Partner for progress

GT-070127
21st September 2007

Quality Aspects of Green Gas

GT-070127
21st September 2007

Quality Aspects of Green Gas

Kiwa N.V.
Sir W. Churchill-laan 273
P.O. Box 70
2280 AB RIJSWIJK ZH
The Netherlands

Tel. +31 (0)70 414 44 00
Fax +31 (0)70 414 44 20
www.kiwa.nl

Colophon

Title
Quality Aspects of Biogas

Project/Order Number
SenterNovem : 2021-07-20-10-003
Order Number: 4700013538
070700220 (Kiwa)

Project Manager
Dr. E.A. Polman

Contractor
SenterNovem

Quality Assurance
Ing. W. Brouwer

Author(s)
Dr. E.A. Polman

Contents

1 Introduction

In the SenterNovem “Green Gas” report of January 2007, the following definition of ‘Green Gas’ is used:
“A gaseous form of energy from renewable biomass with a quality equal to that of the natural gas in the public network”.

Green Gas can be produced, after processing and cleaning of the fermentation product (biogas), originating from:

- Sewage or waste water treatment;
- Landfill sites;
- Composting installations;
- Manure fermentation, possibly combined with co-substrates

It is also possible to produce Green Gas via the methanising of synthesis gas. Synthesis gas is a gasification product from biomass and comprises a mixture of carbon monoxide and hydrogen. Although the separate technologies are available, there is still no installation in which these techniques are combined. A consortium is engaged in the design of a station which is based on this principle. The station in Gothenburg (S) will begin production in 2012.

In the Netherlands, Green Gas has been injected into the gas distribution network for the past twenty years. Twenty years ago, the production, the quality control and the distribution of Green Gas was under one roof. A number of years ago the roles were split and also formally regulated. Since 21st November 2006, the DTe (Dutch Regulator) have set “Quality Standards for Biogas” for regional network controllers. Quality standards or guidelines are also operating in five other European countries.

Since 2003 the EU Directive 2003/55/EC has been in effect. This Directive has the aim of opening the gas network for Green Gas. The European gas industry has joined together in a consortium with the goal of answering the unanswered questions regarding the feeding of Green Gas into the network.

In this report, the recent developments in the areas of regulation for Green Gas, quality standards, biogas locations in Europe and research topics for biogas are described and analysed. This report acts as a background for the established quality standards for biogas for regional network controllers and is written under assignment from SenterNovem.

2 Parties Involved

Before the liberalisation of the gas market, the supply and distribution of gas was carried out by the same company. The classic utilities company was also frequently responsible for the treatment of waste. In this way, a utilities company could keep the exploitation of a landfill site, the extraction of landfill gas, the delivery of landfill gas and the distribution of landfill gas completely to themselves.
Nowadays, a number of roles are differentiated.

2.1 The Supplier of the Biomass

An example of this could be the owner of a sewage treatment plant or a co-operative of farmers which delivers manure for a fermentation installation. The supplier of the biomass will negotiate a contract for the price and quality of the biomass.

2.2 The Producer of Green Gas

Here, a difference can be made between the fermentation installation and the processing and cleaning installation. The producer supplies cleaned biogas to the supplier of Green Gas.

2.3 The Supplier of Green Gas

The supplier offers Green Gas to a number of clients, or sells it on to another supplier. The party which supplies Green Gas to clients must have negotiated a contract with the network controller.

2.4 The Network Controller

The network controller is responsible for the quality of the gas that they distribute. The network controller must therefore guarantee via a contract that the incoming gas is of a good quality. The clauses of such a contract are given in paragraph 4.4. The network controller must check the quality control procedures of the supplier. Another condition for the network controller is that there is sufficient delivery capacity and consumption in their network to be able to distribute Green Gas.

3 International Developments

The Netherlands has a tradition in the production and feeding of Green Gas into the gas network. Most other countries in Europe embarked on this later. There is experience with the injection of Green Gas in five countries, and legislation for this exists in six. In this chapter, attention is given to the development of Green Gas within Europe. The reasons taken into consideration in the drawing up of the standards and directives are also described, so far as these are known.

