Optical investigation of heat release and NOx production in combustion

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Abstract. Two novel optical techniques are presented for non-intrusive, spatially resolved study of combustion, both based on passive Optical Emission Tomography (OET). Firstly, OET is used for non-intrusive study of heat release through the detection of chemiluminescence by the hydroxyl radical that is generated in the burning process. The OET technique presented here is based on a passive fibre-optic detection system, which allows spatially resolved high-frequency detection of the flame front in a combustion flame, where all fibres detect the emission signals simultaneously. The system withstands the high pressures and temperatures typically encountered in the harsh environments of gas turbine combustors and IC engines. The sensor-array is non-intrusive, low-cost, compact, simple to configure and can be quickly set up around a combustion field. The maximum acquisition rate is 2 kHz. This allows spatially resolved study of the fast phenomena in combustion. Furthermore, a method is presented for study of the production of NOx through chemiluminescence from tri-methyl-borate (TMB). In combustion, the tri-methyl-borate produces green luminescence in locations where NOx would be produced. Combining the green luminescence visualisation with UV detection of the hydroxyl radical allows monitoring of heat release and of NOx production areas, thus giving a means of studying both the burning process and the resulting NOx pollution.

1. Introduction

The need for reducing the environmental impact of combustion has led to increased effort in optimising engine efficiency and decreasing emission of harmful combustion products. Two factors considered in this paper are heat release, which determines engine efficiency, and NOx production, which is associated with issues such as increased ground level ozone, acid rain, health risks related to reduced efficiency in oxygen uptake and global warming. This has led to emission standards being introduced limiting the amounts of NOx that can be produced through automotive, gas turbine and furnace combustion.

Many studies have recently been performed on modelling the reaction kinetics [1-3], indicating the type of species present during the different stages of combustion. Several studies have shown that heat release is correlated to the presence of certain molecular species [2, 4, 5]. Thus, localizing and detecting the amount of these species provides a spatially resolved monitoring of heat release. In the present work, a passive Optical Emission Tomography system is demonstrated to relate the hydroxyl radical’s chemiluminescent emission from a combustion flame to spatial heat release.
A similar system is demonstrated for the in situ detection of NOx generation. There are three types of oxides of nitrogen in the atmosphere, nitrous oxide (N\textsubscript{2}O), nitric oxide (NO), and nitrogen dioxide (NO\textsubscript{2}). Collectively the latter two gases are known as NOx. Virtually all anthropogenic NOx enters the atmosphere as a result of the combustion of fossil fuels with the majority due to NO generation by internal combustion engines, where NO is generated at very high temperatures (above 1800K) according to:

\[
N_2 + O_2 \rightarrow 2NO
\]

While complete combustion emits water and carbon dioxide, incomplete combustion emits water, carbon dioxide and impurities such as NOx, SOx and carbon dioxide. Several detectors have been developed for nitrogen dioxide, e.g., by Kebabian et al [6]. Although there are several instruments available commercially for monitoring NOx, however, detection of such harmful gases is currently typically obtained as part of the exhaust products, i.e., not at the production site. The work presented here aims to enable study of NOx production in situ. The approach used in the present paper is based on adding a tracer to the flame in order to make the nitrogen production process visible. The tracer that is used is tri methyl borate (TMB), where boron replaces nitrogen in the combustion reactions. In the process of boron combustion a green chemiluminescent emission is visible, which can be easily recorded using cameras or other visible detectors. By detecting the intensity of the boron chemiluminescence from around the flame, tomographic reconstruction of the location of the NOx production is possible.

The paper shows some preliminary experiments aimed at using optical emission tomography for monitoring the hydroxyl radical as well as boron chemiluminescence, thus allowing study of both heat release and NOx production in situ.

