

A combined multistage corona discharge and catalytic system for gaseous benzene removal

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Abstract

Non-thermal plasma is an effective and economic alternative method for removing volatile organic compounds (VOCs) since it can be operated in ambient conditions, resulting in low energy consumption, compared with the conventional methods. The main purpose of this work was to apply a combined plasma and catalytic system for VOC removal. A four-stage plasma and catalytic reactor system was set up to investigate the oxidation of gaseous benzene. The experimental results showed that an increase in either applied voltage or stage number of plasma reactors enhanced both benzene conversion and CO₂ selectivity, which was in contrast with the effects of frequency and feed flow rate. Commercial TiO₂ (Degussa P25), sol–gel TiO₂, and 1% Pt/sol–gel TiO₂ were used as catalysts in the present study. The presence of all studied catalysts hardly affected the benzene conversion, but markedly increased the CO₂ selectivity. The synergistic effect of catalysts in the plasma reactor system reasonably resulted from the activation of TiO₂ by the energy generated from the plasma, leading to the enhancement of the CO oxidation.

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1. Introduction

The emission of volatile organic compounds (VOCs) is one of the major sources of air pollution. VOCs are liquids or solids containing organic carbon (carbon bonded to carbon, hydrogen, nitrogen, or sulfur, but not carbonate carbon as in CaCO₃ nor carbide carbon as in CaC₂ or CO or CO₂), which vaporize at high rates [1]. The emission of VOCs not only increases the depletion of stratospheric ozone, but also causes widespread environmental contamination, such as groundwater and soil contamination. It is well known that several kinds of VOCs are very harmful to human health because of their carcinogenic and mutagenic effects. In addition, they are recognized as major contributors to air pollution, either directly through their toxicity and malodorous nature or indirectly as ozone precursors, and smog precursors. They also cause acidic precipitation (acid rain) and finally global warming [2].

A number of countries have attempted to assess the toxicity of various environmental pollutants, including VOCs, in order to reasonably establish emission regulations for various pollution sources. To meet the emission standards, various approaches available for air pollution control include liquid absorption, solid adsorption, scrubbing, precipitation, capture devices (fibers, membranes, condensers, etc.), biodegradation, thermal incineration, and catalytic combustion [3]. Catalytic combustion is considered to be the most effective way to achieve the complete destruction of VOCs. However, the energy requirement of catalytic combustion is rather high, while the other methods require further treatment and/or have some disadvantages. Non-thermal plasma or low-temperature plasma processes have been considered promising and economic alternatives for the decomposition of VOCs because they can be operated at ambient temperature and pressure.

Non-thermal plasma is easily generated by applying an electric field across metal electrodes to produce high-energy electrons that can potentially decompose VOCs [4]. During plasma generation, active species, radicals, and ions, as well as UV light irradiation, are produced by the collision of high-energy electrons emitted from the surfaces of electrodes under high voltage

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conditions [5,6]. If oxygen is present at a sufficiently high level, the desirable products from the VOC decomposition are mainly carbon dioxide and water, which are environmentally friendly.

Among VOCs, benzene is an important chemical feedstock and a gasoline ingredient. Moreover, it has distinct volatility, low solubility in water, and very high stability regarding to its chemical structure. It is commonly found in exhaust gases emitted from petroleum storage tanks, coke ovens, and printing offices. In addition, benzene is widely used as a solvent in a number of chemical processes. Hence, it is of interest to remove benzene to ensure that exhaust gases are safe. Many researchers have also focused on benzene removal using various systems [7–9].

In this study, the oxidative removal of gaseous benzene was studied using a multistage corona discharge system in the presence of catalysts. The effect of titania (TiO_2) or platinumized titania (Pt/TiO_2) coated on a glass wool support on benzene oxidation was also determined under the plasma conditions.

2. Experimental

2.1. Materials and reactant gases

Titanium dioxide was obtained from J.J. Degussa Hüls (T) Co., Ltd. Platinum(II) 2,4-pentanedionate, $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$ with 49.8% Pt, was obtained from Alfa Aesar. Tetraethylorthotitanate (TEOT, 100%) was supplied by Fluka. Anhydrous ethanol with 99.8% purity was supplied by Carlo Erba Reagenti. Nitric acid (70%, analytical grade) was supplied by Lab-Scan. All chemicals were used as received without further purification. Distilled water was used throughout this study. For the reactant gases, high purity nitrogen (N_2) and zero grade air were obtained from Thai Industrial Gas (Public) Co., Ltd. Liquid benzene with 99.8% purity, used as a model pollutant, was supplied by Carlo Erba Reagenti.

