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Detection of High Level Carbon Dioxide Emissions using a Compact Optical Fibre Based Mid-Infrared Sensor System for Applications in Environmental Pollution Monitoring.

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Abstract - A novel and highly compact optical fibre based sensor system for measurement of high concentrations CO₂ gas emissions in modern automotive exhaust is presented. The sensor system works based on the principle of open-path direct absorption spectroscopy in the mid-infrared wavelength range. The sensor system, which comprises low cost components and is compact in design, is well suited for applications in monitoring CO₂ emissions from the exhaust of automotive vehicles. The sensor system utilises calcium fluoride (CaF₂) lenses and a narrow band pass (NBP) filter for detection of CO₂ gas. The response of the sensor to high concentrations of CO₂ gas is presented and the result is compared with that of a commercial flue gas analyser. The sensor shows response times of 5.2s and demonstrates minimal susceptibility to cross interferences of other gases present in the exhaust system.

1. Introduction

There are many factors that can affect the rate of environmental pollution. Among others, the major concerns that contribute to the environmental pollution locally are the density of vehicle fleet and their efficiency in combustion, as well as the type of local industrial activities [1]. In most developed countries, like in the European Union, the transport sector is a major source of air pollution especially in the urban area. Emissions from vehicle exhaust, particularly from land transports, contain a substantial portion of harmful gas stream which consists of carbon monoxide (CO), oxides of nitrogen (NOx), volatile organic compounds and particulate matter. Air pollution can cause acute respiratory problems to children and also chronic bronchitis related problems to adults and also been linked with premature mortality and reduced life expectancy [2]. It has also been shown that long-term exposures to severe air pollution can cause, not only adverse health effects to people, but also damage to vegetation and buildings in a heavily polluted area [3].

The rapid increase in the number of motor vehicles has resulted in CO₂ from the internal combustion engines becoming a prime contributor to the current increase of global temperature, also known as the Greenhouse Effect. Greenhouse gases remain in the atmosphere and contribute to global warming long after they were emitted. Research has shown that the United States and European Union alone were responsible for approximately 60% of energy-related CO₂ emissions from year 1850 to 2000, as shown in figure 1 [4]. Because of this, various measures have been taken to control the amount of carbon dioxide emitted to the atmosphere. A major milestone in world pollution control has been achieved by the signing of the Kyoto Protocol in 1997 [5]. The agreement also targeted to cut
down the collective emissions of six key greenhouse gases namely carbon dioxide (CO$_2$), methane (CH$_4$), nitrous oxide (N$_2$O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and also sulphur hexafluoride (SF$_6$). Moreover, the introduction of a succession of increasingly stringent automotive emission control laws by the European Commission is one of the vital actions in its attempt to reduce the levels of pollutants entering the atmosphere from road vehicles, particularly from exhaust emission of motor vehicles [6].

![Cumulative CO$_2$ Emissions (1850–2000)](image)

Figure 1: The cumulative carbon dioxide emissions from various industrialized countries [4].

A number of commercially available gas sensors, which include the NOx sensor for monitoring of nitrogen oxides gas and the lambda sensor for monitoring oxygen, are widely in use by the automotive industry [7]. However, these sensors, which operate based on electrochemical technology, can exhibit some inaccuracies relating to contamination and deposit build up during long term operation. This can shorten the lifetime of the sensor itself and produce a false signal that may lead the car to produce more pollution gases. As a result, the lifetime of lambda sensors in a vehicle is found to be generally far less than the lifetime of the motor vehicles where the sensor operates [8]. At present, based on our findings, there is no exhaust gas sensor systems developed that has the capability of measuring online CO$_2$ gas concentration from the exhaust of an engine of a vehicle. This is a strong indication that an optical fibre based gas sensor for automotive emission monitoring must be developed that is capable of quantifying the levels of CO$_2$ and other gases entering the atmosphere from an engine and that is immune to corrosive elements present in the exhaust system.

2. Absorption theory

Generally, different gas molecules absorb radiation at different wavelength, as each gas species has their own individual fundamental absorption line spectrum [9]. For example, three gases namely NO$_2$, SO$_2$ and NO all have the characteristic absorption lines in the ultraviolet region. On the other hand, carbon dioxide gas (CO$_2$), which is the main focus in this study, has a characteristically strong absorption band in mid infrared region extending from 4.2 µm to 4.5 µm, with its high peaks at 4.23µm and 4.28 µm wavelengths. Apart from that, carbon dioxide also shows a weaker corresponding near infrared overtones absorption band around 2.7 µm with two orders of magnitude lower than that of 4.28 µm wavelength [10]. The sensor system operates at wavelength 4.28µm of where the fundamental absorption lines of CO$_2$ gas as shown in figure 2. There are no gas absorption lines at 3.8µm, enabling a reference signal to be taken at the centre of this wavelength.
The Beer-Lambert law, the relationship between absorbance and concentration of an absorbing species as defined by the Beer Lambert law is shown in equation 1 [11].

