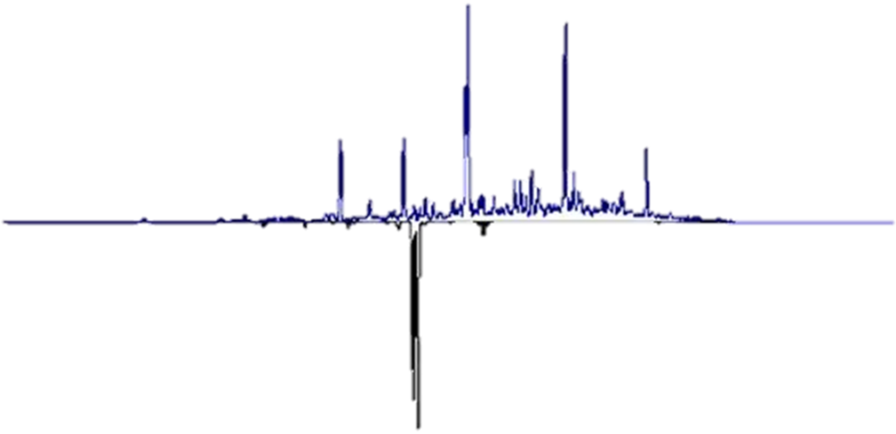
Rapport SGC 246

Characterisation of contaminants in biogas before and after upgrading to vehicle gas



Karine Arrhenius, SP
Ulrika Johansson, SP

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Jörgen Held

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Susanna Pettersson, Göteborg Energi AB

Maria Sandell, Surahammars Kommunalteknik AB

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Contents

1 INTRODUCTION

1.1 Background

Biogas formation from organic material (substrate) is a complex process that takes place over various stages [1]. Complex organic substances are broken down in digesters to form simpler components such as proteins, carbohydrates and lipids. These are then broken down to form acetic acid and other organic acids, carbon dioxide and hydrogen gas. Finally, methane is formed. There are a large number of contaminants in considerably smaller volumes together with the methane. If they were to be present in significant volumes, these contaminants could cause operating problems in the plant itself (corrosion, etc.), but also during use of the clean gas if they are transported with the gas following upgrading. They may also pose a risk to health and the environment. This is why it is of interest to study where these substances are found.

Which contaminants have formed in biogas depending on the substrate and control parameters in digesters has been examined in a number of studies. These studies have shown that many volatile organic compounds (VOCs) which are potentially harmful to humans or the environment may be present in the biogas. Many different groups of chemical substances such as aromatic hydrocarbons, heterocyclic substances, ketones, alkanes, terpenes, alcohols, siloxanes and halogenated substances have been found. However, compiling the results from these studies is all but impossible as the analysis methods vary, what is digested is very much dependent on each country's own rules on waste disposal, and information on the substrates is limited.

Terms

The following terms are used in this report:
- VOCs: volatile organic compounds, organic compounds with a boiling point between 70 and 350° C
The term “contaminants” includes VOCs, but e.g. hydrogen sulphide and ammonia as well.

- Biogas: gas produced in digesters or landfill sites (also termed “landfill gas”)

- Clean gas: biogas after upgrading, i.e. after the removal of carbon dioxide

1.1.1 Survey of the literature relating to contaminants in biogas

Landfill gas

A number of studies on the composition of biogas have focused on biogases from landfill as in many countries, including in Europe, landfill gas represents the primary biogas volume [2]. The contaminants found in landfill gases vary widely from landfill site to landfill site as the items disposed of also vary widely. Moreover, there is variation in how frequently gas is extracted and in what volumes, and the stage of decomposition of the waste.

In a study by Allen [3], seven landfill gases have been analysed with regard to their VOC content. A total of 140 VOCs could be identified, of which 90 were present in all biogases but in differing concentrations. The substrate comprised paper, animal and vegetable material and garden waste.

The dominant VOCs were hydrocarbons (alkanes, aromatic hydrocarbons, cycloalkanes, terpenes), oxygenated hydrocarbons (alcohols and ketones) and halogenated hydrocarbons.

A number of studies focus on certain groups of contaminants which are suspected to be potentially harmful (e.g. corrosive) when using biogas without cleaning. Examples of these groups include siloxanes (chemical compound containing silicon, oxygen and methyl groups (CH_3)), sulphur compounds, ammonia or halogenated substances. Siloxanes generally occur to a greater extent in active landfill sites compared with closed landfill sites [4]. Siloxanes are present in cosmetic products, among other things. Hydrogen sulphide is the most commonly occurring sulphur compound in landfill gas, although mercaptans, disulphides, etc. may also occur. The hydrogen sulphide content is normally lower than 100 ppm at typical landfill sites, but this figure may exceed 1000 ppm, particularly if plasterboard sections have been disposed of. Plasterboard sections are made up mainly of calcium sulphate ($CaSO_4$). Arnold [4] has shown that the three otherwise most commonly occurring contaminants found in three landfill gases from municipal landfill sites in Finland were: aromatic hydrocarbons (ethylbenzene up to 20-25 mg/m^3, xylenes, toluene), aliphatic hydrocarbons (e.g. nonane) and terpenes such as α-pinene (up to 50 mg/m^3 in one case). In another study [5] in which five landfill gases were analysed with regard to VOCs, a large number of VOCs was found in which aromatic hydrocarbons (benzene, toluene and others), siloxanes, sulphur compounds and aliphatic hydrocarbons could be identified. No one substance was clearly dominant. The total VOC content, which varied between 46 and 173 mg/m^3, was a sum of many individual contributions.

VOCs in landfill gas [3] can largely be explained as originating directly from the substrate by means of vaporisation of these substances. In this case, differences in landfill gas composition are due to differences in the composition of the substrates and on the ages of the landfill sites. Terpenes, α and β-pinene are probably vaporised directly from garden waste and scented household products such as detergents. Halogenated hydrocarbons are vaporised directly from cellular plastic, refrigerators and aerosol propellants. Knox et al. [6] noted that alkanes and aromatic hydrocarbons show a tendency to dominate, while at the same time the content of halogenated and oxygenated hydrocarbons is reduced in older landfill sites. If all substances occur in high quantities, this indicates that the gas is extracted from different locations which are at different stages of decomposition. Table 1.1 summarises the substances identified at various landfill sites.

Table 1.1: Identified VOCs at landfill sites

Countries	No. of landfill sites	Identified substances	Content ranges	Source
United Kingdom	7	alkanes, aromatic hydrocarbons, cycloalkanes, terpenes, alcohols and ketones, halogenated hydrocarbons, sulphur compounds	Alkanes (302-1543 mg/m^3) Aromatic hydrocarbons (94-1906 mg/m^3) Cycloalkanes (80-487 mg/m^3) Terpenes (35-652 mg/m^3) Halogenated hydrocarbons (327-1239 mg/m^3)	[3]
Finland	3	aromatic hydrocarbons, aliphatic hydrocarbons, terpenes, siloxanes, sulphur compounds	Ethylbenzene (4.4 - 25 mg/m^3) Limonene (0.6 - 126 mg/m^3) Hydrogen sulphide (25 - 820 mg/m^3) Halogenated hydrocarbons (0.5-7 mg/m^3)	[4]
Finland	1	alkanes, aromatic hydrocarbons, cycloalkanes, halogenated hydrocarbons, sulphur compounds, siloxanes	TVOC: 46-173 mg/m^3 (variations between different days)	[5]

Treatment plants

Rasi [5] studied the composition of biogas produced at four different treatment plants. Methane, carbon dioxide and hydrogen sulphide were analysed at all of these plants (Jyväskylä, Rahola, Viinikanlahti and Espoo, mesophilic municipal treatment plants producing between 0.9 and 1.9 million m^3 biogas per year). At all the treatment plants, the content of hydrogen sulphide was below 5 ppm, i.e. 7 mg/m^3. At the Jyväskylä treatment plant, the biogas was also analysed with regard to VOC content. Many substances were found in the gas, including toluene, siloxanes, oxygenated hydrocarbons, sulphur compounds, aliphatic hydrocarbons, etc. The total VOC content (TVOC) was determined over time by taking eight samples over the course of one month. The TVOC varied widely between 13 and 268 mg/m^3.

The Afsset report of 2008 [7] carried out a survey of the literature in order to compile a list of substances which may occur in biogases. The objective was not to describe the composition of the biogas as thus may vary widely in each individual case. Three of the studies compiled related to treatment plants, two in Germany and one in France. One general conclusion that was drawn is that since the sources vary so widely, the results are not representative for a specific substrate. Many substances (almost a hundred) were found, belonging to many different chemical groups such as terpenes, hydrocarbons, oxygenated hydrocarbons, sulphur compounds and halogenated hydrocarbons. Terpenes (α-pinene, camphene, γ-terpinene) and hydrocarbons (octane, decane, undecane, dodecane and hexadecane) were present in quantities of quantities up to several mg/m^3(maximum quantities measured in a total of four biogases from treatment plants). The maximum hydrogen sulphide content was 3000 mg/m^3.

One clear difference between these two studies is evident in the content of hydrogen sulphide, less than 7 mg/m^3 in the Rasi study and up to 3000 mg/m^3 in the Afsset report. In neither case are details provided on whether the plants use precipitation chemicals.

Waste plants

The Afsset report [7] also compiled results from several studies in which biogas from waste plants was analysed. This includes three studies concerning the composition of a total of four biogases produced by digesting household waste. The report presents the maximum quantities measured in these four biogases. A maximum content of 5000 mg/m^3 hydrogen sulphide was indicated in these samples. Relatively high quantities of terpenes such as d-limonene (220 mg/m^3) and α-pinene, (50 mg/m^3) were also reported. Aromatic hydrocarbons (xylenes, 160 mg/m^3, toluene, approx. 60 mg/m^3, ethylbenzene, approx. 60 mg/m^3) were also indicated. Quantities of individual hydrocarbons (nonane, decane, undecane) in excess of 10 mg/m^3 were also indicated.

Farm-based plants

Rasi [5] studied gases from five different farm-based biogas plants which digest widely varying substrates. The total VOC content was relatively low. Examples of VOCs identified when cow manure and waste from the confectionery industry were digested together were aromatic hydrocarbons (benzene, toluene), disulphides and siloxanes.

A study carried out by KIWA [8] describes the determination of phosphane (PH_3, phosphorus trihydride), sulphur compounds, siloxanes and halogenated hydrocarbons from five plants. Phosphane, a gas which can be formed in the presence of phosphorus, has been found in biogases produced from the digesting of manure and waste sludge, for example [8b]. The siloxane quantities were very low (often below 0.1 ppm). In most cases, hydrogen sulphide was clearly dominant among the sulphur compounds, but there were also significant quantities (several mg/m^3) of other sulphur compounds. No phosphane could be found, and very low quantities of halogenated hydrocarbons were measured.

