Journal of Hazardous Materials 260 (2013) 32–39

Contents lists available at SciVerse ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Decomposition of dimethylamine gas with dielectric barrier discharge

Zhaolian Ye[a,*], Jie Zhao[a], Hong ying Huang[a], Fei Ma[a], Renxi Zhang[b]

[a] *College of Chemistry and Environmental Engineering, Jiangsu University of Technology, Changzhou, 213001, PR China*
[b] *Institute of Environmental Science, Fudan University, Shanghai, 200433, PR China*

HIGHLIGHTS

- The decomposition of DMA gas under high flow rate was investigated.
- Energy yield of DMA removals reached 2781 g/kWh, which is far higher than others.
- Formation of NO_x can be partly suppressed for DMA air abatement by DBD technology.
- DMA can be decomposed into CO_2 when gas residence time was shorter than 0.1 s.
- Hydroxyl radicals play a dominating role in DMA decomposition with DBD technology.

ARTICLE INFO

Article history:
Received 25 February 2013
Received in revised form 9 April 2013
Accepted 23 April 2013
Available online 30 April 2013

Keywords:
Dimethylamine
DBD
Energy yield
Secondary products

ABSTRACT

The decomposition of dimethylamine (DMA) with gas under high flow rate was investigated with dielectric barrier discharge (DBD) technology. Different parameters including removal efficiency, energy yield, carbon balance and CO_2 selectivity, secondary products, as well as pathways and mechanisms of DMA degradation were studied. The experimental results showed that removal efficiency of DMA depended on applied voltage and gas flow rate, but had no obvious correlation with initial concentration. Excellent energy performance was obtained using present DBD technology for DMA abatement. When experiment conditions were controlled at: gas flow rate of $14.9\,m^3/h$, initial concentration of $2104\,mg/m^3$, applied voltage of 4.8 kV, removal efficiency of DMA and energy yield can reach 85.2% and 953.9 g/kWh, respectively. However, carbon balance (around 40%) was not ideal due to shorter residence time (about 0.1 s), implying that some additional conditions should be considered to improve the total oxidation of DMA. Moreover, secondary products in outlet gas stream were detected via gas chromatogram-mass spectrum and the amounts of NO_3^- and NO_2^- were analyzed by ion chromatogram. The obtained data demonstrated that NO_x might be suppressed due to reductive NH radical form DMA dissociation. The likely reaction pathways and mechanisms for the removal of DMA were suggested based on products analysis. Experimental results demonstrated the application potential of DBD as a clean technology for organic nitrogen-containing gas elimination from gas streams.

1. Introduction

Odor control from chemical industries has become an increasing concern because of the detrimental effect on both human health and global environment. Organic nitrogen-containing compounds pollution, mainly trimethylamine (TMA), dimethylamine (DMA), and methylamine (MA) exhaust stream from chemical, dye, pharmaceutical, pesticide and petrochemical industries, has become an urgent problem. Due to their strong fishy odor in low concentrations, frequent complaints from neighbors and many conflicts between surrounding residents and factories have occurred. TMA is a typical odorous gas, which was characterized as odorous gas. MA and DMA are widely used in the chemical industry to make pesticides, surfactants, photographic chemicals, explosives, dyes and pharmaceuticals. They are also used in nylon industry to improve the tensile strength. Therefore, DMA can be detected in waste gas and waste water in related factories. DMA has strong irritative character and can cause headaches, dermatitis, and conjunctivitis. DMA also has been suspected as a possible neurotoxin in uremic patients where it is sequestered intracellularly and occurs in higher concentrations than normal in the intestine, blood, and brain tissues. It is therefore the right time to explore methods of eliminating or reducing DMA gas.

Several groups have surveyed the elimination of TMA, DMA and MA in aqueous solution [1,2]. Helali et al. experimentally studied the photocatalytic degradation of MA and DMA in the presence of

---

* Corresponding author. Tel.: +86 519 86953260; fax: +86 519 86953269.
E-mail address: bess_ye@jstu.edu.cn (Z. Ye).

0304-3894/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jhazmat.2013.04.035

Nomenclature

DBD	dielectric barrier discharge
η_{DMA}	removal efficiency of DMA (%)
$[C_{DMA}]_{in}$	inlet DMA concentration (mg/m^3)
$[C_{DMA}]_{out}$	outlet DMA concentration (mg/m^3)
[CO]	concentration of CO (ppm)
$[CO_2]$	concentration of CO_2 (ppm)
$[NO_2^-]$	concentration of NO_2^- (mg/m^3)
$[NO_3^-]$	concentration of NO_3^- (mg/m^3)
$[NO_2^- + NO_3^-]$	total concentration of NO_2^- and NO_3^- (mg/m^3)
Cb	carbon balance (%)
S_{CO_2}	selectivity of CO_2 (%)
GC–MS	gas chromatogram–mass spectrum
Ey	energy yield (g/kWh)
T	temperature (K)
Rh	relative humidity (%)
Q	gas flow rate (m^3/h)
P_{in}	input power (W)

UV-irradiated TiO_2 aqueous suspensions [1]. Ho et al. introduced a biofilter using granular activated carbon for the elimination of TMA and DMA in solution [2].

