FTIR and QCL diagnostics of the decomposition of volatile organic compounds in an atmospheric pressure dielectric packed bed plasma reactor

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Abstract. Non-thermal atmospheric plasmas can be used to decompose toxic volatile organics. A dielectric packed bed plasma reactor was used to decompose dichloromethane (DCM) in a flowing gas mixture of nitrogen and oxygen. The effect of varying the oxygen concentration on the decomposition of dichloromethane was investigated. A comparison has been made of spectroscopic diagnostics based on FTIR (Fourier Transform Infrared) spectroscopy and infrared quantum cascade laser spectroscopy for the detection of nitric oxide produced in the plasma reactor.

1. Introduction
Volatile organic compounds which have been released to the atmosphere via vehicle exhausts, petroleum storage and distribution, oil refining, surface coating and other industrial processes contribute significantly to both air pollution and human health problems[1]. Some of these VOCs affect the human senses through their odour. Others have much more serious effects such as reducing the birthweight or even causing abortion. Many VOCs are also carcinogens.

Non-thermal plasma has been shown to have a great potential for the decomposition of VOCs. These are non-equilibrium plasmas, in which the energy is delivered to the electrons and not to the translational and rotational energy of the gas molecules thus requiring less input energy. These energetic electrons are responsible for initiating the chemical reactions in the plasma. They can also be generated at atmospheric pressure and room temperature which gives them an advantage for applications such as air pollution reduction[2, 3]. There are a variety of non-thermal plasma reactors such as, dielectric-barrier plasma reactors[4], pulsed corona plasma reactors[5], microwave plasma reactors[6], surface discharge reactors[7] and packed bed plasma reactors[8, 9]. The use of a packed bed reactor provides the advantages of uniform distribution of gas flow and discharge in the reactor. It can also be easily modified to incorporate a catalyst. Indeed the combination between catalyst and packed bed could reduce the amount of some by-products like NOₓ, CO₂ and ozone[10].

In this work, non-thermal plasma generated in packed bed plasma reactor at atmospheric pressure is used to decompose dichloromethane (DCM) as an example of a chlorinated VOC. There have been several previous studies of the decomposition of DCM[5, 9-11]. Experiments have been conducted to
investigate the effect of the addition of oxygen on the decomposition of dichloromethane. For diagnostics of the chemical species in the plasma, in-line FTIR (Fourier Transform Infrared) spectroscopy and mid-infrared quantum cascade laser spectroscopy are used. A comparison is then made of these two complementary techniques.

2. Experimental description

2.1. Packed bed plasma reactor system

Figure 1 shows a sketch of the experimental set-up. The packed bed reactor was constructed using a Pyrex tube of 20 cm length and 31 mm internal diameter and containing two stainless steel electrodes made with funnel ends separated by about 3 cm. A stainless steel mesh was placed in front of the electrodes and the volume filled with barium titanate (BaTiO$_3$) beads. These have a dielectric constant of 2000-10000. The packed bed volume was 24.9 cm$^3$, whilst the volume of the beads was about 9 cm$^3$ and the void volume is about 15.9 cm$^3$. For a 1 L min$^{-1}$ flow rate a residence time of 0.95 s was achieved. The gas mixture passed into the reactor through a 1/4” tube in the centre of the electrodes. The inlet system has been designed to allow the sampling of the gas stream before and after the plasma reactor. In these experiments nitrogen was used as the carrier gas. Air and oxygen cylinders have been used to provide different percentages of oxygen to the plasma. The gases were used as supplied and consisted of an air cylinder (79 % nitrogen, 21 % oxygen), and a nitrogen cylinder (oxygen free) (99.998 % purity). A mass balance calculation allowed the adjustment of the gas flow through mass flow controllers (MKS 247). A total flow rate of 1 L min$^{-1}$ including approximately 500 ppm dichloromethane was used. To obtain 500 ppm, dichloromethane (99.6 %) was cooled down to -20 °C using a coolant of 50 % water and 50 % antifreeze. A neon sign power supply (Hansen) was used to generate a high voltage applied to the reactor electrodes. Electrical measurements of the voltage was made using a Tektronix 1000 to 1 voltage probe and the current was measured using a Pearson 411 current monitor. Plasma is generated in the packed bed reactor at atmospheric pressure and close to room temperature.

