Project Committee - Biomethane for use in transport and injection in natural gas pipelines

CEN/TC 408

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Assistant:
Amelle MOURADI
Direct line : 01 41 62 84 28
amelle.mouradi@afnor.org

Your contact:
Charles-Pierre BAZIN DE CAIX
Direct line : +33 1 41 62 80 73
charlespierre.bazindecaix@afnor.org

CEN/TC 234/WG 9 Contribution to CEN/TC 408 - Requirements and Recom. for Inject. of N.C.S Gases

COMMENTARIES / DECISIONS

The document is the result of the standardization work within CEN/TC 234 WG 9 "Injection of non-conventional gases into the natural gas network" and was planned to be delivered in the next step to CEN CMC as a CEN Technical Report. Following to the launch of M/475 and the creation of the dedicated CEN/TC 408 CEN/TC 234 abandoned the work on the issue and CEN/TC 234 WG 9 is now disbanded.

This document is sent for information and has to be considered as an input from CEN/TC 234 expertise, its content will be helpful in the elaboration of the answer to the mandate M/475 mission. An item on the draft agenda of the 1st CEN/TC 408 meeting (2011-09-16) is related to discussions on this document.

FOLLOW UP

2011-09-16

CEN/TC 408 N010

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Gases from non-conventional sources — Injection into natural gas grids — Requirements and recommendations

Gase aus nicht-konventionellen Quellen — Einspeisung in Erdgasnetze — Anforderungen und Empfehlungen

Gaz d'origines non conventionnelles — Injection dans les reseaux de gaz naturel — Exigences et recommendations

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Foreword

This document (CEN/TC 234 WG 9 N 54:2011) has been prepared by Technical Committee CEN/TC 234 “Gas infrastructure” WG 9 "Injection of non-conventional gases into gas network" (abandoned 07/2011). The secretariat of CEN/TC 234 is held by DIN.

This document is a CEN/TC 234 draft document. Due to the arrival of EU mandate M/475 on biomethane which will be realised by CEN/TC 408 following to CEN BT decisions, this prTR was not presented to enquiry.

It is presented to CEN/TC 408 as a contribution to the standardisation work on the injection of biomethane in natural gas pipelines.

1 Scope

This CEN document covers the state of the art in the injection, transportation, distribution and utilisation of gases from non-conventional sources in the natural gas system. It covers those gases that have similar properties as natural gas in which it is injected, and can replace natural gas without any additional measure. This document also tries to foresee the possible developments in this field in the nearer future. The gases from non-conventional sources include:

- Methane rich gases from gasification or fermentation processes;
- Coal bed or coal mine methane;
- Hydrogen-rich gases from gasification or other chemical processes;
- Hydrogen produced by electrolysis (generally using renewable energy).

The main aspects to be covered by this report are the technical, gas quality and most important (long term) safety and integrity aspects related to the delivery of such gases by the existing natural gas networks, and concern particularly the processes injection in the gas networks, metering and billing, transmission and distribution, and end use. The production and upgrading processes will only be described as far as relevant for the other processes.

This document should be considered in addition to any existing National standards covering installations for manufacture, extraction, treatment, injection, transport and utilisation of these gases. It may also support any future directive or ordinance in this field.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 6974-6 Natural gas - Determination of composition with defined uncertainty by gas chromatography - Part 6: Determination of hydrogen, helium, oxygen, nitrogen, carbon dioxide and C_1 to C_8 hydrocarbons using three capillary columns

EN ISO 6976 Natural gas - Calculation of calorific values, density, relative density and Wobbe index from composition

EN ISO 13734, (Odorants; title to be adapted when ISO 13734.2 is accepted).

ISO 14532 Natural gas - Vocabulary

ISO/TS 16922 *(Odorization; title to be adapted when ISO/TS 16922.2 is accepted).*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply / the terms and definitions given in ISO 14532 and the following apply.

3.1
Biogas
Generic term used to refer to gases produced by anaerobic fermentation or digestion of organic matter, and without further upgrading nor purification

NOTE: this can take place in a landfill site to give landfill gas or in an anaerobic digester to give biogas. Sewage gas is biogas produced by the digestion of sewage sludge. Biogases comprise mainly methane and carbon dioxide.

3.2
Biomass
Organic matter from renewable sources suitable for decomposition into usable energy sources

NOTE: the decomposition may either be thermal or anaerobic.

3.3
Biomethane
Methane rich gas derived from biogas or from methanation of biosyngas by upgrading with properties similar to natural gas

3.4
Bio-substitute natural gas (Bio-SNG)
Biomethane suitable for injection into a natural gas pipeline system

3.5
Biosyngas
Gas manufactured from biomass using thermal gasification processes

NOTE: the production of biosyngas may be optimized either to yield methane or to yield hydrogen.

3.6 Coal associated gases

3.6.1
Coal bed methane (CBM)
Gas emitted from un-worked coal seams. Coal bed methane comprises mainly methane with relatively small amounts of other hydrocarbons, nitrogen and carbon dioxide

3.6.2
Coal mine methane (CMM)
Gas emitted from exposed coal in worked coal seams. Because the coal seam has been exposed to air, either through forced ventilation or natural swings in temperature or pressure, coal mine methane comprises methane with significant quantities of nitrogen and carbon dioxide

3.6
Digester
(Fermenter)
Reactor in which the digestion process takes place, sometimes also called fermenter

3.7
Digestion
Anaerobic degradation of organic matter under the action of specific bacteria

NOTE: The digestion can be natural (like in landfill sites) or subject to process intensification in a digester.

3.8
Gas network
System of pipelines conveying gas from the point of production or delivery to the point of use

3.9
Gas supply
Gas network supplying the general public with gas, under the regime of directive 2003/55/EC

3.10
Gas treatment
Process or series of processes to convert raw gas into one suitable for use, e.g. for delivery into a gas network

NOTE: the treatment of raw gases can be distinguished between upgrading and purification. Upgrading is the process to remove major constituents in the gas not supporting combustion, e.g. carbon dioxide, in order to increase the heating value of the gas. Purification is the process where minor constituents as e.g. hydrogen sulphide, water vapour with only small influence on the heating value are removed.

3.11
Injection
Process in which a gas is introduced into a pipeline system.

3.12
Landfill gas
Biogas produced from natural decomposition processes in landfill sites. Landfill gas comprises mainly methane, carbon dioxide and nitrogen

3.13
Methanation
Process based on a chemical reaction to convert other gases as e.g. hydrogen and carbon monoxide to methane

3.14
Non-conventional source (NCS) gas
Any kind of combustible gas different from natural gas under consideration for pipeline injection

3.15
Point of injection
Location in a pipeline at which a gas is introduced into the pipeline system

NOTE: this may or may not correspond to the point of custody transfer in a commercial agreement

3.16
Raw gas
Any untreated gas that requires further treatment before delivery into a gas network

3.17
Sewage gas
Biogas produced by the digestion of sewage sludge

3.18

Syngas

gas which has been treated and may contain components which are not typical of natural gas

NOTE Manufactured (synthetic) gases may contain substantial amounts of chemical species which are not typical of natural gases or common species found in atypical proportions as in the case of wet and sour gases.

Manufactured gases fall into two distinct categories, as follows :

a) those which are intended as synthetic or substitute natural gases, and which closely match true natural gases in both composition and properties ;

b) those which, whether or not intended to replace or enhance natural gas in service, do not closely match natural gases in composition.

In the case a), the composition of the manufactured gas may be such that the gas is indistinguishable from that of a possible true natural gas. However, more often a manufactured gas, even if it contains inert and lower hydrocarbon gases in satisfactory proportions, does not exhibit the distinctive hydrocarbon “tail” of a true natural gas and may additionally contain small but significant amounts of non-alkane hydrocarbons.

Case b) includes gases such as town gas, (undiluted) coke oven gas, and LPG/air mixtures, none of which is compositionally similar to a true natural gas (even though, in the latter case, it may be operationally interchangeable with natural gas).

3.19
Synthetic Natural Gas (SNG)

Gas produced by gasification, followed by methanisation. Its properties are similar to those of natural gas.