2.2. Catalyst preparation and characterizations

Catalysts used in this study were prepared by dipping glass wool used as the support in a slurry of commercial TiO_2 (Degussa P25) or sol–gel TiO_2 . The glass wool was pretreated to remove all undesirable matter, such as wax and binder, by annealing at 450°C for 2.5 h. The treated glass wool was then cut to $3\text{ cm} \times 3.5\text{ cm}$. To prepare the titania coated on the glass wool, a titania-containing slurry was first prepared by mixing 0.6 g of commercial TiO_2 with 29.4 ml of distilled water. The glass wool was then immersed in this slurry for 5 min, and the slurry-saturated glass wool was dried in an oven at 100°C for 15 min. The coated glass wool was then annealed in a furnace at 300°C for 3 h and cooled to room temperature at a rate of $50^\circ\text{C}/\text{min}$. The TiO_2 catalyst was white after annealing, and the amount of TiO_2 loading was found to be about 0.0126 g. For preparing the glass wool coated with sol–gel TiO_2 , a titania precursor solution was prepared by mixing 1.5 g of TEOT with 20 ml of ethanol and six drops of 70% nitric acid. The coating procedure was the same as the method described above except for using 400°C for 5 h instead of 300°C for 3 h for annealing. To prepare the 1% Pt/sol–gel TiO_2 , 0.005 g of $\text{Pt}(\text{C}_5\text{H}_7\text{O}_2)_2$

and 2.83 g of TEOT were dissolved in 38 ml of ethanol and 14 drops of nitric acid. The same coating and annealing procedures were carried out as described for the preparation of sol–gel TiO_2 coated on glass wool.

The surface areas of all prepared catalysts were determined by a surface area analyzer (Quantachrom, Autosorb-1) using nitrogen adsorption analysis. A catalyst sample was dried and outgassed in a sample cell at 200°C for at least 4 h before adsorption. The specific area of each catalyst was calculated from the five-point adsorption isotherm. The results were analyzed by Autosorb ANAGAS software, version 2.10. The crystalline phases of the catalysts were investigated by an X-ray diffractometer (Rigaku, RINT-2200) equipped with a graphite monochromator and a Cu tube for generating Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) at a generator voltage of 40 kV and a generator current of 30 mA. A nickel filter was used as the $\text{K}\alpha$ filter. The goniometer parameters were; divergence slit = 1° (2θ), scattering slit = 1° (2θ), and receiving slit = 0.3 mm. The catalyst sample was held on a glass slide holder and was examined in the 2θ range of 5° to 90° at a scanning speed of 5° (2θ)/min and a scan step of 0.02° (2θ). The digital output of the proportional X-ray diffractometer and the goniometer angle measurements were sent to an online microcomputer to record the data and to perform subsequent analyses. The surface morphology of all prepared catalysts was examined by using a scanning electron microscope (JEOL, JM-5200).

2.3. Oxidation reaction experiments

A schematic of experimental setup of the multistage plasma reactor system used in this study is shown in Fig. 1. Reactant gases of benzene vapor and air were controlled by mass flow controllers (Sierra, 840L-20V1-SV21-E-V1-S1 and Aalborg, GFC171S) and were mixed before being introduced into the plasma system, which consisted of four plasma reactors. The feed mixture was controlled to 1500 ppm of benzene in air by regulating the bubbling rate of nitrogen and the evaporation temperature of a benzene evaporator unit. The four reactors, which were made of quartz tubes with 10 mm outer diameters and 8 mm inner diameters, were arranged in the vertical position and connected in series. Plasma was generated in each reactor via a pair of stainless steel pin-and-plate electrodes which were located at the center of each reactor. Fig. 2 shows the block diagram of the power supply unit. For the first step, the domestic ac input of 220 V and 50 Hz was converted to a dc output of 70 V by a dc power supply converter. For the second step, a 500 W power amplifier with a function generator was used to convert the dc input to ac output with a sinusoidal waveform and different frequencies. For the final step, the output voltage was stepped up by using two transformers in series. The output voltage and frequency were controlled by the function generator. Since the plasma generated in each reactor was found to have a very high fluctuation, it was not possible to measure the voltage across the electrodes of the reactor (high-side voltage). Therefore, the low-side voltage and current were measured instead, and the high-side voltage and current were then calculated by multiplying and dividing by a factor of 130, respectively. The glass wool