Summary of the survey of the literature:

Biogas may contain a large number of contaminants belonging to many different families. These often include alkanes, aromatic hydrocarbons, cycloalkanes, halogenated hydrocarbons, sulphur compounds, siloxanes and terpenes. To date, landfill gas has been studied most widely.

Studies to date in which the composition of biogas has been determined for different substrates have shown that:

- Biogas composition with regard to contaminants [7] varies widely depending on which substrate is being digested and under what conditions. Siloxanes were indicated as being characteristic for biogas from treatment plants, while terpenes occur in biogases from green waste.

- Biogases produced at farm-based plants [5] contain lower VOC quantities (5 to 8 mg/m^3) than biogases produced at landfill sites (46 to 173 mg/m^3) or treatment plants (13 to 268 mg/m^3).

1.1.2 Contaminants in clean gas

For biogas to be usable as fuel for vehicles or to be discharged to the natural gas network, it needs to be cleaned and upgraded. Cleaning primarily involves removal of particles, water and hydrogen sulphide. The gas is upgraded by removing carbon dioxide in order to increase the calorific value of the gas and achieve a gas with a consistent quality.

Upgrading techniques

There are a number of techniques [9, 10] for removing carbon dioxide from the gas as shown in Table 1.1. The basic principle involves utilising differences in specific properties between methane and carbon dioxide.

Table 1.2: Upgrading techniques

	Principle	Property	Need for cleaning before
PSA (Pressure Swing Absorption)	Adsorption		Yes, water and hydrogen sulphide
Membrane	Permeation		yes
Water scrubber	Absorption	Solubility in water	No
Chemical scrubber, amine scrubber	Chemical reaction	Chemical structure	Yes, hydrogen sulphide
Organic physical scrubber	Absorption	Solubility in a substance	No
Cryogenic upgrading	Boiling point/Sublimation point	Boiling point/Sublimation point	Yes

In this study, three upgrading methods have been studied in order to examine how they influence contaminants found in the biogas.

Water scrubber

This method is based on the fact that gases such as carbon dioxide, hydrogen sulphide and ammonia dissolve more readily in water than methane does. At high pressure and low temperature, carbon dioxide dissolves even more readily in water. The following is an example of how a water scrubber works: the incoming biogas [10b] is compressed and then cooled down. The cold, compressed gas is fed to the bottom of an absorption column. The absorption column may be filled with plastic rings which provide a larger reaction surface. Water runs down the column, meets the gas and absorbs carbon dioxide and hydrogen sulphide, while methane rises to the top of the column. In two subsequent columns, the methane loss is reduced and all gaseous components are released from the process water.

Pressure Swing Adsorption (PSA)

The PSA process utilises the principle whereby gases can be adsorbed under pressure to solid surfaces. The higher the pressure, the more gas is adsorbed. When the pressure is reduced, the gas is released (desorbed).
PSA can be used to separate carbon dioxide from methane as different gases tend to be adsorbed to an adsorption material to a greater or a lesser extent.
Active carbon or zeolites are used as an adsorption material in order to separate carbon dioxide from methane. The biogas is fed into the bottom of the vessel during adsorption. When the gas rises in the vessel, the carbon dioxide is bonded to the active carbon while the methane slips past.

Chemical scrubber

This method is based on the fact that the carbon dioxide is bonded to a chemical, often an amine. This amine may be primary (e.g. MEA, monoethanolamine), secondary (e.g. DEA, diethanolamine) or tertiary (t.ex. MDEA, methyldiethanolamine).
If the amine is primary or secondary, a carbamate is formed when carbon dioxide reacts with the amine in accordance with the following reaction:

$$2\ \mathrm{Am} + \mathrm{H_2O} + \mathrm{CO_2} \leftrightarrow \mathrm{AmCOO^-} + \mathrm{AmH^+} \qquad (1)$$

Tertiary amines cannot form carbamates with carbon dioxide. The reaction between a tertiary amine and carbon dioxide is:

$$\mathrm{Am} + \mathrm{CO_2} + \mathrm{H_2O} \leftrightarrow \mathrm{AmH^+} + \mathrm{HCO_3^-} \qquad (2)$$

The reactions (1) and (2) go towards the right at low temperatures (CO_2 is adsorbed), and towards the left at high temperatures (CO_2 is regenerated). The process comprises two columns, one at low temperature (known as an adsorber) and one at high temperature (known as a stripper).

Adding a primary or secondary amine to MDEA combines a relatively high reaction rate in the absorber with a lower energy consumption in the stripper. Piperazine is thus often used as an activator (also known as a promoter) together with MDEA.

Methane does not react with amines at all.

Composition of clean gas

As far as we are aware, there are few studies involving analyses of how the composition of the clean gas varies depending on the substrate and cleaning technique used.

The Afsset report [7] describes quantities of several contaminants found in two clean gases upgraded from landfill gas. Ethanol, 3-methylbutanal, 2-heptanone, acetone, butanone, limonene, α-pinene, thujone, p-cymene, ethyl acetate, methyl sulphide, dimethyl sulphide, carbon disulphide, methyl propyl disulphide, ethylfuran, methylfuran, dichloroethylene, trichloroethylene, tetrachloroethylene, chlorobenzene, dichlorobenzenes, dichloroethane, chlorobenzonitriles, trichlorobenzene and trichloroethane have been found at levels of between 10 and 5000 $\mu g/m^3$.

The KIWA report [8] describes the quantities of sulphur compounds, siloxanes and chlorinated hydrocarbons for clean gases from biogas produced by digesting slurry and upgrading with a water scrubber. Only sulphur compounds could be detected in the biogas (hydrogen sulphide approx. 400 ppm, mercaptans approx. 3 mg/m^3 mm). The clean gas contained extremely low but measurable quantities (< 0.1 mg/m^3) of hydrogen sulphide, mercaptans, carbon disulphide, thioester and carbonyl sulphide.

1.2 Objective

The primary objective of the project has been to chart the composition of biogas and clean gas, with emphasis on contaminants for different typical plants. This information can then be used as a reference case when investigating any operating problems which have influenced the composition of the gas or which have been caused by substances in the gas.

Another purpose is to study the effects of different upgrading methods on contaminants. At present, there are limited requirements with regard to permitted quantities of contaminants in vehicle gas. However, a number of contaminants such as siloxanes, halogenated hydrocarbons, etc. may be regulated in future. If the gas is analysed before and after a cleaning technique, it is possible to see which substances have been treated and which may have come about.

2 SAMPLING AND ANALYSIS METHODS

In this study, emphasis has been placed on the analysis of organic components. Besides methane and carbon dioxide, hydrogen gas, oxygen, nitrogen gas, carbon monoxide, ammonia, water vapour and hydrogen sulphide were specifically analysed. A “screening” analysis was then carried out for every sample. This analysis does not examine the substances in specific terms, but what the gas contains in terms of significant content is checked. The following families can be examined by means of these analyses: hydrocarbons with 5 to 20 carbon atoms (linear, cyclical, branched, aromatics, alkenes, terpenes), sulphurous substances (mercaptans, thiophenes, sulphides), oxygenated substances (ketones, aldehydes, acids, ether), halogenated organic substances (chlorinated and fluorinated hydrocarbons), siliconic organic substances. On the other hand, inorganic substances (mercury, phosphine, arsenic, etc.), microorganisms and oil have not been analysed.

1.1 Methane, carbon dioxide, oxygen, nitrogen gas, hydrogen gas, carbon monoxide

These substances have been collected in gastight bags of Flexfoil type. The analysis was carried out in the lab using a GC/TCD (Gas Chromatograph with Thermal Conductivity Detector) with external calibration, essentially in accordance with ISO standard 6974.

2.2 Ammonia, water vapour, hydrogen sulphide

These gases have been collected in gastight bags of Flexfoil type. The analysis was carried out using Draeger tubes which give direct results, and also using an OFCEAS instrument (Optical Feedback Cavity Enhanced Absorption Spectrometer). The analysis principle is based on laser IR spectrometry.

2.3 VOCs

An adsorbent, Tenax (a porous polymer based on the monomer 2.6-diphenylene oxide), was used in order to adsorb nonpolar or slightly polar substances with a boiling point in the range 70-320°C (six to thirty carbon atoms). The sample gas was collected by allowing a controlled flow of the gas to pass the adsorbent over a short time.

Analysis of Tenax tubes is carried out by means of what is known as thermal desorption (TD) in which the adsorbed substances are first released with heat and then transferred to a cooling trap for focusing. The cooling trap is reheated quickly and the substances are released and transported on to a gas chromatography column for separation. The outflow from the column is divided up into two flows for detection of individual components in a flame ionisation detector or mass spectrometric detection. The fragmentation pattern in the mass spectrum provides information on the structure of the eluted substances so that they can be identified. This technique is known as TD-GC-FID/MS for short. The quantification limit is at ppb level.

The analyses were carried out on an Agilent Technologies gas chromatograph 6890N equipped with two detectors, a flame ionisation detector and a mass spectrometer 5975C inert MSD in what is known as “electron impact mode” under standard conditions. Adsorbent tubes underwent a two-stage thermal desorption process with the help of a Perkin Elmer TurboMatrix 650 desorber.

The Tenax tubes were analysed on a nonpolar capillary column (5% phenyl polysilphenylene-siloxane, BPX5, 50 m long, 0.32 mm internal diameter, 1 µm film thickness).

3 SAMPLES

The samples were taken either by operating personnel at the participating plants or by personnel from SP. In both cases, two different kinds of gas bags were filled. One of the bags, Flexfoil, is appropriate for primary components, while the other bag, Flexfilm or Tedlar, is appropriate for VOCs with a boiling point of up to approx. 130°C. The gas is also adsorbed on an adsorbent, Tenax, with a controlled flow over a short period (1-4 minutes). The personnel at the plant completed a form of questions relating to the substrates and their characterisations such as DS (%), VFA, pH mm.

A total of 21 biogases (all before cleaning) and 14 clean gases (of which 12 were dry clean gases and 2 were non-dry clean gases) was analysed, as shown in Tables 3.1 and 3.2. In some instances, biogases produced from different digesters (in parallel or in series) were analysed. Biogases were also analysed before and after carbon filters (gas cleaning before the upgrade). Two biogas samples from landfill were also analysed.

Some plants upgrade their biogas using two entirely independent upgrading techniques.

In some cases, the biogas from the waste plant is mixed with the biogas from the treatment plant before the upgrading technique.

