

Development and Demonstration of IR Gas Sensor



EUDP 14-II



Technical University of Denmark





Table of Contents

1.	1. Summary		3		
1.1	. Pr	oject details	3		
1.2	Sh	ort description of project objective and results	3		
1	2.1	English version	3		
1	2.2	Danish version	3		
1.3	Ex	ecutive summary	4		
2.	Proj	ect objectives	5		
2.1	2.1 Objectives		5		
2.2	2 M	ain timelines of the project	6		
3.	Proj	ect results and dissemination of results	7		
3.1	. Re	quirement specification	7		
3	8.1.1	Gas grid requirements	7		
3	8.1.2	Billing related requirements	8		
3	8.1.3	Requirements for regulation and control of burner efficiency	8		
3	8.1.4	ATEX requirements	9		
3.2	2 Pr	nciples and instrumentation	9		
3	8.2.1	Introduction	9		
3.3	5 Te	st of the first prototype	9		
3	8.3.1	Description of the apparatus	9		
3	3.3.2	Tests and results	10		
3.4	Te	st of the second prototype	12		
3	8.4.1	Description of the changes to the first prototype	12		
3	8.4.2	Outdoor test at Risø – Tests and results	12		
3.5	5 St	op/go decision	15		
3.6	i In	stallation and field test MR station Vejen	15		
3	8.6.1	Test method	15		
3	8.6.2	Results of measurements	15		
3.7	' Di	scussion	19		
3	8.7.1	IR gas sensor specifications	19		
3	8.7.2	Service requirements and drift	20		
3	8.7.3	Specification of apparatus components	21		
3	8.7.4	Other applications	21		
3	8.7.5	Potential for further development	21		
3.8	B Di	ssemination of results	21		
4.	4. Commercial outlook – Utilization of project results 22				
5.	Proj	ect conclusion and perspective	23		
6.	6. References				

1. Summary

1.1 Project details

Project title	Development and Demonstration of IR Gas Sensor
Project identification (program abbrev. and file)	64014-0544
Name of the programme which has funded the project	EUDP
Project managing compa- ny/institution (name and ad- dress)	Danish Gas Technology Centre (DGC) Dr. Neergaards Vej 5B 2970 Hørsholm
Project partners	DGC, DTU and Elster
CVR (central business register)	
Date for submission	30-09-2019

1.2 Short description of project objective and results

1.2.1 English version

The amount of biomethane is increasing every year in the Danish natural gas grid and has led to high fluctuations in the gas quality for many end-users.

The objective of the project has been to develop and demonstrate an infra-red (IR) gas quality sensor to ease the integration of biomethane in the natural gas grid. The aim was to develop a sensor able to measure Wobbe Index and heating value of gas with high precision and fast response time.

DTU, DGC and Elster have developed an IR gas sensor that is able to measure C_1 - C_5 and CO_2 . The sensor can execute a full measurement in 22 seconds. The sensor has been tested in DGC's laboratory and field tested in Vejen, Denmark. The field test showed that the IR sensor is stable and has a measurement accuracy of $\pm 1.0\%$ for Wobbe Index.

1.2.2 Danish version

Den stigende mængde bionaturgas på gasnettet har de seneste år ledt til store udsving i gaskvaliteten hos mange slutbrugere.

Projektets formål er at udvikle og demonstrere en infrarød (IR) gaskvalitetsmåler, som kan lette integrationen af bionaturgas på gasnettet. IR sensoren skal kunne måle Wobbe Index og brændværdi med høj præcision og hurtig respons, så den kan benyttes til real-time-styring og -regulering af gasforbrugende apparater.

DTU, DGC og Elster har i samarbejde udviklet en IR gassensor, der kan måle C₁-C₅ og CO₂. Sensoren kan foretage en måling på ca. 22 sekunder. Sensoren er både testet i DGC's laboratorium og ved en field-test i Vejen. Field-testen har vist, at IR sensoren har stabil drift og har en målepræcision på \pm 1.0% for Wobbe Index.

1.3 Executive summary

Development of an IR gas sensor for gas quality measurements aimed at the Danish national gas grid was the overall objective of this EUDP project.