Figure 1. Sketch illustrating the experimental set up.
2.2. Diagnostics with in-line FTIR Spectroscopy:
FTIR spectroscopy (Bruker Equinox 55) was used to identify and determine the concentration of components in the reactor inlet and outlet gas streams. The gas streams were passed alternately into a multiple pass optical gas cell (Specac Ltd) with a White-type mirror arrangement producing an optical pathlength of 5.3 meters. Sampling was carried out about 0.4 sec after the packed bed reactor. FTIR analyses have been obtained at room temperature and atmospheric pressure at a spectral resolution of 2 cm\(^{-1}\). A liquid nitrogen cooled MCT (mercury cadmium telluride) detector was also used for enhanced sensitivity. Concentrations of each species were determined by integrating the area under each peak using Bruker’s OPUS software and then comparing with standard spectra produced by Pacific Northwest National Laboratories\[12\] at atmospheric pressure, one meter path length and different temperatures. The destruction efficiency of dichloromethane was calculated as follows:

\[ \eta = \frac{C_{in} - C_{out}}{C_{in}} \times 100\% \]

where \(C_{in}\) and \(C_{out}\) are the inlet and outlet concentration of dichloromethane respectively.

2.3. Mid-infrared quantum cascade laser measurements of plasma products:
For fast response, high sensitivity and minimal spectral interferences, a thermoelectrically cooled, continuous wave (cw) distributed feedback (DFB) quantum cascade laser (QCL) spectrometer (TDL Sensors Ltd) was used to measure nitric oxide. The wavelength of the laser was current-tuned over two absorption peaks at \(\sim 1900.52\) cm\(^{-1}\) and \(\sim 1900.075\) cm\(^{-1}\) at a QCL temperature of \(-6.5^\circ C\)[13]. The plasma exhaust was connected to an absorption cell of pathlength 21 cm at atmospheric pressure. The exhaust then passes to the multiple pass cell used by the FTIR spectrometer as seen in figure 1. The detector used in this arrangement was a thermoelectrically cooled MCT detector. Figure 2 shows an example spectrum for measuring nitric oxide concentration at the exhaust of the plasma reactor. The inlet gas consists of approximately 500 ppm dichloromethane and 21 % added oxygen. It can be seen that the first 20 channel points are for no current passing through the laser in order to determine the 0% absorption level. The red line is a non-linear least squares fit to lorentzian lineshapes carried out in real-time to extract the concentration. Each spectrum is the result of 1000 averages in approximately 1 s.

![Figure 2. Raw signal and fit in plasma measurements at 300 K and atmospheric pressure. DCM=500 ppm, \(O_2=21\%\), 0.5 L min\(^{-1}\).](image-url)
3. Results

3.1. Effect of adding oxygen to the plasma:
Figure 3 shows the FTIR spectrum, a) before and, b) after the reactor containing a nitrogen plasma with 500 ppm dichloromethane at a flow rate of 1 L.min$^{-1}$. Oxygen was then added to the gas stream by addition of air to the nitrogen plasma. Oxygen percentages were varied between 0 to 21 percent. Figure 4 shows a FTIR spectrum taken after plasma reactor for a gas stream of approximately 500 ppm DCM and 3 % added oxygen in nitrogen plasma. A maximum destruction of about 75 % at 3 % added oxygen to the gas stream has been found with nitrogen plasma.

![Figure 3. Infrared spectrum for 500 ppm dichloromethane in pure nitrogen with flow rate of 1 L.min$^{-1}$ (a) before the plasma reactor. (b) after the plasma reactor.](image-url)
The destruction of dichloromethane as well as the concentration for all species present in the examined plasmas with different percentages of added oxygen in nitrogen is shown in table 1. Phosgene (COCl$_2$), carbon tetrachloride (CCl$_4$) and hydrogen chloride (HCl) were not detected after adding oxygen to the gas stream, whilst HCN concentration was below the limit of detection at oxygen concentration higher than 1%.