4 Description of raw gases

The nature of non-conventional source (NCS) gases varies strongly, depending on type and source and this is summarised in table 1.

The first kind of NCS gas is biomethane obtained from biogas, produced either naturally in a landfill site or in a digester, by a controlled process of anaerobic digestion. The composition of biogas depends on the composition of the organic material treated (crops, green residue, municipal solid waste, agricultural waste, manure slurry, waste from industrial food production, sewage sludge etc.). Due to the nature of their production, such raw gases could also contain some micro-organisms.

Table 1 — Types of non-conventional gas

Source	Production process	Product	Conversion and treatment process	Injectable product
Landfill (municipal and industrial waste)	Digestion	Biogas	Purification Upgrading	Biomethane
Organic waste/by product (agricultural, industrial or municipal)				
Energy crop				
Biomass (wood, crop, etc.)	Gasification, Chemical processes, Reforming	Biosyngas	Purification, Upgrading Water gas shift	SNG, Hydrogen-rich gas
Organic waste/by product (agricultural, industrial or municipal)				
Oil			Methanation Purification, Upgrading	
Hydrogen rich components				
Coal		Towngas		
Coal	Extraction	Coal bed methane, coal mine methane	Purification	Methane
Water	Electrolysis	Hydrogen, Oxygen	Drying	Hydrogen (needs sufficient dilution with other gas)

The second kind of NCS gas is a hydrogen-rich gas e.g. produced by thermal processes. This includes town gas, coke gases, refinery gases, but also gases resulting from the gasification of biomass. In methanation and purification processes, these gases can be transferred into SNG.

SNG can be produced via thermal gasification of biomass and subsequent gas cleaning and upgrading to methane. The main process steps in this process are

- Biomass treatment
- Biomass gasification
- Synthesis gas treatment
- Methanation
- Final gas treatment

In the biomass treatment section, biomass is dried and milled into a form that is suitable for the gasification system. Entrained flow gasifiers use pulverized fuel or liquid fuels and these consequently require more extensive pretreatment than other types of gasifiers.

In the gasification section the fuel is heated to 700°C – 1500°C in presence of steam and oxygen and the volatiles and carbon content is transferred into a combustible gas, containing mainly CO, CH_4, H_2 and CO_2. Gasification at low temperatures yields a tar and methane rich gas and gasification at high temperatures yield a gas with mainly CO and H_2 as main combustible components. Normally 75 – 85% of the heating value in the biomass is transferred into combustible gas.

In the treatment section the gas is cooled and major and minor impurities (e g tars, sulfur, trace elements) are removed from the gas. Under well-controlled temperature and pressure, the CO/H_2-ratio, is adjusted to a value that is suitable for the methanation, normally 1/3,1.

The methanation is carried out according to the formula

$$CO + 3\ H_2 \Leftrightarrow CH_4 + H_2O$$

The reaction is strongly exothermic and is normally cooled by steam production.

Depending on the process configuration the final product needs drying, hydrogen removal and also CO_2-removal before it can be injected into the natural gas grid.

The total efficiency from wood to methane is in the range of 60-70% and surplus heat can be recovered as steam or hot water from the process.

Although related to (and carrying many of the features of) hydrogen-rich gases, pure hydrogen is included in Table 1 as its own kind of NCS gas suitable for injection in the natural gas network after being diluted sufficiently. In a future "hydrogen economy", hydrogen may become an important energy carrier and can be produced in a relatively pure form by electrolysis, using electricity derived from sustainable sources such as wind-, hydroelectric-, geothermal- and photovoltaic power. Emissions of pollutants from combustion of hydrogen are very low. Studies are in progress in assessing the need for a new gas transportation system dedicated solely to hydrogen, or whether the existing natural gas system can be employed, using hydrogen/natural gas mixtures and hydrogen separation techniques[1].

Tables 2 and 3 give some examples of compositions and properties (expressed on a dry basis) of NCS gases.

NOTE 1: The composition and consequently the physical and chemical properties of different raw and treated natural gasses can differ significantly: The figures included for natural gas concern indicative values of gas supplied to European households.

NOTE 2: [1] An integrated project funded by the European Commission's sixth framework programme for research, technological development and demonstration (RTD) has been undertaken under the name “NaturalHy” to examine the effects of hydrogen addition to the natural gas grid. The final report has been published in 10-2009 and is available at www.naturalhy.net

Table 2 — Indicative composition of different raw gases from non-conventional sources and of natural gas

Composition	Units	Natural gas (typical North Sea H)	Biogas		Biosyngas from biomass gasification		Syngas from coal gasification	
			Anaerobic digester	Landfill	O_2-fired	Air-fired	CMM	CBM
Methane		89	65.0 (50-80)	45.0 (30 - 60)	15.6	2.0 (1 – 10)	65.0	90.0
C_{2+} carbons		8			5.8	(0 – 2)	1.5	2.2
Hydrogen	Mol %	-	- (0-2)	1.5 (0-2)	22.0 (20 - 30)	20.0 (10 – 25)	-	-
Carbon monoxide		-	-	-	44.4 (40 - 50)	20.0 (10 – 25)	-	-
Carbon dioxide		2	35.0 (15-50)	40.0	12.2 (15 - 30)	7.0 (7 – 15)	16.0	3.3
Nitrogen		1	0.2 (0-5)	(15-40)	(3 - 7)	approx. 50.0	18.0	4.5
Oxygen		< 0.001	(0-1)	15.0 (0-50) 1.0 (0-10)			(0 – 5)	
Hydrogen sulphide		2	<600 (100-10000)	<100 (0-1000)	-		(0 – 5)	(0 – 5)
Ammonia	mg/m^3	-	100 (0-100)	5 (0-5)	-			
BTX[2,3]		200 -	0-20 (0-100)	0-500 (0-800)				1000-10000
Total chlorine								
Total fluorine	mg/m^3	-	0.5 (0-100)	10 (0-800)	-		-	-
Siloxanes	mg/m^3	-	0-50	0-50	-		-	-
Tar	mg/m^3	-	-	-	0 - 5	0,01 - 100	-	0 - 5

[2] S.Rasi, A. Veijanen, J. Rintala, Trace compounds form different biogas production plants, Energy 32 (2007) p1375-1380

[3] Bridgwater A.V. and Boocock D.G.B. (Eds), 1997, Developments in thermo chemical biomass conversion, IEA Bioenergy

NOTE: 1: all compositions are purely indicative, derived from different sources. Bracket values indicate ranges which may be encountered, depending on the base material fed into the process

NOTE 2: For biomass gasification, different methods are available with significant differences in the composition of the product gases.

Table 3 — Indicative properties of different raw gases from non-conventional sources and of natural gas

Properties	Units	Natural gas (North sea H)	Biogas		Biosyngas		Syngas	
			Anaerobic digester	Landfill	O_2-fired	Air-fired	CMM	CBM
Gross calorific value	MJ/m^3	41.8	32	17	14	6	**25**	**36**
	kWh/m^3	11.6	7	7	4	3	**7**	**10**
Net calorific value	MJ/m^3	37.8	22	21	13	9	**23**	**32**
	kWh/m^3	10.5	6	6	4	3	**7**	**9**
Wobbe number	MJ/m^3	52.7	26	27	29	20	**29**	**45**
	kWh/m^3	14.6	8	8	8	6	**8**	**13**
Relative density		0.63	0.9	0.7	0.2	0.3	**0.8**	**0.6**
Density	kg/ m^3	0.81	0.8	0.8	0.3	0.3	**0.8**	**0.7**
Methane number		76	135	144	64	77	**109**	**90**

NOTE: properties are calculated from the indicative single values given in table 2, on a dry basis (although the raw gas may in practice be saturated)

Gross and net calorific value and Wobbe number are derived from GERG report PC 1 “Biogas characterization WG 1.49

Methane number is generally calculated in accordance with the AVL list

5 Potential additional hazards

5.1 General

The hazard initiated by chemical or biological components is generally associated with the raw gas and hence depends upon the source and/or production process. NCS gases may be characterized by a wide range of composition and by a possible presence of a wide variety of components (either chemical or biological components) which could be corrosive, toxic or could harm the quality of products. This might also be the case for components of the flue gases if these gases are burned.