Table 3.1: Analysed biogases depending on substrate

Type of plant or substrate	Waste plant	Treatment plant (sewage sludge)	Energy crop and byproduct from food industry	Manure
No. of biogases (may be several per plant) (n=)	6	9	3	3
Mesophilic	4	9	3	3
Thermophilic	2	0	0	0
Hygienisation step	Yes	No	No	Yes/No
pH	From 7.2 to 8	From 7.0 to 7.3	From 7.6 to 7.8	From 7.6 to 7.9
DS %	From 2.2 to 5-6	From 1.7 to 3.5	From 4 to 8.2	approx. 5
VFA (g/l)	From 2 to 4-5	From 0.06 to 0.2	No data	18

Table 3.2: Analysed clean gases and upgrading techniques

	Waste plant	Treatment plant	Waste plant + Treatment plant	Energy crop and byproduct from food industry	Manure
No. of clean gases (n=) after drying step	2	2	4	3	1
No. of clean gases (n=) before drying step	0	0	2	0	0
Upgrading technique	PSA Scrubber (water)	PSA Scrubber (amine)	Scrubber (water and amine)	Water scrubber	Water scrubber

4 RESULTS AND COMMENTS

4.1 Chemical characterisation of biogas

4.1.1 Methane, carbon dioxide, oxygen, nitrogen gas, hydrogen gas, carbon monoxide

The results for the primary components, methane and carbon dioxide, are shown in Figure 4.1. This figure shows the average from measurements carried out, divided according to substrate. The span between the lowest and the highest values measured is also shown.

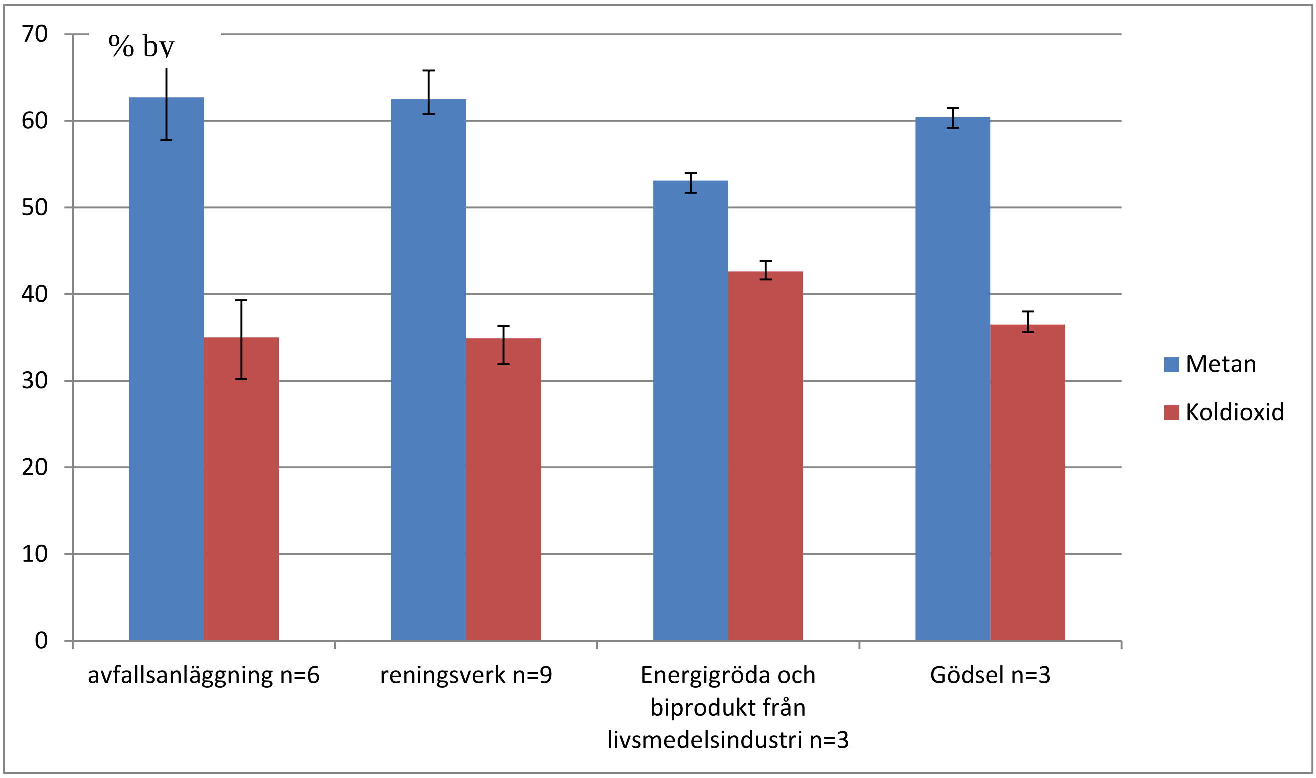

Figure 4.1: Average for methane and carbon dioxide (% by volume) in biogases produced from different substrates and the span between lowest and highest values measured (n stands for the number of samples)

The results are also summarised in Table 4.1.

Table 4.1: Average for primary components (% by volume) in biogases from different substrates and the span between lowest and highest values measured

	Waste plants	Treatment plants	Energy crop and byproduct from food industry	Manure
No. of samples	6	9	3	3

	Medium:	Span	Medium:	Span	Medium:	Span	Medium:	Span
CH_4	62.7	57.8 – 66.8	62.5	60.8 – 65.8	53.1	51.7 – 54.0	60.4	59.2 – 61.5
CO_2	35	30.2 – 39.3	34.9	31.9 – 36.3	42.6	41.7 – 43.8	36.5	35.6 – 38.0

These values match the indicative gas compositions presented in the Marcogaz report “Injection of gases from non-conventional sources into gas networks” [11]. In this report, the authors specify an indicative content of 65% for methane in biogas produced by means of digesting with a span between 50 to 80% In this study, it is possible to see that the content of methane in biogas produced in treatment plants, in waste plants or by digesting of manure is around 60-62% with a relatively small span from 58% to 67%. The content of methane in biogas produced by digesting of energy crop and the food industry is slightly lower, approx. 53.1%. The carbon dioxide content follows an opposing tendency.

The concentration of hydrogen gas and carbon monoxide was lower than the detection limit (< 1000 ppm) in all samples analysed in this study. In some applications, it may be of interest to detect carbon monoxide in the event of lower quantities, for instance if the biogas is intended for use in fuel cells where the content of carbon monoxide is critical. The analysis method used here has the potential for further development in order to detect lower quantities of carbon monoxide and hydrogen gas if so required.

The content of oxygen rarely exceeded 0.5% by volume. In the few instances in which the oxygen content was above 0.5% by volume, there is a risk of the oxygen coming from contamination with ambient air during sampling, which will also affect the nitrogen gas content, while the quantities of methane and carbon dioxide are affected to a moderate extent. This was why we chose not to present all the results for oxygen and nitrogen gas. The nitrogen gas content was between 0.6 and 3% by volume in the samples analysed.

4.1.2 Ammonia, water vapour, hydrogen sulphide

Water

Most of the biogases analysed were saturated with water vapour, which meant that the water content was around approx. 1.7-1.9% by volume.

Hydrogen sulphide

The results of the hydrogen sulphide content are summarised in Figure 4.2.

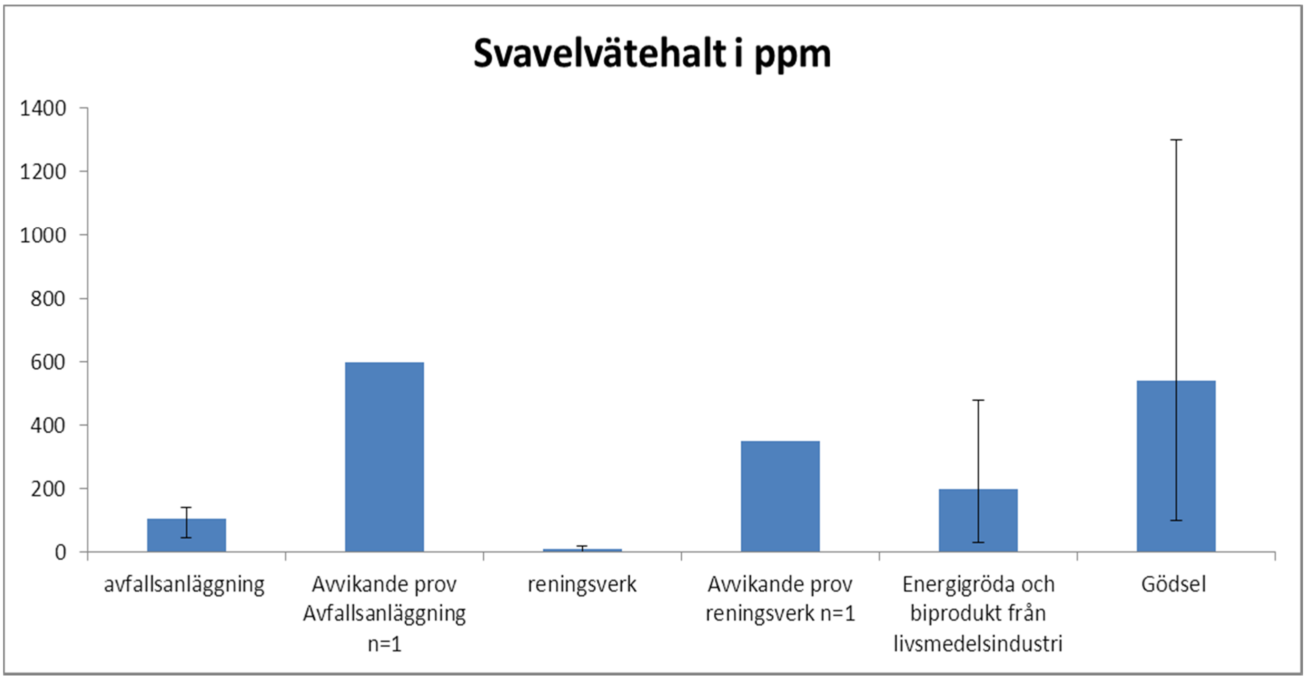

Figure 4.2: Average for hydrogen sulphide in biogases produced from different substrates and the span between lowest and highest values measured

The content of hydrogen sulphide varies widely but nevertheless follows a number of general tendencies. Biogases produced at waste plants where household waste is digested contain around 100 ppm hydrogen sulphide. A content of 600 ppm was found in one case. Biogases produced at treatment plants contain around 10-20 ppm hydrogen sulphide.

Sewage treatment plants often use iron sulphate for chemical precipitation of phosphorus. Iron sulphate reduces the hydrogen sulphide content by bonding the sulphur to iron.

