BIOGAS SUSTAINABILITY
Information from IEA BIOENERGY TASK 37
Energy from Biogas

The Swedish Voluntary system for control of methane emissions



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Foreword

The Swedish system for methane emission control from biogas production and upgrading plants, called the Voluntary Agreement has gained significant international interest in the last years. This report summarises the system, and is written within the framework of IEA Bioenergy Task 37 "Energy from biogas".
More information about Task 37 can be found on the website: www.iea-biogas.net.

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Introduction

Biogas production and use

Biogas is formed during the anaerobic degradation of organic material. It can be produced from any material that is biodegradable and consists mainly of two gases, methane and carbon dioxide. Biogas today is primarily produced from sewage sludge, household waste and energy crops. Biogas production and use has gained increased interest over the last few decades, mainly due to its many environmental benefits. As a result the annual production is increasing.

Biogas, or to be more precise, the methane part of biogas, can be used as an important source of renewable energy. It can be used for heat production or heat and power production, as a raw material in industry and as a vehicle fuel. Biogas can also be used to replace natural gas in the gas distribution grid.

Biogas cleaning and upgrading

In order to use biogas, it needs to be cleaned to a greater or lesser extent, depending on the use. Biogas to be used as a vehicle fuel, or to replace natural gas, needs a treatment whereby the carbon dioxide is separated from the methane. Removing carbon dioxide increases the energy content per volume. This is known as biogas upgrading, and several techniques are commercially available. Emissions from three different technologies have been quantified in the Voluntary Agreement, and are described below.

PSA

PSA (Pressure Swing Adsorption) is a technique by which carbon dioxide in the raw biogas is adsorbed on activated carbon or zeolites. In a PSA plant, there are usually several columns with the adsorbing material working in parallel. The material is regenerated by decreasing the pressure which will make the carbon dioxide desorb. Small amounts of methane that may also have been adsorbed are also released; these end up in the off-gas.

Water scrubbing

Water scrubbing is a technique by which the raw biogas meets a counter flow of water in which carbon dioxide dissolves. Water scrubbers can be of flow-through type, but usually the water is regenerated by a decrease in pressure and by bubbling air through the water. Methane slip will occur in air leaving the desorption column where the water is regenerated. If the water is not regenerated, methane slip will occur in the water stream leaving the plant.

Chemical scrubbing

Chemical scrubbing is similar to water scrubbing, the difference being that in chemical scrubbing carbon dioxide is chemically bound to amines present in the counter flowing liquid. The liquid is regenerated by heat and, since methane has a low solubility in the liquid, only small amounts of methane occurs in the off gas.

Photo 1. The Gårdsbiogas biogas plant at Katrineholm

Environmental benefits and methane emissions

Biogas production and the use of its energy content create several environmental benefits. Replacing fossil energy leads to decreased carbon dioxide emissions. The environmental benefit is dependent on how the biogas is produced and used. Biogas production from manure leads to a "double" positive environmental effect. Not only does the biogas replace fossil energy, thus decreasing carbon dioxide emissions, but also the methane emission that usually occurs during manure storage is avoided. However, while biogas use does lead to decreased emissions of fossil carbon dioxide, methane is, in fact, a strong greenhouse gas and thus emission of methane has to be avoided or minimized during the process. The global warming potential for methane over a 100 year timeframe is 25 times that of carbon dioxide (IPCC, 2005).

Overall, the environmental benefits, and in particular the decrease in fossil carbon dioxide emissions, mean that a certain level of methane emissions can be tolerated while still maintaining a positive environmental effect. How high the emissions can be before the total effect becomes negative depends on the raw material used. A study has shown that for production and upgrading of biogas from manure, the methane emissions can be up to 22–26 %, while for organic waste the level is 12–17 %, and for grass, straw or beet tops 8–16 % (Börjesson and Berglund, 2003). In general though, the greatest environmental benefit is obtained when emissions are minimized. Apart from the environmental aspect, there are also other reasons to avoid methane emissions. There is, of course, an economic incentive not to lose the methane produced. A loss of methane is a loss of income. Safety is also an important consideration, as methane can form explosive mixtures with air. Plus, biogas emissions can lead to odour problems in and around the plant.