In some circumstances the treatment process required to bring the raw gas to general pipeline quality (e.g., calorific value, Wobbe number) may be sufficient to reduce the hazard to acceptable levels. On other circumstances, specific treatment processes may be required. Nevertheless, the effectiveness of countermeasures needs guarantees including checks, and a Quality Assurance system.

The following kinds of hazards shall be kept to a minimum:

- hazards on human health of end-users and for employees of e.g. the gas industry;
- hazards on gas networks integrity;
- hazards to the safe operation of gas appliances.

For human health, the hazards are: direct toxicity in case of exposure to unburned NCS gas and, indirect toxicity by combustion products, water pollution in case of injection in subterranean storage and air pollution.

For gas networks, gas appliances and flue gas systems, major hazards are:

- corrosion and clogging of network facilities,
- failure and blocking of controls and safety devices,
- corrosion, clogging and failure of gas appliances,
- corrosion of the flue gas systems
- undue change of combustion properties.

Furthermore, the safety risks related to the transmission, distribution and end use and the performance of end user appliances may change. Even when the composition of some NCS gases is within the specifications of natural gas, an additional hazard may be raised by the fact that some NCS-gases have a high carbon dioxide content, which has a significant effect on the combustion properties. This is further explained at the end of this sub-clause.

The list of compounds and associated hazards presented here may not be exhaustive.

Table 4 below indicates potential hazards arising from each type of NCS gas under normal and abnormal operational conditions of the biogas production unit, gas treatment facilities etc. Malfunction or non-optimal adjusted facilities in the NCS gas production chain up to and including gas treatment might effect the composition of the gas with subsequent increase of the risks. Furthermore, water in combination with CO_2 or O_2 can initiate system integrity problems.

Risk assessment is recommended in order to evaluate specific requirements (see 7.1).

Table 4 — Additional potential hazards associated with NCS and countermeasures

NOTE These hazards are additional to known potential hazards connected with natural gas

Product	Source	Hazardous components/aspect	Hazard	Countermeasure
Biogas	Digester gas	Ammonia	Corrosive compound: hazard to the integrity of the gas system of the gas system Toxic gas: health hazard Increased NOx emission	Sampling and analysis for ammonia Removal of ammonia from the NCS gas
		Biological agents	Bio corrosion: hazard to the integrity of the gas system Possible presence of pathogenic agents: health hazard Pollution of products	Sterilization of the substrate Long digester retention time Filtration (see note below)
		Halocarbons	Corrosive compounds: hazard to the integrity of the gas system Production of dioxins and furans under burner conditions: health hazard Corrosive, toxic combustion products: hazard to health and equipment of end users (incl. flue gas system)	Sampling and analysis for halocarbons. Exclusion of sources of known halocarbon content Removal of halocarbons from NCS gas
		Siloxanes	Production of silica under burner conditions: hazard to end user equipment	Sampling and analysis for siloxanes. Exclusion of sources of known high silicon content. Removal of siloxanes from the biomass or the NCS gas
		High content of carbon dioxide	Impact on combustion properties: hazard to safety and performance of end user equipment	Mixing with natural gas; Addition of higher – hydrocarbons Maintaining CO_2 content within acceptable limits Extensive gas quality control
		Phosphine (PH_3)	Corrosive compounds: hazard to the integrity of the gas system Toxic gas: health hazard	Sampling and analysis for phosphine. Exclusion of sources of known phosphine content Removal of phosphine from NCS gas
		Phosgene ($COCl_2$)	Corrosive compounds: hazard to the integrity of the gas system Toxic gas: health hazard	Sampling and analysis for phosgene. Exclusion of sources of known phosgene content Removal of phosgene from

				NCS gas
	Landfill gas	Ammonia	Corrosive compound: hazard to the integrity of the gas system Toxic gas	Sampling and analysis for ammonia Removal of ammonia from NCS gas
		Biological agents	Bio corrosion: hazard to the integrity of the gas system Possible presence of pathogenic agents: health hazard Pollution of products	Filtration (see note below)
		Halocarbons	Corrosive compounds: hazard to the integrity of the gas system Production of dioxins and furans under burner conditions: health hazard Corrosive, toxic combustion products: hazard to health and equipment of end users	Sampling and analysis for halocarbons. Exclusion of sources of known halocarbon content Removal from NCS gas
		Polyaromatic hydrocarbons (PAHs)	Affects plastic and elastomere material: hazard to the integrity of the gas system Toxic, carcinogen: health hazard Sooting when burnt: hazard to the performance and safety of end user equipment	Monitoring and removal
		Siloxanes	Production of silica under burner conditions: hazard to end user equipment	Sampling and analysis for siloxanes. Exclusion of sources of known high silicon content. Removal of siloxanes from the biomass or NCS gas.
		Phosphine (PH_3)	Corrosive compounds: hazard to the integrity of the gas system Toxic gas: health hazard	Sampling and analysis for phosphine. Exclusion of sources of known phosphine content Removal of phosphine from NCS gas
		Phosgene ($COCl_2$)	Corrosive compounds: hazard to the integrity of the gas system Toxic gas: health hazard	Sampling and analysis for phosgene. Exclusion of sources of known phosgene content Removal of phosgene from NCS gas
		High content of carbon dioxide	Impact on combustion properties: hazard to safety and performance of end user equipment	Mixing with natural gas; Addition of higher – hydrocarbons Maintaining CO_2 content within acceptable limits Extensive gas quality control

Synthetic natural gas SNG	High temperature gasification	Polyaromatic hydrocarbons (PAHs)	Affects plastic and elastomeric material: hazard to the integrity of the gas system Toxic, carcinogen: health hazard Sooting when burnt: hazard to the performance and safety of end user equipment	Monitoring and removal
		Hydrogen	Corrosion, Hazard to the integrity of the gas system Increased safety risks of transmission, distribution, and end use Safety and performance of gas appliances; Impact on industrial processes	Gas quality control; Removal; Increased pipeline integrity management
		Carbon monoxide	Toxic gas: health hazard	Permanent monitoring and removal
	Low temperature gasification	Polyaromatic hydrocarbons (PAHs)	Affects plastic and elastomeric material: hazard to the integrity of the gas system; Toxic, carcinogen: health hazard Sooting when burnt: hazard to the performance and safety of end user equipment	Monitoring and removal
		Tar	Clogging: hazard to the integrity of the gas system and end user equipment	Monitoring and removal
		Hydrogen	Hazard to the integrity of the gas system Increased safety risks of transmission, distribution, and end use Safety and performance of gas appliances; Impact on industrial processes	Gas quality control; Removal; Increased pipeline integrity management
		Carbon monoxide	Toxic gas: health hazard	Permanent monitoring and removal
Hydrogen	Water gas shift Electrolysis	Hydrogen	Corrosion, Hazard to the integrity of the gas system Increased safety risks of transmission, distribution, and end use Safety and performance of gas appliances; Impact on the performance of industrial processes	Gas quality control; Increased pipeline integrity management

NOTE Micro-organisms can be removed by filtration with mesh size <1µm. However, the effectiveness of filtration systems has not been fully demonstrated for all NCS sources.

5.2 Ammonia

Ammonia is a toxic gas which can induce a risk in case of a leak. Also, it can induce corrosion in gas networks, and when burned, it increases the NOx-emission.

5.3 Halocarbons (Organo-halides)

Efficient combustion of landfill gas should result in destruction of most toxic compounds resulting in largely carbon dioxide, water and traces of oxides of sulphur and nitrogen, and hydrogen chloride. The last mentioned combustion product is highly toxic and corrosive for the equipment. In addition, when materials containing halocarbons are burnt, at the presence of catalytic amounts of copper it is feasible that trace levels of dioxins and furans are produced; the amount depending upon the type of material burnt and the combustion process.

