



Toluene and 4-chlorotoluene decomposition in air mixture in electron beam generated non-thermal plasma reactor and their by-products identification



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ARTICLE INFO

Available online 18 May 2013

Keywords:

Electron beam
Toluene
4-Chlorotoluene
Off-gases purification
Mechanism of VOCs degradation

ABSTRACT

Degradation of toluene and 4-chlorotoluene in air mixture was studied by using electron beam generated plasma reactor. It was found that removal efficiency of toluene and 4-chlorotoluene was influenced by radiation dose, i.e. energy deposited in the gas, and their initial concentration. The by-products formed as a result of degradation of toluene or 4-chlorotoluene under electron beam radiation were identified. The mechanism of their degradation was proposed. $\cdot\text{OH}$ radicals play a main role in degradation process of toluene or 4-chlorotoluene. For degradation of 4-chlorotoluene, reaction of $\cdot\text{OH}$ radicals with 4-chlorotoluene by hydrogen abstraction from the methyl group, followed by peroxy radical formation, is a main reaction pathway. 4-chlorobenzaldehyde and 4-chlorobenzyl alcohol are formed according to the Russel-mechanism. For degradation of toluene, reaction pathway of $\cdot\text{OH}$ radicals with toluene by hydrogen abstraction from the methyl group plays an important role. Besides it, there are the other two important reaction pathways. One is reaction of $\cdot\text{OH}$ radical addition and H atom abstraction from benzene ring; the other is $\cdot\text{OH}$ -adduct reaction. Cresol, nitrotoluene and ring cleavage products are formed from these two reaction pathways. Since Cl is more electronegative than H, H atom abstraction from $-\text{CH}_3$ by $\cdot\text{OH}$ radicals from toluene ($\text{C}_6\text{H}_4\text{CH}_3$) is easier than from 4-chlorotoluene ($\text{ClC}_6\text{H}_4\text{CH}_3$), this may explain why the decomposition efficiency of toluene is slightly higher than that of 4-chlorotoluene in an air mixture under EB radiation.

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1. Introduction

Volatile organic compounds (VOCs), which are emitted from fossil-fuel power stations [1], waste incinerators [2], chemical factories, etc. are very harmful to the environment and human health. They can cause ozone depletion in stratosphere and ozone formation in troposphere. In urbanized area, VOCs are emitted into atmosphere by mainly anthropogenic sources. About 40% of ozone produced photo chemically might be a result of aromatic compounds emission, mainly toluene [3]. Industrial uses of toluene include this compound dealkylation to benzene, and the disproportionation to a mixture of benzene and xylene. Toluene can be used as an octane number booster in gasoline fuels used in internal combustion engines [4]. 4-chlorotoluene, which is emitted from waste incinerators [5], is used as the substrate in manufacturing of organic reagents, e.g. in pharmaceutical industry [6]. Recent studies reported that chlorinated benzenes or phenols were suspected as the precursors for dioxins formation [7]. In Poland [8], 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 chemically 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 dairy products [9]. Therefore, toluene and 4-chlorotoluene must be treated before they are discharged into atmosphere.

VOCs removal from gas phase has been studied in recent years [10,11]. Toluene destruction by using advanced oxidation technologies (AOTs), such as UV/ozone [10], non-thermal plasma (NTP) [11,12], NTP combined with catalyst [13], electron beam (EB) [14–16] and electron beam combined with catalyst technology [17–20], has been studied extensively in recent years. Benzaldehyde, aerosols and benzene were reported as by-products of toluene degradation [14,17–19]. Han et al. [14] also identified acetone, dipropyl 1,2-benzenedicarboxylic acid, nitromethane and trace amount of hexane as by-products of decomposition of toluene. Dechlorination of chlorobenzene in air with electron beam was studied by Hirota et al. [21,22]. Concerning 4-chlorotoluene (4-CT), a few works have been reported for its removal in gas phase [23]. Dechlorination of 4-chlorotoluene in aqueous solution was studied, toluene [24] and benzene [25] were reported as dechlorination products.

Radical species formed from AOTs can oxidatively destroy organic pollutants in gas phase. EB technology is one of the most promising among AOTs. It can simultaneously decompose multiple pollutants in gas phase at relatively low energy consumption [26]. Toluene and

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4-chlorotoluene, commonly used as intermediates of organic reagents in industry, have similar chemical structure. We selected these two compounds as representative non-chlorinated and chlorinated aromatic organic compounds. In our previous work, we studied decomposition efficiency of toluene and 4-chlorotoluene as a function of dose in air mixture under electron beam radiation, and a few products were identified [23,27]. In order to obtain a better insight of decomposition mechanism of toluene and 4-chlorotoluene in air mixture under EB radiation, it is very important to know their degradation by-products. In this work we mainly focused on identification of by-products formed as a result of degradation of toluene and 4-chlorotoluene under EB radiation. Their decomposition efficiency was compared with each other, and their degradation mechanism was proposed.