Thus, the Voluntary Agreement was initiated with the aim of quantifying and minimizing methane slip from biogas production plants and biogas upgrading plants.

Photo 2. Digesters at the Rötkammare biogas plant

Background for the Voluntary Agreement

A Swedish study (Persson, 2003) concluded that in some cases methane emissions from biogas upgrading plant were higher than the 2 % that was at that time the level generally claimed by the plant's manufacturers. A different Swedish study (Gunnarsson et.al. 2005) showed small methane emissions at various points in the plant, with a total methane slip of between 0,5 % and 4 %.

In 2007, the Voluntary Agreement was initiated (Persson et.al. 2007) in order to establish a systematic approach to quantification and minimization of methane emissions. The system for the Voluntary Agreement was then revised in 2009 (Holmgren, 2009). A more detailed description of how to measure and calculate the methane slip was also published by Holmgren in 2011. However, one remaining problem is that methane slip from surfaces such as uncovered digestate tanks can be hard to quantify. To be able to improve the system of the Voluntary Agreement, work is on-going in this area. The results of the system of the Voluntary Agreement have been presented at several national and international conferences.

The title for the Voluntary Agreement in Swedish is "Frivilligt åtagande".

Description of the system

Boundaries

The system boundaries for the different types of biogas plants are presented in Fig. 1-3. Only methane emissions within the following boundaries are quantified:

- Only parts of the plant of which the plant owner has control over are included.
- Only parts connected to production or cleaning/upgrading of biogas are included. Thus methane slip that arises from use of biogas or digestate is not included.

Biogas plant

The Voluntary Agreement system begins when the substrate is delivered to the plant (Fig. 1). The transport to the plant is thus not included. Even though plants can differ, all parts of the biogas production plant are included in the context of the Agreement: from storage of substrate, pre-treatment processes, mixing, digestion, post-digestion and storage of digestate at the plant. The system covers stages up until the point at which the digestate is transported from the plant by truck or in a pipeline. Thus emissions during transport, storage on farms or spreading of digestate are not included. For produced biogas, the system covers up until the point at which the gas is transferred for use to a boiler, engine, a turbine or to an upgrading plant.

Sewage sludge digestion plant

Biogas is often produced at waste water treatment plants. Treatment of waste water includes processes that are not related to biogas production and therefore only the parts of the waste water treatment plants that are directly related to biogas production are included in the Voluntary Agreement. These types of plants will be referred to as biogas plants below. The system of Voluntary Agreement begins when the sewage sludge enters the digester or at the point where the sewage sludge is treated before the digestion (in e.g. mills or centrifuges) and ends after the digestate storage (Fig. 2).

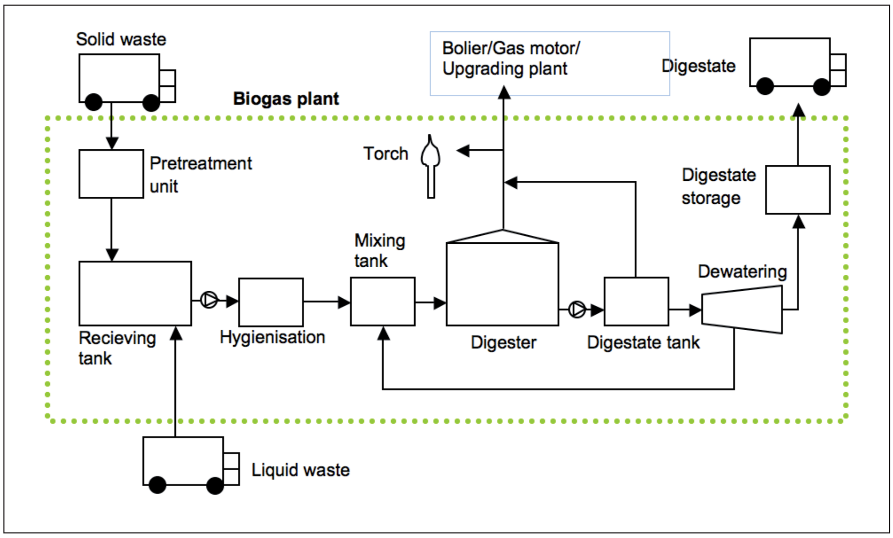

Fig. 1. Green dotted line shows system boundaries for the Voluntary Agreement for a biogas plant.

