ORGANIC POLLUTANTS TREATMENT IN GAS PHASE BY USING ELECTRON BEAM GENERATED NON-THERMAL PLASMA REACTOR

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Introduction

Chlorinated organic compounds, which are emitted from fossil–fuel power stations1, waste incinerators2, chemical factories, etc. are very harmful to the environment and human health. Recent studies reported that chlorinated benzenes or phenols are suspected as precursors for dioxins emission2. In Poland3, dioxins emission from some medical waste incinerators was very high, their concentration in stack gas was up to 32 ng TEQ/m3 [Total toxic equivalency (TEQ), it is a term which describes all the products summed to give a single 2,3,7,8-TCDD equivalent]. Dioxins are relatively chemical inert and demonstrate long life time in environment, therefore they are called persistent organic pollutants (POPs). They are transported by air and are deposited on the surfaces of the soil, water and plants. They can accumulate in the fat of food-producing animals and are transferred into fish, meat, eggs, and diary products5.

Chlorinated aromatic organic compounds (Cl-AOCs) removal from gas phase has been studied in the recent years. In general, there are two ways to realize Cl-AOCs removal, one is reduction Cl-AOCs to their parent hydrocarbons by using metal catalysts6-9, the other is oxidation Cl-AOCs to the corresponding aldehydes and other oxidation products9. Electron beam (EB) process is a promising technology for removal of trace low concentration organic compounds contained in gas mixture by oxidation process. Decomposition of aliphatic chlorinated compounds10 and aromatic hydrocarbons11-12, such as benzene, toluene, xylene etc., have been extensively studied by using this technology and promising results were achieved.

Dioxin’s treatment using EB technology was reported, over 90% dioxins was removed from the waste off gases13,14. Decomposition of chlorobenzene15-16 in gas phase by using electron beam technology have been studied, aliphatic oxygenates were found as gaseous products of chlorobenzene degradation15. No work has been reported concerning 4-chlorotoluene (4-CTO) removal in gas phase. Dechlorination of chlorotoluene in aqueous solution were studied, toluene17 and benzene18 were reported as dechlorination products.

Since the Stockholm Convention on POPs entered into force on 17 May 2004, dioxins emission from off-gases were monitored and their concentration should be lower than 0.1ng-TEQ/m3. In this work, we studied destruction of 4-chlorotoluene in air mixture under electron beam generated plasma reactor, its decomposition efficiency was compared with 1,4-dichlorobenzene (1,4-DCB), the decomposition products of 4-chlorotoluene were identified in the aim of obtain better knowledge to diminish dioxins formation in the waste incineration process using this technology.

Experimental

2.1. Preparation model gas containing 4-chlorotoluene

The set up for preparation model gas of 4-chlorotoluene was similar to that described in our previous work19. 4-Chlorotoluene model gas was prepared by bubbling synthesized air (≥ 99.995 % purity; 21 % O2, N2 as balance gas; CO2 ≤ 1 ppm, BOC gas company, Poland) into liquid 4-chlorotoluene (4-chlorotoluene, Purity 98 % without further purification, provided by Sigma-Aldrich company, Germany). A temperature of 4-chlorotoluene was set to be 21 °C with a water bath (type LW, manufactured by WSL Bytom company, Poland). The concentration of 4-chlorotoluene in the model gas was adjusted by controlling air flow rate by means of valve and rotameters. The model gas of 4-chlorotoluene was introduced into four connected Pyrex glass reactors by parallel connection. When concentration in gas reactors became constant, the glass reactors were sealed with the stop-cocks. The water concentrations in the model gas mixture were measured by a HM141 humidity and temperature indicator (Vaisala company, Finland). Water concentration in gas mixture was 56 ppm. Experiments were carried out at ambient temperature condition and 1 bar atmospheric pressure.
2.2. An accelerator applied for generating plasma generation in the reactor

A pulsed electron beam accelerator ILU-6 (2.0 MeV max, 20 kW max) was used to generate plasma inside glass reactors. Irradiation set up can be referred to our previous work. Pyrex glass reactors were put under scan horn of the accelerator for irradiation. Irradiation conditions were described as follows: 2 Hz (pulse repetition rate), 2 MeV (energy) and 60 mA (pulse current). The absorbed dose (kGy, 1 kGy = 1 kJ kg\(^{-1}\)) inside glass reactors was measured by a cellulose triacetate film dosimeter.

