Research Article

Michał Młotek*, Ewelina Reda, Krzysztof Krawczyk

Conversion of tetrachloromethane in large scale gliding discharge reactor

Abstract: Gliding discharge plasma in a large scale reactor was used for decomposition of tetrachloromethane. The new power supply system based on a power inverter was used. The conversion of CCl₄ was investigated in air at normal pressure. The reactor was made of a quartz-glass tube 60 mm in diameter and contained three converging electrodes 140 mm long. Effects of the initial CCl₄ concentration, gas flow rate and discharge power on CCl₄ conversion have been studied. The conversion of CCl₄ was high in all cases reaching a maximum of 90%. The conversion of tetrachloromethane decreased with increasing initial concentration of CCl₄ in the reaction mixture. Changing the gas flow rate from 1000 Nl h⁻¹ to 1400 Nl h⁻¹ decreased the conversion of tetrachloromethane.

Keywords: plasma, tetrachloromethane, gliding discharge, large scale reactor

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1 Introduction

Volatile organic compounds (VOCs) are particularly problematic for the natural environment. Most of them are harmful to human health and they are responsible for the so-called greenhouse effect and smog [1,2]. Some volatile organic compounds are very stable. Due to low reactivity, some VOCs decompose much later finding their way to high atmospheric layers and are suspected to destroy the stratospheric ozone.

The most important methods for decomposition of toxic compounds under industrial conditions comprise catalytic decomposition, combustion, adsorption, condensation, and biological methods.

In recent years, many studies have been carried out on the application of new technologies for limiting VOC emission. Among such methods is the non-equilibrium plasma generated by glow, corona, gliding, barrier, microwave and surface discharges [2-5]. The energy of electrons in non-equilibrium plasma is much higher than that of molecules. This fact is of particular importance since even processes of high activation energy can be proceed at a high rate at low temperatures.

Studies on the decomposition of tetrachloromethane [4-8] in gliding and pulsed corona discharges have shown that the process is very complex. The discharges give rise to a large number of consecutive reactions in which many intermediate compounds are also involved. The first step of reaction in the air-CCl₄ system consists of the attachment of an electron resulting in the formation of CCl₃ radical and chloride anion Cl⁻ or radical chloride Cl⁻ (Reactions 1,2) [9].

\[
\begin{align*}
\text{CCl}_4 + e & \rightarrow \text{CCl}_3 + \text{Cl}^- \\
\text{CCl}_4 + e & \rightarrow \text{CCl}_3 + \text{Cl} + e
\end{align*}
\]

The conversion of CCl₄ may also be the result of simple dissociation at very high temperatures, which generates Cl radical or Cl₂ [10,11].

\[
\begin{align*}
\text{CCl}_4 & \rightarrow \text{CCl}_3 + \text{Cl} \\
\text{CCl}_4 + \text{Cl} & \rightarrow \text{CCl}_3 + \text{Cl}_2
\end{align*}
\]

In the presence of oxygen, CCl₃ and CCl₄ radicals may react in different ways [12-18].

\[
\begin{align*}
\text{O}^1(\text{D}) + \text{CCl}_3 & \rightarrow \text{CCl}_3 + \text{ClO} \\
\text{CCl}_4 + O_2 + \text{(M)} & \rightarrow \text{CCl}_3O + O + \text{(M)} \\
\text{CCl}_3O + O_2 & \rightarrow \text{COCl}_2 + \text{ClO}
\end{align*}
\]

*Corresponding author: Michał Młotek: Faculty of Chemistry, Warsaw University of Technology, 00-664 Warszawa, Poland, E-mail: Ewelina Reda, Krzysztof Krawczyk: Faculty of Chemistry, Warsaw University of Technology, 00-664 Warszawa, Poland

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ClO + O(3P) → ClO₂ (8)

CCl₃ + O → COCl₂ + Cl (9)

Further stages of the transformations observed in the plasma medium consist of reactions of the radicals with oxidizing agents, which lead to formation of molecules such as CO₂, Cl₂, phosgene or higher halogenated hydrocarbons [11,15].

