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Reaction of dichloromethane under non-oxidative conditions in a dielectric barrier discharge reactor and characterisation of the resultant polymer.

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Abstract

This paper presents the results of dichloromethane (DCM) decomposition to polymers under, utilising dielectric barrier discharge under non-oxidative reaction conditions. The conversion levels, mass balance, reaction mechanism and polymer characterisation in relation to DCM reaction are presented in this paper. Reaction pathways describing the decomposition of DCM and subsequent formation of the major products are outlined. Speculation of the mechanism of formation of CHCl₃ and C₂HCl₃ are supported by quantum chemical calculations. In addition, the effect of introducing methane in the reaction feed on the conversion level of DCM and the polymer structure is also examined in this paper.

Keywords: dichloromethane, non-oxidative treatment, dielectric barrier discharge, polymer characterisation, quantum chemistry.

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1. Introduction

Dichloromethane (DCM) is one of the most versatile and widely used of all chlorinated organic chemicals. It is a popular industrial solvent that finds application in the polymer, paint, pharmaceutical and food industries, for a wide range of uses [1,2]. In addition, it is widely employed as a paint stripper. However, DCM is also a hazardous and toxic chemical, and an estimated 80% of the total production of DCM which is used is ultimately released into the atmosphere [3]. This is mainly due to the dispersive nature of its application and its relatively high vapour pressure.

Human exposure to DCM is most likely to occur through inhalation than other routes such as ingestion. Even short-term exposure to DCM can lead to adverse health effects, most notably the impairment of the central nervous system [3]. The US EPA classifies DCM as a possible carcinogen [4,5]. Given the quantity of DCM released in the atmosphere and the associated hazards, it is imperative to develop improved and novel methodologies for effective remediation of DCM.

Prior investigations on DCM decomposition involved the study of various process parameters and reaction conditions, such as addition of hydrogen/oxygen mixtures, oxidative pyrolysis and the effect of temperature and equivalence ratio, using high temperature technologies [6-8]. In the plasma field, various technologies such as RF, pulsed corona and DBD have been employed to investigate DCM decomposition, using carrier gases such as nitrogen, air and argon under varying experimental conditions [9-15].

However, since majority of these studies are targeted exclusively towards DCM decomposition, its potential for conversion to a value added product such as a polymer remains largely unexplored. Furthermore, the use of O₂ and N₂ in the feed leads to increased probability of formation of toxic by-products such as CO, COCl₂ and HCN during
decomposition. In contrast, the present study focuses on the development of a method that can not only decompose DCM but also convert it to benign and potentially useful polymers. The method encompasses the use of a non-equilibrium plasma generated by using the DBD technique operating at atmospheric pressure. It utilises non-oxidative conditions and argon as carrier gas, which precludes the formation of the aforementioned toxic by-products.

The results from the present research elucidated in the manuscript will indicate that this methodology is capable of DCM decomposition, and results in its conversion into a chlorinated polymer. A detailed mass balance, product distribution and a reaction mechanism that is based on experimental observations and quantum chemical calculations is presented. Characterisation of the chlorinated polymer based on NMR and GPC analyses is also illustrated in the paper. In addition, we investigate the effect of methane addition in the feed on the conversion level of DCM and the structure of the polymer.

2. Experimental and analytical setup

2.1. Experimental setup and parameters

A detailed account of the DBD reactor, experimental and analytical setup is provided in our earlier papers [16,17]. In short, the DBD reactor consists of two quartz dielectrics with cylindrical geometry and arranged in a concentric manner, with the plasma generated in the annular gap. The arrangement of the dielectrics allows for a gap of 4.7 mm and also shields the electrodes from the reactants and corrosive products such as HCl. The custom built power supply is capable of delivering an output up to 20 kV RMS at 21.5 kHz. The delivery of DCM into the reactor is regulated by a syringe pump (SAGE 355). The flow of the carrier gas argon and the additive methane (when required) is controlled using independent mass flow controllers (Brooks).
For all experiments involving the reaction of DCM in absence of methane, the concentration of DCM was retained constant at 1.1 %, the balance being argon. Each experiment was performed for 65 min and the total flow rate of reactants was maintained constant at 200 cm$^3$ min$^{-1}$. The residence time was calculated to be 2.1 s. An experiment to investigate the effect of methane was performed at a representative voltage of 16 kV peak to peak. The experimental conditions for the DCM + CH$_4$ experiment are provided in section 3.5.

