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Accepted Manuscript

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PII: S0304-3894(14)00624-4
DOI: http://dx.doi.org/doi:10.1016/j.jhazmat.2014.07.049
Reference: HAZMAT 16142

To appear in: Journal of Hazardous Materials

Received date: 12-6-2014
Revised date: 21-7-2014
Accepted date: 23-7-2014

Please cite this article as: V. Gaikwad, E. Kennedy, J. Mackie, C. Holdsworth, S. Molloy, S. Kundu, M. Stockenhuber, B. Dlugogorski, Reaction of carbon tetrachloride with methane in a non-equilibrium plasma at atmospheric pressure, and characterisation of the polymer thus formed, Journal of Hazardous Materials (2014), http://dx.doi.org/10.1016/j.jhazmat.2014.07.049

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Reaction of carbon tetrachloride with methane in a non-equilibrium plasma at atmospheric pressure, and characterisation of the polymer thus formed

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Abstract

In this paper we focus on the development of a methodology for treatment of carbon tetrachloride utilising a non-equilibrium plasma operating at atmospheric pressure, which is not singularly aimed at destroying carbon tetrachloride but rather at converting it to a non-hazardous, potentially valuable commodity. This method encompasses the reaction of carbon tetrachloride and methane, with argon as a carrier gas, in a quartz dielectric barrier discharge reactor. The reaction is performed under non-oxidative conditions. Possible pathways for formation of major products based on experimental results and supported by quantum chemical calculations are outlined in the paper. We elucidate important parameters such as carbon tetrachloride conversion, product distribution, mass balance and characterise the chlorinated polymer formed in the process.

Keywords: carbon tetrachloride, non-equilibrium plasma, non-oxidative treatment, dielectric barrier discharge, methane.
1. Introduction

Carbon tetrachloride is one of the most hazardous of all chlorinated hydrocarbons. It not only has a detrimental effect on the environment, but the exposure of mammals, including humans, to this chemical can have serious consequences. Toxicity studies on carbon tetrachloride have indicated that the liver is the primary organ affected by exposure and, depending on the dose the damage can be as severe as liver cancer [1]. Repeated exposure to carbon tetrachloride can also have serious adverse effects on the central nervous system [2].

Carbon tetrachloride is also a potent ozone depleting and greenhouse gas. Its ozone depleting potential (ODP) is 1.2, where ODP is defined as the ratio of the impact of a substance on ozone compared to a similar mass of CFC-11. The ozone depletion potential of CFC-11 is generally defined to be 1.0 [3, 4]. Likewise, 100 year Global Warming Potential (GWP) of carbon tetrachloride is 1400, which implies it is 1400 times more potent greenhouse gas than CO₂ [5]. Carbon tetrachloride that is present as an impurity in industrial effluent streams can lead to water contamination if not treated properly. As it has a higher specific gravity than water, if CCl₄ reaches a ground water source it inevitably becomes a severe environmental hazard. For these reasons, it has been a subject of strict regulatory controls [6].

Historically, carbon tetrachloride served as a dry cleaning agent but was later employed as an intermediate chemical in chlorofluorocarbons synthesis [6]. CCl₄ was used a feedstock in the manufacture of insecticides and other chemical intermediates. In 1987, the annual production of carbon tetrachloride was 9.6 x 10⁸ kg, with United States alone accounting for 3.4 x10⁸ kg of it [7]. Currently, the use of carbon tetrachloride is strictly regulated by the Montreal protocol and its involvement in the production of CFC-11 and CFC-12 was banned globally in 2010. However, carbon tetrachloride continues to be used as a feedstock in the production of HFC-245, HFC-236, and HFC-365 [2]. In spite of the regulatory controls, global consumption of carbon tetrachloride in 2011 was estimated to be 1.37 x 10⁸ kg [2]. Given that
such substantial quantities of the material are still in use, it merits the necessity to develop effective methods for carbon tetrachloride treatment. The disposal of carbon tetrachloride, employing traditional high temperature decomposition or oxidation technologies is well studied. Leylegian et al. [8] examined the oxidation kinetics of carbon tetrachloride and developed a detailed elementary reaction mechanism describing the overall reaction. Hawari and co-workers [9] studied a range of related free radical reactions between alkanes and carbon tetrachloride. Shuprov and Tenser [10] investigated the isothermal pyrolysis of carbon tetrachloride and methane, while Bae et al. [11] examined the disposal of carbon tetrachloride through its reaction with methane. In a more recent study on CCl$_4$, Aghsae et al. [12] employed a shock tube for its pyrolysis to derive the kinetics of the pyrolysis process. These authors outlined several possible pathways for CCl$_4$ decomposition with a focus on the role of transient species such as C$_2$Cl$_2$ in its decomposition and the formation of carbonaceous particles.