3.1 Biogas Plants

3.1.1 France

Currently in France there is still no experience with the injection of Green Gas into the gas network.
In the City of Lille, 200 buses use natural gas as fuel. This fleet will be able to run fully on renewable fuel through the biogas production from a large fermentation installation, in which 100,000 tonnes of organic waste will be processed annually. From this, 4 million $m^3{}_n$ (normal cubic metres) of Green Gas will be produced and injected into the 16 bar network.
Gaz de France has in the past always distanced itself concerning the injection of Green Gas into the gas network. The reason given for this was that the consequences for the end-user are not known. This vision was supported by a decree made in 2004 (2004-555) in which it was determined that the Minister for Energy can, when appropriate, designate an agency to prove by research, that there is no danger to public health.

The controller of the transport network, Gaz de France, has, in the meantime, established technical specifications for the injection of Green Gas (please refer to 4.2).
The results of the public health investigation will be known at the end of 2007, and if a good result is obtained, Green Gas will be injected into the French gas network in 2008.

3.1.2 Austria

In Austria, in the town of Lisbod, 10 $m^3{}_n$ of Green Gas is injected into the distribution network of Erdgas ÖÖ every hour since June 2005.

3.1.3 Switzerland

In Switzerland Green Gas is injected into the net in a total of seven locations. The plant in Bachenbulach was put into service in 1995, and the plant in Samstagern in 1997. In both plants the biogas is generated by the fermentation of organic waste.

Since 2005 in Engelholzli, the Green Gas which is generated from agricultural waste has been added to the gas network. In Emmen 500,000 $m^3{}_n$ of gas, generated from the fermentation of sewer purification sludge, is injected into the net annually.

Since 2006 Green Gas has been injected in the locations: Birs 2, Romanshorn and Bischofzell.

It is not permitted in Switzerland to inject landfill gas into the network. It is also forbidden to add propane to upgrade the gas to the correct calorific value. Without the addition of propane it is not possible to achieve the specifications for H-gas. Requirements are less stringent for injection into the gas transport network, when the amount of biogas can be mixed with large amounts of natural gas (Please refer to 4.2).

3.1.4 Sweden

Green Gas obtained by co-digestion of manure and organic matter has been produced in Laholm since the year 2000. The processed gas is upgraded to the proper specifications with propane before injection into the 4 bar network. 500 $m^3{}_n$ of gas is produced per hour.

In Helsingborg, Green Gas has been produced by the fermentation of waste from the food industry since 2003. Just as in Laholm, the bio-waste is first pasteurised to kill pathogenic bacteria. LPG is then added to the processed gas. 350 $m^3{}_n$ of gas is injected into the 4 bar network every hour. In 2007, gas will be injected into the 4 bar network in two new locations in Helsingborg. The two new plants have a capacity of 650 and 250 $m^3{}_n$ of Green Gas per hour.
In Gothenburg, Green Gas is obtained from the fermentation of sewage treatment sludge. Before this, untreated low calorific gas was distributed in the local city network. Since 2007 the gas has been upgraded to natural gas quality, and injected into the 4 bar network at a rate of 1500 $m^3{}_n$ per hour.

From 2007 in Bjuv, 500 $m^3{}_n$ of Green Gas, obtained by co-digestion of manure and organic waste, has been injected into the gas network every hour.

3.1.5 Germany

In Germany, two plants have been halted (Stuttgart en Viersssen) in which cleaned and upgraded landfill gas was injected into the distribution network. The plant in Stuttgart was in service from 1986 until 1993 and the one in Vierrsen from 1981 until 1996. According to the standard DVGW G-262, drawn up in November 2004, it is not permitted to inject Green Gas obtained from landfill gas, due to the presence of fluoro- and chlorohydrocarbons, which can lead to the formation of dioxins when burnt.
Meanwhile, Green Gas seems to be making a comeback in Germany. A plant was put into service in Pliening (near Munich), where Green Gas is injected into the network, on 21st December 2006. On the 30th December 2006, a plant in Straelen (Aachen region) was opened.
In the following two years, ten new plants will follow: Dorsten (EON-Ruhrgas), Düren (local distribution company: LDC) Düren, RWE), Kerpen (LDC Aachen), Ketzin (E.ON-edis), Lemgo (LDC Lemgo, WINGAS), Mölln (united LDCs; E.ON-Hanse), München-Nord (LDC München), Passau (LDC Passau), Schneeren (Erdgas Münster) and Werlte (EWE).