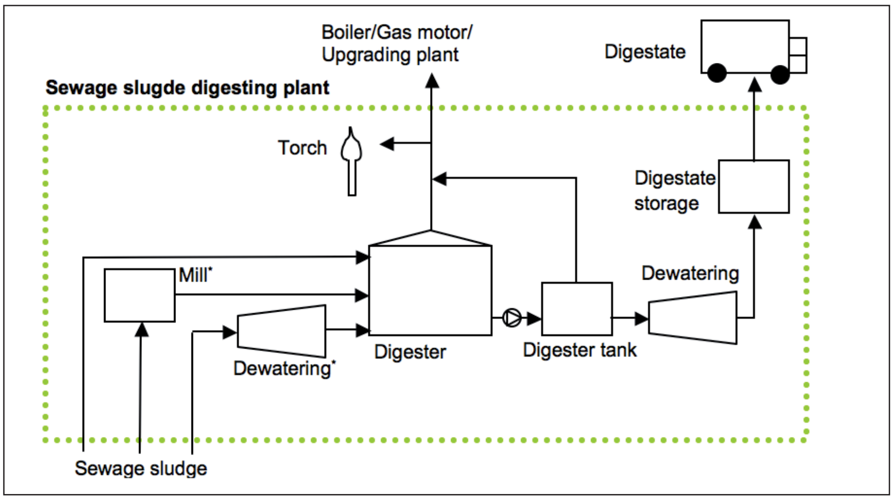

Fig. 2. Green dotted line shows system boundaries for the Voluntary Agreement for a sludge digesting plant.

**Examples of potential pre-treatment processes for sludge prior to digestion.*

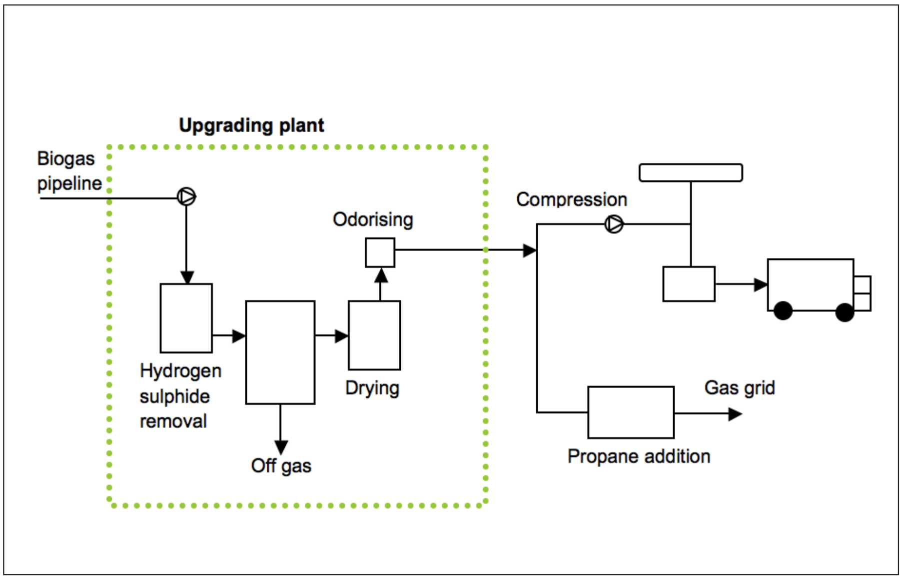

Fig. 3. Green dotted line shows system boundaries for the Voluntary Agreement for a biogas upgrading plant.

For the digestate, the system ends when it is transported from the plant by truck or in a pipeline. Methane emission during the water cleaning process is thus not included in the system. The system ends when the produced biogas is consumed in a boiler, an engine, or a turbine, or is transferred to an upgrading plant.

Biogas upgrading plant

For the upgrading plants, the Voluntary Agreement starts when the gas enters the building containing the upgrading equipment and ends when the gas is cleaned, dried and odorised (Fig. 3). Methane emissions during transport of the upgraded biogas, compression, propane addition, gas storage or emissions at filling stations are not included.