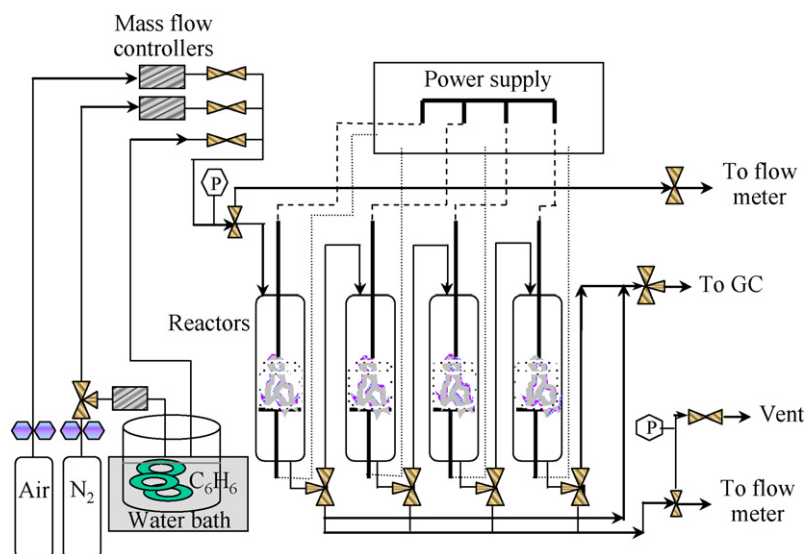


Fig. 1. Schematic of experimental setup.

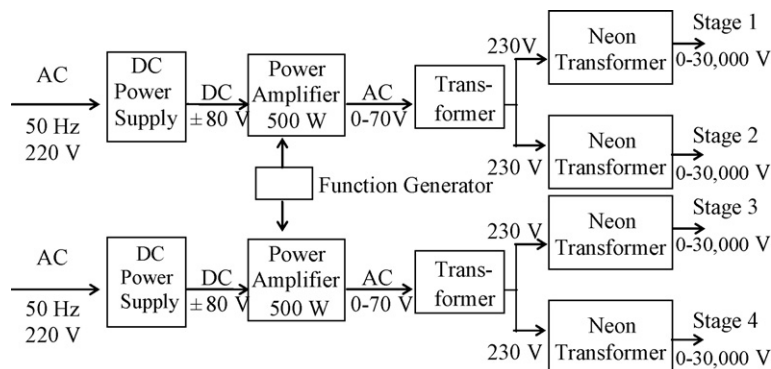


Fig. 2. Schematic of power supply system.

coated with either the commercial TiO₂ or sol–gel TiO₂ was packed in the middle between the pin-and-plate electrodes, as shown in Fig. 3. The plasma system was operated under room temperature and atmospheric pressure. The temperature at the tube wall of the plasma zone was in the range of 150–200 °C.

An experiment was started with the feed gas composition analysis by an on-line gas chromatograph (Perkin-Elmer, AutoSystem GC) equipped with parallel channels to the two detectors, which were a thermal conductivity detector (TCD) and a flame ionization detector (FID). The TCD channel with a packed column (Carboxen 1000) was capable of separating

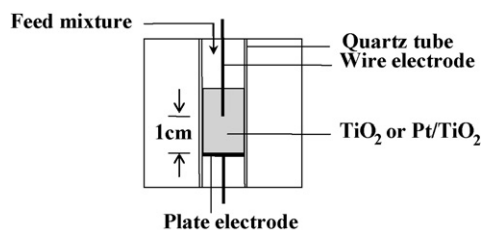


Fig. 3. Configuration of each reactor.