3.1.6 The Netherlands

In the Netherlands the production of Green Gas totals around 14 million nm^3 per year. Due to the landfill gas plants in Tilburg, (from 1987), Wijster (1989), Nuenen (1990) and Collendoorn (1990), the Netherlands has extensive experience with the cleaning, processing and injection of landfill gas which has been upgraded to natural gas quality. Since August 2006, gas has been obtained through the fermentation of sewage and injected into the distribution network of Eneco Netbeheer in Beverwijk.

3.2 Quality Directives

The available quality directives for Green Gas in Europe are given in table 3.1, these are derived from Standards or Directives.

QUALITY REQUIREMENTS OF GREEN GAS

Physical Properties	F	A	CH	S	D	NL	Unit
Calorific Upper Value	38.5 – 46.1 H) 34.2 – 47.8 (L)	38.5 – 46.1	38.5-47.2	39.6 – 43.2	30.2-47.2	31.6 – 38.7	MJ/m^3_n
Wobbe-index	49.1 – 56.5 (H) 43.2 – 46.8 (L)	47.9 – 56.5	47.9-56.5	45.4 -48.6	37.8-46.8 (L) 46.1-56.5 (H)	43.46-44.41	MJ/m^3_n
Qualities							
Water dew point	< -5	< -8 (40 bar)	60% humidity	< -60	Ground temp.	< -10 (8 bar)	^oC
Water				<32 mg/(n)m^3			
Temperature (in the injection gas)				-20 - +20		0 – 40	^oC
Sulphur (in total)	30	10	30	23	30	45	mg/m^3_n
Anorganically bonded sulphur (H_2S)	5	5	5	10	5	5	mg/m^3_n
Mercaptans	6	6			15	10	mg/m^3_n
Odorant level (THT)	15-40		15-25		good	> 10. nominal 18	mg/m^3_n
Ammonia		none		20		3	mg/m^3_n
Chlorine containing Compounds	1	none			none	50	mg/m^3_n

	F	A	CH	S	D	NL	
Fluorine containing compounds	10	none			geen	25	mg/m^3_n
Hydrogen Chloride (HCl)		none				1	ppm
Hydrogen cyanide (HCN)		none				10	ppm
Mercury	1						$\mu g/m^3$
Carbon monoxide (CO)	2					1	mol%
CO2 in dry gas networks (max)	2.5	3	6	3	6	6	mol%
CO2 in wet gas networks						n.a.	Mol%
BTX (Benzene. Toluene. Xylene)						500	ppm
Aromatic hydrocarbons						1	mol%
oxygen in dry gas networks	0.01	0.5	0.5	1	0.5	0.5	mol%
oxygen in wet gas networks							n.a.
Hydrogen	6	4	5	0.5	5	12	mol%
Methane number						> 80	
Methane		>96	>96	>97		-	mol%
Dust		Techn. free		< 1µm	Techn. free	Techn.free	
Siloxans		< 10 (mg/m^3)				5	ppm

Table 3.1: Quality Requirements for Biogas in France, Austria, Switzerland, Sweden, Germany and the Netherlands.

3.2.1 Explanation of Quality Requirements per Country

France:
Gaz de France, the national transporter and distributor, has established technical directives. In the north of France, L-gas is delivered, and in the rest of France H-gas. The planned biogas injection in Lille concerns L-gas. The limit of 2.5% CO_2 places a high demand on the gas processing installation.

Austria:
Austria has the directive OVGW G31 in which the quality standards have been given (table 3.1).

