010,INE, 2011,Observatorio de la sostenibilidad en Espana, 2010,MARM, 2008). Once the waste flow (Fig. 6.2) was determined, and drawn using e!Sankey®, three scenarios were planted and explored.

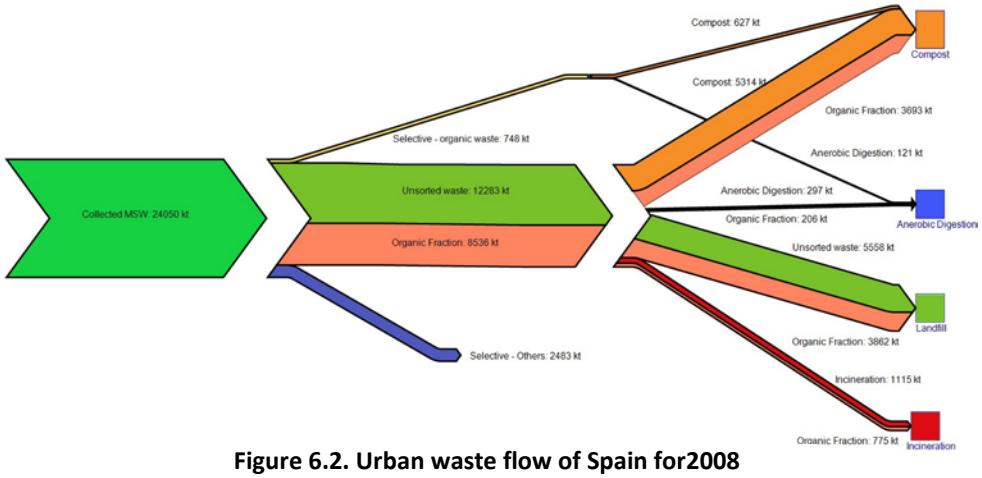


Figure 6.2. Urban waste flow of Spain for2008

The amount of organic matter (OM) within the flow of unsorted waste was calculated at 41% (Farreny, 2011). For the potential amount of biogas generated the following assumptions were made: AD generates 115m^3 of biogas per t of OM (Vicent, 2008), with a capture rate of 100%; and landfills generate 170 m^3 of CH_4 per t of OM (USEPA, 2005), with a capture rate of 30%. The potential amount of BA produced was calculated as 20% of the total waste in MSWI. The potential electricity that can be generated in MSWI was

estimated to be around 0.52 MWh/t of waste and was determined based on information provided for a MSWI in Barcelona in 2008 (Tersa, 2009).

6.3 Results and Discussion

6.3.1 Life Cycle Assessment

Fig. 6.3 shows the g of CO_2 saving by each of the technologies under study. The amount of CO_2 saved varies from 1400 g to almost 2000 g. The BABIU process has the lowest global warming potential (GWP) and actually the largest potential CO_2 savings, 1980 g of CO_2 eq. In general all the other processes generate about 10% more CO_2 emissions than BABIU, except for OPS and MS which generate 15% and 25% more emissions, respectively.

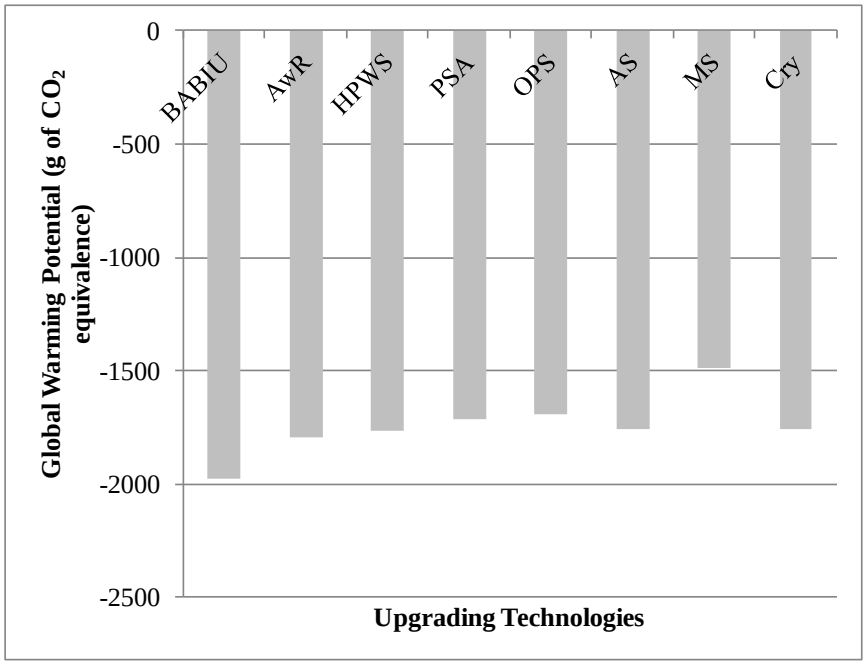


Figure 6.3. Global warming potential of biogas upgrading technologies

Table 6.2 demonstrates the role that each component plays in the carbon balance of each technology. The biomethane processed and the CO_2 stored account for the CO_2 savings while the production of reagents, electricity and any methane slip contribute to CO_2 emissions.

Table 6.2. Breakdown of the global warming impact of biogas upgrading technologies

Impact of components (kg CO_2) / Biogas upgrading process	Heat	Electricity	Reagent	Methane slip	CO_2 storage	Biomethane obtained
BABIU	0	0.009	0.003	0.014	-0.198	-1.805
AwR	0	0.005	0.167	0.043	-0.204	-1.805
HPWS	0	0.021	7.896E-06	0.018	0	-1.805
PSA	0	0.026	0	0.065	0	-1.805
OPS	0.008	0.030	0	0.075	0	-1.805
AS	0.030	0.012	8.478E-04	0.002	0	-1.805
MS	0	0.035	0	0.282	0	-1.805
Cry	0	0.035	0	0.012	0	-1.805

The amount of CH_4 processed and turned into biomethane saves the largest amount and accounts for the fact that these technologies overall save CO_2 rather than contribute to climate change, as was demonstrated in Fig. 6.3. All the processes do emit CO_2 but the amount saved compensates for this impact. Both the BABIU and the AwR process store CO_2 and therefore this contributes to an extra savings of 198 g and 204 g of CO_2 respectively. The BABIU process had the greatest savings as it not only processes a large amount of biogas but it also produces a relatively small amount of CO_2. While AwR stores more CO_2 than BABIU it doesn't have as high of an overall CO_2 savings due to the production of KOH which counts for 8% of AwR's GWP.

For only two of the upgrading technologies, HPWS and Cry, the electricity used produced the largest amount of CO_2 emissions. For AS the production of required heat was the largest source of emissions. Meanwhile, for all the other technologies BABIU, PSA, OPS and MS, the methane slip that occurs during the upgrading process had the highest negative impact. In the case of MS, the methane slip contributes to 13% of the overall impact. For these technologies if the methane loss is reduced then their GWP would improve.

6.3.2 Sensitivity Analysis

Each technology has a final biomethane concentration and methane slip that is inherent to each process. It is therefore of interest to determine whether these characteristics affect their CO_2 balance. A sensitivity analysis done for all the 8 technologies showed that there is no correlation between the GWP of the technologies and the percentage of methane loss nor the final biomethane concentration.

The data obtained for the two novel technologies, BABIU and AwR consist of laboratory scale data that was scaled up to industrial scale. Therefore one can rightfully assume that once these technologies are developed to the industrial level that the data may not be the same. Though in Table 6.1 it is possible to see that values such as biogas input, electricity use, biomethane purity and methane loss for BABIU and AwR fall within the range established by the other six technologies that are currently on the market. From table 2 one can see that the electricity use and methane loss in play a small role in the overall CO_2 impact of the technologies. Therefore one can assume that while there may be changes once the technologies are commercialized, the effect on the GWP would not be significant. This assumption is supported by a sensitivity analysis conducted where the amount of electricity used by both AwR and BABIU was increased to 0.07 kWh (which is the higher end of the electricity use by commercialized technologies). Applying this new value only reduced the CO_2 savings by less than 1.5 %.

6.3.3 Uncertainty Analysis

6.3.3.1 Reagent use in AwR

As was seen in Table 6.2, one of the largest sources of CO_2 for the AwR is the production of the alkaline reagent KOH. Currently, the regeneration rate is around 70%, therefore it was decided to study if improving the regeneration rate would improve the technology enough so that it could be comparable to BABIU and others on the market. As well NaOH is another base that is of interest for this process therefore it was also used in this comparison. The AwR using each base at different regeneration rates were compared to BABIU, AS and HPWS.

As can be seen in Fig. 6.4 even if for AwR the regeneration rate of both KOH and NaOH is improved to 99%, BABIU is still the technology with the greatest CO_2 savings. This is due to the fact that the AwR process has a slightly higher methane slip than BABIU. Though, since both of these technologies are in the development stage the methane slip may improve for both before commercialization.

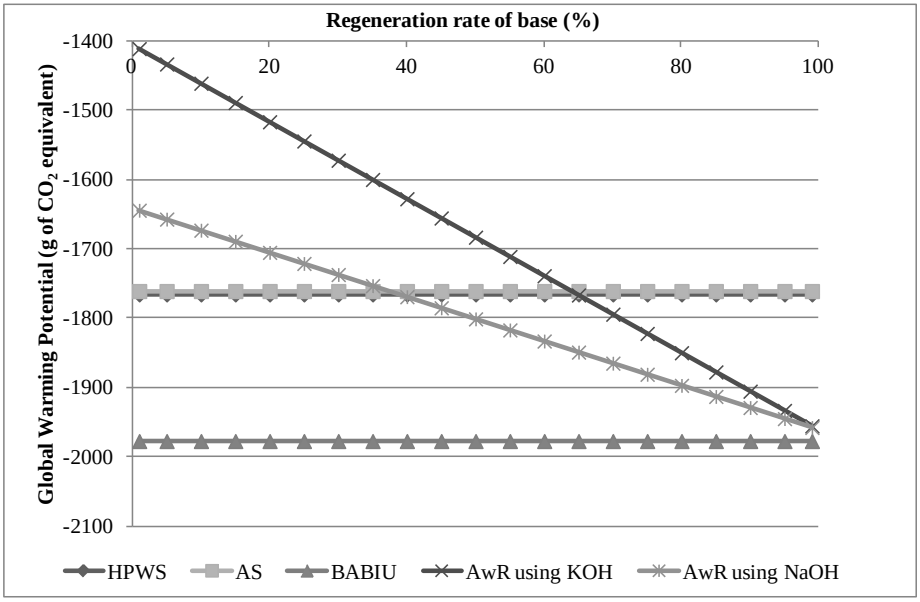


Figure 6.4. Comparison of the global warming potential of using KOH and NaOH at varying regeneration rates in AwR

Using NaOH instead of KOH will result in a greater CO_2 savings for AwR. While using KOH, AwR passed HPWS at a 65% regeneration rate but NaOH passed HPWS at a 40% regeneration rate. If the regeneration rates of either bases is improved a greater CO_2 savings is achieved, though if the regeneration rate is not improved and NaOH is substituted for KOH then an additional savings of 71 g can be achieved.

6.3.3.2 Transport distance and location of technology

A variable in the implementation of the novel technologies that could affect the final CO_2 emissions generated is the location of where the technology is installed. This pertains to both the distance between the upgrading plant and a municipal solid waste incinerator (MSWI), and the country where the upgrading plant is located.

As the novel technologies depend on waste coming from MSWI it is important to determine how the distance between the MSWI and the location of the upgrading technology affects the GWP. As well, large amounts of the waste are needed to run the system, for BABIU it requires 9 kg of bottom ash (BA) and 1 kg of air pollution control residues (APC) for AwR, per functional unit of 1 kWh of biomethane. It was decided to explore the impact related to transport by truck on a small scale with a distance up to 300km.

The electricity production mix of the country where the technology is installed could have an effect on the GWP. For the LCA study the inventory data used was for Spain. We decided to use also the electricity production mix for Italy as the pilot plant of BABIU and AwR are presently located there.

BABIU and AwR were compared to HPWS and AS which are the marketed technologies that showed the greatest CO_2 savings. Though to ensure proper comparability, the energy mixes of both Spain and Italy were used for all four technologies. As well a travel of 50km by truck was applied to any additional reagents used for AwR, BABIU and the amine used in AS.

As can be seen in Fig. 6.5 the impact of the distance travelled becomes increasingly significant when the amount of waste (APC for AwR and BA for BABIU) transported is increased. From 0 to 125 km the BABIU process still shows the greatest CO_2 savings. At around 145 km the AwR process and the BABIU process have the same CO_2 savings. At distances greater than 145 km the AwR achieves a greater CO_2 savings than BABIU, but at the same time they both have a lower CO_2 savings than HPWS and AS. When the distance between the MSWI and a BABIU plant reaches around 1315 km the impact from transport becomes higher than any CO_2 savings and the process begins to have a negative impact on the environment. For AwR, this point is reach at a much further distance of around 10475 km.

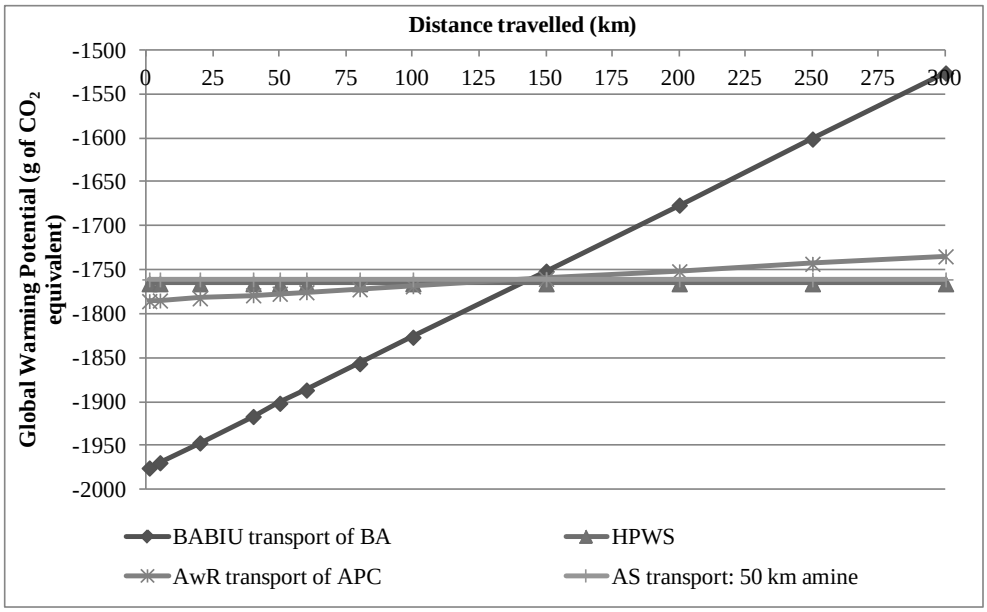


Figure 6.5. Comparison of global warming potential of distance of transport of bottom ash for BABIU and APC of AwR

As the other part of the study, it was determined that comparatively the country where the system is implemented does not have a large effect on the GWP. Overall Spain has a greater CO_2 savings than Italy but one could state that the effect is negligible. This difference exists due to the fact that Spain uses more nuclear and solar energy than Italy (Swiss Center for Life Cycle Inventories., 2010). Only in HPWS is it possible to note a difference and that is because out of all the 4 technologies the HPWS uses the most energy, therefore highlighting better the difference between the two.

6.3.4 Material Flow Analysis

Both BABIU and AwR use waste coming from MSWI in order to remove CO_2 from biogas which comes from landfills or anaerobic digesters (AD). Therefore it is of interest to determine how much BA and APC would be needed and whether enough could be generated. To obtain a general idea, the waste flow of Spain in all of 2008 was studied and the hypothetical situation was applied where all of the biogas generated was upgraded through either BABIU or AwR. This was considered as scenario 1.

Fig. 6.2, which demonstrates the waste flow in Spain, highlights the fact that most of the unsorted waste goes to either the landfill or for composting. On the other hand, Spain currently does not treat a lot of its waste through AD or MSWI.

From Table 6.3 it can be seen that under scenario 1 not enough waste is treated through MSWI to supply sufficient BA or APC to treat all of the biogas emitted from AD and landfills. It might be possible to have enough APC to treat biogas from AD using AwR, but there would not be enough to treat the biogas from landfills and in both cases there would not be enough BA to treat the biogas using the BABIU process.

Table 6.3. Scenarios for implementation of BABIU and AwR based on municipal waste flow of Spain in 2008

	Waste received (kt)	Estimated biogas production (m3)	BA from MSWI needed for BABIU (kt)	APC from MSWI needed for AwR (kt)	Possible BA production (kt)
Scenario 1					
Anaerobic digester	624	37,652,670	1,649	186	
Landfill	9,419	393,917,300	17,251	1,944	
MSWI	1,890				378
Scenario 2					
Anaerobic digester	9,284	1,067,620,203	46,754	5,270	
MSWI	6,672				1,334
Scenario 3					
Anaerobic digester	624	37,652,670	1,649	186	
MSWI	11,309				2,262

In an ideal situation countries would have citizen that are engaged enough to ensure that all organic material (OM) is selectively collected. In scenario 2 all of this OM is treated in the AD and all unsorted non OM waste would be sent to the MSWI. While in this scenario the production of biogas is around 2.5x higher, this would in turn require almost 47,000,000 t of BA for the BABIU process and 5,000,000 t of APC for the AwR, which could not be satisfied as only 6,000,000 t of waste would be treated through MSWI.

Scenario 3 therefore focuses on increasing the amount of BA and APC generated by sending the unsorted waste that would have gone to the landfill to the MSWI instead. In this case there would only be biogas coming from AD. Applying this scenario could generate enough APC for AwR and even enough BA for BABIU. As well, the potential electricity generated through MSWI is greater than the potential electricity from biomethane obtained through upgrading landfill biogas. While this situation seems like the best possible choice, given the current infrastructure of waste management in Spain, it would not be feasible to implement. Currently there are not enough MSWI plants to handle the additional waste.

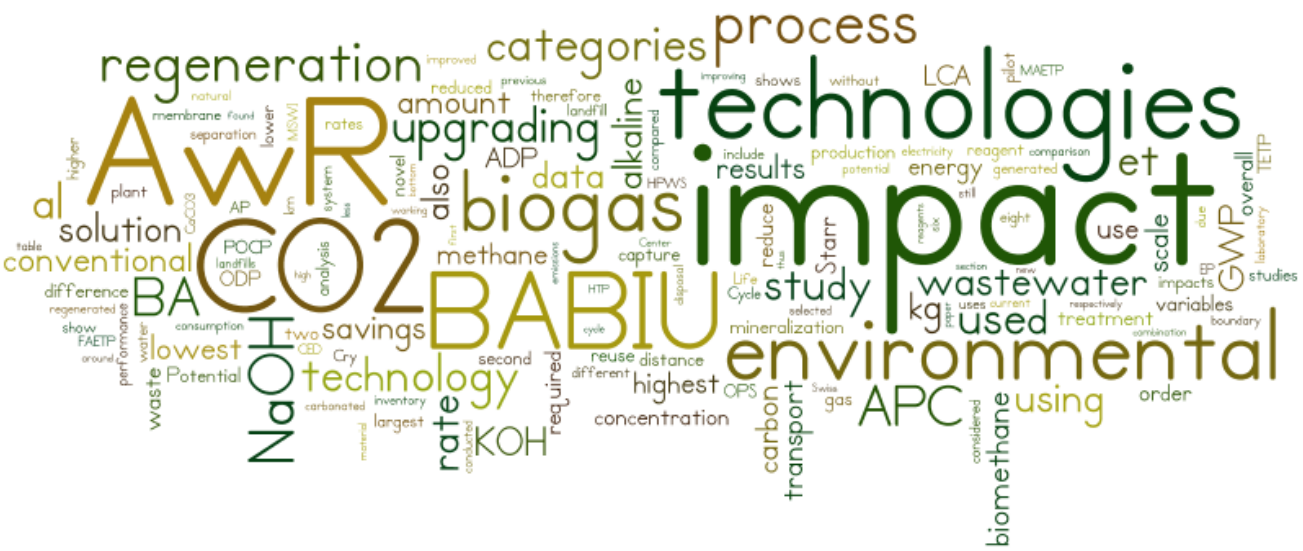
6.4 Conclusion

Out of the technologies that are currently on the market the HPWS and AS showed the greatest potential CO_2 savings followed by Cry. In the former and later processes the impact of electricity used plays the largest role in the CO_2 emissions generated, while for AS the production of heat played this role. In the lower end of the spectrum are located PSA, OPS and at last place MS. For all of these three technologies the impact due to the methane slip plays the largest role. If the technologies are improved in these areas then its potential CO_2 savings could possibly be improved.

The BABIU process showed the overall greatest potential CO_2 savings. Though if one starts to factor in the distance between the MSWI and the location where the technology is installed, then it rapidly decreases in CO_2 savings due to the high amount of BA that must be transported. Therefore in order for the BABIU technology to keep its position as best technology, it must be installed within 125 km of a MSWI. As well since BABIU requires a large amount of BA it was found that applying it as a biogas upgrading solution for all of Spain is not realistic. Therefore based on these two studies the installation of BABIU should be applied at a local scale where an AD plant or landfill can be found close to a MSWI. Therefore it is dependent on whether or not there is a MSWI close enough that produces sufficient BA. Meanwhile AwR, which uses less APC per functional unit, has more of a leeway in both the distance from a MSWI and the production capacity of the MSWI.

The production of the KOH used in AwR plays a large role in its CO_2 impact. If the KOH is changed to NaOH then its impact is reduced. AwR can currently obtain a base regeneration rate of 70%, if this is improved then the GWP is improved as well, though it cannot yet achieve the same CO_2 savings as for BABIU.

These novel technologies show a great potential savings mainly due to the fact that they also store the CO_2 from the biogas. If the CO_2 removed from the current technologies is stored then they may also show similar savings, though it would be necessary to factor in the impact of the storage technology as well.



Chapter 7

Optimization of Environmental Benefits of Carbon Mineralization Technologies for Biogas Upgrading

Chapter 7 - Optimization of Environmental Benefits of Carbon Mineralization Technologies for Biogas Upgrading

based on a manuscript by: Katherine Starr, Xavier Gabarrell, Laura Talens and Gara Villalba.

Abstract

Carbon mineralization is a promising process for carbon dioxide (CO_2) capture and storage, and can also be applied for biogas upgrading. This study uses LCA to identify possible ways to improve and reduce the environmental impact of novel biogas upgrading technologies. The two novel pilot-scale technologies assessed are alkaline with regeneration (AwR) and bottom ash for biogas upgrading (BABIU). These technologies are still at pilot plant scale, which offers the opportunity to identify how their environmental impact can be reduced. The variables that can be modified to optimize the process are: the selection of the alkaline solution and its concentration, wastewater reuse, transport of bottom ash (BA), and electricity consumption. The AwR technology uses as alkaline solution, either potassium hydroxide or sodium hydroxide, to capture the CO_2 and then uses air-pollution control residues to regenerate the solution. The BABIU process uses BA from municipal solid waste incinerators to directly capture CO_2. For AwR focus was placed on the reuse of wastewater and on the type and concentration of reagent. Further improvements focused on the reagent and electricity use in AwR and in the transport of BA for BABIU. The lowest environmental impact for AwR resulted when NaOH and in-process wastewater reuse are used. Despite such lower impacts, AwR still has a higher environmental impact in 11 of 12 categories compared to other conventional carbon capture technologies. Therefore it does not offer a better environmental way to reduce CO_2. In AwR, CO_2 savings begin when the regeneration rate of the NaOH solution is increased by 5%. AwR has a similar environmental impact to current technologies when the regeneration rate is further increased and the electricity requirements are reduced. On average the BABIU process has a 60% lower impact than AwR and it is comparable to conventional technologies. It can achieve CO_2 savings if the total travel distance of BA is less than 1.1 tkm, which can be reached by minimizing the transport distance of BA, or reducing the quantity of BA required.

7.1 Introduction

Landfilled municipal waste has several disadvantages; not only for the space it occupies and the potential leaching of toxic substances but also for the generation of greenhouse gases due to the decomposition of organic matter (OM) (UNEP, 2010). Biogas that is emitted from landfills is largely composed of methane (CH_4) (35-65%) and carbon dioxide (CO_2) (15-50%), as well as lower quantities of other impurities such as nitrogen (5-40%), oxygen (0-5%), hydrogen sulfides (0-100pmm) and VOCs (Petersson and Wellinger, 2009,Lems and Dirkse, 2009). Methane, when generated from the decomposition of OM is often referred to as biomethane and is considered to be 25 times more effective at trapping heat than CO_2 (Guinée et al., 2002). Therefore biogas, even if released in small quantities, is a substance with a high contribution to global warming. It is estimated that by the year 2020 the EU 27 region will emit from landfills alone around 10 billion m3 of biomethane, or roughly 165 Mt CO_2 eq (AEBIOM, 2011). In order to minimize these emissions, the European Commission created the 1999/31/EC directive with the objective that by 2016 the amount of OM delivered to landfills does not exceed 35% of the amount landfilled in 1995. This directive also encourages collection, treatment and usage of biogas from landfills, and states that "If the gas collected cannot be used to produce energy, it must be flared" (European Commission, 1999). Another option for biogas use, which to date is not as widely selected, is to increase the methane concentration of the gas by removing the other components, so that it can be used as a substitute for natural gas. This process is called biogas upgrading and it applies methods used in carbon capture technologies in order to remove CO_2 from the biogas, resulting in a biomethane suitable as alternative to natural gas. Biogas upgrading technologies are two-fold; they increase the content of methane, and capture CO_2 from the biogas. Thus, biogas upgrading technologies use the same or similar techniques as those used for carbon capture applied at large scale.