NOTE There is little dioxin and furan release data available for landfill gas combustion (and in particular landfill gas treated for pipeline injection). Data published on the Internet (www.ping.be/ be/~ping5859/eng/ chlorinediinp.html) shows chlorine input and dioxin output from a variety of process. There does not appear to be a correlation between chlorine content of fuel and the amount of dioxin released. Formally, there is still unclearness about the level of toxicity. Natural gas does not normally contain halocarbons so the risk associated from dioxins and furans posed by landfill gas combustion must be carefully assessed.

5.4 Biological agents

As a number of NCS gases are produced from biomass by biological processes, the transport of micro-organisms as an aerosol has to be considered. Knowledge about the effects of microorganisms in the gas transport system is still limited and will depend on the species. This is a subject of further investigation.

The quality of the treated gas is generally guaranteed by quality assurance (QA) of ingoing raw material to the biogas plant, QA of the biogas production process and QA of upgrading and purification process.

5.4.1 Pipeline integrity

GTI has reported about its investigation of bacteria and spores in biogas and biomethane from dairy waste[4.] In this investigation, the total bacteria and total corrosion-causing bacteria (APB, IOB, and SRB) in gas samples, including both dead and live bacteria, were determined by a genetic method by targeting specific genes present in the target microorganisms. This data quantifies dead and live microbes in the gas sample. The most likely explanation for the presence of dead microbes is that live microbes originating from the digester and entrained in the raw biogas, are killed as they are trapped on the sample filter (succumb to desiccation). The results also indicated that most raw biogas samples analyzed had an average of $10^6/m^3$ (total live and dead) heterogeneous bacteria. Acid-producing bacteria and iron oxidizing bacteria were identified as the two main types of corrosion-causing bacteria present in these samples.
It is recommended that appropriate filters/biocides/microbe removal processes be used to prevent the transfer of microorganisms from the raw biogas to the product biomethane.

There is no information available that proves that bacteria-assisted corrosion by NCS gasses initiates other, less or more problems than experienced with natural gas. Therefore, bacteria-assisted corrosion initiated by NCS- gas is an issue worthwhile further investigation as system integrity is of eminent importance.

5.4.2 Human health

Relatively little information is available on the health risks associated with biological agents in NCS gases. In this respect, the relevant micro-organisms concern, for instance, bacteria, spores, viruses, priones and fungi's. This gap of knowledge is also concluded by recent desk studies performed by LEAVE (NL) and AFSSET (FR),

4 *Pipeline Quality Biomethane: North American Guidance Document for Introduction of Dairy Waste Derived Biomethane Into Existing Natural Gas Networks: Task 2 (*GTI PROJECT NUMBER 20614), 2009

in which the published information was combined and examined. These reports are summarised below as well as a paper of an investigation by the Swedish University of Agricultural Sciences/Swedish Institute for Infectious Disease Control

- The LEAVE report[5] indicates that it is difficult to quantify the health risks initiated by pathogens that might be present in treated biogas as there are many parameters that may have a significant impact on the number of pathogens humans are exposed to. For instance, the quality of the biomass (manure, domestic waste, sewage sludge, etc) is very important for the quality of the biogas produced. Examples of pathogens that might be present are foot-and–mouth disease, Enterobacteria (including Escherichia coli and Salmonella), Campylobacter, spore forming bacteria and Cryptosporidium and Giardia. Manure from healthy animals will generally speaking not contain many human pathogens, and the related risk is expected to be limited. The issue with some pathogens is that they can be present in the animals (and the manure) some time before the animals actually show that they are sick. This is for instance the case with Mycobacterium paratuberculosis. In such cases, the number of pathogens in manure will be significant. It is not yet possible to determine the risks related to the digestion of manure from sick animals.

- The AFSSET report[6] estimates that the general public is exposed to a few litres of treated biogas per ignition. As a consequence of this the quantity of released micro-organisms will be very limited and in the order of several hundreds. Even if this number would strictly concern pathogenic micro-organisms (which is not the case), the dilution effect would lead to a doses which is lower than the infective threshold. Based on the existing information, AFSSET concludes that there seem to be no urgent signals concerning the microbiological risks regarding the utilisation of treated biogas from domestic and similar waste (including waste such as green and animal waste (manure), and fermentable waste from the food industry). Injection of these types of gases does not initiate a bigger health risk than natural gas. However, AFSSET could not draw a conclusion concerning the risks related to gas from sewage sludge and industrial waste other than fermentable organic waste from the food industry. This, because of the lack of data. AFSSET advises not to utilise gas from these sources in the natural gas

- The study on “Biological community in biogas systems and evaluation of microbial risks from gas usage” of Vinnerås, Nordin and Schönning[7] reports on their investigation on mesophilic digesters for sewage sludge and bio waste. The gas was primarily meant for fuelling cars. Most of the micro organisms identified in the gas before treatment and in the condensate were opportunistic pathogens, which may cause infections in immuno-compromised individuals. Some of the bacteria identified (e.g. E. coli) occur naturally in the human intestine and relate to faecal contamination. No significant difference was detected between the concentrations of micro organisms in the upgraded gas and the biogas before upgrading: the microbial load is about 10-100 cfu/m^3. It is concluded that risks from disease transmission from upgraded and dried biogas is low. The possible exposure of personnel to the condensate of the treatment plant is probably the most significant risk. The risk of inhaling pathogens when using gas is overshadowed by the risk of gas intoxication and explosions or similar. The biogas investigated is considered safe to use even in kitchen cookers.

- A recent study of the Gas Technology Institute (GTI) in which samples were examined of biogas and biomethane from dairy waste[4], tested positive for spores with an average spore number of 190 spores/m^3. It is concluded that partial treatment of the biogas or cleanup technologies used in biomethane production may have little impact on spore removal. A preliminary screening of spores found that the majority of spore-forming bacteria were Bacillus licheniformis, Bacillus pumilus, various other Bacillus species, and Paenibacillus species through genbank testing

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[5] Ïnventarisatie van het risico van transmissie van pathogenen uit biogas”, Iemke Bisschops & Miriam van Eekert, LEAF, April 2008

[6] „Risques sanitaires du biogaz; Evaluation des risques sanitaires liés à l’ínjection de biogaz dans le réseau de gaz naturel » AFSSET, October 2008.

[7] Björn Vinnerås, Annika Nordin and Caroline Schönning, Energie I Wasser-praxis 12/2007

5.5 Poly-aromatic hydrocarbons (PAH's)

Poly-aromatic hydrocarbons may be present in NCS-gases including landfill gas. These hydrocarbons may affect PE-pipelines, rubber and other synthetic parts present in the natural gas chain, and some are known carcinogens. In combustion, higher poly-aromatic hydrocarbons may result to the formation of soot.

5.6 Hydrogen

Hydrogen added to natural gas in the natural gas system may affect

- the integrity of the gas system (e.g., hydrogen induced stress corrosion);
- the safety risks related to the transmission, distribution and use of the gas (e.g., unintended gas release, combustion properties as e.g. explosion limits, radiation of flames, ignition energy);
- the performance of end user appliances (e.g. flame speed and flash back);
- the performance of industrial processes (change of chemical composition).

NOTE An integrated project funded by the European Commission's sixth framework programme for research, technological development and demonstration (RTD) has been undertaken under the name "NaturalHy" to examine the effects of hydrogen addition to the natural gas grid. The final report has been published in 10-2009 and is available at www.naturalhy.net

5.7 Siloxanes

Siloxanes may be frequently encountered in municipal sewage and landfill, but were also found in agricultural biogas plants. During combustion they are converted to SiO_2, which is destructive to combustion equipment. Furthermore SiO_2 may deposit on ionisation and ignition pins, causing malfunction of the equipment.

5.8 Carbon dioxide

NCS gases from digestion processes as well as from gasification/methanation processes consist mainly from carbon dioxide and methane. A high CO_2-fraction in combination with a relative high water content may lead to serious pipeline integrity issues.

