JYVÄSKYLÄ STUDIES IN BIOLOGICAL AND ENVIRONMENTAL SCIENCE
202

Saija Rasi

Biogas Composition and Upgrading to Biomethane

JYVÄSKYLÄN YLIOPISTO

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Esitetään Jyväskylän yliopiston matemaattis-luonnontieteellisen tiedekunnan suostumuksella
julkisesti tarkastettavaksi yliopiston Ambiotica-rakennuksen salissa YAA303
heinäkuun 3. päivänä 2009 kello 12.

Academic dissertation to be publicly discussed, by permission of
the Faculty of Mathematics and Science of the University of Jyväskylä,
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UNIVERSITY OF JYVÄSKYLÄ

JYVÄSKYLÄ 2009

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Publishing Unit, University Library of Jyväskylä

Cover pictures by Saija Rasi

URN:ISBN:978-951-39-3618-1
ISBN 978-951-39-3618-1 (PDF)

ISBN 978-951-39-3607-5 (nid.)
ISSN 1456-9701

Jyväskylä University Printing House, Jyväskylä 2009

ABSTRACT

Rasi, Saija Emilia
Biogas composition and upgrading to biomethane
Jyväskylä: University of Jyväskylä, 2009, 76 p.
(Jyväskylä Studies in Biological and Environmental Science
ISSN 1456-9701; 202)
ISBN 978-951-39-3618-1 (PDF), 978-951-39-3607-5 (nid.)
Yhteenveto: Biokaasun koostumus ja puhdistaminen biometaaniksi
Diss.

The feasibility of biogas in energy production was evaluated in this thesis by determining the composition of biogas from different sites and evaluating the effectiveness of water absorption for landfill gas upgrading. Methane, carbon dioxide, oxygen, nitrogen, volatile organic compounds (VOCs), including organic silicon compounds, halogenated compounds and sulphur compounds, were measured in biogas samples from landfills, waste water treatment plants (WWTP) sludge digesters and biogas plants processing different material. Methane content in the studied landfills, WWTPs and biogas plants ranged from 47 % to 70 %, carbon dioxide from 32 % to 43 % and nitrogen from < 1 % to 17 %. Oxygen content in all the measured gases was < 1 %. The highest methane content was found in the gas from one of the biogas plants while the lowest methane and highest nitrogen contents were found in the gases from landfills. Hydrogen sulphide and other sulphur compounds were found in higher amounts in the gases from landfills and biogas plants than in the WWTPs. The total amount of organic silicon compounds was highest (up to 10 mg/m^3) in one of the studied WWTP, and lowest (24 µg/m^3) in the biogas plant processing grass and maize. Organic silicon compounds were also detected in all the biogases produced in the batch assays from energy crops, with higher yields in the grass (from 21.8 to 37.6 µg/kg-volatile solids (VS)) than grass silage or maize assays (from 14.7 to 20.4 and from 7.4 to 12.1 µg/kgVS, respectively). A counter-current absorption process upgraded the landfill gas near to or above 90 % methane content. The carbon dioxide content of the product gas ranged from 3.2 to 4.8 %. With a high pressure water absorption system product gas with methane content ranging from 83 to 92 % was achieved. The carbon dioxide content of the product gas ranged from 4 to 6 %. Hydrogen sulphide was removed from the raw landfill gas with over 99 % efficiency with both upgrading systems, and halogenated compounds with 96 % efficiency with the counter-current process and from 83 to 91 % efficiency with the high pressure process. The silica gel gas drying unit, used in the high pressure process, removed about 66 % of volatile organic compounds from the gas. The results of this study show the feasibility of biogas upgrading for energy production. However, depending on the gas utilization application, the occurrence of trace compounds should be taken into account when planning an upgrading unit for biogas.

Keywords: Biogas; gas upgrading; landfill gas; methane; trace compounds; vehicle fuel.

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LIST OF ORIGINAL PUBICATIONS

ABBREVIATIONS

LIST OF ORIGINAL PUBLICATIONS

The thesis is based on the following original papers, which will be referred to in the text by their Roman numerals I-V.

I planned the articles with my supervisor and co-authors. I did the major part of the experimental work described in articles I-III and in articles IV-V with co-authors. I wrote the first drafts of all articles which were then completed in co-operation with my supervisor.

I Rasi, S., Veijanen, A. & Rintala, J. 2007. Trace compounds of biogas from different biogas production plants. Energy 32: 1375-1380.

II Rasi, S., Lehtinen, J. & Rintala, J. Determination of organic silicon compounds in biogases from waste water treatment plants, landfills, and co-digestion plants. Submitted manuscript.

III Rasi, S., Seppälä, M. & Rintala, J. Organic silicon compounds in biogases produced from grass silage, grass and maize in laboratory batch assays. Manuscript.

IV Rasi, S., Läntelä, J., Veijanen, A. & Rintala, J. 2007. Landfill gas upgrading with countercurrent water wash. Waste Management 28: 1528-1534.

V Rasi, S., Läntelä, J. & Rintala, J. Potential of high pressure water absorption process for landfill gas upgrading. Manuscript.

ABBREVIATIONS

DMS	dimethylsulfide
DMDS	dimethyldisulfide
DMSD	dimethylsilanediol
EU	European Union
EC	European Commission
EPS	extracellular polymeric substance
GC	gas chromatograph
GHG	greenhouse gas
PDMS	polydimethylsiloxane
t	metric ton
TS	total solids
TVOC	total volatile organic compound
VMS	volatile methylsiloxane
VOC	volatile organic compound
VS	volatile solids
ww	wet weight
WWTP	waste water treatment plant

1 INTRODUCTION

1.1 Biogas in energy production

The demand for renewable vehicle fuels is increasing with the growing concern about climate change and air quality. It is estimated that in the European Union (EU) transportation is responsible for 21 % of all greenhouse gas (GHG) emissions. GHG emissions could be decreased, e.g. by using biofuels as vehicle fuel (European Commission 2006). Biofuels often present a good opportunity for energy production, as both the production and consumption of energy can be located in the same area, unlike with fossil fuels. For heat and electricity a wide range of technologies utilising biogas already exist (Lantz et al. 2007). Due to the EU energy policy and concerns about climate change, the production of energy from biogas has increased during the past few years. With the decreasing oil extraction renewable sources of energy as well as energy saving will change the global economic structure (Zittel 2008).

Biogas is produced in different environments, e.g., in landfills, waste water treatment plants (WWTP) and biowaste digesters during anaerobic degradation of organic material. Biogas usually contains from 45 to 70 % methane and from 30 to 45 % carbon dioxide. Depending on the source, biogas can also contain, e.g., nitrogen, hydrogen sulphide, halogenated compounds and organic silicon compounds. Methane is a valuable renewable energy source, but also a harmful greenhouse gas if emitted into the atmosphere. In WWTP and biogas plants the gas produced is generally used for energy production. Also, in several countries methane-rich gas from landfills must be collected and flared, if not used for energy production, so as to prevent the release of methane into the atmosphere.

Biogas is considered a carbon dioxide-neutral biofuel and, if used as vehicle fuel, emits lower amounts of nitrogen oxide, hydrocarbon and carbon monoxide emissions than petrol or diesel engines. Interest in the use of biogas as vehicle fuel and in fuel cells has also increased (Persson et al. 2006). To be utilized for these purposes, in particular, but also increasingly for other purposes, a high methane concentration is required, i.e. the raw biogas has to be upgraded. The number of technologies for upgrading biogas has increased rapidly in recent years along with knowledge about the use of biogas as vehicle fuel (Lantz et al. 2007).

When biogas is used as an energy source, hydrogen sulphide and halogenated compounds, commonly found in biogases, can cause, e.g., corrosion to engines (Schweigkofler & Niessner 2001). Depending on the particular application, biogas may need to be upgraded so that no compounds harmful to engines are combusted. Also, engine manufacturers have set minimum limits on methane content to ensure engine performance.

1.2 Biogas composition

1.2.1 Main compounds of biogas

Biogas from sewage digesters usually contains from 55 to 65 % methane, 35 to 45 % carbon dioxide and < 1 % nitrogen, biogas from organic waste digesters usually contains from 60 to 70 % methane, 30 to 40 % carbon dioxide and < 1 % nitrogen, while in landfills methane content is usually from 45 to 55 %, carbon dioxide from 30 to 40 % and nitrogen from 5 to 15 % (Jönsson et al. 2003).

1.2.2 Trace compounds of biogas

Besides the main components, biogas also contains hydrogen sulphide and other sulphide compounds, siloxanes, and aromatic and halogenated compounds. Although the amounts of trace compounds are low compared to methane, they can have environmental impacts such as stratospheric ozone depletion, the greenhouse effect and/or the reduction in local air quality. Also, some compounds cause engine failure if the gas is used as an energy source. Many volatile organic compounds (VOCs) with high vapour pressure and low solubility, which can occur in biogases, are harmful to the environment and/or to humans. Aromatics, heterocyclic compounds, ketones, aliphatics, terpenes, alcohols and halogenated aliphatics, for example, occur in particular in landfill gas (Allen et al. 1997, Spiegel et al. 1997, Eklund et al. 1998, Shin et al. 2002, Jaffrin et al. 2003). Many toxic VOCs are formed in household waste which includes cleaning compounds, pesticides, pharmaceuticals, plastics, synthetic textiles and coatings (Reinhart 1993).

Sulphur compounds

The main sulphur compound in biogases is hydrogen sulphide (H_2S). Other reduced sulphur compounds, as sulphides, disulphides and thiols, can also be found in biogases. In the presence of water, sulphur compounds can cause corrosion to compressors, gas storage tanks and engines (Persson et al. 2006), and thus these compounds need to be removed before biogas can be utilized as energy. In biogas, in anaerobic conditions hydrogen sulphide and other sulphide compounds originate along several different pathways (Wilber & Murray 1990). For example, methanethiol and dimethyl sulphide (DMS) are formed from the degradation of sulphur-containing amino acids (present, e.g., in manure) and from the anaerobic methylation of sulphide. When DMS is reduced, following to methanogenic conversion, methane and methanethiol are formed. Methanethiol later forms methane, carbon dioxide and hydrogen sulphide (Lomans et al. 2002).

Halogenated compounds

Halogenated compounds are often found in landfill gases and only rarely in biogases produced from sewage sludge or organic wastes. If biogas is used for energy production, compounds containing organochloride contribute to corrosion in vehicle or combustion engines while in certain combustion conditions the formation of dioxins and furans is also possible (Allen et al. 1997, Persson et al. 2006). Aromatic and chlorinated compounds are widely used in industry as solvents, and fluorinated compounds have been used as refrigerating aggregates, foaming agents, solvents and propellants (Scheutz et al. 2004). Levels of alkanes and aromatic compounds as well as those of halogenated and oxygenated compounds are dependent on the composition and stage of decomposition of waste (Allen et al. 1997). In their studies on halocarbons in landfill gases, Allen et al. (1997) and Jaffrin et al. (2003) detected total chloride in amounts from 118 to 735 and 169 mg/m^3 and total fluorine in amounts from 63 to 256 and 25.9 mg/m^3, respectively.

Organic silicon compounds

Organic silicon compounds present in biogas are oxidized during biogas combustion into microcrystalline silicon dioxide, a residue with chemical and physical properties similar to glass. Silicon dioxide collects in deposits on valves, cylinder walls, and liners, causing abrasion and blockage of pistons, cylinder heads, and valves. In gas turbines, siloxane deposits usually form on the nozzles and blades, causing erosion of the turbine blades and subsequently lowering operating efficiency (Tower 2003). Moreover, the glassy residues of silicon dioxide can de-activate the surface of the emission control system catalyst (Schweigkofler & Niessner 1999, Hagmann et al. 2002). According to Tower (2003), there is a correlation between the increasing CO emissions and the build-up of silicate-based deposits from siloxane combustion in generator engines. Some organic silicon compounds can end up in the engine oil after the combustion process. In this case, the engine oil needs to be changed more frequently (Environment Agency 2004). This has led some gas engine manufacturers to introduce a limit on silicon of 1 mg/l in the oil of gas engines (Accettola & Haberbauer 2005).

The subgroups of silicones containing Si-O bonds with organic radicals bonded to Si are called siloxanes. Organic radicals can include methyl, ethyl, and other organic functional groups (Environment Agency 2004). The structure of a siloxane can be linear or cyclic. Siloxanes have the abbreviation L if the structure of the compound is linear and D if the structure is cyclic (Table 1). Most siloxanes have high vapour pressure and low water solubility, and they also have a high Henry's law constant. This indicates that they move easily from water to air (Glus et al. 2001). In waste water digesters and landfills, siloxanes are volatilised into biogas. Along with the most common silicon compounds in biogases (Table 1), biogases may also contain organic silicon compounds other than siloxanes that cause similar detrimental effects in the combustion process. For example methoxytrimethyl silane, tetramethylsilane, trimethylfluorosilane, and trimethylpropoxysilane have been detected in waste water digester biogases (Tower 2003).

TABLE 1 The most common organic silicon compounds and their properties (Schweigkofler & Niessner 2001, Kaj et al. 2005, McBean 2008).

Compound	Abbreviation	Molecular weight [g/mol]	Water solubility at 25 °C [mg/l]	Boiling point [°C]	Vapor pressure at 25 °C [kPa]
Trimethyl silanol	-	90	35000	70	2.13
Hexamethyldisiloxane	L2	162	0.93	107	4.12
Octamethyltrisiloxane	L3	236	0.035	153	0.52
Decamethyltetrasiloxane	L4	310	nk.	194	0.07
Dodecamethylpentasiloxane	L5	384	$3.1*10^{-4}$	230	0.009
Hexamethylcyclotrisiloxane	D3	222	1.56	135	1.14
Octamethylcyclotetrasiloxane	D4	297	0.056	176	0.13
Decamethylcyclopentasiloxane	D5	371	0.017	211	0.02
Dodecamethylcyclohexasiloxane	D6	445	0.005	245	0.003

nk. not known

The use of siloxanes is increasing, for example, in household/industrial cleaning products because volatile methylsiloxanes (VMSs) solvents are aroma-free, and widely available, and because they are not included in volatile organic compound (VOC) regulations, they are not considered a health risk to humans. They are also used in personal care products. VMSs can also originate from the hydrolysis of polydimethylsiloxane (PDMS). PDMS is an organosilicon compound. It is the most widely used silicon compound in household and industrial applications. PDMS is used, for example, as a softener and wetting agent in textile manufacturing, as a component of many surface treatment formulations, and in many domestic products such as shampoos, deodorants, gels, etc. It is estimated that one million tons of siloxanes are produced annually worldwide (Grümpling et al. 1998, Hagmann et al. 2002, McBean 2008).

Most siloxanes are very volatile and decompose in the atmosphere into silanols, which are eventually oxidised into carbon dioxide. These compounds are insoluble in water and have a high adsorption coefficient. Some siloxanes end up in waste water and are adsorbed onto the extracellular polymeric substances (EPS) of sludge flocks. Siloxanes are volatilised from the sludge during anaerobic digestion and end up in biogas (Accettola & Haberbauer 2005, Dewil et al. 2006). Silicones are also sometimes added in digesters as anti-foaming agents, where they can biodegrade into siloxanes (Dewil et al. 2006). Organic silicon compounds end up in landfills from sources such as shampoo bottles and other containers in which some of the product remains, through landfilling of waste water treatment sludge, and from packaging, and construction materials, etc. (Environment Agency 2004, Ohannessian et al. 2008). Degradation of high molecular silico-organic compounds in landfills may also form volatile silicon compounds (Schweigkofler & Niessner 1999). Because of their widespread use, siloxanes are commonly found in air, water, sediment, sludge, and biota, and the variation in concentrations can be high (Kaj et al. 2005).

1.3 Biogas as vehicle fuel

1.3.1 Environmental benefits of biomethane vehicles

Biogas produced from waste or energy crops can be upgraded and used as vehicle fuel in natural gas light-duty or heavy-duty vehicles. The same engine and vehicle configurations are used for biogas as for natural gas. In most cases, light-duty vehicles are so called "bi-fuel" vehicles, i.e. the vehicle can run either with petrol or gas. In some cases the vehicle is designed for natural gas or biomethane and is optimised for operation on a single fuel. In heavy-duty vehicles engines are usually designed to run solely on gas as the engines are based on the larger diesel engines, although "dual fuel" engines which use diesel as pilot ignition, are being developed (NSCA 2006). In 2008 there were over nine million natural gas vehicles in the world, while the annual growth in the number of gas vehicles since the year 2000 has been 30 %. In Asia the annual growth has been over 50 % and in Europe a little over 15 % (IANGV 2009).

When gas fuels are used as vehicle fuels typical air emission reductions compared to diesel fuel emissions have been from 60 to 85 % for nitrogen oxides, from 60 to 80 % for particulates and from 10 to 70 % for carbon monoxide. Gaseous fuels have a higher ignition temperature and a higher lower flammability limit than liquid fuels and in leakage situations gas fuels rise into the atmosphere unlike liquid fuels (Pierce 2007).

If biogas were to replace petrol as a vehicle fuel, non-methane VOC emissions as well as the ozone forming potential of the engine emissions would decrease by 50 %. If biogas were to replace diesel as vehicle fuel, particulate emissions would be reduced significantly and, in the case of heavy-duty vehicles, NO_x emissions would decrease by 25 % (Johansson 1996). According to Tuomisto & Helenius (2008), if biogas produced from energy crops in Finnish conditions were to be used as transport fuel and about 1 GJ of oil was replaced, GHG emissions could be reduced by about 63.3-77.2 kg CO_2-eq GJ^{-1}. When compared to liquid biofuels for vehicles, biogas production has a higher gross energy output and energy output/input ratio than, for example, ethanol produced from the same crops or biodiesel produced from rape seed. Also, compared to petrol, the average life-cycle emissions of greenhouse gases would decrease by about 108 % if biogas produced from manure were used as vehicle fuel (Börjesson & Mattiasson 2007).

Methane enrichment for other purposes than vehicle fuel could in some cases be worthwhile. According to Porpatham et al. (2008) enhanced methane concentrations in biogas improve the performance of spark ignition engines and reduces hydrocarbon (HC) emissions.

1.3.2 Political and economical incentives and barriers

The EU has proposed the target of 20 % for renewable energy in energy consumption and stipulated that at least 10 % of all vehicle fuel sold in each Member State should be from a renewable source (primarily biofuels) by 2020 (European Parliament 2008). For example the increasing regulations and taxes on waste disposal, an increasing need for renewable energy sources to mitigate climate change and measures to improve local air quality are increasing the interest in the use of biogas as a fuel for heat and electricity production and as a vehicle fuel (NSCA 2006). Current policies seek to enhance energy security, slow down climate change and support agriculture and rural development through the use of biofuels. Although biofuels have modest impacts on energy security, the impacts for agriculture are significant (Wiebe 2008). National and European regulations will increasingly include sustainability as precondition for market access. In a proposal for a directive of the European Parliament and of the Council on the promotion of the use of energy from renewable sources, the requirements for biofuels are that the minimum GHG reduction savings from the use of biofuels should be at least 35 % and after 2017 60 %. Also, the cultivation of biomass should be done according to the Cross Compliance criteria, using no feedstock from areas of high biodiversity value, and bioenergy production should take social standards into account (European Parliament 2008).