Up to now, there have been few reports involving in the removal of organic nitrogen-containing gas. A common abatement of gas pollution is incineration, which, for nitrogen-containing compounds, may cause the formation of nitrogen oxides, resulting in the generation of photochemical smog and stratospheric ozone depletion. Many researchers began to focus on the thermal adsorption and decomposition of organic nitrogen-containing compounds on a metal surface [3–6]. Liao et al. [3] investigated the adsorption, thermal reactions, and photochemistry of methylamine on TiO_2 using infrared spectroscopy. Others conducted photocatalytic oxidation research on gaseous DMA and MA [7,8]. Kachina et al. [7] postulated the reaction pathways and kinetics of gas-phase photocatalytic oxidation and thermal catalytic oxidation of DMA on titanium dioxide. In his another report [8], photocatalytic oxidation of MA on titanium dioxide in aqueous and gaseous phases was studied. Microbial degradation was suggested as a useful process capable of eliminating gaseous TMA from contaminated environments [9].

Dielectric barrier discharge (DBD) has been accepted as proven environmental clean-up technology for the removal of pollutants (e.g. nitrogen oxides [10], sulfur oxides [11]). In recent years, DBD has been investigated for the abatement of volatile organic compounds including benzene [12], toluene [13,14] and acetaldehyde [15]. Chen et al. [16] provides laboratory scale experimental data on the removal of malodorants (DMA and dimethyl sulfide) from pesticide factory by a wire-cylinder DBD reactor with pulse forming network type of narrow pulse generator and reasonable removal efficiency was achieved. Relative little attention has been given to the detailed byproducts and carbon balance in previous publication.

In this work, DMA is selected as a representative organic nitrogen-containing compound to be removed from gas stream with DBD technology. Special consideration was given to some factors that may influence DMA decomposition, including applied voltage, DMA initial concentration ($[C_{DMA}]_{in}$) and gas flow rate (Q). The energy yield (Ey), carbon balance (Cb) and CO_2 selectivity (S_{CO_2}) were considered. Secondary products were analyzed by gas chromatogram–mass spectrum (GC–MS) and the likely reaction mechanism for the removal of DMA was suggested as well.

2. Experimental

2.1. Production of stable DMA gas stream

In order to study flowed DMA gas destruction, simulated DMA gas production system was designed since DMA was usually stored in water (w/w 33%). 33% DMA solution was placed in a large glass bottle and some Na_2SO_4 power was added in order to absorb majority of water in DMA solution. Then, the bottle was placed in a container with ice–water mixture to sustain DMA under the environmental temperature of 0 ± 1 °C. The gas from compressed N_2 cylinder flowed through the top of above bottle, carrying gaseous DMA on liquid surface to three buffer chamber at first, subsequently into mixing chamber, where DMA gas was diluted by air from air cylinder. Thus, stable DMA gas stream with certain concentration was generated. By adjusting the volume flowmeter connected to N_2 cylinder, DMA concentration varied from 0 to 6000 mg/m^3.

2.2. Experimental setup

Fig. 1 shows the schematic diagram of the experimental setup, which consists of production system of steady gas stream, DBD reactor, and gas detection system. DMA gas generated by the method mentioned in Section 2.1 was fed axially into the DBD reactor under a tunable air blower (pressure loss is about 1000 Pa). By means of an exhaust fan (2X-3, China) connected with six-way-valve autosampler, samples, before and after discharge reaction, could be taken from the plasma reactor exit and analyzed by two on-line gas chromatographs (GC). To make sure discharge to arrive at steady state, the gaseous sample for analysis was taken at a time around 30 min after discharge started. Noticeably, since the system is an open system, temperature in gas pipeline (T) and relative humidity (Rh) would change along with weather condition. Nevertheless, all contrast experiments were carried out at constant T and Rh to ensure the accuracy of the results. The T and Rh were monitored with an electronic temperature-humidity meter (HD-TE03, China). Q was measured with a wind speed meter (ZRQF-D30J, China).

The DBD reactor was made of two coaxial quartz tubes with wall thickness of 2 mm. The inner one had an outside diameter of 10 mm, while the outer one had an inside diameter of 36 mm. The reactor's length was 200 mm and the total volume of reaction zone was 190 mL. A stainless foil attached tightly to the inside wall of the inner tube serving as an inner electrode. The outer electrode, made of a stainless strip with a width of 4 mm, was wrapped around the outside of the external tube with 4 mm spacing. A homemade square wave power supply with a fixed frequency of 20 kHz was used for generating plasma discharge with applied voltage varying from 0 to 9 kV measured by a high voltage probe (XJ 2370, China). In this research, it was assumed that the power consumed in the circuit could be neglected. This meant that the energy provided by power supply was equal to the energy acted on the two electrodes of DBD. The current can be observed on the relative instrument panel. Detailed measurement of the discharge power has been previously reported by our previous publication [17].

2.3. Analysis methods

GC (Agilent 7820A, America) equipped with a HP-5MS capillary column (30 m × 0.32 mm × 0.25 μm) and nitrogen phosphorus detector (NPD) was used for detecting DMA concentration. The concentration of carbon monoxide (CO) and carbon dioxide (CO_2) in flue gas was measured by GC (SP-6890, China) system with a hydrogen flame ionization detector (FID) and Ni transformer stove. Secondary products were analyzed by Agilent 7890B + 5975 C GC–MS. NO_3^- and NO_2^- concentrations ($[NO_3^-]$ and $[NO_2^-]$) in