Furthermore, calculations show that the combustion velocity of these gases is lower than the velocity of natural gases with a similar Wobbe index. This is predominantly the result of the high CO_2 content compared to natural gases. The very low content of higher hydro-carbons has a further decreasing impact on the flame velocity. The combustion velocity could be reduced to such an extent that flame blow off may occur, resulting in unsafe situations.

5.9 Carbon monoxide

Carbon monoxide is present in gases from gasification plants and is very toxic. Gas leaks in confined rooms can cause fatal accidents.

5.10 Radioactive components

Radon is a radioactive gas that occurs in nature everywhere. It is produced from decay of trace amounts of radioactive uranium present in soils and rocks and is therefore present in both natural gases and in coal-associated gases. European legislation covering the safe handling of radioactive substances and safe disposal of radioactive waste limits also the content of radioactive components in natural gases.

Concentrations of radon in coal-associated gases can vary considerably and can, depending on the respective source, be up to several tens of thousands of Becquerel/m^3. These levels are higher than those seen in natural gas and therefore may lead to denial of access to the natural gas network for a particular gas.

6 Requirements for injection

6.1 Currently used minimum requirements for any type of network entry

In order to ensure the safety, integrity and operability of gas networks, all gases (conventional or non-conventional) must meet certain minimum gas quality requirements. The choice of gas quality parameters and their limiting values are generally specified nationally or in case of transborder transportation, among the parties involved. Table 5 illustrates the parameters that are generally constrained by national legislature.

Table 5 — Gas quality parameters currently specified in national legislation or within EU directives

		AT	BE	DK	DE	FR	IT	NL[4]	ES	UK
Reference Temperature, °C										
Volume		0	0	0	0	0	15	0	0	15
Energy		25/0	25/0	25/0	25/0	0/0	15/15	25/0	0/0	15/15
GCV		X	X		X	X	X		X	
Wobbe index		X	X	X	X		X		X	X
Density		X		X	X		X		X	
Methane number										
Hydrocarbon condensation point		X		X	X		X		X	X
Water dew point		X		X	X	X	X		X	X
Sulfur	Total	X	X	X	X	X	X			X
	H_2S	X	X	X	X	X	X		X	X
	Odorant[2, 3]		X	X			X			
	Mercaptan	X			X		X		X	
	COS	X							X	
Other indices[1]	Comb. Potential									
	Lift Index									
	ICF									X
	Soot index									X
CO									X	
Carbonyl metals										
Impurities (liquids, solids)		X		X	X		X			X
CO_2		X					X		X	
N_2		X								
O_2		X			X		X		X	X
H_2		X								X
Aromatics[5]										
NH_3		X							X	
Hg[5]										
Halogenes		X								

NOTE 1 Other indexes relate to indexes use for interchangeability.

NOTE 2 In every country except the Netherlands there is a national legislation stating that gas shall be odorised. Thus if the table shows an indication for odorant specification it means that an actual concentration of odorant is specified to fulfil this obligation. This specification may be written in a standard. In some countries a specification on mercaptans concentration is made apart from odorization requirement.

NOTE 3 Odorants are not always sulfur-based. In some countries, a sulfur free, acrylate based odorant is used. However, all countries ask for gas to arrive sufficiently odorized at consumers' premises.

NOTE 4 In the Netherlands gas quality parameters are agreed between the gas supplier and its customers.

NOTE 5 Directive 76/769/EEG set further limits on benzene and mercury. Furthermore, the directives 67/458/EEG (concerning classification of compounds in categories), 1999/45/EG (concerning preparations) and 2001/58/EG are directly relevant.

Within the European Union there is a proposal to harmonise natural gas quality specification and a specification has been produced by EASEE-Gas, approved by the Madrid Forum. A Common Business Practice has been prepared by EASEE-Gas which suggests an action plan and timescales for its implementation. The harmonised gas quality specification is currently only applicable for cross-border transportation of gases within gas family H. Gases complying with this specification can be exchanged if the parties involved agree to do so. However, it is intended to produce a European standard for the quality of natural gas H, based on mandate M 400 issued by the European Commission. This standard is envisaged for 2014.

Table 6 indicates the parameters that form part of the harmonised specification, together with limit values and status.

Table 6 — Gas quality parameters from EASEE-gas CBP 2005-01-002, envisaged as base document for the development of a harmonized European standard for natural gas H

Parameter	Value	Status
Wobbe Index	13.6 -15.81 KWh/m^3 (25°C/0°C)	Recommended. A difficulty has been recognised with the lower Wobbe Index value and as a result a starting range of 13.76 – 15.81 has been recommended.
Relative density	0,555 – 0,7	
Total sulfur	Maximum 30 mg S/m^3	
(H_2S + COS)	Maximum 5 mg S/m^3	
Mercaptans	Maximum 6 mg S/m^3	
Oxygen	Maximum 10 ppm molar	From some underground storage facilities, 100 ppm are permitted
Carbon dioxide	Maximum 2.5 % molar	
Water dewpoint	Maximum –8°C at 70 bar a	
Hydrocarbon condensation point	Maximum –2°C over 1 - 70 bar a	
Hydrogen	-	Currently unspecified

Non-conventional supplies of gas must comply with prevailing national and European legislation and must be compatible with those gas quality specifications of the gas to which the non-conventional gas is being added. Where a gas offered to a pipeline owner/operator does not meet the specifications set above, the parties generally examine the possibility of additional treatment of the gas or blending with other gases before it is actually added to the gas system that directly supplies gas to customers.

Increase in magnitude and frequency of gas quality changes may result from the injection - and cessation of injection - of different gases. This may cause operational problems for certain industrial applications of natural gas and safety problems in domestic and industrial applications. Further research in this aspect is required. If the addition of gases leads to a lower content of particularly methane, the commercial value of the gas supplied to industries that use natural gas as a feedstock (for instance producers of H_2, methanol, ammonia, soot) may decrease.

6.2 Requirements particularly relevant for the injection of NCS gases in national networks

Some countries define specific requirements for injection of NCS gases. Some are figured in table 7. It should be noted that the background of quite some of the indicated figures concerning components, cannot be traced and seems, according to the opinion of the authors of this technical report, not to be well based. This does not apply to the values concerning water and sulphur content, and the odorant level.

Table 7 — Specific requirements for the injection of NCS gases into natural gas networks in some European countries

Physical Properties	Unit	France	Czech Republic	Austria	Switzerland	Sweden[8]	Germany	The Netherlands		
								Distribution grid		Transport grid
								2006[9]	2009[10]	2009
Gross Calorific Value	MJ/m^3	38.5 – 46.1 (H) 34.2 – 37.7 (L)		38.5 – 46.0	38.5-47.2	39.6 – 43[11].2	30.2-47.2	31.6 – 38.7	34,5-36,0	34,5-36,0
Wobbe-index	MJ/m^3	49.1 – 56.5 (H) 43.2 – 46.8 (L)		47.7– 56.5	47.9-56.5	43,9 - 47,3	37.8-46.8 (L) 46.1-56.5 (H)	43.46-44.41	43.46-44.41	43.46-44.41
Relative Density		0,555 – 0,7	0,56 – 0,7	0,55 – 0,65	0,55 – 0,7		0,55 -0,7			
Temperature (in the injection gas)	˚C					-20 - +20		0 – 20	0 – 20	10 – 40
Methane number							≥ 70[12]	> 80		-
Water dew point	˚C	< -5	≤-10	< -8 (at 40 bar)		t-5	Ground temp. (subject to change in 2011)	< -10 (at 8 bar)	< -10 (at 8 bar)	< -10 (at 73 bar)
	°C	<-2°C from 1 to 70 bar		0 at op. press.			Ground temperature (subject to	-		5 (T=-3°C, < 70 bar)

8 Swedish standard for use of biogas as a vehicle fuel, SS 155438

9 This set of requirements is part of the technical code for the distribution grid connection of biogas since 2006

10 This set of conditions are additional and preliminary conditions from the grid operator since November 2008, conditions are published in “Feasibility study green gas, P. Jansen and R. van den Boogaard, march 2009, published on the website of Senter Novem

11 No specific requirements on CV in standard

12 Values form DIN 51624 which is applicable not only for natural gas as a vehicle fuel, but also for biogas as a vehicle fuel