The production of biofuels from energy crops has social, environmental and economic impacts on the local inhabitants, especially in the developing countries. In general biofuel production creates jobs in rural areas, creates a reliable market for a farmer's energy crops, and improves the local infrastructure, increasing incomes and, therefore, food security (Hongo 2008).

From an economic point of view, the biogas plants which handle organic waste from municipals and industry today are more favourable than biogas plants handling manure or energy crops as the gate fees bring more economic reliability to the process. Uncertainty about electricity tariffs and the slow increase in the use of gas vehicles is bringing uncertainty into the biofuel business. On the other hand the agricultural sector gains from fertiliser production when manure is transformed into an improved fertiliser, thereby lowering costs, as lower amounts of mineral fertilisers are needed. The fertilisers produced can also be sold to increase the profits of biogas plants. The decrease in odours from spreading digested manure instead of slurry may also act as an incentive for farmers (Lantz et al. 2007).

The main incentives for vehicle fuel production from biogas are the current EU policies favouring alternative fuels and security of energy supplier and the low or non-existing taxation on biofuels which helps to reduce the market price of bioenergy as compared to petrol. The present barriers are the higher cost of bio-fuel vehicles, competing fuels as ethanol, limited biogas distribution systems and storage capacity and the limited number of biogas filling stations (Lantz et al. 2007).

1.4 Biogas upgrading

1.4.1 Biomethane requirements

Different countries have different standards and recommendations for upgraded biogas (biomethane) for gas grid injection and vehicle use. Usually, carbon dioxide, nitrogen, sulphur and halogenated compounds need to be removed from the gas. Commonly used methods for upgrading biogas are water scrubbing and pressure swing adsorption (PSA). Also, liquids other than water are used in absorption processes, and in some locations membrane technology is used (Persson et al. 2006). The upgrading of biogases from sewage and biowaste digesters is rapidly increasing in some countries (Appels et al. 2008a) while studies on upgrading landfill gas and its applications are relatively few.

Biogas upgrading processes need to be designed to avoid or minimize emissions. For example, in absorption processes some of the methane can be absorbed to the absorption liquid and be released into the air with the exhaust gas. Hydrogen sulphide, other reduced sulphur compounds and halogenated compounds in exhaust gas can have environmental and health risks if released into the air untreated. The absorption liquid used in the process should also be treated, for example with other waste waters (Environment Agency 2004).

In general, there are two types of natural gas qualities, high calorific value gas (H-gas) and low calorific gas (L-gas), which are sometimes used as comparison gases for biogas purity requirements. H-gas and L-gas differ in their energy content and λ-shift factor (NSCA 2006).

While there is no international requirements for biomethane purity, some countries have national standards and procedures for biogas injection into the natural gas pipeline (Persson et al. 2006). There is a proposal to harmonize the natural quality specifications within the EU for cross-border transportation of H-level gases (Table 2). The requirements in different countries vary depending on the local natural gas quality and if injection is limited or not. For example, in Switzerland, limited amounts of biogas with > 50 % methane can be injected into the gas grid, while for unlimited injections of biogas the methane content must be over 96 %. In the Netherlands biogas with at least 85 % methane can be injected into the gas grid while in Sweden the methane requirements are over 97 %. Also carbon dioxide, oxygen, hydrogen, water, Wobbe index, gross caloric value, relative density, halogenated compounds and ammonia have to meet specific requirements before the upgraded biogas can be mixed with natural gas. In Austria siloxane concentration is limited to < 10 mg Si/m^3 (Marcogaz 2006).

TABLE 2 Gas quality parameters in proposed harmonised EU specifications for H-gas cross-border transportation (Marcogaz 2006).

Parameter	Value
Wobbe index	13.6÷15.81 KWh/m^3 (25 °C/0°C)
Relative density	0.555÷0.7
Total Sulphur	Maximum 30 mg S/m^3
(H_2S + COS)	Maximum 5 mg S/m^3
Mercaptans	Maximum 6 mg S/m^3
Oxygen	Maximum 100 ppm molar
Carbon dioxide	Maximum 2.5 % molar
Water dewpoint	Maximum –8 °C at 70 bar a
Hydrocarbon dewpoint	Maximum –2 °C over 1 ÷ bar a

1.4.2 Absorption

The process whereby pollutants from the gas stream are dissolved into a solvent liquid stream by mass transfer is called (physical) absorption. The difference in concentration of the solute between the gaseous and liquid phases is the driving force for mass transfer. The process is called chemical absorption if a chemical reaction between the pollutant from the gas stream and the component of the liquid phase occurs. The reaction can be reversible or irreverbible (Kohl & Nielsen 1997).

The solubility of gases into water is dependent on several factors, such as pressure, temperature, liquid/gas ratio etc. According to Henry's law there is a linear relationship between the partial pressure of a gas and its concentration in dilute solution:

$$P_A = X_A H_A \qquad (1)$$

where P_A = vapor pressure of component A above the liquid mixture, X_A = mole fraction of A in the liquid mixture, and H_A = Henry's law constant (Betterton 1992). At higher pressures Henry's law is no longer valid in its simple form (Lekvam & Bishnoi 1997), and temperature becomes a more important factor than pressure for gas solubility (Pierantozzi 1993). Carbon dioxide solubility at high pressures in different temperatures is given in Fig. 1.

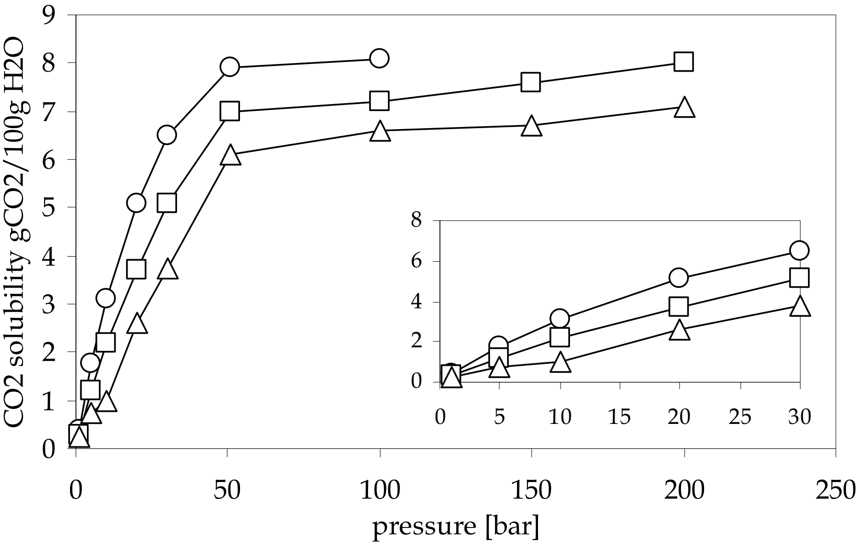

FIGURE 1 Solubility of carbon dioxide in high pressures at different temperatures (○ 0 °C; □ 10 °C; Δ 20°C) (Pierantozzi 1993).

There are several absorber designs, but the primary function of all is to increase the area of contact between the liquid and the gas phases under conditions favouring mass transfer. Usually this is done by dividing the gas into small bubbles in a continuous liquid phase, spreading the liquid into films that flow through a continuous gas phase or forming the liquid into small drops in a continuous gas phase (Kohl & Nielsen 1997). A solvent to absorption process in which the organic contaminant is as soluble as possible should be chosen to decrease the size of the absorption equipment and increase the effectiveness of the process. Liquid and gas should be distributed evenly in the absorption column to avoid gas channelling, which causes a decrease in the removal efficiency of gas components (Hunter & Oyama 2000).

A counter-current flow column has a high absorption efficiency because it provides a long contact time between the vapour and liquid phases. Such a column is often used in biogas purification systems, as it is considered to be a simple, efficient and versatile method capable of treating corrosive compounds at relatively low cost. The biogas is usually pressurised and channelled to the bottom of the counter-current absorption column. The solvent is sprayed from the top of the column. Biomethane is brought out from the top of the column. Before utilisation biomethane is usually dried. Used solvent can be regenerated in the desorption column at low pressure and re-used in the absorption process (Persson et al. 2006). Packed columns can also have co-current flow and the tower can be vertical or horizontal. Other absorption designs include trays or open vessels (Hunter & Oyama 2000).

The most common solvent used in biogas upgrading processes is water. Depending on the site, pure water or treated water from a waste water treatment plant can be used with flow-through or with water circulation. Water washing is an effective upgrading process for biogases produced from different sources, as carbon dioxide ($8.21 \cdot 10^{-4}$, 288.15 K) and hydrogen sulphide ($2.335 \cdot 10^{-3}$, 288.15 K) are more soluble in water than methane ($3.122 \cdot 10^{-5}$, 288.15 K) (Lide 1996), and thus it is possible to produce high quality methane gas. Impurities like ammonia, sulphur dioxide, hydrogen chloride, hydrogen fluoride, chlorine, aldehydes, organic acids, alcohols, silicon tetrafluoride and silicon tetrachloride have also been removed by means of water scrubbing (Kohl & Nielsen 1997). Other commonly used solvents include polyethylene glycol and alkanol amines. Carbon dioxide and hydrogen sulphide are more soluble in organic solvents than in water, and thus the upgrading process is more efficient (Persson et al. 2006); however, organic solvents are more expensive than water. During the absorption process some of methane may also dissolve into the absorption liquid. In many plants, a flash tank is used to recover methane from the absorbent at an intermediate pressure (2-4 bar) before the desorption unit, and thus decrease methane losses (Tynell 2005).

2 OBJECTIVES

The main objective of this study was to assess the composition of biogases in various production sites in order to assess the purification need for different biogas utilisation applications, and to study landfill gas upgrading with two separate water absorption systems.

The specific objectives were:

- To determine the major and trace organic compounds in biogas at different biogas production sites, i.e. a landfill, a waste water treatment plant (WWTP) and a farm biogas plant. The objective was also to determine the variation in biogas composition (I).
- To determine the amounts and the types of organic silicon compounds in biogases from landfills, WWTPs and biogas plants processing different kinds of organic waste (II).
- To study the occurrence of organic silicon compounds in biogases produced from energy crops (III).
- To determine the feasibility of a counter-current water absorption process in upgrading landfill gas to vehicle fuel. For this purpose the effects of pressure and of water and gas flows on product gas composition were studied. Experiments were performed on site using a pilot-scale facility (IV).
- To study the feasibility of a high pressure water absorption process in upgrading landfill gas. Experiments were performed on-site using a pilot-scale facility in which two absorption columns were used for continuous upgrading. Two initial pressure settings were used to determine the optimal process parameters (V).

3 MATERIALS AND METHODS

3.1 Origin of biogas samples

The biogas samples for main and trace compound analyses (I) were obtained from a municipal landfill (W1) and a mesophilic municipal sewage treatment plant sludge digester (S1) both in Jyväskylä, Finland from February to July 2004 and from June to August 2005 and from a mesophilic farm biogas plant in Laukaa, Finland from June to August 2005. For the organic silicon compound analyses (II) gas samples were obtained from four municipal landfills and four mesophilic municipal WWTP digesters in three cities in Finland and four biogas plants in Finland and Germany from September 2007 to April 2008 (Table 3).

TABLE 3 Biogas production sites and biogas samples (I,II).

Sites		Description
Landfills:		
Mustankorkea, Jyväskylä	W1	Municipal landfill established in 1963. Gas recovery is about 3.5 million m^3/year. Sample taken after condensation.
Koukkujärvi, Tampere	W2	Municipal landfill established in 1962. Gas recovery is about 1.7 million m^3/year. Gas taken after condensation.
Tarastenjärvi1, Tampere	W3	Municipal landfill established in 1977 with two gas pumping stations. Capacity of gas pumping station W3 is 800 m^3/h and W4 1000 m^3/h. Gas recovery is about 6 million m^3/year. Samples from W3 taken after condensation and from W4 before condensation.
Tarastenjärvi2, Tampere	W4	
Ämmässuo, Espoo	W5	Municipal landfill established in 1987. Gas recovery is about 60 million m^3/year. Samples taken before and after condensation.
Waste water treatment plants:		
Jyväskylä	S1	Mesophilic municipal WWTP producing 1.5 million m^3 biogas/year. No gas treatment.
Rahola, Tampere	S2	Mesophilic municipal WWTP producing 0.9 million m^3 biogas/year. No gas treatment.
Viinikanlahti, Tampere	S3	Mesophilic municipal WWTP producing 1.9 million m^3 biogas/year. No gas treatment.
Espoo	S4	Mesophilic municipal WWTP producing 1.5 million m^3 biogas/year. No gas treatment.
Biogas plants:		
Kupferzell	B1	Mesophilic (42 °C) co-digestion plant in Germany. Input: pig manure, cow manure, waste from sugar factory, grapes, mallas grane, salad and vegetable waste, 13500 t waste/year. Samples taken after condensation.
Remlingen	B2	Mesophilic (40 °C) 2500 m^3 digestion plant in Germany. Input: grass and maize. Samples taken after condensation.
Vaasa	B3	Thermophilic co-digestion plant. Input: sludge from wastewater treatment plant (15000 t/a) and biowaste (8000 t/a). Samples taken after condensation.
Ilmajoki	B4	Mesophilic Co-digestion plant. Input: sludge from waste water treatment plant and municipal and industrial biowaste (10 % of all input). Biogas production about 700 Nm^3/h. Samples taken after condensation.
Laukaa	B5	Farm scale mesophilic co-digestion plant producing 0.06 million m^3 biogas/a. Input: cow manure and industrial confectionery.

3.2 Experimental set-up

3.2.1 Laboratory biogas batch assays (III)

The batch assays with crops for the organic silicon compound analysis were performed in duplicate or triplicate 2 l and 5 l glass bottles (liquid volume 1.6 l and 4.5 l) at 35 ± 1 °C. Inoculum and substrate in a volatile solids (VS), $VS_{substrate}/VS_{inoculum}$ ratio of 1 were added into the bottles, water was added to produce a liquid volume of 1.6 l or 4.5 l, and sodium bicarbonate ($NaHCO_3$, 3-4 g/l) was added as buffer. The bottles were flushed with N_2 and then sealed with butyl rubber stoppers (Lehtomäki 2006). The inoculum for the biogas batch assays (average values of total solids (TS) 4.7 ± 0.7 %, VS 3.6 ± 0.6 %) was obtained from a mesophilic farm digester processing cow manure, industrial confectionery by-products and energy crops. Grass silage (S), grass (G) and maize (M) were collected from two farms in central Finland. For the grass silage assays, 77, 650 and 873 g/bottle of crop, inoculum and water, respectively, were added; for the grass assays 80.9, 650 and 869.1 g/bottle; and for the maize assays 208.1, 600 and 753.1 g/bottle. To determine the organic silicon compounds of the biogas produced from the inoculum, assays of inoculum only were carried out under the same conditions. The gas produced was collected in Napholan NA© bags. Methane production potential was determined in similar batch assays in 1 l, 2 l and 5 l bottles, and the gas produced was collected in TECOBAG (PETP/AL/PE 12/12/75) aluminium gas bags (volume 10 l).

To obtain the biogas samples for the volatile organic silicon compound measurements, the biogas was collected in gas bags until the required amount of gas (about 1 l) was produced. Thus the duration of the batch assays and number of gas samples taken were dependent on the amount of biogas produced in the actual assay. For each of the assays with crops two to three gas samples were taken, while for the assays with inoculum only one sample per bottle was taken, because of the low amount of gas produced. The yields of the organic silicon compounds were calculated from all the biogas produced during the incubation period per bottle as µg/kg-VS, minus the yields of the organic silicon compounds from the biogas produced from inoculum only. After the incubation period samples were taken from the digestates with the crops and inoculum only (the inoculum and crop material not degraded during the incubation period). Samples were also taken from the inoculum before it was used in the batch assays. The volatile organic silicon compounds in these samples were measured as µg/kg-ww.

3.2.2 Landfill gas upgrading (IV,V)

The biogas upgrading pilot plant, including a courter-current water wash process and high pressure water wash process (IV, V), supplied by Metener Ltd., was deposited at Mustankorkea landfill in Jyväskylä, Finland. The raw landfill gas was taken for the upgrading processes from a collector pipe in the landfill gas collection system after condensation (considered dried gas). Gas samples for analysis were taken from the raw gas, product gas before and after the drying unit (V), and exhaust gas.

Counter-current water wash process

The pilot scale counter-current water wash upgrading facility contained an absorption column (500 l, height 185 cm, diameter 60 cm), desorption column (500 l, height 155 cm, diameter 65 cm) and water storage tank (500 l). Both the absorption column and desorption column were (randomly) filled with pall-rings (4 x 4 cm) to create a larger contact surface between the gas and water. The pilot-scale upgrading plant was able to treat 6 m^3 of raw gas per hour and was built inside a movable container.

First the raw gas was channelled into the gas storage tank and compressed to the upgrading pressure. Compressed raw gas and absorbent were then channelled into the absorption column in which the pressure was maintained. The absorbent used in the process was tap water (pH 7) at a temperature of ca 10 °C. Water was sprayed from the top of the column and the raw gas was channelled from the bottom of the column (Fig. 2). After the absorption column, water and the compounds absorbed into it were channelled into the desorption column. In this column water was regenerated at a low pressure (0 and –0.3 bar), exhaust gas was released from the column and the product gas (upgraded landfill gas) was piped to the landfill gas collection system.

Upgrading efficiency was studied using different pressures (10, 15, 20, 25 and 30 bar) and water (5 and 10 l/min) and gas (50 and 100 l/min) flows in trials which typically lasted 30 min each. The conditions were initially selected on the basis of preliminary studies showing, e.g., that at pressure below 10 bar the methane content of the product gas was less than 80 %.

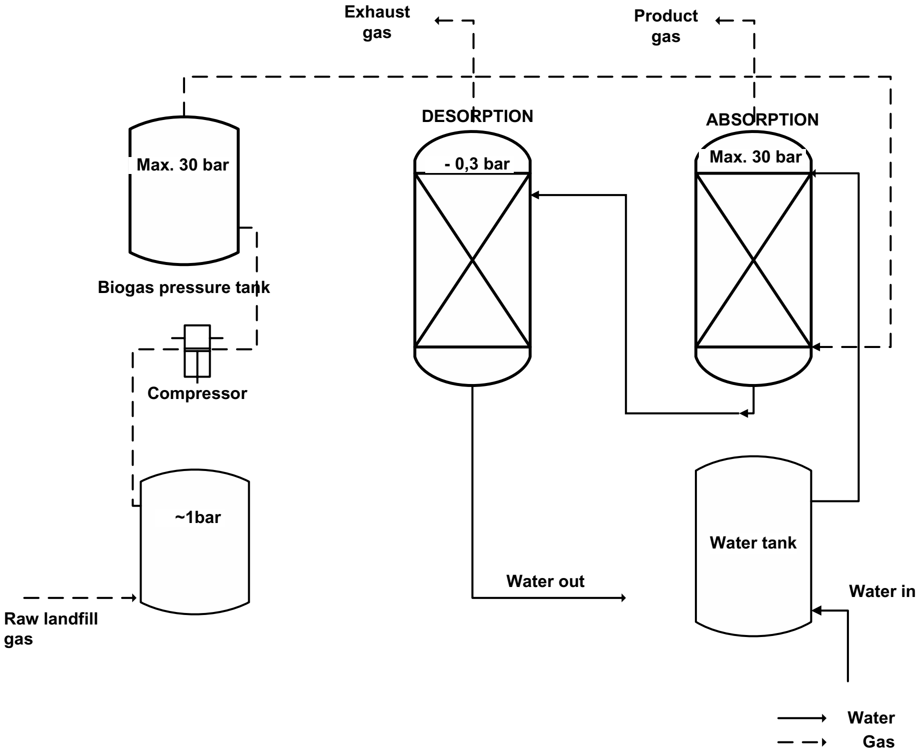

FIGURE 2 Simplified diagram of the counter-current water wash upgrading process.