In one case, a hydrogen sulphide content of 350 ppm was found: the plant states that iron sulphate is not used. The quantities of several thousand ppm may occur at treatment plants which do not add a precipitation chemical.

Ammonia

Ammonia could not be demonstrated in samples from treatment plants or from waste plants which digest household waste. On the other hand, ammonia (approx. 100 ppm) could be demonstrated in samples from waste plants which digest slaughterhouse waste. Ammonia was also demonstrated in one sample from the digesting of manure (10 ppm) and in one sample from the digesting of food industry residues. Ammonia originates from nitrogenous proteins.

4.1.3 Volatile organic compounds

The composition relating to volatile organic compounds (VOC) is characteristic of the substrates, although some substances can be found in almost all biogases such as toluene and 2-butanone.

Waste plants

Biogas samples from waste plants at which household waste is digested have a very characteristic composition in respect of VOCs. Two substances are entirely dominant. Together, their quantities are equivalent to up to 90% of all VOCs. These two substances are p-cymene and d-limonene. P-cymene is very dominant in most cases, with a content approx. four times greater than the limonene content, but in one case the content of limonene is the same as the content of p-cymene. The results are shown in Figure 4.3.

P-cymene occurs naturally in more than 200 food products [13]. Data shows that p-cymene is mainly ingested by consumption of food products such as butter, carrots, nutmeg, orange juice, oregano, raspberries and lemon oil, and nearly all spices [14]. It is estimated that approx. 30000 kg of p-cymene is consumed every year as a natural element of these food products.

D-limonene [15] occurs naturally in lemon rind, dill, fennel, celery and plants, and in many essential oils. It can also be produced synthetically. D-limonene is frequently used as a food additive in order to give a lemon flavour, as a fragrance additive in perfumes, body care products, and as a natural substitute for petroleum-based solvents in paints and detergents.

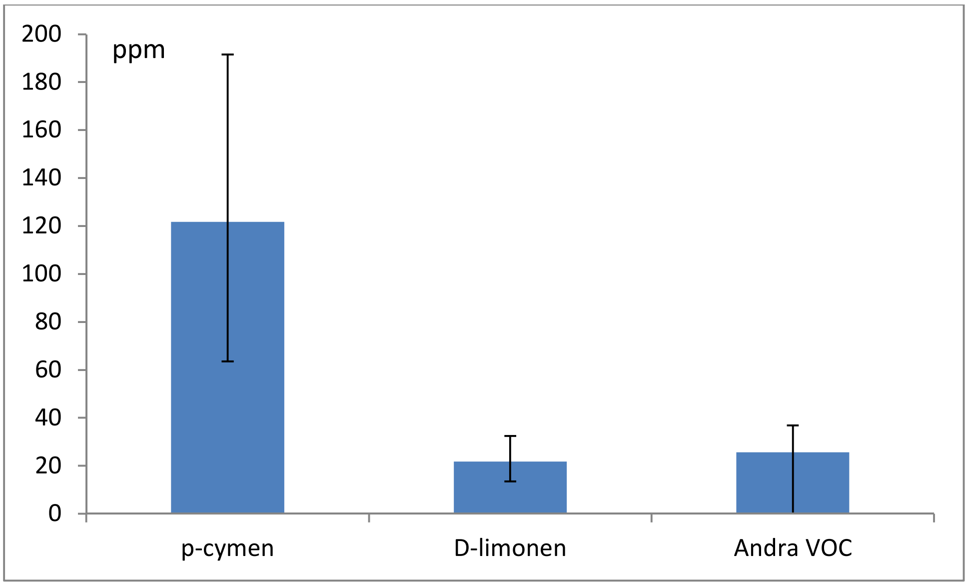

Figure 4.3: Average of p-cymene, d-limonene and total other VOCs in biogases produced from waste plants which digest household waste. Span between lowest and highest values measured

A characteristic chromatogram of VOCs in biogases produced in waste plants where household waste is digested is shown in Figure 4.4. The structures of p-cymene and d-limonene [12] are shown in Figure 4.5.

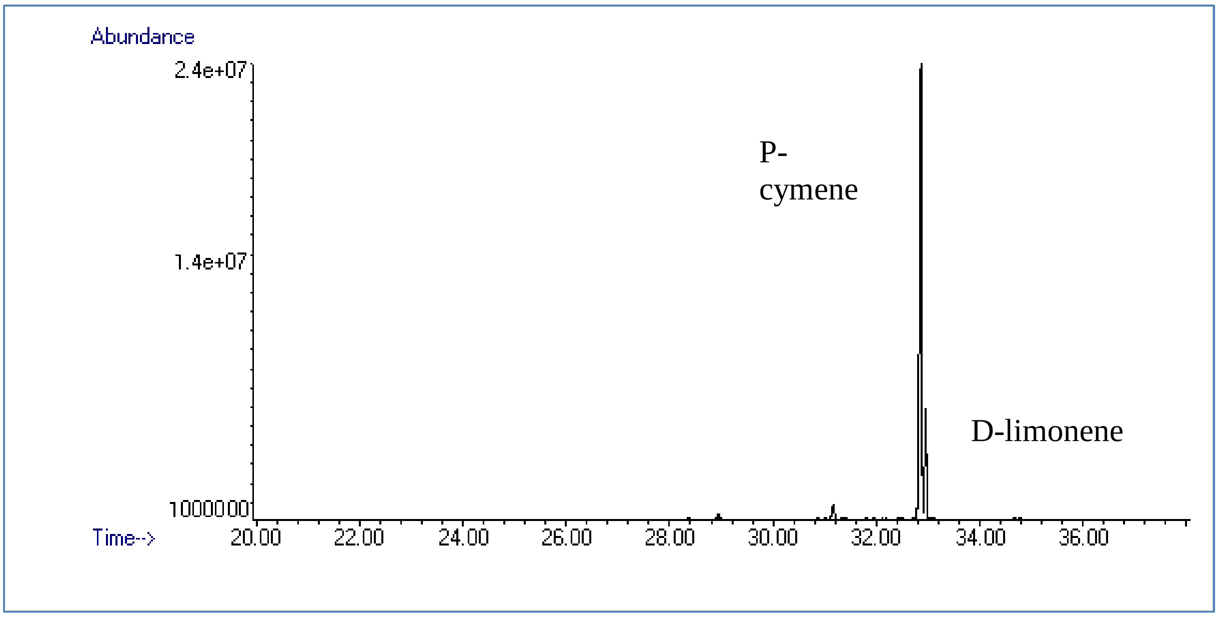

Figure 4.4: Characteristic chromatogram of biogas from digesting of household waste

P-cymene

D-Limonene

Figure 4.5: Structure of p-cymene and d-limonene ($C_{10}H_{16}$)

Household waste contains many more volatile substances (flavourings, etc.), probably in higher quantities than p-cymene and d-limonene. To be able to understand why p-cymene and d-limonene are so dominant in biogas compared with other contaminants, it would be interesting to carry out a more in-depth characterisation of the substrates. This would answer the question as to whether the substances are present in the substrates or formed in digesters through conversion from similar substances.

Biogas composition with regard to VOCs varies widely between waste plants where household waste is included in the substrate and waste plants which only digest slaughterhouse waste and food industry waste. In the latter case, hydrocarbons such as linear and branched alkanes and alkenes with 9 to 13 carbon atoms and furans such as tetrahydrofuran, methylfuran, etc. dominate. Furans are heterocyclic organic compounds comprising an aromatic ring of four carbon atoms and one oxygen atom.

The composition of food waste varies slightly between households, restaurants and catering establishments.
Waste food from restaurants and catering establishments may contain more fat, while the composition of waste food from households includes a higher proportion of carbohydrates [16].
Slaughterhouse waste has a high content of fat and protein. The high protein content may explain the relatively high concentration of ammonia occurring in biogas samples (approx. 100 ppm).

Other substances found in biogases from waste plants include other terpenes such as α-pinene, β-pinene, 3-carene, etc., ketones such as 2-butanone, hydrocarbons with 9 or more carbon atoms.

Sewage treatment plants

Biogas samples from treatment plants also have a very characteristic composition in respect of VOCs. On the chromatogram it is possible to see a fraction with approx. 50-70 hydrocarbons, of which linear hydrocarbons such as undecane are dominant, but it also includes decane, dodecane, nonane, tridecane and many branched hydrocarbons with 9 to 13 carbon atoms. This fraction also includes aromatic hydrocarbons such as trimethylbenzenes, tetramethylbenzenes and cyclical hydrocarbons such as decahydronaphthalene, methyl decahydronaphthalene, etc. Besides this fraction, the biogas contains toluene and siloxanes, decamethylcyclopentasiloxane, abbreviated D5, dominating. The composition of this fraction (besides siloxanes) resembles the composition of vehicle fuel (oil). The results for the dominant substances are shown in Figure 4.7.

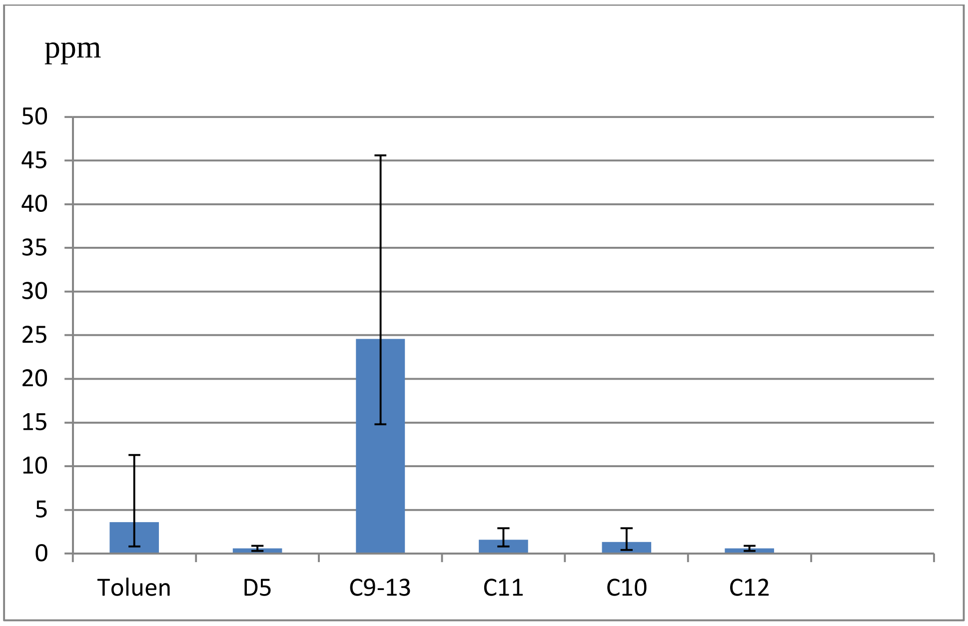

Figure 4.7: Average for toluene, decamethylcyclopentasiloxane (D5), fraction C9-C13 including decane (C10), undecane (C11), dodecane (C12), d-limonene and total other VOCs in biogases produced from waste plants which digest household waste and the span between lowest and highest values measured

Other substances also occur at lower levels, such as sulphur compounds, chlorinated hydrocarbons (in at least one case) and dioxolanes. Dioxolanes are a group of organic compounds which contain a dioxolane ring. The dioxolane ring consists of three carbon atoms and two oxygen atoms.