nitrogen (N₂), oxygen (O₂), and C₁–C₂ hydrocarbons; whereas the FID channel with a capillary column (DB-5) was capable of separating benzene and by-products. Once the benzene concentration of the feed mixture was relatively invariant, the power supply unit was turned on. After 30 min, the composition of the effluent was analyzed every 16 min until the outlet gas composition was invariant, indicating that the plasma system reached a steady state. The experimental data taken after steady state were averaged and the values were used to evaluate the performance of the plasma system. The effect of the stage number of the plasma and catalytic system on benzene removal and product selectivities was investigated by turning off the power supply unit of each reactor one by one, with the fourth one first. In this study, the variable process parameters were frequency, applied voltage, and feed gas flow rate. It is worth mentioning that the plasma system was operated at high feed gas flow rates to avoid the complete removal of benzene, which, in turn, allowed the observation of the effects of all process parameters and the presence of catalysts.

To evaluate the process performance of the plasma system, the conversion of benzene and the selectivities of CO and CO₂

were considered. The conversion of benzene is defined as:

$$\text{benzene conversion (\%)} = \frac{\text{mole of benzene in} - \text{mole of benzene out}}{\text{mole of benzene in}} \times 100$$

The selectivities of CO and CO₂ are calculated based on carbon balance as follows:

$$\text{selectivity of CO (\%)} = \frac{\text{mole of CO in a product}}{6 \times \text{mole of benzene removed}} \times 100$$

$$\text{selectivity of CO}_2 (\%) = \frac{\text{mole of CO}_2 \text{ in a product}}{6 \times \text{mole of benzene removed}} \times 100$$

The specific energy consumption is calculated in a unit of W s per molecule of converted benzene using the following equation:

$$\text{specific energy consumption} = \frac{P \times 60}{\tilde{N} \times M_C}$$

where P is the power (W s); \tilde{N} is the Avogadro's number = 6.02×10^{23} molecules g-mole⁻¹; and M_C is the rate of benzene in feed gas converted (g-mole min⁻¹).

3. Results and discussion

3.1. Catalyst characterization results

The BET specific surface areas of the commercial TiO₂ (Degussa P25), sol-gel TiO₂, and 1% Pt/sol-gel TiO₂ are 63.77, 103.1, and 103.5 m²/g, respectively. The crystal structures of the studied catalysts identified by XRD patterns are shown comparatively in Fig. 4. All catalysts show the anatase peaks, predominantly at the same position of 2θ , whereas the rutile peak was only observed for the commercial TiO₂. It is worth noting that no peak of platinum at $2\theta = 40^\circ$ was observed, suggesting that Pt was highly dispersed on the synthesized sol-gel TiO₂ catalyst. The XRD results indicate that the commercial TiO₂ is more crystalline than both sol-gel TiO₂ catalysts. Interestingly, the sol-gel TiO₂ catalysts do not exhibit the rutile peak since they were calcined at a low temperature of 400 °C, whereas the phase transformation from anatase to rutile is reported to occur at a temperature of approximately 600 °C [10]. The surface morphology of the studied catalysts coated on glass wool was also examined by using SEM analysis. Fig. 5 shows the topography of the commercial TiO₂, sol-gel TiO₂, and 1% Pt/sol-gel TiO₂ coated on glass wool. According to the SEM images, all catalysts agglomerate on the surface of the glass wool in their own crystal shape. However, the surface characteristics of both sol-gel TiO₂ and 1% Pt/sol-gel TiO₂ coated on glass wool are much smoother than that of the commercial TiO₂.

3.2. Benzene oxidation results

As known, the complete removal of VOCs is needed for real applications, but under these operating conditions we cannot rule out the effects of any process parameters of the studied plasma system. Hence, the oxidation reaction experiments were

