Study of dichloromethane decomposition in dielectric barrier discharge plasma reactors using advanced spectroscopic diagnostics techniques

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Abstract: Non-thermal atmospheric plasma generated in a packed-bed plasma reactor at room temperature was used to decompose dichloromethane (DCM) as an example of a volatile organic compound. The effect of varying the oxygen and propylene (C\textsubscript{3}H\textsubscript{6}) concentrations on the destruction efficiency of dichloromethane was investigated. A variety of advanced optical diagnostic techniques have been used to characterize the plasma inlet and products.

Keywords: Packed bed plasma reactor, VOCs remediation, Dichloromethane, Propylene.

1. Introduction

Volatile organic compounds (VOCs) are important air pollutants which negatively affect both the environment and human health\[1, 2\]. Non-thermal atmospheric plasmas have the potential to decompose VOCs\[3, 4\]. Non-thermal plasma is a non-equilibrium plasma in which the electrons gain high temperature and energy while the gas components remain unheated. These electrons initiate the reactions in the plasma region by colliding with VOC molecules and bulk gas molecules, generating excited atoms and molecules. These excited species drive the decomposition of VOCs and the formation of end products\[5, 6\].

Non-thermal plasma has been generated in a variety of plasma reactors such as: dielectric-barrier, pulsed corona, electron beam, radio frequency, microwave, surface discharge and packed-bed plasma reactors\[5\]. The use of packed-bed plasma reactors for VOC remediation has the advantage of uniform distribution of gas flow and discharge in the reactor as well as the possibility to be easily modified to include a catalyst\[7-9\].

The aim of this study is focused on the destruction of dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) as an example of a volatile organic compound. The work uses advanced optical diagnostic techniques such as tunable infrared laser spectroscopy and FTIR to investigate the effect of plasma conditions and additives on the destruction efficiency of dichloromethane.

2. Experimental set up

Non-thermal plasma was generated in a packed-bed plasma reactor at room temperature and atmospheric pressure. The reactor consists of a Pyrex tube with an internal diameter of 31mm and two stainless steel electrodes with funnel ends to achieve an evenly distributed gas flow entering the reactor volume. The distance between the electrodes was set to about 3 cm and packed with barium titanate beads with a diameter of 1.5 - 3 mm giving a bed volume of 24.9 cm\textsuperscript{3}. A neon sign power supply provided a high voltage of about 14 kV\textsubscript{pk-pk} at a frequency of 20 kHz. A Tektronix 1000 to 1 voltage probe and a Pearson 411 current monitor were used to measure the voltage and current provided to the reactor. The applied power measured in these experiments was estimated to be about 15 W corresponding to an energy density of about 900 J L\textsuperscript{-1}. Fig.1 illustrates the experimental arrangement.

In these experiments nitrogen was used as a carrier gas with a total flow rate of 1 L min\textsuperscript{-1}. Nitrogen was controlled via MKS 247 mass flow controllers to pass through a bubbler full of liquid dichloromethane at about -20 °C to obtain 500 ppm. Gases were used as supplied, nitrogen (oxygen free) 99.998% purity, oxygen (99.5 %), propylene (99.95 %) and dichloromethane 99.6 % purity.

FTIR absorption spectroscopy (Bruker Equinox 55) was used to characterize the species present in the plasma product and to determine their concentrations. Measurements were made about 0.4 seconds from the plasma reactor through a multiple-pass optical gas cell (Specac Ltd) with a White-type mirror arrangement producing an optical pathlength of 5.3 meters. The destruction efficiency of dichloromethane has been carried out using the following equation:

\[
\text{DCM \%} = \left( \frac{\text{DCM}_{\text{in}} - \text{DCM}_{\text{out}}}{\text{DCM}_{\text{in}}} \right) * 100 \quad (1)
\]

where DCM\textsubscript{in} and DCM\textsubscript{out} are the inlet and outlet concentration of dichloromethane respectively.
A thermoelectrically cooled, continuous wave distributed feedback quantum cascade laser (QCL) spectrometer (TDL Sensors Ltd) was used to measure nitric oxide from the plasma exhaust. The wavelength of the laser was current-tuned over two absorption peaks at about 1900.52 cm\(^{-1}\) and 1900.075 cm\(^{-1}\) at a QCL temperature of -6.5 °C. An absorption cell of 21 cm pathlength at atmospheric pressure was connected after the plasma reactor. The plasma exhaust then passed to the multiple pass cell used by the FTIR spectrometer[10, 11].