### 2.2. Components characterisation

Qualitative and quantitative analyses of gas phase products were accomplished using a range of analytical equipment such as micro-Gas Chromatograph (micro GC-Varian CP-4900), Fourier Transform Infrared spectrometer (FT-IR- Perkin Elmer Spectrum 100), Gas Chromatograph (Shimadzu GC-17A), Gas Chromatograph-Mass Spectrometer (GC-MS-Shimadzu QP 5000). Polymer analyses were performed using a Nuclear Magnetic Radiation spectrometer (NMR- Bruker Avance 600 MHz) for chemical structure and Gel Permeation Chromatography (GPC- Waters GPCV 2000) for molecular weight determination. CDCl$_3$ was used as solvent for NMR analyses, while tetrahydrofuran for GPC. Since the GPC instrument was calibrated for a 470 to 2,300,000 g mol$^{-1}$ number average molecular weight ($M_n$) range using polystyrene standards, all molecular weights reported in this paper are relative to polystyrene. A low thermal mass J-type thermocouple in thermal contact with the outer dielectric, coupled with a digital thermometer was used to estimate the reactor temperature. A detailed description of the temperature measurement setup is provided in one of our prior publications [16].
3. Results and discussion

3.1. Conversion of dichloromethane and temperature measurements

The data pertaining to the effect of applied voltage on the conversion level of dichloromethane is illustrated in Table 1. As is evident, the conversion level of dichloromethane increases with an increase in applied voltage. An increase in applied voltage results in an increased dissipation of power in the reactor and the plasma system in general. Higher power dissipation inevitably results in higher conversion levels due to an increased rate of collision of the reactant molecules with excited species such as metastable argon and high energy kinetic electrons leading to their fragmentation and eventually their conversion to a range of products as mentioned in the subsequent sections of the paper.

Abd Allah et al. and Li et al. reported similar trends in the conversion profile in their investigation of DCM decomposition using DBD and RF plasma reactors respectively [9,15]. Huang et al. too, described a similar effect of applied voltage on the conversion level of DCM in their study using a pulsed corona reactor [11]. In addition, a similar trend in the conversion profile of chlorinated hydrocarbons is observed in our other publications [17–20]. The non-equilibrium nature of the plasma is sustained at all examined voltages in the present study, as indicated by the temperature measurements of the bulk gas. In the present study, the highest conversion level of DCM (~81 %) is attained at an applied voltage of 16 kV and the corresponding bulk gas temperature is 144 °C.

3.2. Product distribution and mass balance

We present the product distribution and mass balance for the experiment performed at 16 kV in Table 2. Some of the major products formed include methane, ethylene, acetylene, 1,1-dichloroethylene, 1,2-dichloroethylene, vinyl chloride, chloroform and trichloroethylene. As indicated in the table, an overall mass balance of 97 % was obtained for this experiment. Qualitatively, the products obtained for experiments for all the voltages examined in this
study were identical. The mass balance encompasses both solid and gaseous products, including acid gases i.e. HCl. Since the reaction is conducted under non-oxidative experimental conditions, formation of toxic gases such as COCl₂ and other oxygenates is precluded.

As mentioned in the earlier sections of the paper, there are several researchers who have examined DCM decomposition, however, their experimental conditions are different from those employed in the present study. This invariably implies that there will be significant differences in the product distribution from the present study compared to data described in the literature.

Penetrante et al. in their study of DCM decomposition in dry air using pulsed corona and electron beam report the formation of oxygenates such as CO and CO₂ as their main products in addition to HCl [10]. Abd Allah et al. investigated DCM decomposition under various conditions in their packed bed DBD reactor with BaTiO₃ beads as the packing material, one of which was using argon as background gas and without oxygen addition. They reported HCl and CCl₄ to be the main products under these conditions [15].

Similarly Li et al. also reported CCl₄ formation while examining DCM decomposition under low pressures (1-5 Torr) using an RF plasma reactor. However, Li et al. also reported formation of products such as HCl, C₂Cl₄, C₂H₂, CHCl₃ and C₂HCl₃, which are similar to those obtained in the present study [9]. Although HCl is a major product observed in our experiments, we detected only trace amounts of CCl₄ in the product stream. Quantitatively, the largest carbon containing gas phase product generated in our experiments is trichloroethylene.