**Table 1.** Decomposition efficiency for dichloromethane and the concentrations of all species detected in the plasma exhaust by FTIR as a function of oxygen concentration in nitrogen plasma.
The maximum destruction of dichloromethane in a nitrogen plasma occurs at 3 % added oxygen. This can be seen in figure 5 where the concentrations of the byproducts: nitrosyl chloride (CINO), carbon monoxide (CO) and carbon oxide (CO$_2$) in nitrogen plasma are also shown as a function of oxygen concentration.

The effect of oxygen concentration on the formation of nitric oxide has been simultaneously studied by both FTIR and infrared quantum cascade laser absorption spectroscopy. Figure 6 shows the results of two repeated experiments. The measured NO concentrations were very similar up to an oxygen concentration of 10%. After this there is a slight divergence of the QCL and FTIR measurements. This may be due to further oxidation of NO in the exhaust stream in between the QCL sample cell and the FTIR sample cell. Also shown are the DCM concentrations which again show the minimum level of DCM in the exhaust achieved for an oxygen concentration of around 3%.

Figure 7 shows the results of monitoring the NO concentration over time with the QCL for an oxygen concentration of 21% and then for 10%. Step changes of about 50 ppm in the concentrations of NO occur every five minutes. This effect had not previously been observed with the FTIR. The origin is thought to be due to slight changes in the injected power into the plasma. Measurements of the voltage and current have been made using a 1000 to 1 high voltage probe and a Pearson 411 current monitor connected to a digital oscilloscope. Typical measurements are shown in figure 8. Here it can be seen that the power supply generates pulses with a repetition of 100 pulses per second and a pulse duration of 3.25 ms. The peak to peak voltage is about 14 kV at a frequency of 20 kHz during the pulse. An average deposited power of about 15 W, with an energy density of 900 J L$^{-1}$ was calculated where the energy density was calculated as a ratio of the deposited power to the gas flow rate. Closer analysis of the voltage and current waveforms reveals a phase change in the leading edge of the voltage pulse every 5 minutes or so, however further investigation is required to ascertain the effect of this on NO formation.

![Figure 5](image_url)  
**Figure 5.** Comparison among the concentrations of dichloromethane (DCM), carbon monoxide (CO), carbon oxide (CO$_2$) and nitrosyl chloride (CINO), all the concentrations are in ppm.
Figure 6. NO and DCM concentration versus percentage of oxygen in nitrogen in the plasma reactor with a flow rate of 1 L.min\(^{-1}\) and a power of ~15 W. The initial DCM concentration was ~500 ppmv. QCL spectrometer with a 21 cm optical cell, V=103 cm\(^3\) (t=6.1 s). FTIR with an 5.3 m optical White cell, V=1300 cm\(^3\) (t=78 s).

Figure 7. Nitric oxide concentration over time with 21 % and 10 % of added oxygen in nitrogen plasma with approximately 500 ppm DCM and total flow rate of 1 L min\(^{-1}\) measured via QCL laser spectroscopy.
4. Discussion and conclusions

This work has shown that the optimum destruction of DCM in nitrogen at atmospheric pressure in a dielectric packed bed reactor occurred at an oxygen concentration of 3%. This is in general agreement with Fitzsimmons et al[9]. At higher oxygen concentrations the formation of ozone becomes more likely which is less reactive than atomic O and OH in the destruction process. When there is no oxygen present the chlorine forms phosgene (COCl₂), carbon tetrachloride (CCl₄) and hydrogen chloride (HCl), whilst they were substantially reduced or not detected after adding oxygen.

The simultaneous measurement of NO by QCL and FTIR spectroscopy demonstrated the complementary nature of the two techniques. The laser approach provides a very rapid and highly sensitive measurement technique but for only a single species in this case whereas the FTIR has broad spectral coverage for multispecies detection but is less sensitive. It was encouraging to observe that the same NO concentrations were derived except for the situation of high oxygen concentration where the differing gas cell volumes and positions led to different measured NO concentrations. The QCL measurements of NO also showed up some instability in the power supply that was not detected by FTIR.

Further work is being directed towards direct in situ measurements with the QCL and FTIR with time-resolved detection on the microsecond timescale. Additionally multiple packed beds are also being explored and the addition of catalyst to enhance the conversion.

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