Hydrocarbon dew point							change in 2011)			

Components	**Unit**	**France**	**Czech Republic**	**Austria**	**Switzerland**	**Sweden**[13]	**Germany**	**The Netherlands**		
								Distribution grid		Transport grid
								2006[14]	2009[15]	2009
Water					Prevent conden-sation	<32 mg/m^3				
Sulphur (in total)	mg/m^3	30	30	10	30	23	30 10 mg/kg[12]	45		30
Inorganically bonded sulphur (H_2S)	mg/m^3	5 (H_2S + COS)	7	5	5	10	5	5		5
Mercaptans	mg/m^3	6	5	6	5 ppmV		6	10		6
COS	mg/m^3			5					5 (H_2S+COS)	
Odorant level (THT)	mg/m^3	15-40			15-25		Min. 10 (THT)	> 10. nominal 18		
Ammonia	mg/m^3	3	None	Techn. free	20	20		3		-
Chlorine containing Compounds	mg/m^3	1	1.5 (F + Cl)	none	Halogenes < 1 mg/m^3_n		none	50		-
Fluorine containing compounds	mg/m^3	10		none			none	25		-
Hydrogen Chloride (HCl)	ppm			none				1		-
Hydrogen cyanide	ppm			none				10		-

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13 Swedish standard for use of biogas as a vehicle fuel, SS 155438

14 This set of requirements is part of the technical code for the distribution grid connection of biogas since 2006

15 This set of conditions are additional and preliminary conditions from the grid operator since November 2008, conditions are published in “Feasibility study green gas, P. Jansen and R. van den Boogaard, march 2009, published on the website of Senter Novem

(HCN)										
Heavy Metals		Hg <1 µg/m^3			< 5 µg/m^3					
Carbon monoxide (CO)	Mol-%	2			0.2 Vol-%			1		-
CO_2 (dry gas networks, max)	Mol-%	2.5	5	2.0	6	3	6	6	< 10,3	< 8
Components	**Unit**	**France**	**Czech Republic**	**Austria**	**Switzerland**	**Sweden**[16]	**Germany**	**The Netherlands**		
								Distribution grid		Transport grid
								2006[17]	2009[18]	2009
CO_2 (wet gas grids)	Mol-%							n.a.		
Nitrogen	Mol-%		2					-		
BTX (Benzene. Toluene. Xylene)	ppmV				Tar <50			500		250
Aromatic hydrocarbons	Mol-%							1		0,025
Oxygen (dry gas grids)	Mol-%	0.01 (1000ppmV)	0.5	0.5	0.5	1	3	0.5		0,5 (40 bar) 0,0005 (73 bar)
Oxygen (wet gas grids)	n.a.						0.5			
Hydrogen	Mol-%	6		4	4	-	5 2[12]	12		0,02
Dust		<5 mg/m^3	None	Techn. Free		< 1µm	Techn. Free	Techn.free		
Siloxanes	ppm		6 mg/m^3	< 10 mg/m^3				5		-
Pathogens/ corrosive micro organisms									Techn. Free	Techn. Free
Phosphines									Techn. Free	Techn. Free

16 Swedish standard for use of biogas as a vehicle fuel, SS 155438

17 This set of requirements is part of the technical code for the distribution grid connection of biogas since 2006

18 This set of conditions are additional and preliminary conditions from the grid operator since November 2008, conditions are published in “Feasibility study green gas, P. Jansen and R. van den Boogaard, march 2009, published on the website of Senter Novem

Sources:

EU: Mercury and benzene: Directive 76/769/EEG, in combination with 67/458/EEG, 1999/45/EG and 2001/58/EG (value to be added!!!)

Austria: ÖVGW codes of practice G 31, G 33

France: prescriptions techniques du distributeur Gaz de France prises en application du décret n° 2004-555 du 15 juin 2004 relatif aux prescriptions techniques applicables aux canalisations et raccordements des installations de transport, de distribution et de stockage de gaz. However, for density and impurities, two other specifications exist..

Note: Depending on the nature of the gas to inject in the French natural gas grid, others maximal concentrations of some compounds must be added according to the risk of damages which can be caused on the grid.

Germany: DVGW codes of practice G 260, G 262, *DIN 51624 for use as vehicle fuel only

Sweden: Swedish Standard SS155438

Switzerland: SVGW codes of practice G 13

NOTE Depending on the nature of the NCS, specific requirements not mentioned in this table may apply.

6.2.1 Minimum gas quality requirements for grid delivery of gases

NCS gases suitable for injection in the network, should at least meet the specifications of the natural gas in the network.

With the exception of those based on hydrogen, the main component of NCS gases and of natural gas is methane. Biomethane and SNG therefore have many properties similar to those of natural gas. However, NCS gases differ from natural gas in a number of key aspects that must be addressed by appropriate specification of quality, which is additional to the specifications of the natural gas in the network.

6.2.1.1 General requirements

Risk assessment prior to injection of any gas, irrespective of source, is recommended in order to assess requirements for measurement, control and safety devices. Such risk assessment should therefore consider the additional risks associated with NCS gases.

Gas Transporters will generally require that treatment plants feeding gases into a natural gas grid should be equipped with continuous determination of calorific value, density and water content and, depending on the source of gas and requirements in place, also methane, CO, higher hydrocarbons, sulphur and oxygen. Systems to shut down the delivery in case of deviations from minimum requirements may also be required. The selection of the components and parameters to be determined, and the accuracy and frequency with which such determination should be carried out, are a subject to be agreed between the party taking care of the injection and the grid operator, and is often based on the needs for custody transfer and a risk assessment.

The addition of NCS gases as e.g. Hydrogen to natural gas may initiate modification to the measurement system for the determination of the calorific value of gas delivered to end users for billing purposes, depending on the rules in place for legal metrology.

Measurement of gas properties from non-conventional sources should where possible be performed with standardized methods defined by international, European or national standards. ISO/TC 193 “Natural gas” has developed a number of relevant standards, however standards relevant to some NCS gases are not available (for example PAHs, micro-organisms).

6.2.1.2 Requirements concerning biological compounds

Gas that is distributed on the natural gas grid shall not contain substances that can cause danger to the health of gas users or other persons that may come into contact with the gas or its products of combustion. Also, any additional hazard to the natural gas transport system and of its components shall be avoided. NCS gases with high risk from biological agents, such as biogas plants feeding gas into the natural gas grid should therefore have a quality assurance system or equivalent proof for handling raw material, gas production and gas treatment in order to eliminate the risk for contamination.

Biomethane distributed on the natural gas grid shall be specified in a safety data sheet in accordance with Directives 91/155/EEC and 2001/58/EC.

6.2.1.3 Requirements concerning silicon compounds

Siloxanes may be frequently encountered in municipal sewage and landfill. During combustion they are converted to SiO_2, which is particularly destructive in combustion engines. To avoid damage to engines, silicon compounds in gas that is delivered to the natural gas grid may require limitation. In Austria, e.g., Siloxanes are required to be at a level of < 10 mg/m³ (as Si).

6.2.1.4 Requirements concerning halogenated compounds

Gas conveyed to the general public shall be technically free of halogenated hydrocarbons. Under the conditions of a gas burner in the presence of copper, dioxins and furans may be produced. Halogenated hydrocarbons are often encountered in landfill gases and where this is so, these gases should not be admitted to the natural gas grid unless the grid only supplies a defined number of industrial customers with the capability for fully monitored use of the gas. In the UK, National Grid has indicated in its annual Ten Year Statement, a limit on the maximum content of organo-halides permitted for network entry of 1.5 mg/m^3.

6.2.1.5 Requirements concerning ammonia

Ammonia is corrosive in the presence of oxygen for ferrous metals (carbon steel) and non ferrous metals (brass). It induces risks of cracking, especially with high strength steels (> 400 MPa). Above 0,2% of water in the gas, this tendency decreases.

The corrosion with ammonium chloride is known to be fast.