Carbon capture methods used in the biogas upgrading technologies that are available in the market are based on absorption, adsorption, membrane separation and cryogenic separation. CO_2 can be absorbed through high pressure water scrubbing (HPWS) which uses water, chemical scrubbing (AS) which uses an amine, and organic physical scrubbing (OPS) that uses polyethylene glycol. CO_2 can also be captured by pressure swing adsorption (PSA) which uses activated carbon. By membrane separation (MS), CO_2 is filtered using a membrane and in cryogenic separation (Cry) the biogas is cooled until the CO2 changes phase (Petersson and Wellinger, 2009,Persson, 2003,de Hullu et al., 2008). All these technologies capture the CO_2 from the biogas and release it back into the environment. While this CO_2 is of biogenic origin, it is wasting a potential source of highly concentrated CO_2 which can be used for industrial purposes or simply stored (Lems and Dirkse, 2009). Carbon mineralization is an emerging technology (MacDowell et al., 2010,IPCC, 2005) in which carbon is captured as calcium carbonate ($CaCO_3$) when calcium oxides (CaO) react with CO_2 (eq.7.1).

(7.1) $CaO_{(s)}+CO_{2(g)} \rightleftharpoons CaCO_{3(s)} + heat$

Therefore the advantage of carbon mineralization is that the CO_2 is captured (as opposed to released back into the atmosphere) and forms calcium carbonate, a solid and stable compound with low reactivity. Its use in industries generating high amounts of CO_2 is still under review (MacDowell et al., 2010) and at present, there are few studies about using carbon mineralization for the upgrading of biogas from waste treatment facilities such as landfills and anaerobic digesters.

This study assesses two pilot-scale technologies that upgrade biogas by carbon mineralization using CaO contained in waste generated by municipal waste incinerators (MSWI). These technologies convert biogas from landfill, with CaO-rich wastes, into biomethane. Using CaO rich wastes from MSWI, namely bottom ash (BA) and air pollution control (APC) residues, and also biogas generated in landfills help close their material cycle. However, before developing these technologies at industrial scale, it is necessary to assess them from a life cycle perspective to ensure they have a lower environmental impact than current CO_2 capture technologies.

The first carbon mineralization technology uses BA from MSWI in a direct gas-solid phase interaction, and is abbreviated as BABIU (Mostbauer and Lenz, 2007a,Olivieri et al., 2011). In this process the BA is first weathered and placed in a reactor. The reactor is filled with nitrogen in order to remove any air. The biogas is pumped through the reactor to make the CO_2 react with the bottom ash and convert the CO_2 into $CaCO_3$ (eq 7.1). The bottom ash, which is now rich in $CaCO_3$, is then removed and sent for disposal in the landfill. This is a batch process and four reactors run in tandem to ensure continual upgrading (Mostbauer and Lenz, 2007a).

The second carbon mineralization technology addressed in this study is called alkaline with regeneration (AwR) (Baciocchi et al., 2011b,Baciocchi et al., 2012). AwR uses an alkaline solution to strip the CO_2 from the biogas. The biogas enters a column containing an alkaline solution, either potassium hydroxide (KOH) or sodium hydroxide (NaOH). The exiting gas, rich in methane, is then dried and the alkaline solution is regenerated, by passing it through a stirred tank filled with APC from MSWI that has been prewashed. The CO_2 is adsorbed from the alkaline solution and forms $CaCO_3$. The APC residue that is saturated with CO_2 is filtered, post-washed to remove additional base and then is dried and disposed of in a landfill. Equations 7.2 and 7.3 show the chemical reactions using KOH as the base, while equations 7.4 and 7.5 show the same for NaOH.

(7.2) $2\ KOH_{(aq)}+CO_{2(g)} \rightarrow K_2CO_{3(aq)} + H_2O_{(l)}$

(7.3) $K_2CO_{3(aq)} + CaO_{(s)} + H_2O_{(l)} \rightarrow CaCO_{3(s)} + 2\ KOH_{(aq)} + heat\ )$

(7.4) $2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$

(7.5) $Na_2CO_{3(aq)} + CaO_{(s)} + H_2O_{(l)} \rightarrow CaCO_{3(s)} + 2\ NaOH_{(aq)} + heat$

AwR can use either NaOH or KOH at varying concentrations without compromising its yield (Lombardi and Carnevale, 2013). It can also reuse the wastewater generated from

post-washing the carbonated APC to pre-wash the non carbonated APC upstream, without affecting its adsorption ability. This study investigates how the diverse combination of variables such as the alkaline reagent and its concentration, and wastewater reuse can reduce the environmental impact of each technology. Further variables examined in AwR and BABIU include: increasing the regeneration rate of the alkaline and lowering the electricity consumption of AwR; and decreasing the transport and amount of BA in BABIU. All of which aimed to lower environmental impacts of the technologies.

These novel technologies, already assessed in previous papers (Chapter 6, Starr et al., 2012b) using lab-scale data, generate CO_2 savings. Yet, when compared to current technologies, the AwR had the highest environmental impact in 11 of the 12 categories reviewed, while BABIU had one of the best environmental performances overall. This study assesses AwR and BABIU using data from pilot plant production, which is more realistic and comparable to conventional technologies.

The aims of this work are to run an environmental assessment of two new biogas upgrading technologies, AwR and BABIU, both tested at pilot scale, and give examples on how reusing a waste can help close its material cycle, and generate an alternative to natural gas, all by using cleaner technologies with low environmental impact.

7.2 Methodology

The environmental evaluation was conducted with life cycle assessment (LCA) in accordance with the ISO 14040 (ISO, 2006).

7.2.1 Goal and Scope

There are many variables in the alkaline with regeneration (AwR) technology affecting their environmental impact. The main variables for AwR process under study are: the selection of the alkaline solution and its concentration, the regeneration rate of the selected alkaline solution, and the use of wastewater to pre-wash air pollution control residues (APC). The alkaline solution can be either potassium hydroxide (KOH) or sodium hydroxide (NaOH) (as these alkalis have a high reaction rate with CO_2 (Lombardi, 2013b)). The concentration of the alkaline solution can vary from 10% and 13% (by volume) for NaOH and by 14 and 18% for KOH (Lombardi, 2012b). The concentration affects the regeneration rate of the alkaline solution. Solutions with the higher concentrations have a regeneration rate of 50% while solutions with lower alkaline concentration have regeneration rates of 60%. AwR process generates wastewater when APC residues are washed before and after use. The wastewater generated from the post washing can be used without treatment to wash the APC residues before use. For this study, we define eight possible process settings for biogas upgrading by AwR. The objective is to assess the environmental impact of all these possible settings, to later select the combination that provides the lowest environmental impact. Table 7.1 describes the eight different combinations of variables for the AwR process along with the codes defined for easy identification.

The results obtained would also be compared to the pilot plant data of the bottom ash for biogas upgrading (BABIU) technology. The selection of process variables will influence the life cycle assessment (LCA) results, and the goal is to identify the process setting which generates the lowest environmental impact. Previous studies (Starr et al., 2012b, Chapter 6) at the laboratory scale found that BABIU had overall the lowest environmental impacts; therefore the need to adjust variables to reduce its environmental impact did not exist. The combination with the lowest impact will be then compared to six other conventional biogas upgrading technologies in a second LCA study, along with BABIU. The six conventional technologies reviewed in this study are high pressure water scrubbing (HPWS), pressure swing adsorption (PSA), chemical scrubbing (AS), cryogenic separation (Cry), membrane separatio (MS) and organic physical scrubbing (OPS) (Starr et al., 2012b). Additional optimization studies are conducted on AwR and BABIU to determine how to further improve their environmental performance.

Table 7.1 The eight different combinations of variables for AwR process

Code	Base	Concentration of base (wt %)	Regeneration rate (%)	Wastewater reuse for washing of APC residues
K14	KOH	14	60	No
K14ww	KOH	14	60	Yes
K18	KOH	18	50	No
K18ww	KOH	18	50	Yes
N10	NaOH	10.1	60	No
N10ww	NaOH	10.1	60	Yes
N13	NaOH	13	50	No
N13ww	NaOH	13	50	Yes

Source: (Lombardi, 2012b)

7.2.2 Functional Unit

The functional unit for this study is the potential generation of 1kWh from biomethane produced by the different biogas upgrading technologies in Spain. To perform a study about the effectiveness of the two novel CO_2 capturing technologies, we assume that biogas is composed of 50% CH_4 and 50% CO_2. Impurities such as hydrogen sulphide and siloxanes are assumed to be removed beforehand (Petersson and Wellinger, 2009,Persson, 2003).

7.2.3 System Boundaries

Fig. 7.1 shows the LCA boundary used in the two studies that were conducted. The LCA study that compares the novel and conventional technologies includs the heat, electricity and reagents necessary for the process and takes into account the biogas that

is upgraded. The system boundary is expanded for the study between solely AwR and BABIU as more information about the systems is available.

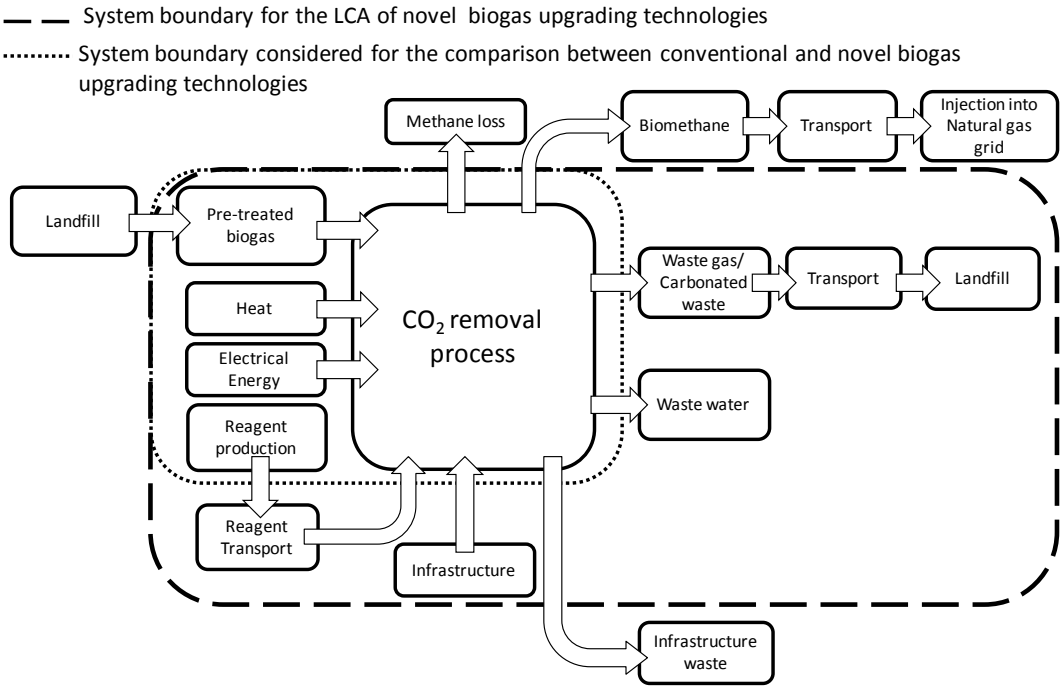


Figure 7.1 LCA System Boundaries
Based on figure 5.3

The transport by lorry/truck for BABIU and AwR is the sum of all the transport required of the reagents, waste (APC residues and BA), and carbonated waste. The distance is assumed to be 50 km. All the studies excluded the disposal of the infrastructure, the final treatment and transport of the biomethane, and methane loss.

CO_2 stored by APC and BA is counted as a CO_2 savings, while the input of methane and any other input of CO_2 not stored are considered as neutral

7.2.4 Life Cycle Inventory

The inventory information for the AwR and BABIU is based on pilot plant scale data that was scaled up to industrial scale and was gathered from direct email communications with the developers of each technology (Lombardi, 2012b,Lombardi, 2012a,Mostbauer, 2010).

Data for the high pressure water scrubbing (HPWS) was obtained through email communications with two manufacturers (Starr et al., 2012b,Kruit, 2010,Rowntree, 2010). Data for the six conventional biogas upgrading technologies was obtained from a literature review. The median point was selected for data with more than one value. For example, the methane slip of the membrane separation (MS) which ranges from 5% to 29% was assumed to be 17% (de Arespacochaga et al., 2010,Dachs and Zach, 2008). Tables 2 and 3 include the inventory data for all the processes assessed. Table 7.2 shows the inventory data for the six conventional technologies under review, as well as the

BABIU process while table 7.3 gives the inventory data for the eight different combinations of AwR. Both tables show the electricity and heat required, reagents used, biomethane purity, methane loses and the amount of biogas processed, all inherent to each technology. In some cases, the information for reagents used in certain processes, such as the amount of polyglycol ether solution used in organic physical scrubbing (OPS), was not available. As their environmental impacts were considered to be negligible, they were not included in the study (Starr et al., 2012b).

Table 7.2 Inventory data for conventional processes and BABIU process

	BABIU	HPWS	PSA	OPS	AS	MS	Cry	reference
Inputs								
Electricity (kWh) [a]	0.020	0.044	0.053	0.062	0.025	0.071	0.073	c,d,e-j, k-n
H_2O (kg) [a]		0.026						m,n
N_2 (kg) [b]	0.018							k,l
diethanolamine (kg) [a]					2E-04			o
BA (kg)	17.67							k,l
Diesel (kg) [a]	0.008							k,l
Biogas (m^3)	0.212	0.212	0.217	0.219	0.210	0.243	0.211	
Heat (kWh) [a]				0.064	0.104			f,i,p
Total Transport via lorry (tkm) [a]	1.781							k,l
Stainless steel (kg)[b]	1E-04							k,l
Gravel (kg)[a]	0.011							k,l
Mastic Asphalt (kg)[a]	0.008							k,l
Concrete (kg)[b]	0.003							k,l
Outputs								
Carbonated BA (kg)	17.94							k,l
Properties								
Biomethane purity (%)	98	98	97.5	97	99	85	98	c,d,f,h-j,k-n, q
Methane loss (%)	1.02	1	3.5	4	0.1	13.5	0.65	c,d,e-h, j, k-n,q

[a] (Swiss Center for Life Cycle Inventories., 2010) [b] (PE International, 2010) [c] (Petersson and Wellinger, 2009) [d] (Lems and Dirkse, 2009) [e] (MT- BIOMETHAN, 2010) [f] (Dachs and Zach, 2008) [g] (Pertl et al., 2010) [h] (Urban, 2007) [i] (Bekkering et al., 2010) [j] (de Arespacochaga et al., 2010) [k] (Lombardi, 2012a) [l] (Mostbauer, 2010) [m] (Rowntree, 2010) [n] (Kruit, 2010) [o] (Bailey and Feron, 2005) [p] (Beil et al., 2012) [q] (de Hullu et al., 2008)

Table 7.3 Inventory data for AwR process with diverse combination of variables

		K14	K14 ww	K18	K18 ww	N10	N10 ww	N13	N13 ww	ref
Inputs	Electricity (kWh) [a]	0.092	0.092	0.092	0.092	0.092	0.092	0.092	0.092	[b]
	KOH (kg) [a]	0.160	0.160	0.200	0.200					[b]
	H_2O (kg) [a]	7.994	4.866	7.950	4.809	8.029	4.901	7.990	4.848	[b]
	NaOH (kg) [a]					0.115	0.115	0.142	0.142	[b]
	APC (kg)	0.766	0.766	0.780	0.780	0.776	0.776	0.780	0.780	[b]
	Biogas (m^3)	0.212	0.212	0.212	0.212	0.212	0.212	0.212	0.212	[b]
	Total transport by lorry/truck (tkm) [a]	0.073	0.073	0.103	0.103	0.070	0.070	0.100	0.100	[b]
	Stainless steel (kg)[b]	4E-05	4E-05	4E-05	4E-05	4E-05	4E-05	4E-05	4E-05	[b]
Outputs										
	Wastewater (kg) [a]	6.538	3.418	6.568	3.434	6.538	3.419	6.568	3.434	[b]
	Carbonated APC (kg)	0.519	0.519	1.086	1.086	0.519	0.519	1.086	1.086	[b]
Properties										
	Biomethane purity (%)	98	98	98	98	98	98	98	98	[b]
	Methane loss (%)	1.22	1.22	1.22	1.22	1.22	1.22	1.22	1.22	[b]

[a] (Swiss Center for Life Cycle Inventories., 2010) [b] (Lombardi, 2012b)

7.2.5 Life Cycle Impact Assessment Phase

The life cycle assessment (LCA) for this study was conducted using the GaBi 4.4 software. Databases for this study came from the Ecoinvent 2.2 (Swiss Center for Life Cycle Inventories., 2010) and GaBi PE (PE International, 2010). The energy mix selected was based on the technologies used in Spain. The impact assessment method used was the CML 2001 method (Guinée et al., 2002) as it allows for comparison of the new results with previous work. This includes the following impact categories:

- Abiotic depletion, elements (ADP E) kg Sb eq
- Abiotic depletion, fossil (ADP F) MJ
- Acidification potential (AP) kg SO_2 eq
- Eutrophication potential (EP) kg Phosphate eq
- Freshwater aquatic ecotoxicity potential (FAETP) kg DCB eq
- Human toxicity potential (HTP) kg DCB eq
- Marine aquatic ecotoxicity potential (MAETP) kg DCB eq
- Ozone layer depletion potential, steady state (ODP) kg R11 eq
- Terrestrial ecotoxicity potential (TETP) kg DCB eq
- Global warming potential, 100 years (GWP) kg CO_2 eq

- Photochemical ozone creation potential (POCP) kg Ethene eq

The primary energy demand from renewable and non-renewable resources, considered by Ecoinvent as cumulative energy demand (CED) (Swiss Center for Life Cycle Inventories., 2010), was included as well.

7.3 Results and Discussion

In this section we examine which combination of variables of alkaline with regeneration (AwR) results in the lowest impact, along with the bottom ash for biogas upgrading (BABIU) process. The combination for AwR with the overall lowest impact is compared to the conventional technologies and also BABIU using a reduced system boundary (Fig. 1). Possible ways of further optimizing the environmental impacts of AwR and BABIU were examined with focus placed on global warming potential (GWP) for both technologies and on the remaining 11 impact categories for solely AwR. We then summarize the results and compare them to previous LCA results based on laboratory scale inventory data.

7.3.1 Selection of environmentally optimized alkaline with regeneration variables

Fig. 7.2 shows the results of the environmental assessment of AwR for the different working conditions as defined in table 1, as well as BABIU. The impact of AwR is reduced for all of the environmental categories when wastewater was reused to pre-treat air pollution control residues (APC). This is in line with the concept that if you use fewer resources, and thus close the material cycle of inputs and outputs then the overall impact is lowered. In 7 of the 12 categories reusing wastewater reduces the impact by 1% or less. In four other categories, which include acidification potential (AP), eutrophication potential (EP), ozone layer depletion potential (ODP) and photochemical ozone creation potential (POCP), the difference in the impact results are between 0.6% and 2.8% for the KOH combinations and between 1.4% and 4.8% for the NaOH variables. This is due to the fact that the impact of water consumption and wastewater treatment is comparatively low in relation to the impact of the KOH and NaOH, often two to three orders of magnitude lower. The treatment of wastewater is an important contributor for the GWP impact category. It has the second largest contribution after the reagent, though even in this case its impact is one order of magnitude lower than the reagent. The results show that when using NaOH, the reuse of wastewater in N13 and N10 reduces the GWP by 40% and 68% respectively. When using KOH the wastewater reuse lowers the impact of K18 and K14 by 11% and 15% respectively.

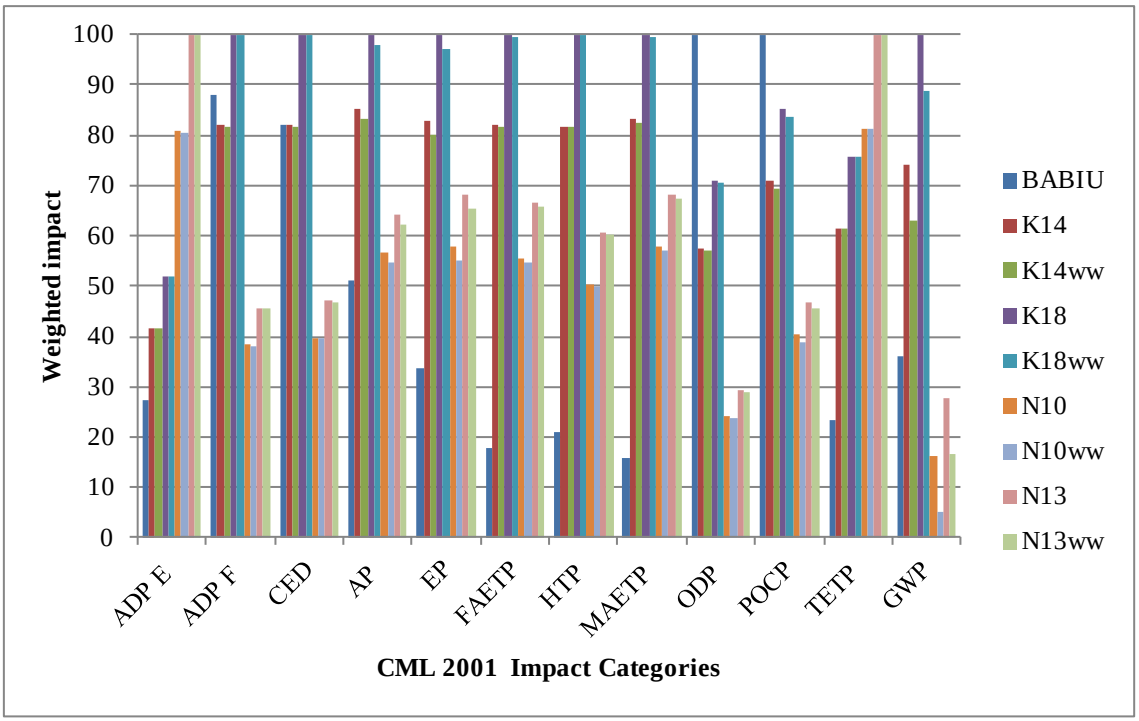


Figure 7.2 LCA of combination of AwR variables and BABIU

In 8 out of the 12 categories using KOH at an 18% concentration resulted in the highest impact followed by KOH at 14%, NaOH at 13% and NaOH at 10%. In these eight impact categories, it is clear that the production of NaOH and KOH play a major role in the overall impact of the system. The production of KOH requires heat, meaning it is more energy intensive than NaOH (Swiss Center for Life Cycle Inventories., 2010), which results in a 32-84% higher environmental impact in those eight categories. Using NaOH has a higher impact in abiotic depletion elements (ADP E) and terrestrial ecotoxicity potential (TETP) due to use of mercury cells for the electrolysis of sodium chloride (Swiss Center for Life Cycle Inventories., 2010). The process data used for the study attributed 55% of the total production of NaOH to mercury cells (Swiss Center for Life Cycle Inventories., 2010). The production mix of NaOH is due to change in the years to come as the European Union (EU) plans to replace mercury cells by membrane cells by 2020 (European Commission, 2001a,Euro Chlor, 2009). Such replacement would reduce the environmental impact of AwR in the categories ADPE and TETP.

The BABIU process has the lowest impact in most of the environmental categories under review, 7 out of 12. It has a higher impact only for ODP and POCP. The impact for ODP and POCP is 29-75% and 14-60% higher than for the other technologies. BABIU also had a large impact in abiotic depletion fossil (ADP F) and cumulative energy demand (CED). Compared to the AwR with the highest impact, which in these categories is K18, BABIU had an 18% and 12% lower impact in ADP F and CED respectively. The increased environmental impact in these four categories can be attributed to the transport and the amount of BA required by the process, which is 23 times heavier (at 18 kg per kWh biomethane) than the APC required for AwR.

Overall AwR carbon mineralization process using NaOH at 10% concentration and reusing wastewater (N10ww) showed the lowest impact. This process is then compared along with BABIU and other conventional carbon capture technologies.

7.3.2 LCA of eight biogas upgrading technologies

As mentioned in section 7.3.1, AwR using NaOH at 10% concentration with wastewater reuse was selected to be compared to BABIU and six other conventional biogas upgrading technologies, which include pressure swing adsorption (PSA), high pressure water scrubbing (HPWS), cryogenic separation (Cry), chemical scrubbing (AS), membrane separation (MS) and organic physical scrubbing (OPS). This study used a smaller system boundary than the first analysis as shown in Fig. 7.1. Fig. 7.3 shows the results of the LCA for all the technologies assessed.

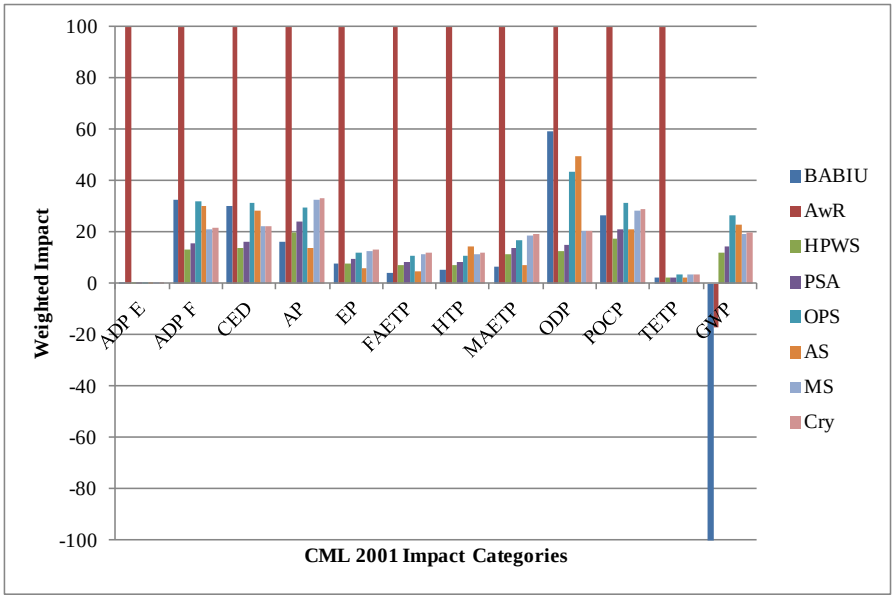


Figure 7.3, LCA of novel and conventional biogas upgrading technologies

Despite selecting the AwR process with the lowest environmental impact, it can be seen in Fig. 7.3 that AwR still has the highest impact in all environmental categories except for GWP, which is due to the production of NaOH. The differences between AwR and the upgrading process with the second highest impacts (which vary between BABIU, AS, OPS and Cry) were quite marked in some cases, such as a 99% difference in abiotic depletion elements (ADP E) and 96% for terrestrial ecotoxicity potential (TETP). The category where AwR had the least difference in impact was in ozone depletion potential (ODP) where its impact was 41% higher than BABIU.