2.3. Analytical methods

Concentrations of 4-chlorotoluene (4-CTO) before and after irradiation contained in reaction vessels were measured by a gas chromatography (GC-17A, Shimadzu Corporation, Japan) equipped with a flame ionizing detector (GC-FID). A capillary column (Supercowax\(^{TM}\)-10, 30 m \(\times\) 0.32 mm \(\times\) 0.25 \(\mu\)m, Supelco Company, USA) was used. Stock solutions of 4-chlorotoluene (200 \(\mu\)g ml\(^{-1}\) in methanol, AccuStandard company, USA) were used for preparation calibration curve. Analytical conditions of 4-chlorotoluene were given as follows: column temperature was kept at 40 °C for 1 min, then increased to 160 °C at 20 °C min\(^{-1}\); flow rate of He as carrier gas was 47 mL min\(^{-1}\); injector temperature was 100 °C and detector temperature was 250 °C; Injection mode was split, split ratio was 40:1. The injection volume of 4-chlorotoluene air mixture was 1 mL.

By-products analysis after electron beam irradiation was carried out in this work. Organic compounds contained in reaction vessels (before and after irradiation) were adsorbed by coconut charcoal adsorbents (SKC Inc, USA) and then were desorbed by 5 mL ethyl acetate (HPLC purity, provided by J.K.Baker, USA). The solid-free extract solution was obtained by using syringe filters and then was concentrated to approximately 0.3 mL by using a micro-extractor under continuously blowing high purity N\(_2\) (99.995 % purity, BOC gas company, Poland). A Gas Chromatography equipped with a mass detector (GCMS-QP 5050A, Shimadzu Corporation, Japan) was used to identify by-products, a HP-5MS column (30 m \(\times\) 0.25 mm \(\times\) 0.25 \(\mu\)m, Agilent technologies Incorporation, USA) was used. The oven was held at 40 °C for 1 minute, then programmed at 20 °C min\(^{-1}\) to 290 °C, held for 1 minute. Total flow rate of carrier gas helium was set to be 15 mL min\(^{-1}\). Injector temperature was 280 °C and detector temperature was 280 °C. The injection volume of the concentrated extract solution was 1 \(\mu\)L with split mode, split ratio was 12:1. Electron impact ionization mode of MS was applied, 70 eV energy was used.

2.4. Dose dependence of removal efficiency or decomposition efficiency

In electron beam process, it is very important to consider energy consumption for degradation of pollutants, how much energy (unit: kJ) is consumed/absorbed to decompose amount of pollutants in the base gas (unit: kg). Energy absorbed by per amount of gas is defined as a term of dose, unit is kGy.

1 kGy = 1 kJ kg\(^{-1}\).

Removal efficiency or decomposition efficiency of organic pollutants is defined as R: \(R = \frac{C_0 - C_i}{C_0}\)

where \(C_0\) is initial concentration of organic pollutants, unit: ppm (v/v), \(C_i\) is concentration of organic pollutants at i kGy absorbed dose, unit: ppm (v/v).

Results and discussion

3.1. 4-Chlorotoluene decomposition

Decomposition of 4-chlorotoluene at different initial concentrations versus dose in an air mixture was studied in an electron beam generated non-thermal plasma reactor and results are presented in fig. 1. Water vapor concentration in an air mixture was 58 ppm (v/v). It can be seen that concentration of 4-chlorotoluene decreases with the absorbed energy increasing for the initial concentration of 4-chlorotoluene being 15.39 ppm, 51.93 ppm and 95.30 ppm, respectively. About 46.8 % 4-chlorotoluene is decomposed at 15 kGy for the initial concentration of 4-chlorotoluene being 95.30 ppm, and 69.39 % 4-chlorotoluene is decomposed at 15 kGy for the initial concentration of 4-chlorotoluene being 15.39 ppm.