2. Optical emission tomography

Optical Emission Tomography (OET) provides a cross-sectional spatially resolved reconstruction of the location of light emission sources based on intensity levels measured from around the field. In combustion, it has been used to monitor the location and dynamics of hydroxyl radicals (OH\textsuperscript{*}) in a flame. These radicals are generated during the initial stages of burning in the combustion of hydrocarbon fuels and provide a qualitative indicator for the boundary between burnt and unburnt fuel [7]. These radicals can be detected optically as they produce light in the UV band through chemiluminescence. It has been shown that the OH radical emission is directly proportional to heat release in premixed flames [4]. The chemiluminescence from the hydroxyl radical forms clear, well-separated peaks in the spectrum allowing simple spectroscopic filtering to isolate the light coming from the hydroxyl radical at 309 nm from the total emission spectrum of the burning process. Using a sensitive detector, this can be measured at very high speeds (kHz range) and by using a range of detectors positioned around the field of interest the spatial distribution can be tomographically reconstructed. In experiments performed earlier an array was developed consisting of a set of forty fibre-optic detectors, mounted annularly so that they can be fitted around a combustion field [8]. This configuration allows mounting of the array on real engines and combustors requiring only little modification in most cases. The detectors are arranged in such a way that the sensitivity of the array is as homogeneous as possible across the circular area surrounded by the detectors. The OET system was designed to operate using different detectors, depending on the need (high sensitivity, high-speed, etc.). Also, it can be used to monitor a specific wavelength, used e.g., for tracking of heat release, or a wavelength range can be detected. The intensities detected by each detector are used as input to a tomographic reconstruction algorithm based on the Multiplicative Algebraic Reconstruction (MART) technique [9, 10]. The intensity of emission in the flame is reconstructed on a 10 by 10 grid, resulting in a spatial resolution of approximately 1/10th of the viewing area. The system can be used to study instabilities in premixed combustion. It allows high-speed data-capture (up to ~2 kHz) and also a high, instantaneous spatial resolution (~10 mm\textsuperscript{2} for an area of 70 mm diameter) to map out the spatial behaviour of the instabilities. Furthermore, being passive, it does not interfere with the combustion processes taking place (i.e., be non-intrusive). Its capabilities are illustrated in figure 1, where the
spatial and temporal variation in heat release inside a cylindrical combustor during unstable, lean combustion is shown, with the tomographic reconstruction indicating the basic annular shape of the heat release region. Data was captured at 1 kHz, allowing recording of the high-speed oscillation.

This tomographic technique is further developed to monitor heat release through chemiluminescent emission from OH radicals, as well as for localisation of NOx generation.

Figure 1. Tomographic reconstruction of time-varying OH* distribution in RR combustor based on OET measurements. Two slices are shown: The horizontal one shows the spatial distribution of chemiluminescence intensity from the OH radical indicating an overall annular shape, indicating heat release being primarily concentrated around the edges of the combustion chamber, despite the flame being present throughout the chamber. The vertical slice indicates the temporal evolution of the hydroxyl radical chemiluminescence, indicating a regular oscillation at a frequency of approximately 0.3kHz.

3. Location of NOx production

There are two primary forms of NOx production. Thermal NOx and Fuel NOx. A further, less important source of NOx formation is through the ‘Prompt NOx’ or ‘Fenimore mechanism’. Thermal NOx is formed when nitrogen and oxygen in the combustion air combine with one another. It is determined by a set of highly temperature-dependent chemical reactions known as the extended Zel’dovich mechanism:

\[
N_2 + O \rightarrow NO + N
\]
\[
N + O_2 \rightarrow NO + O
\]
\[
N + OH \rightarrow NO + H
\]

Here it is assumed that oxygen atoms are available through the equilibrium reaction: O2→2O. The Zel’dovich mechanism is rate-limited by the first reaction, as breaking the triple bonds in the nitrogen molecule requires high activation energy. The further reactions require less energy and in most combustion cases, except fuel-rich ones, there is excess oxygen, so that the rate of consumption of free nitrogen atoms becomes equal to the rate of its formation and therefore a quasi-steady state can be established. The rate of formation of NOx is dependant on concentration and temperature, but independent of fuel type. The rate will increase with increasing oxygen concentration.