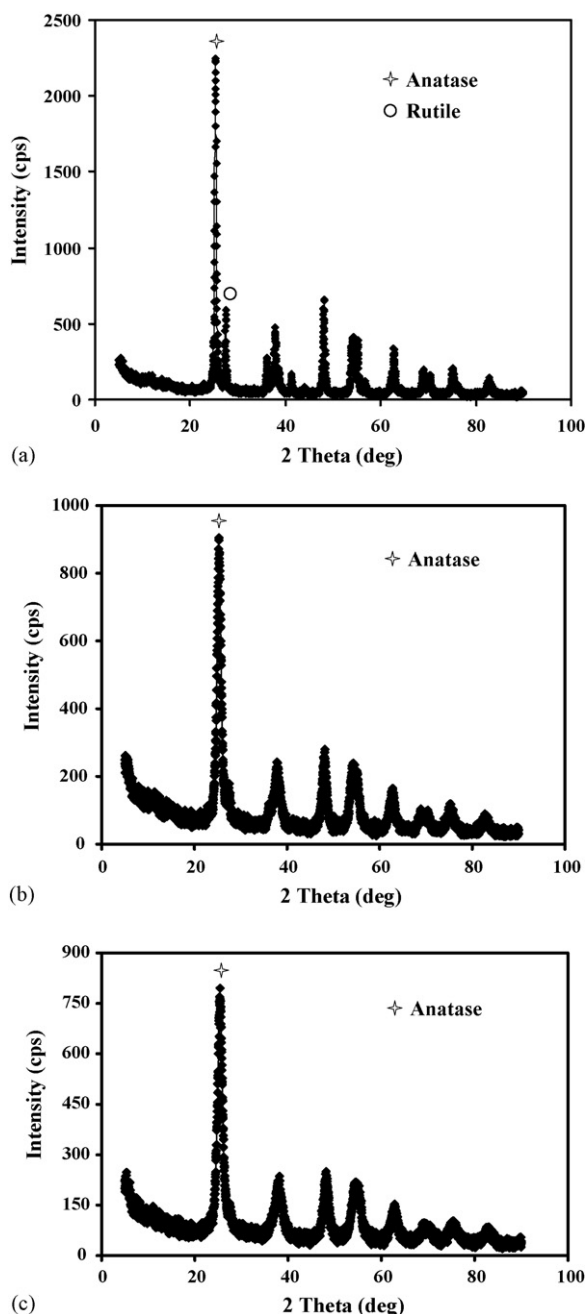


Fig. 4. XRD patterns of (a) commercial TiO₂, (b) sol-gel TiO₂, and (c) 1% Pt/sol-gel TiO₂.

conducted at high feed gas flow rates to ensure benzene removal lower than 100% in order to observe the effects of all process parameters and the presence of catalysts.

3.2.1. Effect of frequency

Fig. 6 shows the effect of frequency on the benzene conversion at an applied voltage of 21 kV and different stage numbers of plasma reactors. The studied plasma system could not be operated at a frequency lower than 50 Hz since the reaction temperature was found to be very high, which would damage both the electrodes and the catalysts due to the high current, as shown in Fig. 7. Meanwhile, the plasma did not occur when the