In contrast to technologies based on thermal decomposition, the literature on the disposal or treatment of carbon tetrachloride using plasma based technologies (both thermal and non-equilibrium) is comparatively limited. Some notable studies in the field are those reported by Indarto et al. [13, 14], Penetrante et al. [15], Rubio et al. [16, 17] and Foeglein et al [18]. Kovacs et al. [19] provided a mechanism for carbon tetrachloride decomposition in a thermal plasma. However, most of these studies were aimed at destruction or complete decomposition of carbon tetrachloride. With the exception of the studies by Kovacs et al and Foeglein et al., most investigations were undertaken under oxidative conditions. These conditions inevitably lead to the production of toxic gases, such as phosgene, as reaction products.

The present study is directed towards exploring the application of a non-equilibrium plasma capable of decomposing carbon tetrachloride and converting it into a benign, and potentially valuable commodity such as a polymer. For this purpose, we have employed a double
dielectric barrier discharge reactor, which uses quartz as dielectric. With the dielectric barrier
discharge technology, a stable non-equilibrium plasma can be effectively maintained during
operation at atmospheric pressure [20]. The introduction of methane in the reaction feed
provides a source of hydrogen and carbon moieties to react with CCl₄ and its decomposition
products. The chlorinated polymer which is generated can potentially be used in various
industrial and commercial applications. The research presented in the current manuscript
discloses that under non-oxidative conditions, the reaction between carbon tetrachloride and
methane yields a chlorinated polymer and a range of gas phase products. Along with a
detailed mass balance in this paper, we propose possible pathways of some of the major gas
phase products, as well as a preliminary characterisation of the polymer formed.

2. Experimental and analytical setup

The reactor used in this study is a double dielectric barrier discharge reactor with quartz as
the dielectric material. A detailed description of the reactor, the experimental setup and
analytical train is provided in our prior publications [21, 22]. Briefly, the two dielectrics are
of cylindrical geometry and are arranged in a concentric manner with the plasma being
generated in the annular gap. This arrangement of the dielectrics creates an annular gap of 4.7
mm and also isolates the electrode from contact with the reactants or the products. The power
supply is purpose built, and capable of delivering an output voltage of 20 kV (peak to peak)
at a frequency of 21.5 kHz. A SAGE 355 syringe pump is utilised to regulate the delivery of
the CCl₄ liquid into the reactor, and argon was used a carrier gas for CCl₄. The feed rates of
argon and methane are controlled via mass flow controllers (Brooks).

The analytical equipment used for gas phase product analysis comprise of a micro-GC
(Varian CP-4900), FT-IR (Perkin Elmer Spectrum 100), GC (Shimadzu GC-17A), GC-MS
(Shimadzu QP 5000), NMR (Bruker Avance 600 MHz) and GPC (Waters GPCV 2000). The
micro-GC and FT-IR are online instruments. Quantitation of all carbon containing gas phase products was achieved using the dedicated micro-GC, while the quantitation of acid gases, i.e. HCl, was performed by an FT-IR equipped with a teflon gas cell. Quantitation and identification of hydrogen was performed on the GC. In addition, FT-IR spectroscopy (Perkin Elmer Spectrum Two) was utilised for determining the functional groups present in the polymer. The reactor temperature measurements were performed using a low thermal mass J-type thermocouple which was in thermal contact with the outer dielectric in the plasma region and coupled with a digital thermometer. A detailed description of the temperature measurement setup is provided in our prior publication [22]. NMR analyses were performed to enable a better understanding of the structure of the polymer formed during the reaction. The molecular weight of the polymer was determined by GPC analysis (Waters GPCV 2000). The instrument was equipped with 3 columns (Waters Styragel HR5E, HR3 and HR0.5) and was calibrated for a 470 to 2,300,000 g mol$^{-1}$ number average molecular weight ($M_n$) range. The GPC instrument was calibrated using polystyrene standards and the polymer molecular weights reported in this paper are relative to polystyrene.

