Experimental study of the reaction of 1,2-dichloroethane in a non-thermal plasma – effect of methane addition

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Abstract: This paper examines the effect of methane on the reaction of 1,2-dichloroethane in a non-thermal plasma in a double dielectric barrier discharge (DBD) reactor, under non oxidative conditions and at atmospheric pressure. Commercially important products such as vinyl chloride and polyvinyl chloride were produced. The addition of CH₄ to the feed stream reduces the concentration of unsaturation in the polymeric material.

Keywords: non-thermal plasma, DBD, dichloroethane, methane, polymer

Introduction

1,2-dichloroethane (EDC) is in mass terms, the highest quantity synthetic chlorinated hydrocarbon produced in the world [1]. An estimated 1.6x10⁷ tons of EDC is produced annually worldwide [1]. The majority of EDC is used in production of vinyl chloride (VC), which is the monomer used in the synthesis of polyvinyl chloride (PVC) [2]. However, EDC is also an environmental pollutant, listed as a priority pollutant by the US EPA and is also identified as a human carcinogen [2]. The vinyl chloride manufacturing process is the primary contributor to EDC emissions, with losses usually occurring during the disposal of heavy end products [3] and leakage of EDC from storage tanks [4]. The heavy ends from the VCM manufacturing process consist of toxic and persistent by-products and their disposal by incineration can lead to release of toxic gases in the atmosphere [5]. The leaks from the storage tanks can cause formation of ‘Dense Non-Aqueous Phase Liquids’ or ‘DNAPL’, which are insoluble in water [6]. The DNAPLs are generally heavier than water and affect groundwater resources. They tend to percolate downward through the aquifer until they reach an impervious layer of rock or a low permeability layer like clay, where they then tend to accumulate [6]. These problems necessitate the need to explore new methods and techniques to treat waste EDC. We examined the reaction of EDC in a DBD reactor to explore the possibility of using a DBD as the basis of an alternative treatment process for chlorinated hydrocarbons. In contrast to the majority of research on EDC in the non thermal plasma field, (which normally examines its oxidative decomposition under reduced pressure in an RF plasma environment [7] [8]), the present research is focussed on the non oxidative treatment of EDC operating at atmospheric pressure using a DBD to beget commercially important products like vinyl chloride and polyvinyl chloride. In this paper, we focus in particular on the use of methane as an additive to the non thermal plasma treatment of EDC using a double dielectric barrier discharge reactor.

Experimental facility and analytical techniques

The experimental setup, including the advantages of the geometry of reactor used in this research, is described in detail elsewhere [9]. The discharge gap between the dielectrics was 4.7 mm. The flow of EDC was regulated by a syringe pump (SAGE 355) and the flow of the carrier gas, argon and CH₄ were controlled by mass flow controllers (Brooks). Argon (and CH₄ as added in some experiments) was mixed with EDC, and the resultant gas mixture was introduced into the plasma reactor. Products were identified and quantified using GC-MS, micro-GC and GC. HCl was quantified using FT-IR. NMR and GPC analysis were performed for polymer characterisation. Analytical techniques are described in detail elsewhere [9].

Results and Discussion

The concentration of EDC and CH₄ in the reactant stream was maintained at constant level of 1.15 % for all experiments, the balance bath gas being argon. The flow rate of the reactant stream was constant at 200 cm³ min⁻¹. All experiments were performed for 63 minutes duration. The values of all voltages noted are peak to peak. The residence time for all the experiments described in this paper was kept constant at 1.12s. The residence time was calculated using the formula [10]:

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Where, \( L \) is the length of electrode, \( F \) is the total volumetric flow rate and \( A \) is the area in the annular space of the reactor.

**EDC and CH\(_4\) conversion:** The conversion of EDC and CH\(_4\) increases with increasing applied voltage, where an increase in applied voltage implies higher input power, increasing the production of reactive species in turn leading to a higher level of conversion.