Plants which digest sewage sludge often accept other substrates such as grease trap removal sludge or discarded milk, glycol water, etc. in limited volumes compared with sewage sludge. As the substances named above do not occur at all plants, it is possible to suspect that their presence is due to these supplementary substrates. The mixture of other substrates is typically 1-3% of the total substrate volume.

Again, more information is needed on the substrates and the process so as to be able to understand why these substances occur in the biogas. Are they present in the substrates, adsorbed to the substrates or formed in digesters? Siloxanes are used in many different applications such as the manufacture of hygiene and cosmetic products (deodorants, shampoos, conditioners, hairsprays, shaving gels), paint removal products, food additives, implants for cosmetic surgery, nail polishes, pacemakers, production of babies' dummies and additives in paints and oils and for dry cleaning. They can be adsorbed to some solid materials, such as digested sludge. During anaerobic breakdown of substrates, they are volatilised and end up in the biogas.

Significant quantities of p-cymene and d-limonene were found in the biogas in two cases. It may be assumed that these substances occur in the biogas due to the other substrates digested together with the sewage sludge in these plants.

A characteristic chromatogram of VOCs in biogases produced at treatment plants is shown in Figure 4.8.

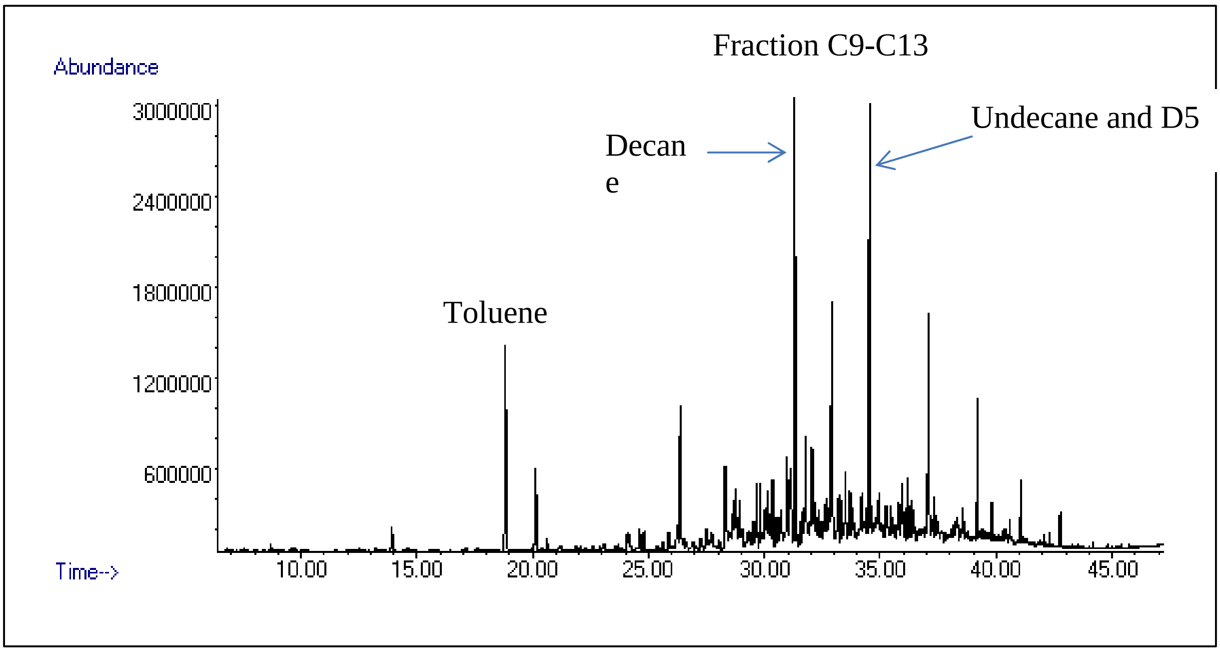

Figure 4.8: Characteristic chromatogram of biogas from digesting of sewage sludge

Food industry residues and energy crops

VOCs in biogas samples from digesting food industry residues and energy crops occur in considerably lower quantities (a few ppm per substance) than in biogases from treatment plants or waste plants. Ketones, including 2-butanone, pentanones, hexanones and heptanones often dominate, but furans are also common. Sulphur compounds also occur in significant quantities in two cases, but in one sample they were not found in detectable quantities. Other substances occurring in some samples were chlorinated hydrocarbons, esters, terpenes such as α-pinene, santolina triene, p-cymene, d-limonene, dioxolanes and also the nitrogen compound ethyl methyl pyridine. The determination of content for the dominant substances is shown in Figure 4.9.

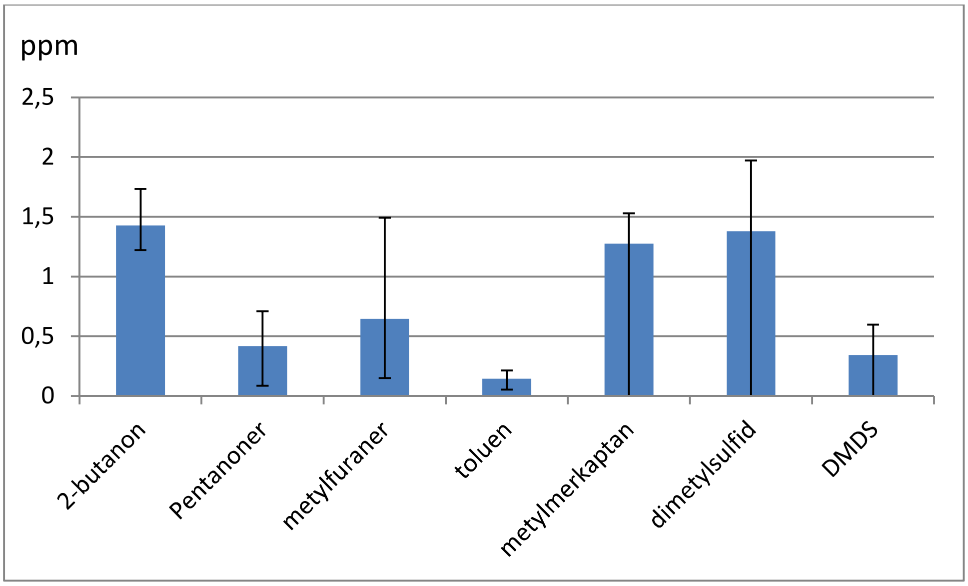

Figure 4.9: Average for 2-butanone, pentanones, methylfurans, toluene, methyl mercaptan, dimethyl sulphide, dimethyl disulphide (DMSDS) in biogases produced from waste plants which digest food industry residues and energy crops, and the span between lowest and highest values measured

Manure

In this study, the data (n = 3 of which two for the same plant but from two different digesters) from biogas samples from the digesting of manure is too limited to draw conclusions on the VOC content of these samples. These samples have a mutually different gas composition in respect of VOCs. In one case, ketones and linear hydrocarbons are the dominant VOCs, and in the other case terpenes (α-pinene, β-pinene, 3-carene) and toluene dominate. These substances probably originate from animal feeds of different kinds. Moreover, in one case a foam reducer was used in the digester which may affect the gas composition with regard to VOCs. In the other case, byproduct from the food industry were digested together with manure. As many more farm-based plants planning to digest manure are in the pipeline, collecting more samples in order to acquire representative data is of interest.

Landfill

In terms of VOCs, the two landfill gases analysed in this study are of a composition similar to biogas samples from plants which digest household waste. P-cymene and d-limonene are clearly dominant.

Besides these two substances, a large number of hydrocarbons with 5 to 12 carbon atoms (linear, branched or cyclical), aromatic hydrocarbons (benzene, toluene, xylenes, etc.), chlorinated and fluorinated hydrocarbons and sulphur compounds are present. I a study from Allen et al. [3], the composition of VOCs from seven landfill sites in the United Kingdom was charted. The substances occurring there were alkanes (302-1543 mg/m^3), aromatic hydrocarbons (94-1906 mg/m^3), cycloalkanes (80-487 mg/m^3), terpenes (35-652 mg/m^3) and halogenated hydrocarbons (327-1239 mg/m^3), i.e. more or less the same families as those found in this study, albeit not in the same proportions. The composition of the waste and the progress of the decomposition process are the two parameters which control the composition of the gas. In Sweden, sending organic waste to landfill has been prohibited since 2005, while landfill sites in the United Kingdom still accepts such waste. Moreover, waste landfill sites in the United Kingdom accept garden waste, while such waste is often composted in Sweden. It is assumed that terpenes, in particular α-pinene and β-pinene, are vaporised [3] from garden waste, and these are the dominant terpenes in the British study, while p-cymene and d-limonene – which probably originate from fruit – are dominant in this study.

4.2 Composition of substances occurring in biogas samples

Table 4.2 provides an overview of total VOC content in biogases depending on which substrate is digested.

Table 4.2: Total VOC content depending on substrate

mg/m^3	Medium:	Span
Waste plants (which digest household waste, among other things)	700	400-1200
Treatment plant	200	120-400
Byproducts from food industry	18	10-30

Table 4.3 provides an overview of substances found to be present in biogas from different substrates.

