International Gas Research Conference 2011

ALTERNATIVE BIOMETHANE ANALYSIS

MSc. M.J.T. Geurds, MSc. E.L. Huijzer, MSc. E.E.Hardi

The Netherlands

Subject: **Transmission/distribution; Injection of "new" gases, Pipeline integrity**
Keywords: **biomethane, biogas, natural gas, analysis, spectroscopy, infrared**

ABSTRACT

The objective of the alternative gas analysis method is to provide a simple, thorough and robust gas analysis. Due to increased import of natural gases and injection of biomethane, monitoring of the gas quality and composition is increasingly important. Nowadays a thorough biomethane gas analysis is done by laboratory analysis. These are singular and costly measurements. Infrared spectroscopic analysis can possibly be used for gas component analysis locally throughout the gas grid. The analysis is done relative to laboratory reference analyses. This could provide a simple, thorough and robust gas analysis method.

CONTENTS

Background

In the Netherlands Groningen natural gas quality is the standard by which the infrastructure and end user appliances operate. Due to international trade and local injection of biomethane the gas origin and composition is changing. The Netherlands has ambitious goals for the transition towards renewable energy. 45% of the Dutch primary energy consumption (1466 PJ in 2009) is based on natural gas. On the short term 8-12% is to be substituted by renewable gases. In 2050 up to 50% is to be substituted. For safe and continuous operation however all gases have to meet the strict Groningen natural gas quality standard. Due to the changing gas origin and composition monitoring of the gas quality and composition in the gas grid is increasingly important. This requires a simple, thorough and robust gas analysis system for local gas analysis.

New gases

Natural gas

Groningen natural gas is low calorific gas. It consists of 81% methane and 14,3% nitrogen with small amounts of larger hydrocarbons and carbon dioxide. The general Groningen natural gas composition and properties are shown in table 1.

Table 1: Groningen natural gas composition and properties

Component		
Methane	81,2	mol%
Ethane	2,9	mol%
Propane	0,4	mol%
Butane	0,2	mol%
Pentane	0,1	mol%
Nitrogen	14,3	mol%
Carbon dioxide	0,9	mol%
Properties		
Higher heating value	35,2	MJ/m^3
Lower heating value	31,7	MJ/m^3
Relative density to air	0,65	-
Wobbe index	43,7	MJ/m^3

Due to international trade other natural gases are increasingly replacing Groningen natural gas. Each natural gas source has a specific gas composition. Often these gases have a higher heating value containing more higher hydrocarbons like propane and butane. All natural gases also contain several trace components. This is a unique set of components by which the origin of the gas can be identified. Table 2 shows several trace components identified in Groningen natural gas.

Table 2: Groningen natural gas trace components

2-methylpropane	n-hexane
n-butane	benzene
2.2-dimethylpropane	2-methylhexane
2-methylbutane	heptane
n-pentane	methylcyclohexane
cyclopentane	toluene
2.2-dimethylbutane	iso-oktanes
2.3-dimethylbutane	n-oktane
3-methylpentane	

Biomethane

Biomethane is upgraded biogas which complies with the strict Groningen natural gas quality standard. The biogas which is used to produce biomethane can originate from manure (co-)digesters, landfills and waste water digesters. It is low calorific gas containing mainly methane and carbon dioxide. The composition can vary by source and location. Biogas also contains volatile organic compounds. Table 3 gives a non limiting list of volatile organic components reported by Rasi et al.

Table 3: Volatile organic components [Rasi et al.]

1-chloro-1-fluoroethane	1, 2-Dichloroethene	1-propanethiol
Ethyl chloride	1,1,1-trichloroethane	Thiophene
Dichlorofluoromethane	Hexamethyldisiloxane	Methylthiophenes
Methylene chloride	Tetrachloroethylene	DMS (Dimethyl sulfide)
Carbon disulphide	Hexamethylcyclotrisiloxane	DMDS (Dimethyl Disulfide)
1-chloropropane	Octamethylcyclotetrasiloxane	Alkyl disulphides
Thiols	2, 4-bis(trimethylsiloxy)benzaldehyde	Alkyl trisulphides
1-Trimethylsilanol	Decamethyltetrasiloxane	

Gas measurements

Alliander is a network company which holds a larger part of the Dutch gas distribution grid. It is responsible for the management, control, safety and operation of this distribution grid. It plays a key role in facilitating the transition towards renewable gases. Because of the changing source and origin of gasses, gas component and quality measurements are increasingly important. This requires a simple, thorough and robust gas analysis system for local gas analysis.