6.2.2 Minimum gas quality requirements particularly relevant for grid delivery of gases produced from biomass by fermentation processes

These requirements are covered by the general requirements for the injection of NCS gases in the network, as indicated in the previous paragraph.

6.2.3 Minimum gas quality requirements particularly relevant for grid delivery of gases produced by thermal process

Gases produced from for instance biomass and coal by thermal process will be of a similar composition to town gas produced from coal or lignite, because the production processes available are based on coal gasification processes. Depending on the process chosen the product gas will contain a significant percentage of methane, or will be predominantly a mixture of hydrogen and carbon monoxide. Gases produced from biomass gasification in general contain less sulfur components and ash residue than gases from the gasification of coal. After cleaning, (utilising the same methods developed for raw town gases) such gases are suitable as a replacement for town gas. However, as town gas is hardly ever encountered in Europe, its use is limited to augmenting gas in natural gas grids. Such use demands more thorough treatment, including total removal of carbon monoxide, partial removal of carbon dioxide and eventually hydrogen. Drying is required as such gases (like their coal-based counterparts) are generally wet.

Polyaromatic hydrocarbons (PAHs) and tars are formed when thermally gasifying any kind of solid carbon containing fuel. PAHs are generally defined as organic compounds containing two or more condensed aromatic rings. PAHs can condense in gas pipes and cause clogging, and because they decompose only very slowly can accumulate in the human body if exposed. Tars may also lead to clogging of the gas system and to the formation of soot when burned.

PAHs are normally formed in the gasifier but removed in subsequent processes to produce a gas suitable for grid injection.

In Germany, DVGW specifies, for towns gases, a maximum content of single ring aromatics of 10 g/m^3 and the maximum content of double ring aromatics (naphthalene) to be 50/P mg/m^3 (where P = max pressure in bar where gas is injected) in order to avoid condensation. DVGW also requires a hydrocarbon dew point to be less than the temperature of the pipe where gas is injected.

Carbon monoxide can be present in gases from gasification plants and is very toxic. Very little town gas production is practiced today, but in Denmark and Sweden, typical towns gas specifications limit carbon monoxide level to 3 mol%.

6.2.4 Minimum gas quality requirements particularly relevant for grid delivery of coal-associated gases

Due to their similarity to natural gas, for these gases, after treatment, the same network entry requirements apply as for natural gas. However, for some sources of this type radioactive gases, e.g. radon content, may exclude them from grid entry.

In the UK, the Radioactive Substances Act 1993, as modified by the Radioactive Substances (Natural Gas) Exemption Order 2002 requires registration of all natural gas installations where a content (for each nucleotide) of 5 Becquerel per gram is exceeded. This threshold value is around ten times the typical radon content of UK natural gases.

6.2.5 Minimum gas quality requirements particularly relevant for grid delivery of hydrogen containing gases

Some NCS-gases may contain a significant percentage of hydrogen, and as a consequence of this, the chemical and physical properties of these gases may differ significantly from natural gas. Hydrogen affects:

- the safety related to the transmission, distribution and use of the gas,
- the performance of end use appliances as it affects the combustion properties of the gas and
- the mechanical properties of pipeline materials and consequently it may have a major impact on both safe utilisation and pipeline integrity.

The amount of hydrogen to be delivered depends amongst others on the specifications and condition of the end user appliances, the materials, the condition and on operating conditions of the respective grid and may vary from 0,02% for some high-pressure grids up to 60% in some low-pressure towns gas grids. The NATURALHY project (www.naturalhy.net) that defines the conditions under which hydrogen can be added to natural gas with acceptable consequences was completed in October 2009, and further investigative research on this issue is ongoing and should be extended.

End user perception and acceptance of gases containing hydrogen are also relevant (and critical) issues. Hydrogen content is currently unspecified in the proposed EASEE-Gas harmonised gas quality specification (see Section 5.1).

7 Measurement and control

7.1 General considerations

When injecting NCS gases into a natural gas pipeline, several factors need to taken into consideration:

— Quality control of the injected gas in order to avoid any damage or hazard to the downstream gas system or any adverse effects to gas utilization. This implies usually that the injection facility is equipped with a emergency shutdown which comes into action when the properties of the injected gas leave an accepted range;

— Energy determination for legal purposes. This includes usually a measurement of the gas volume and the measurement of the calorific value thereof. See also EN ISO 6974-6 and EN ISO 6976-6.

It depends on at which conditions the NCS gas changes custody, either as raw gas, as treated gas (all disturbing components removed, but nothing added for upgrading), or as fully upgraded gas, how many measurements will be necessary.

7.2 Measurement

7.2.1 Gas Quality control and measurement methods

During the fermentation process some parameters have to be controlled such as methane, carbon dioxide, oxygen and hydrogen sulphide content.

In order to control the upgrading process and the gas quality before injection of the biogas in the gas grid, the following parameters should be controlled continuously:

— Methane

— Carbon dioxide

— Hydrogen sulphide

— Wobbe number

— Calorific value

— Dew point

For the determination of the calorific value or Wobbe number it is convenient to comply to ISO 6974 and 6976. The accuracy is not directed in these standards, but complies in corresponding accuracies for natural gas standards.

A daily calibration of the measurement system with certified test gases is recommended. Furthermore a yearly maintenance and control of the measurement system is recommended.

7.2.2 Control and Quality system Grid owner

For the requirements for biogas injection, the table refers to existing regulations are recommendations for continuous gas quality control.

Continuous is defined as at least, two times a day, but in most cases about every 15 minutes.

Table 8 — Biogas components that are recommended or obliged to be measured continuously

	DE[19][20]	FR[21]	NL[22]	CH[23]	Canada[24]	SE[25]
Responsibility						
Grid owner	X					
Producer		X	X	X	X	X
Obliged						
Wobbe-index	X	X	X			X (1)
Calorific value	X(1)	X(1)			X	
Density		X			X	
Methane			X	X		X (1)
H_2S	X	X	X		X	X(2)
CO_2		X	X	X	X	X(3)
O_2	X		X	X	X	X(3)
N_2			X			X(3)
H_2	X					
Temperature			X			
Pressure			X			
Water dewpoint	X	X	X	X	X	X(4)
THT		X				
Octane number						X(5)
Accuracy requirements	Calibrated measurement	Methods indicated 1: according to ISO 6976	Not yet specified			1: ISO 6974 and 6976 2: ISO 6326 3: ISO 6974 4: ISO 10101 5: ISO 15403

[19] D. Henning Pruss, Energie-Wasser Praxis 11, 2008, p22-26

[20] N. Grassmann, GasErdgas 4, 2008 p 222-230

[21] Document informative, Cahier des charges fonctionnel du controle des characteristiques du biogaz

[22] Draft: conditions for biogas injection in the local gas grid

[23] G. Muller, DBI, Intelligent Energy Europe EIE-06-221 presentation 16.11.2007

[24] Contractual arrangement for first biogas injection plant, no law

[25] Standard for use of biogas as a car fuel, SS 155438

The accuracy of these measurements is mostly agreed on in agreements between the producer and the grid owner. The methodology is mostly prescribed in standards. For e.g. the caloric value and the Wobbe number ISO 6974 (methodology) and 6976 (calculation method) are commonly applied. The accuracy is in most cases not arranged in the national standards for biogas. As a rule of thumb in first instance the accuracies agreed on in the standards for natural gas may be used.

Periodic quality control measurements are done for the remaining components that are in the list of quality requirements.

The procedure defined in EN-ISO 4259 shall be used in case of disagreement on how to interpret results based on the methods accuracies.