BABIU had the second highest impact in abiotic depletion potential fossil (ADP F) and ODP, while the impact in human toxicity potential (HTP), marine aquatic ecotoxicity potential (MAETP) and freshwater aquatic ecotoxicity potential (FAETP) was the lowest. Focusing solely on the conventional technologies, OPS, Cry and AS all had the highest impact in four different categories each. OPS was the conventional technology with the highest impact in abiotic depletion potential fossil (ADP F), cumulative energy demand (CED), photochemical ozone creation potential (POCP) and TETP. Cry was found to have the highest value in the impact categories of abiotic depletion potential (AP), eutrophication potential (EP), FAETP and MAETP. Meanwhile AS had the largest impact in ADP E, HTP, ODP and GWP and the lowest impact in AP and EP, FAETP, and MAETP. Out of all of the technologies currently on the market, HPWS was found to have the lowest overall environmental impact as it had the lowest impact in 8 of the 12 categories. Compared to both the conventional and novel technologies, HPWS still has overall the lowest impact in 6 of the 12 categories (ADP E, ADP F, CED, ODP, POCP and TETP) whereas AwR and BABIU, the two novel technologies have the lowest environmental impact in GWP.

7.3.3 Improving carbon dioxide savings

In the comparison between the novel technologies (section 3.1) both AwR and BABIU generate CO_2 despite the fact that they inherently store CO_2. On the other hand in the comparison between both the novel and the conventional technologies (section 3.2) the mineralization technologies did demonstrate a CO_2 savings. The reason for this difference is that the system boundary was expanded for the comparison between only the novel technologies (Fig. 7.1) and therefore the impacts of transport, wastewater and infrastructure are included. With the expanded boundary it was seen that transport of bottom ash played the largest role in the GWP for the BABIU process, though for the AwR it only had the third largest GWP impact after the reagent and wastewater treatment. Further analyses were conducted to determine how the performance in the GWP impact category could be improved for the carbon mineralization technologies.

7.3.3.1 Optimization of BABIU process for CO_2 impact

As mentioned, the GWP of the BABIU process is largely impacted by the transport of the bottom ash to and from the upgrading site due to the amount required shown in table 7.2 (17.67 kg of BA per kWh of biomethane compared to 0.766 kg of APC residues per kWh of biomethane for AwR). For both processes we assume a distance of 50 km to the upgrading plant and another 50 km from the upgrading facility to the disposal site for used BA. For this analysis, it was presumed that the final carbonated BA will be disposed in the same landfill where the upgrading took place and therefore will have 0 km. The variation on transport distance therefore focused on the BA that goes to the landfill. As the amount of BA that comes in and goes out vary by a few kg, one can use this analysis as an overall estimation of the total distance. Based on such estimation, we calculate the maximum distance at which the BABIU process starts saving CO_2.

The BABIU process obtains CO_2 savings when the total combined distance between its facility, the municipal solid waste incinerator (MSWI), as well as the BA disposal site do not exceed 60 km (as shown in Fig. 7.4). When the total amount of the BA transported is taken into account it can be considered as 1.1 tkm. Locating BABIU facilities near MSWI and BA disposal sites would considerably reduce the GWP for the entire process. Another option to minimize the GWP is to reduce the amount of BA required by the process. One way to achieve this reduction would be to upgrade the biogas to a gas with has a methane content that is lower than required for natural gas substitution, but enough for direct burning for electricity. On the other hand, this would obviously also reduce the overall amount of CO_2 saved by the technology, as less biogas would be processed, and therefore less CO_2 captured by the BA. The second largest contributor to CO_2 emissions, which can be also reduced, is the energy used by the process. Achieving a significant reduction of the energy input to the process requires a more in-depth analysis of the equipment used by the facilities.

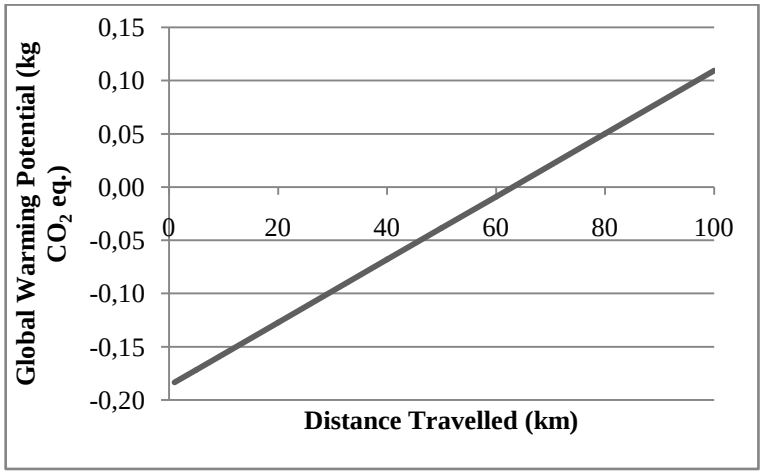


Figure 7.4. CO_2 emissions of the BABIU process in relation to distance between upgrading plant and source of bottom ash

We considered the BA as a resource input to the BABIU process and therefore we associated the burden of transport to BABIU. As the BA is a waste that would be landfilled, and the BABIU facility for this study is located in a landfill, other authors may attribute this impact to the waste itself as opposed to the BABIU process. As this technology would have other possible applications as for example the treatment of biogas from anaerobic digestors and wastewater treatment plants, we feel that including the impact of transport in the study is inherent for understanding the overall impact of BABIU.

7.3.3.2 Optimization of AwR regeneration rates for improved CO_2 impact

The AwR process uses a solution of base and water in order to create the alkaline solution (NaOH or KOH) that captures the CO_2 from the biogas. This alkaline solution is regenerated while in contact with APC residues to create fresh alkaline solution. However not all the alkaline solution that enters the column is regenerated and therefore more has to be made up. The amount of alkaline solution regenerated is known as the regeneration rate. Increasing the regeneration rate of AwR helps reduce its environmental impact. The current regeneration rates for each AwR working conditions can be found in table 1. While they ranged from 50-60%, an additional analysis was conducted in order to see at which regeneration rate there is a CO_2 savings.

Fig. 7.5 shows the GWP for different regeneration rates for AwR, at different working conditions, compared with the GWP of BABIU. The figure shows CO_2 savings when NaOH has a regeneration rate of 65% and reuses wastewater (N10ww and N13ww), which can be achieved by improving the regeneration rate of N10ww and N13ww by 5 and 15% respectively. AwR using NaOH without wastewater reuse starts saving CO_2 at approximately 77%. AwR using KOH solutions has to achieve a regeneration rate of 85 and 90% with and without water reuse respectively to achieve CO_2 savings. This would require a regeneration rate improvement of between 25 and 40%.

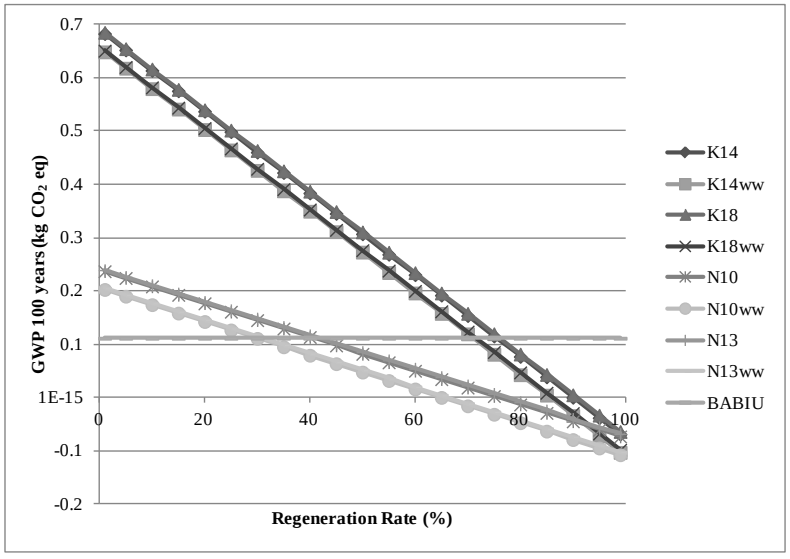


Figure 7.5. GWP of AwR variables at different regeneration rates

From this analysis, it is quite clear that the NaOH solution at 10% with wastewater reuse has the highest potential for CO_2 savings as the regeneration rate would have to be improved by 5% in order to begin saving CO_2. Whether CO_2 savings can be reduced without compromising the quality of the technology, needs to be studied further by the developers.

7.3.4 Optimization of AwR for overall environmental performance

Based on the analysis described in section 7.3.2 we concluded that AwR is the technology that has the highest impact all categories except GWP. Improving the regeneration rates of the alkaline solution can further reduce the CO_2 emissions generated by the AwR process. Further analysis was run in order to determine if the performance in other impact categories can also be improved by adjusting the regeneration rate.

Even with a regeneration rate of 100%, AwR still has the highest impact in 7 out of 12 categories out of all of the technologies studied. Table 7.4 highlights the difference in impacts between the AwR technology and the technology with the second highest impact in those seven categories. The technologies with the second highest impact include: cryogenic separation (Cry) for acidification potential (AP), eutrophication potential (EP), freshwater aquatic ecotoxicity potential (FAETP) and marine aquatic ecotoxicity potential (MAETP); chemical scrubbing (AS) for human toxicity potential (HTP) and terrestrial ecotoxicity potential (TETP); and organic physical scrubbing (OPS) for photochemical ozone creation potential (POCP).

Table 7.4. Difference between AwR and technology with second highest impact in CML 2001 ecoindicator.

Impact category	Difference between AwR and technology with second highest impact (%)		Energy reduction required to reach second highest Impact (without reagent) (kWh per FU)
	With reagent included	Without reagent	
AP	67	23	0.024
EP	87	25	0.028
FAETP	88	26	0.030
HTP	86	9	0.016
MAETP	81	24	0.026
POCP	69	18	0.019
TETP	97	26	0.056

The main contribution to the impacts in six of the seven cases refered to above, comes from the energy consumption (as shown in inventory data of table 7.2 and 7.3), while for AP the wastewater treatment played the major role. The environmental impact of AwR would be comparable to that of the technologies with the second highest impact in HTP and POCP, if the impact from the reagent is considered negligible and the electrical energy use is reduced by around 20%. If the electricity consumption was reduced to around 30% then it would reach levels similar to technologies in AP, EP, FAETP and MAETP. If it was reduced further by 61% then its impact would be comparable to technologies in TETP (table 7.4). The main energy input for AwR comes from the membrane filter presses which are used to dry the APC residues at three different stages. There is a prewashing of APC, separation of the regenerated NaOH from the carbonated APC, and lastly the final washing of the carbonated APC. The filters that are

used require a lot of energy and account for 92% of the electricity requirements of the system. This may be improved once the technology reaches industrial scale.

As for the other impact categories, it was found that improving the regeneration rates can bring the environmental impact on par with other conventional technologies, though in most cases at very optimistic rates, which is currently not technically possible. For abiotic depletion potential elements (ADP E) a regeneration rate of around 99.9% would need to be obtained. The other categories also needed high regeneration rates at 98.5% necessary for cumulative energy demand (CED), 97% for abiotic depletion potential fossil (ADP F) and 87% for ozone layer depletion potential (ODP).

7.3.5 Summary and comparison to life cycle assessment based on experimental data

Past studies show that the reagent had the largest impact for the AwR process (Starr et al., 2012b, Chapter 6). In this study, we have shown that changing the reagent from KOH to NaOH and reducing its concentration helps minimise the environmental impact of AwR. Though, further studies will have to be conducted by the developers to find how to reach a level of regeneration without compromising the upgrading performance. The environmental impact of the AwR technology can also be reduced when the wastewater generated from the post-washing phase is reused in order to pre-wash APC residues. The technology provides CO_2 savings by improving its current regeneration rate by 5%. This differed from a previous study (Starr et al., 2012b) in which the AwR showed a CO_2 savings. This difference is due to the fact that with the pilot plant more materials and reagents are required for not only AwR but also for BABIU. For example, laboratory scale data showed a regeneration rate of 70% for the KOH used in AwR which resulted in less KOH required by the process. Previously, the CO_2 that was stored recompensed for any CO_2 emissions and also had additional savings, but this new data shows that improvements are required for both technologies in order to save CO_2.

To reduce the environmental impact of AwR in the other 11 impact categories focus would have to lie in not only the reagent but also in the energetic needs of the technology. Through the development of this technology it was found that in addition to the filter needed to separate the regenerated NaOH from the carbonated APC it would be necessary to pre and post-wash the APC which would require additional filters. The developers currently selected membrane filter presses, which have resulted in a much higher energetic consumption since the previous laboratory scale did not include a filtration system (Olivieri et al., 2010). This tenfold increase in energy consumption means that the technology has a larger energy need in comparison to all of the other conventional technologies studied, and as a result a higher environmental impact. Therefore, in addition to improving the regeneration rate of the reagent, the selection of the separation technology is also important to make AwR a viable technology for biogas upgrading.

Improving the performance of BABIU depends on reducing the amount of BA required for the process, and locating the biogas upgrading facility less than 60 km away from the incineration plant and its final disposal location. This is a great difference in comparison

to a previous study (chapter 6) which showed that CO_2 savings would begin at a distance of 1315 km. There are several factors for this difference. The first is, as mentioned above, the material requirement at pilot plant scale is greater than estimated in the first study. The experimental data suggested that 9 kg of bottom ash was needed per kWh of biomethane, while new data suggests that the amount required is 18 kg. As a result the impact from transport is higher and thus the additional material amount results in a smaller allowable transport distance.

The greatest difference between the results of these two studies depends on the allocation of the CH_4 contained in the biogas. This study does not include the impact of methane contained in the biogas in the GWP impact category, as it is biogenic and thus not derived from fossil fuels. Also, we do not consider any future use of the resulting biomethane, therefore we do not account for the positive effect its use may have when substituting natural gas. Chapter 6 considered biomethane as a CO_2 savings while CH_4 losses were categorised as emissions. CO_2 savings were assumed because the upgraded biogas diverted CH_4 from being emitted into the atmosphere in order to be combusted for electricity generation.

Despite the fact that the LCA results of AwR and BABIU are different using laboratory and pilot plant data, AwR still has a greater environmental impact than BABIU and other conventional technologies. Adjusting the working conditions or parameters when scaling up processes helps to identify areas for improvement and to understand better how those changes affect the environmental impact of these technologies.

7.4 Conclusion

While these carbon mineralization technologies are still in the development stages, it is important to evaluate their environmental performance in order to pinpoint where potential improvements and measures to reduce their environmental impact can be made. For that reason, in this study, we performed an LCA for eight carbon capture technologies, including two pilot scale technologies: AwR and BABIU. The results show that the environmental impact of AwR can be minimised by using NaOH at 10% concentration and reusing in-process wastewater to pre-wash the APC residues. It can be further reduced by improving the regeneration rate of NaOH and lowering its overall energetic consumption by changing the current filtering equipment used. The environmental impact of the BABIU process can also be improved by optimising the quantity of BA and reducing the transport distance between the source of BA and the biogas upgrading facility.

Once technologies with lower environmental impacts are developed at an industrial scale it would be of interest to compare them to other landfill biogas operations such as direct combustion for energy production. A combined study with an economic analysis would help estimate the feasibility of applying these technologies, and show how they can contribute to reduce global warming potential and other environmental impacts.

Chapter 8

Using Exergy Analysis for the Assessment of Novel Biogas Upgrading Technologies

Chapter 8 - Using Exergy Analysis for the Assessment of Novel Biogas Upgrading Technologies

based on a manuscript by: Katherine Starr, Laura Talens, Gara Villalba and Xavier Gabarrell

Abstract

In this study we analyse the main differences by the diverse methods available to calculate exergy, including one used in LCA. Although cumulative exergy demand (CExD) is included in LCA software programs it is not yet included in many LCAs and its significance is not well understood. The calculations of exergy values from "cradle-to-gate" can be done by using diverse indicators which leads to further confusion about how exergy can be calculated and its usefulness. This study uses exergy analysis in order to analyse the resource use and efficiency of diverse biogas upgrading technologies. Exergy is calculated using cumulative exergy consumption (CExC), CExD, a mix between the two (CExM), and exergy efficiency (e_2). The results show that the different studies achieve similar ranking for the biogas upgrading technologies. Despite the similarity, it was found that CExD is not a substitute for CExC, because indirect flows are accounted for. Also discrepancies between the three cumulative methods assessed can also be attributed to the production processes used. The overall results were compared to a previous LCA study, and it was found that the results generally reflected the resource based indicators, except for the CML 2001 impact category of ADP elements.

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8.1 Introduction

The environmental impact of systems and products is generally assessed by life cycle assessment (LCA). LCAs are performed based on various environmental impact categories. One such method is CML 2001 developed by Leiden University. This method consists of 10 environmental impact categories which include: abiotic depletion (elements and fossil), acidification potential, eutrophication potential, freshwater aquatic ecotoxicity potential, human toxicity potential, marine aquatic ecotoxicity potential, ozone layer depletion potential, terrestrial ecotoxicity potential, global warming potential, and photochemical ozone creation potential (Guinée et al., 2002).

While these methods do allow for the estimation of the potential environmental impact of technologies they do not provide information about the system performance and how the natural resources are used. Both of these indicators however can be assessed using exergy analysis. Szargut et al (1988) used exergy analysis and efficiency to study the individual production of several chemicals and developed further the method to assess chemicals from a cradle-to-gate perspective (Szargut et al., 1988). Efficiency is often applied to energy conversion technologies in order to determine how much energy input is required for the energetic output. This is often based on the first law of thermodynamics which states that energy in conserved. However this calculation doesn't take into account how much of the input or output energy is available to do work (Ayres et al., 2011). The second law of thermodynamics however gives a measure on how the quality of the energy is degraded, and helps determine the potential available work. Exergy efficiency (e_2) applies both the first and second laws of thermodynamics in the assessment of processes and products. Exergy is defined as the maximum amount of useful work obtained when a system is brought to equilibrium with its surroundings through a series of reversible processes, in which the system interacts only with its reference environment (Szargut et al., 1988). Exergy is not a conserved quantity, in contrast with energy. It can measure not only energy, but also material and chemical compounds. In other words, it can be used to measure natural resources, as well as wastes and emissions (Szargut, 2005,Ayres et al., 1998,Talens, 2009). Szargut et al. use the term cumulative exergy consumption (CExC) to refer to the consumption of exergy from cradle-to-gate. This methodology, developed by Szargut and Morris, sums up the exergy used in the lifespan of a product or system (Szargut and Morris, 1987,Szargut et al., 1988), which is total amount of resources required by the product over a lifetime starting from the product and going backwards to the extraction of raw materials.

Initial work to integrate exergy as an indicator of LCA was done by Cornelissen (Cornelissen, 1997). Despite the fact that the term used was different, the reasoning behind was the same as CExC: to account for the material and energy inputs during the life cycle of a product in the form of exergy. In 2007 Bosch et al. proposed a new methodology focused on integrating LCA and cumulative exergy analysis using a method called cumulative exergy demand (CExD) (Bösch et al., 2007). CExD takes advantage of the Ecoinvent database which contains information on the production of chemicals and

products. This method is currently found as an impact category in SimaPro, leading LCA software and due to its availability has appeared in various LCA publications (Carvalho et al., 2013). The advantage of this method is that practitioners of LCA can easily apply CExD to their LCAs as opposed to going through the analytical calculations required for CExC. Despite the fact that these methods provide insight into resource consumption, they do not provide a way to measure how effectively resource inputs are used. This latter aspect can be estimated by e_2, which is defined as the difference between the exergy of the useful output and the sum of all the inputs.

This study uses e_2 as an indicator to complement an LCA study performed on four biogas upgrading technologies (chapter 7). CExC and CExD are explained in further detail and applied to the four case studies in order to understand better the discrepancies of results and the challenges associated with using this indicator.

8.2 Case Study

In municipal waste landfills, the anaerobic digestion of organic matter produces biogas, a mixture of methane (CH_4) and carbon dioxide (CO_2). When methane in the biogas is isolated, through a process called biogas upgrading, the resulting biomethane, which has a high calorific value, can be used as substitute to natural gas (Petersson and Wellinger, 2009). Biogas upgrading technologies concentrate CH_4 by removing impurities such as hydrogen sulphide, nitrogen and most importantly CO_2.

Current commercial biogas upgrading technologies remove CO_2 to later release it back into the environment (Lems and Dirkse, 2009). The novel biogas upgrading technologies under study are two-fold as they capture and store the CO_2. These technologies apply the concept of carbon mineralization whereby, waste from municipal solid waste incinerator (MSWI) rich in calcium oxide (CaO) reacts with CO_2 to form calcium carbonate ($CaCO_3$). These novel technologies show a potential environmental benefit over conventional methods as they store CO_2. It is important to conduct studies about their efficiency in order to better assess their benefits before industrial scale plants are built. Data concerning the exergy or e_2 of biogas upgrading technologies is scare, if not difficult to find.

The two carbon mineralization technologies under development include alkaline with regeneration (AwR) and bottom ash for biogas upgrading (BABIU). These two processes were studied, along with high pressure water scrubbing (HPWS) a conventional technology. HPWS was selected as a point of comparison, as not only it is one of the widely applied conventional upgrading technologies (Bauer et al., 2013), but previous studies from the author have shown through LCA that it has one of the lowest environmental impacts (Starr et al., 2012b). A description of these three technologies can be found in table 8.1. AwR and BABIU were selected as they present novel methods to upgrade biogas with a potential to store CO_2 while also removing it from biogas. The reagents for AwR used in this study were KOH and NaOH (Lombardi and Carnevale, 2013).

Table 8.1. Description of biogas upgrading technology

Technology	Acronym	Description of the process
Alkaline with Regeneration[a]	AwR	An alkaline solution of either sodium hydroxide (NaOH) or potassium hydroxide (KOH) absorbs CO_2 in biogas. The solution is mixed with air pollution control residues (APC) in order to regenerate the alkaline solution by adsorbing the CO_2 through the conversion of the calcium oxide (CaO) in the APC into calcium carbonate ($CaCO_3$). The APC is disposed. Any make-up water and base are added. *Process: carbon mineralization*
Bottom Ash for Biogas Upgrading[b]	BABIU	Bottom ash (BA) from municipal solid waste incinerator is placed in a reactor. Using nitrogen, the air is purged from the reactor. The BA is exposed to biogas. The calcium oxide (CaO) reacts with CO_2 to form calcium carbonate ($CaCO_3$) and isolating the biomethane. The BA is removed and disposed. *Process: carbon mineralization*
High Pressure Water Scrubbing[c]	HPWS	Pressurized water is used to absorb CO_2 from biogas, isolating the biomethane. The water is depressurized to release the CO_2 and to regenerate the water. *Process: absorption*

[a] (Baciocchi et al., 2011a,Baciocchi et al., 2012) [b] (Olivieri et al., 2011,Mostbauer and Lenz, 2007a) [c] (Petersson and Wellinger, 2009,Lems and Dirkse, 2009)

The information required to calculate the exergy of material is the compositional data on the inputs and outputs, which allows performing consistent mass balance of the process, and it requires a detailed process description. Information was obtained through direct communication with the developers or manufacturers (Kruit, 2010,Rowntree, 2010,Lombardi, 2012a,Lombardi, 2012b). Datasets were standardized for the production of 1 kWh of biomethane from biogas with a theoretical composition of 50% CH_4 and 50% CO_2.

8.3 Methodology

Exergy represents the ability to do work, therefore exergy is calculated as the work involved to bring the system under study from a reference state to state 1 (Talens, 2009). Exergy, as with energy, can be in different forms: kinetic, potential, physical, and chemical. Like energy, kinetic exergy is based on velocity with respect to the surface of the earth, while potential exergy is based the position of a body in reference to a force, such as gravity (Szargut, 2005,Talens, 2009).

Physical exergy is calculated by determining the work required to bring a substance from one temperature and pressure to the temperature and pressure of the surrounding environment. Thus, it is calculated using equation 8.1 (Szargut, 2005):

(8.1) $b_{ph} = \Delta H - T_0 \Delta S$

Where b_{ph}= physical exergy (J/kg), H= enthalpy (J/kg), *S*= entropy (J/(kgK)) and T = temperature (K)

Chemical exergy is based on the difference in the chemical composition of a substance in relation to the chemicals which are commonly found in the environment, referred to as the reference state. The chemical exergy is calculated using the Szargut reference state and its standard chemical exergies (Szargut, 2005). For the analysis of biogas upgrading technologies exergy for substances was taken from literature sources (Szargut, 2005,Dewulf et al., 2007). When data was not available, we used equation 8.2 (Szargut, 2005):

(2) $b_{ch} = \Delta_f G + \sum n_e b_e$

Where b_{ch}= standard chemical exergy of the compound (J/kg)$\Delta_f G$ = Gibbs free energy of formation (J/kg), n_e= number of moles of element per unit of compound, and b_e= standard chemical exergy of the element (J/kg).

This study considers the chemical exergy of the inputs and outputs, the physical exergy of steam and the exergy of direct electrical energy. For chemical processes, kinetic and potential exergies are considered to be steady; therefore they were excluded from the analysis.