The increasing amounts of biomethane in the Danish national gas grid and increasing amounts of imported gases have led to more fluctuations in the gas quality than previously experienced. The purpose of the developed gas sensor is to mitigate the problems associated with rapid changes in gas quality, such as "knocking" problems with gas engines, problems with billing and performance problems related to gas quality variations. Cheap, fast and accurate measurements of gas quality can be utilised to ease the above stated problems.

The development of the IR gas sensor was performed in three steps. First a prototype was developed and tested. The initial learnings from the first prototype was used to build a second model of the IR gas sensor. The second model was subject to a large testing programme in DTU's laboratories and in DGC's laboratories.

After a successful test programme, it was decided to move forward with the project and adjust the second model of the IR gas sensor to a field-test-ready unit. The adjustments were mainly ATEX area qualifications and data handling. The measurement principles were not changed.

A successful field test of the IR gas sensor was performed at the MR station in Vejen from the 26th of February to the 23rd of August 2019. The field test went very well with high accurate measurements and no fallouts of the equipment.

The IR gas sensor measures C_1 - C_5 and CO_2 , and from these data the Wobbe Index and heating value are calculated with accuracies of 1.0% and 0.7%, respectively. The measurement time for all components is 22 seconds. The gas sensor is free from calibration as regular zero-measurements are automatically performed. If drift is observed, it can be reported back to the operator who can take action. No drift occurred in the field test.

There is further development potential in making ultrafast gas quality measurements by only looking at one component such as C_1 . This makes it possible to detect gas quality changes within seconds.

The involved project participants are preparing further development of a commercial product. The commercial rights for the developed technology are shared equally between DTU and DGC as initially agreed upon.

2. Project objectives

2.1 Objectives

The production and distribution of new green gases in the Danish natural gas grid leads to fluctuations in the gas quality at many end-users, see Figure 2-1. This puts strain on efficiencies of gas consuming units in the industry, the safety and the correct fiscal metering (for billing purposes) of the gas consumers. Today this challenge is mainly addressed by using gas chromatographs (GC).

The objective of this project is to develop an IR based method for detection of the real time gas composition and thereby gas quality parameters such as the Wobbe Index and the heating value. The sensor must be relatively cheap and with fast response time compared to gas chromatographs. The aim is that the final sensor has an accuracy that allows for fiscal metering at the end-customers. Furthermore, the sensor should be able to allow the customers to adapt to rapid changes of the gas quality by real-time regulation and control of burner settings.

The starting point for the project is a previously developed IR system at DTU. This system has been modified to allow analysis of multiple gas components from methane to butane and CO_2 .

The development in this project is focused on two customer segments: Those who operate a gas grid and need accurate information on the gas quality, and those who operate large gas consuming equipment and who will be able to gain in energy efficiencies by using the developed sensor.



Figure 2-1: Fluctuating Wobbe Index measured at three MR stations in Denmark. Nybro is the entry point for North Sea gas of stable quality, and Frøslev and Terkelsbøl are located near biogas plants.

2.2 Main timelines of the project

The original start and end dates for the project were 1-1-2015 and 31-12-2016, respectively. The project has been significantly delayed due to reasons which have been communicated to the EUDP committee in a timely manner.

3. Project results and dissemination of results

This section of the report presents the main results of the project.

3.1 Requirement specification

As mentioned earlier, gas quality variations can lead to different challenges. Meeting and dealing with the challenges define different requirements for accuracy for the developed instrument. Different requirements are discussed in this section.

3.1.1 Gas grid requirements

The formal requirements to introduction of green gasses to the gas grid are defined by the concentration of various trace components as well as e.g. Wobbe Index. The main requirements are shown in Table 3-1.

There are no specific requirements for heating value or methane content for gas in the gas grid. However, these are indirectly limited by the stated Wobbe index requirement.

- Г				
	Wobbe index	MJ/Nm ³	50.76	- 55.8
	Relative density	-	0.555	- 0.7
	O2	% (mole)	max	0.5
	CO ₂	% (mole)	max	3
	H2S + COS	mg/Nm3	max	5
	Total - S	mg/Nm3	max	30
	Siloxanes	mg/Nm3	max	1
ſ	NH3	mg/Nm3	max	3
	Water dew point	°C @ p up to 70 bar	max	-8
ſ	Hydrocarbon dewpoint	°C @ p up to 70 bar	max	-2

Table 3-1: Gas quality requirements for the gas grid according to the Danish regulation(Bekendtgørelse nr. 230 af 21/03/2018) (1)

The heating value is reflected in the Wobbe Index, which is derived from the heating value and relative density of the gas. Figure 3-1 shows an example of how the Wobbe Index limits for the gas grid are met. This includes the measurement error for the measured parameters.