Ho et al. and Srgo et al. examined DCM decomposition via the conventional thermal pathway. There are several similarities in the product distribution reported by these
researchers and in the results obtained in the present study. For instance, the product distribution reported by Srgo et al. included species such as C₂HCl₃, C₂H₃Cl, cis and trans C₂H₂Cl₂, CHCl₃, C₂H₂, C₂H₄ and HCl [6,8].

3.3. Reaction mechanism

In this section of the paper, we qualitatively expound on the possible pathways for argon excitation, DCM decomposition and formation of the significant products as outlined in section 3.2. In addition, we have utilised quantum chemistry calculations employing the Gaussian09 software to abet in understanding the mechanism of formation of chloroform and trichloroethylene, two of the major products obtained during the reaction.

Argon excitation [17,19]

Argon ions and metastable argon can be formed because of argon excitation in the plasma. The formation of both these species is presented in the reactions below

\[ \text{Ar} + e^- \rightarrow \text{Ar}^+ + 2e^- \quad \text{(R1)} \]

\[ \text{Ar} + e^- \rightarrow \text{Ar}^m + e^- \quad \text{(R2)} \]

DCM decomposition [13,15]

\[ \text{CH₂Cl₂} + e^- \rightarrow \text{CH₂Cl}^- + \text{Cl}^- + e^- \quad \text{(R3)} \]

\[ \text{CH₂Cl₂} + e^- \rightarrow \text{CHCl₂}^- + \text{H}^- + e^- \quad \text{(R4)} \]

\[ \text{CH₂Cl₂} + \text{H}^- \rightarrow \text{CH₂Cl}^- + \text{HCl} \quad \text{(R5)} \]

\[ \text{CH₂Cl₂} + \text{H}^- \rightarrow \text{CHCl₂}^- + \text{H₂} \quad \text{(R6)} \]

\[ \text{CH₂Cl₂} + \text{Cl}^- \rightarrow \text{CHCl₂}^- + \text{HCl} \quad \text{(R7)} \]
Since the energy of the lowest metastable state of argon (11.55 eV) is higher than that of the ionisation energy of DCM, Penning ionisation is another pathway through which DCM can decompose (see reactions R8 and R9) [17,19,21,22]. Penning ionisation, followed by the dissociative electron-ion recombination of the CHCl₂⁺ ion, is another pathway through with a CH₂Cl radical can be generated.

\[
\text{CH}_2\text{Cl}_2 + \text{Ar}^m \rightarrow \text{CH}_2\text{Cl}_2^+ + \text{Ar} \quad \text{(R8)}
\]

\[
\text{CH}_2\text{Cl}_2^+ \rightarrow \text{CH}_2\text{Cl}^+ + \text{Cl}' \quad \text{(R9)}
\]

\[
\text{CH}_2\text{Cl}^+ + e^- \rightarrow \text{CH}_2\text{Cl}^- + \text{Cl}' \quad \text{(R10)}
\]

In addition to the aforementioned reactions, dissociative ionisation of DCM can also be a possible pathway for its decomposition.

The formation of **methane** can occur via the following pathways [23] ;

\[
\text{CH}_3\text{Cl}^- + \text{H}' + \text{M} \rightarrow [\text{CH}_3\text{Cl}]^* \quad \text{(R11)}
\]

where M is a third body

\[
[\text{CH}_3\text{Cl}]^* \rightarrow \text{CH}_3^- + \text{Cl}' \quad \text{(R12)}
\]

\[
\text{CH}_3^- + \text{H}' + \text{M} \rightarrow \text{CH}_4 + \text{M} \quad \text{(R13)}
\]

While that of **ethylene** by [8]:

\[
\text{CH}_2\text{Cl}^- + \text{CH}_3^- \rightarrow \text{C}_2\text{H}_4 + \text{HCl} \quad \text{(R14)}
\]

The formation of **1,1-dichloroethylene** is via [7,8];
Likewise that of 1,2-dichloroethylene can occur via [7,8];

\[
\text{CH}_2\text{Cl}^- + \text{CHCl}_2^- + \text{M} \rightarrow [\text{CH}_2\text{ClCHCl}_2]^* \rightarrow \text{CH}_2=\text{CCl}_2 + \text{HCl} \tag{R15}
\]