Switzerland:
The directive SSIGE G13 is used in Switzerland. It is not permitted to inject upgraded landfill gas and the addition of LPG to biogas is also forbidden. The quality requirements given in the table apply to the distribution network. Injection into the transportation network may only occur in limited amounts, to ensure that a good mix with the fossil natural gas takes place. In this case, the injected biogas must contain a minimum of 50% methane, which means that the requirements for the calorific value and the Wobbe-index are no longer valid. For the gas properties, the requirements which apply to Green Gas for injection into the transport network are the same as the requirements given in table 3.1.

Sweden:
The quality requirements for biogas are listed in the standard 155438. The addition of LPG is normal practice in Sweden to raise the gas to the correct calorific value. Landfill gas is not really forbidden in Sweden, but due to the high requirements of the methane content, the processing of landfill gas to the required quality would be difficult. In the Swedish biogas plants, the methane and CO_2 levels, as well as the water dew point are continuously monitored.

Germany:
The DVGW standard G-260 is applied in Germany, in which the quality requirements are determined. According to the standard DVGW G-262, the injection of landfill gas is not permitted due to the presence of halogens which can lead to the formation of dioxins when burnt.

The Netherlands:
In the Netherlands, the connection and transport conditions for the injection of gas into the regional network (8 bar and lower) were set by the DTe on 21st November 2006. The main aim of the DTe is that the integrity of the distribution network is guaranteed and that gas installations and appliances function correctly. It is stated in article 3.3.10 that the network controller can set other requirements for the biogas injector regarding the inspections which need to be carried out and may also carry out inspections themselves. Due to the fact that the network controller is responsible for the quality of the gas

which is distributed through their network, it is necessary for the network controller to set additional requirements regarding the quality control of the injected gas (please refer to 4.4.).

Europe:
In 2003 a directive regarding biofuels (2003/55/EC) was drawn up. In article 24 the following is noted:

"Member States should ensure that, taking into account the necessary quality requirements, biogas and gas from biomass or other types of gas are granted non-discriminatory access to the gas system, provided such access is permanently compatible with the relevant technical rules and safety standards. These rules and standards should ensure, that these gases can technically and safely be injected into, and transported through the natural gas system and should also address the chemical characteristics of these gases."

This article means that at the minimum the member states are compelled to draw up regulations for the quality of biogas.

3.3 Comparison and Analysis of the Values

In a comparison of the values it is interesting to look at the underlying differences and similarities. The Netherlands has the most items mentioned in its directives. This is due to the fact that that the already existing regulations for gas quality, which apply to the national network controllers, have been followed as much as possible. These regulations are very detailed. Due to the fact that landfill gas is permitted in the Netherlands, as opposed to Germany and Switzerland, limits are also set for the components which are typically present in landfill gas (siloxans, halogens, etc). The values for the Netherlands were set in 2004. The regulations are based on the then-available regulations and also on expert opinion.
When the values are compared, it becomes apparent that the permitted values for chlorine and fluorine in the Netherlands are higher than in the other countries. The values for the Netherlands are based on the DVGW (Germany) standard G262 from 1991 and the OVGW G 33 standard from 1992. In the meantime the standards for chlorine and fluorine in both Austria and Germany have been honed.
As yet, there are no indications that the permitted values are too high. The values which appear in biogas are much lower than the standard. For this reason, a change in these values may take place in the future.
The permitted value for hydrogen is higher than in surrounding countries. The value of 12% is determined by research completed by Kiwa Gas Technology in 1999. It is unlikely that percentages of 10 to 12% of hydrogen will be found in Green Gas. In the Netherlands, limits exist for the methane number to guarantee the operation of gas engines. Furthermore, there is an extremely small Wobbe range.
Switzerland is the only country where it is possible to inject biogas which does not conform to the specifications for the calorific value. However, this is

only applicable to the transport network and under the condition that there is sufficient mixing with the fossil natural gas.
The limit for CO_2 is not set in the conditions for Regional Network Controllers and national Network controllers. If the gas networks are completely dry there is, strictly speaking, no reason to limit the level of CO_2, except for the fact that with an extremely high CO_2 level, the requirements for the Wobbe index can no longer be met. The limit of 6% in the Dutch regulations is nevertheless higher than in the other countries. Outside the limits set by the Wobbe index, it appears however, that there is no restriction to raising the level of 6%. This would give the biogas injectors more possibilities regarding the separation of methane / CO_2 mixtures.