Figure 3-1: Example of how the uncertainty is used when evaluating whether or not the Wobbe Index requirements are met (2).

3.1.2 Billing related requirements

The allocation of heating value in the distribution gas grid has a maximum allowable yearly error of 2%. Due to this requirement, the measurement uncertainty for heating value has been set to $\pm 0.5\%$ to be able to meet the maximum allowable yearly error (3). If the developed IR gas sensor can determine the heating value of the gas with an uncertainty lower than $\pm 0.5\%$, it can be used for fiscal metering.

There are no specific limits for how precisely the concentration of the hydrocarbon molecules is measured, as long as the heating value requirement is met. According to the standard EN 16726 (4) there is a requirement stating that the methane number of the gas should be minimum 65 in order to avoid knocking when the gas is used as engine fuel.

3.1.3 Requirements for regulation and control of burner efficiency

There are no specific requirements for the detection rate of gas quality variations. Gas flows continuously through the IR sensor and one loop of measurements on all the components (C_1 - C_5 and CO_2) currently takes approx. 20 seconds. This would allow industrial consumers to react relatively swiftly to changes in gas quality if an online monitor system is set up and changes the burner configuration to match the gas quality which is received at the current moment. Further development of the gas sensor can reduce the detection rate to less than a second, if another sensor is added which only measures changes of the C1 content.

Figure 3-2 shows an example of Wobbe Index changes to illustrate the rapid shifts that are observed at different places in the gas grid.



Figure 3-2: Example of rapid Wobbe Index changes at Frøslev.

The impact of gas quality changes is different dependent on the usage in the industry.

For power and heat production, gas turbines and gas engines are affected by changing gas quality. In Denmark, the major impact is on gas engines as the decentralized power plants have installed many of these, approx. 700. Low methane number can lead to knocking problems etc. In addition, engine emissions and power output and efficiency are affected by changes in the gas quality. The number of gas turbines is relatively low in Denmark, and the major impact of gas quality change on gas turbine operation is related to calorific value (CV), hydrogen content and Wobbe Index (5).

Among thermal processing applications, glass and ceramics production is acknowledged by many to be especially vulnerable to fuel gas quality fluctuations. Discoloration and reduced glaze quality constitute a problem with fluctuating gas quality (6).

3.1.4 ATEX requirements

The gas sensor needs to adhere to general ATEX requirements when installed in critical environments.

3.2 Principles and instrumentation

3.2.1 Introduction Section removed due to confidentiality

3.3 Test of the first prototype

3.3.1 Description of the apparatus Section removed due to confidentiality



Figure 3-3: Electronics developed by DTU Fotonik for temperature control, scanning and reference of spectrometer, digitalisation of detector signal, analog output, etc. The size of IR gas analyser electronic module is approx. 100x100 mm.

Standard electronic modules were used in the first laboratory version of the gas analyzer (Figure 3-6), which was a very costly and clumsy solution and designed for general use and experimental-like instrumentation. The electronics is an important part of the gas analyzer, and it must have all features needed to control all functions, e.g. low noise data sampling of the detector signal, temperature and pressure measurement, control spectrometer, valves and temperature regulation, etc. The developed electronic module is shown in Figure 3-9. It is connected to a small computer for data processing and data handling.

Section removed due to confidentiality

3.3.2 Tests and results

Test results at DTU and DGC with the first prototype were successful, i.e. it was proven that the concept works as foreseen. Reliable and stable gas measurements were performed.

It was decided by all partners to proceed to the next step, i.e. a major redesign and update of the first prototype.

The IR analyzer electronics was tested in June 2018 with prototype mechanics and optics at DTU to evaluate performance. The signal is best at short wavelengths (angle 325-345°) and very low noise in the signal is seen comparable to SNR of FTIR spectrometers, Figure 3-10. The signal drop at long wavelengths, i.e. for the CO_2 band at 15 µm, is due to a low efficiency of the grating (angle 350-360°).