Vinyl chloride may be produced by the following pathway [7,8,24];

\[
\text{CH}_2\text{Cl}^- + \text{CH}_2\text{Cl}^- + \text{M} \rightarrow [\text{CH}_2\text{ClCH}_2\text{Cl}]^* \rightarrow \text{CH}_2=\text{CHCl} + \text{HCl} \tag{R16}
\]

Further decomposition of vinyl chloride can lead to formation of acetylene by [7]:

\[
\text{CH}_2=\text{CHCl} + e^- \rightarrow \text{C}_2\text{H}_2 + \text{HCl} \tag{R18}
\]

Chloroform formation can be as a result of [25];

\[
\text{CHCl}_2^- + \text{Cl}^- + \text{M} \rightarrow \text{CHCl}_3 \tag{R20}
\]

A qualitative diagrammatic representation of the pathways for DCM decomposition and formation of products is illustrated in Fig. 1.

3.3.1. Quantum chemical calculations

All quantum chemical calculations were performed using the Gaussian09 software [26]. Initial geometry optimisation and zero point vibrational energy (ZPVE) calculations of all molecular structures were achieved at B3LYP/6-31G (2df,p) level of theory. The structures were then subjected to G4MP2 level of theory for increased accuracy of energy calculations. Transition state structures for this study were determined using the Synchronous Transit-Guided Quasi-
Newton (STQN) method, more specifically the QST3 function. The transition state was identified by the presence of a single negative or imaginary vibrational frequency in structure. Intrinsic reaction coordinate (IRC) calculations were performed to link reactants and products to their transition state.

As is evident in reactions R19 and R20, the CHCl₂ radical is critical in formation of both chloroform and trichloroethylene. Hence, the pathway leading to its formation i.e. attack of a Cl⁻ radical on dichloromethane, was studied initially.

\[ \text{CH}_2\text{Cl}_2 + \text{Cl}^- \rightarrow \text{CHCl}_2^- + \text{HCl} \quad (R7) \]

The modredundant option in Gaussian09 was adopted to determine the transition state (TS) for this reaction, wherein the approach of Cl radical towards the H atom in CH₂Cl₂ was examined. This was achieved by arbitrarily fixing the distance between the atoms (H and Cl) and subjecting the structure to an initial optimisation at the previously noted level of theory. This procedure was repeated several times until an optimised TS structure (having removed the modredundant constraint) with the highest possible negative frequency was obtained. The distance between the Cl radical and H atom in this optimised TS structure was 1.49 Å. In addition, the exothermicity of the reaction was estimated to be 37.4 kJ mol⁻¹ at 0 K.

However, the value of barrier for the TS, which was determined from the difference between the \( E_0 \) (ZPVE) of the reactants and the TS, was negative and small (~ -10.4 kJ/mol). Such outcomes are not uncommon in quantum chemistry calculations and generally imply that the reaction is almost barrier-less or has very small activation energy, as is also indicated by data from various experimentally determined values. The NIST database for this particular reaction provides the activation energy value in the range of just 8.37 kJ mol⁻¹ [27]. Overall, the formation of CHCl₃ radical as presented in reaction R7 can be said to be a thermodynamically favourable process.
Reaction R20 depicts the formation of chloroform by the attack of a Cl radical on the CHCl₂ radical. Since a TS state for such reactions is non-existent, calculations to predict the exothermicity of this reaction were undertaken and it was estimated to be 307 kJ mol⁻¹ at 0 K.

As illustrated in reaction R19, two CHCl₂ radicals combine to form [C₂H₂Cl₄], from which HCl is eliminated by chemical activation to eventually form trichloroethylene i.e. C₂HCl₃. Quantum chemical calculations were then focused on HCl elimination, which can proceed via two pathways, i.e., either by H and Cl elimination from the same carbon atom (ipso elimination) or from adjacent carbon atoms. Based on quantum chemical modelling, a potential energy diagram for two pathways of reaction R19 was developed and is presented in Fig. 2. The details pertaining to the quantum chemical modelling and calculations are provided in the subsequent paragraphs.

The TS structure for both types of elimination has been determined, however, the TS structure for ipso elimination did not yield a useful IRC. Nonetheless, by using a very small step size, one or two points on both products’ side and on reactants’ side were computed before failure of the simulation. However, this did not enable identification of the products or reactants linked to the TS. The reasons for this can be explained from relaxed potential energy (PE) scans going forward and reverse, depicted in Fig. 3 and 4 respectively.