2CCl₃ → C₂Cl₆ (10)

2CCl₃ → C₂Cl₄ + 2Cl (11)

2CCl₂ → C₂Cl₂ + 2Cl (12)

Phosgene (COCl₂) is one of the unwanted toxic products of these reactions. However, it is readily destroyed by the reactions described hereinafter [13,8,14,16].

COCl₂ + e → CO + Cl₂⁻ (13)

COCl₂ + e → COCl + Cl⁻ (14)

COCl₂ + Cl → COCl + Cl₂ (15)

Two reactions that produce COCl are followed by reactions that produce Cl₂ and CO. COCl is also easily oxidized to CO₂ in the presence of oxygen [15,16].

COCl + Cl → CO + Cl₂ (16)

COCl + M → CO + Cl + M (17)

COCl + O → CO₂ + Cl (18) [19]

CCl₃ radicals may result in CCl₄ regeneration [6,11,12, 14 - 16].

CCl₃ + Cl + (M) → CCl₄ + (M) (19)

CCl₃ + Cl₂ → CCl₄ + Cl (20)

In the presence of nitrogen, NOCl may be generated.

N +O₂ → NO + O (21)

NO + Cl → NOCl (22)

The decomposition of NOCl is a very fast reaction in plasma in the presence of Cl or O radicals.

This mechanism shows that the CCl₄ decomposition in the plasma environment is very complex.

The gliding discharge is one of the electroplasma methods tested in recent years for the decomposition of toxic and particularly stable chemical substances [20,21]. The method is especially attractive due to the high quantity of radicals produced. Another advantage of this method is the possibility of using gas mixtures containing solid particles with considerable humidity, and to perform the process at high flow rates. Previous studies were carried out mainly in laboratory scale in two electrode reactors with low gas flow rate. The following sections present results of our studies on the kinetics of decomposition of tetrachloromethane in a large scale gliding discharge reactor.

2 Experimental procedure

Tetrachloromethane was used as a model compound for the study because of the simplicity and the stability of its structure. The conversion of CCl₄ was investigated in air at normal pressure in a large scale gliding discharge reactor. For this study, a 3-phase gliding discharge reactor (Fig. 1) with three electrodes was used. The reactor was made of a quartz-glass tube of 60 mm in diameter and contained three diverging electrodes 140 mm long.

Electrodes were placed in a reaction chamber with ceramic lining. The reactor was powered by a 50 Hz system (Fig. 2). The new power supply [22] applied for the presented gliding discharge reactor was manufactured by Ertec-Poland. The electric power supplied to the gliding reactor was in the range of 1 – 4 kW and it was measured by an energy meter. The active power supplied was measured in the low voltage (primary) circuit.

Gas stream was introduced through the capillary nozzle, located below the electrodes, at the bottom and flowed upward between electrodes across the plasma zone. The gas temperature measured at the vessel axis over the upper ends of the electrodes reached 200–560°C depending on the discharge power (Tables 1 and 2).

During the decomposition of tetrachloromethane in air, the following concentrations of tetrachloromethane were used: 0.04%, 0.09%, 0.15%, and 0.29% for 1000 Nl h⁻¹ and 1400 Nl h⁻¹ gas flow rate.

The content of CCl₃ in the gas mixture before and after the reaction was determined by gas chromatography using Chrompack CP-9002 with Carbowax 20M column and
FID detector. The content of NO was determined using an industrial photometer *URAS 10P*. The content of chlorine and phosgene was determined by iodometric and acid-base titration methods respectively. Chlorine, trace amounts of COCl₂ and nitric oxide observed in the outlet gas were compounds which could be removed from gas by absorption in appropriate absorbents or by catalytic reduction with ammonia. No chlorinated organic compounds other than CCl₄ have been found in off gases. The highest overall CCl₄ conversion of about 90% was observed.

**3 Results and discussion**

Parameters and definitions:

\[ W_{0}[\text{CCl}_4], \text{[mol h}^{-1}] \] – tetrachloromethane flow rate at the inlet

\[ W[\text{CCl}_4], \text{[mol h}^{-1}] \] – tetrachloromethane flow rate at the outlet

\[ P \text{[W]} \] – power computed from energy meter,

\[ x = \frac{W_{0}[\text{CCl}_4] - W[\text{CCl}_4]}{W_{0}[\text{CCl}_4]}. \]

\[ S_v = \frac{P \times 3.6}{W[\text{CCl}_4]}. \]

\[ \text{UEC} = \frac{P \times 3.6}{X \times W_{0}[\text{CCl}_4]}. \]

The results of CCl₄ conversion for gas flow 1000 NL h⁻¹ and 1400 NL h⁻¹ are given in Tables 1 and 2.

