



# The role of ozone in the plasma-catalytic destruction of environmental pollutants

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## ABSTRACT

The destruction of low concentrations of toluene and cyclohexane in air streams using the combination of a novel multistage, non-thermal plasma reactor with either a MnO<sub>2</sub> or a MnO<sub>2</sub>-CuO catalyst has been investigated. It is found possible to get complete destruction of the organic pollutant when the plasma and catalyst were combined. The different catalysts produced different outcomes in terms of the residual ozone in the outlet stream and the extent of oxidation to CO<sub>2</sub>. Neither of these compounds react to any measurable extent with ozone in the gas-phase nor are they decomposed by the catalyst at the temperature of the experiment. It is deduced that adsorption of ozone onto the catalyst surface and its subsequent dissociation into reactive atomic oxygen species is the key step in the heterogeneous destruction of toluene and cyclohexane.

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## 1. Introduction

Volatile organic compounds (VOCs) are contaminants that are emitted from a wide range of sources including semiconductor manufacturing plants and chemical processing plants. Their presence in air contributes significantly to photochemical smog production; VOCs also pollute soil, surface water and groundwater. Emission of VOCs into the atmosphere is detrimental to both human beings and the environment. The remediation of dilute VOCs from waste gas streams is both a health and environmental concern. It is necessary to remove VOCs from waste gas streams due to increasing emission control legislation. Toluene is widely used in many applications, such as in the pharmaceutical industry and it is an important feedstock in chemical processes. It is often used as a solvent because of its excellent ability to dissolve substances. Toluene is also used to make spray and wall paints, medicine, dyes, explosives, detergents, spot removers, lacquers, adhesives, rubber, and antifreeze. Cyclohexane is a widely used non-polar solvent and is also a raw material for intermediates used in the production of nylon.

Non-thermal plasma processing can be more efficient in decomposing VOCs than conventional technologies, such as catalytic combustion or thermal incineration, as no energy is wasted in heating the gas molecules [1]. A disadvantage, however,

of plasma technology is often incomplete oxidation, leading to potentially toxic by-products [2]. This problem can be solved by combining a non-thermal plasma system with a catalyst [2,3]. This is because there is an increase in reaction time due to adsorption of intermediates and contaminants on the catalyst surface, resulting in a shift towards total oxidation [2]. There is also preferential consumption of active species by surface reactions on the catalyst instead of undesired gas-phase reactions [2].

In recent years, this hybrid plasma-catalysis process, combining the use of plasma and catalysis methods has been extensively investigated and developed [2,4–8]. It is now well established that the performance of non-thermal plasma systems for the removal of low concentrations of pollutants can be improved particularly by the addition of catalyst material into the discharge region of the reactor [9]. The performance of a plasma-catalytic reactor has been found to be superior to a plasma reactor for a range of VOCs [3]. Advantages of using plasma-catalysis systems over plasma alone include enhanced conversion of pollutants, lower energy input giving improved energy efficiency for the plasma process, higher CO<sub>2</sub> selectivity and extended catalyst lifetime [9,10]. A synergistic effect has been reported in some cases for the plasma-catalytic decomposition of VOCs, where the effect of the combined treatment is found to be higher than the sum of the individual steps [11–13]. The excited species produced by the non-thermal plasma have a high catalytic ability; their concentration increases with increasing plasma energy which means that the synergic effect also increases with energy [12]. Another advantage is that the VOCs can be decomposed at ambient temperatures so there is

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no need to heat the catalysts [12]. In addition, the catalyst reduces the formation of by-products as well as increasing the removal efficiency [12]. The main oxidising species formed by non-thermal plasma in oxygen-containing gas streams is ozone due to the dissociation of oxygen molecules [14]; it can either react directly with the VOCs or decompose on the catalyst to give reactive atomic oxygen in surface sites [15].

There are two types of arrangements for these hybrid plasma-catalysis systems, sometimes known as one- and two-stage configurations. The role of the non-thermal plasma is highly dependant on the configuration used [16,17]. In the one-stage configuration, the catalyst is placed directly in the discharge region allowing the plasma to directly activate the catalyst. In the two-stage configuration, the catalyst is placed downstream from the plasma reactor. This means that only long-lived species such as ozone and some stable organic intermediates produced by the plasma will be involved in reactions with the catalyst. Synergistic effects are thought to be limited to when the catalyst is placed inside the discharge region (one-stage system) [9]. In a one-stage configuration, the synergistic effect will be greater due to the increase in concentration of short-lived excited species on the surface of the catalyst and the effect of photons and electrons generated in the plasma.

The presence of highly reactive species and electrons in the plasma trigger physical changes in the catalyst material, consequently affecting the VOC surface adsorption. Plasma-catalytic systems have been shown to exhibit zero-order kinetics during VOC decomposition, indicating the importance of surface reactions [18]. The addition of a catalyst in the one-stage configuration may change the discharge characteristics and in both configurations it can change the chemical reactions involved in the processing [10]. In a one-stage configuration, electron-induced processes, surface discharges and short-lived radicals are potential active species as opposed to long-lived species in a two-stage configuration. In a two-stage configuration, by moving the catalyst away from the plasma where the excited species are created, it is possible to look at the effect of the lifetimes of various radicals and excited species on the destruction of pollutants [12]. In the one-stage configuration, the catalysts are directly activated by the non-thermal plasma at lower temperatures than applies in conventional thermal catalysis [17], even at temperatures as low as room temperature where normally thermal catalysis does not occur [16]. Additional advantages of the combined plasma-catalysis over conventional thermal catalysis include rapid start-up and shutdown and simple construction requiring no heat insulation [17].