Table 1. EDC, CH4 conversion with respect to applied voltage

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>EDC conversion (%)</th>
<th>CH(_4) conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>63.3</td>
<td>11.6</td>
</tr>
<tr>
<td>13</td>
<td>73.5</td>
<td>19.1</td>
</tr>
<tr>
<td>14</td>
<td>77.1</td>
<td>21.9</td>
</tr>
<tr>
<td>16</td>
<td>78.6</td>
<td>22.7</td>
</tr>
</tbody>
</table>

The conversion of EDC is much higher than the level of conversion of CH\(_4\) at all the reported voltages (see Table 1). This may be a result of the relative ionisation potential of CH\(_4\) (12.62 eV) [11] which is higher than that of EDC (11.05 eV) [12]. EDC would be activated at a higher rate compared to CH\(_4\), thus leading to a higher level of conversion of EDC:

\[
\text{C}_2\text{H}_4\text{Cl}_2 + e^- \rightarrow \text{C}_2\text{H}_4\text{Cl} + \text{Cl} + e^- \quad (1)
\]

\[
\text{C}_2\text{H}_4\text{Cl}_2 + \text{Ar}^{m} \rightarrow \text{C}_2\text{H}_3\text{Cl}^+ + \text{Ar} + e^- \quad (2)
\]

Mechanistically, reaction (1) represents the interaction between EDC and kinetic electrons capable of cleaving C-Cl bonds [8] while reaction (2) represents the Penning ionisation of EDC i.e. reaction with metastable argon (Ar\(^{m}\)) [13]. Excitation mechanisms of CH\(_4\) are described elsewhere [11]. The increasing level of CH\(_4\) conversion with higher power input is also in accordance with our previous work [11]. When compared with EDC treatment under similar conditions (in absence of CH\(_4\)), the conversion of EDC in the presence of CH\(_4\) is much lower at the respective voltages. For example, EDC conversion at 12 kV and 16 kV in absence of CH\(_4\) is 86.4 % and 87.9 % respectively [9], as compared to 63.3 % and 78.6 % in the presence of CH\(_4\). CH\(_4\) thus has an inhibiting effect on the conversion of EDC, and functions as a neutral species that tends to deactivate excited molecules on collision.

**Yield of vinyl chloride:** The yield of vinyl chloride increases when the applied voltage increases from 12 to 13 kV. Any further increase in applied voltage results in a drop of the yield of vinyl chloride. This increase in yield is attributed to an increase in input power, increasing production of reactive species, leading to formation of more vinyl chloride.

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>Vinyl chloride Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>6.2</td>
</tr>
<tr>
<td>13</td>
<td>11.3</td>
</tr>
<tr>
<td>14</td>
<td>9.99</td>
</tr>
<tr>
<td>16</td>
<td>8.56</td>
</tr>
</tbody>
</table>

Any increase in voltage above 13 kV results in a near quantitative decomposition of vinyl chloride to acetylene and HCl [8] which leads to the dramatic drop in yield of vinyl chloride above 13 kV. A similar phenomenon is observed in the experiments of EDC treatment in absence of CH\(_4\), where it was observed that an input voltage above 16 kV resulted in a decrease in the yield of vinyl chloride [9]. Values for vinyl chloride yield under various reaction conditions are presented in Table 2. The vinyl chloride yield at 12 kV and 16 kV for EDC treatment in similar conditions but in absence of CH\(_4\) is much higher. The yield is 13.6 and 16.8 % respectively at these voltages [9]. This observation is not unexpected, as the conversion of EDC in absence of CH\(_4\) is also higher and thus more vinyl chloride is produced. The reactions which are suggested to contribute to the formation of vinyl chloride as well as its decomposition to HCl and acetylene are provided below [9].

\[
\text{C}_2\text{H}_4\text{Cl}_2 + \text{Cl} \rightarrow \text{C}_2\text{H}_3\text{Cl}_2 + \text{HCl} \quad (3)
\]

\[
\text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3\text{Cl} + \text{Cl} \quad (4)
\]

\[
\text{C}_2\text{H}_3\text{Cl} \rightarrow \text{C}_2\text{H}_2 + \text{HCl} \quad (5)
\]

![Fig.1 FT-IR spectrum of product stream with HCl, CH\(_4\) and EDC reference spectra](image)

Table 2. Vinyl chloride yield with respect to applied voltage
The formation of HCl in the products can be confirmed from the FTIR spectrum given in Fig. 1. The spectrum contains the standard spectra of HCl, CH₄ and EDC for comparison along with the product spectrum.