High pressure water wash process

The high pressure water wash process contained two adjacent absorption columns (10 l), a collector column (10 l) and a product gas storage bottle (75 l) (Fig. 3). The raw gas was obtained from the landfill gas pumping station after condensation (considered dried gas). The two absorption columns were operated alternately to ensure continuous operation. The upgrading facility also included a raw gas storage column (50 l) and two columns for water treatment (500 l each) (Fig. 3). The collector column was filled with plastic pall rings to prevent water foaming in the column. The gas drying unit was placed between the collector column and the product gas storage bottle.

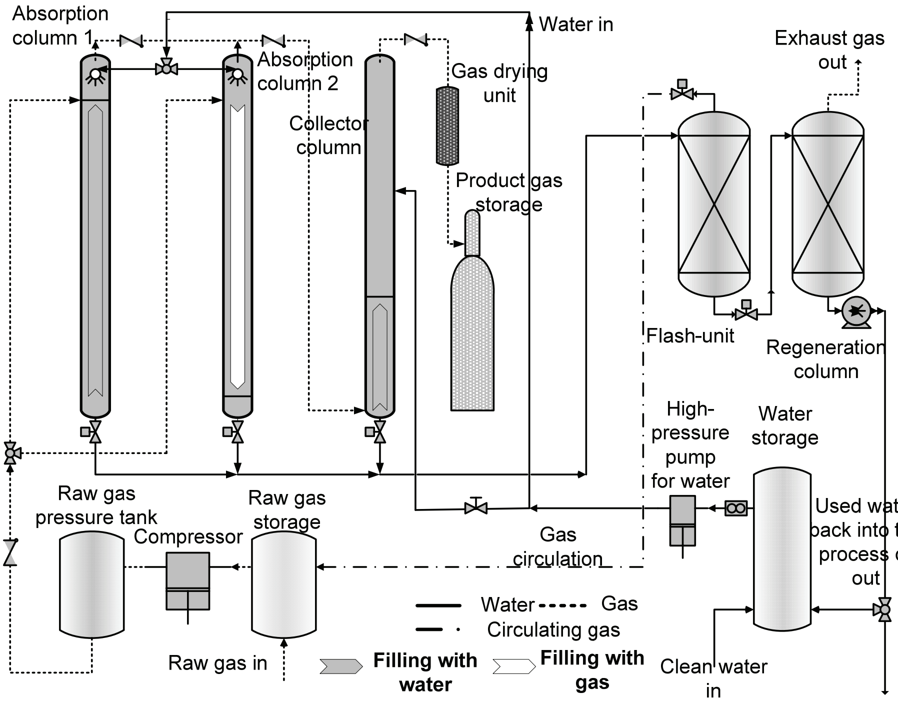

FIGURE 3 Simplified diagram of the high pressure upgrading process.

First, the raw landfill gas was channelled into the raw gas storage column. The raw gas was then pressurised in the raw gas pressurising unit up to 8 and 10 bar (initial pressure). The initial pressure controlled the water and raw gas flow ratio in the absorption columns, since at the lower initial pressure less raw gas was channelled into the absorption columns (ideal gas equation) and, because the water flow was kept constant, more water per gas volume was used for upgrading. The initial pressures of 8 and 10 bar were selected after pre-trials of initial pressures of 10 and 14 bar in which 10 bar was found to produce higher methane enrichment. The pressurised raw gas was then channelled into the absorption column 1. After the absorption column 1 was filled with gas, the raw gas was channelled into the absorption column 2 and water (ca 16 °C) sprayed into the column 1 from the top of the column. The rising water level pressurised the gas in the column 1 and absorption was performed at pressures ranging from 50 to 170 bar in all trials. When the pressure in the column 1 reached the pressure of the collector column, the gas and the water in the column 1 were channelled into the collector column. The upgrading continued in the collector column as the gas from the absorption column 1 was channelled into the collector column from the bottom of the column and fresh water from the middle of the column. The gas was upgraded to its final purity in the collector column and then channelled into the gas storage bottle. The pressure in the collector column was dependent on the pressure in the gas storage bottle so that when the pressure in the collector column reached the product gas storage pressure, the upgraded gas was channelled into the product gas storage bottle from the collector column. The pressure in the product gas storage bottle was maintained at over 100 bar at all times. The pressure in the product gas storage bottle increased during the trial. At the end of the trial the gas was pressurised to about 180 bar. After all the gas had been channelled from the collector column into the product gas storage bottle, the absorption column 2 was filled with water and the process continued as with the column 1. One cycle lasted 36 sec.

The water used in the absorption and collector columns was channelled into a flash tank from where the absorbed methane was released from water at a pressure of 4 bar and returned to the absorption process. From the flash tank the water was channeled into the desorption column (–0.3 bar) where the absorbed carbon dioxide was released from water. After desorption, the water could be reused in the upgrading process. In this study the upgrading process was studied with and without water circulation and with two initial pressures.

3.3 Analysis and calculations

3.3.1 Analysis of main components of biogases

Samples for methane, carbon dioxide, oxygen, nitrogen and sulphur compound measurements were collected in TECOBAG (PETP/AL/PE 12/12/75) aluminium gas bags (volume 10 l). Methane, carbon dioxide, oxygen and nitrogen (I,IV,V) were measured with a Perkin Elmer Autosystem XL gas chromatograph by using a thermal conductivity detector (TCD). Injector, oven and detector temperatures were 50, 45 and 160 °C, respectively. Methane in biogas batch assays (III) was measured using a Perking Elmer Clarus 500 gas chromatograph with flame-ionisation detector (FID). Injector, detector and oven temperatures were 225 °C, 225 °C and 100 °C, respectively. Argon was used as carrier gas. Methane enrichment efficiency was calculated from the upgrading results,

$$Enrichment\,CH_4 = 100 \times \frac{C_p - C_r}{C_r} \tag{2}$$

where C_p is methane content in product gas and C_r is methane content in raw gas. The results of methane potentials (III), main components of biogas and upgrading efficiencies (IV, V) below are given as mean value ± standard deviation.

3.3.2 Analysis of trace compounds of biogases

Ammonia was analysed (I) using Rae Systems gas detection tubes (range 1-30 ppm). Methylmercaptan, dimethylsulphide (DMS) and dimethyldisulphide

(DMDS) were measured (I) with a portable gas chromatograph (Photovac GC/PID). Hydrogen sulphide (I,II,IV,V) was also measured with an infra-red gas analyser (GA 94) equipped with an electro-chemical cell (detection limit 1 ppm), Dräger and Rae Systems gas detection tubes (range 0.2-6 ppm, 2.5-60 ppm, 1-200 ppm, 25-250 ppm and 200-2000 ppm), and a portable gas chromatograph (Photovac GC/PID) (detection limit 0.1 ppm).

Samples of the VOC and organic silicon compounds in biogas (I, II, III, IV, V) were collected in Nalophan NA© bags. The samples were directly drawn into metallic sampling tubes at a rate of 90 ml/min (sample volume typically from 0.5 to 1.5 l/sampling tube) using a Gillian Personal Air Sampler (LFS-113DC). The adsorption material in the sampling tubes was Tenax GR (200 mg in each sampling tube). Before use, the sampling tubes were preconditioned by heating under a stream of nitrogen (flow 0.4 ml/s) at 300 °C for 8 h. Parallel samples were drawn at the same time with branching pieces. Secondary sampling tubes were attached after the primary tubes to collect compounds that have possibly passed through the primary tubes. After sampling the tubes were capped and stored at –18 °C until analysed.

The adsorbed VOC samples were analysed using thermal desorption gas chromatograph-mass spectrometry (Tekmar Purge & Trap Concentrator 3000/Agilent 6890+/5973 N MSD). The GC capillary column used in all the analyses was Agilent Technologies HP5 (film 1 µm, diameter 0.25 mm, 30 m length). The desorption temperature was 230 °C held for 10 min (I, IV,V) and 250 °C held for 10 min (II,III). During desorption compounds are transferred into a cryogenic trap (–120 °C). After desorption the cryogenic trap was heated to 250 °C. The initial GC oven temperature was 40 °C for 2 min and then ramped at 5 °C/min up to 150 °C and 15 °C/min up to 250 °C and held at this temperature for 5 min.

Concentrations of single VOCs (I,IV,V) were calculated according to an external standard. Total concentrations of volatile organic compounds (TVOC) were calculated from hexane to hexadecane as a toluene equivalent. Halogenated, reduced sulphur and organic silicon compounds were calculated as 1,1,1-trichloroethane, DMDS and toluene equivalent, respectively. Qualitative identification was done according to library spectra (NIST D.01.00/NIST D.04.00). For the organic silicon compound analyses (II,III) the MSD was operated in the selected ion mode (SIM). Target ions were selected for each compound (Table 4) with a SIM dwell time of 100. Concentrations of silicon compounds were calculated according to an external standard which comprised seven different organic silicon compounds.

TABLE 4 Selected target silicon compounds and retention times.

Compound	Target ions *m/z*			Retention time [min]	Detection limits [μg/m^3]
Trimethyl silanol	75	76	77	3.7	0.65
L2	147	148	149	6.4	0.65
D3	207	208	209	11.2	0.83
L3	221	222	223	13.3	0.77
D4	281	282	283	17.6	0.57
L4	207	208	209	20.2	0.71
D5	267	268	269	23.3	1.30
L5	281.1	282.1	283.1	25.6	0.64

3.3.3 Analysis of water and digestate from batch assays

In the upgrading experiments absorption water samples (IV,V) were collected before and after the desorption column, and pH, dissolved sulphide and VOCs were determined. Dissolved sulphide was determined by the methylene blue method (Trüper & Schlegel 1961), using an UV/VIS spectrophotometer (Hitachi U-1500). Samples if the inocula used in the batch assays and digestate from batch assays (III) were collected before and after the assays and volatile organic silicon compounds were determined. The VOCs in the water, inocula and digestate samples were analysed using thermal desorption gas chromatograph-mass spectrometry (Tekmar Purge & Trap Concentrator 3000/Agilent 6890+/5973 N MSD). Samples were placed into a sample tube (Tekmar purge and trap tube) and purged with helium for 12 min (80 ml/min). The desorption temperature was 230 °C and held for 10 min. With digestate samples desorption was performed at 250 °C for 10 min. During desorption compounds are transferred into a cryogenic trap (–120 °C). After desorption the cryogenic trap was heated to 250 °C. The initial GC oven temperature was 40 °C for 2 min, then ramped at 5 °C/min up to 150 °C and 15 °C/min up to 250 °C and held at this temperature for 5 min. With the digestate samples the MSD was operated in the selected ion mode (SIM). The GC capillary column used for the analyses was Agilent Technologies HP5 (film 1 μm, diameter 0.25 mm, length 30 m).

3.3.4 Other analyses

The volume of produced biogas in the aluminium gas bags was measured by water displacement. TS and VS were determined (III) according to the Standard Methods (APHA 1998). Methane and carbon dioxide in the biogases (II) were also measured on site with an infra-red gas analyser (GA 94).

For Si determination (III), the materials (grass, maize and inocula) were first dried (24 h, 105 °C), and then pulverized in a Pulverisette 14 (Fritsch, Germany) rotor mill and stored at 22 °C until analyzed. The concentration of Si was measured with a Perkin-Elmer (Norwalk, CT, USA) Optima 4300 DV ICP-OES using different default parameters of the instrument (nebulizer flow 0.5-1.0 L/min, auxiliary gas flow 0.2 L/min, plasma gas flow 15 L/min and plasma power of 1300 or 1400 W) (Väisänen et al. 2008).

4 RESULTS

4.1 Biogas composition (I,II)

The content of methane, carbon dioxide and hydrogen sulphide were determined in all the 14 biogas production plants studied. In the biogases from one landfill (W1) and one WWTP (S1), and from the farm biogas plant oxygen, nitrogen and ammonia were also determined. The highest methane content, 70 %, was detected in the gas from the biogas plant in Ilmajoki, Finland (B4) and the lowest, 47 %, in the landfills in Jyväskylä and Tampere (W1 and W2) (Table 5). The amount of hydrogen sulphide in the landfill gases varied from 27 to 500 ppm and in the biogas plants from 3 to 1000 ppm, while hydrogen sulphide in the gas from the WWTPs was below 4 ppm in all sites.

Variation in the main components of the biogases was determined from the landfill and WWTP in Jyväskylä (W1 and S1) and the farm biogas plant (B5). The lowest variation in the methane (less that 4 %) and carbon dioxide, oxygen and nitrogen (less than 2 %) content of the biogas were detected in the WWTP (S1) and the farm, while in the landfill (W1) the methane and nitrogen contents varied from 10 % to 15 % (Fig. 4). The concentration of ammonia was below the detection limit (1 ppm) in the gas samples from the landfill (W1) and WWTP (S2), while in the samples from the farm biogas plant (B5) the amount of ammonia ranged from 0.5 to 2 ppm.

TABLE 5 Content of methane, carbon dioxide, oxygen, nitrogen, and hydrogen sulphide in biogas from the different biogas producing plants investigated in this study.

Plant		CH_4 [%]	CO_2 [%]	O_2 [%]	N_2 [%]	H_2S [ppm]
Landfills:						
Mustankorkea	W1	47-57	37-43	< 1	< 1-17	36-230
Koukkujärvi	W2	47-62	37-41	n.a.	n.a.	27-32
Tarastenjärvi 1	W3	49-57	32-35	n.a.	n.a.	108-125
Tarastenjärvi 2	W4	51-61	35-37	n.a.	n.a.	53-84
Ämmässuo	W5	50-52	36-38	n.a.	n.a.	300-500
WWTPs:						
Jyväskylä	S1	60-65	34-38	< 1	< 2	< 1-4
Tampere	S2	61-67	33-38	n.a.	n.a.	2-4
Tampere	S3	61-66	35-36	n.a.	n.a.	2-4
Espoo	S4	64-66	34-36	n.a.	n.a.	< 1-2
Biogas plants:						
Kupferzell	B1	56	n.a.	n.a.	n.a.	300
Remlingen	B2	55	44	n.a.	n.a.	300
Vaasa	B3	56-65	38-40	n.a.	n.a.	500-1000
Ilmajoki	B4	65-70	29	n.a.	n.a.	3-5
Laukaa	B5	55-58	37-38	< 1	< 1-2	32-169

n.a. not analysed

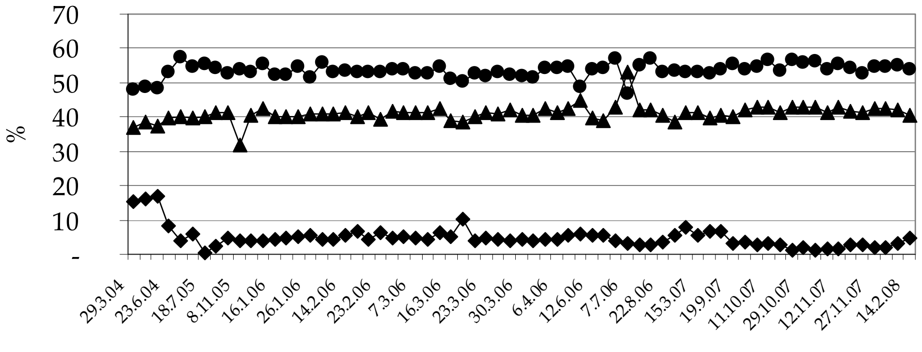

FIGURE 4 Contents of methane, carbon dioxide and nitrogen of landfill gas (W1) at different measurement times (• CH_4; ▲ CO_2; ♦ N_2).

4.2 Trace compounds in biogases

4.2.1 Volatile organic compounds in biogases (I)

The occurrence of VOCs in the landfill (W1), WWTP (S1) and farm biogases was studied. The farm biogas contained lower amounts of TVOCs (from 5 to 8 mg/m^3) than the other gases (Fig. 5), and the variation between samples was small. In the landfill and WWTP, the amounts of TVOCs varied from 46 to 173 mg/m^3 and from 13 to 268 mg/m^3, respectively. Reduced sulphur compounds were found in all the biogas samples (Fig. 6).

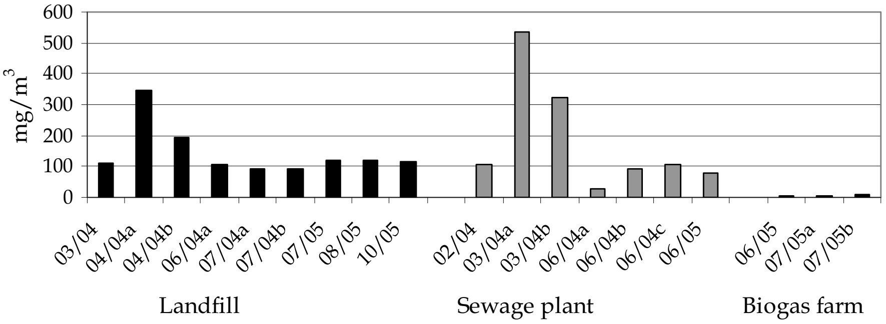

FIGURE 5 TVOC contents in the landfill (W1), WWTP (S1) and farm-scale biogas plant (B5).

Chromatograms from the different gas samples were compared and differences in VOC qualities evaluated. Differences in the amounts and quality of VOCs are shown in Fig. 6, which shows example chromatograms of biogas samples from the landfill (W1), WWTP (S1) and farm, with a list of the major trace components. Gas samples from different plants are on the same scale and thus comparable with each other. In the landfill gas the molecular weights of most of the compounds varied from 62 to 140 g/mol and in the sewage digester gas from 92 to 198 g/mol, as the retention times in the chromatograms show. In the farm biogas, the molecular weights of the compounds varied more widely but their concentrations were lower. Most of the VOCs, especially in the landfill and WWTP gas samples, were aliphatic and aromatic hydrocarbons although organic silicon, halogenated and reduced sulphur compounds were also detected. The landfill gas contained more aromatic and halogenated hydrocarbons than the biogas from either the WWTP or farm. Most of the VOCs from the WWTP were aliphatic, but some aromatic compounds were also present. The biogas from the farm mostly contained reduced sulphur compounds and only small amounts of aromatic and aliphatic hydrocarbons.