The very shallow minimum at about 1.85 Å is the ‘product’ associated with the TS. It is a complex between the carbene and HCl and can be fully optimised. With further increase in C-H distance the potential energy monotonically rises (with no discrete barrier) to the completely dissociated carbene and HCl. Decreasing the C-H distance initially leads to a very slight drop in PE from that of the TS until it dramatically drops at around 1.36 Å (see Fig. 4). Examination of the structure at this point showed that the Cl atom had now bonded to the C
atom (of the carbene) and further decrease in the C-H distance leads to the reactant. With this abnormal PE variation, an IRC cannot succeed.

There was no such issue involved for determination of TS structure for H and Cl elimination from adjacent carbon atoms, and the IRC was able to link the reactants and products with the TS. In addition, it was determined that this type of elimination is energetically more favourable since its TS barrier (calculated at 0 K) was 256 kJ mol\(^{-1}\) compared to 279 kJ mol\(^{-1}\) for the initial H and Cl elimination in ipso route (TS\(_2\)).

Furthermore, as depicted in Fig. 2, post the initial H and Cl elimination, the ipso route involves another transition state (TS\(_3\)), for Cl transfer in the carbene leading to the C\(_2\)HCl\(_3\) formation. Thus, formation of trichloroethylene (C\(_2\)HCl\(_3\)) will proceed via H and Cl elimination from adjacent carbon atoms rather than the ipso route. Overall, the reaction has an exothermicity of 282 kJ mol\(^{-1}\) at 0 K.

### 3.4. Polymer characterisation

The polymer deposited during reaction was collected by rinsing the annular space of the DBD reactor with tetrahydrofuran (THF) after each experiment. The polymer was found to be readily soluble in THF, thus indicating that it is non-crosslinked. Characterisation of the polymer obtained from the experiment at 16 kV is reported in the following sections of this paper.

#### 3.4.1. Molecular weight determination

In general, GPC analyses indicate that the polymer is constituted of high and low molecular weight fractions. The high molecular weight fraction has a number average molecular weight \((M_n)\) of 3340 g mol\(^{-1}\) and a weight average molecular weight \((M_w)\) of 4780, thereby having a polydispersity index \((\text{PDI} = M_w/M_n)\) of 1.4. For the low molecular weight fraction, \(M_n\) is 811 g mol\(^{-1}\) and \(M_w\) is 885 g mol\(^{-1}\), thus making its PDI = 1.1.
3.4.2. NMR analyses

The aim of NMR analyses presented in this paper is to identify the functional groups that constitute the polymer and postulate possible chain structures. The analyses are based on data obtained from 1-D and 2-D NMR experiments, as well as being based on information available in literature.

There are various factors that contribute to the complexity of NMR analyses of this polymer and make it a challenging task. The starting material is not a typical monomer, and the nature of the plasma process introduces structural defects such as branching and unsaturation in the polymer. In addition, there exists considerable overlap in the spectral features from different functional groups. The combination of these factors makes definite identification of peaks in the NMR virtually impossible. The $^1$H NMR is a more sensitive technique compared to the $^{13}$C, DEPT and DEPTQ 135 techniques, and has a substantially higher signal to noise ratio. Thus some functional groups that register a signal in the $^1$H NMR spectrum might have a very weak or at times no signal in the $^{13}$C, DEPT and DEPTQ 135 spectra. This limitation can be overcome to some extent by utilising the 2-D NMR (HMQC) techniques.

In the present research, the DEPT and DEPTQ 135 NMR spectra are utilised for analyses and representation purposes since they are of a better resolution and provide similar information to the $^{13}$C NMR spectrum. The DEPT and DEPTQ spectra are essentially similar in that they allow distinguishing between $\text{CH}_2$ and $\text{CH/CH}_2$ peaks. The only difference is that the DEPTQ NMR is capable of displaying quaternary carbons, unlike the DEPT.

3.4.2.1. $^1$H NMR analysis

The $^1$H NMR spectrum of the polymer is depicted in Fig. 5. The peaks in the range 1.2-2.2 ppm chemical shift are characteristic of $\text{CH}_2$ groups in the polymer. However, the peaks in the region from 1.2-1.5 ppm are attributed to $\text{CH}_2$ groups that are not in proximity of any Cl
containing functional group, while those in the region from 1.8-2.2 ppm belong to CH₂ groups adjacent to or in proximity of a Cl-containing functional group [17,19,28–30].