The method for determining the location and rate of thermal NOX production used here is based on the theory that the Zel’dovich mechanism, \( N_2 + O \rightarrow NO + N \), is similar to that of boron combustion, \( BO + O + M \rightarrow BO_2^* + M \), as both reactions have a first order dependence on the oxygen atom concentration [11-13]. Thus, boron combustion can be used as a tracer for NOx production, which allows passive OET measurement as in the process of boron combustion a green chemiluminescent emission is visible. Of the three known boron sources that combust with a reaction with the oxygen atom (two diborane seeds and tri methyl borate), here the use of tri-methyl-borate (TMB) as first proposed by Annen et al [11, 12, 14] is explored as their experiments showed that the intensity of boron chemiluminescence is closely related to NO production rate in specific regions.
4. Experimental set-up

4.1. Meker burner
For ease of access while developing the techniques, the experiments described here are performed on the optically thin flame generated by a modified meker burner of 0.043 m outer diameter and 0.040 m effective burner diameter (Farnell Industrial Components, REXALOY 4101/52) that is designed to run on natural gas. The gas is supplied via a hose, which is connected to a fitting located at the base of the burner. The meker burner is modified slightly by a collar fitted around the base, where two air-supplies are connected, one of which contains TMB. The mixture then passes through a 0.5 mm diameter circular jet nozzle.

4.2. Tri-methyl borate seeding
TMB is added to the air supply via vaporization in a dreschel bottle. To calibrate the TMB flow rate, two dreschel bottles are used, one of which contains a small amount of (liquid) TMB. This first one is connected to an input line with the air supply and an output line, which is connected to an empty dreschel bottle. The empty bottle is weighed, and then the first bottle is heated to vaporise the TMB. The air supply is turned on for a set period. The second dreschel bottle is then weighed to calculate the TMB flow rate. Once the desired flow rate is attained, the first dreschel bottle can be connected directly to the flame. Airflow is measured using a bubble meter.

5. Results
Results obtained for the natural gas flame using the sensor array with 40 UV sensitive diodes (AlGaN photo-diode detectors (A0250-07-00001.18, APA Optics Inc) are shown in figure 2. The detectors used here have no sensitivity beyond 325 nm, which from spectroscopic measurements for this flame implies only light emitted by OH* will be detected. The fibre-detector systems have a linear sensitivity and are calibrated to allow intensity comparison between fibres. Tomographic reconstructions are obtained for positions of 1mm intervals from the burner top upwards (right side of figure 2). The highest intensity of hydroxyl radical chemiluminescence is found in the centre at approximately 4 mm above the burner surface. The results for each ‘slice’ are averaged over 1000 measurements, taken simultaneously for the 40 detectors.

![Image of Meker flame and tomographic reconstruction](image)

Figure 2. Meker flame (left), tomographic reconstruction of hydroxyl radical emission (right)

In subsequent experiments, different concentrations of TMB were added. Images of the resulting flames at different TMB concentration levels are shown in figure 3 (taken using an Olympus Camedia C-2500L, running in auto exposure mode). The flame on the left contains no TMB, while in the flame...
shown on the right 12.25 ml/s air and 0.06125 ml/s of TMB was used (0.5% TMB, highest concentration used), displaying a clear green chemiluminescence.

![Meker flame](image)

**Figure 3.** Meker flame. Left: no TMB, right: some TMB, centre: ~0.5% TMB (maximum used).

A preliminary tomographic analysis was obtained by using a mini fibre-array that was moved around the flame. In the present experiment the mini-array consists of 5 colour sensitive sensors, filtered to be especially sensitive to green light. To obtain data for a full tomographic reconstruction, the array of five sensors was rotated eight times to simulate a full forty-sensor array, assuming a stable flame (simulated by averaging over a set period, again 1000 samples were used per sensor position). As the signal was very small a gain of 100 was used. The height above the burner was increased from 0 mm to 69 mm, with varying increments. Measurements were obtained at 1, 2, 3, 4, 9, 14, 19, 24, 32, 38, 43, 45, 48, 60 and 69 mm.