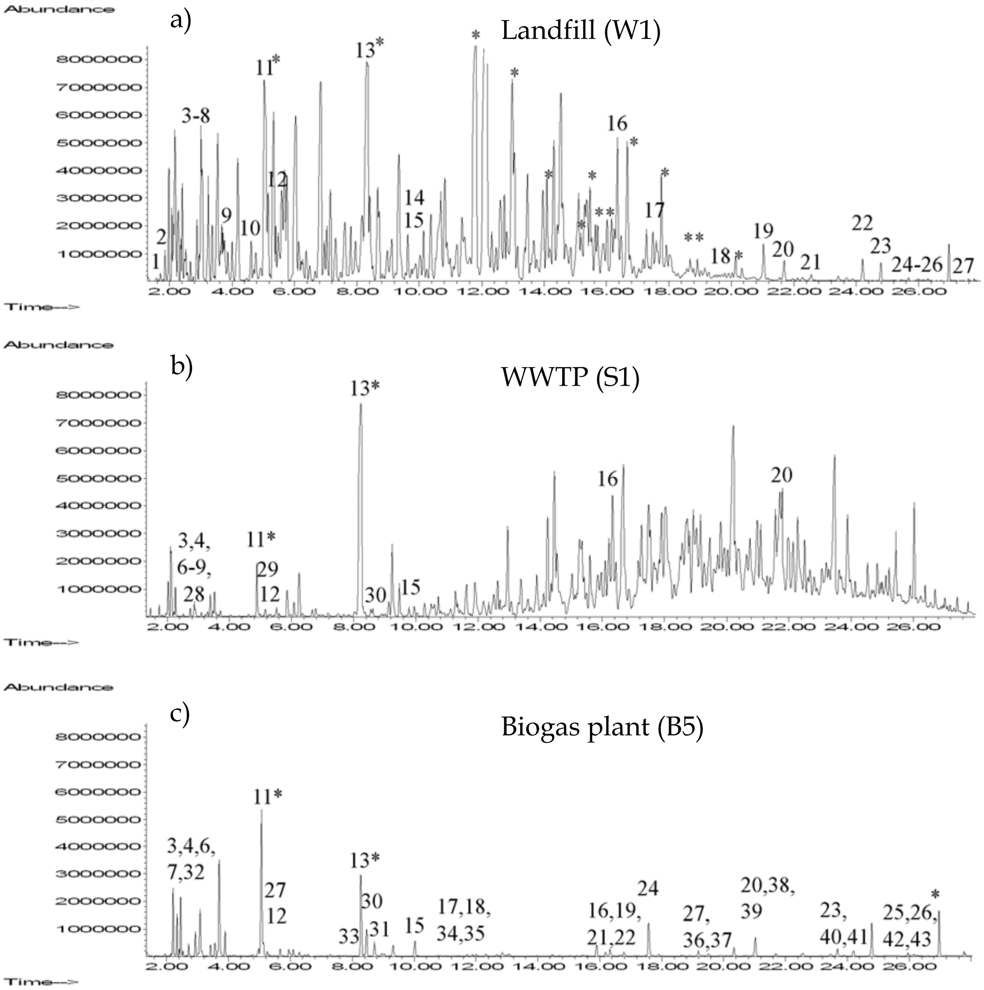

FIGURE 6 Total ion current chromatograms (TIC) of VOCs in a) landfill gas (above), b) WWTP gas (middle) and c) farm biogas plant (below).
(1.) 1-Chloro-1-fluoroethane (1.71), Ethyl chloride (1.80); (2.) Dichlorofluoromethane; (3.) Methylene chloride; (4). Carbon disulphide; (5.) 1-Chloropropane; (6., 8.) Thiols; (7.) Trimethylsilanol; (9.) 1,2-Dichloroethene; (10.) 1,1,1-Trichloroethane; (11.) Benzene; (12.) Hexamethyldisiloxane; (13.) Toluene; (14.) Tetrachloroethylene; (15.) Hexamethylcyclotrisiloxane; (16.) Octamethylcyclotetrasiloxane; (20.) 2,4-bis(trimethylsiloxy) benzaldehyde; (26.) Decamethyltetrasiloxane; (28.) 1-Propanethiol; (29.) Thiophene; (30., 31.) Methylthiophenes; (32.) DMS; (33.) DMDS; (34., 35.) Ethylthiophenes; (17., 18., 19., 21., 22., 24., 27., 36., 37., 38., 39., 40., 41., 42., 43.) Alkyl disulphides (C3-C10); (23., 25.) Alkyl trisulphides (C6); *Aromatic hydrocarbons

Benzene, toluene, halogenated and organic silicon compounds were determined from the VOC samples (Table 6). The landfill gas contained more benzene than either the WWTP gas or farm biogas while toluene content was higher in the

WWTP gas. The benzene concentration in the farm biogas was higher than that in the WWTP gas. The highest variation in concentrations of organic silicon compounds was found in the biogas from the WWTP.

TABLE 6. Concentrations of halogenated and organic silicon compounds, benzene and toluene in biogases from landfill, WWTP and farm biogas plant.

Plant	Halogenated compounds [mg/m^3]	Organic silicon compounds [mg/m^3]	Benzene [mg/m^3]	Toluene [mg/m^3]
Landfill (W1)	0.3-1.3	0.7-4	0.6-2.3	1.7-5.1
WWTP (S1)	< 0.1	1.5-10.6	0.1-0.3	2.8-11.8
Farm biogas plant (B5)	b.d.	< 0.4	0.7-1.3	0.2-0.7

b.d. below detection limit.

4.2.2 Organic silicon compounds in biogases (II)

Eight selected volatile organic silicon compounds (Table 4) were also measured in four landfills (sites W1, W2, W3, W4, W5), four waste water treatment plants (sites S1, S2, S3, S4), and four biogas plants (sites B1, B2, B3, B4) processing different organic material. Trimethyl silanol, L2, D3, L3, D4 and D5 were identified in the landfill gases. Trimethyl silanol, L2, D4 and D5 were found in higher concentrations than L3 or D3. In the biogas from one of the WWTPs (S1), L4 and L5 were also identified along with the same six compounds found in the gas in the landfill and other WWTPs. In the Finnish biogas plants processing WWTP sludge and other waste (B3 and B4), the same six silicon-containing compounds were identified, along with L4 in one sample (B4). In the German biogas plants, processing mainly manure and biowaste (B1) and energy crops (B2), only trimethyl silanol, D3, and D5 were identified (Fig. 7). The concentration of the compounds varied both between plants and between the measurement times in each plant. The highest variations were observed in the landfills, but variation was also noted in the amount of cyclic compounds present in the biogases from the WWTPs. The total amount of organic silicon compounds varied from 24 to 2460 µg/m^3, being lowest in the biogas plant handling energy crops (B2) and highest in one WWTP (S1) (Fig. 8). At one of the WWTPs (S1), one of the samples contained L5 20 µg/m^3 and L4 46 µg/m^3, and at the biogas plant in Ilmajoki (B4) one of the samples contained L4 1.6 µg/m^3. In the other samples, L5 and L4 levels were below the detection limit.

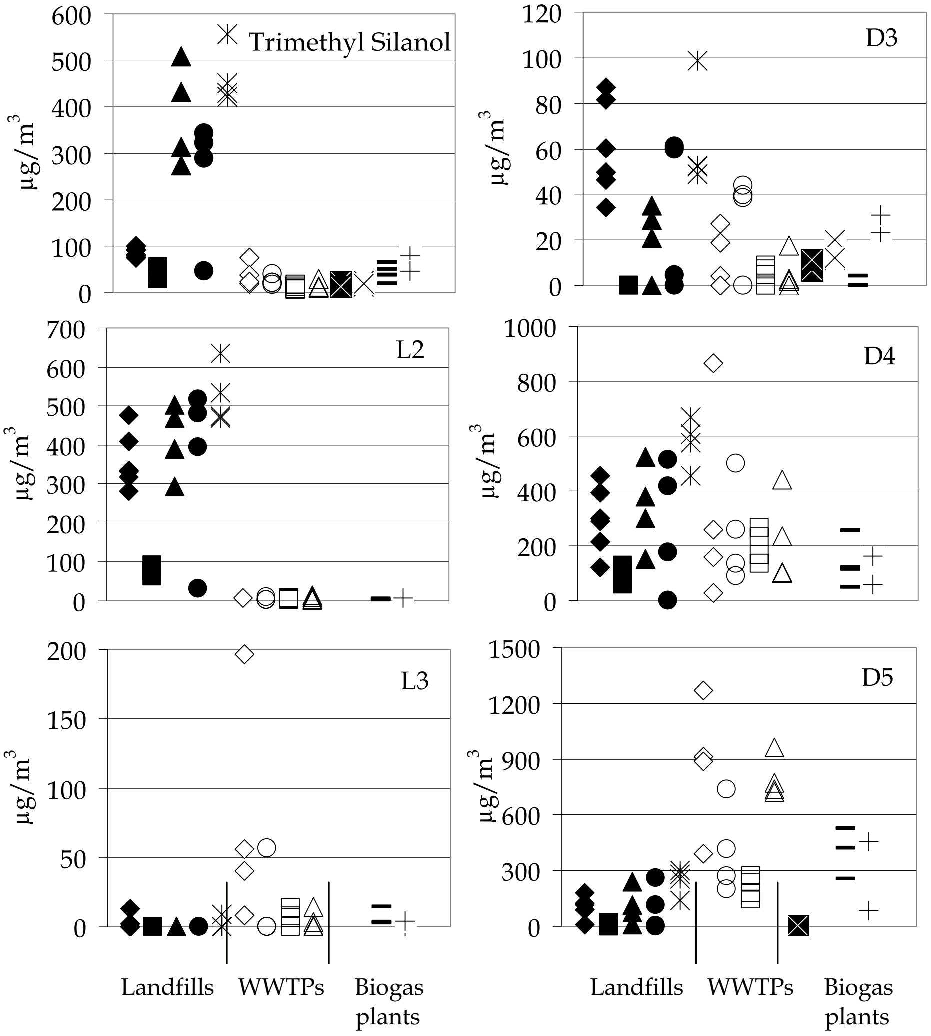

FIGURE 7 Amounts of trimethyl silanol, and different siloxane compounds (L2, D3, L3, D4, and D5) in the studied landfills, WWTPs and biogas plants at different measurement times. All the measured concentrations are presented for each site separately (♦W1; ■W2; ▲W3; ●W4; ЖW5; ◊ S1; ○ S2; □ S3; Δ S4; ☒ B1; x B2; – B3; + B4).

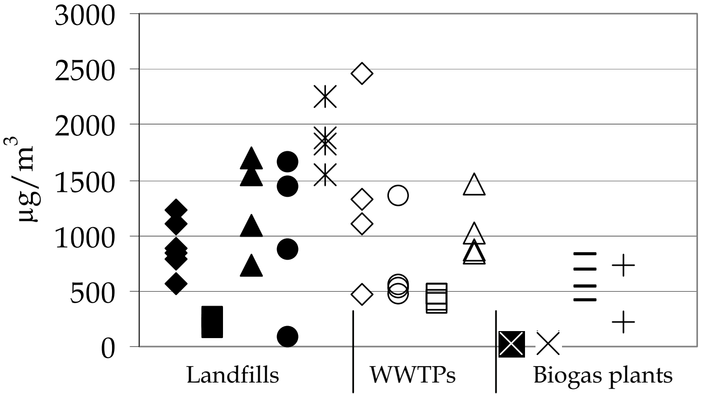

FIGURE 8 Total amounts of organic silicon compounds in the studied landfills, WWTPs and biogas plants at different measurement times. All the measured concentrations are presented for each site separately (♦W1; ▪W2; ▲W3; ●W4; Ж W5; ◊ S1; ○ S2; □ S3; Δ S4; ☒ B1; x B2; – B3; + B4).

The most common silicon compound in the WWTP gas was D5. Together with D4, D5 represented over 90 % of all the organic silicon compounds in the WWTP gas. Also in the biogas plants processing partly sewage sludge, over 80 % of all the organic silicon compounds measured were D5 and D4. In the landfill gas, trimethyl silanol, L2, and D4 were more common than D5, L3, or D3. In the biogas plants processing only manure and biowaste or energy crops, the most common compounds were trimethyl silanol and D3 (Table 7). Fig. 9 shows the chromatographs for a single measurement from a landfill (W5), a WWTP (S1), and two biogas plants (B2 and B3). The chromatograms for the different biogas samples are on the same scale and thus comparable with each other.

TABLE 7 The proportion of different silicon compounds (% of total) in the studied landfills, WWTPs and biogas plants.

	Trimethyl silanol	L2	D3	L3	D4	D5
Sites			[% of total]			
Landfills (W1-W5)	9-30	28-40	0-7	0	27-42	3-13
WWTPs (S1-S4)	1-3	0-1	1-4	0-6	21-45	48-76
German biogas plants (B1-B2)	56-59	0	29-44	0	0	0-11
Finnish biogas plants (B3-B4)	7-13	1	0-6	0-1	22-23	57-70

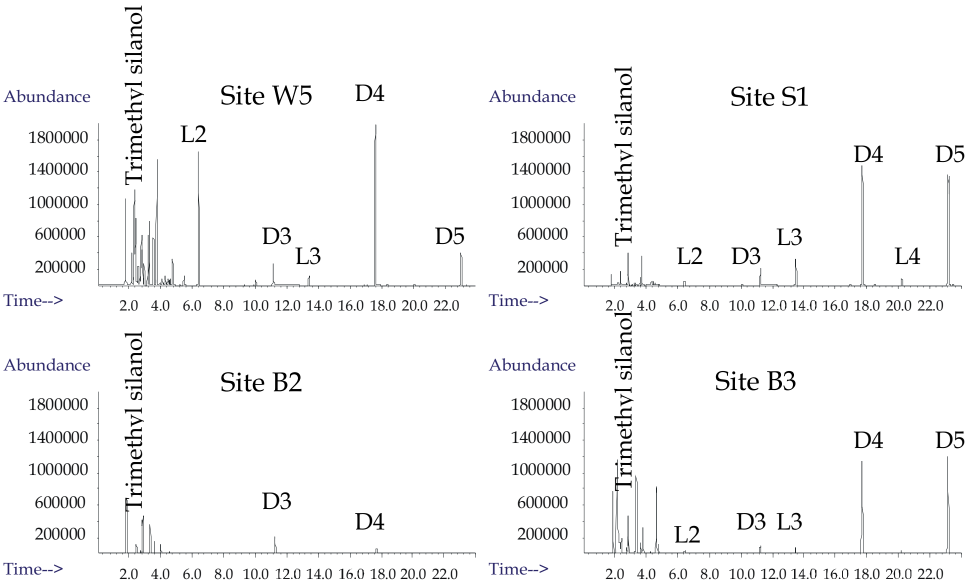

FIGURE 9 An example of a selected ion mode (SIM) chromatograph for biogas from one of the landfills, a WWTP, and two biogas plants (W5, S1, B2, and B3).

The effect of water separation on the concentrations of organic silicon compounds was studied by measuring the organic silicon compounds in one of the landfills (W5) before and after water separation (Table 8): no siloxane removal during condensation was detected.

TABLE 8 The total amounts of organic silicon compounds at site W5 before and after condensation in four samples.

	Total amount of organic silicon compounds [mg/m^3]			
Sample	1	2	3	4
Raw gas	1.6	2.3	1.4	1.9
Gas after 1st condensation	1.8	2.5	1.9	1.8
Gas after and condensation	1.5	2.3	1.9	1.8

4.2.3 Organic silicon compounds in biogas produced from energy crops in the laboratory batch assays (III)

In order to evaluate the occurrence of organic silicon compounds in biogases produced from energy crops, laboratory batch assays were performed using grass silage, grass and maize. The VS, TS, biogas production and methane potential of the different feedstocks were determined. The total amount of biogas produced for the organic silicon measurements varied from 4.1 to 7.3 l/assay, depending on the crop species and duration of the batch assays. The average methane potentials for grass silage, grass and maize, 0.38, 0.42 and 0.34 $Nm^3CH_4/kgVS$, respectively, were determined from duplicate batch assays (Table 9).

TABLE 9 Duration of batch assays, biogas production, TS and VS of crops and inocula and methane potential of grass silage, grass and maize.

Substrate: Code for duplicate and triplicate sample bottles	Organic silicon compound analysis		TS [%]	VS [%]	CH_4 potential analyses	
	Duration of the batch assays [d]	Amount of biogas [l]			Duration of the batch assays [d]	Methane potential [$Nm^3CH_4/kgVS$]
Grass silage:						
S1/S2	10/17	5.1/7.3	33.7	30.9	84	0.38 ± 0.08
Inoculum	20/35*	0.9/1.8*	4.7	3.8		
Grass:						
G1/G2	21/64	5.4/6.1	24.9	23.3	77	0.42 ± 0.05
Inoculum	64	0.6	3.8	2.9		
Maize:						
M1/M2/M3	23	4.1/4.4/5.5	13.6	12.5	88	0.34 ± 0.12
Inoculum	23	2.6	5.5	4.3		

*two inoculum experiments were performed with different durations

The concentrations of volatile organic silicon compounds were measured in the biogases produced in the batch assays during the incubation period (Table 9). Trimethyl silanol and cyclic siloxanes (D3, D4 and D5) were detected in the gases (Fig. 10) produced by the crops and by the inoculum used in the grass silage and grass experiments, while the gas produced by the inoculum used in the maize experiment did not contain D4 or D5. In all the batch assays D3 showed the highest yield [μg/kgVS] while the yields of trimethyl silanol, D4 and D5 were minor. The biogas produced from maize had a lower yield of total silicon compounds than the gas from grass or grass silage. From the gas produced by the inoculum only in the grass silage and grass experiments, L2 was detected at concentrations of 0.006 and 0.06 μg/kgVS, respectively, but was not detected in the biogas produced in the crop assays.

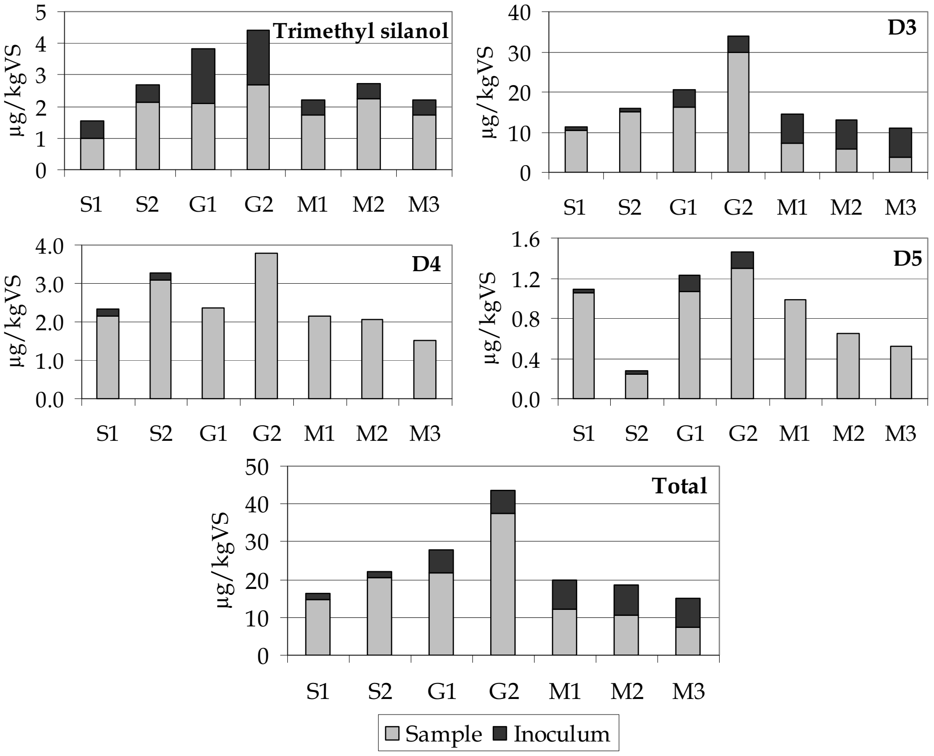

FIGURE 10 Yields of trimethyl silanol and cyclic siloxanes (D3, D4 and D5) detected in biogases in batch assays (effect of inocula subtracted) in two (grass silage, S, grass, G) or three (maize, M) parallel samples and inocula (note different y-scales).