As the novel technologies are in the pilot plant stage, not all of the inputs are fully defined, for example the complete chemical composition of the BA that is required by the BABIU process both before and after carbonation, and the APC residues needed by AwR. Both APC and BA come from municipal solid waste incinerators (MSWI) and are therefore normally considered as wastes however for these upgrading technologies they are used as a raw material. The composition of these wastes depends on the composition of the waste that is incinerated; though the BA and APC often contain a mixture of calcium oxide (CaO) like compounds. We use as a reference substance calcium hydroxide ($Ca(OH)_2$) as it is a common compound present in both wastes (Baciocchi et al., 2013,Mostbauer et al., 2013). Therefore the chemical exergies of BA and APC are calculated as $Ca(OH)_2$.

Electrical exergy is considered as fully useful work; therefore its exergy is considered the same as its energy content. In other words 1 MJ of energy is equivalent to 1 MJ of exergy (Ayres et al., 2005,Ertesvåg, 2001).

8.3.1 Exergy Analysis

Exergy can be used to perform a balance in a defined system, thus compare inputs and outputs. Exergy efficiency (e_2) is defined as the ratio of the exergy of the useful product and the sum of the exergies of all the inputs. For biogas upgrading technologies, it is calculated by dividing the exergy (Ex) of the main product of the system under analysis,

which in this case is biomethane (CH_4), by the sum of the exergy of the inputs such as CH_4, $Ca(OH)_2$, and CO_2 as seen in equation 8.3.

(8.3) $$e_2 = \frac{Ex_{product}}{\sum Ex_{inputs}}$$

The e_2 can also be used to study systems from a "cradle-to-grave" perspective, however in this study we focus on the immediate inputs into the biogas upgrading process as most of the inputs are traditionally considered as waste products (fig 8.1).

In this study we also use cumulative exergy demand (CExD) and cumulative exergy consumption (CExC). The CExD (Bösch et al., 2007), was calculated based on the inventory data of a previous LCA conducted by the authors (chapter 7). The functional unit for this and all exergy analyses was for the potential production of 1 kWh of biomethane. The estimate of CExD for biogas upgrading was conducted following the LCA guidelines set out in ISO 14040 (ISO, 2006). The database used was Ecoinvent 2.2 (Swiss Center for Life Cycle Inventories., 2010) and SimaPro 7.3® was used to perform the calculations. The system boundaries include the main infrastructure, transport, reagents and electricity used (fig 8.1).

The CExD was compared to CExC, which is a more analytical approach. For CExC, the inputs into the system are added up from the point of extraction, up to the point of use. Therefore exergy involved in the manufacturing of the chemical compounds are taken into account. In this study, the CExC was centered on the AwR process. A literature review was necessary in order to obtain information on the production processes of KOH and NaOH (European Commission, 2001b,Schultz et al., 2000), as well as that of NaCl and KCl (Faith et al., 1975) (which are products required for the production of NaOH and KOH respectively). For the CExC the production of KOH and NaOH was based on the membrane cell electrolysis. For the production of KCl, it was assumed that KCl had a 50% production from brine using solar evaporation, and 50% from fractional crystallization of sylvenite. For NaCl it was assumed that the production was split 50-50 between multiple effect evaporation of saturated brine and open pan process of saturated brine.

A third cumulative exergy method was examined which aims to answer whether it is advisable to complement CExC with process data of CExD. This is done to take advantage of the readily available data in ecoinvent and to avoid conducting literature searches for inventory data information. For example, as opposed to calculating the CExC of the production of KOH, the CExD could be obtained and therefore used in order to calculate the CExC of AwR. In order to avoid confusion between methods, we call this cumulative exergy mix (CExM).

APC, BA, and biogas are considered as raw materials for biogas upgrading, as opposed to waste products. For their calculation in CExC and CExM they are considered as being at the first stage of their respective life cycle. The waste management treatment they undergo and the previous steps are not considered.

Figure 8.1 shows a general flow diagram of biogas upgrading technologies. The different dotted lines indicate the flows included in each cumulative exergy analysis.

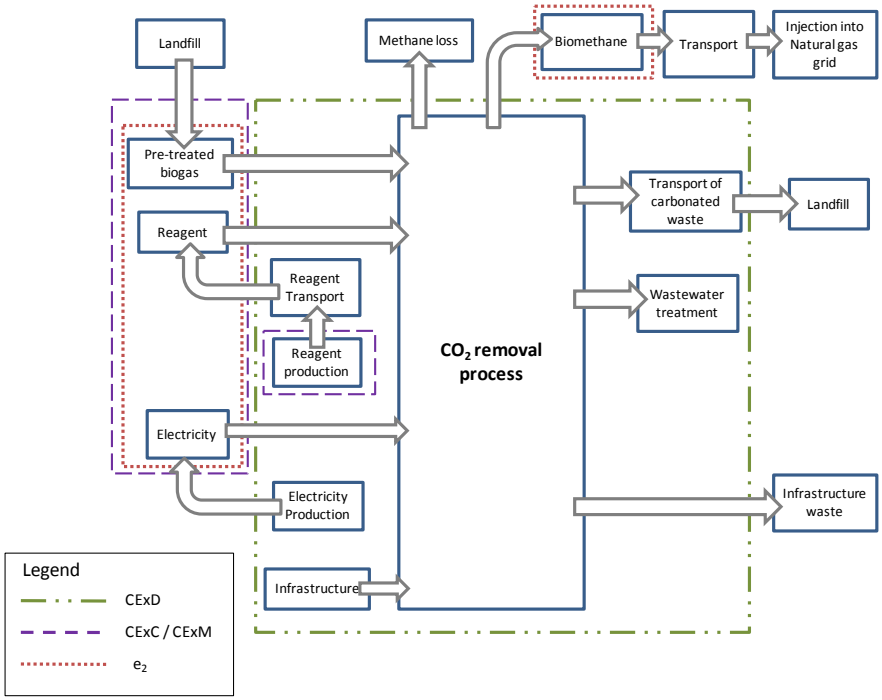

Figure 8.1 Biogas upgrading flows included and excluded in various exergy analysis

A literature review was conducted to obtain information on the production processes of KOH and NaOH (European Commission, 2001b,Schultz et al., 2000), as well as NaCl and KCl (Faith et al., 1975) (which are product required for the production of NaOH and KOH respectively). For the CExC the production of KOH and NaOH were based on the membrane cell electrolysis. For the production of KCl, it was assumed that it has a 50% production from brine using solar evaporation, and 50% from fractional crystallization of sylvenite. For NaCl, it was assumed that the production was split 50-50 between multiple effect evaporation of saturated brine and open pan process of saturated brine.

8.4 Results and Discussion

8.4.1 Exergetic Efficiency

As shown in table 8.2 high pressure water scrubbing (HPWS) is the biogas upgrading technology with the greatest e_2 (93%). Then BABIU, followed by the AwR NaOH and KOH with an efficiency of 89.5%, 74.32% and 73.12% respectively.

Table 8.2. Exergetic efficiency (e_2) of biogas upgrading technologies

Process	Exergetic Efficiency (%)
BABIU	89.50
AwR KOH	73.12
AwR NaOH	74.32
HPWS	93.00

Using input and output exergy data provided by Shudo et al (2009) it was possible to calculate the e_2 of a biogas upgrading technology, which uses a membrane separation (a conventional technology) to selectively separate CO_2 and CH_4, as roughly 84% (Shudo et al., 2009). These results are in line with our estimates. Even though the AwR process has the lowest e_2 out of the biogas upgrading technologies under review, it is still higher than the e_2 of burning landfill biogas directly for electricity and heat, which has an efficiency of 36% (for biogas with a composition of 56% CH_4 and 36% CO_2) (Carolino and Medeiros Ferreira, 2013).

Table 8.3 shows the breakdown of each input for the four biogas upgrading processes and how they affect the e_2 results. The useful output of the upgrading system is the biomethane, which has a high exergy and consequently influences the final e_2. All the other inputs that are not methane are considered as losses, and therefore lowers the efficiency of the technology.

Table 8.3. Breakdown of each input in the exergetic efficiency (e_2) study

Compound/element	Exergetic efficiency - Breakdown of input exergy of component in each process (%)			
	BABIU	AwR KOH	AwR NaOH	HPWS
CO_2 (biogas)	2.17	1.78	1.81	2.26
CH_4 (biogas)	90.43	74.02	75.24	93.94
$Ca(OH)_2$	5.75	4.71	4.78	
N_2	0.01			
KOH		5.77		
NaOH			4.19	
H_2O		7.49	7.64	0.03
Energy	1.64	6.24	6.34	3.77

For both AwRs the methane only accounts for 75% of the total input of exergy, therefore resulting in a lower efficiency. In AwR, the second largest contributor of exergy is the amount of water used in the make-up of the alkaline solution. KOH has a slightly (1.6%) larger contribution to the e_2 than NaOH. The NaOH also has a lower effect on e_2 compared to the APC residues ($Ca(OH)_2$). Meanwhile in the BABIU process, the BA ($Ca(OH_2)$) has the highest exergy contribution after the methane. Water requirements for the HPWS are low that for the e_2 estimation its exergtic contribution is the lowest (at < 1%) whereas the energy used by the system has the largest impact. For both BABIU and AwR, the exergy analysis on APC and BA focused solely on the $Ca(OH)_2$ for its

carbonation ability, yet if the metals and other elements found in the BA and APC were to be included in the study, it could be possible that these processes would lower in efficiency. Though as the presence and concentration of each metal depends on the waste entering the MSWI, the e_2 of each process changes on a case by case basis.

8.4.2 Cumulative Exergy

As previously explained, we calculated the CExC, using process data information, and CExD using process information from the ecoinvent database. We also calculate the CExM which uses CExD to supplement process information for CExC. The latter is done to simplify the calculations involved. Table 4 shows how the cumulative exergy of each biogas upgrading process changes depending on the method used to calculate it. In all methods it was found that HPWS consumes the least amount of exergy, followed by BABIU. AwR consumed the greatest amount of exergy when using KOH. Despite the similarity in ranking, the numerical value of the total exergy consumption changes between the three methods that were examined. CExM values are around 4 to 5 MJ larger than CExD for all the processes except for BABIU that has 20 MJ less. Cumulative exergy values depend on the main source of exergy. The BABIU process had a lower value because in the CExD the transport of the bottom ash to and from the upgrading plant accounts for 95% of the total exergy in CExD. Transport of BA is not included in the CExM, which accounts for the decrease. For HPWS, the production of water accounted for 64% of the CExD. Since this production was also included in the CExM the value did not decrease, which meant that the final value increased once the chemical exergies of each input were included.

Table 8.4. Cumulative exergy results for biogas upgrading

	Cumulative Exergy Method (MJ per 1 kWh biomethane)		
	CExD	**CExM**	**CExC**
HPWS	0.25	4.20	-
BABIU	24.52	5.48	-
AWR KOH	80.67	84.85	1299
AwR NaOH	50.84	55.05	7.78

As for AwR, the main source of exergy was the one associated with the production of the bases, both NaOH and KOH. Therefore as this is also included in the CExM, the values increase slightly from CExD when the chemical exergies are included. Since it was found that the production process of the bases accounted for the largest source of exergetic consumption, an analytical process was run to determine the difference between the CExD and the CExC. As seen in table 4, applying a more analytical approach with CExC changes the results greatly between the KOH and NaOH. While KOH still consumes more exergy than NaOH, the difference between them markedly increases from around 30MJ for both CExD and CExM, to over 1250 MJ in CExC. The reason for this difference is due to how the production of KOH and NaOH are accounted for.

For NaOH, the analytical CExC method found a cumulative exergy of the production to be 1.2 MJ (per 1 kWh biomethane), while the ecoinvent based CExD found it to be 48 MJ (per 1 kWh biomethane). The production process of NaOH from the ecoinvent database, that is used for CExD, relates to a production mix consisting of electrolysis of NaCl by 55% mercury cells, 21% membrane cells, and 24% diaphragm cells (Swiss Center for Life Cycle Inventories., 2010). However in CExC we assume all was by membrane cell as the European Union has decided to replace mercury cells with membrane cells by the years 2020 (European Commission, 2001a,Euro Chlor, 2009). When calculating the CExD on solely the membrane process in Ecoinvent, the value lowers to 43 MJ, which is still higher than the 1.2 MJ determined through the CExC method. In the production of NaOH the salt, NaCl, is a necessary reagent and the cumulative exergy of its production is also different, which may account for part of the difference in results. The CExD method calculates 16 MJ which is ten times larger than the 0.09 MJ that was determined through the CExC. The ecoinvent database divides the production of NaCl between solution mining (41%) and rock salt (59%) (Swiss Center for Life Cycle Inventories., 2010), while by analytical method we calculated the processes that involve extraction from saturated brine (Faith et al., 1975). Apart from the differences due to the production methods selected the difference can also be attributed to the CExD method itself. CExD, as it uses the ecoinvent database, includes indirect flows such as infrastructure, waste disposal, water treatment, transport and the cumulative exergy of electricity. These additional flows account for the higher exergy result. In some aspects it can be seen as a positive as it takes into account all of the indirect flows. However, analytical CExC is based on mass balance, which makes it more consistent when assessing the performance of a particular process as system boundaries are better defined.

On the other hand, the difference in results for the KOH production was inversed. The cumulative exergy values for KOH production jumped from 78 MJ (per 1 kWh biomethane) in CExD to 1292 MJ (per 1 kWh biomethane) in CExC. It was found that the large difference was attributed to the production of KCl, which is a salt necessary for the production of KOH. For the production of KCL, the analytical CExC method used a 50-50 split between solar evaporation of brine and fractional crystallization of sylvinite, the latter of which accounts for the large CExC value at 1291MJ. The reason for this is that fractional crystallization is a process that requires a high quantity of water (151 million litres (Faith et al., 1975)) and therefore accounts for 99.99% of the total exergy for the process. For KCl the ecoinvent database focuses on solely the mining of the mineral by three different processes: solution in hot water, flotation and electrostatic separation (Swiss Center for Life Cycle Inventories., 2010), which results in a CExD of 73 MJ. In this process the water also accounts for the largest source of exergy at 85%. The main reason for the difference between the two results is therefore the input of each process and also the process that is selected. If the production of KCl was based solely on solar evaporation of brine, the CExC of the AwR KOH would be reduced to 8.9 MJ, which is similar to the analytical value of AwR NaOH and is also closer to the CExC of HPWS and BABIU.

Both of these exergy analyses are similar to the conclusions obtained in life cycle assessment (LCA) studies by the authors (chapter 7, Starr et al., 2012b). The LCA had shown that for CED and ADP (calculated using the CML 2001 method (Guinée et al., 2002)) HPWS had the lowest environmental impacts followed by BABIU, with AwR having the highest environmental impact. The only difference was the results for AwR. AwR using KOH has the highest and less efficient use of resources compared to AwR using NaOH. Such results were also obtained from impact categories CED and ADP fossil, but not for ADP elements where NaOH had a higher impact than KOH (chapter 7).

8.5 Conclusion

The results from the exergetic efficiency (e_2) and the cumulative exergetic consumption (CExD) demonstrate that HPWS has the highest e_2 and also the lowest natural resource use. This is followed by BABIU, AwR NaOH and AwR KOH. The HPWS only requires small quantities of water, while AwR requires a base, water and source of CaO, and BABIU requires a source of CaO, as well as nitrogen. AwR had the more intensive exergy consumption due to the requirement of the base. While in this study CExD and e_2 provided similar final results, they do provide different information which helps give a better understanding of the product or system under study.

Using exergy analysis is a useful complement to LCA as it gives further insight into resource consumption and burden on the environment. CExD is a valuable method that makes it possible for researchers who are not experts in exergy to obtain an estimated exergy assessment, though it includes many indirect elements that are not included when performing the analysis analytically. Among the indirect factors are transport and infrastructure, which are not generally considered as the focus of exergy analyses. It has a different focus than LCA, and therefore while CExD is a useful indicator for LCA practitioners, it is important to check the limits of the system under study. Using the CExD of a process within a traditional CExC, as was tried in CExM, does result in a more complete analysis, but still provides results that differ from a fully analytical CExC. Apart from the difference in the flows, the difference also lays in the type of processes used for the production of reactants. CExC relies on literature search that in some cases could be complicated or result in general estimations and assumption. Therefore CExD, while similar, is not a substitute for CExC but it can provide an understanding of the exergy consumption of a system if information about sub processes are lacking.

Chapter 9

Potential Substitution of Natural Gas using Upgraded Biogas from Municipal Solid Waste and Potential CO_2 Reduction

Chapter 9 - Potential Substitution of Natural Gas using Upgraded Biogas from Municipal Solid Waste and Potential CO_2 Reduction

based on a manuscript by: Katherine Starr, Gara Villalba, Xavier Gabarrell and Laura Talens

Abstract

Biogas is rich in methane and can be further purified through biogas upgrading technologies, presenting a viable alternative to natural gas. Landfills and anaerobic digestors treating municipal solid waste are a large source of such biogas and therefore present an attractive opportunity to tap into this potential source of natural gas, at the same time minimizing the global warming impact resulting from methane emissions in waste management schemes (WMS). This study looks at the current solid waste flows of Spain, Italy and Austria in order to determine how much biogas is generated via their WMS based on waste generation for one year (2009) and as such, how much natural gas could potentially be substituted via four different biogas upgrading technologies. Two additional WMS scenarios are presented where biogas production is incremented by increasing the amount of organic matter sent to anaerobic digestors and increasing landfill biogas capture. We find that the potential substitution of natural gas by biogas resulting from the present WMS seems rather insignificant: 0.3% for Austria, 0.9 % for Italy and 1.4% for Spain. However, if the WMS is redesigned to maximize biogas production, these figures can increase to 0.9% for Austria, 1.9 for Italy and 3.8% for Spain. Furthermore, the potential CO_2 reduction as a consequence of capturing the biogas and using it instead of natural gas can result in up to a 2.2% reduction of the annual national GHG emissions.

9.1 Introduction

More than 80% of our global energy consumption is supplied by fossil fuels, which are quickly being depleted (IEA, 2013). Furthermore, the combustion of fossil fuels results in carbon dioxide emissions (CO_2), which contribute to the climate change (IPCC, 2006a). In addition, the landfilling of waste plays an important role in climate change. In 2009 in Europe, 190 kg of waste per captia was landfilled (roughly 38% of the total waste), which generated over 140 million tons of CO_2 eq (Eurostat, 2013a). The use of waste as a source of energy offers the unmatched opportunity to reduce CO_2 emissions by minimizing fossil fuel consumption and optimizing the life cycle of materials. In this respect, biogas resulting from landfill and anaerobic digestion of waste is an attractive potential substitute of natural gas.

The decay of organic matter (OM) in waste accumulated in landfills results in methane (or biomethane) emissions, which, depending on the amount of OM present in the waste, can be up to 170 kg CH_4/ tonne of organic landfill waste (USEPA, 2005). Anaerobic digesters (AD) used in digestion of organic waste also result in methane emissions (115m^3 of biogas per t of digested waste (Vicent, 2008)). However, the methane emissions do not come alone: other gases such as carbon dioxide (CO_2), nitrogen, siloxanes, hydrogen sulphides, and more are also included forming what is normally called biogas. The average composition of biogas is 35-70% CH_4 and 15-50% CO_2 (Petersson and Wellinger, 2009,Dirkse, 2009). In order for biogas to be a suitable substitute of natural gas, the biogas needs to be purified or “upgraded” by further increasing the methane concentration through elimination of the CO_2. Given the large amounts of organic waste produced yearly, it is worthwhile to investigate the potential source of biomethane as a significant supply to the energy mix.

Presently most of the biogas collected in landfills is captured and flared in order to transform the CH_4 to CO_2, to reduce the global warming potential from 25 to 1 (Forster et al., 2007). Alternatively, in some waste management facilities, the biogas is burned to generate electricity with an efficiency of approximately 38% (Carolino and Medeiros Ferreira, 2013). Upgrading biogas to biomethane for vehicle fuel or to supply the gas grid are currently implemented in around 100 sites over the world (Petersson and Wellinger, 2009). The two most commonly used biogas upgrading technologies are based on the absorption of CO_2 and include high pressure water scrubbing (HPWS) and chemical scrubbing with amine (AS). These technologies, which use water and an amine solution respectively to capture the CO_2, release the captured CO_2 into the atmosphere upon regeneration of that water and amine solution. If the CO_2 is of a high enough quality some upgrading sites may choose to capture the gas and sell it to industries (Lems and Dirkse, 2009), though this option is not always selected.

There are two pilot-scale biogas upgrading technologies that in addition to removing CO_2 (via carbon mineralization), are also able to store the CO_2 as calcium carbonate ($CaCO_3$). These novel technologies are bottom ash for biogas upgrading (BABIU) and alkaline with regeneration (AwR). BABIU was developed by the University of Natural

Resources and Life Sciences in Austria (Mostbauer and Lenz, 2007a,Olivieri et al., 2011) and uses a direct gas-solid phase interaction with bottom ash from municipal solid waste incinerators (MWSI). The AwR process was created by the Universita degli Studi di Firenze and the Universita di Roma "Tor Vergata" in Italy (Baciocchi et al., 2011a,Baciocchi et al., 2011b) and uses an alkaline solution to capture the CO_2 and this solution is regenerated through contact with air pollution control residues (APC) from MSWI.

BABIU and AwR are better options than the water scrubbing and amine solution in terms of GHG emission reduction. Previous studies by the authors found that due to the inherent ability to store CO_2 these technologies have a lower GHG impact than standard technologies that are currently on the market (Chapters 5, 6 and 7). The authors have also found that based on exergetic analysis (Szargut, 2005,Ayres et al., 1998,Talens, 2009), resources are consumed more efficiently when biogas upgrading technologies are used as opposed to direct burning for electricity. The exergetic efficiency (e_2) of biogas upgrading technologies ranges from 73 to 93% (Chapter 8, Shudo et al., 2009) - more than twice the efficiency of directly combustion for energy, which is estimate to be 36% (Carolino and Medeiros Ferreira, 2013).

Motivated by the opportunity to reduce waste, minimize global warming impact, and lessen our dependence on natural gas, we quantify the potential biogas production of Austria, Spain, and Italy based on a material flow analysis (MFA) of the current municipal solid waste (MSW) management schemes based on 2009 data. We determine the amount of biomethane that can be produced based on each of the technologies of HPWS, AS, AwR, and BABIU. Furthermore, we develop two theoretical scenarios for each country in which the waste management scheme (WMS) is redesigned to maximize the production of bottom ash and APC residues thereby increasing the production of biomethane. Based on these scenarios the potential amount of natural gas that could be replaced is quantified, as well as the potential CO_2 savings.

9.2 Methodology

The main method used for this study is material flow analysis (MFA). This is a widely used methodology in the field of industrial ecology. MFA is the quantification of the material (and energy) inputs and outputs of a system based on the mass balance principle which states that mass, matter and energy are conserved (1^{st} law of thermodynamics) (Ayres and Ayres, 1999). On this principle it is possible to examine the flows through the system and any accumulations that may occur within the system. This is not only useful for visualization but also when combined with environmental, economic, or social indicators gives better understanding of the metabolism of a system. It is often used for the study of waste inflows and outflows on a territorial scale (Font Vivanco et al., 2012,Fragkou et al., 2010).

9.2.1 System Definition

This study looks at the MSW flows of Spain, Italy and Austria in 2009. It examines the flows from the point of collection of the waste to final disposal. Since the objective of this study is to examine the amount of biogas generated, waste flows without organic matter, such as the collection of glass for recycling, were not quantified. Thus the system considers the waste flows that enter the waste management scheme (WMS) to be treated in mechanical biological treatment plants (MBT) for composting and anaerobic digestion, as well as waste flows that go to landfill and incineration

With the MSW flows defined, it is possible to determine the potential biomethane generation by applying the four biogas upgrading technologies, AS, HPWS, BABIU and AwR to landfills and anaerobic digestors (AD).

9.2.2 Data Collection and Calculations

9.2.2.1 Waste Flows

Data on MSW flows were collected through discussion with experts and literature reviews, including statistics and reports generated from federal agencies of Spain, Italy and Austria (Lebensministerium, 2011,INE, 2012,ISPRA, 2011). When data was unavailable estimations were made. For example, 2009 data for Spain's MBT and composting facilities was estimated based on 2008 data (MARM, 2011,MAGRAMA, 2010,Farreny, 2011).

Table 9.1 demonstrates the variables and waste fractions that were applied in order to calculate the organic content of the waste flows. The flows of paper and organic matter (OM) were taken into consideration due to the large carbon content and high biogas generation potential.

Table 9.1. Variables of the MSW flow per country

	Spain	Italy	Austria
All Waste			
OM (%)	44[a]	33[a]	27[c]
Paper (%)	21[a]	24[a]	22[c]
Mixed Waste			
OM (%)	51[b]	41[b]	21[c]
Paper (%)	21[b]	23[b]	12[c]
Impurities in OM selective collection (%)	20[a]	10[a]	10[a]
Landfill biogas capture rate (%)	17[a]	48[a]	N/A

[a] source: (Farreny, 2011) [b] Value estimated by subtracting total amount in selective collection from total [c] (Lebensministerium, 2011)

The waste flows of the WMS of each country are defined as follows. The "all waste" or "municipal solid waste collection" is the total waste generated by each municipality, which enters the WMS in two separate ways: 1) selective collection, in which the waste is separated by individuals into OM, paper and cardboard, plastics, metal, bulky waste, electronics, batteries etc, and 2) mixed waste. The latter includes fractions of OM,

paper, plastics, metal, and others. Depending on the WMS of the municipality, the composition of the fractions can vary considerably. For example, in certain parts of Spain there is selective organic waste collection, which considerably reduces the amount of OM found in mixed waste. Austria has the highest selective collection rate of all three countries and thus the OM fraction in mixed waste is the lowest (see table 9.1).