3.4 Directives for the Treatment of Bio Waste.

The European directive 1774/2002 is applicable to the pre-processing of bio-waste which is to be used for fermentation.
The waste from abattoirs and hotels and restaurants is often added to manure to obtain a high return of biogas from co-digestion. This waste must be pasteurised beforehand. The residue after fermentation must be salmonella-free and limited to the permitted level of enteriobacteriaceae[1]

3.5 Research Activities

In 2005 and 2006, GERG (European Gas Research Group), under the name BINGO, carried out research into the insertion of Green Gas in the European transport and distribution network. In this context, research was completed into the current legislation, the status of biogas injection in Europe, existing technology for biogas purification and production and the prevention of contaminants in biogas. These contaminants could present a danger for health or for the function of the gas pipes or appliances.

It is the intention that the remaining questions will be answered after further investigation. This investigation will take place in the 7th Framework Programme of the European Union. It must deliver the basis for widely supported specifications for the gas quality in the distribution and transport network. This research is expected to start in the autumn of 2008.

---

[1] The family Enterobacteriacea contains bacteria which appear in the bowels of mammals naturally, but which also thrive in other environments. This concerns the types of bacteria *Escherichia*, *Citrobacter*, *Enterobacter* and *Proteus*, and some of the most important causes of bowel diseases such as *Salmonella*, *Shigella*, *Yersinia enterocolitica* and the pathogenic *E. coli*. Enterobacteriacea are useful indicators of hygiene.

4 Quality Aspects

4.1 Possible Compositions of Biogas

Biogas can contain many compounds. The composition of biogas is dependent on the nature of the biomass. Some components will only appear in certain types of biogas.
Fossil natural gas also contains many differing components. For example, in fossil natural gas there are many higher hydrocarbons and aromatic hydrocarbons. When biomass is fermented, these components will almost never appear. Higher hydrocarbons and aromatics could well appear in landfill gas as contaminants from the landfill site.

The quality of landfill gas can vary tremendously, depending upon the contaminants present in the landfill site.

4.1.1 Siloxans

Siloxans appear in landfill gas and can result in the wearing of gas engines.

4.1.2 Halogens

Halogen hydrocarbons occur in landfill gas. Due to the fact that these compounds can give rise to the formation of dioxins when burnt, it is important that a limit is set on the content of these compounds.
During a research by Kiwa Gas Technology on gas samples, it was discovered that more halogen hydrocarbons are present in landfill gas than in biogas from sewer sludge fermentation. For hydrocarbons this is typically 1 to 10 mg per m^3_n for landfill gas and 1 to 3 mg per m^3_n for purified landfill gas.
The levels for fluorohydrocarbons are, respectively, 1 to 5 mg and 1 to 2 mg per m^3_n.
In biogas produced from sewer sludge fermentation, the levels are less than 1 mg per m^3_n in the raw gas.

	Chlorohydrocarbons (mg/ m^3_n)	Fluorohydrocarbons (mg/ m^3_n)
Raw landfill Gas	1 – 10	1-5
Purified landfill gas	1-3	1-2
Raw sewer sludge fermentation gas	<1	<1
Purified sewer sludge fermentation gas	<<1	<<1

Table 4.1 Typical Values of Halogen Hydrocarbons

These values are far under the limit which is currently set in the connection and transport conditions for the injection of gas into the regional network. Halogens can form dioxins under unfavourable conditions (long presence times in the flame and high flame temperatures.) With a well-designed burning process, dioxin formation should not easily occur. In the 1970's there were problems with the burning of waste with high concentrations of chlorohydrocarbons, from which dioxins arose.

4.1.3 Aromatics and Higher Hydrocarbons

Aromatics and higher hydrocarbons can appear in the landfill gas as contaminants from the landfill. These compounds can be present in the range of 10 to 100 ppm in raw landfill gas. In purified landfill gas this will at most be several ppm's. These levels are no higher than normal natural gas. For raw fermentation gas produced from sludge and manure, these compounds appear in the range of 10 to 20 ppm. After purification this will be a maximum of a few ppm.