The cumulative yield of the different organic silicon types in the different gas samples were measured in all the gas samples (2-3 per assay in duplicated bottles) collected during the batch assays (Fig. 11). From one of the grass bottles (G2) one sample was taken after incubation for 64 days and the cumulative yields of trimethyl silanol, D3, D4 and D5 were 4.4, 34.0, 3.8 and 1.5 μg/kgVS, respectively.

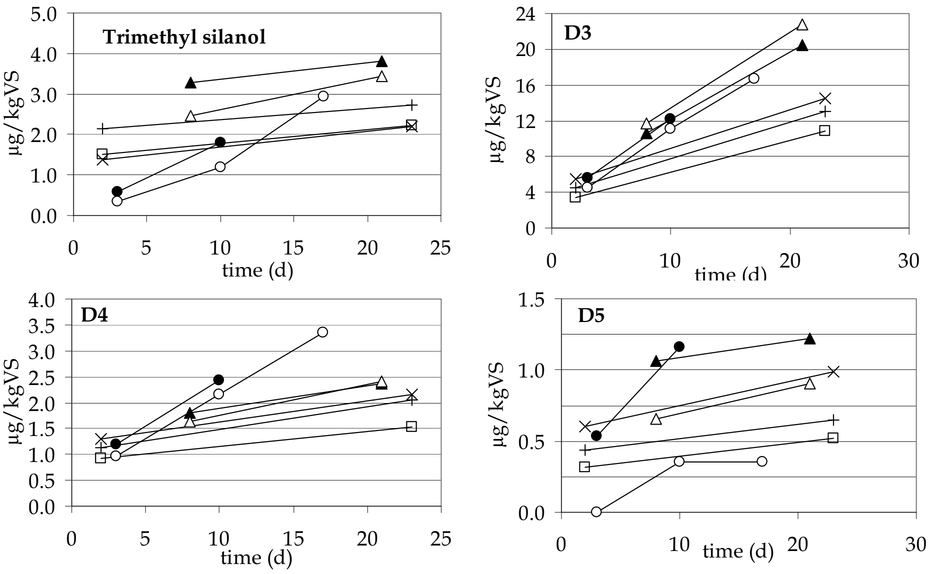

FIGURE 11 Cumulative yields of trimethyl silanol, D3, D4 and D5 in gas samples from batch assays (effects of inoculum not subtracted) with grass silage (● S1; ○ S2), grass (▲G1; Δ G2) and maize (x M1; + M2; □ M3).

The volatile organic silicon compounds in the digestate after the batch assays and in the inocula used for the batch assays were also measured (Table 10). In the grass silage and grass batch assays, the same inoculum was used. The digestate sample from the grass silage assay was taken after 84 days, the sample from the grass assays after 64 and sample from the maize assays after 23 days of incubation. Trimethyl silanol, D3 and D4 were detected in the inocula used for the grass silage and grass assays, in the inoculum digestate from the grass assay and in the digestates from the grass and maize assays. D3 and D4 were also detected in the inoculum digestate from the maize assays. Variation was found in the results for the digestates and inocula used in the experiments between the parallel samples analysed in each crop assay and between the digestates from different crops. No correlation between the inoculum concentration of silicon compounds before or after the batch assays was detected.

TABLE 10 Concentrations of detected organic silicon compounds in the digestates and in inocula used in the assays.

Sample		Trimethyl silanol	D3	D4	Total
		[μg/kg-ww]			
Grass silage	Inoculum (S and G)	0.15	4.82	0.33	5.30
	Digestate, inoculum only	b.d.	b.d.	b.d.	b.d.
	Digestate	b.d.	b.d.	b.d.	b.d.
Grass	Digestate, inoculum only	0.2-0.34	3.6-7.22	0.1-0.41	3.9-8.0
	Digestate	< 0.21	< 0.92	b.d.	< 1.13
Maize	Inoculum	b.d.	b.d.	b.d.	b.d.
	Digestate, inoculum only	b.d.	1.72	0.1	1.8
	Digestate	< 0.1	< 6.3	< 0.4	< 6.7

b.d. below detection limit (for trimethyl silanol, D3 and D4 the detection limits were 0.037, 0.157 and 0.043 μg/kg, respectively), S grass silage, G grass.

The silicon (Si) concentration in the grass, maize and inocula used in the experiments was determined. The concentrations varied, the lowest (387 mg/kg-TS) occurring in grass and the highest (3071 mg/kg-TS) in the inoculum used in the maize experiments (Table 11). The yield of Si volatilized from the batch assays was calculated for grass silage, grass and maize: the values were 3.0 ± 0.7, 5.2 ± 2.0 and 1.7 ± 0.4 μgSi/kg-TS, respectively.

TABLE 11 Silicon concentrations in grass, maize and inocula.

Sample	Si [mg/kg-TS]
Grass	383 ± 67
Maize	578 ± 79
Inoculum for grass experiments	1579 ± 125
Inoculum for maize experiments	3071 ± 374

4.3 Upgrading landfill gas with a counter-current water wash process (IV)

The effects of pressure, and of water and gas flows in the counter-current water wash process on the product gas were studied. During the trials, the methane, carbon dioxide, oxygen and nitrogen contents in the raw landfill gas were 53.2 ±

1.4 %, 40.8 ± 1.0 %, 0.4 ± 0.3 % and 4.9 ± 1.2 %, respectively. The methane content of the product gas was close to or above 90 % at over 20 bar pressure with 10 l/min water flow and at 30 bar pressure with 5 l/min water flow (Fig. 12). Over 68 % methane enrichment and over 90 % carbon dioxide removal efficiencies were obtained with 10 l/min water flow at over 20 bar pressure and with 5 l/min water flow at 30 bar (Fig. 12). Oxygen and nitrogen were not removed under any of the conditions studied, and nitrogen concentration in the product gas increased by about 2 % over that in the raw gas (data not shown). During the trials, the hydrogen sulphide content of the raw landfill gas ranged from 30 to 120 ppm, and it was removed from the product gas below the detection limit (0.1 ppm) in all the conditions studied (data not shown).

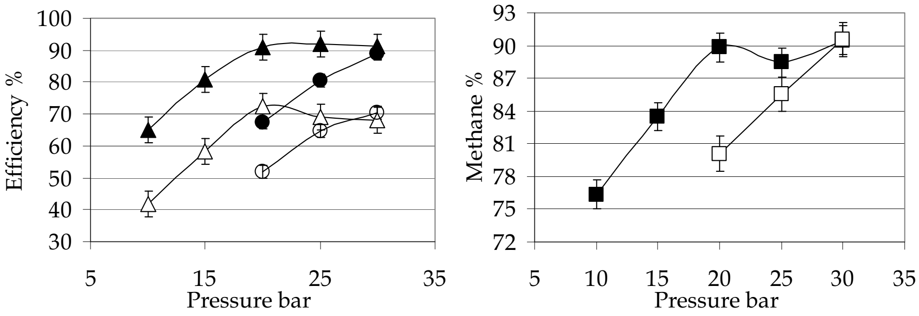

FIGURE 12 The effects of pressure and water flow rates of 5 and 10 l/min on carbon dioxide removal, methane enrichment efficiencies (left) and methane content (right) (▲ CO_2, water flow 10 l/min; Δ CH_4, water flow 10 l/min; • CO_2, water flow 5 l/min; ○ CH_4, water flow 5 l/min; ■ water flow 10 l/min; □ water flow 5 l/min).

The effects of the gas/water flow-ratio (ratios 5-20, gas flows 50 and 100 l/min, water flows 5 and 10 l/min) on methane enrichment and carbon dioxide removal efficiencies were studied at 30 bar. The highest pressure was selected for these trials due to its high upgrading efficiency, as found in the present studies. In all the gas/water flow-ratios studied, the product gas contained over 90 % methane and less than 4.5 % carbon dioxide, indicating that the gas and water flows applied had no effect on the upgrading efficiency (Table 12).

TABLE 12 The effect of gas and water flow ratio on upgrading efficiency and on the contents of the main components of the product gas at 30 bar pressure (from 6 to 10 trials in each condition settings).

Water flow rate [l/min]	Gas flow rate [l/min]	Product gas [%]			CH_4 enrichment efficiency [%]	CO_2 removal efficiency [%]
		CH_4	CO_2	N_2		
10	100	90.5 ± 1.2	3.7 ± 0.9	7.0 ± 0.5	68.0 ± 4.7	91.1 ± 2.3
10	50	91.5 ± 2.5	4.5 ± 1.3	6.8 ± 0.7	68.4 ± 5.6	88.2 ± 3.3
5	100	90.5 ± 1.2	4.5 ± 0.8	7.1 ± 1.0	70.4 ± 5.5	89.0 ± 2.0
5	50	90.1 ± 1.4	4.2 ± 1.7	7.4 ± 1.0	68.4 ± 5.2	89.7 ± 4.1

Removal of VOCs in the raw gas was studied at 30 bar pressure, with water flow of 10 l/min and gas flow of 100 l/min. The raw gas contained mainly aliphatic and aromatic hydrocarbons, which were not removed in the upgrading process. Also, reduced sulphur compounds, halogenated compounds and organic silicon compounds were detected in the raw gas. Organic silicon compounds were not removed while reduced sulphur compounds and halogenated compounds were removed from the product gas (Table 13).

TABLE 13 The amounts of TVOCs, organic silicon compounds, reduced sulphur and halogenated compounds in raw gas and product gas (30 bar pressure, 10 l/min water flow, 100 l/min gas flow).

	Raw gas [mg/m^3]	Product gas [mg/m^3]
TVOC	24.2-149.4	33.8-142.8
Organic silicon compounds	0.3-2.8	0.5-3.1
Reduced sulphur compounds	0.3-1.3	< 0.3
Halogenated compounds	1.7-4.6	< 0.2

The effects of pressure (10, 15, 20, 25 and 30 bar) and water flow (5 and 10 l/min) on the methane content of the exhaust gas was studied using pressures of 0 and –0.3 bar (vacuum) in the desorption column. The methane content of the exhaust gas increased with increasing pressure up to 15 % at 30 bar pressure (Fig. 13) with both water flows. With the lower (5 l/min) water flow the methane content in the exhaust gas was lower than with the higher (10 l/min) water flow. The carbon dioxide content of the exhaust gas ranged from 73 % to 82 %, and hydrogen sulphide content was over 100 ppm in all of the conditions studied.

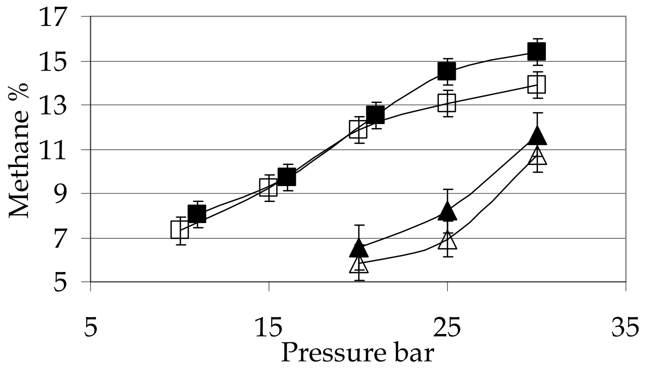

FIGURE 13 The effect of pressure and water flow on methane content in exhaust gas. (■ water flow 10 l/min, 0 bar; □ water flow 10 l/min, –0.3 bar; ▲ water flow 5 l/min, 0 bar; Δ water flow 5 l/min, –0.3 bar).

The VOCs in the exhaust gas were analysed at 30 bar pressure, with a water flow of 10 l/min, gas flow of 100 l/min and pressure in the desorption column of 0 bar. The concentrations of TVOCs, organic silicon compounds, benzene, reduced sulphur and halogenated compounds in the exhaust gas were 46.2 ± 17.1 mg/m^3, 1.0 ± 0.3 mg/m^3, 1.1 ± 0.5 mg/m^3, 1.0 ± 0.1 mg/m^3 and 3.1 ± 1.4 mg/m^3, respectively.

The absorbent water quality was studied before and after desorption. It was not possible to separate the effect of the absorption or desorption unit conditions on water quality because of the slow rate of water circulation in the process. The TVOC concentration in the water samples increased during the studied period, but in the individual trials the TVOC concentrations were lower after than before desorption (data not shown) (Table 14). The pH of the water increased after desorption (Fig. 14), while the dissolved sulphide concentration after desorption was below the detection limit of 0.01 mg/l in all the water samples.

TABLE 14 TVOC, benzene, organic silicon, reduced sulphur and halogenated compounds in process water before and after the desorption unit.

	Before [μg/l]	After [μg/l]
TVOC	730-1380	515-1250
Benzene	12-25	10-14
Organic silicon compounds	9-13	3-19
Reduced sulphur compounds	3-22	4-8
Halogenated compounds	18-96	11-75

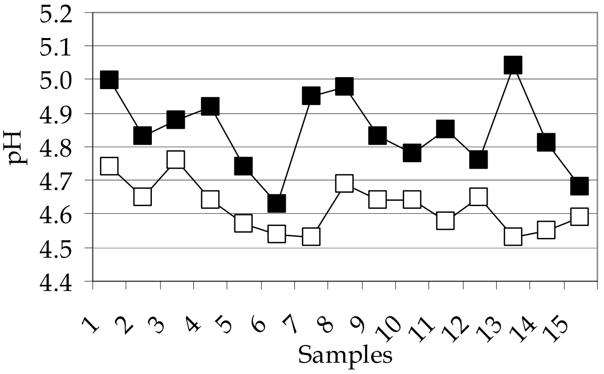

FIGURE 14 pH of absorbent water before (□) and after (■) desorption.

4.4 Upgrading landfill gas with a high pressure water wash (V)

The upgrading of the landfill gas in a high pressure water absorption process was studied using an on-site pilot facility with two (8 and 10 bar) initial pressure settings and with and without circulation of the absorbent water. The water flow in the process was kept constant but water circulation decreased the amount of pure water needed. The initial pressure affected the amount of raw gas upgraded per hour. With the higher initial pressure settings the amount of raw gas increased and less water was used per volume of upgraded gas (Table 15). During the experiment ca 45 trials were conducted. A typical trial lasted from 1.5 to 3 h and from 4 to 12 m^3 of raw landfill gas was upgraded in each trial.

TABLE 15 Raw and product gas composition with different process parameters.

Initial pressure [bar]	Water circulation	Water [m^3/h]	Raw gas [m^3/h]	Water / Raw gas [m^3/m^3]
8	off	0.5 ± 0.07	2.8 ± 0.4	0.20 ± 0.03
10	off	0.6 ± 0.05	3.6 ± 0.4	0.17 ± 0.01
8	on	0.2 ± 0.04	2.7 ± 0.5	0.06 ± 0.01
10	on	0.1 ± 0.02	3.1 ± 0.5	0.04 ± 0.01

The methane content of the raw gas was 55 ± 1.5 % during the trials. The methane content of the product gas was 88 ± 2 % with both initial pressures and with and without water circulation (Table 16). Carbon dioxide content was 42 ± 2 % in the raw gas and 5 ± 0.5 % in the product gas. The nitrogen and oxygen contents of the raw gas were 4 ± 2 % and < 1 %, respectively, and neither were removed in the upgrading process.

TABLE 16 The raw and the product gas composition with different process parameters (from 6 to 8 trials in each condition).

Initial pressure [bar]	Water circulation	Raw gas [%]	Product gas [%]		
		CH_4	CH_4	CO_2	N_2
8	off	54 ± 1.0	88 ± 1.7	4.8 ± 0.4	5.9 ± 1.7
10	off	55.3 ± 2.3	86.8 ± 2.8	5.0 ± 0.6	7.2 ± 2.5
8	on	55.0 ± 1.3	89.0 ± 1.9	5.3 ± 0.3	3.8 ± 0.9
10	on	55.4 ± 1.3	87.0 ± 0.6	5.9 ± 0.3	5.9 ± 1.0

The efficiency of methane enrichment and carbon dioxide removal was 60 ± 4 % and 87 ± 1 %, respectively (Fig. 15), the value for methane enrichment efficiency being higher with 8 than 10 bar initial pressure. With the initial pressures of 8 and 10 bar 0.84 and 0.82 g CO_2/100 g H_2O, respectively, was dissolved in water. Water circulation had no effect on methane enrichment at either initial pressure.

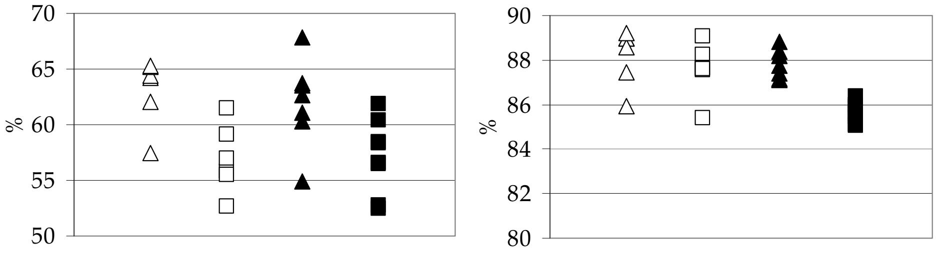

FIGURE 15 Methane enrichment (left) and carbon dioxide removal (right) efficiencies with and without water circulation and with two initial pressures in different trials (Δ 8 bar, no water circulation; □ 10 bar, no water circulation; ▲ 8 bar, water circulation; ■ 10 bar, water circulation).

The initial pressure had no effect on the efficiency of carbon dioxide removal, while the efficiency slightly decreased with water circulation when the initial pressure was 10 bar. The drying unit had no effect on methane, carbon dioxide, nitrogen, oxygen nor hydrogen sulphide removal (data not shown).

During the trials, the hydrogen sulphide content of the raw landfill gas ranged from 42 to 150 ppm, while in the product gas it was below the detection limit (1 ppm) in all the conditions studied (data not shown). The amounts of reduced sulphur compounds, halogenated compounds, toluene and benzene in the VOC samples were analyzed (Table 17). The removal efficiencies were: for reduced sulphur compounds from 79 to over 99 %, for halogenated compounds from 83 to 91 %, for toluene from 30 to 85 % and for benzene over 99 %. The drying column had no effect on the removal efficiencies of these compounds, since they were removed in the absorption columns (data not shown).

TABLE 17 Amount of reduced sulphur, halogenated compounds, toluene and benzene in raw gas and in product gas.

	Reduced sulphur compounds	Halogenated compounds	Toluene	Benzene
		[mg/m^3]		
Raw gas	0.5-1.6	1.0-2.5	1.6-3.1	0.6-1.2
Product gas	< 0.3	0.1-0.6	0.2-2.0	< 0.03

The organic silicon compounds in the VOC samples were analyzed before and after the gas drying unit. Trimethyl silanol, hexamethyldisiloxane (L2), hexamethylcyclotrisiloxane (D3) and octamethylcyclotetrasiloxane (D4) were detected in the samples (Table 18). The concentration of the compounds varied across the samples, and in some samples the concentration was higher in the undried product gas than in the raw gas. Concentrations of organic silicon compounds were lower after the gas had been channeled through the drying unit. The removal efficiencies for L2, D3 and D4 were 4 %, 70 % and 98 %, respectively, and the total removal of organic silicon compounds was 66 %. Trimethyl silanol was detected in one raw gas sample (10 μg/m^3) but not in the product gas samples.