Mechanical biological treatment (MBT) is a waste treatment process that accepts unsorted municipal waste and through mechanical treatments sorts out waste that can be further treated such as recyclables (paper, metal, glass, plastic) and organic matter. How the waste is distributed and treated in MBT depends on various conditions, including the input waste. Therefore the following assumptions were applied to Italy and Spain: in the MBT 3.2% of the total waste is sorted as paper, and 57% is sorted as organic fraction for biological treatment, for either AD followed by composting or directly to composting. Of this organic fraction 74% is OM and 9% is paper and cardboard (Montejo et al., 2013,Di Lonardo et al., 2012). The amount of unsorted residual waste that is sent to the landfill is 35% (Montejo et al., 2013), of which 24% is OM and 28% is paper and cardboard (Montejo et al., 2011). As further data was obtained for Austria, of the waste that enters the MBT, 41% goes to the incinerator and 49% goes for biotechnical treatment (Lebensministerium, 2011). The waste flow of separated paper and of the composition of each flow remained the same as above.

Biogas generation was attributed to anaerobic digestors (AD) and landfills. For AD, we assumed that all biogas is generated within the year under study (2009). The rate of biogas generation in AD is 115m^3 of biogas per tonne of OM (Vicent, 2008), with a capture rate of 100%. Landfills, on the other hand, emit biogas over a period of years after the waste is deposited, according to decay rates of organic matter. The gas emissions related to the landfill were calculated by using the IPCC model (Pipatti et al., 2006,IPCC, 2006b). As this model is based on the first order decay rate (Pipatti et al., 2006) it was important to take into account the waste that had been gradually deposited over the previous years. We considered the emissions resulting from waste landfilled between 1995 and 2009. The data on landfilled waste was obtained from Eurostat (Eurostat, 2012,Eurostat, 2013h).The OM and paper fractions of the landfilled waste were assumed constant at 2009 values during the 15 years for lack of better data. However, we are aware that this could result in an underestimation of the biogas produced from landfills, since in the earlier years we can expect higher paper and OM content in the landfills due to simpler WMS. The landfill biogas generation was only attributed to Italy and Spain, as Austria no longer uses landfills.

In order to determine the production of BA and APC needed for the mineralization process of the BABIU and AwR technologies, we used the production rates given by Lombardi and Carnevale, namely that 20% of municipal solid waste that is treated by incineration results in BA, and 3% results in APC (Lombardi and Carnevale, 2013,Quina et al., 2008)

9.2.2.2 Natural Gas Consumption

Statistics about the natural gas consumption was obtained from the International Energy Agency (IEA, 2013) and from British Petroleum (British Petroleum, 2011). Table 9.2 presents the transformation efficiency, total production, export, and domestic supply, the latter of which is broken down into its final uses of all three countries. Both Austria and Spain import more gas than they consume as the imported gas also includes gas that is eventually exported.

Table 9.2. 2009 Natural Gas Distribution per Country [a]

	Austria	Italy	Spain
Amount of natural gas			
Domestic Supply[b] (TJ)	333 400	2 973 000	1 452 000
Imported (TJ)	442 300	2 638 000	1 478 000
Produced (TJ)	66 670	305 300	568
Uses of natural gas (% based on domestic supply)			
Energy industry	40	42	58
Energy (transformation)	35	41	53
Own uses[c]	5	1	5
Consumption	60	57	43
Industry	53	27	62
Transport	4	2	< 1
Residential	27	46	24
Other [d]	15	25	14
Additional information			
Transformation efficiency (%) [e]	65	59	47
CO_2 impact of natural gas before use [f] (kg/MJ of natural gas)	0.0222	0.0121	0.0100

[a] Unless otherwise stated, source: (IEA, 2013) [b] Domestic supply refers to the net amount of gas in the country. It is calculated by: production + import – export = domestic supply. [c] refers to the direct consumption of the plant required to produce energy. [d] Includes commercial and public service, agriculture, forestry, petroleum feedstocks, as well as other undefined non-energy uses. [e] refers to the gas lost during conversion. Data not provided, therefore estimated by applying the following calculation: 1-(transformation/domestic supply) x 100 = transformation efficiency. [f] data obtained from ecoinvent 2.2 (Swiss Center for Life Cycle Inventories., 2010) process "natural gas, high pressure, at consumer". The CO_2 impact was calculated using the CML 2001 method (Guinée et al., 2002). While the data set is valid for 2000, the values are similar to other found in literature of 0.010 kg/MJ for the extraction, fuel production and distribution of compressed natural gas (Hekkert et al., 2005).

9.2.2.3 CO_2 Emissions and Savings

The potential CO_2 savings calculated in this study were based on three factors. Firstly, we considered the amount of CO_2 emissions attributed to the biogas upgrading technologies. Information about the CO_2 impact of different biogas upgrading technologies was based on previous work by the authors (Chapter 7), in which it was found that AwR can save 32 g CO_2 eq/kWh and BABIU can save 185 g CO_2 eq/kWh, whereas HPWS generates approximately 22 g CO_2 eq/kWh and AS 42 g CO_2 eq/kWh. Secondly, we take into account the amount of methane that is diverted from being emitted into the atmosphere by landfills and AD, which is achieved through the application of biogas upgrading. Thirdly, we consider the CO_2 savings generated by reducing fossil-based natural gas consumption.

CO_2 emissions related to the waste collection and transport were not accounted for. The CO_2 emissions resulting from MSWI were also excluded. The IPCC guidelines do not

include these items in waste CO_2 emission inventories; however we believe that it would be well worth considering these emissions to have a more integrated assessment of the WMS. For the sake of our argument, we believe our limited study suffices to have an estimate of the potential CO_2 savings and natural gas substitution.

In order to understand the magnitude of the CO_2 savings resulting from the scenarios, we compared them to the overall nationwide CO_2 emissions resulting from waste in 2009, as well as the total national emissions for that year (see table 9.3).

Table 9.3. 2009 statistics for Austria, Italy and Spain

	Austria	Italy	Spain
Population [a]	8 355 260	60 045 068	45 828 172
Annual CO_2 emissions (t CO_2 eq) [b]			
Total	79 739 350	491 528 490	366 272 600
Waste [c]	1 913 300	18 556 870	14 784 530

[a] source: (Eurostat, 2012) [b] source : (UNFCCC, 2013) [c] waste emissions are based solely on the direct emissions from landfills and calculated by each country using first order decay rates and historical information.

9.2.3 Scenarios

Based on each country's municipal solid waste generation for 2009 and the OM and paper fractions given in table 9.1, we carry out a MFA of the following scenarios.

1. Actual situation in each country. The MSW flows for each country for 2009 are quantified. The biogas collection rate from landfills (17% for Spain and 48% for Italy) and the flow of organic matter and paper is based on table 9.1. Selective collection of OM often contains impurities, such as plastic from bags and containers. The quantities of impurities of each country can also be found in table 9.1.

2. Actual situation of the waste flows is maintained as (1) except the entire waste going to landfill is sent to the MSW Incineration (MSWI) instead

3. The third scenario is designed to maximize the amount of biogas produced. In this scenario, no waste is sent to the landfill, rather all of the organic matter (OM) is selectively collected and sent to the AD and all non organic matter is sent to the MSWI. This scenario reflects the EU's waste framework preference for reducing landfill waste through better sorting and processing of waste (i.e., composting or energy recovery) (European Commission, 2008). We assume that other carbon-containing waste such as plastics and paper is not removed from the mixed waste flow that under scenario 1 would have gone to the landfill and/or MSWI, and therefore now all goes to the MSWI. We also include an improved sorting of the selective collection of OM and it is therefore free of impurities (non OM waste) when sent to the AD. The impurities resulting from the improved sorting are sent to the MSWI.

4. Actual situation of the waste flows in (1) is maintained. The amount of biogas that is collected from the landfills is 100%.

Scenarios 2, 3 and 4 were created as hypothetical scenarios in order to explore and increase the potential application of biogas upgrading technologies.

A study by Starr et al (Chapter 6) found that a limiting factor of the BABIU and AwR technologies is the requirement of APC and BA, resulting from waste incineration, for the CO_2 sequestration. Thus a Scenario 2 in which incineration is maximized was designed in order to increase the amount of APC and BA that could be produced.

Scenarios 3 and 4 were created to maximize the amount of biogas theoretically available for upgrading from the waste management schemes of the three countries. Scenario 3 does so by increasing the amount of OM that goes to the AD, which hypothetically collects 100% of the biogas generated, unlike landfills. Scenario 4 increases the biomethane potential by collecting all of the biogas emitted from landfills. Both scenarios 3 and 4, although being hypothetical scenarios, are potentially conceivable with proper social engagement as well as with adequate restructuring of the each country's MSW flow.

9.3 Results

9.3.1 Municipal solid waste flow

In order to better visualize the waste flow data of the three WMS belonging to Spain, Italy, and Austria, the MFA's are represented by Sankey diagrams. As can be seen in figure 9.1 Spain has the lowest rate of selective collection, with 82% (20,342 kt) of the municipal waste going into the mixed waste category. Approximately 10,330 kt (51%) of the unsorted waste is sent to the landfill, 8747 kt (43%) to MBT (both composting and AD facilities) and the rest to MSWI. In the MBT the waste is sorted into OM, recyclables such as paper and plastics, and unvalued residual waste which is sent to landfill. The OM is sent to aerobic stabilization through composting. Of the waste that is sent to the MBT, 407 kt, or 4.5%, is sent to be anaerobically digested before composting. This MBT aids in the separation of OM as the selective collection of OM only accounts for around 3% of the total collection, roughly 724 kt. Of that selective collection only 116 kt is treated in AD with the rest going straight for composting.

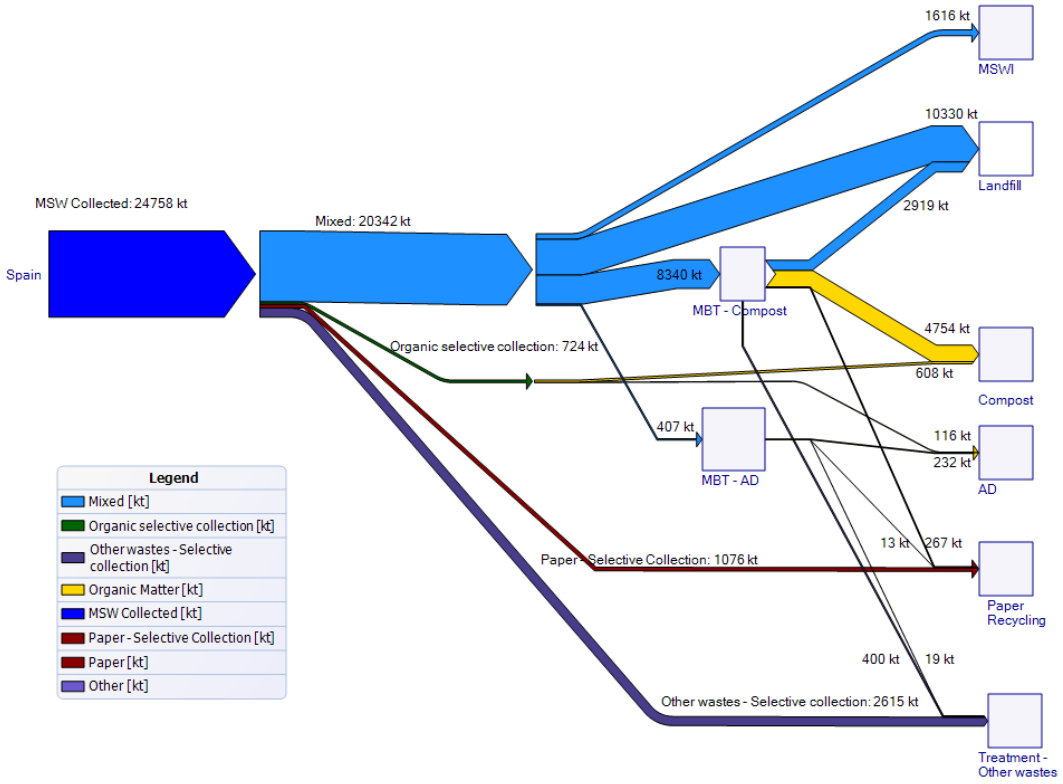

Figure 9.1. 2009 MSW Flow Spain (Scenario 1)

Italy has a similar WMS as Spain, as can be seen in figure 9.2. The amount of unsorted municipal waste that ends up in the mixed waste bin amounts to 20,909 kt (65%). Of this mixed waste 11,431 kt (55%) is sent to landfills and 2,829 kt (14%) is sent to incinerators. The remaining mixed waste is sent to MBT plants that are limited to compost treatment, since none of the MBT facilities in Italy are equipped with anaerobic digestors. As with Spain, the OM, paper and other recyclables are sorted out and the unvalorized waste is sent to the landfill. The selective OM collection is 2,183 kt (7%), of which 547 kt is sent for AD, while the rest is directly composted.

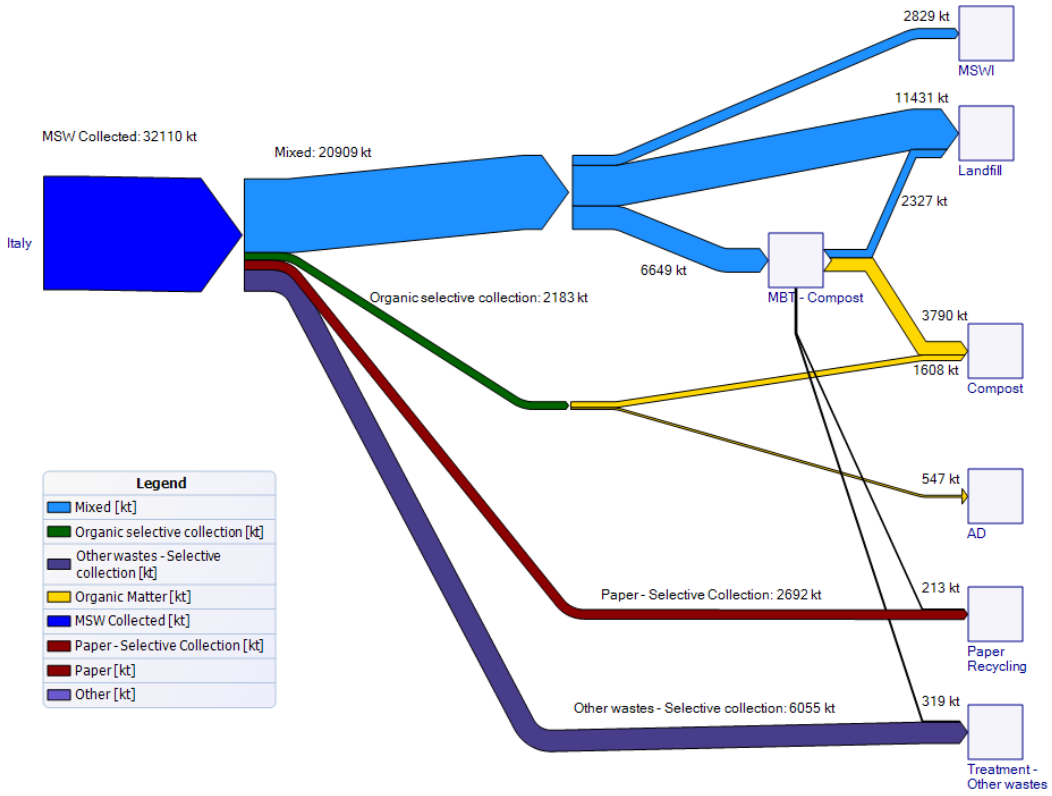

Figure 9.2. MSW flow Italy 2009 (Scenario 1)

Austria has a significantly different WMS than both Spain and Italy, and also has the lowest waste generation rate per capita. As of 2009, Austria no longer uses landfills, and all mixed and unvalorized waste is sent to incineration. Due to the high preliminary sorting by Austrian residents, only 43% (1,661 kt) of the total waste generated is collected as mixed waste. As shown in figure 9.3 roughly half of that goes to incineration (835 kt) while the other half (826 kt) goes for further sorting at MBT plants. As with Italy, the Austrian MBT plants only handle composting and do not do anaerobic treatment beforehand. Unlike Italy and Spain, the unvalorized waste from the MBT plants is sent to incinerators. After incineration the ashes are sent to the landfill. Of the total collected waste in Austria 752 kt (19%) of that waste is selectively collected as OM. In turn, 410 kt (56%) is sent for anaerobic digestion, while the rest is sent for composting.

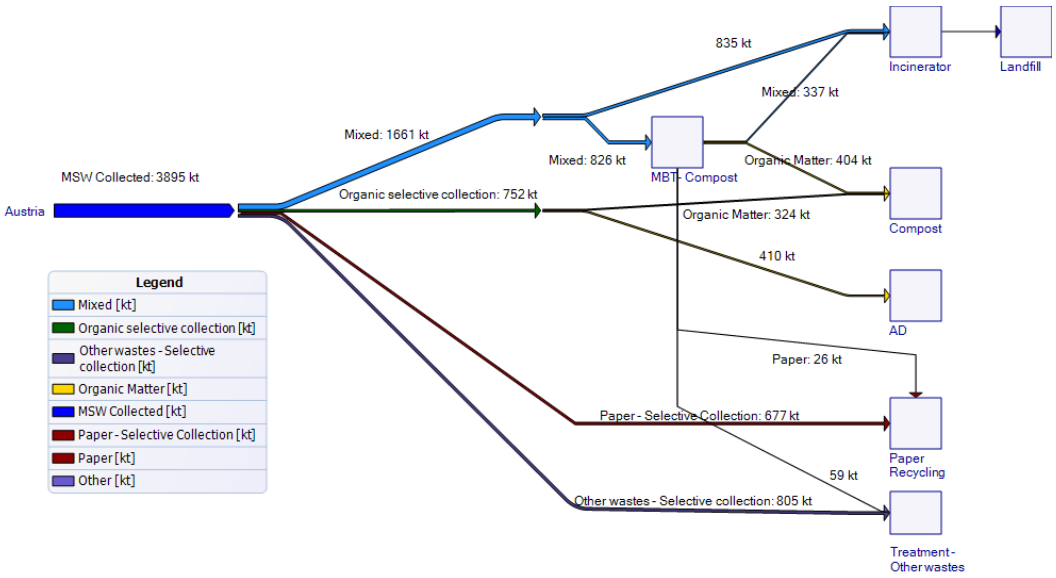

Figure 9.3. MSW flow Austria 2009 (Scenario 1)

Based on the waste flows represented by figures 1-3, the scenarios described in section 2.3 were applied to each country and are summarized in table 9.4.

Table 9.4. Annual waste flow per scenario

Country	Waste collection		Scenarios	Waste Treatment (kt)						Biogas generation (m^3)	
	Total (kt)	Per capita (t/per)		Landfill	MSWI	AD	Compost	Paper	Other	Landfill	AD
Austria	3895	0.47	1	0	835	410	728	703	805	-	$4.2x10^7$
			2	0	835	410	728	703	805	-	$4.2x10^7$
			3	0	1373	1040	0	677	805	-	$1.2x10^8$
			4	0	835	410	728	703	805	-	$4.2x10^7$
Italy	32110	0.53	1	13758	2829	547	5398	3175	6055	$9.0x10^8$	$5.7x10^7$
			2	0	16587	547	5398	3175	6055	-	$5.7x10^7$
			3	0	12560	10532	0	2962	6055	-	$1.2x10^9$
			4	13758	2829	547	5398	3175	6055	$1.9x10^9$	$5.7x10^7$
Spain	24758	0.54	1	13391	1616	348	5362	1356	2616	$2.5x10^8$	$3.3x10^7$
			2	0	15008	348	5362	1356	2616	-	$3.3x10^7$
			3	0	10172	10894	0	1076	2616	-	$1.3x10^9$
			4	13391	1616	348	5362	1356	2616	$1.5x10^9$	$3.3x10^7$

9.3.2 Potential replacement of natural gas

We determined how much bottom ash (BA) air pollution control residues (APC) could be produced from incineration and how much biogas could be generated from landfills and AD based on the waste flows quantified for each scenario. Based on these calculations, it was possible to determine how much biomethane could be produced through the application of the conventional biogas upgrading technologies as well as BABIU and AwR which also capture the CO_2 emissions.

As table 9.5 demonstrates for scenario 1, AwR and BABIU produce significantly less biomethane than the conventional upgrading technologies that do not require BA and APC from MSWI. AwR can replace between 0.1 - 0.5% of the primary natural gas consumption of a country, while the BABIU can only substitute less than 0.02% of a country's primary consumption. This is in contrast with the conventional technologies that can replace around 0.33% of Austria's consumption, 1% of Italy's and 1.4% of Spain's. The amount of natural gas that is produced in each country is less than what is consumed (table 9.2), which means a higher substitution rate can be achieved for the produced gas, as opposed to the primary consumption. This is specifically the case for Spain, in which, if AwR, AS, or HPWS are applied, over 100% of the produced natural gas can be substituted.

Table 9.5. Scenario 1 results (actual 2009 WMS)

			Substituted Natural Gas			CO_2 Avoided Emissions		
		Biomethane (m^3)	Total (TJ)	Primary consumption (%)	Production (%)	Total (Mt CO_2 eq)	National Total (%)	National waste emissions (%)
Austria	AwR	6.7×10^6	347	0.10	0.52	0.15	0.18	7.67
	BABIU	1.4×10^6	73	0.02	0.11	0.03	0.04	1.73
	HPWS	2.1×10^7	1,106	0.33	1.66	0.46	0.57	23.88
	AS	2.1×10^7	1,116	0.33	1.67	0.46	0.58	24.19
Italy	AwR	1.6×10^7	930	0.03	0.30	0.36	0.07	1.95
	BABIU	3.4×10^6	197	0.01	0.06	0.08	0.02	0.44
	HPWS	4.9×10^8	27,795	0.94	9.10	10.55	2.15	56.8
	AS	4.8×10^8	28,048	0.94	9.19	10.68	2.17	57.6
Spain	AwR	9.3×10^6	658	0.05	> 100%	0.22	0.06	1.46
	BABIU	2.0×10^6	139	0.01	24.48	0.05	0.01	0.33
	HPWS	2.8×10^8	19,938	1.37	> 100%	3.37	1.7	43.3
	AS	2.8×10^8	20,119	1.39	> 100%	3.41	1.8	43.9

In terms of CO_2 emissions, the novel upgrading technologies can reduce the national emissions by less than 0.2%, while the conventional technologies can reach up to around 2%. The conventional technologies achieve significant savings when we consider CO_2 emissions associated to each country's waste sector, resulting in 24% savings for Austria, 43% for Spain and 57% for Italy. The reason behind poor CO_2 savings by implementing BABIU and AwR is that these technologies depend on BA and APC resulting from incineration. In scenario 1, only 1% of the collected biogas can be upgraded by the BABIU process in Italy and Spain, and 7% of the biogas can be upgraded in Austria. Since the AwR process requires less APC than BABIU does BA, a higher amount of gas can be upgraded: 3% of the gas in Italy, 6% of the gas in Spain, and 31% of the biogas in Austria. However, the conventional technologies are able to upgrade all of the biogas that is captured, resulting in higher CO_2 savings.

9.3.3 Application of Hypothetical WMS Scenarios

In scenario 2, the WMS is modified in order to increase the amount of waste diverted to the MSWI, and therefore increase the amount of BA and APC produced. Despite the fact that less biogas is generated compared to the scenario 1 (less waste goes to landfill because more waste is being incinerated), scenario 2 results in that both Spain and Italy can upgrade more biogas. As shown in table 6 the biomethane generation in Spain is approximately doubled for AwR from 9,200,000 m^3 to 17,000,000 m^3 while the BABIU process results in an eight -fold increase from 1,900,000 m^3 to 15,000,000 m^3. In Italy, the AwR process also roughly doubles its biomethane production from 16,000,000 to 28,000,000 m^3, while BABIU increases by a factor of 7 from 3,400,000 to 20,000,000 m^3. This upgraded biogas increase results in higher natural gas substitution and the CO_2 emission avoidance as can be seen in table 9.6.

Table 9.6. Results of Hypothetical WMS Scenarios[a]

Country	Scenario	Biomethane (m^3)	Substituted Natural Gas			CO_2 avoided emissions		
			Total (TJ)	Primary Consumption (%)	National Production (%)	Total (Mt CO_2 eq)	National Total (%)	National Waste Emissions (%)
Austria	2	1-21x10^7	73-1116	0.02-0.33	0.11-1.67	0.03-0.46	0.04-0.58	1.7-24
	3	6x10^7	3,100	0.9	4.7	1.29-1.41	1.6-1.8	67-73
	4	2x10^7	1,000	0.3	1.7	0.46-0.50	0.6	24-26
Italy	2	2-3x10^7	1,100-1,600	0.04-0.06	0.4-0.5	0.5-0.6	0.1	2.6-3.4
	3	6.1x10^8	35,000	1.2	11.5 - 11.6	13-15	2.7-3.0	72-78
	4	9.8x10^8	56,000	1.9	18.3-18.5	21-23	4.3-4.7	> 100
Spain	2	2x10^7	1,100	0.07-0.08	> 100	0.37-0.38	0.1	2.5-2.6
	3	6.3x10^8	45,000	3.1	> 100	14-16	4	98 - >100
	4	7.8x10^8	55,000	3.8	> 100	18-19	5	> 100

[a] This table summarizes the results for the four different biogas upgrading technologies. Values are rounded and when noticeable differences are found the ranges are presented. Therefore some categories have ranges, when values were found to be different.

Scenarios 3 and 4 were created to maximize the amount of biogas theoretically available and thus determine the full potential of natural gas substitution and CO_2 savings that could be generated by upgrading the biogas for the three countries. For both of these scenarios we assume that all of the BA and APC needs of BABIU and AwR technologies are met by importing the required amounts or supplementing with other CaO-rich sources, such as steel slag, or minerals like olivine.

Scenario 3 is similar to scenario 2 in which all of the landfill waste is sent to the MSWI. However, in scenario 3 all OM is selectively collected and sent to the AD and all non organic matter is sent to the MSWI. Under this scenario the amount of biomethane increases by a factor of 3 for Austria, and by a factor of 30 for Italy and by 44 for Spain. The additional biomethane is lower for Austria because there is less OM in the mixed waste (21%) than Italy and Spain, which had 41% and 51% OM content respectively. The CO_2 savings also show an increase in all three countries and it is possible to counteract the emissions of the waste sector by over 75%.