2.1 Experimental parameters examined

For all the experiments conducted in this study, the concentration of CCl$_4$ and methane was maintained at a constant value of 1% for each component, the balance of the feed being argon. The total flow rate of gas into the reactor was 200 cm$^3$ min$^{-1}$ and each experiment continued for 65 min duration. The residence time was estimated to be 2.1 s. All voltages in the paper are peak to peak.

3. Results and discussion

3.1. Conversion of carbon tetrachloride, methane and temperature measurements
Table 1 presents the conversion profile of the feed species with respect to the applied voltage, and the conversion level of CCl₄ and CH₄ with respect to the applied voltage. As is evident from the data, an increase in the applied voltage results in an increase in the conversion level of both, carbon tetrachloride and methane, and increasing the applied voltage elevates the power dissipation in the reactor and plasma system. The increase in power input also leads to an increase in the rate and extent of molecular fragmentation of reactant molecules due to collisions with metastable argon atoms as well as in the collisions with other species formed during the reaction as described later in this paper. A similar trend was reported by Rubio et al. [16, 17] in their study utilising a microwave plasma for CCl₄ destruction, and by Wang et al. [22] on the thermal decomposition of CCl₄. In our previous work we observed similar behaviour in the conversion profile of chlorinated hydrocarbons [24, 25, 21]. Measurements of the temperature of the bulk gas indicate that the plasma substantiates its non-thermal or non-equilibrium behaviour at all the voltages examined in this study, although the temperature increased with increasing applied voltage. The lowest temperature recorded was 117 °C at an applied voltage of 16 kV, where the conversion level of CCl₄ and CH₄ was 19.1 % and 30.6 % respectively. The highest temperature recorded in the present study was 157 °C at an applied voltage of 18 kV, at which the conversion level of CCl₄ was 37 % and that of CH₄ was 44.5 %.

3.2. Product distribution and mass balance

The product distribution and mass balance for the reaction of CCl₄ with methane at an applied voltage of 16 kV are presented in Table 2. An overall mass balance of 98.7 % was obtained for this experiment and includes both, solid and gaseous species, including HCl. It is uncommon to find studies with such exhaustive and complete mass balances for comparison purposes; however, in one such study on CCl₄ decomposition, Foeglein et al, reported a mass balance in excess of 99 % [18]. Identification and quantification of HCl is provided by FT-IR
spectrum analysis; a typical spectrum is presented in Fig. 1. The major carbon-containing gas phase products generated during the reaction are CHCl₃ and C₂Cl₄. To our knowledge, the reaction of CCl₄ and CH₄ in non-equilibrium plasma, employing dielectric barrier discharge, has not been previously reported and hence there is no literature to directly compare the product distribution from the present study. However, there are a number of studies pertaining to the CCl₄ and methane reaction employing the conventional thermal pathway. The research study by Bae et al. [11] examined the reaction of CCl₄ with methane over various catalysts. In their study, they reported formation of products such as CHCl₃, C₂Cl₄, and CH₂Cl₂, similar to the product spectrum observed in the current study. Although the formation of HCl was not specifically described, these authors speculated on the effect HCl had on the MgO catalyst used in the study. Wang et al. [23] in their study of CCl₄ and methane reaction in presence of O₂ and N₂ also reported formation of a range of products which are similar to those detected in the present study, species such as C₂H₂, C₂H₄, CHCl₃, CH₂Cl₂, C₂H₂Cl₂, C₂Cl₄ and HCl were reported. In addition to these species, toxic oxygenated products, including COCl₂ were also reported. However, since oxygen was deliberately excluded from the reaction in the current study, the formation of toxic products such as COCl₂ is not possible. Wang et al. and Bae et al. [23, 11] both reported formation of CH₃Cl during the reaction, but in the present study, CH₃Cl was not detected.