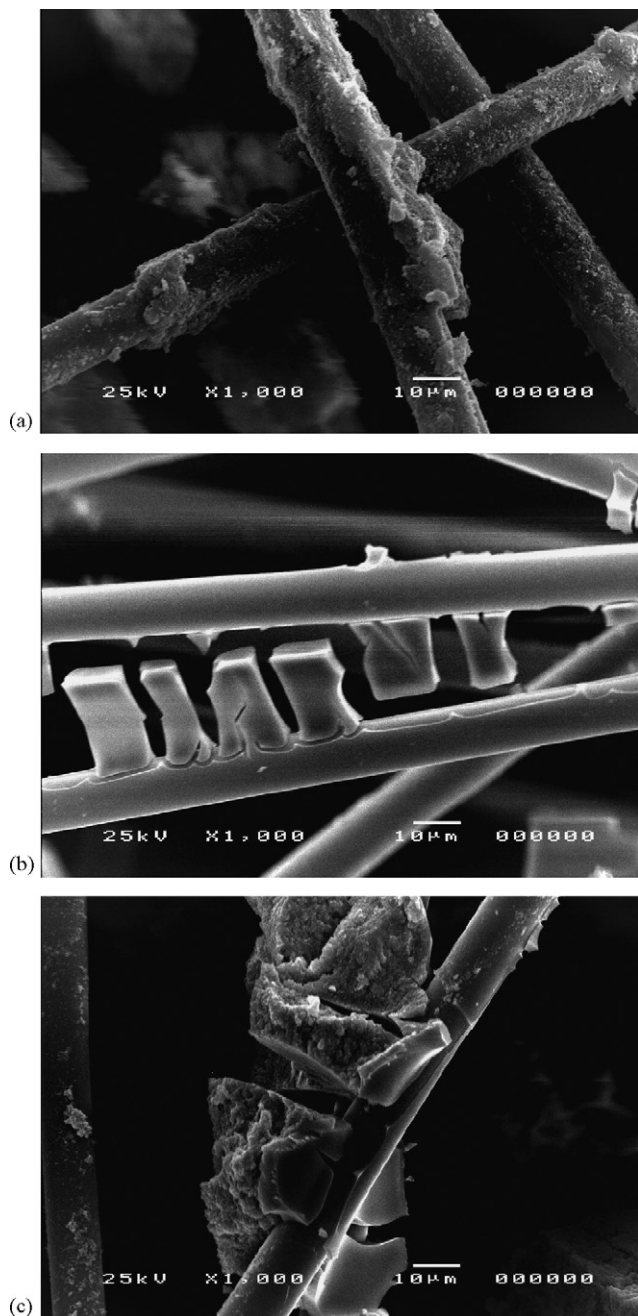


Fig. 5. SEM images of (a) commercial TiO_2 , (b) sol-gel TiO_2 , and (c) 1% Pt/sol-gel TiO_2 coated on glass wool (bar = 10 μm).

frequency was greater than 700 Hz. The conversion of benzene decreased with increasing frequency in the range of 50–700 Hz. The reason is that a higher frequency results in a lower current [11,12], as confirmed in Fig. 7. Therefore, the opportunity of collision between electrons and O_2 molecules declines with the decrease in the current. For any given frequency, the conversion of benzene increased with the increase in the stage number of plasma reactors. This is because the residence time is increased with the increase of the stage number.

The effects of applied frequency on the CO and CO_2 selectivities are illustrated in Fig. 8. When the frequency increased, the CO selectivity increased, whereas the CO_2 selectivity con-

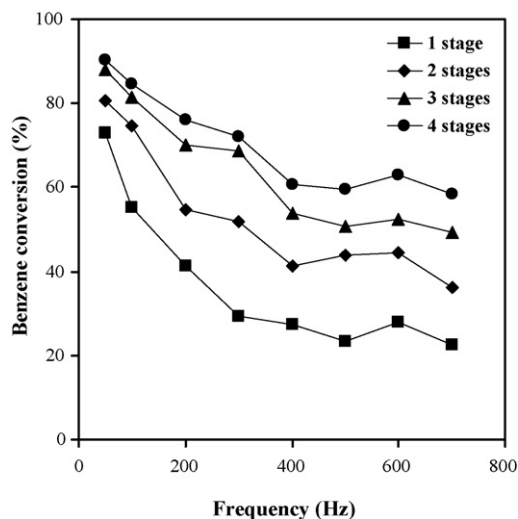


Fig. 6. Effect of frequency on benzene conversion at different stage numbers of plasma reactors (initial benzene concentration in air = 1500 ppm; applied voltage = 21 kV; electrode gap distance = 1 cm; feed flow rate = 500 cm^3/min).

versely decreased. As mentioned earlier, at a lower frequency, the system current increases, leading to a larger number of electrons generated from the electrodes, as shown in Fig. 7. The higher the number of electrons, the higher the amount of oxygen active species generated. Therefore, it enhances the oxidation of benzene, as well as the reaction between oxygen active species and CO becomes more effective, leading to a higher CO_2 selectivity. For any given frequency, the CO_2 selectivity increased while the CO selectivity decreased with the increase in the stage number of plasma reactors, due to the increase in the residence time or reaction time. As a result, the electrons produced have a higher possibility to break down O_2 to produce the oxygen active species for further CO oxidation to form CO_2 .

When an ac discharge is applied, each electrode performs alternatively as an anode and cathode. The space charge between the two electrodes is eliminated and then a new space dis-

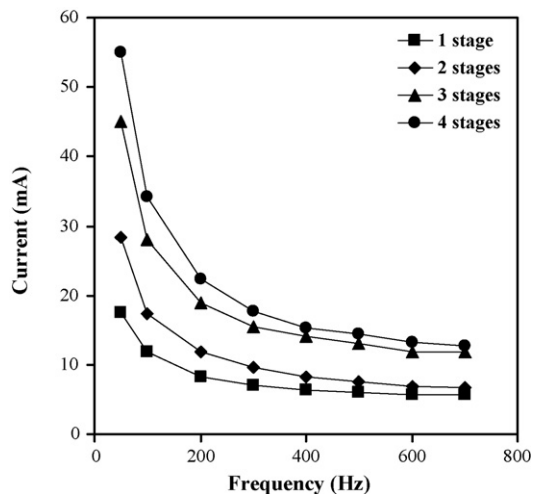


Fig. 7. Effect of frequency on current at different stage numbers of plasma reactors (initial benzene concentration in air = 1500 ppm; applied voltage = 21 kV; electrode gap distance = 1 cm; feed flow rate = 500 cm^3/min).