Context of the Voluntary Agreement

The Voluntary Agreement consists of three main parts:

- Inventory of systemic emissions
- Leak detection
- Emission measurements and calculations

Inventory of system emissions

In the Voluntary Agreement, the plant's staff is required to make an inventory of systemic emissions. These should be marked on a map or plan of the plant. The map or plan with marked systemic emissions is then reviewed together with a measurement consultant. To be able to do this, staff needs a thorough knowledge of the plant. At least one of the staff members participating in the inventory should have taken the course on the Voluntary Agreement (these are regularly organised by the Swedish Waste Association).

A classification plan can be helpful in making the inventory of systemic emissions. A classification plan is mandatory for Swedish biogas plants and it describes where explosive gas mixtures can occur and thus where systemic emissions may be expected.

Below is a description of where methane emission may occur in biogas plants, in sewage sludge digestion plants and in biogas upgrading plants. The parts of the plants that are identified are recommended for inclusion in the inventory of systemic emissions.

Biogas plant and sewage sludge digesting plant

Ventilation

Ventilation is the single most important point for systemic emissions. Some plants have one overall ventilation system where smaller flows are collected for odour reduction. Other plants have several different ventilation systems for different parts of the plant. The emissions should be determined downstream of any gas treatment processes, i.e. at the point of emission to air. Both mechanically ventilated objects and natural ventilation should be included.

Mixing tanks

Some plants use a mixing tank before digestion. Under certain circumstances methane production can start in this tank. The measurements should be done in the ventilation. Note that there is also the possibility that hydrogen can form in this tank.

Process Water tank

Some plants have process water tanks from which methane emissions can occur. The measurements should be done in the ventilation.

Digester

Systemic emissions from the digester can occur at overflows. The overflows may be either opened at regularly intervals or, in some cases, permanently open. If the top of the digester is built inside a building the emissions can be determined by detecting methane in the air leaving the ventilation system.

Digestate tank
After passing through the digester, the digestate is pumped to a digestate tank. Some biogas is formed in this tank and some plants also collect this gas. If the biogas formed here is not collected, the tank can be a source of high emissions (estimated up to approx. 10 % of the total methane produced).

Dewatering
Several technologies are commercially available for dewatering of the digestate. Methane emissions can occur through the ventilation system. Measurements of emissions should be done at the top of the dewatering column. For other types of digestate treatments, such as sieving, the emissions should also be measured.

Digestate storage
Digestate storage systems vary for different plants. Some plants only have a liquid fraction, whereas other plants have both a liquid and a solid fraction. Some plants do not have a separate digestate storage tank. Solid digestate is often stored in open containers and methane production and emission can occur here. Methane emissions from open or semi-open tanks are difficult to measure directly, and therefore a mathematical model may be applied (see more under Calculations).
It is common that the digestate is transported from the plant to other storage tanks outside the biogas plant before spreading. This storage is normally not included in the Voluntary Agreement system (see system boundary figures above).

Instruments for gas analysis
Through permanently installed gas analysis equipment at the plant, biogas is constantly flowing. The methane content in this gas is known and the flow of the gas is determined by readings on a rotameter on the measuring instrument.

Biogas upgrading plant

Off-gas
The most important source for methane emissions from the upgrading plant is the off-gas. Optimally the off-gas consists of only carbon dioxide, but it can also contain methane in varying concentrations. To lower the methane slip, the off-gas at some plants is treated to break down methane by e.g. catalytic burning. In those cases the methane emission is measured after the treatment.

Ventilation
The ventilation of the upgrading plant should be taken into account since small emissions occurring at different points are collected here. At some plants the total emissions in ventilation can be as high as or even higher than off-gas emissions.

Instruments for gas analysis
If analysis instruments are permanently installed in the upgrading plant, the methane emission from them should be included (see above regarding biogas plant).

Leak detection

Every plant should carry out regular and systematic leak detection. It should be done at least once a year, but it is strongly recommended that it is performed on a monthly basis. It can be an advantage to use an external resource for this to avoid "domestic blindness". It is recommended to use an external consultant from time to time, say every third year.
A checklist should be prepared that is used as a protocol for the leak detection and it should be archived for checking by an external consultant every third year.