Table 4.3: Composition of identified substances in biogas

a) Hydrocarbons

	Sewage sludge	Household waste	Slaughterhouse waste	Residual products	Manure	Landfill
Terpenes	X	X	(X)	X	(X)	X
P-cymene		D		X		D
D-limonene	X	D	(X)	X		D
α-pinene				X	(X)	
β-pinene						
Alkanes	X	X	(X)		(X)	X
Decane	X		(D)		(X)	X
Undecane	D		(D)		(X)	X
Dodecane	X		(D)		(X)	X
Pentanes						X
C6, C7, C8, C9						X
Alkenes			(X)			

Decene			(X)			
Undecene			(X)			
Cyclical hydrocarbons	X					X
Cyclohexane						X
Decahydronaphthalene	X					
Methyl decahydronaphtalene	X					
Aromatic hydrocarbons	X					X
Toluene	D					X
Xylenes	X					X
Tri-, tetramethylbenzenes	X					X

b) Oxygenated substances

	Sewage sludge	Household waste	Slaughterhouse waste	Residual products	Manure	Landfill
Dioxolanes	X			X		
Ethyl methyl dioxolane	X					
Trimethyl dioxolane				X		
Furans			(X)	X		
Tetrahydrofuran			(X)			
Methylfuran			(X)	X	(X)	
Ketones		X		X		
2-butanone		X		D	(X)	
Pentanones		X		X		
C6-, C7-, C8-ketones				X		

c) Other substances

	Sewage sludge	Household waste	Slaughterhouse waste	Residual products	Manure	Landfill
Nitrogen compounds				X		
Ethyl methyl pyridine				X		
Sulphur compounds		X			(X)	
1-propanethiol		X			(X)	
Methyl mercaptan				D	(X)	
Dimethyl sulphide				D	(X)	
Dimethyl disulphide				X		
Thiophenes					(X)	

Chlorinated and fluorinated hydrocarbons Di-, tri-, tetrachloroethylene Fluorodichloromethane, chlorofluoroethane	X X			X X		X X X
Siloxanes	X			X		X
D4	D			X		X
D5				X		X

D: dominant, i.e. the quantities correspond to more than 10% of the total content of contaminants measured for a specific substrate
X: present
(X) and (D): identified, but insufficient data

4.3 Chemical characterisation of clean gases

As some upgrading techniques require the gas to be cleaned first to remove hydrogen sulphide, some plants have a carbon filter which treats the biogas before it is to be upgraded. The main task of the carbon filter is to reduce the hydrogen sulphide content. Hydrogen sulphide is corrosive even in low quantities, which results in a risk of corrosion of gas pipes and equipment when upgrading or using biogas.

It will also be interesting to study how these carbon filters handle the other contaminants present in the biogas. In this study, biogas samples have been taken before and after four carbon filters for analysis of hydrogen sulphide and contaminants.

The results show that all carbon filters included in this study perform their primary task of removing a large proportion of the hydrogen sulphide. That said, the results show very varying effects on VOCs. In some cases, most VOCs are removed very effectively (sample 3), while in other cases, the effect on contaminants is very limited (samples 1, 2 and 4) (see Figure 4.10).

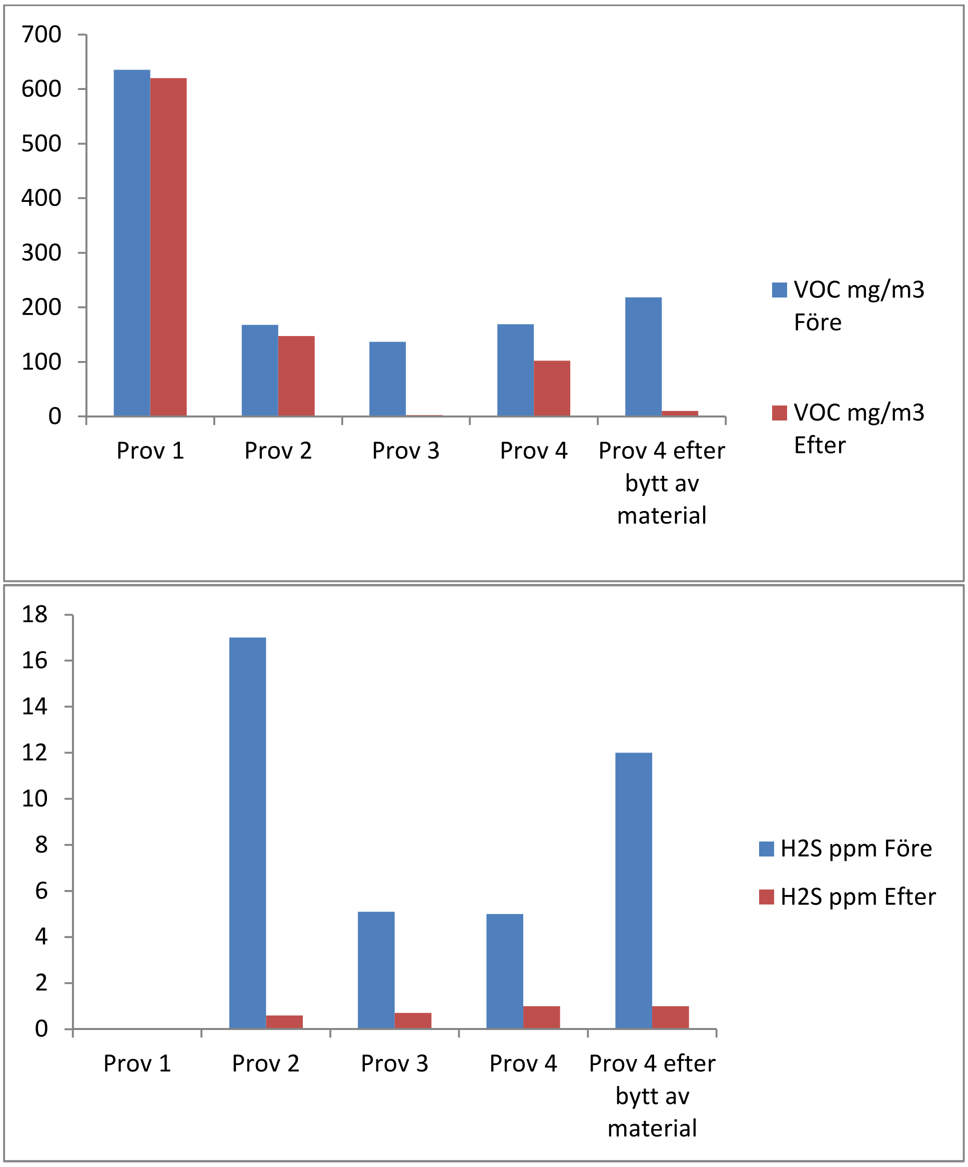

Figure 4.10: VOC content (above, expressed in mg/m^3) and hydrogen sulphide content (expressed below in ppm) before and after carbon filters

The most likely explanation is that the carbon filter material is more or less saturated. This hypothesis was confirmed when analyses were repeated directly after replacing the carbon filter material at a plant. After replacement, the carbon filter was considerably more effective at removing the VOCs. The fact that different types of filter material are used may also be a possible explanation of the variation in effectiveness.

4.4 Chemical characterisation of upgraded gases

4.4.1 Methane, carbon dioxide, oxygen, nitrogen gas, hydrogen gas, carbon monoxide

The quantities of the primary components methane, oxygen and nitrogen gas are shown in Figure 4.11. This figure shows the average from measurements carried out, divided according to upgrading techniques.

As things stand at present, a Swedish standard (SS 15 54 38 “Krav på biogas som fordonsdrift” [Motor fuels – Biogas as fuel for high-speed otto engines] [17]) for renewable vehicle gas is used informally. This standard lays down requirements for primary components: a methane content of 97 ± 1% and total content for carbon dioxide + oxygen + nitrogen gas of max. 4% (oxygen content max. 1%). It is therefore important to indicate the measurement uncertainty for these components. The relative measurement uncertainty (95% confidence interval) for methane and carbon dioxide is estimated at 1.0% in the range 6-100%. The absolute measurement uncertainty (95% confidence interval) for carbon dioxide, oxygen, nitrogen gas, hydrogen gas and carbon monoxide is estimated at 0.1% in the range 0.1-6% by volume.

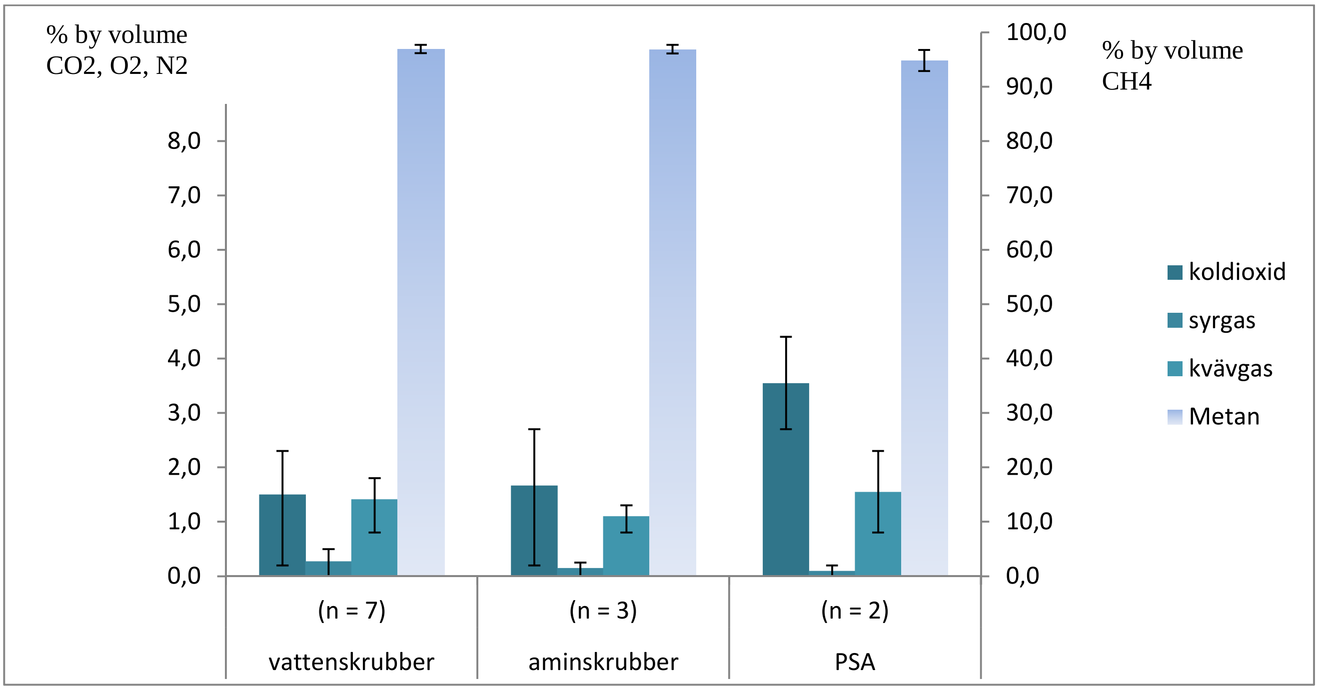

Figure 4.11: Average for methane, carbon dioxide, oxygen and nitrogen gas in clean gases upgraded using different upgrading techniques and the span between lowest and highest values measured

The results are also summarised in Table 4.4.