Bibliography

Relevant standards to be applied for the injection of biomethane and other gases from non-conventional reesources

[1] EN ISO 4259 Petroleum products - Determination of accuracy of testing methods (ISO 4259:1995)

[2] EN ISO 10101-1 Natural gas – Determination of water content using the Karl Fischer method Part 1: Introduction (ISO 10101-1:1993)

[3] EN ISO 10101-2 Natural gas - Determination of water content using the Karl Fischer method Part 2 (ISO 10101-2:1993)

[4] EN ISO 10101-3 Natural gas - Determination of water content using the Karl Fischer method Part 3 (ISO 10101-3:1993)

[5] ISO 6326-Natural gas - Determination of sulfur compounds - Part 1: General introduction

[6] ISO 6326-2 Gas analysis - Determination of sulfur compounds in natural gas - Part 2: Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulfur compounds

[7] EN ISO 6326-3 Natural gas – Determination of sulfur compounds – Part 3: Determination of hydrogen sulfide, mercaptanes and carbonyl sulfide by potentiometric methods. (ISO 6323-3:1989)

[8] ISO 6326-4 Natural gas - Determination of sulfur compounds - Part 4: Gas chromatographic method using a flame photometric detector for the determination of hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants

[9] EN ISO 6326-5 Natural gas – Determination of sulphur compounds – part 5: Combustion method according to Lingner (ISO 6326-5:1989)

[10] ISO 6327 Gas analysis - Determination of the water dew point of natural gas - Cooled surface condensation hygrometers

[11] ISO 6974 Natural gas - Determination of hydrogen, inert gases and hydrocarbons up to C8 – Gas chromatographic method

[12] ISO 6976 Natural gas – Calculation of heating value, density, relative density and Wobbe index based on the gas composition.

[13] ISO 10715 Natural gas – Guidelines for sampling

[14] ISO 15403 Natural gas - Designation of the quality of natural gas for use as a compressed fuel for vehicles

[15] ISO 13734 Natural gas - Organic sulfur compounds used as odorants. Requirements and test methods

Annex A
(informative)

Gas treatment

A.1 General considerations

The treatment of NCS gases depends on the way of their production. For gases from fermentative production basically the following cleaning and upgrading steps are required:

- Desulfurization;
- Drying;
- Separation of CO_2/methane enrichment;
- Gas filtration

The processes shall be, depending on the technical and economic conditions, combined with each other and be adapted to the respective composition of the raw gas and to the local conditions.

A.2 Basic treatment

A.2.1 Pressurized water washing

The method is based on the different solubility of methane and carbon dioxide. The raw gas is compressed because the solubility increases with pressure. In the detergent water polar substances as the acidic components (CO_2, H_2S) and the basic components (NH_3) dissolve better than non polar, hydrophobic components as e.g. hydrocarbons.

To separate the biomethane from CO_2 and H_2S, single stage compression to 7 bars is used and the gas is given into an absorption column at its bottom. From the top of the column water is sprayed so that it encounters the gas stream when dripping downwards. Commonly, the absorption column is equipped with some packing material to ensure a large surface for the gas to liquid contact. In the column the polar components of the raw gas dissolve in water, but also small amounts of CH_4 are dissolved. In plant with a closed water circuit, the components solved in the water are removed in a stripping unit at atmosphere pressure and the regenerated water is reused in the absorption column. In the stripping unit the solved components are desorbed form the washing liquid by partial pressure decrease, often in an air stream. To minimize methane slippage at this method a “flash box” is installed upstream to the stripping unit in which the detergent solution is decompressed to a mediocre pressure level. The released, methane rich flash gas is reguided into the raw gas stream upstream to the washing unit. However, to avoid climatically dangerous methane emissions, often a retreatment of the gas stream evolving from the stripping unit will be required.

A.2.2 Pressure swing adsorption (PSA)

The pressure swing adsorption method uses principally kinetic and steric, but also balance effects for gas separation. Usually, activated coal, molecular sieve (Zeoliths) and hydrocarbon molecular sieves are used as adsorbent. Low temperatures and high operating pressures enhance the adsorption of gases at solid active surfaces.

PSA plants consist out of several adsorption units which in sequence are either in the adsorption or in the desorption phase. In the adsorption phase, the raw gas is flowing through the unit at high pressures. This leads to the adsorption predominantly of CO_2 with small amounts of CH_4 almost until saturation of the sieve material. In the desorption phase, the pressure in the unit is decreased and the desorbing CO_2 is removed. Further pressure reduction leads to the desorption of the CH_4 which is subsequently reinjected into the raw gas. For complete regeneration of the adsorbent a vacuum pump is employed.

A.2.3 Amine method

This method is used for the separation of the acidic components as CO_2, H_2S, COS and others. It uses a aqueous amine solution with up to 40 % amine and is therefore in particular applicable for the treatment of wet gases. Amine washes are state of the art von the separation of CO_2 and H_2S from natural gases and from refinery gases. The CO_2 reacts with the detergent, is thus bound and can be removed from the gas by use of a column.

As detergent for CO_2 separation predominantly amines which can be mixed with water are considered. Therefore, mono-ethylamine (MEA), di-ethylamine (DEA), di-glycolamine (DGA), di-isopropanolamine (DIPA) and methyl-diethyl-ethanolamine (MDEA) are suitable.

Compression to higher pressure is not required if physical cleaning effects are not used. The detergent can be recovered in a desorption unit by heating which will release CO_2 and other sour gas components. During operation, the detergent is slowly spent due to chemical disintegration which is enhanced by elevated desorption temperatures. To encounter this, the recovery of the detergent solution is done incompletely at a lower temperature level to increase the economics of the method.

A.2.4 Selexol™ method

This method is based, similar to pressurized water washing, on the different solubility of methane and carbon dioxide. It employs an absorption stage and a regeneration stage. As solvent Selexol™, an organic solvent consisting out of polyethylenglycolethers, is used, which, like water, is non toxic and is non corrosive, but features a larger solubility of CO_2.

System pressure in the absorption column is usually around 7 bars, removing CO_2, H_2S and water from the gas in a single step. To decrease methane losses. Flash boxes are used downstream to the absorption column.

A.3 Membrane separation method

A.3.1 Dry method

CO_2 is separated by a membrane due to different pressure drops. To improve the separation performance, modules with back flows may be used.

A.3.2 Wet method

CO_2 is separated by a membrane due to different solubility and velocity of diffusion and is absorbed by a suitable liquid (soda lye for H_2S or amine solution for CO_2).

A.4 Low temperature method (Cryogenic method)

There are two method summarized as cryogenic gas treatment:

- Liquefaction of the gas (rectification) yielding liquid CO_2;
- Low temperature separation yielding solid CO_2.

These methods are mainly used for air separation, gas liquefaction, production of rare gases and for the treatment of natural gas rich in nitrogen.

A.4.1 Carbonate based washing methods

Some long known washing methods are so far almost neglected for the treatment of gases from non-conventional sources, as e.g. the hot potash washing method or the Sulfinol washing method.

The design of the potash washing method is similar to the amine wash. Potash washing units operate pressure less up to temperatures of 100°C. The method will deliver a cleaning performance comparable to amine washing methods, but the washing liquid is more stable and is less sensitive towards the environment. However, regeneration of the potash in the desorption unit will require more heating energy.

A.5 Rectisol™ method

The Rectisol™ method is a physical washing method using methanol as solvent for the CO_2. Absorption temperatures are at -30°C which needs to be considered when choosing the material for the plant, and it asks for proper insulation. On the other hand, it is a pressure less method. The advantage of the method is the uncomplicated removal of the CO_2 from the methanol by stripping with air, but problems may rise from the methanol content and thus emission problems in that carbon dioxide.

A.6 Gas conditioning

A.6.1 Calorific value adjustment

Depending on the requirements of legal metrology in the country, the supply of clients with gas in a certain area may require to keep the calorific value within given limits over a billing period.

This is, in most cases, done with LPG or, in order to lower the calorific value, nitrogen or air.

A.6.2 Odorization

As a primary safety measure, gases in distribution to the general public shall carry in all European countries a warning smell, i.e., these gases shall be odorized. Odorization practices, types of odorants used and minimum odorant concentration levels differ from country to country, depending on national habits and environmental conditions. They are not harmonized.

However, this implies that also NCS gases when injected into a pipeline conveying odorized natural gas shall be odorized with the same odorant, at the same odorization level as the gas in the pipeline. Most countries have issued technical regulations for odorization. As a guideline, the practice of odorization is described in ISO/TS 16922. EN ISO 13734 specifies odorants which are used either pure or as mixture of several odorants.