TABLE 18 Amount of organic silicon compounds in the raw gas and in the product gas before and after the drying unit.

	L2	D3	D4	Total
		[μg/m^3]		
Raw gas	308-603	135-223	183-1179	627-1751
Product gas before drying	499-1084	84-266	142-1013	741-2182
Product gas after drying	250-685	12-102	1-43	342-698

During the first six trials the methane content of the exhaust gas ranged from 2.5 % to 4 %, thereafter increasing to 8 %, and varying during the last trials from 8 to 12 %, indicating that methane recovery from the flash tank was not working properly. The pressure of the flash tank was reduced from 4 to 2 bar in some trials, after the methane content had increased to 10 %, to study the effect of the flash tank on the efficiency of methane circulation and methane losses. With lower pressure in the flash tank the methane content varied from 8 to 10 %. In the exhaust gas carbon dioxide content ranged from 65 to 81 %, nitrogen content from 2 to 12 % and hydrogen sulphide content from 24 to 200 ppm during all the trials and no correlation with time or flash-tank pressure was detected. No effect of water circulation or initial gas pressure on exhaust gas content was observed.

The composition of the gas circulated at the beginning of the upgrading process from the flash tank was measured when the initial pressure of the process was 10 bar and water circulation was on. The content of methane, carbon dioxide and nitrogen ranged from 57.7 ± 0.6 %, 37.5 ± 1 % and 5.5 ± 1.2 %, respectively.

The process water was sampled before and after the desorption column and from the water storage tank when water circulation was on. The pH of the water increased from 4.7 to 5.8 after desorption. Despite the input of fresh water, the pH of the water in the water tank was lower than that of tap water (pH about 7) during water circulation (Table 19). The concentration of dissolved sulphide after desorption was below the detection limit of 0.01 mg/l both with and without water circulation (data not shown).

TABLE 19 The pH in the water samples when water circulation was on.

pH	Before desorption	After desorption	Water tank before trials	Water tank after trials
With water circulation	4.7-5.2	5.1-5.8	5.1-5.3	5

5 DISCUSSION

5.1 Biogas composition –major components (I, II)

The higher methane content observed in the biogases from WWTPs and biogas plants in this study makes the utilisation of biogas easier and apparently less expensive, although the concentration of methane in some of the landfills was on the same level as in the studied WWTPs and biogas plants. The amount of methane and carbon dioxide determined in the different biogases in the present landfills and WWTPs resemble those found in previous studies in landfills and WWTPs (Table 20).

The content of nitrogen and oxygen in biogases from WWTP and biogas plants is usually low, as was also the case in this study, because the biogas is produced in sealed tanks, preventing contact with air. The presence of nitrogen and oxygen in the landfill gas is due to air flow in the gas collection pipes. In landfills gas recovery (and gas composition) is controlled by the vacuum pressure in the gas collection system. If the vacuum pressure is small, the air flows from the surface of the landfill into the collection system are also small, but the gas also can pass through the gas recovery system. On the other hand, if the vacuum pressure is high, the air flows into the collection system will also be high and may reduce anaerobic degradation and, by increasing nitrogen and oxygen contents, reduce the energy value of the landfill gas (Popov 2005). High amounts of air in landfill gas can also be harmful because higher concentrations of oxygen increase the risk of explosion, although the levels of oxygen in the landfill gas studied here were less than 1 %.

In the present study the lower methane and higher nitrogen contents observed in the landfill gas (W1) at the beginning of the study were either due to adjustments in the gas recovery system or due to differences in landfill gas production. In landfills gas production is dependent on the degradation status of the waste material as well as on moisture and temperature, all of which may vary greatly in different parts of the landfill body. Because the process is relatively constant, variation in the methane content of the biogas in WWTP

TABLE 20 Methane, carbon dioxide, oxygen, nitrogen and hydrogen sulphide contents in biogas from different biogas-producing plants.

Biogas	CH_4 [%]	CO_2 [%]	H_2S [ppm]	Reference
Landfills	47-62	32-43	27-500	This study
Landfill	59-68	30-37	15-427	Shin et al. 2002
Landfill	37-62	24-29	n.a.	Allen et al. 1997
Landfill	55	37	n.a.	Eklund et al. 1998
Landfill	44	40	250	Jaffrin et al. 2003
WWTPs	60-67	33-38	< 1-4	This study
WWTP	58	38	63	Spiegel & Preston 2003
WWTP	63	37	n.a.	Stern et al. 1998
WWTP	58	34	24	Spiegel & Preston 2000
Biogas plants	55-70	37-40	3-1000	This study

n.a. not analysed

and biogas plants is usually lower than in landfills. The variation in methane content between different biogas plants may be more of greater importance as the different raw materials used in the processes produce different methane yields (Lehtomäki 2006). In this study the methane content in different biogas plants varied from 55 to 70 %.

The hydrogen sulphide content of the biogas in the WWTPs studied here was lower than that in the other biogases or in previously reported digester biogases (Table 20). In Finland in WWTPs, ferro sulphate ($FeSO_4$) is generally used to precipitate phosphorus from sewage. $FeSO_4$ also precipitates hydrogen sulphide under the anaerobic sludge digestion condition. In biogas plants adding oxygen or air into the digester chamber is a method commonly used to remove hydrogen sulphide from biogas. With this method hydrogen sulphide is commonly reduced to concentrations below 50 ppm (Persson et al. 2006).

5.2 Trace compounds in biogases

5.2.1 Volatile organic compounds in biogases (I)

The present results showed some differences in the contents of trace compounds in the biogases from the plants producing biogas from different and varying proportions of substrates under different conditions. Levels of trace compounds are dependent on the stage of decomposition and on the composition of the feedstock (Allen et al. 1997). Differences in biogas composition should be taken into account when planning biogas utilisation because certain compounds, such as the VOC and sulphur compounds found in all the biogases in the present study, can cause health problems to humans, have negative environmental impacts, such as GHG emissions, and damage engines when used as a source of energy (Shin et al. 2002).

The fact that the TVOC content and variation in that content was lower in the farm biogas (B5) than in the landfill (W1) and WWTP (S1) gases in this study was probably due to the more homogenous feedstock (manure and confectionery by-products) used in the farm biogas plant. Although much waste material is recycled, wastes in landfills continue to contain a wide range of different materials, and probably some hazardous waste from the time before segregation. In the WWTP, biogas production takes place in a stable environment, but the source of the treated material is both industrial and household. The presence of and variation in biogas VOC content in landfills has also been reported by other researchers (Allen et al. 1997, Shin et al. 2002). Although the concentration of TVOCs in this study varied across the different samples and different biogas producing plants, the trace components were similar from sample to sample for a given location. In the case of landfill gases this has also been reported by other researchers (Eklund et al. 1998, Shin et al. 2002). The higher amounts of aromatic compounds in the present landfill compared to sewage digester or farm biogases (Fig. 6) are probably associated with older waste (Allen et al. 1997), although high concentrations of aromatic compounds have also been measured in urban waste disposal bins (Statheropoulos et al. 2005). Aromatic compounds are produced during the anaerobic process via the breakdown of abundant lignins (Wilber & Murray 1990). Levels of alkanes and aromatic compounds as well as those of halogenated and oxygenated compounds are dependent on the stage of decomposition and on the composition of waste (Allen et al. 1997). In their studies on halocarbons in landfill gases, Allen et al. 1997 and Jaffrin et al. 2003 detected from 118 to 735 and 169 mg/m^3 of total chloride, respectively, and from 63 to 256 and 25.9 mg/m^3 of total fluorine. In the present study the total amount of halogenated compounds was even lower (0.3-1.3 mg/m^3) than either of the above mentioned alone.

In the present study the biogas from the farm contained greater amounts of different reduced sulphur compounds than the gas from either the landfill (W1) or WWTP (S1) (Fig. 6). In biogas, hydrogen sulphide and other sulphide compounds originate in anaerobic conditions along several different pathways (Wilber & Murray 1990). For example, methanethiol and DMS are formed from the degradation of sulphur-containing amino acids (present, e.g., in manure) and from the anaerobic methylation of sulphide. DMS is reduced to form methane and methanethiol, following methanogenic conversion. Methanethiol later forms methane, carbon dioxide and hydrogen sulphide (Lomans et al. 2002).

5.2.2 Organic silicon compounds in biogases (II)

The present study shows that in the landfills and WWTP biogases studied, the total amount of organic silicon compounds ranged from 77 to 2460 µg/m^3 and that no typical concentration could be defined for any one site. From one of the landfills (W1) and one of the WWTPs (S1) total concentrations of organic silicon compounds up to 4.0 and 10.6 mg/m^3, respectively, were also detected but these results are not included in this comparison as these measurements were analysed by a different method and only total amounts of organic silicon compounds were determined. In addition, the biogas plants processing partly sewage sludge had organic silicon compound concentrations ranging from 220 to 820 µg/m^3, which was lower than in most of the studied landfills and WWTP biogases but higher than in the biogas from one of the landfills (W2) and one of the WWTPs (S3). The biogases from the plants processing only manure, food waste, or energy crops had fewer organic silicon compounds, these ranging from 24 to 44 µg/m^3, than the other measured biogases.

The total amount of the different organic silicon compounds in the plants studied here varied from 24 to 2460 µg/m^3, which is lower than the total siloxane values previously reported for WWTP digester gases and landfill gases, which have ranged, for example, from 20 to 59.8 mg/m^3 and from 4.8 to over 50 mg/m^3, respectively (Schweigkofler & Niessner 2001, Hagmann et al. 2002, McBean 2008). On the other hand, the concentrations of individual organic silicon types have shown significant variation between different studies (Table 21). In fact, concentrations as low as and even lower than those in the present study have been measured for individual types. For example, in the studies by Schweigkofler & Niessner (1999, 2001) concentrations of D4 and D5 in WWTPs were higher than in the present study while the concentrations of other organic silicon compounds resembled those found here. The differences could be due to differences in the raw materials and process conditions used in different sites, but no conclusion can be drawn as this type information is not commonly given in reports on biogas composition. Studies on biogas composition have also used different sampling and analytical methods, and thus the possible effects of these should be systematically studied to ensure the comparison of absolute concentrations. Engine manufacturers have set limits for siloxane concentrations varying from 0.03 to 28 mg/m^3. Some of the lowest limits are set by microturbine and gas turbine manufacturers, due to turbine failures experienced earlier with biogas, although examples exist of turbines operating continuously for months on biogas without problems. Although internal combustion (IC) engines are more tolerant of siloxanes than turbines and biogas is commonly used in these engines without any treatment, with IC engines too, SiO_2 deposit increases the need for engine maintenance and thus more engine manufacturers have now set limits on values for siloxanes (Wheles & Pierce 2004). Notwithstanding the variation in the concentrations of organic silicon compounds in this study at each site, the types of compounds and their proportions remained similar in each site when compared to the total concentrations (Table 7).

TABLE 21 Siloxane concentrations in landfill gas and WWTP gas.

	Trimethyl silanol	L2	D3	L3	D4	L4	D5	Ref.
				[mg/m³]				
Landfills	n.d.	6.07	0.49	0.32	12.53	n.d.	4.73	1.
	2.8-3.2	0.7-0.9	0.4-0.44	n.d.	4.8-5.1	n.d.	0.6-0.65	2.
	6.62-7.43	1.04-1.31	0.01	0.03-0.05	7.97-8.84	< 0.01	0.5-1.09	3.
	2.41-3.21	0.38-0.77	0.31-0.45	0.04	4.24-5.03	< 0.01	0.4-0.53	3.
	11-12	3.1-5.0	0.5-0.84	n.d.	10.6-15	< 0.1	3.0-3.3	4.
	n.d.	0.87	0.088	n.d.	2.06	n.d.	0.473	5.*
	n.d.	0.14	0.083	n.d.	1.207	n.d.	0.395	5.*
	n.d.	0.12	0.81	n.d.	2.0	n.d.	3.33	5.*
	n.d.	0.23	n.a.	n.d.	5.03	n.d.	0.83	5.*
	0.03-0.56	0.03-0.63	< 0.1	< 0.01	< 0.67	b.d.	< 0.3	6.
WWTPs	n.d.	0.02	0.04	0.02	0.93	n.d.	6.03	1.
	n.d.	< 0.05-0.08	0.24-0.42	n.d.	6.3-8.2	n.d.	9.4-15.5	2.
	n.d.	< 0.05	0.32-0.35	n.d.	7.5-7.7	n.d.	11.3-12.0	2.
	0.13-0.15	0.05	0.14-0.17	0.03	6.40-6.98	0.13-0.15	8.96-9.65	3.
	0.06-0.08	0.01	0.18-0.2	0.02	2.87-3.02	0.02	2.75-2.81	3.
	0.006-0.07	0.001-0.008	< 0.04	< 0.2	0.03-0.87	< 0.04	0.1-1.27	6.

n.d. not detected, b.d. below detection limit, n.a. not analyzed, * mean values 1. Accettola & Haberbauer, 2005, 2. Schweigkofler & Niessner 2001, 3. Schweigkofler & Niessner 1999, 4. Urban et al. 2009, 5. McBean 2008, 6. This study

Comparison of organic silicon compound concentrations in biogases between different sites is difficult because of the different analytical and sampling techniques used by different laboratories. At the moment there is no standard method for the analysis for organic silicon compounds. Metal canisters, Tedlar bags, the methanol impingement method and Chromosob or Tenax adsorption tubes have all been used for sampling by different authors. Samples have been analyzed, for example, using GC-MS full scan or SIM, GC/FID, CI-MS or GC-MS/AES (Schweigkofler & Niessner 1999, Hagmann et al. 2002, McBean 2008, Popat & Deshusses 2008, Urban et al. 2009).

In the landfill gases in this study, D4 and L2 were the most common compounds followed by trimethyl silanol. This finding mirrors that of Sweigkofler & Niessner (1999), who found the most common organic silicon compounds in landfill gas to be trimethyl silanol, L2, D4, and D5. Similarly, in the study conducted by Wheles & Pierce (2004), approx. 60 % of total siloxanes were found to be D4, followed by L2, D5, and L3. Moreover, in the study by McBean (2008), the majority of the siloxanes in the landfill gases studied were D4 and D5. The differences in the concentrations of siloxanes may be due to the different age of the landfills studied. Indeed, it has been found that the landfills with older waste contain fewer siloxanes than landfills with fresh waste. This may be because the use of siloxanes has increased in recent years. This was also detected in the present study, the lowest concentrations of organic silicon compounds being found in the Koukkujärvi landfill (W2), which was also the oldest landfill studied. The gas from active landfills also has more siloxanes than gas from closed landfills (Wheles & Pierce 2004). However, variations in siloxane concentrations have been detected even with similar municipal waste in landfills in the same country (McBean 2008). All the present landfills receive both industrial and domestic waste and all the landfills are active.

In the WWTP digester gases studied here, the most common organic silicon compound was D5. Together with D4, D5 represented over 90 % of all the organic silicon compounds. In Schweigkofler & Niessner's (1999) study of WWTP gas, a tendency towards less volatile compounds was also observed; the most volatile silicon containing compounds, trimethyl silanol, and L2 were found only in low concentrations and the most common organic silicon compounds were D4 and D5. In a study carried out by Wheles & Pierce (2004), the most common siloxanes in the digester gases studied were D4 and D5, which accounted for over 90 % of the total, with L2 and L3 not being detected. In the present study, trimethyl silanol, L2, L3, and D3 were detected in minor concentrations in WWTP biogas. In one sample from a WWTP in Jyväskylä, Finland (S1), the L3 concentration was 197 $\mu g/m^3$, which was higher than in other samples from both the same site and other sites. In that same sample, L4 and L5 were also detected. The levels of methane and carbon dioxide in that sample were the same as in the other samples and there were no reported differences in the process itself; however, as industrial waste water also enters the plant, the material in the digester varies and this also affects the concentrations of siloxanes.

Differences in the types of silicon compounds present were detected between the German biogas plants (B1/B2) and the Finnish plants (B3/B4). The main organic silicon compounds in the German plants (B1 and B2) were trimethyl silanol and D3, whereas D4 and D5 were more common in the Finnish plants (B3 and B4). The main difference between the processes is the feedstock used; in the Finnish sites (B3 and B4) WWTP sludge was also added to the process. In the German plants (B1 and B2), only manure, food waste, or energy crops were used as raw materials in the process. These differences in the types of the silicon compounds present indicate that the source of silicon in the German plants (B1 and B2) was different from that in the landfills and WWTP studied here.

Trimethyl silanol was more common in the landfill gases than in the biogases from the WWTPs or biogas plants. This was also detected by Grümping et al. (1998), who found from 3.4 to 17.5 mg/m^3 of trimethyl silanol in landfill gases, while in WWTP gases, trimethyl silanol was not detected.

Furthermore, L2 was more common in landfills than other biogases. In the present study D4 and D5 were the most common silicon compounds in all the measured gases, except for the gases from the German biogas plants (B1 and B2), while contributed from 21 to 76 % of all the detected silicon compounds.

In the present study, there were no major differences between the landfill and WWTP digester gases in the total amounts of siloxanes present. The same observation was made by Schweigkofler & Niessner (2001). According to Wheles & Pierce (2004) and McBean (2008), siloxane concentrations are usually higher in digester gases than in landfill gases. This difference has been assumed to be due to the higher operating temperature in WWTP digesters than in landfills. Moreover, if landfills are operated as bioreactors at higher temperatures, siloxane concentrations in the landfill gases may increase (McBean 2008). In the present study, the methane content of the different biogases was also measured and no correlation was found between methane production and the amounts of organic silicon compounds. Although methane content is lower in landfills and the temperature in the landfill body is, in Finnish conditions, also usually lower (from 10 to 39 °C in Ämmässuo landfill (Sormunen 2008)), than in WWTP and biogas plant digesters, organic silicon compounds volatilize to the landfill gas.

Gas condensation had no effect on the amount or types of organic silicon compounds; in the Ämmässuo (Finland) landfill (W5), the compounds were measured before and after gas condensation. In fact, in one sample from Tarastenjävi (Finland) landfill (W3), condensation was not on, while all the samples from the other pumping station in Tarastenjärvi landfill (W4) were taken before condensation, yet no differences were detected between these and the other landfill gases in this study. Schweigkofler & Niessner (2001) studied the effect of biogas refrigeration on siloxane removal. They cooled the biogas temperature down to 5 °C and found that over 88 % of the initial siloxane concentration continued to be present in the biogas. The concentration of trimethyl silanol was decreased in the same study by 27 %. This is most likely a result of its water solubility (Table 1). In the present study, the concentration of trimethyl silanol was decreased by 8 %, and removal of the other organic silicon compound types was not detected. 50 % removal of siloxanes has been reported when the gas is chilled to 4 °C at 25 bar pressure (Wheles & Pierce 2004).