Figure 3-4: Laboratory test of the signal-to-noise ratio (SNR) with short (full line) and long measurement time (broken line). Several repeated measurements are shown with different colors to visualize noise in signal (1=low noise). Blue curve is the detector signal (Y-axis right). The SNR can be improved by longer measurement time (square root of the measurement time).

The response time of the IR analyzer is affected by the design and volume of the gas cell.

The gas cell is designed for a plug flow, i.e. the inlet gas enters the gas cell in a diffuse manner in one side of the cell and moves to the opposite side, i.e. turbulent mixing in the gas cell is avoided. The response time was measured to 3 s with a high gas flow through the gas cell, Figure 3-11. The response time can be lowered further by a reduction of the gas cell volume, e.g. the volume can be reduced by a factor 4 using $\frac{1}{2}$ " windows instead of the present 1" windows. A response time of less than one second has been obtained in an earlier project looking for gas leaks in gas bottles.



Figure 3-5: The response time of gas cell with ca. 5 m long 6/4 mm tubing is approx. 3 s with high flow rate. Laboratory test result June 2018. The measurement time per data point is 1.28 second. It is seen that the response time of the IR gas cell system can be very fast as expected due to plug gas flow design of gas flow through the system.

3.4 Test of the second prototype

3.4.1 Description of the changes to the first prototype

The design of the IR gas analyzer was improved in many ways and changes were needed for going from laboratory to field measurements. The IR analyzer was built into an enclosure with insulation. Plastic tubing was replaced by stainless steel tubing and a CH₄ alarm was installed to disconnect power if a gas leak occurs (ATEX, method can be used for test and demonstration). Electronics was installed in a separate enclosure together with the safety system held by a metal frame for easy installation. Software was updated to handle data storage, i.e. data stored on SD card locally and in a database (Amazon Web Service was selected). Mobile Ethernet connection was set up, and it worked trouble-free during test at DTU and in field tests.

3.4.2 Outdoor test at Risø – Tests and results

The gas analyzer setup was tested at Risø (see Figure 3-6) before installation on MR station Vejen Vest.



Figure 3-6: Outdoor test winter 2018-2019 at Risø.

The gas analyzer is heated and temperature controlled to a certain temperature over ambient. In all final tests, the set point was fixed to 40.0°C. Best performance was obtained at fixed conditions. A common problem in FTIR gas analyzers is base-line drift, which is eliminated using fixed, stable temperature conditions.

The instrument can work at different temperatures, e.g. a summer and winter mode, to save energy. The instrument can also be operated without temperature control, but a more complex software must be used for correction of the temperature effects.



Figure 3-7: Ambient temperature variation (red) and temperature of temperature stabilized parts of gas analyzer (black, blue and green curves). The temperature variation of the instrument is within a few milli-Kelvin.

The temperature control system is better than ± 0.003 °C, see Figure 3-7, i.e. excellent temperature stability and no drift of the instrument due to the 3-zone temperature control.



Figure 3-8: Gas analyzer setup used during test at the MR station Vejen in the period 2019. The instrument is insulated and kept at 40.00°C by temperature regulation in an insulated wall enclosure. Electronics and the safety system are placed below.

3.5 Stop/go decision

A discussion of the progress, validation of the technical concepts and the obtained laboratory results during the project were carried out during a project meeting with all partners, e.g. results show that all needed gas components $(C_1-C_5 + CO_2)$ can be measured in order to calculate the Wobbe Index, the price level of components and instrument was within the expected range, and a market was still seen for the instrument. It was, therefore, decided to look for a field-test site with a GC analyzer for comparison of results, large variations in the gas composition and typical temperature variations found during a winter-summer period.

3.6 Installation and field test MR station Vejen

The gas analyzer setup was installed on MR station Vejen Vest, as large variations in gas composition are seen at this location in the cold period. Finn Iversen from Dansk Gas Distribution A/S was so kind as to find this location for test of the gas analyzer and to send data from the GC-TCD gas analyzer for comparison during the 6-month test period.

The installation was made together with Erik Fyhn from Dansk Gas Distribution A/S on 26th February 2019 at MR station Vejen Vest, Boulevarden 6, 6600 Vejen. The gas analyzer was turned off 23rd August 2019 after 6 months' operation without any technical problems.