Methods
Recommended methods include traditional leak detection instruments, leak detection sprays and ocular and odour control. It is recommended that every plant has at least one leak detection instrument available, as well as having access to a leak detection spray.
Leak detection instruments are often based on semiconductor sensors or catalytic sensors. It is important to distinguish between leak detection instruments and gas alarms. It should be possible to connect a probe to the instrument to be able to reach parts that are otherwise hard to access. The instruments should be serviced and calibrated as recommended by the manufacturer.

Photo 3. Digestate storage at the Gårdsbiogas plant

Careful leak detection

A systematic leak detection should be done throughout the entire plant with a leak detection instrument and leak detection spray. Before starting, the leak detection instrument should be checked and calibrated. The instrument is moved along potential leakage points, both at a distance from the equipment, and very close to it. Detected methane slips are noted in a protocol. If possible, the exact source of the leakage should be determined and noted, and if possible the leakage should be addressed and stopped immediately.

Intermediate leak detection

If careful leak detection is performed too often there is the risk that it is carried out less thoroughly. To overcome this, intermediate leak detection should be done at more regular intervals, say weekly or monthly. The level of methane should be checked at a number of well-defined places, not close to potential leaking equipment, but at least 1 m away. The methane levels concentrations for each spot should be plotted on a diagram, which will enable detection of a trend. If a diagram indicates a possible leakage, careful leak detection should then be done.

Emission measurements

Every third year measurements should be done by an external measurement consultant, during normal production conditions. The methane emissions are then extrapolated to a yearly basis. To be able to make a careful quantification of emissions, measurements should be done during a longer time and data should be logged. The measurement should continue until a stable signal is detected or a stable pattern is found. As a general rule, measurement should be done during one hour at each point. Methane slip at each point is related to the total flow of methane in the plant. The slip is always related to the methane flow in the raw gas, but for upgrading plants, the slip is also related to the measured total flow of upgraded methane.

How to measure methane

Methane concentrations should be measured by a Flame Ionization Detector (FID)-instrument equipped with a cutter (that filters out other hydrocarbons than methane). FID-instruments usually have broad area of measuring, up to 100 000 ppm (10 vol.-%). The methods of measuring methane with this instrument are described in the international standard EN ISO 25140:2010. It is important to know if, and how, the methane measurement by the instrument is affected by carbon dioxide. For higher levels of methane than the instrument can show, gas samples are taken in bags for later analysis in a laboratory with a Gas Chromatography (GC). This method is described in the international standard EN ISO 25139:2011

If the slip in a measuring point is lower than 0.1 % of the total amount of methane in the plant and less than 10 % of the total slip, the concentration can be measured by simpler leak detection instruments. The petroleum and the chemical industry use statistical methods to estimate emissions based on leak detection measurements. Some of these methods have been published in a European standard (EN 15446:2008) and parts of that standard are applicable to biogas plants.

How to measure flow

Measuring the flow is quite a challenge since the conditions vary between different measuring points and different plants. The measurement points are rarely prepared for flow measurements. When it is technically or practically impossible to perform measurements, other methods have to be used, such as using fan data or default values.

The general method for measuring flow in a duct is Pitot tube measurements which are described in the international standard ISO 10780:1995. In this type of measurement the speed of gas is measured and the flow is then calculated by multiplying the speed by the cross section area of the duct.

The flow from a ventilation opening can be determined by a sensitive hot wire instrument. For natural ventilation valves, an instrument with a low detection level is needed.

When it is not possible to measure, the flows have to be estimated. For a wall mounted axial fan the flow can be estimated by the following equation:

$$Q = 16.5 * P + 500$$

where Q is the flow in m^3/h and P is the fan's nominal effect in W.

As a last resource, the following table (Tab. 1) can be used to get a rough estimate of flows.