4.2 Effect of Bacteria

The fermentation process is induced by methane producing bacteria.
The formation and spreading of pathogenic bacteria is undesirable. This can lead to health risks in the vicinity of the biogas plants. Network controllers will also wish to prevent bacterial colonies being spread via the distribution network. Moreover, bacteria can cause microbiological corrosion in pipelines. There is very little information available in the literature on either subject.

4.2.1 Pathogenic Bacteria

At the request of the Swedish Gas Centre (SGC), the Swedish Institute for Veterinary Medicine conducted a study into the presence of micro-organisms (MO) in biogas and natural gas.
The study involved two biogas reactors, namely, a co-digestion reactor (manure and organic waste) and a sewage sludge fermenter. According to the European legislation (EC No. 1774/2002), it is not necessary to include pasteurisation as a procedure. It is therefore possible that pathogenic bacteria can appear in the produced biogas.
In the comparison between the gases produced in the two biogas plants, it appeared that there was no difference between the types of MO which are present in natural gas and in biogas. The number of MO in biogas is no higher than in natural gas.
In bacteriology, a differential is made between pathogenic MO and commensal MO. Pathogenic MO can cause serious and even deadly diseases. Commensal MO appear in nature and can only cause sickness in people with an exceptionally low immunity. No pathogenic bacteria were found. Some commensal pathogenic bacteria were present in very low concentrations. The biogas from sewage sludge fermentation contains a higher concentration of commensal pathogenic bacteria than the biogas produced by co- digestion.

The report recommends the filtering of biogas with a 1 micrometre filter. Care must also be taken with waste water from biogas plants. SGC concluded that the health risks from biogas are low.

Marina Moletta has conducted an exhaustive study into the presence of micro-organisms in biogas. She has discovered 15 groups of bacteria which each have a level of more than 3% in the biogas. A surprisingly high total of 183 groups were discovered. What is also apparent is that the ratio between

the various bacteria in the biomass is different from that found in the biogas. Molina explained this by the aerosol formation of bacteria. The transport of bacteria in the air takes place by means of aerosol formation. Molina specifies three different mechanisms: active formation of aerosols, inactive formation of aerosols and passive formation of aerosols.
The study is to be considered as a first analysis of the types of bacteria in biogas and is not directly usable to research the corrosive behaviour or the impact on health of MO. Molina acknowledges that no detailed description exists of the number and concentration of MO in normal air or in fossil natural gas.

4.2.2 Microbiological Corrosion

It was observed in an article of Zhu that bacteria can survive and grow in the microfilm which lines the inside of natural gas pipelines. No relation was found between these and the bacteria which appear in biogas.

4.2.3 Conclusions

There is no evidence that the bacteria in biogas are hazardous to health. There is also no evidence that biogas gives rise to microbiological corrosion. However, this research is very limited, and further research is required.

4.3 Other Hazardous Substances in Biogas

A short literature study was performed in the BINGO research into the presence of compounds in biogas which could pose a risk to health or to the correct functioning of the gas infrastructure. The results of this are summarised below:

4.3.1 BTX

BTX stands for the aromatic contaminants benzene, toluene and xylene. In landfill gas, these compounds can appear as contaminants. BTX also appears in natural gas and the levels found in biogas are no higher than those in natural gas. For this reason, the presence of BTX in biogas is not considered a risk.

4.3.2 Cyanides

Hydrogen cyanide can arise in low concentrations as a contaminant in landfill gas. Application of a gas scrubbing procedure is very effective in significantly reducing any possible present concentrations. For this reason, the presence of hydrogen cyanide in biogas is not considered a risk.

4.3.3 Phosphines

The presence of phosphines (PH_3) with the fermentation of cattle and pig manure is registered in a few publications. It appears that higher concentrations of phosphines are present in pig manure than in cattle manure, as much as microgrammes per cubic metre of air. Due to the fact that phosphines are extremely poisonous, this must be taken seriously. There is little known regarding the mechanism of the formation of phosphines. It is recommended that further research is completed into the effect of gas purification on the levels of phosphines and into the effects on health. An investigation is also recommended to determine the phosphine content in natural gas.