Scenario 4 attempts to further increase the biomethane generation potential by considering the WMS flows as depicted in scenario 1, yet increasing the landfill biogas collection to 100%, from the present 17% of Spain and 48% of Italy. This scenario only affects Spain and Italy, since there is no landfill waste in Austria for 2009. Spain and Italy increase their biomethane production to 780,000,000 m^3 and 930,000,000 m^3 respectively. The additional biomethane results in the potential replacement of 4% and

2% of the primary consumption of natural gas of Spain and Italy, respectively, and a 5% reduction in their national CO_2 emissions inventory. Table 9.6 presents all the results for scenarios 4 and includes the results from scenarios 2 and 3 to facilitate the comparison.

In both scenarios 3 and 4 it is possible to see in table 9.6 that the avoided CO_2 emissions have a range. This is due to the fact that each biogas upgrading technology has different CO_2 savings, in the case of the novel technologies, or CO_2 emissions in the case of the conventional technologies. Though in most cases this range is not very large and this is because as mentioned in section 9.2.2.3 three factors are taken into consideration, impact of biogas upgrading technology, the emissions avoided by not using natural gas, and the methane in biogas diverted towards biomethane. The difference between the upgrading technologies does not play a large role in the overall total of the carbon savings. It plays less that 8% of the role for the CO_2 savings of BABIU, and less than 1.5% for AwR. For the conventional technologies the CO_2 emissions account for 1% of their total. It was found that the largest contribution to the savings comes from the avoided methane emissions, which corresponds to around 80% of the total savings.

9.4 Discussion and Conclusion

The biogas captured by the current WMS of each country is too low to provide a significant substitution to present natural gas consumption. Austria could potentially substitute 0.02-0.33% of its natural gas consumption, depending on the upgrading technology used. For Italy and Spain, the figures are slightly higher, at 0.01-0.94% and 0.01-1.4%, respectively. We found that AwR and BABIU were limited in their ability to upgrade biogas as they require more APC residues and BA from MSWI than is presently available in the current WMS of the countries under study. Currently, it is only possible for 1% -7% of the biogas to be treated by BABIU and 6-31% of the biogas to be treated by AwR. One way to offset the limitation of reactants for BABIU and AwR is to divert the landfill waste to the MSWI, although this also reduces the amount of biogas being produced (scenario 2). While this does increase the amount of natural gas substitution for HPWS and AwR, the conventional technologies see a decrease as the landfill source is eliminated. Another way to reduce the limiting factor of the novel technologies is to replace or supplement the BA and APC residues with another source of CaO, for example with steel slag.

When pre-sorting of OM by the population is increased to 100%, and such waste is sent to the AD, with the remaining sent to the MSWI (Scenario 3), then an increased biomethane generation is obtained. It is possible to replace over 75% of the CO_2 emissions of the waste sector. If the biogas collection rate from landfills is increased to 100% (scenario 4) then the potential substitution of natural gas is rather significant. Spain is the country that could potentially benefit the most from such substitution, reducing its national natural gas consumption by 3.8%. As Spain produces around 0.04% of the natural gas that it consumes, the 3.8% substitution that it achieves can both replace and supplement the national production rate by a large margin. Increasing

biogas recovery from WMS offers an opportunity for minimizing dependency on natural gas imports, not only for Spain but for the other countries as well.

With 100% of the OM selectively collected and sent to the AD, while the remaining sent to the MSWI (Scenario 3), it is possible to increase the natural gas substitution of all three countries. Compared to scenario 2 it is possible for Spain to increase substitution values 44 times over, and compared to scenario 1 it can increase up to 310 times over for BABIU, and 62 times for AwR. These are reflected to a lesser extent with Italy. In order to obtain this modified WMS, not only does new infrastructure have to be put in place, but also public participation and awareness has to be improved in order to increase selective collection of OM.

If the biogas collection rate from landfills is increased to 100% (scenario 4) then the potential substitution of natural gas is rather significant. Spain is the country that could potentially benefit the most from such substitution, reducing its national natural gas consumption by 3.8%. As Spain produces around 0.04% of the natural that it consumes, the 3.8% substitution that it achieves can both replace and supplement the national production rate by a large margin. Increasing biogas recovery from WMS offers an opportunity for minimizing dependency on natural gas imports, not only for Spain but for the other countries as well.

The application of these technologies also presents an opportunity for lowering the greenhouse gas contribution of the countries in this study. Under present WMS conditions, the savings could be up to 0.58 % of total national GHG inventory of Austria, 1.8% of that of Spain and 2.2% of Italy's. Though it was found that on a national scale that which biogas upgrading technology is applied does not make much of a difference in terms of CO_2 savings. The main contribution (80%) comes from the methane that is diverted from being emitted. Other biogas treatment options such as flaring and direct burning for electricity may therefore have similar CO_2 savings, though further studies would be required. Scenarios 2, 3 and 4, all showed an increase in potential CO_2 savings. Scenario 4 shows that the CO_2 emissions of the waste sector of Italy and Spain can be reduced by over 100%, and the national emissions by 5%.

This study focuses on an either-or application of the biogas upgrading technologies on a national scale. As we can see, this is not feasible for the novel technologies. By combining their application with those of conventional technologies it would be possible to draw upon the potential biomethane from landfills and AD. As well by furthering the application to sewage sludge and small scale AD from agricultural facilities even more natural gas could be substituted.

Overall, applying biogas upgrading technologies provides an opportunity for reducing natural gas consumption, thereby minimizing dependency on fossil fuels. We find that even though BABIU and AwR technologies provide carbon capture, they are limited by the need of BA and ACP resulting from MSWI. Thus, these technologies are more appropriate and will result in the highest GHG reductions and natural gas substitutions for those countries that incinerate a large waste fraction. For other countries, such as

Spain and Italy, a combination of conventional and novel technologies will be necessary in order to optimize upgraded biogas production. While upgraded biogas does not substitute a large amount of natural gas, it does help contribute to the overall total energy production and to significant GHG emission reductions. As European countries divert more waste from landfill to other final disposal treatments such as incineration, composting and AD, in accordance to the Waste Framework (European Commission, 2008), it may be more beneficial to focus on applying biogas upgrading to AD (or other biogas sources as previously mentioned) such as was presented here for Austria

Part III

Economic Assessment

Chapter 10

Economic Analysis of Biogas Upgrading Technologies using Carbon Mineralization. A Case Study for Spain.

Chapter 10 - Economic analysis of biogas upgrading technologies using carbon mineralization. A case study for Spain.

based on a manuscript by: Katherine Starr, Andrea Ramirez, Hans Meerman, Xavier Gabarrell, Laura Talens, and Gara Villalba,

Abstract

This section studies the potential application of a novel biogas upgrading technology called alkaline with regeneration (AwR). This technology uses an alkaline solution, along with carbon mineralization, to remove and store CO_2 from biogas in order to create biomethane, which is a substitute for natural gas. Three different applications of biogas were explored for their potential economic benefits along three different biogas generation capabilities of landfills in Spain. The scenarios include upgrading biogas using AwR and injecting the biomethane into the natural gas grid, or selling the gas as a vehicle fuel. The third reference scenario assessed directly burning the biogas for the production of electricity. The latter showed an annual profit of 0.2 - 4 million $€_{2025}$ while upgrading the biogas to obtain biomethane showed an annual loss of 3 - 36 million $€_{2025}$. This was due to the operational costs involved in AwR, namely the cost of NaOH (principal reagent) and the treatment of wastewater. Another option, that could be applied instead of, or as a supplement to, lowering operational costs is to raise CO_2 credits to 165 $€_{2025}$/t or increase the price of biomethane sold, through feed in tariffs, to 0.30 $€_{2025}$/kWh. In those cases it would be possible to obtain an annual profit.

10.1 Introduction

It is predicted that in the year 2020 Europe will produce 10 billion m^3 of biomethane solely from landfills (AEBIOM, 2009). While this biogas can be considered as an environmental contaminant due to its high concentrations of methane (CH_4) (35-65%) and carbon dioxide (CO_2) (15-50%) (Petersson and Wellinger, 2009,Dirkse, 2009), for the same reasons it can be considered as a potential source of energy. CH_4 is a powerful greenhouse gas (GHG) that is 25 times more potent than CO_2 in trapping heat in our atmosphere (Forster et al., 2007) and therefore concerns have been raised in minimizing such emissions (European Commission, 1999,Bogner et al., 2007). Furthermore, as it has a high calorific value it is also a potential source of energy. By removing the CO_2 from biogas through the application of carbon capture technologies, it is possible to obtain a high concentration of methane, often referred to as biomethane, which is comparable to commercial natural gas. This allows for biogas to become a potential source of alternative natural gas, and therefore this biomethane could be fed into the natural gas grid, or used as a fuel for vehicles.

The application of carbon capture to biogas in order to form biomethane is called biogas upgrading. While it utilizes carbon capture technology it does so at a smaller scale than what is currently envisioned when referring to carbon capture (for example power plants). This smaller scale also allows for the deployment of novel capture techniques which have not yet been tested on or proved at larger scale. One such example is carbon mineralization. This process has been gaining interest as a viable route for carbon storage (Mun and Cho, 2013,Santos et al., 2013,Olajire, 2013) as it uses a chemical reaction to convert the CO_2 into a non-soluble solid compound. Materials that contain metal oxides (such as calcium oxide (CaO) or magnesium oxide (MgO)) are put in contact with CO_2. The metal oxides react with the CO_2 to form a carbonate (calcium carbonate ($CaCO_3$) or magnesium carbonate ($MgCO_3$). Metal oxides occur naturally in minerals such as silicate, serpentine and olivine. High levels of CaO can also be found in industrial wastes such as air pollution control (APC) residues from municipal solid waste incinerators (IPCC, 2005). There has been growing interest in using carbon mineralization for biogas upgrading and one such technique that is being developed is called *alkaline with regeneration* (AwR) (Baciocchi et al., 2011b,Baciocchi et al., 2012). This process uses an alkaline solution to strip CO_2 from biogas and then this solution passed through the APC residues in order to store the CO_2 while at the same time regenerate the alkaline solution. This technology, currently at the pilot plant stage, presents an advantage over current biogas upgrading technologies as it stores CO_2 while it captures it.

There are currently six biogas upgrading technologies that are on the market, which include high pressure water scrubbing, chemical scrubbing with amine, pressure swing adsorption, cryogenic separation, membrane separation and organic physical scrubbing. These technologies all isolate methane from the biogas. However, currently most captured CO_2 is then released back into the atmosphere, unless it is of a high enough purity for industrial purposes (Lems and Dirkse, 2009). Interest has been growing in

biogas upgrading technologies and various facilities exist, though their application has not been very widespread (Petersson and Wellinger, 2009,Bauer et al., 2013). Application of biogas upgrading technologies focuses on facilities that have anaerobic digestion of organic matter, e.g., agricultural facilities that deal with waste crops and manure, and waste treatment facilities such as wastewater treatment, anaerobic digestion of municipal solid waste and landfills for municipal solid waste. While non-upgraded biogas can be burned directly for electricity, when it is upgraded the biomethane is an alternative source of natural gas and can therefore be injected into the natural gas grid, or be used as a vehicle fuel, all of which could bring a profit to the owner of the biogas upgrading facility.

The novel technology, AwR, poses an interesting issue in that it can be profitable while capturing and storing CO_2 at the same time. Though as this technology is still at the pilot plant stage it is important to review whether the application of this technology can be economically feasible and where focus should be placed in order to maximize profits. Therefore this article explores the potential application of AwR in three different landfill sizes in Spain, with increasing biogas generation, and explores the potential costs involved in the upgrading and injection into the gas grid, as well as selling it as vehicle fuel.

10.2 Methodology

This article follows a techno-economic study conducted by Lombardi and Carnevale (2013) in which the total cost of a 250 Nm^3/h AwR facility (under different working conditions) in Italy was determined (Lombardi and Carnevale, 2013). This article looks to apply the AwR technology, which was determined to have the lowest specific cost, in landfills in Spain and examine under which economic conditions and technological scale a profit can be obtained by selling biomethane for different final applications. As the technology is still in the pilot plant stage, and considering the time needed to upscale to operational level, it is assumed that the upgrading facility will become operational in 2025.

10.2.1 Technical Information

The technology under review is the Alkaline with Regeneration (AwR) process (Fig. 10.1). During the development of this technology there were various different combinations of working conditions that could be applied. It was decided to select the working condition that presented the lowest environmental impact for this technology (Chapter 7), which is AwR using a 10% concentration of NaOH and re-using the wastewater. This working condition was also found to have the lowest annual cost in the study by Lombardi and Carnevale (2013).

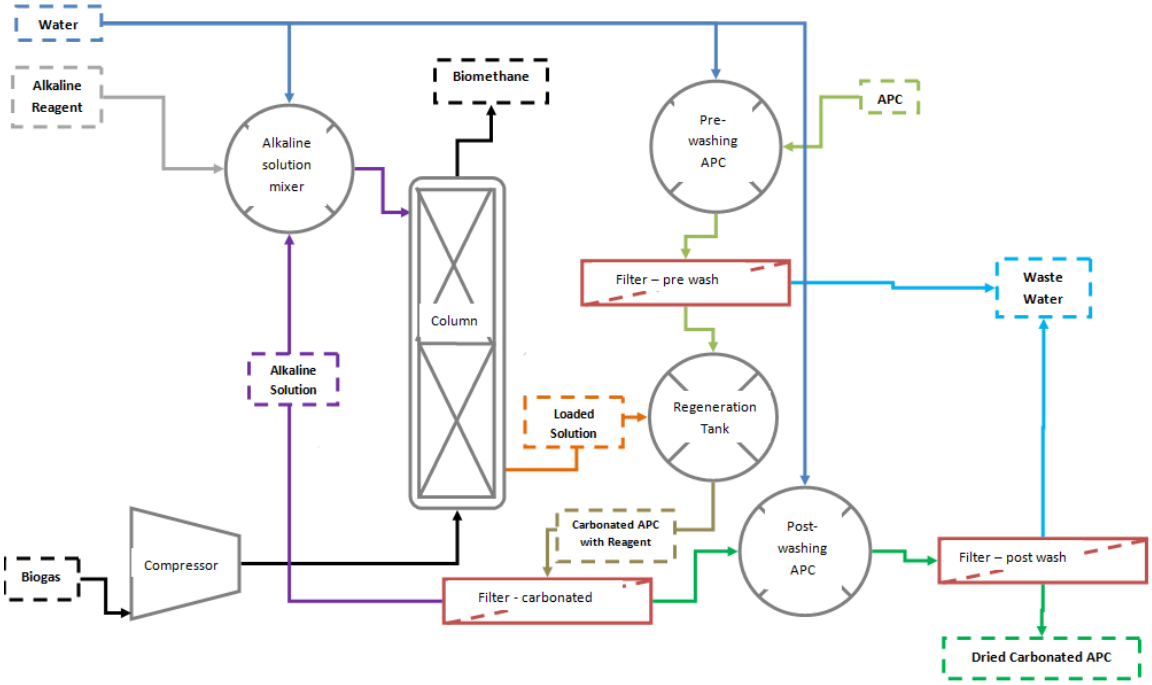

Figure 10.1. Alkaline with regeneration process

In this process, water and NaOH are first mixed to form a solution of 10% concentration by volume. This is passed through a packed column in which the biogas is pumped through. The CO_2 absorbs to the NaOH according to equation 10.1 and the biogas is upgraded to 98% CH_4 and leaves the system.

$$(10.1)\ 2\ NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3\ (aq)} + H_2O_{(l)}$$

The loaded solution is then pumped into a mixer that is filled with APC residues that has been prewashed and filtered to remove the heavy metals and chlorine (Lombardi and Carnevale, 2013). The sodium carbonate (Na_2CO_3) reacts with the CaO to form $CaCO_3$ as seen in equation 10.2.

$$(10.2)\ Na_2CO_{3(aq)} + CaO_{(s)} + H_2O_{(l)} \rightarrow CaCO_{3(s)} + 2\ NaOH_{(aq)}$$

The slurry is passed through a filter to separate the regenerated NaOH solution and the carbonated APC residues. The regenerated solution, at 61% regeneration, is pumped back into the column, with the necessary make-up of water and NaOH. The carbonated APC residues are then washed again to remove any excess alkaline solution and this wastewater is sent back into the process as the water to pre-wash the APC residues. The final wastewater is sent for treatment and disposal.

10.2.2 Conditions and Scenarios

Three cases were selected for potential biogas generation, based on landfill data in Spain (MAGRAMA, 2011) and standard sizes of conventional biogas upgrading

technologies (Petersson and Wellinger, 2009). The first case is a landfill that generates 250 Nm^3/h of biogas, which is the size at which the developers of AwR focused their study (Lombardi and Carnevale, 2013) and can be considered as a mid-range biogas collection rate. The second case is a landfill that generates 1000 Nm^3/h which is found generally in larger landfills that collect at least over 100 000 t of municipal solid waste per year. The third case is an extreme size of 5000 Nm^3/h, which can be found in landfills that accept roughly over 500 000 t of waste per year (though smaller landfills with the correct set up can also collect this amount) (MAGRAMA, 2011,MAGRAMA, 2007). Technical input data for the three different biogas generation rates can be found in table 10.1.

Table 10.1. Biogas data for AwR[a]

		Unit	250 Nm^3/h	1000 Nm^3/h	5000 Nm^3/h
Entering biogas flow rate		Nm^3/h	250	1000	5000
Biogas composition	CH_4	% (vol)	55	55	55
	CO_2	% (vol)	45	45	45
	H_2S[b]	ppm (vol)	200	200	200
Exiting biomethane flow rate		Nm^3/h	138	552	2760
Biomethane composition	CH_4	% (vol)	98	98	98
	CO_2	% (vol)	2	2	2

[a] Source: (Lombardi and Carnevale, 2013) [b] Approximated level based on: (Petersson and Wellinger, 2009,Rasi et al., 2007)

To each of the cases three different scenarios were considered, namely injecting in the natural gas grid, as fuel for LNG vehicles or as fuel for electricity production (Fig. 10.2). These scenarios were selected based on literature review of current uses for landfill biogas (Petersson and Wellinger, 2009,Persson et al., 2006). For all scenarios the biogas is pre-cleaned to remove hydrogen sulphide (H_2S). Apart from CO_2, biogas consists of other gases that should be removed beforehand, such as H_2S, NH_3, N_2, O_2, and siloxanes. Which gas should be removed before treatment depends on the composition of the waste in the landfill, the final use of the upgraded gas, and on the upgrading technique itself. For this study, it was decided to focus on the removal of H_2S, because apart from the environmental and health issues related to H_2S (as well as the SO_2 that is produced upon its combustion) and the fact that its levels in natural gas is generally regulated (de Arespacochaga et al., 2010,Persson et al., 2006), the gas can pose a problem for the AwR (Lombardi, 2013a), as well as the gas generator (Maizonnasse et al., 2013).

In scenario 1 the biogas pre-cleaned, upgraded with AwR and the biomethane is sold to and injected into the natural gas grid.

Scenario 2 follows a similar process, though in this case after upgrading by AwR the biomethane is used as fuel for vehicles. The landfills themselves have trucks and heavy machinery on site that require diesel. However, it was found that for every m^3/h of biogas that a landfill site produces the landfill requires roughly 0.091 m^3 of diesel per year (Inedit, 2013). Therefore, as biomethane production greatly surpasses these needs, it was decided to focus on providing biomethane to nearby communities within a 2 km radius of the landfill.

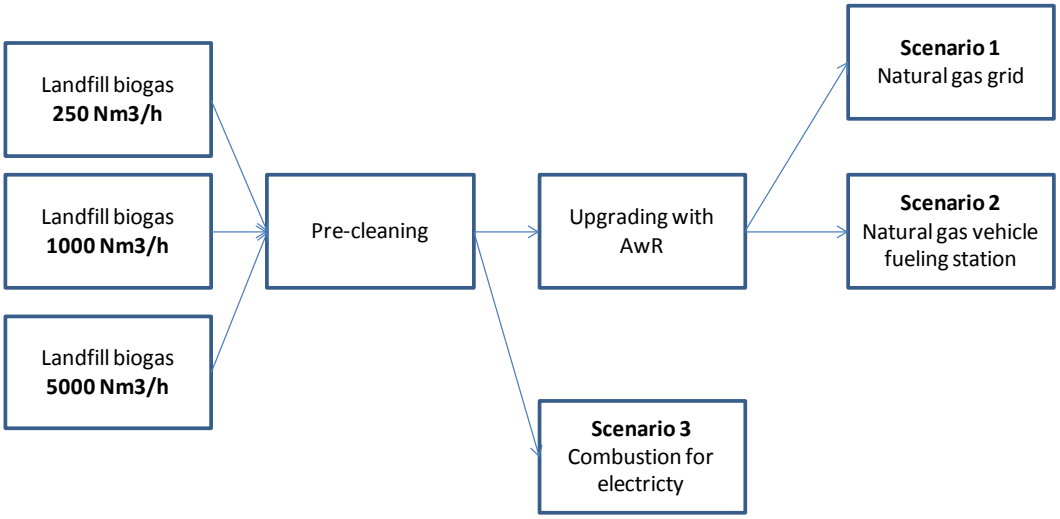

Figure 10.2. . Schematic overview of investigated systems

Scenario 3 was selected as a reference case whereby the biogas, after having been pre-cleaned, is not upgraded but rather burned onsite for electricity, and the CO_2 is not captured but emitted into the atmosphere.

It is assumed that the AwR plant is located on a landfill and a municipal solid waste incinerator (MSWI) pays the landfill to accept the APC residues as hazardous waste. Since after the upgrading process the APC residues are of a more stable quality, the landfill then sends it for treatment but it is now considered a non-hazardous waste, which reduces its treatment and disposal costs.

10.2.3 Economic Model

The economic model was divided into three parts. Firstly, the capital cost of the upgrading technology was assessed. Secondly, the operation and maintenance costs were assessed. Thirdly, the different scenarios were examined.

The equipment costs and operational flow rates of the AwR were provided by the developers (Lombardi and Carnevale, 2013,Lombardi, 2012c). As it was necessary to resize the capacity of the technology from 250 Nm^3/h to 1000 Nm^3/h and 5000 Nm^3/h, a factored estimation method was used and a scaling factor was applied to each individual component using equation 10.3 (Meerman et al., 2012,Blok, 2007). Table 10.2 shows a breakdown of the components and the scaling factors that were applied, which include the column, pumps, stir tank, filters and other components. The building in which the upgrading facility is housed was assumed to be 16% of the total capital cost. Interest on construction is ignored.

(10.3) $$z_s = z_0 * \left(\frac{x_s}{x_0}\right)^{SF}$$

Where, z_s= scaled cost, z_0= initial cost, x_s = actual scale, x_0= initial scale and SF= scaling factor.

Table 10.2. Costs associated to components required for AwR

Component	Quantity [i]	Base Cost [i]	Base Scale [i]		Scaling Factor
		(€$_{2012}$)	Value	Unit	
Absorption column (tank) [a]	1	17417	250	Nm^3/h biogas processed	0.67
Absorption column (packing) [b]	1	17917	250	Nm^3/h biogas processed	1
Stir tank [c]	4	8 000	2 000	liters	0.67
Compressor [d]	1	10 000	250	Nm^3/h gas intake	0.67
Pump A [e]	8	3 000	0.18	kW_e	0.72
Pump B [e]	2	3 000	0.28	kW_e	0.72
Pump C [e]	1	3 000	1.18	kW_e	0.72
Filter (pre-treatment) [f]	1	205 500	1	m^2 membrane surface	1
Filter (carbonation) [f]	1	151 650	0.64	m^2 membrane surface	1
Filter (final treatment) [f]	1	157 770	0.64	m^2 membrane surface	1
Conveyer belt [g]	3	10 000	250	Nm^3/h biogas processed	0.62
Pipes [h]	1	16 500	250	Nm^3/h biogas processed	0.75

[a] Scaling factor from (Larson et al., 2005) [b] It is assumed that the required packing material increases linearly as the volume treated increases [c] Volume includes the stirrers. Scaling factor from (Larson et al., 2005) [d] Although efficiency is unknown, we still assume that efficiency remains constant with scaling. Scaling factor from (Kreutz et al., 2005) [e] Pumps are based on a flow rate of 2000-3000 l/h. Assumed capacity of up to 24 kW therefore only one pump is required. Scaled size is linear as we assume that the efficiency of the pump stays the same as the size is relatively small. The difference in energy input for the pumps is due to the different viscosities of the liquids (Lombardi, 2012c). Scaling factor from (Turner, 2013) [f] The cost difference between the three filters is a result of the different size requirements for the membrane used. This membrane accounts for roughly 50% of the total cost of each filter (Lombardi, 2012c). Scaling factor of 1 selected as membrane capacity is linear to the surface area of the membrane (van Reis et al., 1997,van Reis and Zydney, 2013) [g] Technical analysis was not performed for this component, therefore base scale based on processed biogas (Lombardi, 2012c). Scaling factor from (Black et al., 2012) [h] A specific technical analysis was not performed and the cost of the pipes were assumed to be 50% of the pumps (Lombardi, 2012c). Scaling based on (NETL, 2010). [i] (Lombardi, 2012c,Lombardi and Carnevale, 2013)

Once the total capital for each biogas upgrading capacity was determined, the annual capital cost was calculated using equation 10.4 using the discount rate and lifetime defined in table 10.3. The same equation was applied to all other infrastructures used in the study, for example the pre-cleaning equipment, vehicle fuelling station, turbine, etc.

$$A = I * \frac{r}{(1-(1+r)^{-L})} \quad (10.4)$$

Where, A = annual capital cost, I= investment (total capital cost), r = discount rate, and L = lifetime.