Tab. 1. Standard values for airflows

Emission point	Characteristics	Flow
Ventilation fan, ceiling/wall (smaller)	Smaller rooms, e.g. gas equipment rooms or containers for upgrading	3000 Nm^3/h
Ventilation fan, ceiling/wall (bigger)	Bigger rooms	6000 Nm^3/h
Natural ventilation	Noticeable, but not measurable flow	0.1 m/s

Calculations

The following information about a biogas plant needs to be known:

- Current methane concentration in the biogas (vol-%)
- Current amount of produced biogas (raw gas) (Nm^3/h)
- Annual average methane concentration (vol-%)
- Annual production of biogas ($Nm^3/year$)

The following information must be known about an upgrading plant:

- Current methane concentration in the raw biogas (vol-%)
- Current amount of incoming raw biogas (Nm^3/h)
- Annual average methane concentration in the raw biogas (vol-%)
- Annual amount of incoming raw biogas ($Nm^3/year$)
- Current methane concentration in the upgraded biogas (vol-%)
- Current amount of upgraded biogas (Nm^3/h)
- Annual average methane concentration in the upgraded biogas (vol-%)
- Annual amount of upgraded biogas ($Nm^3/year$)

Gas flow (Q) should be given in Nm^3/h. A measured flow in e.g. a ventilation duct has to be recalculated based on measured temperature and pressure to flow in standard conditions 0°C (273.15 K) and 1 atm (101.3 kPa). The flow is calculated to standard conditions by the ideal gas law. For the most part, it is acceptable to assume atmospheric pressure in ventilation systems.

For a single emission point, the methane loss is then calculated by multiplying the methane concentration by the flow at that point. Methane emissions are reported in relation to the total methane flow through the plant. The total flow through the plant is calculated by multiply the methane concentration (vol-%) in the raw gas by the raw gas flow (Nm^3/h) (Form.1) .

For upgrading plants, the emissions should also be related to the methane content in the cleaned gas. The reason for this is the lower measurement uncertainty for measuring the methane flow in the cleaned gas compared to the raw gas (Form. 2).

The losses in different points are then added to give a total loss for the plant. The calculated loss can be extrapolated to a yearly loss (Form. 3).

For an upgrading plant the total emission in also calculated based on the yearly production of cleaned methane gas (Form. 4).

Form. 1

$$Loss_{raw}(\%) = \frac{CH_{4(emission)}(vol-\%) * Q_{emission}\left(\frac{Nm^3}{h}\right)}{CH_{4(raw)}(vol-\%) * Q_{raw}\left(\frac{Nm^3}{h}\right)} * 100$$

Form. 2

$$Loss_{clean}(\%) = \frac{CH_{4(emission)}(vol-\%) * Q_{emission}\left(\frac{Nm^3}{h}\right)}{CH_{4(clean)}(vol-\%) * Q_{clean}\left(\frac{Nm^3}{h}\right) + \sum CH_{4(emission)} * Q_{emission}} * 100$$

Form. 3

$$Emission_{raw}\left(\frac{Nm^3}{year}\right) = \frac{Loss_{raw}(\%) * Total\ flow_{raw}\left(\frac{Nm^3}{year}\right)}{100}$$

Form. 4

$$Emission_{clean}\left(\frac{Nm^3}{year}\right) = \frac{Loss_{clean}(\%) * Total\ flow_{clean}\left(\frac{Nm^3}{year}\right)}{100}$$

In Holmgren, 2011 a number of examples of calculations for different emission points are described in detail.

Mathematical modelling of methane loss from digestate

In a Danish study (Hansen et.al. 2006) the following equation for calculating methane production in digestate is suggested:

$$E_{CH_4} = 0{,}0004 * e^{0{,}159 * t}$$

where ECH_4 is the methane production (Nm^3 CH_4/Mg Volatile Solids h) and t is the temperature in the digestate (between 5-35°C). With an average storage volume of V (m^3) the methane emission can be calculated in the following way:

$$Emission\left(\frac{Nm^3}{year}\right) = \frac{E_{CH_4} * V * \rho}{1000} * 24 * 365$$

where ρ is the density of the digestate which can be set to 1000 kg/m^3.

Results

The first series of measurements were performed from 2007 – 2009 at a total of 18 biogas plants and 20 upgrading plants, and the results showed considerable differences in methane emissions from the plants. Since then, a further 6 upgrading plants have joined the Voluntary Agreement (September 2011). The system requires that methane emissions are quantified every third year, and so the next results for these plants will be available accordingly.

The results of the quantification in biogas plants are shown in Fig. 4. The result is shown for the different types of biogas plants treating: waste water, household waste and industrial waste.

From the results of the leak detections it could be concluded that the biogas plants in general had few, but larger leaks. Typical leakage points were relief valves and digestate storage tanks.