**Preliminary polymer characterisation:** The polymer obtained in the experiment at 12 kV was characterised by various techniques. Based on ¹H and ¹³C NMR analyses, it was concluded that the polymer obtained in the reaction displayed all the characteristic chemical shifts of polyvinyl chloride (CH₂CHCl)n, along with some evidence of the presence of structural defects such as branching in the polymer. Other NMR techniques such as DEPT 135 and 2-D NMR techniques such as HMQC and COSY were also used in conjunction with ¹H and ¹³C techniques to elucidate the structure of the polymer. The presence of low and high molecular weight species is disclosed by the presence of narrow and broad peaks in the NMR.

![Fig. 2 ¹H NMR of the polymer](image2.png)

The chemical shifts for the main chain repeating group, CH₂ (1.8-2.7 ppm in H and 44.5-47.9 ppm in C) [14-15] and the main chain CHCl repeating group (4.2-4.7 ppm in H and 56-64 ppm in C) [14-15] are observed in the ¹H and ¹³C NMR depicted in Fig. 2 and Fig. 3 respectively. The analysis suggests the polymer has additional functional groups, which might be a part of the branching or even the main polymer chain. For example, the peaks in the region from 3.7-3.9 ppm are characteristic of a CH₂Cl group [9]. This group can be introduced in the main chain as a result of initiator radical attack or it can be a part of branching chain formed during the process of polymerisation.

![Fig. 3 ¹³C NMR of the polymer](image3.png)

. The molecular weights of the polymer have been estimated as $M_n = 49,800$ g mol⁻¹ and $M_w = 107,000$ g mol⁻¹, with a polydispersity index of 2.1. The most significant effect of introducing CH₄ as an additive to the EDC feed is the virtual elimination of unsaturation in the polymer, which was previously observed in polymer (5.6-5.9 ppm in ¹H NMR) [14-15] from EDC treatment in absence of CH₄.

**Product distribution and Mass Balance:** A summary of the product distribution and mass balance is presented in Table 3 for the experiment conducted at 12 kV for 63 min. Although the quantity of products formed varies with respect to input voltage, the product distribution remains virtually unchanged for all the input voltages examined. The product spectrum is similar to that obtained in the non thermal plasma treatment of EDC in absence of CH₄ under similar experimental conditions. The addition of methane has an inhibiting effect on the conversion of EDC, the effect of which can be seen in the comparatively smaller quantity of products being produced when methane is present in the feed stream. Comparing the product spectrum observed in the present study to that of oxidative treatment of EDC, though in absence of CH₄, as reported by Li et al. [8], it is evident that the non-oxidative condition obviates the formation of toxic gases such as COCl₂ and polychlorinated hydrocarbons such as C₂HCl₅, CHCl₃ were not detected in our analysis of the products obtained.
Table 3. Product distribution and mass balance for experiment at 12 kV

<table>
<thead>
<tr>
<th>Species</th>
<th>Feed (mg)</th>
<th>Products in gas Phase</th>
<th>Polymer+Oligomer In (mg)</th>
<th>Out (mg)</th>
<th>Mass Balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed Products in gas Phase</td>
<td>102 %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass (mg)</td>
<td>EDC</td>
<td>CH₄</td>
<td>CH₄+</td>
<td>C₂H₆</td>
<td>C₂H₅Cl</td>
</tr>
<tr>
<td>640</td>
<td>103</td>
<td>91.5</td>
<td>10.7</td>
<td>0.711</td>
<td>2.52</td>
</tr>
</tbody>
</table>

[a: 1,1-dichloroethylene, b: trans-1,2-dichloroethylene, c: 1,1-dichloroethane, d: cis-1,2-dichloroethylene]

**Conclusion:** This paper examines the reaction of EDC in the presence of CH₄, which yields commercially important products like vinyl chloride and polyvinyl chloride. The major advantage of the non oxidative reaction conditions is the notable absence of toxic gases like phosgene in the reaction products mixture. Conversion levels up to 79% of EDC were achieved, and although CH₄ acts as an inhibitor to EDC conversion, the addition of CH₄ has a desirable effect on the polymer produced as it eliminates unsaturation from the polymer backbone chain which is a structural defect observed in the polymer obtained from EDC treatment in absence of CH₄.

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**References**