The spectral region between 3-5 ppm chemical shift constitutes a peak which is a composite of a considerable overlap between two functional groups i.e. CH₂Cl and CHCl. The peaks in the region of 5.2-5.5 ppm suggest formation of a structural defect such as CHCl-CH=CHCl, while the peaks around 6.5 ppm can be attributed to another structural defect such as CHCl-CH=CH₂ [17,19,29]. Peaks above 7 ppm tend to indicate formation of aromatic structures.

### 3.4.2.2. DEPT, DEPTQ and HMQC NMR analyses

In the DEPT and DEPTQ spectra, the CH₂ groups are oriented above the axis, while the CH and CH₃ groups are oriented below. In addition, for DEPTQ spectrum, the quaternary carbons (QC) will be oriented above the axis. The CH₂ groups which are not in proximity of any Cl-containing functional group register their signal between 21-28 ppm chemical shift [19,29].

The broad peaks, in the region of 40-45 ppm, correspond to the CH₂ groups in proximity of a Cl-containing functional group. The spectral region between 57-70 ppm consists of signals from both CHCl and CH₂Cl groups. The sharp signal around 67 ppm is most likely from CH₂Cl groups; however, there is a possibility that it might also contain a signature from some residual THF in the polymer. The peaks in the 57-70 ppm region oriented below the axis are attributed to CHCl groups from main chain as well as a branch [17,19,29,30]. The peaks in the region 105-107 ppm can be attributed to the structural defect CHCl-CH=CHCl, while the broad peak between 125-127 ppm can be related to another structural defect CHCl-CH=CH₂ [19,29].

The broad peak at 135 ppm (evident in DEPTQ spectrum) suggests the presence of quaternary carbons. This can be inferred from the observation that, this peak is displayed in only the DEPTQ spectrum (and ^13C) but not in the DEPT spectrum. In addition, the HMQC
spectrum too does not show any correlation between C and H signals in this range. The HMQC spectrum (see Fig. 8) displays the correlation between C and H in the form of contours and supplements the data obtained from 1-D NMR analyses. The $^{13}$C and $^1$H NMR spectra are represented on the vertical and horizontal axes respectively.

Contour A represents the C-H correlation between CH$_2$ groups that are not in proximity of a Cl-containing functional group (21-28 ppm in $^{13}$C and 1.2-1.5 ppm in $^1$H) as well as the CH$_2$ groups adjacent to a Cl-containing functional group (40-45 ppm in 13C and 1.8-2.2 ppm in 1H). C-H correlation between CHCl groups (57-60 ppm in $^{13}$C and 3-5 ppm in $^1$H) and CH$_2$Cl groups (~ 67 ppm in $^{13}$C and 3-5 ppm in $^1$H) is reflected in contour B. The contours C and D represent the C-H correlation between the structural defects –CHCl-CH=CHCl and CHCl-CH=CH$_2$ respectively.

Based on the inferences drawn from the 1-D and 2-D NMR analysis, the polymer can be said to be a random block co-polymer comprising more than one chain structure such as – (CH$_2$-CH$_2$)- and -(CH$_2$-CHCl)-. The polymer is likely to have additional structural defects to those mentioned before and will also be branched.

3.5. Effect of methane addition

The experiment of methane addition was performed mainly to investigate its effect on the polymer structure as in one of our previous publications, the addition of methane resulted in the elimination of structural defects such as unsaturation in the polymer [18]. Moreover, the effect of methane addition on DCM conversion level and product distribution was also studied as a part of the present investigation. This experiment was conducted at an applied voltage of 16 kV and the concentrations of methane and DCM in the feed were maintained constant at 0.9 % or 9000 ppm. Since the change in feed concentration is likely to affect the conversion, an additional experiment with only DCM in feed and 0.9 % feed concentration
was conducted at 16 kV. This experiment served as a better benchmark to compare the effect of methane addition. The conversion level of DCM obtained in this case was 86.1 %.

Addition of methane to the feed results in a drop in the conversion level of DCM. The conversion level of DCM in presence of methane is 79.9 %, which is much lower than the 86.1 % obtained in its absence. This effect can be attributed to the fact that the net reactant concentration has now increased; thereby increasing the probability of collision of species such as excited DCM molecules and argon metastable atoms with neutral methane molecules. The resultant collisional relaxation of such excited species will invariably amount to decreased conversion levels. The methane conversion level for this experiment was 30.3 %. Qualitatively, the product distribution obtained from DCM reaction in presence and absence of methane is identical.