3.3. Reaction mechanism

We present a qualitative reaction mechanism that aims to elucidate the pathways leading to the formation of some of the major products detected during the reaction. An additional CCl₄ experiment was conducted at 16 kV in absence of CH₄. This experiment was targeted towards understanding the mechanism of product formation. The only product observed in this experiment was C₂Cl₄. The conversion of CCl₄ was extremely low, about 5 % under the experimental conditions.
In order to assist with unravelling the mechanism of product formation, quantum chemical calculations have been carried out on ionic and neutral species of importance. The quantum chemical calculations along with the inferences drawn from the CCl$_4$ experiment in absence of methane are described in detail in the later section of this paper. The reaction mechanism includes proposed pathways for argon excitation, CCl$_4$ and CH$_4$ decomposition, formation of CHCl$_3$, C$_2$H$_2$Cl$_2$ (1,1-dichloroethylene), C$_2$HCl$_3$, C$_2$Cl$_4$ and HCl.

Argon excitation

Argon excitation results in formation of argon ions via ionisation and the formation of metastable argon atoms. Metastable argon is denoted by Ar$^m$ and has excitation energy of 11.55 eV for its lowest metastable state [21] [26, 27].

$$\text{Ar} + e^- \rightarrow \text{Ar}^+ + 2e^- \quad (1)$$

$$\text{Ar} + e^- \rightarrow \text{Ar}^m + e^- \quad (2)$$

CCl$_4$ decomposition [8, 19]

$$\text{CCl}_4 + e^- \rightarrow \text{CCl}_3^- + \text{Cl}^- + e^- \quad (3)$$

$$\text{CCl}_4 + \text{H}^- \rightarrow \text{CCl}_3^- + \text{HCl} \quad (4)$$

$$\text{CCl}_3^- + \text{Ar}^m \rightarrow :\text{CCl}_2 + \text{Cl}^- + \text{Ar} \quad (5)$$

In addition to the reactions mentioned above, CCl$_4$ may decompose via other routes such as dissociative ionisation. Our experimental results highlight the absence (below our estimated 10 ppm detection limit) of C$_2$Cl$_6$ in the product stream. This observation leads us to suggest that, it is likely the carbene CCl$_2$ plays a dominant role, in contrast to the CCl$_3$, radical under the prevailing experimental conditions.
The ionisation energy of CCl$_4$ is 11.47 eV [28], less than the excitation energy of the lowest metastable state of argon. This suggests that there is possibility of CCl$_4$ decomposition via Penning ionisation [26], where the reaction results in formation of a radical cation of carbon tetrachloride. The Penning ionisation of CCl$_4$ is represented below [26]

\[
\text{CCl}_4 + \text{Ar}^m \rightleftharpoons \text{CCl}_4^+ + \text{Ar} + e^- \quad (6)
\]

\[
\text{CCl}_4^+ \rightarrow \text{CCl}_3^+ + \text{Cl}^- \quad (7)
\]

\[
\text{CCl}_3^+ + e^- \rightarrow \text{:CCl}_2 + \text{Cl}^- \quad (8)
\]

Reaction (6) is represented as a reversible reaction because CCl$_4$ is known to be re-formed as a product of its own decomposition, at temperatures similar to those encountered in the present study [18]

The major pathways for CH$_4$ decomposition include the following reactions [22];

\[
\text{CH}_4 + e^- \rightarrow \text{CH}_3^- + \text{H}^+ + e^- \quad (9)
\]

\[
\text{CH}_4 + \text{Ar}^m \rightarrow \text{CH}_3^- + \text{H}^+ + \text{Ar} \quad (10)
\]

While CHCl$_3$ formation is likely to occur as follows [8];

\[
\text{:CCl}_2 + \text{HCl} \rightarrow \text{CHCl}_3 \quad (11)
\]

and C$_2$H$_2$Cl$_2$ formation (1,1-dichloroethylene) [8, 19]

\[
\text{CHCl}_3 + e^- \rightarrow \text{CHCl}_2^- + \text{Cl}^- + e^- \quad (12)
\]

\[
\text{CHCl}_2^- + \text{H}^+ \rightarrow \text{CH}_2\text{Cl}_2 \quad (13)
\]
\[ \text{CH}_2\text{Cl}_2 + \text{H}^- \rightarrow \text{CH}_2\text{Cl} + \text{HCl} \]

\[ \text{CH}_2\text{Cl}^+ + :\text{CCl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl}_2 + \text{Cl}^- \]