Table 4.4: Average for primary components (% by volume) in all clean gases (irrespective of substrate) upgraded using different techniques and the span between lowest and highest values measured

	Water scrubber		Amine scrubber		PSA	
No. of samples	7		3		2	
	Medium:	Span	Medium:	Span	Medium:	Span
CH_4	97.0	96.2-97.7	96.9	96.1-97.7	94.9	92.9 – 96.8
CO_2	1.5	0.2-2.3	1.7	0.2-2.7	3.6	2.7-4.4
O_2	0.3	< 0.1-0.5	0.3	< 0.1-0.3	0.1	< 0.1-0.2
N_2	1.4	0.8-1.8	1.1	0.8-	1.6	0.8-

				1.3		2.3
$CO_2+O_2+N_2$	3.0	2.3-3.9	3.0	1.7-3.7	5.2	3.5-6.9

All except one of the clean gases analysed are compliant with the two requirements laid down in the Swedish standard SS 15 54 38 with regard to primary components, i.e. a methane content of 97 ± 1% and a total content for carbon dioxide + oxygen + nitrogen gas of max. 4% (oxygen content max. 1%).

4.4.2 Hydrogen sulphide, ammonia, water

According to the standard SS 15 54 38, the total sulphur content must not exceed 23 mg sulphur/Nm^3. Most of the sulphur originates from the addition of odorous substances for safety reasons, known as odorisation [18]. THT (tetrahydrothiophene, approx. 6 mg S/Nm^3) is used in Sweden. If hydrogen sulphide is the only remaining sulphur compound in detectable quantities, this means that the content of hydrogen sulphide must not exceed approx. 17 mg sulphur/Nm^3, i.e. approx. 13 ppmv hydrogen sulphide. All biogases analysed in this study meet this requirement as the content of hydrogen sulphide in all clean gases was less than 2 ppmv.

According to the standard SS 15 54 38, the total content of nitrogen compounds (excluding nitrogen gas) counted as ammonia must not exceed 20 mg/Nm^3. Small amines (methylamine, ethylamine, etc.) have not been analysed in this study. Besides these amines, only ethyl methyl pyridine could be detected in one biogas sample, and in a low quantity (less than 1 ppmv). It may be assumed that ammonia should be the dominant nitrogen compound in terms of content. Ammonia occurs in quantities of up to approx. 100 ppm in some biogas samples. The ammonia content in all clean gas samples was found to be less than 1 ppmv, i.e. less than 1 mg/Nm^3, which means that ammonia is removed effectively in the upgrading plants tested. As small amines are relatively soluble in water, it may be assumed that if they were present in significant quantities in biogas, these would be removed effectively in the extraction system at the same time as water.

The method used to measure the water content in clean gases was not fully tested, and there was insufficient time for validation. Thus no conclusions can be drawn regarding water content in clean gases.

4.4.3 Volatile organic compounds

Effectiveness of removal

A comparison between VOC content in biogases and clean gases for every upgrading technique tested (including cleaning and drying stages) is summarised in Table 4.5.

Table 4.5: Comparison of VOC content in biogases and clean gases

	Waste plant	Treatment plant	Waste plant + Treatment plant	Energy crop and byproduct from food industry	Manure
No. of clean gases (n=)	2	2	3	3	1

Average VOCs in biogas, mg/m^3	700 mg/m^3	200 mg/m^3	400 mg/m^3	10-30 mg/m^3	20 mg/m^3
PSA VOCs in clean gases	5 mg/m^3	3 mg/m^3	-	-	-
Water scrubber VOCs in clean gases	100 mg/m^3	-	70 mg/m^3 < 5 mg/m^3	< 1 mg/m^3 (n = 3)	< 1 mg/m^3
Amine scrubber VOCs in clean gases	-	10 mg/m^3	10 mg/m^3	-	-

In biogases upgraded in treatment plants and waste plants, the VOC content was approx. 700 mg/m^3 and 200 mg/m^3 respectively. In five cases, a total of less than 10 mg/m^3 VOCs remain in clean gases after upgrading and drying. In the other two cases, the VOC content in clean gases was 70 mg/m^3 and 100 mg/m^3 respectively. All these clean gases contain the substances that have been demonstrated as being characteristic for the substrate: p-cymene and d-limonene for waste plants (with digesting of household waste) and an oil fraction containing hydrocarbons with 9 to 13 carbon atoms for treatment plants.

There are negligible quantities of VOCs in clean gases upgraded from biogas produced by digesting food industry byproducts or energy crops. The biogas already contained much lower quantities of VOCs than biogases from treatment plants or waste plants.

As the number of samples for each combination of substrate/upgrading technique is very limited (often just one sample), the results show how individual plants operate. The objective of the project is not to study each individual case, but to show how effective specific upgrading techniques are on contaminants. Therefore, the conclusions considered to be representative for a specific technique, i.e. which have been found at a minimum of two of the participating plants, are reported here.

Biogases upgraded with chemical scrubber

Samples were taken before and after the adsorption tower and after the drying stage. It is possible from these samples to check what effect the adsorption tower has on contaminants.

The results show that the adsorption tower just removes ketones and esters effectively from the biogas and generally does not affect the composition of other contaminants. Ketones and esters contain a carbon-oxygen group with a double bond (C=O) (in other words, they share a structural element with carbon dioxide, O=C=O) which reacts with amines in the same way as carbon dioxide. A chromatogram of VOCs in biogas before and after the adsorption tower is shown in Figure 4.12.

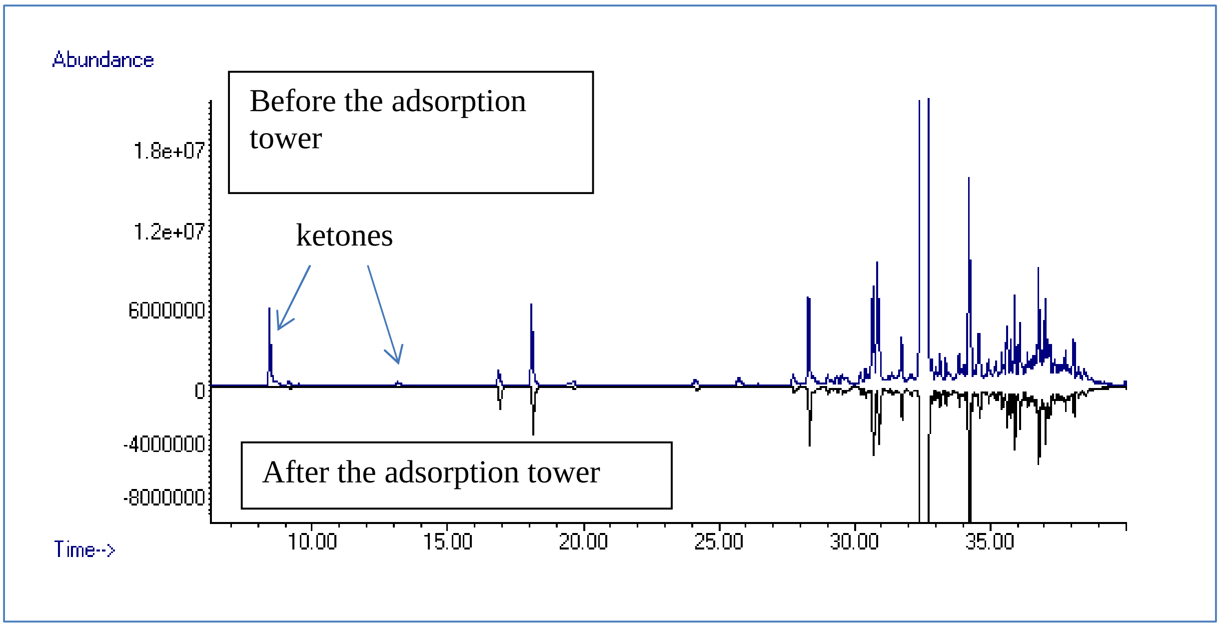

Figure 4.12: Chromatogram before (above) and after (below) the adsorption tower in an upgrading plant with an amine scrubber

At least 95% of the compounds passing the adsorption tower are then removed effectively during the drying stage.

The water is normally adsorbed on a desiccant. The desiccant may be a silica gel or an aluminium oxide. The damp gas is fed through a drying tower filled with the desiccant. Water is present in the form of a condensate. On one occasion, a flask was filled with the condensate water. The air above the condensate was analysed. Its composition in respect of VOCs was compared with the composition of biogas. The results are shown in Figure 4.13.