2. Experimental

2.1. Preparation of gas mixture of 4-chlorotoluene and toluene

The set-up for preparation of gas mixture of 4-chlorotoluene was similar to the set-up for preparation of gas mixture of 1,4-dichlorobenzene described in our previous work [28]. 4-chlorotoluene gas mixture was prepared by bubbling synthesized air ($\geq 99.995\%$ purity; $21\% \text{O}_2$, N_2 as balance gas; $\text{CO}_2 \leq 1$ ppm, provided by BOC gas company, Poland) into liquid 4-chlorotoluene (4-chlorotoluene, Purity 98% without further purification, provided by Sigma-Aldrich company, Germany). The 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 gas mixture was adjusted by controlling air flow rate by means of valve and rotameters. The gas mixture of 4-chlorotoluene was introduced into four connected Pyrex glass reactors by parallel connections. Active carbon adsorbents were connected at the outlet of glass reactors before the gas discharged into the atmosphere. When concentration of toluene or 4-chlorotoluene inside the glass reactors became constant, the glass reactors were sealed with the stopcocks. The water concentration in the model gas mixture was measured by a HM141 humidity and temperature indicator (Vaisala company, Finland). Water concentration in gas mixture was 56 ppm (v/v). Experiments were carried out at ambient temperature condition and 1 bar atmospheric pressure.

We used the similar set-up and conditions for preparation of toluene gas mixture. Liquid toluene (toluene, purity $>99.7\%$ without further purification, provided by J. K. Baker, USA) was used.

2.2. An accelerator applied for 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 [28]. 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, $1 \text{ kGy} = 1 \text{ kJ/kg}$) inside the glass reactors was measured by a cellulose triacetate (CTA) film dosimeter and was calculated on the basis of an empirical formula giving correlation between $\text{dose}_{(\text{CTA})}$ and $\text{dose}_{(\text{N}_2\text{O})}$ [29]:

$$\text{dose}_{(\text{N}_2\text{O})} = 2.897 * \text{dose}_{(\text{CTA})} \quad (1)$$

2.3. Analytical methods

Concentrations of toluene and 4-chlorotoluene (4-CT) in the air contained the glass reactors before and after irradiation were measured by a gas chromatography (GC-17A, Shimadzu Corporation,

Japan) equipped with a flame ionizing detector (GC-FID). A capillary column (SupercowaxTM-10, $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$, Supelco Company, USA) was used. Stock solution of 4-chlorotoluene ($200 \mu\text{g/ml}$ in methanol, AccuStandard company, USA) and stock solution of AK-101AA-ARO ($2000 \mu\text{g/ml}$ in methanol, AccuStandard Company, USA) containing toluene were used for preparation of calibration curves. Parameters for 4-chlorotoluene and toluene analysis were following: column temperature was kept at 40°C for 1 min, then increased to 160°C at 20°C/min ; injector temperature was 100°C and detector temperature was 250°C ; injection mode was split, split ratio was 40:1. The injection volume of toluene and 4-chlorotoluene air mixture was 1 ml, respectively.

By-products analyses after electron beam samples irradiation were carried out in this work. Analytical method for identification of by-products was improved based on the results of our previous work [23,27]. A gas chromatography equipped with a mass detector (GCMS-QP 5050A, Shimadzu Corporation, Japan) and a HP-5MS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$, Agilent technologies Incorporation, USA) were used to identify by-products. By-products (in gas phase) of degradation of 4-chlorotoluene and toluene were analyzed by directly injecting $250 \mu\text{l}$ gas mixture into the GC-MS. By-products (in solid phase) formed as a result of degradation of 4-chlorotoluene and toluene were analyzed according to the following procedures: 5 ml organic solvent (CH_3OH for 4-chlorotoluene and CH_2Cl_2 for toluene, HPLC purity, provided by J.K.Baker, USA) was used to wash the glass plasma reactor which contained by-products to obtain solution I, then this solution I was concentrated to approximately 0.3 ml by using a micro-extractor under continuously blowing high purity N_2 (99.995% purity, provided by BOC gas company, Poland) to obtain solution II. $1 \mu\text{l}$ of the concentrated extract solution II was injected to the chromatograph sampling port. The parameters of analytical conditions were following: the oven was held at 40°C for 1 min, then programmed at 3°C/min to 139°C , then 10°C/min to 269°C and held at 269°C for 1 min. Injector temperature was 210°C and detector temperature was 280°C . Electron impact ionization mode of MS was applied, and its energy was set for 70 eV.

For by-products (in gas phase) of 4-chlorotoluene, GC-MS following analytical conditions were set: the oven was held at 40°C for 1 min, then programmed at 5°C/min to 140°C , then 10°C/min to 270°C and held at 270°C for 1 min. Injector temperature was 210°C and detector temperature was 280°C .

For by-products (in gas phase) of toluene, GC-MS following analytical conditions were set: the oven was held at 40°C for 1 min, then programmed at 5°C/min to 200°C , and held at 200°C for 1 min. Injector temperature was 50°C and detector temperature was 280°C .

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, it gives information 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.

$$1 \text{ kGy} = 1 \text{ kJ/kg.}$$

Removal efficiency or decomposition efficiency of organic pollutants is defined as R

$$R = (C_0 - C_i) / C_0$$

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).

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