The polymer structure remains virtually unchanged as compared to the polymer obtained in absence of methane. The $^1$H spectrum indicates that the polymer from DCM+CH$_4$ experiments consists of the same characteristic functional groups as the polymer obtained from only DCM experiments. The only difference in polymer due to methane addition is the introduction of additional CH$_3$ groups, seen around 0.1 ppm in the $^1$H spectrum (see Fig. 9). Thus, unlike in the case of our previous publication pertaining to dichloroethane [18], the addition of methane did not result in any specific advantages for DCM experiments.

4. Conclusion
The decomposition of DCM, and its conversion to a chlorinated polymer, was achieved by using a dielectric barrier discharge reactor. The chlorinated polymer is proposed to have chain structures comprising of -(CH$_2$-CH$_2$)$_n$- and -(CH$_2$-CHCl)$_m$-, along with structural defects such as unsaturation and branching. Non-oxidative reaction conditions prevented the formation of toxic oxygenates such as COCl$_2$ or CO. When the DCM concentration in the
feed was 1.1 %, the highest conversion level achieved was 80.9 % at an applied voltage of 16 kV. Addition of methane was not advantageous to the reaction chemistry or the polymer structure and had an inhibiting effect on the conversion of DCM. Quantum chemical calculations indicated the most probable pathways for decomposition of DCM as well as for formation of two of the major products i.e. CHCl₃ and C₂HCl₃.

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6. References


Figure 1. Diagrammatic representation of the reaction mechanism

Figure 2. Potential energy diagram for reaction R17

TS₁: Transition state for H and Cl elimination from adjacent carbon atoms
TS₂: Transition state for ipso elimination of H and Cl
#: Carbene + HCl complex
TS₃: Transition state for Cl transfer in the carbene
Figure 3. PE scan for increase in C-H bond length

Figure 4. PE scan for decrease in C-H bond length

Figure 5. $^1$H NMR spectrum of the polymer obtained from DCM experiment at 16 kV
Figure 6. DEPT135 NMR spectrum of the polymer obtained from DCM experiment at 16 kV

Figure 7. DEPTQ135 NMR spectrum of the polymer obtained from DCM experiment at 16 kV
Figure 8. HMQC NMR spectrum of the polymer obtained from DCM experiment at 16 kV

Figure 9. Comparison of $^1$H NMR spectra of the polymers obtained from DCM and DCM+CH$_4$ experiments at 16 kV
Table 1. Conversion level and reactor wall temperature data

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<thead>
<tr>
<th>Applied voltage (kV)</th>
<th>Conversion level (%)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>62.5</td>
<td>88.1</td>
</tr>
<tr>
<td>13</td>
<td>64.4</td>
<td>101</td>
</tr>
<tr>
<td>14</td>
<td>67.8</td>
<td>118</td>
</tr>
<tr>
<td>15</td>
<td>69.2</td>
<td>133</td>
</tr>
<tr>
<td>16</td>
<td>80.8</td>
<td>144</td>
</tr>
</tbody>
</table>
Table 2. Product distribution and mass balance data for the experiment at 16 kV

<table>
<thead>
<tr>
<th>Feed</th>
<th>Products</th>
<th>Mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>Mass (mg)</td>
<td>Species</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>542</td>
<td>CH₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₄+C₂H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂H₃Cl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₃Cl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CHCl₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>aC₂H₂Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>bC₂H₂Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cC₂H₂Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2-C₂H₄Cl₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,1,2-C₂H₃Cl₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂HCl₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CCl₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C₂Cl₄</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₂Cl₂(unreacted)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polymer +</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Oligomer</td>
</tr>
</tbody>
</table>

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

Reaction of dichloromethane under non-oxidative conditions in a dielectric barrier discharge reactor and characterisation of the resultant polymer.

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

- Non-oxidative treatment of DCM is explored using non-equilibrium plasma
- The reaction mechanism relies on experimental data and quantum chemical analysis
- Comprehensive mass balance for the reaction is provided
- DCM is converted to an environmentally benign and potentially useful polymer
- Characterization of the polymer structure based on NMR analyses is presented