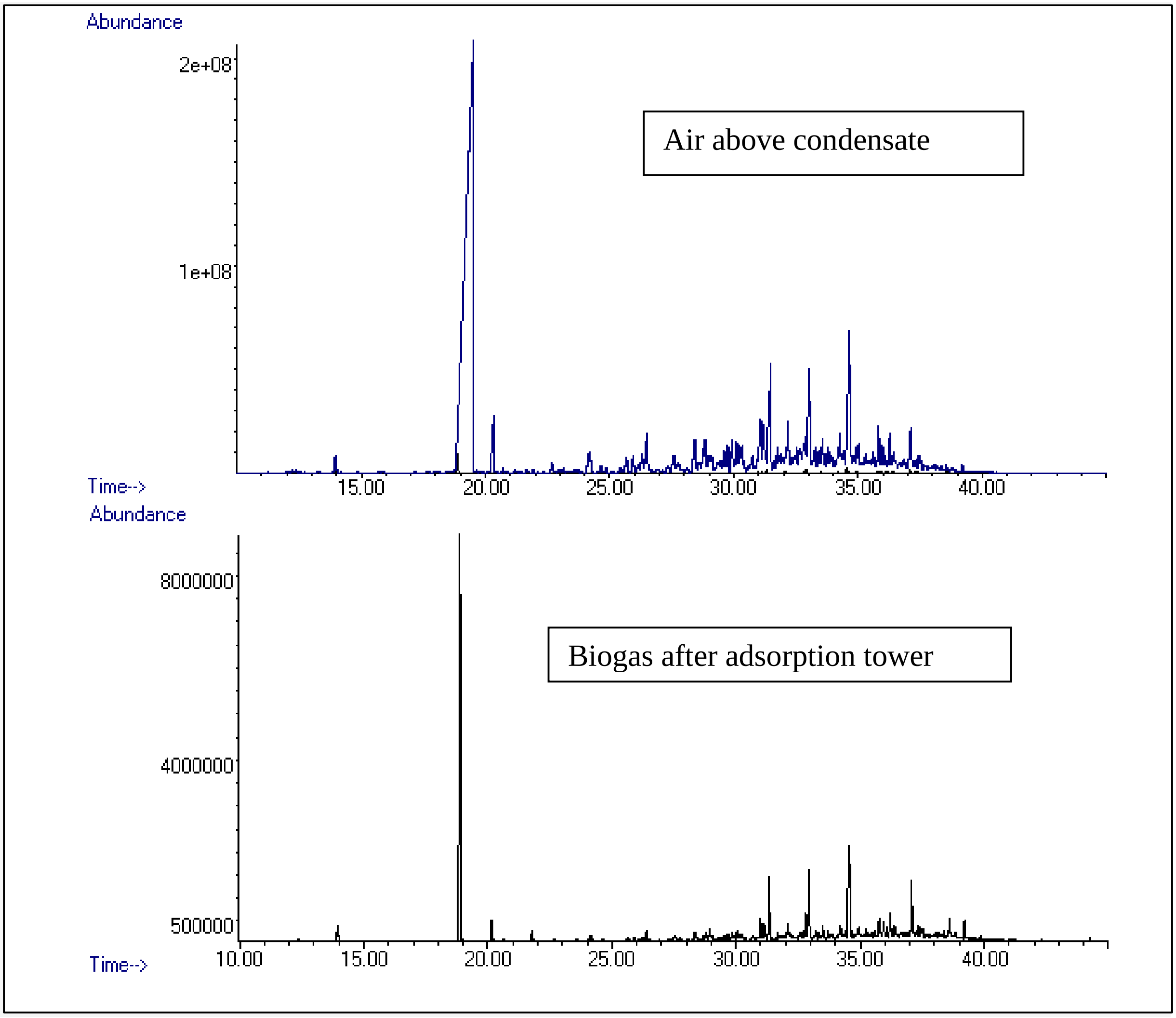

Figure 4.13: Chromatogram of the air above the condensate (above) and chromatogram of biogas after the adsorption tower

It is clearly apparent from Figure 4.13 that the same substances are found in the biogas after the adsorption tower and in the air above the condensate, which indicates that these substances are condensed together with the water.

In a small number of cases, clean gases from amine scrubber plants have been observed to contain significant quantities of amines. These amines have accompanied the gas out of the adsorption tower and can be found in the dry clean gas (the end product) as shown in Figure 4.14. No study has been carried out to observe the conditions under which these substances accompany the upgraded gas out from the adsorption tower.

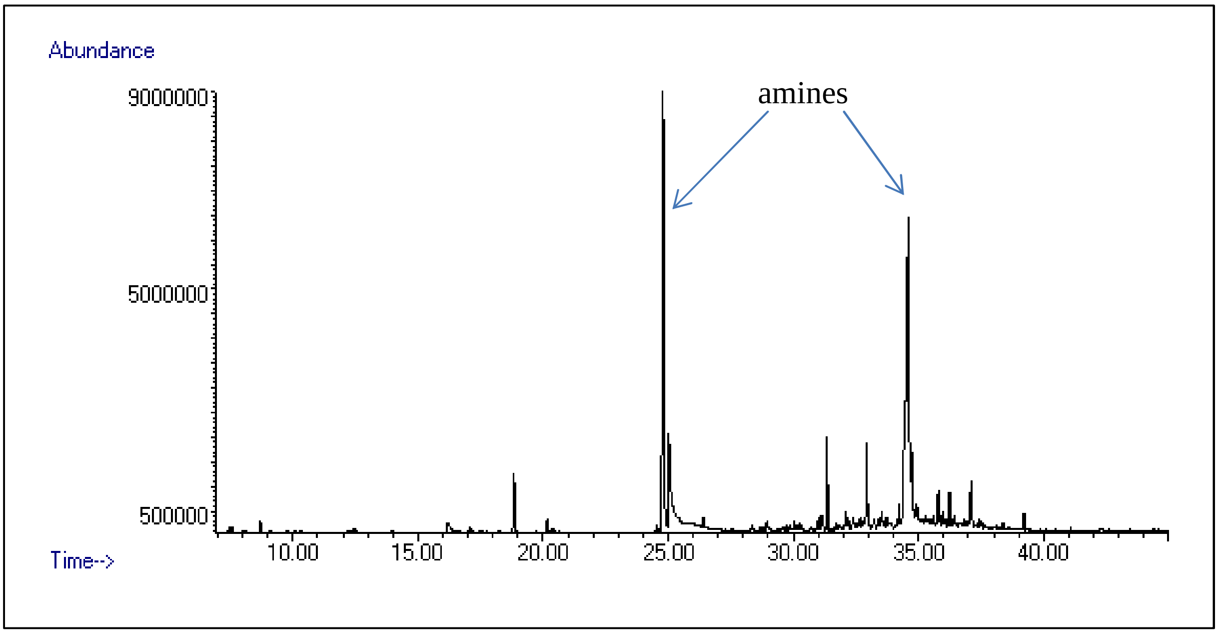

Figure 4.14: Chromatogram of clean gas containing significant quantities of amines used in amine scrubber

Biogases upgraded with water scrubber

All clean gas samples were taken from the upgraded and dry gas. Hence it is only possible to assess how the upgrading plant functions as a whole.

A total of seven clean gases from water scrubber plants were analysed. In five cases, less than 5 mg/m^3 VOCs remained in the clean gases. In four of these cases, the VOC content in biogas was already relatively low (approx. 10-30 mg/m^3), but in one case there was approx. 400 mg/m^3 VOCs in the biogas. A water scrubber is used in parallel with other upgrading techniques at two of the participating plants. In both cases, clean gases upgraded with a water scrubber contained considerably more VOCs than the gas upgraded in parallel with other upgrading techniques. Up to 100 mg/m^3 VOCs were measured in clean gas upgraded with a water scrubber.

Biogases upgraded with PSA

In this study, two gases were analysed after upgrading with PSA.

The biogas first passes a carbon filter, the primary task of which is to significantly reduce the hydrogen sulphide content, and the gas is then dried before it reaches PSA columns. In one case, gas samples were taken before the carbon filter, after the carbon filter, after drying and after upgrading. The carbon filter removed most of the contaminants except for chlorinated hydrocarbons with an efficiency in excess of 90%. In the other case, only the dry and upgraded gas was analysed. The gas then contained a total of 5 mg/m^3 VOCs, while the biogas contained approx. 400 mg/m^3.

5 CONCLUSIONS

5.1 Primary components

Biogas

The quantities of methane and carbon dioxide in biogases studied as part of this project match the indicative gas compositions presented in the Marcogaz report “Injection of gases from non-conventional sources into gas networks” [11], i.e. approx. 65% for methane in biogas produced by digesting with a span between 50 and 80%. In this study, it is possible to see that the quantity of methane in biogases produced at treatment plants, at waste plants or by digesting manure is around 60-62%, with a relatively small span from 58% to 67%. The content of methane in biogas produced by digesting of energy crop and the food industry is slightly lower, approx. 53.1%. The carbon dioxide content follows an opposing tendency.

The content of oxygen rarely exceeds 0.5% by volume.

The concentration of hydrogen gas and carbon monoxide is lower than the detection limit (< 1000 ppm) in all samples analysed in this study.

Most of the biogases analysed were saturated with water vapour, which meant that the water content was around approx. 1.7-1.9% by volume.

The hydrogen sulphide content varies widely but nevertheless follows a number of general tendencies. Biogases produced at waste plants where household waste is digested contain around 100 ppm hydrogen sulphide. Biogases produced at treatment plants contain around 10-20 ppm hydrogen sulphide.

Ammonia could not be demonstrated in samples from treatment plants or from waste plants which digest household waste. On the other hand, ammonia (approx. 100 ppm) could be demonstrated in samples from waste plants which digest slaughterhouse waste. Ammonia was also demonstrated in one sample from the digesting of manure (10 ppm) and in one sample from the digesting of food industry residues.

Clean gas

Ten out of eleven upgraded and dry clean gases analysed in this study are compliant with the two requirements laid down in the Swedish standard SS 15 54 38 with regard to primary components, i.e. a methane content of 97 ± 1% and a total content for carbon dioxide + oxygen + nitrogen gas of max. 4% (oxygen content max. 1%).

The quantities of hydrogen sulphide and ammonia in all clean gases was less than 2 ppm.

5.2 Volatile organic compounds

Biogas

Which VOCs are present and dominate in biogas is dependent on the substrate.

P-cymene and d-limonene, two terpenes, have been identified as characteristic for biogas samples from plants where household waste is digested. These substances are clearly dominant, and together these quantities represent approx. 90% of the total VOC content. The presence of an “oil” fraction containing alkanes with 9 to 13 carbon atoms is characteristic for biogas from treatment plants. Siloxanes occur in significant quantities in biogases from treatment plants. Ketones (particularly 2-butanone) and sulphur compounds normally occur in biogas samples from the digestion of energy crops and byproducts from the food industry. The composition of volatile organic compounds (VOCs) in biogas samples from the digestion of manure has not been mapped as insufficient numbers of samples have been analysed.

Typical VOC quantities are 700 mg/m^3 at waste plants, 200 mg/m^3 at treatment plants and 20 mg/m^3 when energy crops and byproducts from the food industry are digested.

Some substances occur in almost all biogases, irrespective of which substrate has been digested. These substances include 2-butanone, toluene, d-limonene and undecane.

Clean gases

Clean gases studied here often contained less than 10 mg/m^3 VOCs, except in two cases where the VOC content in clean gas was 70 mg/m^3 and 100 mg/m^3 respectively (including 50 mg/m^3 d-limonene). Even if the biogas has been upgraded and there is only a small quantity of VOCs remaining, it contains the VOCs which indicate which substrate has been digested.

As regards VOCs, there are currently no requirement for permitted quantities although discussions are under way in Sweden and Europe with a view to setting requirements for siloxanes and halogenated hydrocarbons as these substances have been cited as a possible cause of undiagnosed running problems in gas vehicles. That said, this is no data to indicate whether other contaminants identified in this study (including terpenes, hydrocarbons and ketones) affect the running of gas vehicles. At a certain content, d-limonene can affect the odour of the upgraded biogas and mask/alter the odour from the sulphurous odour additive.

As some VOCs are potentially hazardous to humans and the environment, it is important to trace the location of the VOCs cleaned from biogases. Some results from this study indicate that they are adsorbed to the adsorption material in effective carbon filters or end up in condensate water from the drying stage in plants with amine scrubbers. In some plants, VOCs are processed with the aid of what is known as a vocsidizer. Where VOCs are has not been studied in some cases. There is a risk of a certain proportion of these VOCs emerging from the upgrading plant without being processed.

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Svenskt Gastekniskt Center AB

Scheelegatan 3, 212 28 Malmö ● Tel 040-680 07 60 ● Fax 040-680 07 69
www.sgc.se ● info@sgc.se