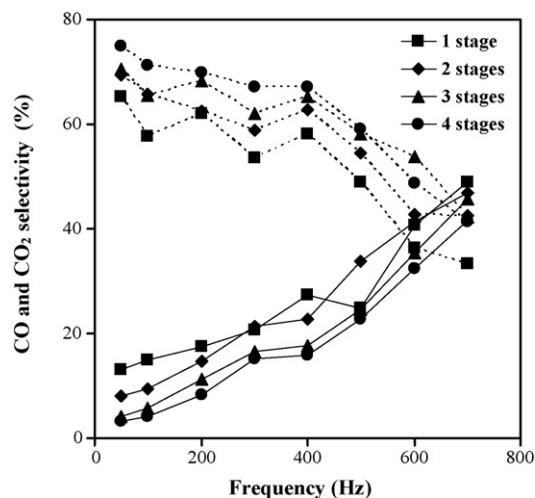


Fig. 8. Effect of frequency on CO and CO₂ selectivities at different stage numbers of plasma reactors (solid line: CO selectivity; dotted line: CO₂ selectivity) (initial benzene concentration in air = 1500 ppm; applied voltage = 21 kV; electrode gap distance = 1 cm; feed flow rate = 500 cm³/min).

charge is initiated every half cycle. With increasing frequency, a faster reversal of the electric field reduces the decay of the space charge. Acceleration of the remaining space charge by the reversing electric field can diminish the amount of current needed to maintain the discharge [13]. In addition, the alternating behavior has been proven to be remarkably efficient in eliminating contaminant accumulation on the electrodes, resulting in increasing conversions, as compared with a dc discharge [14]. Although the power is constant, the effect of frequency on the conversion and selectivity originates from the differences in both the space charge (electrons, radicals, and ions) contents and the characteristics of the discharge. Therefore, ac discharge was selected in this present work.

The effect of frequency on power consumption to decompose each benzene molecule is shown in Fig. 9. It can be clearly

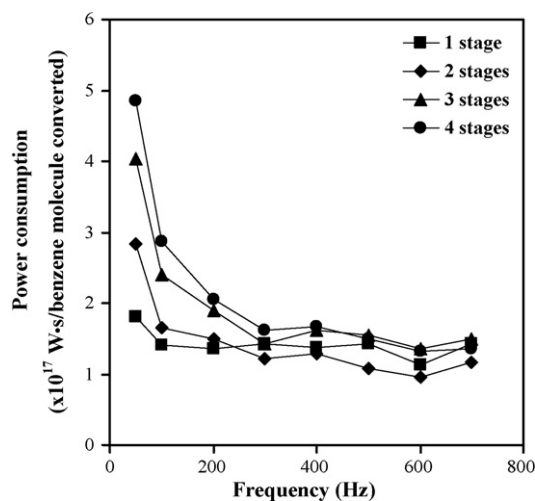


Fig. 9. Effect of frequency on power consumption to convert one benzene molecule at different stage numbers of plasma reactors (initial benzene concentration in air = 1500 ppm; applied voltage = 21 kV; electrode gap distance = 1 cm; feed flow rate = 500 cm³/min).