It is well known that non-thermal plasma in air can produce high levels of ozone [13]. Although decomposition of ozone to oxygen is a thermodynamically favoured process, ozone is stable up to 100–250 °C. At lower temperatures, a catalyst is necessary for ozone decomposition, producing active species on the catalyst surface, which may induce secondary oxidation reactions. Due to its long lifetime, ozone is of importance in both one- and two-stage plasma systems [15]. In the two-stage configuration, ozone may still be present in significant concentrations and partial oxidation of the VOCs may take place with ozone in the gas-phase [17] and also over a downstream catalyst bed [2,19–22]. Holzer et al. [2] have suggested that in a two-stage configuration hydrocarbon species may be adsorbed on the catalyst deactivating its effectiveness for ozone decomposition. It is believed that the conversion of VOCs is mainly due to ozone acting either directly or indirectly via adsorption or decomposition on catalyst surfaces, leading to the formation of strongly oxidizing species, such as atomic oxygen [9,14].

This work tries to identify the mechanism of VOC destruction using plasma-catalysis by looking at the action of plasma and ozone separately on the decomposition of toluene and cyclohexane

including the addition of a catalyst using a novel, energy-efficient, multistage plasma reactor [13,23]. Ozone has a longer lifetime than other plasma-generated species, so it is thought that only ozone will be present in this system when the VOC is injected into the system downstream of the plasma cells. This work shows that ozone on its own is incapable of destroying pollutants in the gas-phase but when combined with a catalyst, successful destruction is seen.

## 2. Experimental

This work is carried out in a similar manner to that described previously [13]. A schematic of the system is shown in Fig. 1. The apparatus consists of three plasma reactors in series contained in a gas-tight box with external power supplies. Each plasma cell contains two copper mesh electrodes spaced by a distance of 1.65 cm, the copper mesh area of each electrode being 63 cm<sup>2</sup>. Between the electrodes is an air-permeable fixed bed of glass beads (6 mm in diameter). The spacing between the cells is 3.7 cm and each cell is mounted in such a way as ensures that the gas passes through the cell and does not by-pass it. Each plasma cell is individually powered by a high voltage, high frequency, neon sign transformer power supply. The output from the neon sign transformer is 10 kV, 30 mA at full supply voltage with a frequency of 21 kHz. The input voltage of these power sources is controlled by a variac (Zenith Electric Company Ltd.). The input or wall-plug energy consumption is measured by a plug-in power and energy monitor (Prodigit Electronics, 2000MU). Separate experiments with high voltage and current probes indicate that the plasma power is ~20% of the input electrical power for this system. We choose to reference our cell performance to the input power as this is a true measure of the “real” performance of the system in terms of energy consumption.

Two different catalysts are used in this work. The first catalyst is Honeycyle ZA (Nichias Corporation) (catalyst A) which is an ozone destruction catalyst. It is a MnO<sub>2</sub> catalyst supported on an aluminium honeycomb monolith of thickness 2 cm. The second catalyst tested (catalyst B) is Moleculte (Molecular Products Limited). This is a MnO<sub>2</sub>-CuO catalyst capable of decomposing ozone and oxidising carbon monoxide. The catalyst has a surface area of 20–30 m<sup>2</sup> g<sup>-1</sup>, size 4–6 mesh and a total volume of 154 cm<sup>3</sup> is loaded into a polycarbonate filter box. Either or both catalysts may be placed downstream after the plasma cells as required, as shown in Fig. 1, and are unheated.

In the experiments, a mixture of air and the vapour of the VOC pass through the reactor controlled by mass flow controllers

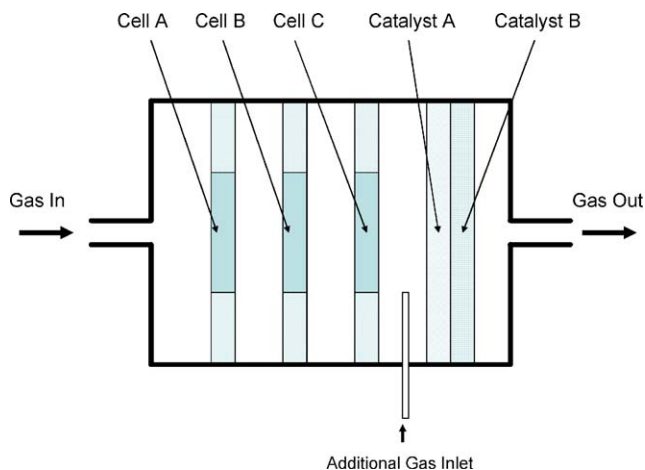


Fig. 1. Schematic diagram of the reactor.

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