For 1000 NL h⁻¹, the increase of CCl₄ conversion with increase of discharge power was observed (Fig. 3a, Table 1). In the studied range of initial concentration of tetrachloromethane, the relationship between electric power and conversion of CCl₄ did not significantly depend on the initial concentration of CCl₄. The conversion depended only on electric power. The effect of the specific energy on the CCl₄ conversions was studied. Using a gas flow rate of 1000 NL h⁻¹, the highest conversion was observed for higher initial concentrations of CCl₄ (0.15 and 0.29% by vol). For the lower initial concentration of CCl₄, lower conversion was observed (Fig. 4a). For a gas flow rate of 1400 NL h⁻¹, the highest conversion for the lowest initial concentration of CCl₄ (0.04%) was observed. However, it was obtained for a much higher specific energy. It should be noted that for the specific energy in the range of 40 - 480 MJ mol⁻¹, the conversion of CCl₄ was 40 - 70% for all studied CCl₄ initial concentrations (Fig. 4b) For a gas flow rate of 1400 NL h⁻¹, the effect of the initial concentration of tetrachloromethane on conversion was observed. An increase of the initial concentration of CCl₄ decreased tetrachloromethane conversion (Fig. 3b, Table 2).

The results of the study of CCl₄ decomposition in a large scale gliding discharge reactor showed that when the gas flow rate of 1000 NL h⁻¹ was used, the highest energy consumption was obtained with an initial concentration of 0.04%. Higher initial concentrations of CCl₄ caused lower energy consumption in the process of CCl₄ decomposition (Fig. 3a,5b, Table 1).

Using a gas flow rate of 1400 NL h⁻¹, the highest energy consumption was obtained for an initial concentration of CCl₄ of 0.04%. With higher concentrations of CCl₄ (0.29%), lower energy consumption was observed (Fig. 6a,6b, Table 2). The increase in the initial concentration of tetrachloromethane in the inlet gas caused a reduction in unit energy consumption. The study of the effects of the initial concentration of CCl₄ on its conversion, for 1500 W and gas flow rate of 1000 and 1400 NL h⁻¹, showed that it was preferable to conduct the process when the gas flow rate was lower.
For 1000 Nl h⁻¹, higher conversions of tetrachloromethane was achieved (Fig. 7a). With an increase of the initial concentration of tetrachloromethane in both cases, a different character of relation was observed. For 1400 Nl h⁻¹, conversions of CCl₄ decreased with the increase of CCl₄ initial concentration. The inverse relation was observed when lower gas flow rate was used. Comparing the process of tetrachloromethane conversion, in which the gas flow rate of 1000 Nl h⁻¹ and 1400 Nl h⁻¹ and electric power to 1500 W was used, this process should be carried out with gas flow rate of 1000 Nl h⁻¹ for economical reasons (Figs. 7a,7b).

![Figure 3: Effect of the discharge power on overall conversion of CCl₄. a: Gas flow rate of 1000 Nl h⁻¹, b: Gas flow rate of 1400 Nl h⁻¹.](image)

| Initial conc. of CCl₄ | Power [W] | T [°C] | x | Eᵣ [MJ mol⁻¹] | UEC [MJ mol⁻¹] |
|----------------------|-----------|--------|---|---------------|---------------|
| 0.04%                | 909       | 300    | 0.54 | 167.80       | 308.40        |
|                      | 1154      | 300    | 0.63 | 212.98       | 340.02        |
|                      | 1429      | 420    | 0.63 | 263.69       | 416.68        |
| 0.09%                | 1250      | 330    | 0.62 | 115.37       | 186.47        |
|                      | 1364      | 380    | 0.68 | 125.85       | 184.99        |
|                      | 1579      | 420    | 0.67 | 145.72       | 216.56        |
| 0.15%                | 1648      | 440    | 0.79 | 91.28        | 116.16        |
|                      | 2190      | 500    | 0.77 | 121.26       | 157.72        |
|                      | 3000      | 530    | 0.89 | 166.13       | 186.92        |
| 0.29%                | 1714      | 460    | 0.70 | 47.46        | 67.34         |
|                      | 2068      | 440    | 0.71 | 57.25        | 80.51         |
|                      | 2234      | 540    | 0.77 | 61.85        | 79.84         |
|                      | 3052      | 560    | 0.80 | 84.50        | 105.51        |