Section removed due to confidentiality

3.6.1 Test method

Section removed due to confidentiality

3.6.2 Results of measurements

The measured C_2H_6 concentration by the IR gas analyzer is in excellent agreement with the GC in the range 0-6% over the 21 days, Figure 3-9.





Figure 3-10: Same data as in the Figure 3-9 in a situation with high C_2H_6 concentration. The IR gas analyzer measures slightly less, approx. 0.03%, than the GC.



Figure 3-11: Same data as in the Figure 3-9 in a situation with low C₂H₆ concentration. The IR gas analyzer (blue curve) has a lower detection level than the GC (red curve).

Measurement results are shown for CH_4 , C_3H_8 and CO_2 in Figure 3-12 to Figure 3-14.



Figure 3-12: Measured C_3H_8 (blue curve with crosses for each measurement) by IR gas analyzer compared with GC (red). Deviations up to 0.15% are observed. The lower detection limit of the IR analyzer is approx. 0.1%



Figure 3-13: Measured CO₂ (blue curve with crosses) by IR gas analyzer compared with GC (red) in period with large CH₄ variation due to switch between NG and bio gas.

The CO₂ concentration data measured by the IR analyzer is noisier than for the GC, Figure 3-13, and an offset in measured concentration is seen. The offset of the IR analyzer values can be reduced by optimization of the calibration method. The noise of the IR analyzer can be reduced by longer measurement time, e.g. going from present 2.3 s to 20.7 s for CO₂ will reduce noise by a factor 3. Another way to improve the CO₂ measurement is by hardware changes (higher signal at CO₂ position).



Figure 3-14: Measured CH₄ (blue curve with crosses) by IR gas analyzer compared with GC (red) over a period of 21 days with large CH₄ variation due to switch between NG and bio gas.

Deviations in CH₄ concentration between IR analyzer and GC are typically within 0.5%, Figure 3-15. Results from the IR analyzer are noisier than the GC. SNR can be improved by longer measurement time. Some variation in the offset between GS and GC is seen over 21 days. Probably an effect that can be reduced by improvements.

The Wobbe Index can be calculated from the measured gases. The IR analyzer does not measure O₂ and N₂; therefore, unknown component is calculated as N₂ for the IR analyzer. The calculated Wobbe Index for the IR analyzer and the GC is shown in Figure 3-16 over 21 days. Results for the IR analyzer is as expected noisier than the GC with 22.3 s measurement time of gas components. The noise can be reduced by a rule of thumb with the square root of the measurement time, e.g. half noise of the results from IR analyzer with less than 89 s measurement time. Deviations in the Wobbe Index of the two systems vary typically in the range ± 0.2 or $\pm 0.4\%$, see Figure 3-16.



Figure 3-16: Calculated time variations of the Wobbe Index from 08-04-2019 until 29-04-2019. Grating spectrometer (GS, blue line with crosses) vs GC-TCD (red line). Zones with high (NG)/low (biomethane) Wobbe Index numbers are marked.

3.7 Discussion

3.7.1 IR gas sensor specifications

Specification of the IR gas sensor is given below based on the setup and operation parameters used in the field tests. It should be noted that the instrument can operate in many different ways controlled by the software, e.g. the measurement time is 3.2 s for each gas component despite the fact that more accurate measurements can be obtained using longer measurement time for gases with low signal.

Table 3-2: Specifications of the IR gas analyzer

Table removed due to confidentiality

Gas	Range ¤	Reference/Detection	Accuracy#
		limit *	
CH ₄	80 - 100%	90% / 0.1%	0.3%
C ₂ C ₆	0 - 10%	5.8%/0.004%	1.8%
C ₃ H ₈	0 – 5%	2.4% /0.006%	1.2%
iC4H10	0 – 2%	0.4% /0.017%	2.4%
nC_4H_{10}	0 – 2%	0.6% /0.003%	1.2%
C ₅ H ₁₂	0 - 1%	0.15% /0.003%	2.4%
CO ₂	0 – 5%	0.6% /0.04%	25%

Table 3-3: Gas measurement range and estimated accuracy

*: 3.2 s measurement time per component, gas composition measurement takes 22 s, #: compare to GC-TCD, x: can be modified or extended

Based on the data in Table 3-3, the accuracy of heating value determination is 0.7% and the accuracy Wobbe Index determination is 1.0%.