For \( \text{C}_2\text{HCl}_3 \) formation (trichloroethylene) the following reactions are likely to dominate [24,19]:

\[ :\text{CCl}_2 + \text{CHCl}_2^- \rightarrow \text{C}_2\text{HCl}_3 + \text{Cl}^- \]

\[ \text{C}_2\text{Cl}_4 + \text{H}^- \rightarrow \text{C}_2\text{HCl}_3 + \text{Cl}^- \]

Likewise for \( \text{C}_2\text{Cl}_4 \) (tetrachloroethylene) formation [8]

\[ :\text{CCl}_2 + :\text{CCl}_2 + [\text{M}] \rightarrow \text{C}_2\text{Cl}_4 + [\text{M}] \]

where \( \text{M} \) is a third body

While HCl formation is a result of [8]:

\[ \text{CCl}_4 + \text{H}^- \rightarrow \text{HCl} + \text{CCl}_3^- \]

\[ \text{CHCl}_3 + \text{H}^- \rightarrow \text{HCl} + \text{CHCl}_2^- \]

3.3.1. Quantum Chemical Computations

All computations were carried out with the Gaussian 09 [29] suite of programs. Optimized geometries and zero point vibrational energies (ZPVE) were calculated at the B3LYP/6-31+G(d,p) level of theory. Stationary points located were either minima or transition states (TS) determined by an analysis of the vibrational frequencies wherein a transition structure contains only one imaginary frequency along the specified reaction co-ordinate. Intrinsic
reaction coordinate calculations (IRC) were performed to link reactants and products with their transition state.

From the distribution of products from the CCl₄/CH₄ experiments, it would appear that no products which can be attributed to the presence of CCl₃ radicals have been observed. In particular, we do not observe any C₂Cl₆, which would arise from recombination of two CCl₃ radicals. This is further emphasised in experiments conducted in CCl₄ alone (in the absence of CH₄). Indeed, in the absence of methane, conversions are low and the only product observed is C₂Cl₄ whose presence strongly suggests it arises from recombination of two CCl₂ carbone radicals and that, in the presence of methane, the gaseous product distribution is driven by CCl₂ reactions.

The quantum chemical calculations suggest why CCl₂ carbenes and not CCl₃ radicals determine the product distribution. Optimized structures of the following equilibrium structures were obtained: CCl₄, CCl₄⁺, CCl₃, CCl₃⁺ and CCl₂ together with Cl atoms. Atomic coordinates, zero point energies at electronic energies at 0 K (E₀) are given in Supplementary Information. Ionization potentials of CCl₄ and CCl₃ were evaluated as the difference in E₀ values of neutral molecule and ion. Computed values were 11.1 eV for CCl₄ and 8.2 eV for CCl₃ which are in reasonable agreement with experimental values of 11.5±0.1eV [30] and 8.109±0.005 eV [31].

We assume that initial reaction results from ionization of CCl₄ by electrons and/or metastable Ar atoms to produce CCl₄⁺. Our quantum calculations then show that fission of a Cl atom from CCl₄⁺

\[ \text{CCl}_4^+ \rightarrow \text{CCl}_3^+ + \text{Cl}^- \]  \hspace{1cm} (21)
has an exothermicity of 38.9 kJ/mol at 0 K. Furthermore, we have located a transition state (TS) for this fission and the barrier is only 3.8 kJ/mol at 0 K. (Atomic coordinates, zero point energies and $E_0$ are also shown in Supplementary Information). Thus formation of the CCl$_3^+$ ion should be a very facile process. We then believe that this ion undergoes the well-known process of dissociative electron-ion recombination [32]

$$\text{CCl}_3^+ + e^- \rightarrow \text{:CCl}_2 + \text{Cl}^-$$  \hspace{1cm} (8)

According to our quantum chemical computations, production of both CCl$_2$ and Cl in their respective ground electronic states would release up to 536 kJ/mol of energy at 0 K. There is sufficient energy for formation of these two products in several of their excited states. However, to determine which states of the products are actually favoured, would depend on a detailed knowledge of crossing of potential energy surfaces of CCl$_3^+$ and excited Rydberg surfaces for the neutral CCl$_3$ molecule in the region of the lowest vibration level ($v=0$) of the ion.