| Initial conc. of CCl₄ | Power [W] | T [°C] | x | Eᵣ [MJ mol⁻¹] | UEC [MJ mol⁻¹] |
|----------------------|-----------|--------|---|---------------|---------------|
| 0.04%                | 1267      | 200    | 0.56 | 167.03       | 298.13        |
|                      | 1526      | 300    | 0.61 | 201.19       | 332.07        |
|                      | 2830      | 410    | 0.69 | 373.15       | 542.48        |
|                      | 3614      | 430    | 0.71 | 476.55       | 670.34        |
| 0.09%                | 1429      | 260    | 0.43 | 94.18        | 221.26        |
|                      | 1807      | 260    | 0.47 | 119.14       | 254.69        |
|                      | 2500      | 280    | 0.50 | 164.81       | 330.72        |
|                      | 3297      | 320    | 0.50 | 217.33       | 434.61        |
| 0.15%                | 1500      | 290    | 0.40 | 59.33        | 149.09        |
|                      | 2143      | 310    | 0.55 | 84.76        | 153.53        |
|                      | 2500      | 330    | 0.58 | 98.88        | 171.04        |
|                      | 3947      | 340    | 0.57 | 156.13       | 276.28        |
| 0.29%                | 1765      | 280    | 0.36 | 34.90        | 96.69         |
|                      | 2239      | 320    | 0.43 | 44.28        | 103.35        |
|                      | 2857      | 320    | 0.48 | 56.51        | 117.84        |
|                      | 4000      | 390    | 0.48 | 79.11        | 165.71        |
Figure 4: Effect of the specific energy on overall conversion of tetrachloromethane. Gas flow rate of (a) 1000 Nl h⁻¹, (b) 1400 Nl h⁻¹.

Figure 5: Effect of power (a) and the specific energy (b) on unit energy consumption. Gas flow rate of 1000 Nl h⁻¹.

Figure 6: Effect of power (a) and the specific energy (b) on unit energy consumption. Gas flow rate of 1400 Nl h⁻¹.

Figure 7: Effect of the initial concentration of tetrachloromethane on CC₄ conversion (a) and on unit energy consumption (b). Gas flow rate of 1000 and 1400 Nl h⁻¹. Electric power of 1500 W.
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NOCl was not observed in the outlet gas. Kinetic calculations have shown that the reaction rate constant of formation of NOCl (Reaction 22) is lower than the one of decomposition (Reactions 23, 24). Those are $k_{22} ≈ 5 \times 10^{-14}$, $k_{23} ≈ 8 \times 10^{-11}$, $k_{24} ≈ 6 \times 10^{-11}$ [cm$^3$ molecule$^{-1}$ s$^{-1}$] respectively. The content of NO in outlet gas was about 1.2%. NO could be formed directly from elements or by NOCl decomposition (Reactions 23, 24). Catalytic reduction with ammonia is the most common method of removal of NO. In order to avoid obtaining NO, the decomposition of chlorinated compounds can be conducted in inert gas in the circuit system.

4 Conclusions

The tetrachloromethane conversion preferably occurred at a gas flow rate of 1000 Nl/h containing high initial concentrations of CCl$_4$. Unit energy consumption increased with the decrease of initial concentration of tetrachloromethane. The process of CCl$_4$ was energetically favorable for higher initial concentrations of tetrachloromethane. For gas flow rate of 1400 Nl/h, the highest conversion occurred for the lowest initial concentration of CCl$_4$ but only at appropriately high energies. An increase in the initial concentration of CCl$_4$ caused the decrease of energy consumption in the process of tetrachloromethane decomposition. Higher conversion and a lower consumption of energy for gas flow rate of 1000 Nl h$^{-1}$ were observed.

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