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

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HIGHLIGHTS

- 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.
- Characterisation of the polymer structure based on NMR analyses is presented.

ARTICLE INFO

ABSTRACT

This paper presents the results of dichloromethane (DCM) decomposition to polymers 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 $CHCl_3$ and C_2HCl_3 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.

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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

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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 destruction, its potential for conversion to a value added product such as a polymer remains largely unexplored. Furthermore, the use of O_2 and N_2 in the feed leads to increased probability of formation of toxic by-products such as CO, $COCl_2$ 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 the absence of methane, the concentration of DCM was maintained 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 was 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 Resonance 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 analy-

ses, 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 previous 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 ($\sim$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 $COCl_2$ 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 reported the formation of oxygenates such as CO and CO_2 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 $BaTiO_3$ beads as the packing material, one of which was using argon as background gas and without oxygen addition. They reported HCl and CCl_4 to be the main products under these conditions [15].