4.3.4 Halogens

Halogens can be present in landfill gas and in fermentation gas. Under unfavourable conditions, these compounds can be transformed into dioxins during the burning process. It is expected that this will only become a problem at very high concentrations (in the order of 1%), high flame temperature and long presence in the flame.
Although the risk is not considered great, it is nonetheless recommended that research is carried out to gain increased knowledge about the formation of dioxins upon burning of gases with chloro- or fluoro- contaminants .

4.4 Risks According to the Marcogaz Study.

A study by Marcogaz was revealed in December 2006 in which a risk analysis was also made for each origin of the biogas. Please refer to paragraphs 4.1 to 4.3 for a description of the risks from these compounds.

Biogas from fermentation (manure and sludge) can give rise to the following compounds:

- Siloxans;
- Bacteria;
- Fluorohydrocarbons;
- Chlorohydrocarbons;
- Ammonia.

Landfill gas can contain the following compounds :

- Siloxans;
- Bacteria;
- Fluorohydrocarbons;
- Chlorohydrocarbons;
- Ammonia ;
- BTX .

Hydrogen-rich synthesis gas (product of gasification)

- Hydrogen (influences the combustion properties);
- Carbon monoxide (poisonous);
- BTX.

SNG (methane-rich gas obtained after the methanization of synthesis gas):

- Carbon monoxide;
- BTX.

4.5 Quality Control

The network controller and the supplier of Green Gas must mutually agree on a number of issues. There are no set directives about what and how they must regulate. The summary below is based on the expertise and knowledge of Kiwa Gas Technology and can be treated as a checklist.

4.5.1 Continuous Measurements

The usual quality controls for the processing of biogas to ensure a good quality gas are:

- Continuous monitoring of the Wobbe-index;
- Continuous monitoring of the sulphur levels;
- Continuous monitoring of the oxygen levels.

When it appears from the gas analyses that there are critical parameters, such as the water dew point, it can also be chosen to monitor this continuously.
It is recommended that agreements are made with the supplier regarding the carrying out of checks of the odourisation installation and the continuous monitoring apparatus.

In the case of the gas not conforming to the specifications, a procedure must be in place in which it is stipulated what will occur with the non-conforming gas.
Examples of actions to be taken are the recirculation of the biogas through the processing installation or the burning off of the biogas.

4.5.2 Semi-Quantitative and Quantitative Measurements

Before a plant begins production, it needs to be recorded which compounds can occur in the biogas, and which of these will be monitored. Following this the frequency of the inspections needs to be established.

With the inspections, a distinction is made between semi-quantitative and quantitative analyses.
Quantitative analyses mostly follow a specific standard and are usually conducted in a laboratory environment, using a gas chromatograph analysis on a supplied biogas sample.
Semi-quantitative analyses are usually carried out at the location of the biogas injection. An appropriate and much used method is the use of so-called colour tubes ("Dräger" tubes), which are available on the market for almost every specific component which could occur in biogas. This testing method is not as accurate as the above named quantitative determination methods (laboratory measurements). However, by using this method the biogas injector can monitor that the gas supplied by him satisfies the set requirements more frequently and against a reasonable cost. The accuracy of this method differs per type of specification (the gas component to be measured) and is in the (relative) order of size from 10% to 30%.

In a report to a regional network controller, Kiwa Gas Technology has advised the following monitoring regime for the semi-quantitative measurements:

- Annually, when the last determined value of the property was less than 25% of the set limit value.
- Monthly, when the last determined value of the property was between 25% and 75% of the set limit value.

- Weekly, when the last determined value of the property was between 75% and 90% of the set limit value.
- If the last determined value of the property was greater than 90% of the set limit value, further consultation is needed between the biogas injector and the network controller. Dependent upon the cause, this consultation can result in (amongst other things) the (temporary) stopping of the injection, or in a request for a mandatory quantitative analysis.