3.2. Gaseous products

A GC-MS spectrum of gas mixture of 4-chlorotoluene with air after electron beam irradiation is presented in fig. 2. A compound eluted at retention time (RT) 7.590 min of the GC-MS spectrum, which was eluted at the same retention time of GC-MS spectrum obtained for 4-chlorotoluene/air mixture before irradiation, was identified as 4-chlorotoluene, its mass spectrum is shown in fig. 3. Two compounds eluted at retention time 4.91 min and 12.50 min, respectively, were identified by our carefully comparing their mass spectrums with reference mass spectrums provided by WILEY7N2 library. The mass spectrums of these two compounds and their reference mass spectrums are presented in fig. 4a, 4b & 5a, 5b, respectively. They are chlorobenzene (\(C_6H_5Cl\), RT = 4.910 min) and 4-chlorobenzaldehyde (\(C_6H_4ClCHO\)).
RT = 12.502 min), respectively. There is one unknown compound eluted at 8.9 min.

3.3. Mechanism of 4-chlorotoluene decomposition

When fast electrons from electron beams are absorbed in the carrier gas, they cause ionization and excitation process of nitrogen, oxygen and H$_2$O molecules in the carrier gas and generate non-thermal plasma reactor. Primary species and secondary electrons are formed. The secondary electrons are thermalized fast within 1 ns in air at 1 bar pressure. The G-values (molecules /100eV) of main primary species are simplified as follows:

\[ 4.43 \text{N}_2 \rightarrow 0.29 \text{N}_2^* + 0.885 \text{N}_2(3^2D) + 0.295 \text{N}_2(3^2P) + 1.87 \text{N} + 2.27 \text{N}_2^+ + 0.69 \text{N}_2^+ + 2.96 \text{e} \]

\[ 5.377 \text{O}_2 \rightarrow 0.077 \text{O}_2^* + 2.25 \text{O}_2(1^1D) + 2.8 \text{O} + 0.18 (\text{O}^*) + 2.07 \text{O}_2^+ + 1.23 \text{O}^+ + 3.3 \text{e} \]

\[ 7.33 \text{H}_2\text{O} \rightarrow 0.51 \text{H}_2 + 0.46 \text{O}_2(3^1P) + 4.25 \text{OH} + 4.15 \text{H} + 1.99 (\text{H}_2\text{O}^+) + 0.01 (\text{H}_3^+) + 0.57 (\text{OH}^+) + 0.67 (\text{H}^+) + 0.06 (\text{O}^+) + 3.3 \text{e} \]

These primary species and thermalized secondary electrons formed initiate and cause decomposition of 4-chlorotoluene. In our previous work we carried out computer simulation of decomposition 1,4-dichlorobenzene in air mixture in an electron beam generated non-thermal reactor and learnt that two reaction pathways are play main roles for 1,4-DCB decomposition. Because chemical structure of 4-chlorotoluene (ClC$_6$H$_4$CH$_3$) is very similar to 1,4-DCB (ClC$_6$H$_4$Cl), decomposition mechanism of 4-chlorotoluene can be referred to 1,4-DCB, two main reaction pathways are given below (3.3.1 −3.3.2).

3.3.1. Positive charge and negative charge transfer reaction pathways

As described above, when the carrier gas air is ionized by electron beam, positive ions (such as N$_2^+$, O$_2^+$ etc.) and secondary electrons etc. are formed. These positives ions transfer energy rapidly to the species with the lowest ionization energy (IE)$^{27}$. The IE of 4-chlorotoluene is 8.69 ± 0.03 eV, it is smaller than the IE of N$_2^+$, O$_2^+$ etc. Some important positive charge transfer reactions causing 4-chlorotoluene decomposition are proposed as follows (R1 − R3):

\[ \text{O}_2^+ + \text{C}_6\text{H}_4\text{Cl} = [\text{C}_6\text{H}_4\text{Cl}^+] + \text{O}_2 \quad (R1) \]
O₂(H₂O)⁺ + C₇H₇Cl = [C₇H₇Cl⁺] + O₂ + H₂O (R2)

N₂ + C₇H₇Cl = [C₇H₇Cl⁺] + N₂ (R3)

where O₂(H₂O)⁺ in reaction R2 might be formed by a following reaction R4:

O₂ + H₂O + M = O₂(H₂O)⁺ + M (R4)

M is any specie in the gas phase.