A liquid nitrogen cooled lead salt diode laser (Laser Components GmbH) with a tuning range of 2230 – 2250 cm\(^{-1}\) at an injection current of 220 – 400 mA and about 83 K operating temperature was used to detect N\(_2\)O from the plasma exhaust after the FTIR multiple pass cell[12]. The laser was scanned across R (8) of the v\(_3\) band around 2231 cm\(^{-1}\). A liquid nitrogen cooled InSb photovoltaic (Infra red Associates Inc.) detector connected to a pre-amplifier NSB-1000 (Infrared System Development Corp.) was used to monitor the laser intensity signal. A data acquisition card (ADwin) was used to provide an external laser current modulation at a frequency of about 91 Hz and to transfer the signal to a dedicated PC. A single cell with KBr windows with an optical pathlength of about 13 cm at atmospheric pressure was used for the in-line detection of N\(_2\)O. A Ge etalon with free spectral range (FSR) of 0.0475 cm\(^{-1}\) at 4.55 µm was inserted within the optical path for wavenumber calibration. Two off-axis parabolic mirrors (OAP mirror) were used to collect and collimate the laser beam from the laser head and focus the beam onto the detector. Fig. 2 illustrates the lead salt diode laser arrangements.

**Fig. 2 Experimental setup with lead salt diode laser**

### 3. Results and discussion

#### 3.1. The effect of adding oxygen and propylene on the destruction of dichloromethane:

In these experiments, 500 ppm dichloromethane in a nitrogen gas stream was used. Oxygen concentrations varying between (0 – 21%) were added to the gas stream to investigate the effect of oxygen on the destruction efficiency of dichloromethane. These experiments showed a peak of destruction at about 75% with 3% oxygen. After this point the destruction of DCM decreased with increasing oxygen concentration[10]. The destruction of dichloromethane in non-thermal atmospheric pressure plasma occurs due to electron impact as well as the reaction with excited atoms and molecules such as O(^{3}\text{P}), O(^{1}\text{D}), OH, Cl, N(^{2}\text{P}), N(^{2}\text{S}), N(^{2}\text{D}) and N\(_2\)(A\(^{2}\Sigma^+\))\(_u\)). Increasing the concentration of oxygen in the plasma region leads to the formation of ozone via recombination between the oxygen atoms and molecules. The formation of ozone consumes O(^{3}\text{P}) atoms which cuts the route of destruction of dichloromethane via the reaction with O(^{3}\text{P}) leading to decreased destruction efficiency.

\[
\text{O}^{3}\text{P} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \tag{2}
\]

The effect of adding different concentrations of propylene to the gas stream has also been investigated. The first set of experiments has been carried out using 200 ppm of propylene, whilst 800 ppm was added in the second set.

**Fig.3** shows FTIR spectra for the plasma product of a gas stream of 500 ppm DCM, 800 ppm propylene and nitrogen before and after adding 5% of oxygen. The spectra are taken at atmospheric pressure and room temperature with a resolution of 2 cm\(^{-1}\).

**Fig.3** FTIR spectra for approximately 500 ppm DCM and 800 ppm propylene in nitrogen plasma. (a) without adding oxygen (b) with 5% added oxygen.

Adding propylene to the gas stream leads to the reaction with ozone and the formation of OH and H radicals via the following reactions[13]

\[
\text{O}_3 + \text{CH}_2 \rightarrow \text{HCHO} + \text{CH}_3\text{CHOO} \tag{3}
\]
\[
\text{CH}_3\text{CHOO} \rightarrow \text{CH}_3 + \text{CO} + \text{OH} \tag{4}
\]
\[
\rightarrow \text{CH}_3 + \text{CO}_2 + \text{H} \tag{5}
\]

When 200 ppm of propylene has been added to the gas stream the destruction of dichloromethane decreased significantly. However, adding 800 ppm of propylene improved the destruction of dichloromethane after 7% of added oxygen and did not show a peak of destruction at 3% added oxygen. **Fig.4** shows the destruction of di-
chloromethane at different oxygen and propylene concentrations.