Current situation

Natural gas quality is monitored and controlled within the high pressure (64 bar) transport grid. Samples are taken at specific locations for laboratory analysis. Up to now no gas quality measurements were necessary further downstream in the regional distribution network. Biomethane is however injected into the regional distribution grid. The biomethane quality is controlled by continuous monitoring of seven main components (methane, hydrogen sulphide, carbon dioxide, oxygen, nitrogen and water). In addition to these continuous measurements biomethane samples have to be laboratory analysed at least twice a year. Legislative compositional requirements for biomethane injection are given in table 4. The gas quality and composition is the sole responsibility of the gas producer. Alliander is however also interested in monitoring the gas quality and composition throughout the grid.

Table 4: Legislative compositional requirement for biomethane

Component	*Limiting values*	
Carbon monoxide (CO)	1	mol%
BTX (benzene, toluene, xylene)	500	ppm
Sulphur (total)	45	mg/m^3
Hydrogen sulphide (H_2S)	5	mg/m^3
Carbon dioxide (CO_2)	6	mol%
Oxygen (O_2)	0,5	mol%
Hydrogen (H_2)	12	mol%
Mercaptanes	10	mg/m^3
Ammonia	3	mg/m^3
Hydrogen chloride (HCl)	1	ppm
Hydrogen cyanide (HCN)	10	ppm
Chloride containing components	50	mg/m^3
Fluor containing components	25	mg/m^3
Aromatic hydrocarbons	1	mol%
Siloxanes	5	mg/m^3
Phosphine (PH_3)	0	ppm

Alternative gas analysis

Qualitative and quantitative gas component analysis is mainly done by gas chromatography. There is a large variety of commercially available gas chromatograph analysers, both for industrial and laboratory applications. Standard gas chromatograph analysers capable of monitoring the main natural gas components nitrogen, carbon dioxide, and methane up to hexane are readily available. The gas components mentioned in table4 are generally laboratory analysed making use of several laboratory gas chromatograph analysers. Mobile gas analysis units for field measurements are under development. These however contain several gas chromatograph analysers and can only monitor a subset of the required components. As a whole this makes a thorough gas component analysis quite complex and costly.

Near infrared spectroscopy

Near infrared spectroscopy is in theory capable of detecting all gas components except all homonuclear diatomic molecules like hydrogen, oxygen en nitrogen. Infrared absorption makes atomic bonds vibrate. Each gas component has a specific absorption profile by which it can be identified. The gas component concentration can be quantified by the amount of absorption. Industrial infrared spectrometers are commercially available. They are for example applied for flue gas component analysis. An infrared spectrometer can provide a robust and easy to use alternative for in field gas component analysis. Infrared spectroscopy has however not yet been applied for a full biomethane or natural gas component analysis. It is not clear which components a spectrometer can detect and quantify. There are two main concerns limiting the detectability of components. The first concern is the methane content. Because methane is present in large concentrations (more than 80 vol%) it will absorb a large part of the infrared spectrum limiting the detectability of other components. The second concern is the large amount of components present (component matrix). Individual gas component absorption profiles may overlap limiting their detectability.

Testing

Laboratory tests are scheduled to determine if biomethane and natural gas components are detectible by infrared spectroscopic analysis. The laboratory tests will take place in two parts. The first part consists of a limited amount of reference measurements to determine the detectability of components. The second part consists of at least 20 reference measurements to determine how accurately the gas component concentrations can be quantified. All measurements will be carried out with a nitrogen flushed spectrometer at 1 cm^{-1} resolution with 64 scans.

Initial results

Nine reference tests have been carried out on nine different gas samples to determine the detectability of gas components. These samples include both calibration gases and laboratory analysed gas samples containing a wide range of components like siloxanes, fluor containing compounds and aromatic hydrocarbons. Both natural gas, biogas and biomethane samples have been analysed. Test results will be available during the IGRC 2011.

Future application

The current field and laboratory measurement regime is quite intensive and expensive. Currently only a small amount of biomethane is injected into the grid. Considering the required 8 - 50% natural gas substitution in the near future, the current measurement regime cannot be maintained. Safe and continuous gas supply is however the primary concern and responsibility of the network company.
In this light infrared spectroscopic analysis can be of interest. It is not expected that an infrared spectrometer can replace laboratory analysis. If tests are successful mobile infrared spectroscopic analysers can monitor gas composition throughout the network. Monitoring is done relative to all available laboratory reference analyses. When an individual infrared spectroscopic analyser cannot relate a gas sample to one of the reference measurements this sample will be laboratory analysed. This sample then serves as a new reference sample. The more reference analyses the smarter the system. This makes it a simple, thorough and robust system.

References

1. S. Rasi et al., Trace compounds of biogas from different biogas production plants, Energy 32, 1375-1380, 2006.
2. CBS Statline: Energy balance, http://statline.cbs.nl/statweb/?LA=en, 2011
3. Hoezoandergas: http://www.hoezoandergas.nl, 2011
4. Platform Nieuw gas: Volume 2, Vol gas vooruit, platform Nieuw gas , 2007