Overall, the tomographic results obtained for different concentrations of TMB confirm that the boron chemiluminescence increases with increased concentration of TMB. Example results obtained from tomographic reconstruction are shown in figure 4 for the highest TMB concentration used (0.5%). Although these results are very preliminary, they do indicate peak emission for boron chemiluminescence (NOx production) to take place further from the burner surface than the hydroxyl radical chemiluminescence (heat release).

![Reconstruction](image)

**Figure 4.** Reconstruction for green emission at ~0.5% TMB. Slices shown at 1, 9, 19, 24, 32, 43, 60 and 69 mm above burner surface; maximum emission found at 38 mm.

### 6. Conclusions
The preliminary investigation of heat release and NOx production based on optical emission tomography is described. Both techniques that are used are indirect in that they monitor through the detection of species related to the variable under investigation. For heat release this species is the hydroxyl radical, which here is indicative of the position of the flame front. In the case of NOx it is
through boron combustion, where the green chemiluminescence is found to occur in the areas in which NOx production would have taken place.

The experiments show that boron chemiluminescence intensity is increased for an increase in trimethyl borate (TMB), indicating possible use for quantifying relative changes in NOx production. The described method, although indirect, can be used to find location of production in situ and thus eliminates the need for sampling of exhaust air.

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References
[1] Smith G P, Luque J, Park C, Jeffries J B and Crosley D R 2002 Low pressure flame determinations of rate constants for OH(A) and CH(A) chemiluminescence, Combust. Flame 131(1-2) 59-69
[2] Najm H N, Knio O M, Paul P H and Wyckoff P S 1998 A Study of Flame Observables in Premixed Methane - Air Flames Combust. Sci. and Tech. 140 369-403
[3] Docquier N, Belhalfaoui S, Lacas F, Darabiha N and Rolon C 2000 Experimental and numerical study of chemiluminescence in methane/air high-pressure flames for active control applications, Proc. Combust. Inst. 28(part 2) 1765-74
[4] Diederichsen J and Gould R D 1965 Combustion Instability: Radiation from Premixed Flames of Variable Burning Velocity Combust. Flame 9 25-31
[5] Hultqvist A, Christensen M, Johansson B, Franke A, Richter M and Alden M 1999A Study of the Homogeneous Charge Compression Ignition Combustion Process by Chemiluminescence Imaging SAE Journal of Engines 108(3) 2114-27
[6] Kebabian P L, Annen K.D, Berkoff T A and Freedman A 2000 Nitrogen dioxide sensing using a novel gas correlation detector Meas. Sci. Technol. 11(5) 499-503
[7] Allen M G, Butler C T, Johnson S A, Lo E Y and Russo F 1993 An Imaging Neural Network Combustion Control System for Utility Boiler Applications Combust. Flame 94 205-14
[8] Dunkley P 2003 The Investigation and Application of OET (Optical Emission Tomography) as a Combustion Diagnostic PhD thesis University of Warwick (Coventry UK)
[9] Herman G T and Lent A 1976 Iterative reconstruction algorithm Comput. Biol. Med. 6 273-94
[10] Fok I T, Gilks D T, Greenshields D D, Horton S J, Moll E, Murray J and Thomas G P 2002 Tomographic Diagnostic Tool (Technical Report) MEng Report University of Warwick (Coventry UK)
[11] Annen K D, Brown R C and Stickler D B 1998 Chemiluminescent Visualization of Spatially - Resolved Thermal Nitric Oxide Production Rates Aerodyne Research Inc Report (Billerica, MA)
[12] Annen K D, Brown R C and Stickler D B 2001 Chemiluminescent Visualisation of Spatially-Resolved Nitric Oxide Production Rates in Industrial burners Aerodyne Research Inc. Report (Billerica, MA)
[13] Annen K D and Knight R A 2003 Chemiluminescent Visualisation of Spatially-Resolved Nitric Oxide Production Rates in Single and Two-stage Industrial Burners Aerodyne Research Inc
[14] Annen K D and Knight R A 1998 Chemiluminescent Visualisation of Spatially-Resolved Nitric Oxide Production Rates in Industrial Burners Aerodyne Research Inc and Gas Technology Institute Report (Billerica, MA)