The following frequency is suggested for the quantitative analyses:

- Annually, independent of earlier findings.
- Quarterly, when it appears from three or more semi-quantitative analyses during the period of one year, that the measured value of the property has been between 75% and 90% of the set limit value.
- Monthly, when it appears from three or more semi-quantitative analyses during the period of one year, that the measured value of the property was higher than 90% of the set limit value.

For well-founded reasons – for example, when the scatter in the measured values is relatively large – a difference agreement can be reached after consultation between the biogas injector and the network controller.

4.5.3 Inspections by the Network Controller

The regional network controller is responsible for the quality of the natural gas transported and supplied to customers by himself (whether or not this is mixed with biogas). The network controller has to fulfil this task by performing measurements or other checks.

Examples of inspections:

The network controller, or a third party appointed by him, checks the compliance of all set technical specifications on-site by means of an audit, at least once per calendar year, as agreed between the network controller and the biogas injector. If requested by the network controller, the biogas injector must allow inspection of all required information, including:

i. Applied measuring techniques
ii. Results of semi-quantitative measurements
iii. Results of quantitative measurements
iv. Written records (logbooks)

The network controller, or a third party appointed by him, must perform control checks of the quality of the injected biogas using random samples. It

is advised that the network controller as well as the biogas injector conduct independent measurements of the agreed properties of the same gas sample, and then compare the results at least once each calendar year.
In accordance with the guidelines for local odourisation, it is also advised to measure the odourant content (THT) as well as the olfactory properties of the gas monthly, at a representative location in the distribution network, downstream from the biogas injection location.

5 Conclusions

The injection of Green Gas into the natural gas network takes place in five European countries. So far as is known, this has taken place without any great problems arising. The capacity of the gas distribution network can set limitations in the amount of Green Gas which can be injected. Specifications for the quality of the gas have been drawn up in six countries.

The limit values for the contaminants in Green Gas are for the most part comparable. For some components such as CO_2 and halogen hydrocarbons there are significant differences in the limit values. The injection of Green Gas derived from landfill gas is prohibited in Switzerland, Austria and Germany. In Switzerland the addition of LPG to Green Gas is also forbidden. In France, a special regulation is in force through which an investigation into the health risks can be requested by the authorities before Green Gas is allowed to be injected.

The limit of 6% for CO_2 in the Dutch legislation is higher than in the other countries. Outside the limits set by the Wobbe index, it appears that there is absolutely no restriction to raising the level of 6%. This would give the biogas injectors more possibilities in the separation of methane / CO_2 mixtures.

For a number of components it can be stated that there is little information available regarding the basis for the limit values. A European consortium, called "BONGO", is planning to analyse these and other gaps. Further investigation is needed regarding:

- The influence of bacteria;
- The influence of phosphines;
- The behaviour of halogen hydrocarbons during incineration;
- The possibility of microbiological corrosion of distribution and transport pipes due to Green Gas.

6 Literature Sources

1. EU Directive 2003/55/EU
2. IEA Bioenergy, Kirchmayer et al.; Animal Byproducts and Anaerobic Digestion
3. Basic Data on Biogas Sweden 2007 (brochure)
4. Oral communication with Owe Jonsson, SGC (Sweden), July 2007
5. Oral communication with Mrs. Fradet, Gaz de France, July 2007
6. M. Moletta, Thesis: Caractérisation de la diversité microbienne aéroportée des biogaz; Université Montpellier; 2005
7. J.H. Wellink, M. Dumont, K. Kwant, Groen Gas, SenterNovem, January 2007
8. SGC: Sampling of Micro-organisms in Natural Gas and Biogas, 2005
9. Aansluit- en transportvoorwaarden gas RNB, November 2006
10. Biogasanalyses Kiwa Gas Technology
11. M. Bensman, C. Trefzger-Betzing: Biogas stromt ins Erdgasnetz, Biogas Journal 1/07
12. Brochure “Biogas Upgrading to Vehicle Fuel Standards and Grid Injection”; IEA Task 37, 2007
13. Marcogaz, Final Recommendation: Injection of Gases from Non-conventional Sources into Gas Networks, 2006