$$I_L = I_0 e^{-εcl}$$  \(1\)

where $I_L$ is the intensity of light after the absorption, $I_0$ is the incident light intensity, $l$ (dm) is the optical path length, $c$ (mol/L) or (mol/dm$^3$) is the concentration of the gas species and $ε$ (L/mol.dm) is the molar absorptivity of the gas species. According to the Beer - Lambert Law, the Transmission or Transmissivity ($T$) of a light intensity has a logarithmic dependence with the product of its absorption coefficient ($α$) and the pathlength ($l$) as shown in equation 2 [12].

$$T = \frac{I_L}{I_0} = e^{-αl} = e^{-εcl}$$  \(2\)

A variation of the Beer-Lambert Law has been derived from equation 2 and rearranged for the concentration of the gas species $c$ in unit of percentage gas concentrations as shown in equation (3):

$$c[\%] = \frac{-ln\left(\frac{I_L}{I_0}\right) \times R \times T \times 10^2}{σ \times N_A \times l \times P}$$  \(3\)

where $c[\%]$ is percentage gas concentrations, $R$ is the gas constant (0.08205 L.atm/K.mol), $T$ is the room temperature at 293.15K, $N_A$ is the Avogadro’s constant, $P$ is the atmosphere pressure (1 atm) and $σ$ is the average absorption line intensity of the gas under study. Figure 3 shows the sensor signal output versus percentage of CO$_2$ gas concentrations during the sensor calibration process.

A specifically designed LabVIEW program has been developed for use in the sensing system as a means of controlling data acquisition from the receiver circuitry and also data output to the user. When the LabVIEW program is initialized, it records the incident intensities from the detector circuitry for a short period of time. The average of this data is then utilised along with other data accessible during testing to calculate the concentration of the gas present using the equation (4) as shown above. These concentrations are then output to the user in real time. Through this method the program can automatically calculate and output the measured percentage gas concentrations in real time. This reading is compared to the commercial gas analyzer simultaneously during experimental tests.
3. Experimental Set-Up
The experimental set-up of the optical fibre based mid-infrared sensor system as assembled in the laboratory is shown in figure 4. The sensor system, developed using low cost and compact mid infrared components, consists of a pulsed broadband infrared light source, chalcogenide infrared fibre bundles, calcium fluoride (CaF$_2$) lenses, two pyroelectric detectors, and a highly compact open-path gas mixing cell for the measurement of the gas concentrations. The pyroelectric detectors are fitted with two separate narrow band pass (NBP) filters. The filters, one with a NBP filter at centre wavelength 4.28µm of where the fundamental absorption lines of CO$_2$ gas and the other is a reference filter at centre wavelength of 3.8µm wavelength. The output signal of the sensor was detected by a computer by using a Data Acquisition card and a LabVIEW program. A commercial gas analyzer was also used simultaneously in the experimental setup to provide a comparison to the concentrations of CO$_2$ gas present in the gas mixing cell.

![Figure 4: The experimental setup of optical fibre based CO$_2$ sensor systems.](image)

4. Results
Experimental results are presented for the calibration of this sensor using laboratory based gas mixtures supplied from gas bottles. The results shown in figure 5, demonstrate that the developed optical fibre sensing system is capable of detecting changes in high concentrations of CO$_2$ between 0.1% and 10%, and compared to the readings of the commercial gas sensor. From the pyroelectric detector voltage outputs, percentage absorption due to changes in gas concentrations was calculated. The commercial gas analyser, which was used to run a simultaneous measurement, has provided reliable and accurate reading of the concentrations present in the gas cell. At the beginning of the experiment, the gas cell was purged with 100 percent zero grade nitrogen (N$_2$) for 5 minutes to remove any atmospheric CO$_2$ that may present. Following this, a 10 percent concentration of CO$_2$ gas from the cylinder was added to the gas cell for a period of 5 minutes. The gas cell was then purged with 100 percent nitrogen for 5 minutes duration by turning off the flow of CO$_2$ gas. The concentration of the gas under study was reduced in step of 2 percent each times, with 100 percent nitrogen purge for 5 minutes each time until the concentration of gas under study was reduced to zero percent. The response time ($t_{10}$ - $t_{90}$), as the CO$_2$ gas concentration was switched from 0% to 6%, was recorded at 5.2s as shown in figure 6.