Table 10.3. Economic parameters

	Unit	Value
Lifetime	Years	20
Discount rate	%	10
Working days per year	Days	330
Hours per day	Hours	24
Annual maintenance cost	% of capital cost	3.5

The annual net benefit was determined by subtracting the operation and maintenance (O&M) costs (tables 10.3 and 10.4) and the annual capital recovery from the total annual income. The net present value (NPV), which is a measure of the current value of future incomes and expenses and therefore determines the profitability of an investment, was calculated using equation 10.5 (Meerman et al., 2012,Blok, 2007).

(10.5) $NPV = -I + \sum_{y=0}^{L} \frac{B_y - C_y}{(1+r)^y}$

Where I= investment (total capital cost), B= annual income, C= annual costs (excluding capital), r = discount rate, L = lifetime and *y*= year.

Table 10.4 defines all of the operational inputs and outputs for a 250 Nm^3/h biogas upgrading facility along with the yearly quantity and their costs per unit. Data on the quantities of the inputs and the APC residues acceptance came from (Lombardi and Carnevale, 2013). The same source was used to calculate the annual biomethane and electricity output in kWh. The costs associated with each input and output came from literature reviews and personal communications with companies and experts

Table 10.4. Operation costs and incomes of AwR for a 250 Nm^3 facility.

Operational costs and incomes	Yearly consumption/production		Costs	
	Quantity [i]	unit	amount	unit
Expenses				
Electricity [a]	899,237	kWh	0.14	€$_{2025}$/kWh
NaOH [b]	1,219,680	kg	1.02	€$_{2025}$/kg
APC final disposal [c]	11,967	t	75.98	€$_{2025}$/t
Water [d]	61,451	m^3	1.56	€$_{2025}$/m^3
Waste water treatment [c]	39,236	t	62.77	€$_{2025}$/t
Labour [e]	1	person	60,576	€$_{2025}$/y
Income				
APC acceptance [c]	8,870	t	126.64	€$_{2025}$/t
Biomethane sold to gas grid [f] (scenario 1)	13,067,735	kWh	0.03	€$_{2025}$/kWh
Biomethane sold as vehicle fuel [g] (scenario 2)	13,067,735	kWh	0.06	€$_{2025}$/kWh
Electricity sold from direct burning [h] (scenario 3)	4,818,220	kWh	0.07	€$_{2025}$/kWh

[a] Based on industrial price 5 year average between 2008 and 2012 (Eurostat, 2013b). Price associated with consumption of between 500 MWh-2000 MWh. [b] Price constantly fluctuates; approximation based on consultation with sellers (Simar, 2013,España Maraver, 2013) [c] Price

includes transport. From consultation with treatment facility (Creus and Casañas, 2013) [d] Taken from (Aeas, 2010) [e] Assumed current staff at landfill can perform all activities. One professional staff hired with specific knowledge about the technology (Eurostat, 2013g). This aspect may be an over-assumption as proper training of the staff, with periodical visits may be sufficient. [f] Price of natural gas based on lowest price for industrial consumer, based on annual consumption of over 4 PJ. Price obtained by 5 year average of 2008-2012 (Eurostat, 2013d) [g] Price of natural gas based on price for domestic consumer, based on annual consumption of over 200 GJ. Price obtained by 5 year average of 2008-2012 (Eurostat, 2013c) [h] Price of electricity based on lowest price for industrial consumer, based on annual consumption of over 150 000 MWh. Price obtained by 5 year average of 2008-2012 (Eurostat, 2013b). [i] The quantities related to the yearly expenses and the income from APC acceptance from: (Lombardi and Carnevale, 2013).

All costs were adjusted to $€_{2012}$ using historical inflation/deflation values (Eurostat, 2013e,Eurostat, 2013f,BEA, 2013,StatCan, 2013) in order to ensure comparability between data. The prices were then indexed to $€_{2025}$ assuming an annual 2% inflation rate. Currencies which had to be converted to Euros were first deflated/inflated to 2012, then an exchange rate was applied (ECB, 2013b,ECB, 2013a), and then indexed to $€_{2025}$.

10.2.4 Additional Associated Costs

10.2.4.1 Pre-cleaning

There are different technologies that can remove H_2S (Petersson and Wellinger, 2009). A literature review suggested that a liquid scavenger is the optimal method for the H_2S concentration in the biogas (Maizonnasse et al., 2013). The total capital cost and annual operation and maintenance (O&M) costs can be found in table 10.5.

Table 10.5. Costs associated with pre-cleaning H_2S. Prices in $€_{2025}$.

	Unit			
Biogas generation rate	Nm^3/h	**250**	**1,000**	**5,000**
Investment cost	€	25,738	37,920	102,952
Annual O&M	€/y	2,971	13,645	148,536

Source: (Maizonnasse et al., 2013)

10.2.4.2 Scenario 1

Apart from the pre-cleaning and upgrading there are fees associated with connecting the biomethane to the natural gas grid. These costs include the capital and O&M associated with preparing the gas for grid injection (compressors, odorizers, control valves, flow meters, sensors and other monitoring equipment) and the pipeline to connect to the natural gas grid (Electrigaz, 2008).

The EC directive 2009/28/EC states that access to the gas grid to any producers of biomethane is guaranteed (European Commission, 2009). Although Spanish regulations state that the gas producer is responsible for monitoring the quality of the gas before injection, it does not refer directly to the actual connection costs (Gobierno de Espana, 2011). In other countries it was found that the costs associated with the connection (pipeline, injection plant and O&M) would depend on the contract between the biomethane producer and the distributor (Viking Strategies, 2012,DECC, 2009,Ontras,

2013). Therefore for the purposes of this study a worst case scenario was assumed whereby all the costs are allocated to the landfill.

A literature search found that the capital costs for the connection has many variables and ranges from approximately 48 000 $€_{2012}$ to 1 000 000 $€_{2012}$ (Electrigaz, 2008,Ontras, 2013,AEBIOM, 2009). This cost can increase if connections over 1 km are required and if more treatment is needed to prepare the gas for injection as additional equipment is required (Electrigaz, 2008,Ontras, 2013). The average price of a simple connection to the gas grid was found to be around 60,000 $\$CAD_{2008}$, or 49,240 $€_{2012}$, for a 240 Nm3/h biogas facility (Electrigaz, 2008). This includes basic equipment such as flow meters, odorizers and valves; therefore a scaling factor of 0.7 was applied (Lombardi and Carnevale, 2013). This cost only includes a short pipe connection and therefore a price of 70 000 $€_{2012}$/ $km_{pipeline}$ (Börjesson and Ahlgren, 2012) was used to supplement the additional pipeline required. It was assumed that landfills as well as main natural gas lines are found outside of cities, therefore in this study a distance of 1 km between the upgrading site and the gas grid injection site was selected. Similar to the upgrading facility, annual O&M costs of 3.5% of the capital costs are assumed.

Income comes from the sale of biomethane and the treatment of APC residues from hazardous waste to non-hazardous waste (see table 10.4).

10.2.4.3 Scenario 2

The landfill takes on the cost of the biogas pre-cleaning and upgrading equipment. In some cases an external company would purchase the biomethane and bring it to a filling station, though for this study it is assumed that the landfill is responsible for the capital and O&M costs involved for a filling station located 2 km from the landfill. The costs associated were determined at 30 $€_{2012}$/$MWh_{biomethane}$ for the filling station, 70 000 $€_{2012}$/ $km_{pipeline}$ for the pipeline to transport the biomethane to the filling station, and 5 $€_{2012}$/$MWh_{biomethane}$ for the O&M of the filling station (Börjesson and Ahlgren, 2012). These costs are comparable to values found in literature (AEBIOM, 2009,Gerbio, 2012,Biogas OST, 2008).

Income comes from the sale of biomethane as vehicle fuel and the treatment of APC residues from hazardous waste to non-hazardous waste (see table 10.4).

10.2.4.4 Scenario 3

The landfill takes on the cost of pre-cleaning equipment as well as the gas generator. Data for the generator was obtained from personal communication with a generator manufacturer (Farzad, 2013). The prices were given for the 250 Nm^3/h and 1000 Nm^3/h sized generator. The 5000 Nm^3/h gas generator price was not provided therefore it was estimated by deriving a scaling factor based on the previous two capacities.

The cost of the connection to the electricity grid is the responsibility of the producer (Gobierno de Espana, 2007). It is assumed that a landfill would already be equipped with a transformer, therefore the distance selected was 500 m. Through consultations with

experts it was determined that the connection cost is approximately 150 000 €$_{2013}$/km (García, 2013).

Income comes from the sale of electricity (see table 10.4).

10.2.4.5 Feed in tariffs

Feed in tariffs were set in 2007 in order to encourage the production of renewable energy in Spain (Gobierno de Espana, 2007), though due to economic downturns these tariffs were suspended for future renewable energy producers in 2012 (Gobierno de Espana, 2012) and retroactively eliminated in 2013 (Gobierno de Espana, 2013). These tariffs only accounted for electricity produced and did not pertain to biomethane production. In this study we did not account for any tariffs in any scenario as their application and prices are not yet known.

10.2.4.6 Specific costs

This study looked at the specific cost of each scenario per (i) m^3 of biogas processed; (ii), kWh of biomethane, and (iii) CO_2 avoided emissions. The costs were calculated using equation 10.6.

(10.6) $$SC_i = \frac{A+C-B}{U_i}$$

Where SC= specific cost, *i* = indicator under study, A= annual capita cost (eq. 10.4), C= annual costs, B= annual benefits, U = annual total of indicator under study, for example annual total m^3 of biogas (Blok, 2007).

For the specific cost of CO_2 in scenarios 1 and 2, two factors were accounted for. Firstly, the amount of CO_2 stored by the biogas upgrading technology was calculated. This was determined by taking the CO_2 that is found in the biomethane stream (2% of the total), and subtracting that from the total CO_2 input. Secondly, the amount of avoided methane emissions from the landfill was determined (see table 10.1). This methane is normally accounted as part of the GHG emissions of a landfill (Bogner et al., 2007) and therefore its mitigation could be considered as a savings and therefore source for CO_2 credit. The global warming potential of 1 t of CH_4 over 100 years is equivalent to 25 t of $CO_{2\text{-eq}}$ (Forster et al., 2007). The sum of these two factors was counted as avoided emissions. This value, along with equation 10.6, were used to determine the CO_2 avoidance cost, in other words the carbon tax required to break even.

In scenario 3 the on-site gas generator directly burns the biogas, thereby producing CO_2. This physical amount is subtracted from the total CO_2 savings associated with methane emission avoidance. This subtraction was not included to the CO_2 credit for scenarios 1 and 2 as the associated final end use falls outside of the system of study. Equation 10.7 shows that the combustion of 1 mol CH_4 produces 1 mol CO_2.

(10.7) $$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

10.3 Results and Discussion

The total annual costs, incomes and net benefit of each scenario can be found in table 10.6. As seen, the scenarios that utilize biogas upgrading have an annual loss of between 3 to 63 million €$_{2025}$, while scenario 3 receives an income of between 0.2 to 4 million €$_{2025}$. Between scenarios 1 and 2, the capital costs of connecting to the natural gas grid are lower than the costs associated with the filling station, but the potential income from the filling station is higher compared to selling to the grid. This means that scenario 2 has an annual loss that is reduced by 0.2-4.7 million €$_{2025}$ compared to scenario 1.

Table 10.6. Total costs associated with each scenario. Prices in €$_{2025}$.

	Unit	Scenario 1			Scenario 2			Scenario 3		
Biogas generation rate	Nm^3/hr	250	1,000	5,000	250	1,000	5,000	250	1,000	5,000
Annual costs[a]	M€/yr	5.08	20.04	99.79	5.23	20.61	102.6	0.05	0.09	0.31
of which AwR	M€/yr	5.06	19.99	99.56	5.06	19.99	99.56			
Annual income	M€/yr	1.5	6.2	30.9	1.9	7.7	38.5	0.32	1.3	6.4
Annual net benefits	M€/yr	-3.5	-13.8	-68.6	-3.3	-12.9	-64.2	0.28	1.2	6.1
NPV	M€/yr	-30.0	-118	-586	-28.1	-110	-546	2.45	10.3	52.2
Specific costs[b]										
Biogas processed	€/m^3	1.79	1.75	1.74	1.67	1.63	1.62	-0.14	-0.15	-0.15
Production costs[c]	€/kWh	0.27	0.27	0.26	0.25	0.25	0.25	-15.9	-17.2	-17.6
CO_2 eq. avoidance costs	€/t CO_2	169	166	165	158	154	153	-16	-17	-18
CO_2 eq. avoided	kt CO_2/yr	20.92	83.67	418.3	20.92	83.67	418.3	17.38	69.51	347.6

[a] Includes annual capital and O&M. [b] Based on annual cost (equation 10.6) [c] Scenario 1 and 2 relate to biomethane generated and scenario 3 to direct electricity production.

With the specific cost it is possible to see that if CO_2 credit were to be applied, the pricing for the 250 Nm^3/h scale would have to be 169 €/t CO_2 in order to break-even for scenario 1 and 158 €/t CO_2 for scenario 2. This is quite high compared to the forecasted CO_2 price for 2020 of around 6 €$_{2020}$/t CO_2 (EEX, 2013). Also, it was determined that in order for scenario 1 to obtain a profit on the sale of biomethane it has to be sold for around 0.30 €$_{2025}$/kWh which is a tenfold increase over the estimated price in 2025 of 0.03 €$_{2025}$/kWh. In scenario 2, the sale price would have to be above 0.25 €$_{2025}$/kWh, which is over a 4x increase from the estimated price of 0.06 €$_{2025}$/kWh. Therefore, large cost reductions are needed if a business case is to be found.

In scenario 1 and 2, the costs of biogas upgrading appear as the key component of the total cost figures (in both scenarios it accounts for over 96% of the annual costs).

The size of the upgrading facility does not play a large role in decreasing the costs as the specific cost per m^3 biogas processed decreases from 1.79 €$_{2025}$ for a 250 Nm^3/h sized facility to 1.74 € for 5000 Nm^3/h for scenario 1 and from 1.67 €$_{2025}$ for a 250 Nm^3/h sized facility to 1.62 € for 5000 Nm^3/h for scenario 2. This is due to the fact that the main costs for scenarios 1 and 2 come from the operational costs, which is linear.

10.3.1 Upgrading technology

Table 10.7 shows that the upgrading step, AwR, was found to have a cost of between 3.53 and 3.60 €$_{2025}$/m^3 of biomethane. This is a significant difference from other upgrading technologies that report a cost of between 0.11 and 0.40 €$_{2007\text{-}2009}$/m^3 of biomethane for a facility between 200-300 Nm^3/h (Patterson et al., 2011), which indexed to 2025 would be around 0.15-0.56 €$_{2025}$/m^3. In order for scenario 1 to be profitable, the AwR technology would have to reach a specific cost below 1.40 €$_{2025}$/m^3 of biomethane, or a reduction of 70%. For scenario 2 a slightly smaller reduction of 65% (or 1.62 €$_{2025}$/m^3) would be needed. Therefore, if the specific cost of the AwR approaches those of other upgrading technologies, such as pressure swing adsorption and cryogenic separation then it could be possible to obtain a profit.

Table 10.7. Capital and O&M costs of AwR. All prices in €$_{2025}$

	Unit	Biogas upgrading plant		
		250 Nm^3/h	1000 Nm^3/h	5000 Nm^3/h
Capital cost	M€	**1.036**	**3.829**	**18.04**
Annual Capital	M€/y	0.122	0.450	2.118
Total Operational Costs	M€/y	4.898	19.41	96.81
Electricity	M€/y	0.130	0.521	2.607
NaOH	M€/y	1.239	4.957	24.78
APC final disposal	M€/y	0.909	3.637	18.19
Water	M€/y	0.096	0.384	1.918
Waste water treatment	M€/y	2.463	9.851	49.52
Labour	M€/y	0.061	0.061	0.061
Annual Maintenance	M€/y	0.036	0.134	0.631
Total annual cost (before income)	M€/y	5.056	19.99	99.56
Income from APC	M€/y	1.123	4.493	22.47
Total annual cost	M€/y	**3.932**	**15.50**	**77.09**
Specific annual cost of AwR				
Biogas processed	€/m^3	1.99	1.96	1.95
Biomethane generated	€/m^3	3.60	3.55	3.53
Biomethane generated	€/kWh	0.301	0.297	0.295
Specific annual cost of AwR, *based on capital cost*				
Biogas processed	€/m^3	0.52	0.48	0.46
Biomethane generated	€/m^3	0.95	0.88	0.83
Biomethane generated	€/kWh	0.08	0.07	0.07

A breakdown of the total annual costs of AwR costs, without including the income, is given in figure 10.3 (as well as table 10.7). It is clear that the wastewater treatment, NaOH requirements and the disposal of the APC residues have the highest contributions to the overall costs. The APC residues that are used are considered hazardous waste before the upgrading and non-hazardous after the upgrading. The price at which APC residues are accepted, which is an income, is projected to be around 126.64 €$_{2025}$/t while the price the landfill would in turn have to pay for its treatment of the non-hazardous waste is 75.98 €$_{2025}$/t. This cannot be viewed as a straightforward profit of 51 €$_{2025}$/t

since for every t of APC residue accepted 1.35 t of carbonated APC residue is obtained after upgrading. In order to ensure a profit from the use of APC residues the following condition must be met: $€_H > 1.35 \times €_{NH}$, where $€_H$ is the price of the hazardous waste, $€_{NH}$ is the price of the non-hazardous waste. In this study these conditions are met, which means that the APC residue provides an overall profit at around 24 $€_{2025}$ per t of APC residue used.

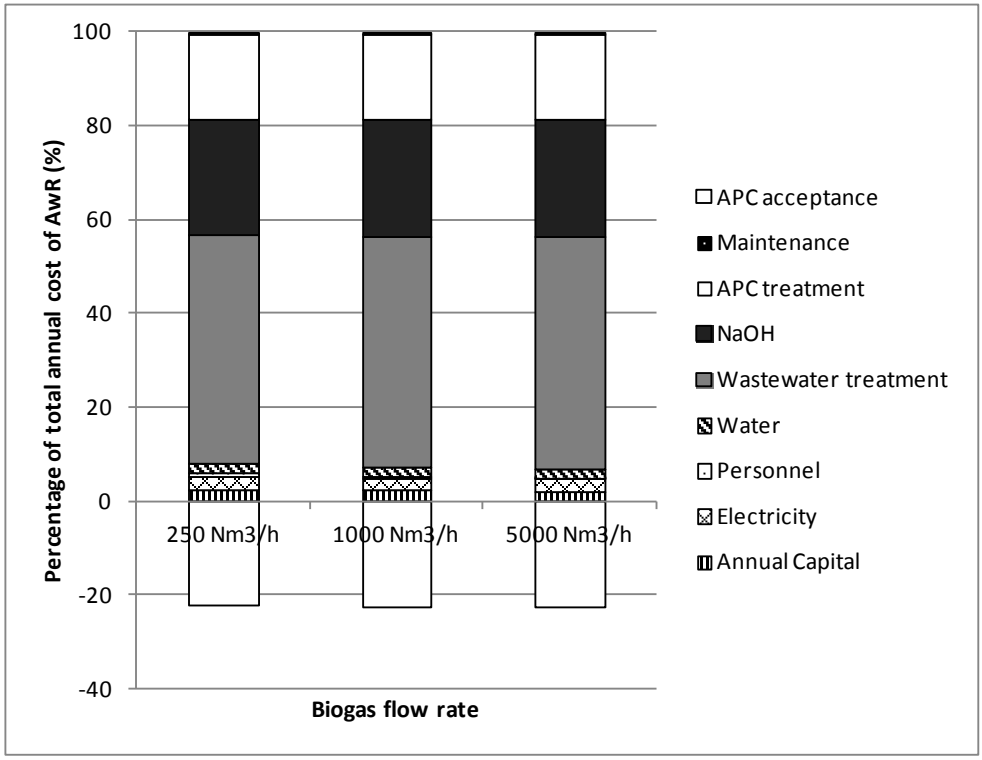

Figure 10.3. Annual cost breakdown of AwR technology at different sizes

Therefore the main costs of AwR come from NaOH (25%) and the treatment of wastewater (49%). The price of NaOH varies over time, though in this study it was assumed that the cost is inflated to 2025 at a rate of 2%. The treatment of wastewater from the biogas upgrading technology is necessary as preliminary tests found that there are heavy metals and chlorine that end up in the water from the washing of APC residues. The APC residues that were tested came from specific incinerators in Italy and as the composition of the residues is inherent to the waste that is incinerated, the concentration of contaminants in the water may change, thereby possibly reducing the need for treatment. A sensitivity analysis on the price of NaOH and wastewater treatment was conducted and can be found in section 10.3.2.

The annual capital cost of the biogas upgrading equipment is around 2% of the total costs (excluding income), though if the prices of NaOH and wastewater treatment can be reduced then this capital would play a more significant role. The specific capital cost of the AwR did not decrease with size, as was expected. The scaling factor was found to be almost linear at 0.95, as opposed to 0.7 which was suggested by the developers (Lombardi and Carnevale, 2013). The largest expense came from the equipment for the

three filtering steps (64% for 250 Nm^3/h, 70% for 1000 Nm^3/h, and 74% for 5000 Nm^3/h) followed by the building that houses the AwR (16%). The membrane has a scaling factor of 1, which results in almost linear scaling for the entire AwR equipment. Therefore the way to considerably reduce capital costs is through the filtering system. The technology currently uses membrane filters, which is a new technology. With advances and increasing market it is likely that the costs would eventually go down, though it would not be enough to make the case studies break-even as the O&M costs are still significant. Even if there were no membrane costs, in order to break-even it would be required to reduce the O&M costs by 86-87% for scenario 1 and by 80-81% for scenario 2.

10.3.2 Sensitivity Analyses

In this section various sensitivity analyses were conducted. They were based on the prices associated with NaOH and wastewater treatment, as well as distances and costs associated with the distribution of biomethane and electricity for the three scenarios, and the allocation of CO_2 credits.

The largest costs in the O&M can be attributed to the price of NaOH and of the wastewater treatment, both of which can and do change over time. Therefore, a sensitivity analysis was performed in order to see at which price for NaOH and wastewater treatment the plant would break-even. It was found that, since both of the costs are significant, eliminating one cost is not sufficient to gain a profit in either scenario 1 or 2. Therefore, both would need to be reduced as shown in figure 4. In order for scenario 1 to break-even, NaOH would need to be reduced by at least 80-87% from 1.02 €2025/kg, if the wastewater treatment would be for free. If the NaOH cost was reduced to zero then the wastewater treatment price would have to be reduced by at least 90-93% from 62.77 €2025/t in order to run break-even. Since it is not feasible to eliminate the cost of either NaOH nor of wastewater treatment, it would be necessary to find a mid-point between the two costs. In figure 10.4 the area below each line denotes prices at which an annual profit can be obtained. Scenario 2 does present a more optimistic case in which the NaOH would have to be reduced by 60-68% (if wastewater treatment is zero) or the wastewater treatment must be reduced by 80-84% (if NaOH price is zero). While the cost reductions are less than in scenario 1 both scenarios do require significant price cuts which may be difficult to achieve. Therefore focus for cost reductions should not be placed solely on these two elements but rather in combination in other areas such as the filter used in the AwR process, increasing the price at which biomethane is sold or a carbon tax

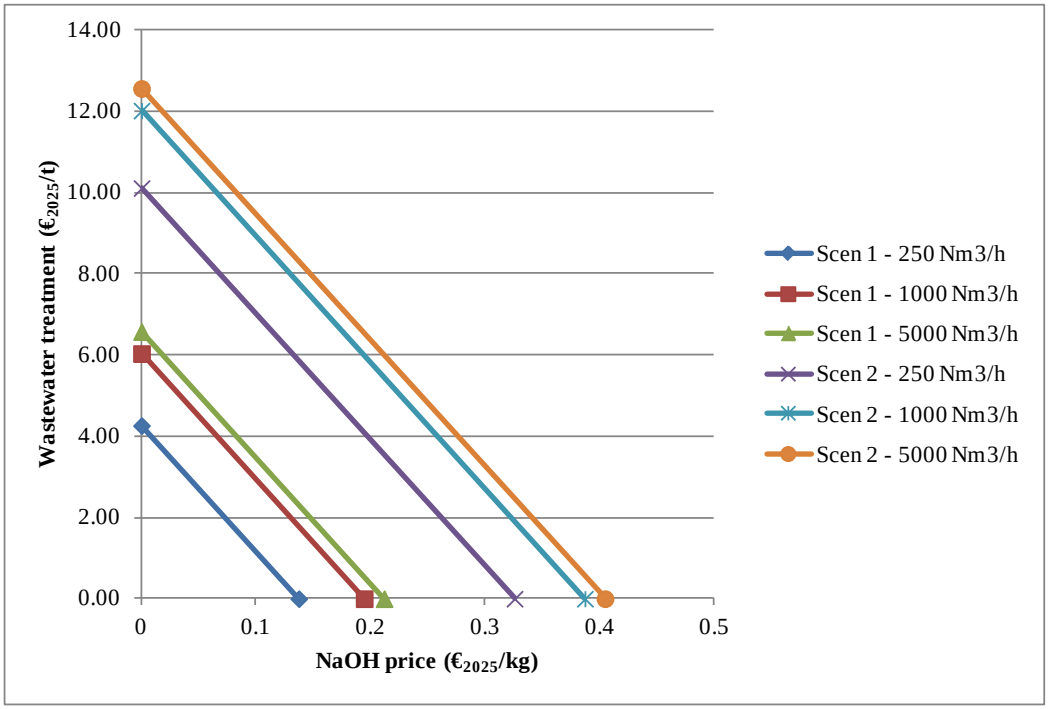

Figure 10.4. Cost reductions of NaOH and wastewater treatment.
Line means annual benefit = 0. Above line means annual loss and below signifies annual profit.