3.4 Polymer characterisation

The polymer formed during each experiment was collected by rinsing the annular space of the DBD reactor with tetrahydrofuran (THF). The polymer is readily soluble in THF, indicating that it is non-crosslinked. In subsequent sections of this article, we report the characterisation of the polymer obtained from the experiment performed at 16 kV. The composition of the polymer was determined from elemental analysis as follows (in wt %): 34.8 % carbon, 1.48 % hydrogen and 63.9 % chlorine.

3.4.1. Molecular weight determination

Broadly, the polymer is characterised by the presence of two distinguishable high and low molecular weight fractions. For the high molecular weight fraction, the number average
molecular weight ($M_n$) was determined to be 3280 g mol$^{-1}$ and the weight average molecular weight ($M_w$) to be 5200 g mol$^{-1}$, and the polydispersity index (PDI = $M_w/M_n$) is 1.6. The low molecular fraction has $M_n$ in the range of 986-252 g mol$^{-1}$ and $M_w$ in the range of 1092-298 g mol$^{-1}$, thus having a PDI of 1.1.

3.4.2. NMR analysis

NMR analysis of the polymer formed in this study is complex and challenging. This is mainly because the starting material is not a conventional monomer and, as a result of the method used for its synthesis, there are some striking structural defects in the polymer. In addition, there is a considerable overlap in its spectral features, making unequivocal identification virtually impossible. The NMR analysis reported in this paper was aimed at identifying functional groups present in the polymer based on 1-D ($^1$H, $^{13}$C) and 2-D (HMQC and COSY) NMR techniques and using data available from literature wherever possible. $^1$H NMR analysis is a highly sensitive technique and provides a very good signal to noise ratio as compared to the $^{13}$C technique. Hence some functional groups which are readily identifiable in the in $^1$H spectrum (see Fig. 2) are undetectable in the corresponding $^{13}$C NMR spectrum. However, using the 2-D analysis technique HMQC, it is possible to overcome this limitation, at least partially. The HMQC spectrum displays the carbon/hydrogen (C-H) correlations in the polymer while the COSY technique is used to explore the hydrogen/hydrogen (H-H) correlations and reveals information on structure of the polymer chain. The vertical axis of the HMQC spectrum depicts the $^{13}$C NMR while the horizontal axis depicts the $^1$H NMR spectrum. The correlation between the $^{13}$C and $^1$H is shown by the contours in the figure. The $^{13}$C NMR spectrum from the HMQC in the present study is of a much higher resolution when compared to the conventional $^{13}$C NMR spectrum. The $^{13}$C spectrum is presented in Fig. 3 while the HMQC spectrum is given in Fig. 4.
3.4.2.1. $^1$H NMR analysis

Peaks in the spectrum region between 2-2.7 ppm correspond to CH$_2$ groups that are adjacent to a chlorine containing functional group, while those in proximity of 1.2 ppm correspond to CH$_2$ groups that are not coupled to Cl atoms or to Cl-containing functional groups [21] [33, 34]. The peaks in region of 3.8-4.8 ppm are characteristic of CHCl and CH$_2$Cl groups [21] [33, 34]. The CHCl group constitutes an important component of the main primary chain of the polymer, while the CH$_2$Cl group will likely be a terminating group in the polymer. The data obtained from 2D NMR analyses (COSY and HMQC) indicate the coupling of CHCl and CH$_2$Cl groups to other functional groups. The CH$_2$Cl group is assigned as terminal group because the carbon has only one vacant valency and thus cannot be located within the bulk of the chain, while the carbon in CHCl has two vacant valencies and hence can be located within the bulk of the chain. Peaks in the region of 5-5.5 ppm are indicative of unsaturation in the polymer due to a structural defect such as –CHCl–CH=CHCl [21, 33]. The peaks in the region around 6.5 ppm also indicate the presence of unsaturation, involving a chlorinated species such as –CHCl–CH=CH$_2$. The peaks above 7 ppm tend to indicate presence of aromatic species.