The formation of OH and H radicals increase the destruction of dichloromethane via the following reactions[14, 15]

\[
\begin{align*}
CH_2Cl_2 + OH & \rightarrow CHCl_2 + H_2O \quad (6) \\
CH_2Cl_2 + H & \rightarrow CH_2Cl + HCl \quad (7)
\end{align*}
\]

When adding 800 ppm of propylene an increase of destruction can be seen after about 7 % of added oxygen. However, adding 200 ppm of propylene decreased the destruction of dichloromethane significantly. This still requires further investigation to explain why this is occurring.

The destruction of dichloromethane as well as the concentration of all the species present in the plasma product as a function of oxygen is illustrated in Table 1. It is noticed that small concentrations of CO, CO_2, NO and N_2O were detected via FTIR even before adding oxygen to the gas stream. These are thought to be due to impurities in the gases used.

A significant increase in carbon monoxide and carbon dioxide concentrations after adding 800 ppm to the gas stream has been detected. This is occurring due to the reactions (4) and (5) as well as other chemical routes of decomposition of propylene in the plasma. Fig. 5 presents a comparison of CO and CO_2 concentrations before and after adding propylene to the gas stream.

![Fig. 5 CO and CO_2 concentration before and after adding propylene to a gas stream of 500 ppm DCM, oxygen and nitrogen](image)

**3.2. Mid-infrared quantum cascade laser measurements of nitric oxide:**

A simultaneous study for nitric oxide concentrations in the plasma exhaust as a function of oxygen concentration by both FTIR and QCL has been carried out. In the presence of oxygen in the gas stream, nitric oxide was formed in the plasma via the reaction of oxygen molecules with metastable nitrogen atoms N(^2D) and N(^4S)[16]:

\[
\begin{align*}
N(^2D) + O_2 \rightarrow NO + O \quad (8) \\
N(^4S) + O_2 \rightarrow NO + O \quad (9)
\end{align*}
\]

![Fig. 6 Comparison of NO concentration measured by FTIR and QCL with different oxygen concentrations. A total flow rate of 1 L min\(^{-1}\) with 500 ppm DCM was used.](image)

Table 1. Decomposition efficiency for DCM and the concentrations of all species detected in the plasma exhaust by FTIR as a function of oxygen concentration in a gas stream of 500 ppm DCM, 800 ppm C_3H_6 and nitrogen.

<table>
<thead>
<tr>
<th>O_2 %</th>
<th>DCM %</th>
<th>Concentration / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CINO</td>
</tr>
<tr>
<td>0</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>34</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>42</td>
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<td>68</td>
</tr>
<tr>
<td>21</td>
<td>67</td>
<td>45</td>
</tr>
</tbody>
</table>
was noticed. This thought to be due to further oxidation of NO between the two measuring optical cells for FTIR and QCL.

3.3. Lead salt diode laser measurements of nitrous oxide:
The N$_2$O measurements were carried out using a lead salt diode laser. As well as nitric oxide, nitrous oxide was produced in the plasma in the presence of oxygen. N$_2$O was produced via the reaction of oxygen molecules with excited electronics states of nitrogen $N_2(A^3\Sigma_u^+)$ [17].

$$N_2(A^3\Sigma_u^+) + O \rightarrow N_2O + O \quad (10)$$

A comparison between FTIR and lead salt diode measurements for N$_2$O concentration has been carried out and is shown in Fig. 7.

In addition, detection of carbon monoxide (CO) and carbon dioxide are possible within this laser tuning range.

4. Conclusion

Adding propylene to the gas stream provides two main advantages for the remediation of dichloromethane. Firstly, it reacts with O$_3$ molecules which do not contribute to the destruction of dichloromethane. Secondly the reaction of propylene with ozone, as highlighted in equations 3, 4 and 5, forms OH and H radicals which contribute significantly to the destruction of dichloromethane via reactions 6 and 7. These reactions cause the destruction of dichloromethane to increase with increased oxygen concentration, which is not the case when propylene is not present.

The use of mid-infra red lasers provides a fast response measurement with minimal spectral interferences and high sensitivity, even with short optical pathlengths. However these lasers can be used for the detection of a single species, whilst FTIR measurements provide a wide spectral coverage but with less sensitivity.

Further work is being directed towards time-resolved in-situ measurements on a microsecond timescale via FTIR. Also, a multiple packed bed plasma reactor is being designed to investigate the effect of catalyst on the destruction efficiency of dichloromethane, as well as on the removal of NOx from plasma product.

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References