The engine tests of the optical fibre based sensor system were carried out in a test facility in Centro Ricerche Fiat, Italy. The results of the test, as shown in figure 7 demonstrate that the developed optical fibre sensor system has been able to reproduce the concentrations of CO$_2$ compared to data that simultaneously recorded on the commercial gas analyser for the whole duration of the test cycle. The similar sensor has also demonstrated operation over a wide range of concentrations and a limit of detection smaller than that present in a modern automobile [13]. Previous testing using a similar sensor showed that the detection and transmission systems are capable of operating over long periods of time [14], [15]. Extensive testing is necessary to quantify if the optical fibre sensor is capable of reliably detecting CO$_2$ over a period of a time when fitted to an automobile during normal operation.
Figure 5: Comparison between the output of developed CO₂ optical fibre sensor systems and commercial gas analyzer in detection of CO₂ gas.

Figure 6: Time response analysis of the sensor system.

Figure 7: Measured concentrations from the sensor for the EUDC test cycle on a Fiat Croma engine exhaust.

5. Conclusions and Future Work
A highly compact optical fibre based sensor system for on-line measurement of CO₂ gas emissions in modern automotive exhaust has been successfully demonstrated. This work offers the possibility of extension the applications of this sensor in environmental pollution monitoring where lower concentrations of CO₂ and other harmful exhaust emissions present. Further work is in progress to optimize the sensor system in term of issues related to noise reduction, response time, stability and reliability over long term operation, software and also hardware interfacing.
References
[1] David H. F. Liu and Béla G. Lipták, Air Pollution, (CRC Press), 2000, pp. 3.
[2] Environment and Human Health Report on The Harmful Effects of Vehicle Exhaust http://www.ehhi.org/reports/exhaust/summary.shtml.
[3] A. Bytnerowicz et al, Integrated effects of air pollution and climate change on forests: A northern hemisphere perspective, Environmental Pollution, Volume 147, Issue 3, June 2007, Pages 438-445.
[4] Global Climate Change on Cumulative CO2 Emissions at http://www.pewclimate.org/facts-and-figures/international/cumulative.
[5] European Environment Agency 2008 EEA Reports on Progress in Greenhouse gas Emissions Reductions in 2006 http://www.eea.europa.eu/references.
[6] European Union Emission Standards 2005 Heavy-Duty Diesel Truck and Bus Engines Dieselnet http://www.dieselnet.com/standards/eu/hd.php
[7] A. J. Ricco, Chemical and Biological Sensors and Analytical Electrochemical Methods: Proceedings of the Symposium on Chemical and Biological Sensors and Analytical Electrochemical Methods, The Electrochemical Society (1997) pp.88.
[8] S Zhuiykov, Electrochemistry of Zirconia Gas Sensors, CRC Press, (2007) pp.95.
[9] C. N. Banwell, Fundamentals of molecular spectroscopy, 4th Edition, McGraw-Hill, (1994) pp.19
[10] Hitran Rothman LS, Rinsland CP, Goldman A, Massie ST, Edwards DP, "The Hitran Molecular Spectroscopic Database and HAWKS (HITRAN Atmospheric Workstation); 1996 Edition", in quantitative spectroscopy and radiative transfer, vol. 60, 1998, pp. 665-710.
[11] I M Campbell, Energy and the atmosphere: a physical-chemical approach, 2nd Edition, John Wiley & Sons, (1986) pp 20.
[12] S Svanberg, Atomic and molecular spectroscopy: basic aspects and practical applications, 4th Edition: 4, Springer, (2004), pp 132.
[13] Muda R., Clifford J., Chambers P., Mulrooney J., Merlone-Borla E., Gili F., Dooly G., Fitzpatrick C. and Lewis E. “Simulation and measurement of carbon dioxide exhaust emissions using an optical fibre based mid infrared point sensor.”. J Opt A: Pure Appl. Opt. 11 No 5 (May 2009) 054013 (7pp).
[14] G. Dooly, J. Mulrooney, E. Merlone-Borla, G. Flavia, J. Clifford, C. Fitzpatrick and E. Lewis, In-situ monitoring of Carbon Dioxide Emissions from a Diesel Automobile using a Mid-Infrared Optical Fibre Based Point Sensor, IEEE International Instrumentation and Measurement Technology Conference, Canada, May 12-15, 2008.
[15] Jim Mulrooney, John Clifford, Colin Fitzpatrick, Paul Chambers and Elfed Lewis, "Monitoring of carbon dioxide exhaust emissions using mid-infrared spectroscopy", Journal of Optics A, Opt. 9, 2007, pp. 87 - 91.