Negative charge transfer reactions causing 4-chlorotoluene decomposition are given below (R5, R6):

e + O₂ + M = O₂⁻ + M (R5)

O₂⁻ + C₇H₇Cl = [C₇H₇Cl⁻] + O₂ (R6)

[C₇H₇Cl⁻] and [C₇H₇Cl⁺] formed from above reactions might go neutralization through ionic recombination reactions (R7, R8):

[C₇H₇Cl⁻] + A⁻ = C₇H₇Cl + A (R7)

[C₇H₇Cl⁺] + A⁻ = C₇H₇Cl + A (R8)

A⁻, A⁺ are any negative ions and positives ions in the gas phase, respectively.

3.3.2. OH radicals decomposition pathway

Based on our previous work21, we learn that OH radical decomposition reaction pathway plays main role for 1,4-DCB decomposition. During irradiation of low-humidity air with 4-chlorotoluene mixtures, OH radicals are formed. The reaction of OH radicals with 4-chlorotoluene at room temperature, 1 bar pressure is possible H atom elimination reaction23 from –CH₃ group of 4-chlorotoluene based on by-products which were identified by the GC-MS analysis. From information of by-products identified, we learn only –CH₃ function group of 4-chlorotoluene involving in reaction with OH radical. The ClC₆H₄CH₂⁺ radical produced in reaction (R9) may be decomposed by the reaction with oxygen molecules in the carrier gas as follows:

OH + ClC₆H₄CH₂⁺ = H₂O + ClC₆H₄CH₂ (R9)

ClC₆H₄CH₂⁺ + O₂ = ClC₆H₄CH₂(O₂)⁺ (R10)

2 ClC₆H₄CH₂(O₂)⁺ = 2 ClC₆H₄CH₂O⁺ + O₂ (R11)

ClC₆H₄CH₂O⁺ + O₂ = ClC₆H₄CHO + HO₂ (R12)

ClC₆H₄CHO⁻ = C₆H₅Cl + HCO (R13)

HCO + O₂ = CO + HO₂ k = 5.0·10⁻¹² (R14)

OH + CO = CO₂ + H k = 2.4·10⁻¹³ (R15)

4-chlorobenzaldehyde (ClC₆H₄CHO) and chlorobenzene (C₆H₅Cl), which were identified as by-products in the experimental work, are might be formed from reactions R12 and R13, respectively.

In fact, mechanism of 4-chlorotoluene decomposition is very complicated, many reactions are involved, we just listed most important reactions we supposed.

3.4. 4-Chlorotoluene and 1,4-dichlorobenzene decomposition comparison

In order to find out whether functional group has influence on decomposition efficiency of aromatic compounds or not, we compared decomposition of 4-chlorotoluene (ClC₆H₄CH₃) with decomposition of 1,4-dichlorobenzene (ClC₆H₄Cl) in air mixture in an electron beam generated non-thermal plasma reactor. The experimental results are presented in fig. 6. It is found that decomposition efficiency of these two compounds is almost same at the same absorbed dose for the same range initial concentration of 4-chlorotoluene and 1,4-dichlorobenzene. Here should mention that water vapor concentration in 1,4-dichlorobenzene/air mixture was 170 ppm, this value is higher than 58 ppm water vapor in 4-chlorotoluene/air mixture.
Conclusions

4-Chlorotoluene in air can be decomposed in an electron beam generated non-thermal plasma reactor, decomposition efficiency of 4-chlorotoluene is similar to 1,4-dichlorobenzene, about 46.8% 4-chlorotoluene is decomposed at 15 kGy for the initial concentration of 4-chlorotoluene being 95.30 ppm. Chlorobenzene and 4-chlorobenzaldehyde are identified as by-products.

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REFERENCES