5.2.3 Organic silicon compounds in biogas produced from energy crops in the laboratory batch assays (III)

The results of this study suggest that organic silicon compounds may be present in biogas produced from plant material. Organic silicon compounds have been detected in biogases produced in landfills and sewage digesters (Schweigkofler & Niessner 1999, Hagmann et al. 2002). The source of these compounds is clear since they are widely used in industry and the waste from materials containing silicon ends up in sewage treatment plants and landfills. The presence of siloxanes in crop biogas may also derive from their wide use in industry as these compounds are commonly found in air, water, sediment, sludge and biota

(Kaj et al. 2005). Lehmann et al. (1998) studied the fate of dimethylsilanediol (DMSD) in different soils. They added leaf litter to soil and after 30 weeks varying amounts of DMSD were found in grass, corn and pine litter, possibly through DMSD volatilization. It is also possible that DMSD was degrading within the litter layers. Degradation and volatilization are the mechanisms of DMSD loss from soils. Which of these two mechanisms is more important will depend on both the soil type and field conditions. PDMS has been reported to degrade in all soils, although the rate of degradation is faster in soils with lower moisture content (Griessbach & Lehmann 1999). In the study by Lehmann et al. (1996) varying fractions of PDMS degraded to water soluble molecules with low molecular weight after PDMS had been applied to the soil as a component of sludge. Although large amounts of PDMS were degraded and volatilized, ≤ 2 % of the total was found in plant shoots. According to Grümping et al. (1998), trimethyl silanol is a product of PDMS degradation. However, it is also assumed that other environmental pathways to trimethyl silanol formation exist. VMSs are also widely used in industry but these are also detected as degradation products of PDMS (Accettola et al. 2008).

In the present study the yield of organic silicon compounds was higher in biogas produced in the grass assays than grass silage or maize assays (Fig. 10). For the present experiments the grass silage and maize were collected from the same farm on which the fermentation digestate was used as a fertilizer. The grass was from a farm where chemically produced fertilizers were used. More research needs to be conducted on the effects of fertilizers and soil types on concentrations of organic silicon compounds in plant materials.

The results of the batch assays showed that linear siloxanes were not detected in the biogases from energy crops: however, trimethyl silanol and cyclic siloxanes (D3, D4 and D5) were detected in higher yields than in biogas produced from inoculum only. Linear siloxane (L2) was detected in the biogases from inoculum only, in the grass silage and grass assays. D3 is commonly used in, e.g., chemical products and D4 and D5 in, e.g., fuel additives while linear siloxanes such as L3 and L4 are commonly used in, e.g., paints and varnishes (Kaj et al. 2005). Hence it can be assumed that cyclic siloxanes can more easily end up in plants through the use of fertilisers or farm machinery than linear siloxanes. In other studies cyclic siloxanes, in particular D4 and D5, have also been found in higher concentrations in different media and in biogases from waste water treatment plants than linear siloxanes (Kaj et al. 2005, Appels et al. 2008b). In the European Union, D4, D5 and L2 are chemicals with a high production volume. In the Nordic countries more extensive use of D4 and D5 has been reported while the use of L2, L3 and L4 is limited. In Finland there is no reported use of D3, but as importers are not obliged to register the full content of chemicals for most products, it is difficult to estimate the total use of siloxanes (Kaj et al. 2005). Moreover the soil type may affect the concentrations of siloxanes in plant materials. It has been reported that cyclic siloxanes are PDMS degradation products from pure kaolinite clays while silanols are the major degradation products from montmorillonite clays (Lehmann et al. 1995). According to Griessbach &

Lehmann (1999) DMSD is more rapidly volatilised into the air from soils with lower clay content than from soils with finer textures, after which it is expected to be oxidised in the atmosphere like other small siloxanes and silanols.

In the present study the volatilisation rate of organic silicon compounds varied in the different assays. The increase in the volatilisation rate of D3 was higher with all crops than the rates of the other organic silicon compounds, and the results from one of the grass assays showed that organic silicon compounds continued to be volatilised after 64 days of incubation. This is probably due the capacity of some siloxanes to adsorb into the EPS of sludge flocks. Volatilisation of these compounds depends mainly on the sludge temperature (Dewil et al. 2006) and the properties (e.g. molecular weight, vapour pressure) of different compounds. From the grass silage and maize experiments no samples after 17 and 23 days, respectively, were taken (Table 9), and thus the effect of a longer incubation time in these assays was not studied. The duration of the present batch assays should have been longer to confirm the effect of duration on incubation.

The results of the digestates from the grass silage batch assays showed that trimethyl silanol, D3 and D4 were present in the inoculum used in the experiments, but not in the digestates (Table 10). This was not the case with the grass and maize experiments as the concentrations in parallel samples varied and some of the inocula samples contained more silicon compounds after the assays than they did before the batch assay. The results indicate that longer incubation time affects the concentration of volatile organic silicon compounds in the residue as the digestate samples for the grass silage assays were taken after 84 days of incubation while for the grass and maize assays the samples were taken after 64 and 23 days of incubation. The method used measured the amount of volatile organic silicon compounds in both the inocula and digestates, and thus it was not possible to determine the amounts of organic silicon compounds that were adsorbed to the material and not volatilised during the analysis.

The results of this study showed higher concentrations of silicon in the inocula than in the crops. Also, the silicon concentration was higher in maize (578 mg/kg/TS) than in grass (383 mg/kg/TS); for example, no correlation was found between the concentration of silicon in the substrate and the concentration of organic silicon compounds in the biogas. According to Pahkala & Pihala (2000) the concentration of silicon increases with plant development, and that high silica content is typically found in grass plants because grasses accumulate silicon in the form of silica to protect against herbivores and fungi. Moreover leaf blades have a higher concentration of silica compared to stems and leaf sheaths. The grass for the present measurements was collected in late June and the maize in late August. The results of this study indicate that not all of the organic silicon compounds may volatilise during anaerobic digestion. Differences in the duration of assays and in gas production rates during the batch assays caused differences in the total amounts of organic silicon compounds.

5.3 Landfill gas upgrading with a counter-current and with a high pressure water wash (IV, V)

5.3.1 Product gas quality (IV, V)

This study shows that landfill gas can be upgraded to > 90 % methane content using a counter-current water absorption process at over 20 bar pressure and to 89 ± 2 %methane content using a high pressure (up to 180 bar) system. With the counter-current process used in this study, the optimal operating pressure was 20 bar, with 10 l/min water flow, as higher pressures did not have any significant effect on the upgrading efficiency (Fig. 12). The lower methane content in the product gas at 25 bar pressure than at 20 bar pressure was probably due to variation in the methane content of the raw gas. It also appeared that with the high pressure process studied here, product gas of this quality could be achieved with an initial pressure of from 8 to 10 bar and with water circulation, the consumption of water ranging from 0.04 to 0.06 m^3H_2O/m^3 raw gas. Counter-current water washing has been used in other landfills, resulting in gas with a methane content of about 95 % (Halldórsson 2006) and about 97 % (Roe et al. 1998). In these cases the methane content of the raw landfill gas was around 55 %, i.e., similar to that in the present study; however concentrations of other compounds, such as nitrogen, were not reported. With the membrane technology, landfill gas was upgraded up to 96 % methane content in a system where air intrusion was minimized, and the nitrogen content was kept below 5 % by collecting the gas from wells in the deep core of the landfill (Roe et al. 1998).

The present upgrading processes removed halogenated and sulphur compounds from the landfill gas, although these concentrations in the raw gas were low compared to those found in other studies (Stoddart et al. 1999, Shin et al. 2002) and lower than the concentrations of over 250 mg organic Cl/Nm^3 and over 1500 ppm of hydrogen sulphide considered damaging (corrosive) to gas engines (Stoddart et al. 1999, Environment Agency 2004). For the vehicle use and injection into the natural gas grid, the limits are stricter, < 23 mg/m^3 or < 30 mg/m^3 for total sulphur, < 1 mg/m^3 for chlorine and < 10 mg/m^3 for fluorine (Persson et al. 2006). These parameters were achieved with the present upgrading process.

Most of the VOCs present in the raw gas, mostly aliphatic and aromatic hydrocarbons, were not removed in either of the water wash processes and neither were organic silicon compounds. In fact, slight enrichment of silicon compounds during the absorption process was found as the amounts of organic silicon compounds in the product gas were higher than in the raw gas. This is probably due to the low solubility of these compounds in water. In the present study the drying unit used in the high pressure process removed up to 66 % of total organic silicon compounds. Some organic silicon compounds were removed in the drying unit, which contained silica gel, more efficiently than others: for example, the removal efficiency of L2 was 4 % while that of D4 was 98 %. Removal efficiencies of 75 % and over 98 % were achieved for total organic silicon compounds when silica gel and meadow ore were used as gas pre-treatment installations in a sewage treatment plant (Schweigkofler & Niessner 2001). During the upgrading trials in this study the amounts of organic silicon compounds in the raw gas were less than 2.8 mg/m^3, which were lower than those reported in some previous studies (22 mg/m^3 and up to 50 mg/m^3) (Schweigkofler and Niessner 1999, Stoddart et al. 1999). The total amount of organic silicon compounds in the product gas in the high pressure process (from 0.3 to 0.6 mg/m^3) was below many engine manufacturers recommendations (15 mg/m^3) (Schweigkofler & Niessner 2001), although, with microturbines and gas turbines amounts as low as < 0.03 and < 0.1 mg/m^3, respectively, have been recommended (Wheles & Pierce 2004). In Austria the maximum silicon (Si) content permitted in biogas delivered to the natural gas grid is 10 mg/m^3 (Marcogaz 2006). Because amounts of organic silicon compounds can vary in different locations, upgrading needs have to be estimated separately for every landfill.

5.3.2 Upgrading efficiency (IV, V)

In the present study a methane enrichment efficiency of over 68 % was obtained with a counter-current process operated at a pressure of over 20 bar, which was higher than that obtained in the high pressure process (ca 62 ± 4 % and 57 ± 3 % at initial pressures of 8 and 10 bar, respectively). Carbon dioxide removal efficiencies were similar with both processes. The differences between the two processes were small and did not have an effect on the methane content of the product gas, although strict comparison of these processes is not justified because of variation in the composition of the raw gas in the landfill. The methane enrichment efficiency of ca 60 % achieved with both processes would mean that, e.g., in a situation where the raw gas contained ca 60 % methane and no nitrogen, the product gas would be expected to contain about 96 % methane.

With the counter-current process, carbon dioxide removal increased with increasing pressure at a constant absorbent flow rate, as expected according to Henry's law (Hunter & Oyama 2000), until 20 bar pressure was attained at a water flow of 10 l/min after which maximum removal efficiency was achieved. On the other hand, a higher absorbent flow rate could compensate for lower pressure when the gas and water phase contact surface is higher; for example, at 20 bar pressure at an absorbent flow of 10 l/min a similar upgrading efficiency was obtained as at 30 bar with a flow rate of 5 l/min. The effects of pressure and absorbent flow rate on methane enrichment in this study were not as straightforward because the methane content of the raw landfill gas varied. The variation in carbon dioxide removal efficiency was smaller, as was the variation in carbon dioxide content in the raw gas. In this study the variation in raw gas content was not significant and had a minor effect on the upgrading process. A higher variation, for example in methane content, which has been reported in other landfill gas studies (Shin et al. 2002, Bove & Lunghi 2006), can have a greater effect on the upgrading process.

5.3.3 Effects of pressure, water and gas flow (IV,V)

The dependence of upgrading efficiency on the water and gas flow-ratios applied in the counter-current process studied here was negligible. In previous reports, where the column design have been different, water and gas flow-ratios were more important to upgrading efficiency than the dimensions of the absorption column (Kapdi et al. 2005). A high gas flow rate can cause flooding in the column, and with a high liquid flow rate flooding can occur even at lower gas flows (Schnelle & Brown 2002). In the present study flooding was not experienced at any of the water or gas flow rates. Carbon dioxide removal efficiency was highest at the highest water and gas flows (10 l/min and 100 l/min, respectively), but the differences between the different water/gas ratios were small.

The pressure used in the process may be the main reason for the absence of an effect of a high gas/water ratios. At 20 bar or lower pressure, methane enrichment and carbon dioxide removal efficiencies were more dependent on the water flow rate than at 30 bar pressure. At the higher water flow rates, the highest carbon dioxide removal was achieved at lower pressures while with nitrogen in the raw gas higher methane content could not be achieved. This means that at 30 bar pressure, less water is needed for gas upgrading. Since water is one of the major costs in this process, especially if pure water is used without water circulation, it would be important to consider means to minimize the amount of water. In cases where landfill leachate or other waste water can be used in the process, upgrading at lower pressure and at a higher water flow rate is probably more economical. It is also possible that with higher pressure the life of the equipment is shorter, while pumping and compression energy costs are higher. Both water circulation and use of waste water increases the possibility of biological growth on the packing material, and can lower the upgrading efficiency if the packing material is not regularly cleaned (Tynell 2005). Because of the high solubility of hydrogen sulphide in water over a wide pressure range, neither pressure nor water flow rates had any effect on hydrogen sulphide removal as its concentration in the product gas, in all the conditions studied, remained below the detection limit of 0.1 ppm.

With the high pressure process used in this study, neither water circulation nor initial pressure had an effect on the upgrading efficiency. The fact that the methane enrichment efficiencies (Fig. 15) in the high pressure process varied across different trials (in the same conditions) could be due, apart from variation in the raw gas composition, also to the fact that gas from the flash tank was circulated in the absorbent unit in cycles, thereby causing additional random variation in gas composition and flow to the absorbent unit.

5.3.4 Effect of water circulation on product gas (V)

The fact that circulation of water in the high pressure process did not decrease the methane enrichment or carbon dioxide removal efficiency (as compared to flow-through) suggests that the regeneration process (desorption column) applied in these experiments was effective in removing carbon dioxide from the absorbent water. Also, neither the initial pressure nor water circulation had any effect on the removal of hydrogen sulphide, reduced sulphide compounds, halogenated compounds, toluene and benzene, as these were removed from the raw gas with all the process parameters used. If the water used is not regenerated properly and the same water is used again in the process, the remaining carbon dioxide in water can decrease its absorption capacity. As water circulation did not reduce the efficiency of upgrading in this study, the regeneration of water is the preferred option to reduce the volume of fresh water consumed in the process.

In the high pressure gas upgrading system studied here, the gas was pressurised with water and thus water consumption was not optimized from the absorption standpoint; instead more water was used than was needed for total carbon dioxide solubility. A strict comparison of the water consumption in the present pilot-scale process with that of the other gas upgrading processes is not relevant, but in general from 0.1 to 0.2 m^3 water/Nm^3 raw gas is used in the existing counter-current water wash processes, if they do not include water circulation (Persson 2003). As many of the upgrading plants are in sewage plants they apparently use treated sewage, and thus the cost of water is lower than would be for tap water (Table 22).

5.3.5 Implications for field applications (IV,V)

Depending on the biomethane standards applied in different countries (Persson et al. 2006, Pierce 2007), the upgraded landfill gas obtained with both the processes studied here could be used in several biogas utilisation applications, including vehicle fuel, as 86 % methane is the minimum quality parameter for natural gas vehicles (European Commission 2001) and as compounds harmful to engines, as classified by the EnvironmentAgency (2004), were not found in high concentrations. However, a methane content of from 95 to 97 % is generally expected by many engine manufacturers. The higher relative nitrogen content found in the product gas than raw gas in the present study indicates nitrogen enrichment in the upgrading process, which can be prevented by adding a separate upgrading unit, such as an activated carbon adsorption process (Yang 1987) for nitrogen, or by lowering the nitrogen content in the raw gas, e.g., through changes in the landfill gas collection system. On the other hand, an additional adsorption unit would complicate the process. The nitrogen content of product gas is restricted by Swedish biomethane standards (CO_2+O_2+N_2 < 5 %) but not apparently, by other national standards (Persson et al. 2006). Nitrogen lowers the caloric value of biomethane but does not harm

TABLE 22 Examples of biogas upgrading plants using a counter-current water wash process (Roe et al. 1998, Hagen et al. 2001, Tynell 2005, Halldórsson 2006, Persson et al. 2006).

Country/City	Plant	Type of upgrading plant	Methane in raw gas [%]	Methane in product gas [%]	In operation since
Sweden/					
Eskilstuna	co-digestion	regenerating	64	> 95	2003
Henriksdal	sewage sludge	regenerating	62-64	> 95	2003
Linköping	co-digestion	regenerating	68-69	> 95	1997
Trollhättan	co-digestion	regenerating	60-70	> 95	1996
Eslöv	co-digestion	single pass	55-62	> 95	1999
Jönköping	co-digestion	single pass	65	> 95	2000
Kristianstad	co-digestion	single pass	60-70	> 95	1999
Uppsala	co-digestion	single pass	63-70	> 95	1997
Kalmar	co-digestion	regenerating & single pass	64-67	> 95	1998
Island/Reykjavik	landfill	nk.	55	95	2000
France/Lille	landfill	regenerating	nk.	97	1994
Japan/Kobe	sewage sludge	nk.	nk.	97	2004
Netherlands/ Tillburg	landfill	nk.	nk.	88	1987
Spain/Madrid	nk.	nk.	nk.	96.5	2007

nk. not known

engines; in fact, the reference fuel for natural gas vehicles is 86 % methane and 14 % nitrogen (European Commission 2001).

The current techniques used to upgrade biogas are not new as raw natural gas has been upgraded for years using the same methods. For example, in North America the methane content of raw natural gas can vary from 45 % to 97 %, carbon dioxide from 0 % to 54 % and nitrogen from 0.2 % to 21 %, depending on the location of the source. Raw natural gas also contains hydrogen sulphide and other sulphur compounds, and hydrocarbons like propane, butane and pentane. Many upgrading technologies exist especially for the removal of carbon dioxide and hydrogen sulphide from natural gas and biogas produced in co-digestion plants (Table 22); however, knowledge about upgrading landfill gas remains limited (Woodcock & Gottlieb 1994).

5.3.6 Exhaust gas (IV, V)

The results of this study show that, for example, methane, hydrogen sulphide and VOCs can be emitted into the air from exhaust gas and absorbent in the absence of exhaust gas or waste water treatment. Also, methane circulation from the flash tank back to the upgrading process is important in order to minimize methane losses. In particular, high pressure in the absorption process may increase methane absorption into water and, furthermore, can lead to the loss of methane, if a flash tank is not used. For example, the solubility of methane (molefraction) in water at 12 °C at pressures of 23, 88 and 91 bar is $0.656*10^{-3}$, $1.881*10^{-3}$ and $2.002*10^{-3}$, respectively (Lekvam & Bishnoi 1997), indicating that methane solubility increases with increasing pressure despite the fact that Henry's law is not valid in its simple form. In the present high pressure experiment, although the pressure in the process varied from 50 to 170 bar, methane losses were minimized by circulating the methane from the flash tank back to the upgrading process.

The effect of the flash tank on the methane content of the exhaust gas could be seen when the two processes studied here were compared; in the counter-current process, no flash-tank was used and the methane content in the exhaust gas rose to 15 %. In the high pressure process the low methane content (from 2.5 to 4 %) in the exhaust gas at the beginning of the present trials showed that the methane absorbed into water was circulated back to the absorption process. With the gas upgrading techniques commonly used, the suppliers guarantee maximum methane losses of 2 % yet methane losses of 8 to 10 % have been measured at some plants (Persson 2003). In the present study it was not possible to measure either the exhaust gas or methane circulation flows, and thus total methane losses were not calculated. Also, the increase in methane content in the exhaust gas in the high pressure process observed throughout the research period (from 2 to 12 %) indicates possible failure in the flash tank and methane recovery; however, the reason for this was not found during the trials.