3.4.2.2. $^{13}$C and HMQC NMR spectrum analysis

Signals associated with CH$_2$ groups that are not in proximity of any Cl containing functional groups are observed between 20 and 30 ppm [33], while the peaks between 40 and 45 ppm correspond to CH$_2$ groups adjacent to a chlorine containing functional group [21] [33, 34]. The region between 45-65 ppm may constitute overlapping signal attributable to CH$_2$Cl and CHCl groups; with the CH$_2$Cl group exhibiting a shift between 45 and 50 ppm and the CHCl group between 55 and 65 ppm. The peak at 107 ppm can be attributed to –CHCl–CH=CHCl-type defect [33]. The broad peak from 120 to 140 ppm may be indicative of more than one
species including aromatic structures. Species such as –CHCl-CH=CH\textsubscript{2} are likely to have a signature in this region \[33\].

In the HMQC spectrum, the point A represents C-H correlation between both types of CH\textsubscript{2} groups i.e species not in proximity of Cl (1.2 ppm in H and 20-30 ppm in C) and groups adjacent to a Cl containing functional group (2-2.7 ppm in H and 40-45 ppm in C). Point B represents the C-H correlation in the CH\textsubscript{2}Cl (3.8-4.8 ppm in H and 45-50 ppm in C). Point C represents the correlation in CHCl (3.8-4.8 ppm in H and 55-65 ppm in C). Point D represents the C-H correlation in the –CHCl-CH=CHCl defect in the polymer chain, while point E represents the C-H correlation in a –CHCl-CH=CH\textsubscript{2} type structural defect. The HMQC contours provide a clear picture of the existence of the functional groups that were assigned in the \textsuperscript{1}H and \textsuperscript{13}C spectra. Based on the data from the 1-D and 2-D analysis the polymer chains might have structures such as CH\textsubscript{2}Cl-(CH\textsubscript{2}-CH\textsubscript{2})\textsubscript{n}-CH\textsubscript{2}Cl and -(CH\textsubscript{2}-CHCl)\textsubscript{n}-. It is likely that the polymer chains are branched and have structural defects in addition to those discussed here.

3.4.3. FT-IR analysis

In conjunction with the NMR analyses, FT-IR spectroscopy (see Fig.5) was used to ascertain additional information about the functional groups present in the polymer. The C-Cl stretching vibration is characterised by the broad peak from 650 cm\textsuperscript{-1} to 800 cm\textsuperscript{-1} \[35-38\]. The peaks in the proximity of 920 cm\textsuperscript{-1} and 1035 cm\textsuperscript{-1} are due to a C-H bending vibration from a Cl substituted alkene \[38,39\], most likely from the structural defects, as discussed previously. The peak at 1260 cm\textsuperscript{-1} corresponds to a C-H bending vibration from a chlorinated alkane species such as CHCl \[36-39\], while the peak at 1585 cm\textsuperscript{-1} is indicative of a C=C stretching vibration from an aromatic species. The peak around 1726 cm\textsuperscript{-1} is most likely due to a C=C stretching vibration from a substituted alkene species, but may also be an artefact,
due to residual THF in the polymer [39]. The C-H stretching vibration from CH$_2$ groups exhibits its signature at about 2960 cm$^{-1}$ [35-38] Based on these data, it is evident that the result obtained from the FT-IR analysis is in good agreement with the conclusion drawn from NMR analysis.

Chlorinated polymers with structure similar to that obtained in this study often display good chemical resistance and desirable thermal properties, and as such can potentially find application in a wide variety fields such as in manufacturing of corrosion resistant paints, textile coatings and inks [40]. Their deposition onto surfaces can modify the surface tension thereby changing the wettability and adhesion properties of the surface [41, 42].

4. Conclusion

This paper demonstrates the successful implementation of a non-equilibrium plasma process for treatment of carbon tetrachloride and its conversion to a potentially valuable product by reacting it with methane. Both, carbon tetrachloride and methane increase in conversion level with respect to increasing applied voltage to the plasma system. The non-oxidative conditions prevent formation of hazardous oxygenated products such as CO or COCl$_2$. In addition, a potentially useful chlorinated polymer is obtained in this process. The results for polymer characterisation from NMR (1-D and 2-D) and FT-IR complement each other. The polymer is likely to be branched and to consist of some structural defects. Possible chain structures such as CH$_2$Cl-(CH$_2$-CH$_2$)$_n$-CH$_2$Cl or -(CH$_2$-CHCl)$_n$- have been proposed.