For the biogas upgrading plants there was also a large difference in methane emissions (Fig. 5).

The leak detection results showed that in general the upgrading plants had many, but smaller leaks. Typical leakage points were gas equipment parts and compressors.

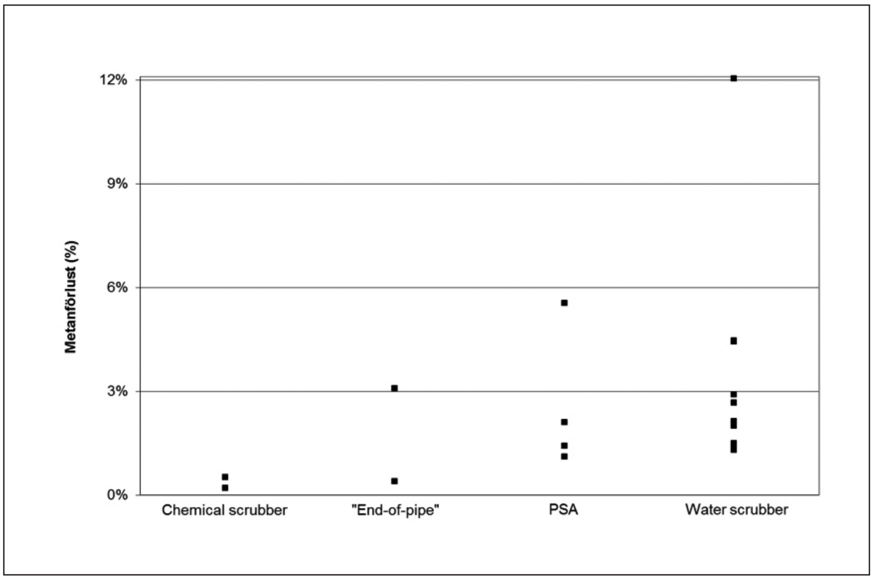

Fig. 5. Methane emissions from upgrading plants, divided in different types: chemical scrubber, PSA (Pressure Swing Adsorption) and water scrubber. "End-of-pipe" refers to plants with off-gas treatment equipment such as Vocsidizer.

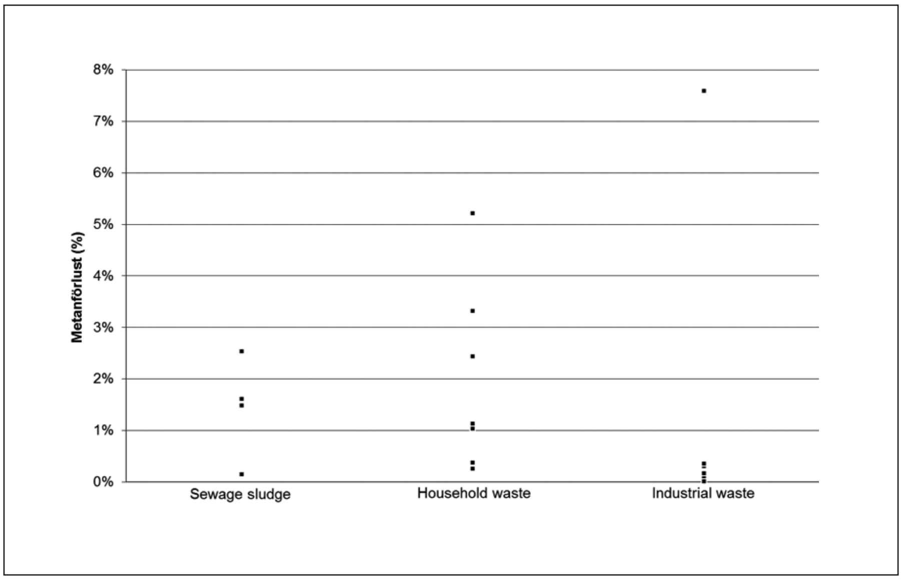

Fig. 4. Total methane losses for the participating biogas plants.

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IEA Bioenergy

Task 37 – Energy from Biogas

IEA Bioenergy aims to accelerate the use of environmentally sound and cost competitive bioenergy on a sustainable basis and thereby achieve a substantial contribution to future energy demands

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