With such high prices for wastewater treatment, the landfill would most likely opt to invest in increasing the capacity of its existing wastewater treatment facility (use for leachates). If the AwR is not installed on a landfill or on a site where wastewater is not treated then a new facility may have to be built. Further research is required to estimate the impact of on-site waste water treatment.

A second sensitivity analysis was done for the distance between the biogas upgrading facility and the natural gas grid in scenario 1 and the natural gas fuelling station in scenario 2, which were assumed to be 1 km and 2 km respectively. It was determined that the impact of is minor. For instance, if the distances increased to 10 km, annual costs increase by less than 3%. A 250 Nm^3/h sized facility has the greatest increase in annual cost with a 2.7% increase for scenario 1 and a 2.6% increase for scenario 2. The 1000 Nm^3/h facility increases the annual costs of scenario 1 by 0.69% and scenario 2 by 0.66%, while the 5000 Nm^3/h facility sees an increase of less than 0.14% for both scenarios. Scenario 3 on the other hand has a more noticeable impact as the cost to connect to the electricity grid is double that of the gas pipeline connection cost. Currently, scenario 3 generates an annual income when a connection distance of 0.5 km is applied. If this was increased to 10 km then the income would decrease by 78% for a 250 Nm^3/h facility, by 18% for a 1000 Nm^3/h facility and by 3.5% for a 5000 Nm^3/h facility. At a distance of 13 km the 250 Nm^3/h facility would no longer generate an annual profit. This point would be reached at 54 km and at 272 km for a 1000 and 5000 Nm^3/h facility respectively.

In the original assessment it was assumed that the landfill would be responsible for the cost of distributing the biomethane after its upgrading, or in the case of scenario 3, the cost to connect to the electricity network. An analysis was run to determine how the annual costs would change if the connection costs would be taken on by a second or third party, as opposed to the landfill. For scenario 1annual costs could drop by between 0.5% for the 250 Nm^3/h facilities and 0.1% for a 5000 Nm^3/h facility if the gas distributor took on the connection costs. As the infrastructure and connection costs are higher for the vehicle filling station, eliminating these costs have a larger impact. In this case the annual costs drop by between 5% for 250 Nm^3/h and 4.5% for 5000 Nm^3/h. Scenario 3 sees a small impact with reductions between 4% and 0.1% for the 250 and 5000 Nm^3/h plant respectively.

In the assessment it was assumed that the CO_2 credit that the upgrading technology obtains would be applied solely to the technology itself. If the landfill emits biogas then it could be possible that they will be charged for their emissions. If this is the case then it is of interest to know whether treating the biogas through upgrading can reduce the costs for the landfill. This sensitivity analysis was conducted at the forecasted price of 6 €/t CO_2 (EEX, 2013). At this price it was found that both scenario 1 and 2 have an annual cost that surpasses that of a landfill that does not treat their biogas. Table 10.8 demonstrates that under this cost scheme scenario 3 lowers the cost that the landfill has to pay. This analysis was also applied to flaring, which is another biogas management option that is not profit-oriented, yet is often enforced by law as the minimal treatment (European Commission, 1999). Under the applied CO_2 credit price it was noted that flaring also reduces the overall costs of the landfill, though not as much as scenario 3. The costs listed in table 8 are applicable to all biogas collection rates. Landfills do not collect 100% of the biogas they emit, therefore if a landfill collects 1% or 50% of their biogas, it was found that the price difference between letting all of the biogas escape and treating the collected gas will differ by that exact amount listed in table 10.8. Therefore if a landfill collects and treats only 1% of its biogas then the landfill will still have to pay for their emissions under scenario 3, but it was found that if it collects and treats 50% then the landfill will generate an income under scenario 3.

Table 10.8. Reduction or savings of landfill costs due to biogas emissions through the addition of various treatment options, at at 6 €/t CO_2 (M€/y)

	250 Nm^3/h	1000 Nm^3/h	5000 Nm^3/h
Scenario 1	3.3	12.8	63.7
Scenario 2	3.1	11.9	59.1
Scenario 3	- 0.5	-2.2	-10.9
Flaring	- 0.2	-0.9	-4.4

It was found that in order for scenarios 1 and 2 to have an annual cost that is lower than not treating the gas, the price per tonne would have to reach between 81 -83 €/t CO_2 for scenario 1 and between 76-78 €/t CO_2 for scenario 2. Figure 10.5 show how the price range changes over biogas plant size.

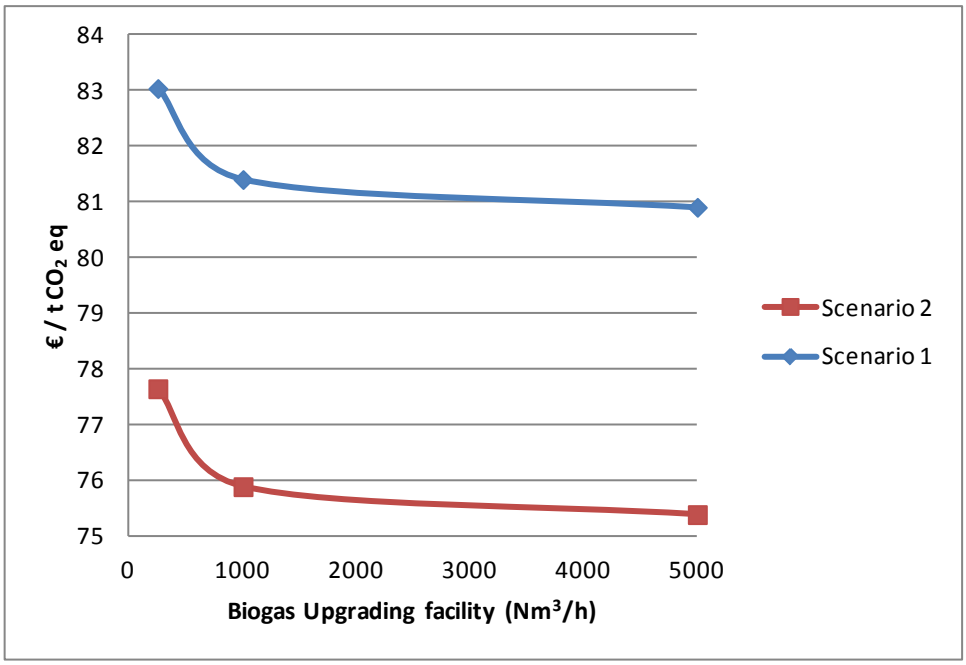

Figure 10.10.5. Price at which upgrading scenarios have the same annual cost of not treating biogas in landfills

10.4 Conclusion

This study aimed to determine whether it is economically feasible to use AwR to generate biomethane from landfill biogas and to sell the biomethane to the natural gas grid (scenario 1) or as vehicle fuel (scenario 2). It was also compared to directly generating electricity from the biogas (scenario 3).

Of the three case scenarios that were investigated, only the direct burning of biogas for electricity makes a profit of 276,000 €/y for a 250 Nm^3/h biogas flow rate. For a plant of the same size the application of this technique can reduce the landfill GHG emissions by around 17,000 t CO_2 eq./y, which increases to around 350,000 t CO_2 eq./y for a 5000 Nm^3/h facility (if one does not include the CO_2 impact of the process itself). If the biogas is first upgraded, then the GHG that can potentially be reduced is increased to around 21,000 and 420,000 t CO_2 eq./y, for a 250 and 5000 Nm^3/h facility respectively. Despite the higher GHG savings, the two other cases studies, which involve biogas upgrading using AwR, are not economically feasible. This is due to the high O&M costs of the upgrading process itself, which is mainly attributed to NaOH (25%) and wastewater treatment (49%).

In order for scenarios 1 and 2 to break even it would be necessary to either sell biomethane at a price of around 0.26 - 0.30 €/ kWh or sell carbon credit at a price of over 169 €/t CO_2. Another option would be to reduce the price of the process itself through a combination of improving the selected de-watering system, increasing the profit from APC, and reducing the required amount and/or the cost of the NaOH and

wastewater treatment. These modifications, along with possible feed-in tariffs from the sale of biomethane and CO_2 credits, would reduce the cost of AwR and make it possible to profit from the sale of upgraded biogas. Selling upgraded biomethane for use as vehicle fuel is slightly more cost effective than injection into the gas grid as the biomethane can be sold at a higher price. Though, if feed-in tarrifs for biomethane are implemented then the prices may even out, thus making injection into to the gas grid a more desirable option. The filling station may also have more long term potential as it could obtain biomethane from other sources once the landfill stops emitting sufficient methane. It is important to be aware that costs would increase the further away the filling station is from the upgrading site. Therefore, location is an important factor to ensure reduced costs. This is also an important factor for the injection into the gas grid. The gas distributor determines where the gas can be injected. Therefore, if the distance is too large then costs can increase to a point where injection is no longer economically feasible. If distance proves to be the limiting factor for the biogas upgrading facilities, then other options should be explored such as symbiosis with a neighbouring industry or even localized distribution to residents in a neighbouring city for use as cooking fuel.

Biogas upgrading technologies provide an alternative to reduce GHG emissions as it limits the methane emissions from landfills. In particular, the application of carbon mineralization to biogas upgrading is a promising technology due to the additional reduction of GHG emissions through direct CO_2 storage. Though, in order for the AwR process to reach commercialization, significant reductions in the operating costs are required.

Part IV

Conclusions

Chapter 11

Conclusion and Future Recommendations

Chapter 11 - Conclusions

This thesis determined that while the novel technologies, alkaline with regeneration (AwR) and bottom ash for upgrading (BABIU), can potentially be a positive impact on the environment, improvements need to be made before it reaches industrial scale in order to not only be competitive but also in order to have a true environmental advantage over current conventional technologies.

In this chapter, a summary of the main results and conclusions will be discussed. This will be followed by recommendations to the technology developers and final remarks.

11.1.1 Summary of results and conclusions

This section summarizes the main results of the thesis within the framework of the objectives listed in chapter 2 of the thesis.

***Objective I* – To determine whether the environmental benefits of the novel biogas upgrading technologies outweigh the environmental impacts created.**

Through the use of LCA, BABIU seemed to be the best environmental option in both **Chapter 5** and **Chapter 6**. Though, in **Chapter 7**, when pilot plant scale data was available, the BABIU process no longer excelled over all of the other biogas upgrading technologies. Rather, it was found to be in the mid-range. The only impact category where it consistently demonstrated the lowest impact, in comparison with both the conventional and novel technologies, was in global warming potential (GWP). This was because the amount of CO_2 that is stored outweighs the overall amount of CO_2 eq that is produced.

Chapter 5, which had a functional unit based on the removal of 1 tonne of CO_2, determined that the BABIU process has the lowest environmental impact when compared to high pressure water scrubbing (HPWS) and AwR. It also had the lowest impact when the system boundary is collapsed to exclude infrastructure and transport and it is compared to additional biogas upgrading technologies. This chapter revealed that the electricity use played the largest role overall, followed by the transport required for bottom ash (BA).

The chapter also demonstrated how expanding the system boundary to account for the methane diverted from the atmosphere would increase the potential CO_2 savings of BABIU as well as those of all the other processes. **Chapter 6** continued the expansion of the system boundary but used a different functional unit, the generation of 1kWh of biomethane instead of the separation of 1 tonne of CO_2 from raw biogas. Despite changing the functional unit, the BABIU process still shows the highest potential CO_2 savings at 2 kg of CO_2 saved per 1 kWh biomethane.

Unfortunately upon obtaining and applying final pilot plant data the overall environmental impact performance of the BABIU process increased. **Chapter 7** found that when looking at the full system boundary, thus when items such as transport and

infrastructures are included, and applying finalized pilot plant data, the BABIU process had a higher impact than AwR in two categories, photochemical ozone creation potential (POCP) and ozone layer depletion potential (ODP). This is due to the transport of BA required. Though, most notably, ***in this analysis it was found that the BABIU process now produces more CO_2 eq than what it stores through carbon mineralization.*** The inverse occurred when the system boundary was collapsed to exclude transport and infrastructure and the process was compared to other conventional technologies.

The reason for the difference of the results between **Chapter 7** and **Chapters 5** and **6**, is that once the BABIU process was brought from laboratory to pilot scale, the amount of BA required is higher than previously thought. This therefore increases the need to transport and thus emits more CO_2. Adjusting this factor can help to reduce the overall impact. In **Chapter 6**, which is based on laboratory scale data, the BABIU required 9 kg of BA per kWh of biomethane. CO_2 savings occur when the overall transport between the upgrading facility and the source of BA is less than 1315 km away. This is reduced to 60 km in **Chapter 7** as the pilot plant BABIU process requires 18 kg. This difference in distance can also be attributed to the fact that for the pilot plant data the other inputs increased as well, for example the electricity use went from 0.017 to 0.020 kWh per 1kWh biomethane. As well in **Chapter 6** the main infrastructure was not included while it was included in **Chapter 7** (as well as **Chapter 5**).

The AwR process did not perform overall as well as the BABIU process; therefore early on different variables were explored in order to see how its environmental impact could be reduced. **Chapter 5** found that compared to all biogas upgrading technologies, that AwR had by far the highest environmental impact in all of the impact categories, except for GWP, due to the CO_2 that it stores. It was found that the production of KOH, which is the main reagent, was the reason for the environmental burden. By replacing KOH by another alkali agent like NaOH, it was possible to reduce the environmental impact by around 34%. ***When the system boundary included the methane that is diverted, AwR did not have a significant CO_2 savings compared to other technologies.*** At 8 tonnes of CO_2 saved per functional unit (one tonne of CO_2 removed), the AwR was found to be in the mid range savings wise, only surpassing two novel technologies.

By shifting the perspective of the study to a functional unit of 1 kWh biomethane, the AwR appeared to have a better performance. In **Chapter 6**, where the diverted methane is taken into account, the AwR had the second highest CO_2 savings, after BABIU, at 1.8 kg of CO_2 saved per 1 kWh of biomethane. Even with these results, the reagent used again showed to be the highest source of impact. It was determined that even if KOH is substituted for NaOH reducing the reagent rate to 100% (i.e.: no losses in the system) would not enable AwR to have the same CO_2 savings as BABIU, but it does improve its CO_2 savings overall.

Chapter 7, which used pilot plant scale data, explored how changing the base, as well as other working conditions, affects the overall environmental impact. Eight different combinations were explored and while KOH did show lower environmental impact in two categories, abiotic depletion elements (ADP E) and terrestrial ecotoxicity potential

(TETP), overall it did have a higher environmental impact than NaOH. It was found that out of all of the working conditions, the one with the lowest environmental impact was AwR using NaOH at 10% concentration and also reusing wastewater from post washing of APC to pre-wash APC. Despite the improvements, AwR still had the highest impact compared to all other conventional technologies. As well, ***in the LCA study where transport and infrastructure were included, the AwR did not have a CO_2 savings as it produced more than it stored in the APC.*** Though, it was found that by improving the regeneration rate of best performing working condition from 60% to 65% that CO_2 savings can begin. However, improving the regeneration rate alone would not bring the AwR to comparable environmental impact of the other conventional technologies. Additionally, the electricity consumption would have to decrease as well, which may not be feasible given the current layout of the technology.

To summarize, BABIU showed the lowest environmental impact in both laboratory and pilot plant scale. AwR performed better than conventional biogas upgrading technologies in only one category: GWP. AwR's environmental performance could be further improved, reducing impacts by 34%, if KOH is replaced by NaOH. Even so, the other conventional technologies have a lower impact.

Objective II – **To determine whether the novel upgrading technologies consume natural resources in an efficient manner.**

Exergy analysis was applied in **Chapter 8** in order to examine the efficiency of resource consumption through exergetic efficiency (e_2). It was found that the results reflect those demonstrated in Objective I, in which ***BABIU is more efficient than AwR***, and within AwR, NaOH is more efficient than KOH. In contrast to the LCA results, it was found that the lower AwR efficiency (compared to BABIU) was due to the exergy of water and energy as opposed to the base. In BABIU, the exergy of methane (which is the useful product) had the highest exergy, followed by the bottom ash.

AwR had e_2 of 73-74% while BABIU had an e_2 of 90%, which in comparison to direct burning of biogas for energy has a very good efficiency as the latter has an e_2 of around 36%. These results are also found to be comparable with conventional biogas upgrading technologies. Therefore one can conclude that the novel upgrading technologies are more efficient in consuming resources than other biogas treatment processes, but similar in efficiency to other upgrading processes.

Objective III **– To determine how much natural gas can be substituted by biomethane, upgraded from biogas, under different municipal waste management system scenarios**

Biogas upgrading provides an alternative to natural gas. In **Chapter 9** scenarios were created in which upgrading technologies, AwR (using NaOH) and BABIU, as well as other conventional technologies, HPWS and AS, were applied to landfills and anaerobic digestors (AD) on a country wide scale in Spain, Italy and Austria. ***By examining the municipal solid waste flow*** over the course of one year it was possible to estimate how much biogas could be generated in landfills and AD. ***Through the application of biogas***

upgrading technologies it was possible to determine that biomethane could replace 1.4% of the primary natural gas consumption of Spain. This was more advantageous to Spain which has a low natural gas production and therefore can supplement its natural gas production by over 100%. Italy which produces a similar amount of waste per capita, also substituted 0.9% of the primary consumption of natural gas. As it has a larger national production, the biomethane would increase the national production rates by around 9%. Austria, which no longer sends municipal waste directly to landfills, had less potential natural gas replacement as the isolated organic matter mainly goes to compost, while only 35% of the isolated OM goes to AD for biogas production, resulting in a potential primary consumption gas replacement of 0.3%.

When the waste management schemes were adapted to produce more biogas, increased substitution was observed. For Italy and Spain high levels of biomethane could be achieved when landfill gas capture rate is increased to 100%, and for Austria its biogas upgrading rate increased when all of the OM was sent to the AD. Both of the scenarios are ideal, though they require not only social engagement, but also technological improvement to the waste treatment facilities in order to take advantage of the potential resource.

Objective IV **– To determine whether there is enough carbon mineralization material available for wide scale application of the novel technologies.**

Both the AwR and BABIU technologies rely on wastes from municipal solid waste incinerators (MSWI) as the source of CaO, which is necessary for carbon mineralization. In **Chapter 6** the 2008 waste management scheme of Spain was examined. It was determined that under the current layout if all landfills and AD were equipped with AwR or BABIU, that not enough APC or BA would be generated to fulfill the needs. If the landfill waste was diverted to the MSWI and only the AD produced biogas, then enough BA and APC could be generated.

Chapter 9 examined this further with a more in-depth analysis and exploring the requirements if the technologies were applied in Austria, Italy and Spain in 2009. It was determined that ***for all three countries not enough BA or APC could be produced to meet the needs of the upgrading technologies*** if it was applied to every landfill and AD. It was found as well that for Italy and Spain, if the landfilled waste is diverted to MSWI then enough APC could be produced to meet the needs of the AwR. Unlike the findings in **Chapter 6** it was not possible to meet the BA requirements of the BABIU process, though it came close. The difference between the two chapters not only lay in the fact hthat two different years were studied, but also that **Chapter 9** ran a more detailed assessment of the waste flows and therefore a different conclusion was reached.

These results demonstrate that due to the amount of waste required and produced, the application of AwR and BABIU is not appropriate for country wide application. Yet there is enough waste to fill the needs of some facilities.

Objective V **– To determine whether the application of a novel biogas upgrading technology is economically feasible.**

Chapter 11 determined that the ***application of AwR in Spain is currently not an economically feasible option***. This is mainly due to the costs involved in the operation of AwR. The use of NaOH and the wastewater treatment resulted in annual operational cost that was higher than the annual projected income. Reducing these factors, along with supplementing the income with subsidies such as CO_2 credit or feed in tariffs would help the AwR reach commercial viability.

It was also found that selling the biomethane as vehicle fuel has more potential for economic feasibility in Spain versus direct injection into the natural gas grid. Despite this, the direct burning for electricity did have the best business case and generated an annual profit.

11.2 Compatibility of Tools in Industrial Ecology

Transversal Question 1: **How can different industrial ecology tools serve to assess technologies and how do they complement each other?**

By applying and integrating different industrial ecology tools it is possible to get a broad understanding of the environmental impact of a system. Life cycle assessment (LCA), exergy analysis, and material flow analysis (MFA), along with economic assessment are useful in assessing the sustainability and the viability of a new technology, further identifying potential for future development.

The LCA and exergy assessments yielded similar conclusions, in that BABIU has a lower environmental impact than AwR, and within AwR the NaOH had a lower impact than KOH. Through LCA it was possible to see a wide range of potential impacts and from that it was possible to see that while AwR and BABIU do save more CO_2 than conventional technologies, this does not necessarily translate to environmental savings in other categories such as ozone depletion potential (ODP). LCA also makes it possible to determine which areas cause each environmental burden. Exergy analysis provides additional insight into resource consumption and it also determines how efficiently they are consumed, which is not covered in LCA.

Both of these tools require MFA in order to understand and quantify the flows involved in the upgrading processes. By running an MFA on a national scale it is possible to understand the potential applicability of the upgrading technologies on a large scale, in terms of both material availability and potential replacement of natural gas. It was found that the novel biogas upgrading technologies were not feasible for wide scale implementation, and even if they were only a small portion of the natural gas that is consumed would be replaced.

Applying an economic assessment helped to determine whether investment in AwR would be worthwhile. It was also possible to pinpoint what improvements should be made in order to have a business case. This assessment also found that the treatment of wastewater resulted in higher costs, and therefore its generation would need to be reduced. The LCA and exergy analysis did not identify this as an issue. What these three assessments do have in common is in identifying that the NaOH consumption would have to be reduced. This could be done by increasing its regeneration rate. The way in which the regeneration rate can be improved is through increasing the amount of solution that is removed from the APC resdues. After regeneration of NaOH it was found that the APC residues contain a humidity of around 40-55%, thus requiring a good filter to remove as much solution as possible. Yet it was determined that the price of the filter was the highest capital cost in the economic assessment. Therefore an increase in capital cost (through investment in a better filter) may be required in order to lower the environmental impact of NaOH.

Each of these tools is useful on its own, but in combination they provide a more well rounded understanding of emerging technologies, as they each provide different and unique perspectives. These tools helped determine that while the novel technologies, alkaline with regeneration (AwR) and bottom ash for upgrading (BABIU), can potentially have a positive impact on the environment, improvements need to be made before it reaches industrial scale in order to not only be competitive but also in order to have a true environmental advantage over current conventional technologies.

11.3 Recommendations to Developers

Transversal Question 2: **As the technologies are still in the development stage, what changes can be made in order to improve the environmental and economic performance? How can environmental assessment at the pilot scale be used at industrial scale? What are the limitations?**

While not yet applicable to large scale processes, carbon mineralization is a promising option for carbon capture and storage (CCS). Therefore applying it on the smaller scale of biogas upgrading allows developers to understand the main environmental and economic hurdles.

For AwR the base was the biggest issue for both the environmental and economic performance. Therefore focus should be placed on either finding an alkali, or another chemical such as amine, that has a lower cost and impact without compromising the performance. Also, focus should be placed on the regeneration process in order to improve its performance. After filtration the APC still contains 40-55% humidity therefore exploring methods to improve extraction of the solution would be important.

In BABIU the main issue was the amount of BA required since this material has a lower CaO content than APC residues. For this process APC residues cannot be used because it

is a powder which means that when it is placed on a fixed bed air cannot pass through it. APC residues are more suitable for AwR where the liquid can pass through it via a stir tank. Therefore BABIU either needs to explore different reactors that will encourage better contact, or explore other sources of CaO.

For both technologies different residues can be explored for capturing the CO_2. Other industrial waste options include steel slag, and there are options found in nature such as serpentine and olivine (the latter of which may have high environmental impact due to excavation). Changing the CaO source can increase the carbonation ability achieved in BABIU while for AwR it could mean that no pre or post washing is required, therefore lowering the operational costs.

As the technologies are at the development stage there is a lot of work that can still be done. Apart from the suggested areas of improvements, developers can look to apply carbon mineralization in tandem with another process or may look for other applications.

Any technical developments that are explored should be done so in parallel with environmental and economic assessments, as to ensure that there are no hidden impacts or negative side effects.

11.3.1 Future Work

Sustainability assessments are important for any technology and can be especially advantageous for technologies under development. There are some constraints as the data is often estimated and can continually change during the development process. Therefore if and when these or other upgrading technologies reach full commercialization, it would be of interest to run another environmental analysis in order to examine not only the impacts, but also if and how results changed. Knowing this can help future researchers to have better insight into projecting future environmental impacts of emerging technologies.

Improved cooperation with current manufacturers of upgrading technologies would be advantageous so that more complete assessments and comparisons could be run. In terms of all environmental and economic assessments, if more information is made available to the researcher then a more complete assessment can be obtained.

An exergy efficiency and cumulative exergy analysis could be conducted with expanded system boundaries as more information becomes available. Further information about the sub processes leading up to biogas upgrading, along with industrial scale data, would allow for a more complete picture and would help build the exergy analysis system. This would hold true for the other analyses as well, though often it requires cooperation with industries.

All of this work could be complemented with a social and political assessment in order to get a broader understanding of the sustainability of carbon mineralization technologies used in biogas upgrading.

11.4 Final Remarks

Biogas upgrading is an advancing field with a lot of promise. During the development of this thesis the number of articles and reports related to this type of technology has grown, thus demonstrating the increasing interest in developing further the upgrading of biogas. Interest in carbon mineralization has grown as well, not only for large scale industries but for biogas upgrading. Using carbon mineralization for biogas can be advantageous as it is possible to study the potential application at a smaller scale, before it is adapted to a larger scale.

The overall results of the thesis demonstrate that, at the current state, the carbon mineralization technologies used for biogas upgrading are not as environmentally friendly as they set out to be, and one is not economically feasible. Yet it does provide valuable information as it pinpoints what improvements are required for the two technologies under review. These results can also be used by other developers of biogas upgrading technologies, as well as developers of carbon capture technologies used for industry. The work contained in this thesis provides guidance into what aspects need to be examined and improved upon in order to reduce costs and reduce environmental impacts.

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