



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



Vaibhav Gaikwad^a, Eric Kennedy^{a,*}, John Mackie^a, Clovia Holdsworth^b, Scott Molloy^a, Szal Kundu^a, Michael Stockenhuber^a, Bogdan Dlugogorski^c

^a Process Safety and Environment Protection Research Group, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

^b Centre for Organic Electronics, Chemistry Building, School of Environmental and Life Sciences, University of Newcastle, Callaghan, NSW 2308, Australia

^c School of Engineering and Information Technology, Murdoch University, Murdoch, WA 6150, Australia

HIGHLIGHTS

- CCl₄ remediation using non-equilibrium plasma and 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.
- Characterisation of the polymer structure based on NMR and FTIR analyses is presented.

ARTICLE INFO

Article history:

Received 12 June 2014

Received in revised form 21 July 2014

Accepted 23 July 2014

Available online 1 August 2014

Keywords:

Carbon tetrachloride

Non-equilibrium plasma

Non-oxidative treatment

Dielectric barrier discharge

Methane

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.

© 2014 Elsevier B.V. All rights reserved.

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, the 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

* Corresponding author. Tel.: +61 4985 4422.

E-mail address: Eric.Kennedy@newcastle.edu.au (E. Kennedy).

chlorofluorocarbons synthesis [6]. CCl_4 was used a feedstock in the manufacture of insecticides and other chemical intermediates. In 1987, the annual production of carbon tetrachloride was 9.6×10^8 kg, with United States alone accounting for roughly 3.4×10^8 kg [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 1.37×10^8 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 , Aghsaee 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_2Cl_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 CCl_4 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 electrodes 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 CCl_4 liquid into the reactor, and argon is used a carrier gas for CCl_4 . 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 470–2,300,000 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 $200 \text{ cm}^3 \text{ min}^{-1}$ 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 CCl_4 and CH_4 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,

Table 1
Conversion level and temperature data.

Applied voltage (kV)	CCl_4 conversion level (%)	CH_4 conversion level (%)	Temperature ($^{\circ}\text{C}$)
16	19.1	30.6	117
16.5	21.9	35.1	126
17	28.6	36.4	135
17.5	31.5	39.0	154
18	37	44.5	157

Download English Version:

<https://daneshyari.com/en/article/6971246>

Download Persian Version:

<https://daneshyari.com/article/6971246>

[Daneshyari.com](https://daneshyari.com)