The accuracy of CO_2 concentration is limited by the SNR, i.e. the accuracy of the present setup can be improved using a longer measurement time for the CO_2 channel, e.g. accuracy from 25% to 8% going from 22.3 s to 48 s measurement time. A modification of the grating or selection of a different CO_2 absorption band can also raise the accuracy of the CO_2 significantly. However, that will only improve the accuracy of the Wobbe Index modestly as CO_2 is only present in low concentrations in the gas grid, see Table 3-1. The heating value determination is not affected by improved CO_2 accuracy.

As the instrument can determine heating value with an accuracy of 0.7%, it is not suitable for billing purposes in the current state. However, it is likely that the accuracy can be improved with modifications of the current setup.

3.7.2 Service requirements and drift

The gas analyzer does not need any periodic calibrations, except for validation calibrations if demanded. The gas analyzer is calibration free as seen for some on-line laser systems for emission monitoring. However, the analyzer needs a periodic reference measurement with a gas without gas absorption features, e.g. air, nitrogen, argon, etc., to remove long-term drift. Nitrogen was used instead of air due to ATEX requirements in the conducted tests. A 10-50-liter nitrogen bottle can last 1-5 years for reference measurements.

The gas analyzer can detect if no reference gas is passed through the analyzer. The scanner part of the instrument has a built-in optical sensor used at start-up to find the reference position. This sensor signal is furthermore used in each scan to verify the accuracy of each scan. An error message can be sent if any parameters deviate from the valid range.

Drift of the pressure sensor will affect the gas concentration measurement, i.e. a drift of +0.1% of the pressure sensor will be seen as a similar drift of +0.1% in measured gas concentrations. The atmospheric pressure is measured by weather stations and can be compared with the pressure measurement in the gas analyzer in an installation like the one used in Vejen.

Drift in temperature also leads to errors, but the temperature drift is likely to be less than 0.1° C per year, i.e. equal to a drift of 0.03% per year (0.1K/313.15K).

No or very minor drift was observed during the field test in Vejen, see Figure 3-17.



Figure 3-17: Plot of spectrometer measurements with nitrogen in gas cell performed at Vejen MR station 29th March (red dashed curve) and 4th April 2019 (black line). No or very minor drift in signal is observed over 2 months as the red and black lines are superimposed.

3.7.3 Specification of apparatus components Section removed due to confidentiality

3.7.4 Other applications

Section removed due to confidentiality

3.7.5 Potential for further development Section removed due to confidentiality

3.8 Dissemination of results

Due to delays of the original project timeline, limited results have been disseminated in the project phase as the results have not been ready for dissemination. The progress of the project was presented in 2019 at a forum for gas measurements, where relevant persons for the gas companies were briefed about the project and the likely outcome.

The results were also shared with relevant personnel working with the MR station in Vejen, who found the results very interesting.

Furthermore, it is planned to present the project at the conference Gastekniske Dage 2020 (Danish Gas Association) if accepted by the planning committee for Gastekniske Dage.

4. Commercial outlook – Utilization of project results Section removed due to confidentiality

5. Project conclusion and perspective Section removed due to confidentiality

6. References

1. **Sikkerhedsstyrelsen.** Retsinformation.dk. [Online] 21. 3 2018. [Citeret: 27. 9 2019.] https://www.retsinformation.dk/Forms/R0710.aspx?id=200169.

2. **Dansk Gasteknisk Center a/s.** *Kontrolmanual til måling af biogas og bionaturgas.* Hørsholm: DGC, 2015. 3. udgave.

3. **Dansk Gasteknisk Center a/s.** *Naturgasselskabernes kontrolmanual for allokering af brændværdi .* Hørsholm : DGC, 2012. ISBN: 978-87-7795-330-9.

4. **Dansk Standard.** *Gasinfrastruktur – Kvalitet af gas – Group H.* København : Dansk Standard, 2015. DS/EN 16726:2015.

3. **Schweitzer, Jean, et al.** *Danish natural gas utilisation today (WP2 Future Gas project).* Hørsholm: Futuregas, 2017.

4. Leicher, Jörg og Giese, Anne. Changing natural gas qualities: impact on industrial gasfired applications: Heat Processing, 2013.