Photoacoustic Monitoring of CO_2 in Biogas Matrix Using a Quantum Cascade Laser

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Abstract — *The renewable energy source biogas gains in market importance. New developments promote the supply of biogas by the local gas distributor. Regulations about the composition of the supplied biogas ask for an appropriate quality control of the gas content.*
This work demonstrates the outstanding capability of photoacoustic detection (PA) based on quantum cascade laser (QCL) for the in-line measurement of CO_2 in the difficult matrix biogas. Compared to standard techniques QCL-PA shows several distinct advantages as higher selectivity and faster response.

I. Biogas – a renewable energy source

In the past decades, global energy consumption has exhibited a remarkable increase. Unlike natural gas, biogas (i.e. fermentation gas) is CO_2-neutral [1]. Consequently, it helps to reduce the amount of greenhouse gases in the atmosphere when used as a substitute for fossil fuels [2]. Biogas consists of 50 – 70% methane, 25 – 45% carbon dioxide, 0 – 5% nitrogen, as well as small quantities of hydrogen sulphide and ammonia [3.] After the purification of the biogas for the achievement of natural gas quality, biogas can be inducted into the local gas supply system. However, a gas analysis has to be conducted beforehand. A market survey, also with regard to economic aspects, showed that in practice such an analysing system is not available yet.

II. Photoacoustic – An innovative detection scheme

The high sensitive photoacoustic (PA) scheme is particularly attractive in combination with recently available compact QCL sources. The signal, which is recorded by a microphone, is directly proportional to the absorbed incident laser power [4]. Furthermore, the signal is recorded on a zero background. Photoacoustic sensors offer the advantage of a simple and robust setup, low maintenance and room temperature operation and compact size.

III. Experimental – The Proof of concept

In order to comply with the requirements of biogas analysis, a mobile prototype based on photo-acoustic laser spectroscopy has been developed [5]. As a light source, a Peltier-cooled quantum cascade laser, emitting at 4.29 µm, was chosen. The photoacoustic cell was adapted to the geometry of the laser beam and consists of a Helmholtz resonator. Carbon dioxide was used as a test-analyte to demonstrate the applicability as an online technique. Calibration was performed by measuring carbon dioxide concentrations ranging from 1 to 100 %vol., directly within the gas flow. The quality-factor (Q) was found to be 9 with a resonance frequency range from 1.6 to 2.8 kHz due to the variable gas composition. A detection limit of 250 ppmv CO_2 and a response time of 6 minutes were determined. Furthermore, the photoacoustic sensor was qualified for flow rates of up to 400 ml min^{-1}. Field measurements at a pilot plant in St. Martin, Austria confirmed the road capability of the sensor in noisy surroundings.

The linear relationship between the PA signal and the reference concentration is shown in Figure 1. The evaluated concentration range is of high relevance for the control system of the purification plant (set point is 2.0 %vol). Reference analytic was realized with the commercial carbon dioxide analyzer NGA 2000 (Emerson AG, Switzerland).

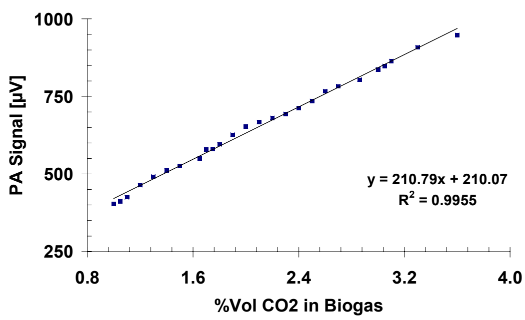

Figure 1: Measurements of CO_2 in Biogas

IV. CONCLUSIONS

This work shows the potential of a portable sensor system based on quantum cascade lasers for the detection of industrial relevant analytes in complex matrices such as biogas. It has been demonstrated that a continuous monitoring of the CO_2 concentration in biogas is possible directly in the gas flow. Carbon dioxide concentrations ranging from 1 to 100 %Vol are detectable with high temporal resolution. The sensor is fast enough to react on small changes in concentration and provide detailed information's to optimize the purification process.

Photoacoustic detection shows several distinct advantages such as higher selectivity, faster response, on-line analysis, and portability compared to standard technologies. The construction of the prototype was designed to enable a quick and easy exchange of the laser source. Thus, as a future prospective, other analytes could be detected in the biogas as well. This option is of particular relevance for the trace components ammonia and hydrogen sulphide.

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