Neither the different upgrading parameters nor different desorption pressures used in the counter-current process had any effect on the hydrogen sulphide content of the exhaust gas. Samples were taken over a short period, hence variation in exhaust gas composition may not have had time to occur. To minimize emissions, including odour emissions, into the air, the compounds removed from the raw gas during the landfill gas upgrading process can be upgraded, for example with a bio-filter. Or, if a flash tank is not used to circulate the absorbed methane, the exhaust gas should be collected and burnt or channelled back to the upgrading process. If the exhaust gas is not treated, some of the released compounds, such as hydrogen sulphide and halogenated compounds, may have adverse effects on the environment or on humans health. Emissions from landfill gas flaring can contain high levels of NOx, CO and PAHs and, in some cases, vinyl chloride and dioxin (Wiemer & Widder 1996). On the other hand the health risk from a gas upgrading plant is not different from the risks from other landfill gas utilization plants.

5.3.7 Water regeneration (IV, V)

During the water absorption processes studied here, carbon dioxide and hydrogen sulphide are absorbed into water and some of the carbon dioxide molecules form carbonic acid (H_3CO_3), which lowers the pH of the water, making it slightly acidic (Tynell 2005). In both the present upgrading processes, after desorption, the pH of water was higher than before desorption, but still acidic, indicating that some of the dissolved compounds leave water during the regeneration step and become part of the exhaust gas. The pressure in the desorption column also affected the methane content of the exhaust gas, while was lower when a pressure of –0.3 bar was used in desorption in the counter-current process. When water was circulated in the high pressure process, the gradual decrease in pH of the absorbent water did not affect the methane content of the product gas. The differences, however, were negligible, and a longer measurement time in each trial would have been needed to evaluate the total effect of desorption pressure or water circulation during long-term continuous operation.

In general, the amounts of TVOCs in water increased across the measurements in the counter-current process, which indicates some enrichment the of VOCs in water during the upgrading process. The amounts of VOCs were lower after than before the desorption step, except for organic silicon compounds. The amounts of organic silicon compounds varied during the measurements, and no difference was observed between samples taken after and before desorption. The effect on the environment of the water used can be decreased if water is regenerated and re-used in the process. Gas upgrading plants with water absorption and no water circulation are mainly used in waste water treatment plants where treated waste water can be used as an absorption liquid and channelled back to the waste water treatment process after use (Tynell 2005). In landfills the water used can be channelled to the water treatment unit and treated with leachate or it can be used for irrigation of the landfill.

6 CONCLUSIONS

The present results showed some differences in biogas contents and its variations in the studied plants producing biogas from different and varying substrates under different conditions. It is important that biogas composition is determined in order to identify the need and a suitable method of purifying the gas for energy utilisation. Especially, when introducing new technologies, as compounds which do not have an effect on the conventional gas engines may damage machinery and increase the need of maintenance. The present results indicate that if biogas is to be considered to utilization purposes where higher methane content is required, it might be more advantageous to produce it from manure or sewage sludge as the lower content of nitrogen and halogenated compounds. Although the landfill gas upgrading results were promising, the nitrogen that remains in the product gas decreases the energy content of the gas. On the other hand, the global level, in many landfills gas is not collected and thus biogas, together with all its compounds, is being emitted into the atmosphere, creating environmental and health problems.

From the point of view of upgrading the organic silicon compounds found in various concentrations in all the types of biogas determined in this study present a challenge for applications that utilize biomethane. Especially in landfill and WWTP gases as from these sources siloxane concentrations were detected in higher concentrations than in biogases produced from manure or energy crops. The occurrence of these compounds is probably because of the wide use of siloxanes in industry. When only energy crops are used as raw material in a biogas process, the amounts of organic silicon compounds are lower, but not eliminated in all cases. Moreover, it is important that concentrations of organic silicon compounds are determined with reliable analytical method as these compounds may damage some of the engines even in low concentrations and especially in these cases the method used to remove organic silicon compounds should be carefully designed.

The study shows that the methane content of landfill gas can be upgraded to 90 % methane by a counter-current water absorption process and to 89 ± 2 % using a high pressure water absorption system. During upgrading the carbon dioxide content fell to below 6 % and sulphur and halogenated compounds were removed with high efficiency with both, the counter-current and high pressure processes used. Also, from 68 to 70 % methane enrichment and 88 to 91 % carbon dioxide removal efficiencies were obtained with the counter-current water wash process. With the high pressure process methane enrichment efficiencies of ca 62 ± 4 % and 57 ± 3 % were achieved at initial pressures of 8 and 10 bar, respectively, and 87 ± 1 % carbon dioxide removal efficiency was obtained with the parameters used. Comparison of these processes is, however, difficult because of variation in the composition of the raw gas. Further work is also needed on the trade-offs related to the energy requirements and absorbent water treatments needed for low and high pressure absorption systems. Depending on the biomethane standards applied in different countries, upgraded landfill gas could be used in several biogas applications, including vehicle fuel, as 86 % methane is the minimum quality parameter for natural gas vehicles. Nitrogen lowers the caloric value of biomethane but does not harm engines, as indicated by the fact that the reference fuel for natural gas vehicles is 86 % methane and 14 % nitrogen.

Acknowledgements

The research for this thesis was carried out at the Department of Biological and Environmental Science, University of Jyväskylä. The work was funded by the Maj and Tor Nessling Foundation, the Finnish Funding Agency for Technology and Innovation (Tekes, Grant no. 70045/03), Grenovia Ltd. and Tampere Regional Solid Waste Management Ltd. Thanks go to Mustankorkea Waste Management Ltd. for providing the site for this study and to Tampere Regional Solid Waste Management Ltd., YTV Waste Management, the waste water treatment plants in Jyväskylä, Tampere, and Espoo, the waste management companies Stormossen and Lakeuden Etappi Ltd., Greenvironment GmbH and Erkki Kalmari for providing the opportunity to take biogas samples. In addition I want to acknowledge support from the Finnish Graduate School for Energy Science and Technology (EST).

I am indebted to my supervisor Prof. Jukka Rintala for providing me with the opportunity to undertake PhD studies. I highly appreciate his patience and support throughout the research process. I gratefully acknowledge my co-authors Anja Veijanen, Jussi Läntelä, Jenni Lehtinen, and Mari Seppälä for their contribution, especially to the planning of the experiments, and guidance. Special thanks go to Bastien Ménard, Ville Pyykkönen and Viljami Kinnunen for their assistance in the experiments. I also thank Leena Siitonen and Mervi Koistinen for their help in the laboratory, and the technical and office personnel of the Department of Biological and Environmental Science. I also wish to thank everyone in the Environmental Science section for all their help and support and for cheerful discussions in the coffee room and, especially Jenni, Hanne, Outi, Veli-Heikki and Ulla, who have shared an office with me and helped me to troubleshoot many problems.

My warmest thanks go to my family and friends for their support. Most of all I thank my husband Jukka for his love, support and encouragement and my daughter Tetta for bringing such joy into my life.

YHTEENVETO (RÉSUMÉ IN FINNISH)

Biokaasun koostumus ja puhdistus liikennepolttoaineeksi

Euroopan yhteisö on edistänyt uusiutuvien polttoaineiden käyttöä etenkin ympäristönäkökohtiin vedoten, mutta fossiilisiin polttoaineisiin kohdistuvan riippuvuuden vähentäminen on korostunut yhä enemmän viime vuosina. Fossiilisten polttoaineiden korvaaminen uusiutuvilla polttoaineilla vähentää kasvihuonekaasupäästöjä sekä terveydelle haitallisia päästöjä.

Biokaasua voidaan käyttää sähkön ja/tai lämmön tuotantoon ja jalostettua kaasua (biometaania) ajoneuvojen polttoaineena. Biokaasua voidaan tuottaa jätevedenpuhdistamoiden lietteistä ja yhdyskuntien ja teollisuuden biohajoavista jätteistä ja sivuvirroista, maatalouden lannoista, peltobiomassoista sekä mm. teollisuuden lämpimistä ja väkevistä jätevesistä. Biokaasua muodostuu toistaiseksi myös kaatopaikoilla, joissa on runsaasti biohajoavaa ainesta. Monissa maissa kaatopaikkakaasun kerääminen on suurimmilla kaatopaikoilla pakollista, tavoitteena kasvihuonekaasupäästön (metaani) estäminen. Tällä hetkellä kaatopaikoilta kerättävä kaasu joko poltetaan, tai käytetään lämmön ja/tai sähköntuotantoon.

Biometaanin käyttö liikenteen polttoaineena vähentää ajoneuvon kasvihuonekaasupäästöjä parhaimmillaan yli 90 %. Biokaasun käyttö vähentää erityisesti typenoksidi-, hiilivety- ja hiilimonoksidipäästöjä sekä haju- ja melupäästöjä. Kaatopaikkakaasun käyttö liikennepolttoaineena on noussut viime aikoina kiinnostuksen kohteeksi, mutta liikennekäyttö on toistaiseksi vähäistä.

Biokaasu sisältää yleensä 45 – 70 % metaania, 30 – 45 % hiilidioksidia ja < 1 – 15 % typpeä. Lisäksi kaasussa voi olla mm. rikkivetyä, ammoniakkia, vetyä, tyydyttyneitä tai halogenoituja hiilivetyjä sekä happea. Biokaasussa on usein myös kosteutta ja se voi sisältää pölypartikkeleita sekä orgaanisia silyyliyhdisteitä (siloksaaneja). Ajoneuvojen polttoaineeksi tarkoitettu kaasu tulee puhdistaa sekä haittaa aiheuttavista että lämpöarvoa alentavista yhdisteistä. Yleensä ajoneuvokäyttöön tarkoitetulle biokaasulle suositellaan yli 95 %:n metaanipitoisuutta. Biokaasun puhdistusmenetelminä voidaan käyttää mm. absorptiota, korkeapaineadsorptioprosessia (PSA) sekä membraaneja. Yleisin puhdistusmenetelmä on absorptioon perustuva vesipesu. Vesipesussa biokaasussa esiintyvät hiilidioksidi ja rikkivety liukenevat veteen ja metaanipitoinen tuotekaasu johdetaan ulos puhdistustornista. Käytetty vesi voidaan puhdistaa desoptiokolonnissa, jonka jälkeen vesi voidaan johtaa takaisin puhdistusprosessiin. Puhtaan veden käyttö ei ole välttämätöntä, joten prosessissa voidaan käyttää myös jätevedenpuhdistamon puhdistettua jätevettä tai kaatopaikkavettä, jolloin vettä ei yleensä kierrätetä. Vesipesulaitteiston etuja ovat sen yksinkertainen rakenne sekä veden verrattain alhainen hinta.

Tämän työn tavoitteena oli tutkia biokaasun koostumus kaatopaikoilla, jätevedenpuhdistamoilla sekä biokaasulaitoksilla ja selvittää mahdollisten energiakäytölle haitallisten yhdisteiden pitoisuudet eri kohteissa. Metaanin, hiilidioksidin, hapen ja typen lisäksi kaasuista analysoitiin rikkivety, ammoniakki sekä haihtuvat orgaaniset yhdisteet (VOC). Lisäksi tavoitteena oli tutkia kahden vesiabsorptioon perustuvan kaasunpuhdistusmenetelmän toimivuutta kaatopaikkakaasun puhdistuksessa.

Tässä tutkimuksessa tutkituilla neljällä kaatopaikalla kaasun metaanipitoisuus oli hieman alhaisempi (47 – 62 %) kuin neljällä jätevedenpuhdistamolla (60 – 67 %). Tutkitulla viidellä eri biokaasulaitoksella kaasun metaanipitoisuus vaihteli (55 – 70 %), riippuen mm. laitoksen syötteestä sekä laitostyypistä. Kaatopaikkakaasussa havaittiin enemmän typpeä (< 1 – 17 %) kuin muissa tutkituissa biokaasuissa (< 1 %), mikä voi johtua siitä, että kaatopaikkakaasuun pääsee alipaineeseen perustuvassa keräysjärjestelmässä ilmaa. Rikkivetyä havaittiin jätevedenpuhdistamoiden biokaasussa vähemmän (< 4 ppm) kuin kaatopaikkojen (27 – 500 ppm) tai biokaasulaitosten (3 – 1000 ppm) kaasuissa. Alhainen rikkivetypitoisuus johtunee siitä, että Suomessa jätevedenpuhdistamoilla käytetään yleisesti ferrosulfaattia saostuskemikaalina, joka reagoi rikkivedyn kanssa ja rikkiyhdisteet voivat poistua lietteestä jo ennen mädättämöä. Biokaasun VOC pitoisuuksia analysoitiin yhdeltä kaatopaikalta, yhdeltä jätevedenpuhdistamolta sekä maatilakokoluokan biokaasulaitokselta. Kaatopaikkakaasussa ja jätevedenpuhdistamon kaasussa VOC-pitoisuudet vaihtelivat paljon yli vuoden mittaisen seurantajakson aikana (kaatopaikka 46 – 173 mg/m^3, jätevedenpuhdistamo 13 – 268 mg/m^3). Maatilan biokaasussa VOC-pitoisuudet olivat alhaisia ja suuria vaihteluja pitoisuuksissa ei havaittu (5 – 8 mg/m^3).

Orgaanisten silyyliyhdisteiden esiintymistä biokaasussa tutkittiin kaatopaikkojen (4 kpl), jätevedenpuhdistamoiden (4 kpl) sekä eri materiaaleja prosessoivien biokaasulaitosten (4 kpl) kaasuista. Lisäksi tutkittiin laboratoriokokeissa orgaanisten silyyliyhdisteiden pitoisuuksia energiakasveista tuotetussa biokaasussa. Neljältä eri kaatopaikalta ja jätevedenpuhdistamoilta tutkituissa biokaasuissa orgaanisia silyyliyhdisteitä havaittiin enemmän (217 – 1878 µg/m^3 ja 437 – 1341 µg/m^3) kuin neljän biokaasulaitoksen kaasuista. Kahden sekä jätevedenpuhdistamoiden lietettä ja biojätettä käsittelevien biokaasulaitosen kaasuista mitattiin orgaanisia silyyliyhdisteitä 479 – 620 µg/m^3, kun kahden lantaa ja energiakasveja käsittelevien laitosten biokaasussa esiintyi orgaanisia silyyliyhdisteitä 30 – 33 µg/m^3. Eri biokaasun käyttökohteisiin on orgaanisille silyyliyhdisteille erilaisia raja-arvoja. Useat kaasumoottorivalmistajat ovat asettaneet raja-arvoksi < 5 – 28 mg/m^3, jotka tässä tutkimuksessa mitatuissa kaasuissa alittuivat. Erityisesti mikroturbiinivalmistajat ovat asettaneet myös alhaisempia raja-arvoja (< 0,03 mg/m^3), joka alittui vain yhdellä biokaasulaitoksella. Laboratoriopanoskokeissa rehusta, ruohosta ja maissista tuotetuissa biokaasuissa määritettiin orgaanisten silyyliyhdisteiden tuotto. Rehusta tuotetussa biokaasussa orgaanisia silyyliyhdisteitä oli 12 – 20 µg/kg orgaanista ainesta (VS), ruohosta tuotetussa biokaasussa 22 – 38 µg/kgVS ja maissista tuotetussa biokaasussa 7 – 12 µg/kgVS.

Kaatopaikkakaasun puhdistamista liikennepolttoainekäyttöön tutkittiin pilot-mittakaavan vastavirtavesiabsorptio- sekä korkeapainevesipesuprosesseilla. Kaasunpuhdistuslaitteistot sijoitettiin Mustankorkean kaatopaikalle Jyväskylään kaasunkeräyspumppaamon viereen. Kaasu puhdistuslaitteistolle otettiin kaatopaikkakaasun keräysjärjestelmän kokoojaputkesta. Kaikista koeajojen kaasunäytteistä (raakakaasu, tuotekaasu, poistokaasu) analysoitiin metaani-, hiilidioksidi-, happi-, typpi- ja rikkivetypitoisuudet. Lisäksi tiettyjä ajoasetuksia käytettäessä kaasunäytteistä analysoitiin VOC-pitoisuudet. Kaasunpuhdistuksen toimivuutta arvioitiin vertaamalla puhdistetun kaasun koostumusta ajoneuvokäytön edellyttämiin laatuvaatimuksiin.

Käytettäessä vastavirtavesiprosessia koeajojen aikana raakakaasun metaanipitoisuus oli noin 53 % ja painepesuprosessin aikana noin 55 %. Tuotekaasun metaanipitoisuus oli noin 90 % vastavirtavesiprosessissa yli 20 bar paineessa, kun prosessissa käytettiin veden virtausta 10 l/min. Samaan puhdistustulokseen päästiin 30 bar paineessa 5 l/min veden virtauksella. Painepesuprosessilla metaanipitoisuus tuotekaasussa oli 89 ± 2 % kaikilla prosessiparametreilla. Puhdistusprosessit eivät poistaneet happea eivätkä typpeä. Typpi rikastui prosessien aikana, pitoisuuden ollessa tuotekaasussa noin 2 % korkeampi kuin raakakaasussa. Rikkivetypitoisuus vaihteli raakakaasussa tutkimusten aikana 30 – 150 ppm. Kumpikin prosessi poisti rikkivedyn (tuotekaasussa < 0,1 ppm). Noin 90 %:ista metaanikaasua voidaan teknisesti käyttää mm. ajoneuvojen polttoaineena, sillä kaasun seassa oleva typpi ei vahingoita ajoneuvojen moottoreita, mutta alentaa kaasun lämpöarvoa. Typpi voidaan poistaa kaasusta mm. adsorptiomenetelmillä tai sen esiintymistä kaatopaikkakaasussa voidaan vähentää tekemällä muutoksia kaasun keräysverkostoon, jolloin tutkituilla puhdistusmenetelmillä voidaan päästä yli 95 %:n metaanipitoisuuteen.

Raaka- ja tuotekaasun VOC -pitoisuudet vaihtelivat. Suurin osa yhdisteitä sekä raaka- että tuotekaasussa oli alifaattisia ja aromaattisia hiilivetyjä, mutta myös alhaisia pitoisuuksia pelkistyneitä rikkiyhdisteitä, halogeeniyhdisteitä sekä orgaanisia silyyliyhdisteitä havaittiin. Puhdistusprosessilla ei ollut kokonaispitoisuuksiin suurta merkitystä, sillä alifaattiset ja aromaattiset hiilivedyt, bentseeniä lukuun ottamatta, sekä orgaaniset silyyliyhdisteet eivät poistuneet ko. olosuhteissa vesipesujen aikana. Pelkistyneet rikkiyhdisteet poistuivat kaasusta vastavirtaprosessilla noin 90 %:n ja painepesuprosessilla 79 – 99 %:n tehokkuudella. Halogeeniyhdisteet poistuivat vastavirtaprosessilla noin 96 %:n ja painepesuprosessilla noin 83 – 91 %:n tehokkuudella. Painepesuprosessissa tuotekaasu johdettiin silikageeliä sisältävän kuivausyksikön läpi. Kuivausyksikkö poisti orgaanisista silyyliyhdisteistä 66 %.

Tämän tutkimuksen tulokset osoittavat biokaasun soveltuvuuden energiakäyttöön puhdistusprosessin jälkeen. Riippuen biokaasun käyttökohteesta haitallisten yhdisteiden esiintyminen eri biokaasun tuotantokohteissa tulee ottaa huomioon puhdistusprosessia suunniteltaessa.

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