5. Acknowledgements

The authors would like to thank the Australian Research Council for financial support of this project. Vaibhav V. Gaikwad and Sazal K. Kundu are indebted to the Department of Education, Science and Training (DEST) of the Australian Government and the University of Newcastle, Australia for postgraduate research scholarships. We also acknowledge the
assistance of Dr. Monica Rossignoli at School of Environmental and Life Sciences, The University of Newcastle, with the NMR analyses. The authors are thankful to the Micro-Analytical Unit of the Australian National University for their assistance with the elemental analyses of the polymer. Computational support of the National Computational Infrastructure Facility in Canberra, Australia, is also acknowledged

References


Fig. 1. FT-IR spectrum confirming HCl formation

Fig. 2. $^1$H NMR spectrum of the polymer

Fig. 3. $^{13}$C NMR spectrum of the polymer
Fig. 4. HMQC NMR spectrum of the polymer

Fig. 5. FT-IR spectrum of the polymer

Table 1. Conversion level and temperature data

<table>
<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>CCl₄ conversion level (%)</th>
<th>CH₄ conversion level (%)</th>
<th>Temperature (°C)</th>
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</thead>
<tbody>
<tr>
<td>16</td>
<td>19.1</td>
<td>30.6</td>
<td>117</td>
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<tr>
<td>16.5</td>
<td>21.9</td>
<td>35.1</td>
<td>126</td>
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<tr>
<td>17</td>
<td>28.6</td>
<td>36.4</td>
<td>135</td>
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<tr>
<td>17.5</td>
<td>31.5</td>
<td>39.0</td>
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<tr>
<td>18</td>
<td>37</td>
<td>44.5</td>
<td>157</td>
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</table>
Table 2. Product distribution and mass balance

<table>
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<tr>
<th>Feed</th>
<th>Products</th>
<th>Mass In (mg)</th>
<th>Mass Out (mg)</th>
<th>Mass balance (%)</th>
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</thead>
<tbody>
<tr>
<td>CCl₄</td>
<td>CH₄ (unreacted)</td>
<td>891</td>
<td>64.4</td>
<td>984</td>
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<tr>
<td>CH₄</td>
<td>C₂H₄+C₂H₂</td>
<td>92.8</td>
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<td>C₂H₆</td>
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<tr>
<td></td>
<td>C₂H₃Cl</td>
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<tr>
<td></td>
<td>CHCl₃</td>
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<td>25.5</td>
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<tr>
<td></td>
<td>CH₂Cl₂</td>
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<td>1.04</td>
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<tr>
<td></td>
<td>aC₂H₂Cl₂</td>
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<td>4.61</td>
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<td>bC₂H₂Cl₂</td>
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<tr>
<td></td>
<td>cC₂H₂Cl₂</td>
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<td>0.62</td>
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<tr>
<td></td>
<td>HCl</td>
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<td>99.4</td>
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<tr>
<td>CCl₄ (unreacted)</td>
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<tr>
<td>C₂HCl₃</td>
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<tr>
<td>H₂</td>
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<tr>
<td>Oligomer</td>
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</tbody>
</table>

a: 1,1-dichloroethylene, b: trans 1,2-dichloroethylene, c: cis 1,2-dichloroethylene
Highlights

Reaction of carbon tetrachloride with methane in a non-equilibrium plasma at atmospheric pressure, and characterisation of the polymer thus formed

Vaibhav Gaikwad, Eric Kennedy, John Mackie, Clovia Holdsworth, Scott Molloy, Sazal Kundu, Michael Stockenhuber and Bogdan Dlugogorski.

- CCl₄ remediation using non-equilibrium plasma & non-oxidative conditions is proposed
- The reaction mechanism relies on experimental data and quantum chemical analysis
- Comprehensive mass balance for the reaction is provided
- CCl₄ is converted to an environmentally benign and potentially useful polymer
- Characterization of the polymer structure based on NMR and FTIR analyses is presented