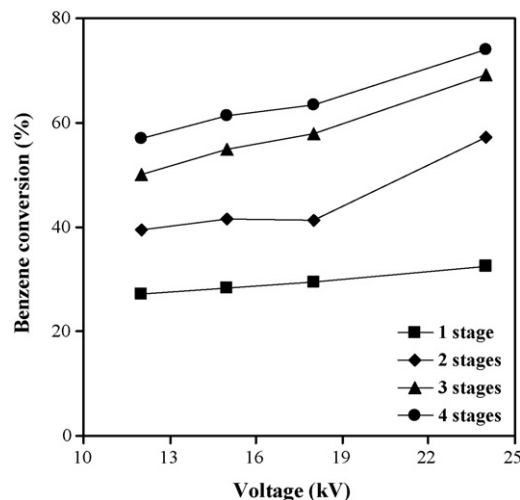


Fig. 10. Effect of applied voltage on benzene conversion at different stage numbers of plasma reactors (initial benzene concentration in air = 1500 ppm; frequency = 300 Hz; electrode gap distance = 1 cm; feed flow rate = 500 cm³/min).

seen that optimum power is obtained with the frequency in the range of 200–700 Hz. Since a lower frequency results in a higher current and a larger number of generated electrons, this leads to a higher power consumption. The lower the frequency, the higher the amount of active oxygen species used to oxidize all intermediate products, especially CO. On the other hand, a higher frequency corresponds to the reduction of the amount of electrons generated from the electrodes, causing lower benzene decomposition. Based upon both relatively high benzene conversion and minimum power consumption, a frequency of 300 Hz was selected for further experiments. In addition, amounts of intermediate products produced at 300 Hz were not detected at significant levels. It was also reported that other hydrocarbon (C₁–C₂) by-products from the aromatic decomposition in a packed-bed plasma reactor were detected with very low levels [15,16]. However, in this study, coke deposit was observed at the surface of the pin and plate electrodes. The amount of coke deposit was found to increase with decreasing frequency. It can then be concluded that under the experimental conditions, CO and CO₂ are the main products of the plasma system. This is because the feed gas contained a very low benzene concentration of 1500 ppm and very high excess oxygen. Hence, all intermediate products are further oxidized by the active oxygen species generated from the collision between oxygen molecules and the high-energy electrons of the plasma.

3.2.2. Effect of applied voltage

Fig. 10 depicts the effect of applied voltage on the benzene conversion for different stage numbers of plasma reactors. The plasma system could not be operated at an applied voltage lower than 12 kV, known as the breakdown voltage, since the plasma did not exist. Meanwhile, the experiments were conducted at the highest voltage of 24 kV, which is quite close to the maximum limit of the power supply units. The conversion of benzene increased with increasing the applied voltage in the range of 12–24 kV, which is in contrast to the effect of frequency. The explanation is that a higher voltage results in a

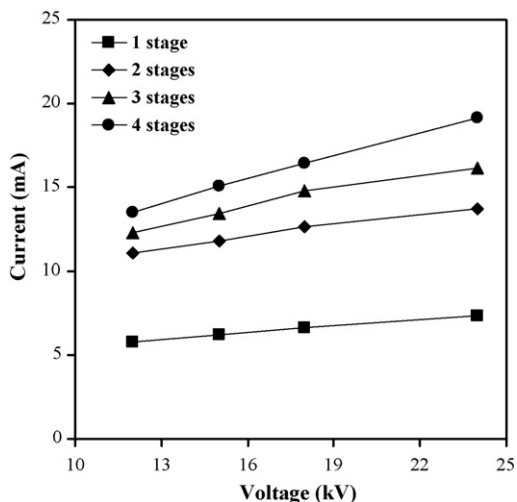


Fig. 11. Effect of applied voltage on current at different stage numbers of plasma reactors (initial benzene concentration in air = 1500 ppm; frequency = 300 Hz; electrode gap distance = 1 cm; feed flow rate = 500 cm³/min).

higher electric field strength, as shown in Fig. 11, leading to a rising average electron energy as well as an increasing number of electrons which sequentially increase the amount of active oxygen species available for reacting with benzene. From previous literature, it was found that with a fixed reactor geometry, the quantity of electricity transferred between electrodes increased as the applied voltage increased [12]. It was also observed that a decrease in applied voltage resulted in a lowering of toluene decomposition [17]. Additionally, an increase in the stage number of plasma reactors in operation enhanced the conversion of benzene because of a longer residence time, leading to a higher chance of electrons to collide with oxygen to produce active oxygen species, as well as to break down benzene molecules.

The effects of applied voltage on the CO and CO₂ selectivities are shown in Fig. 12. As the applied voltage increased, the CO selectivity decreased, whereas the CO₂ selectivity increased.

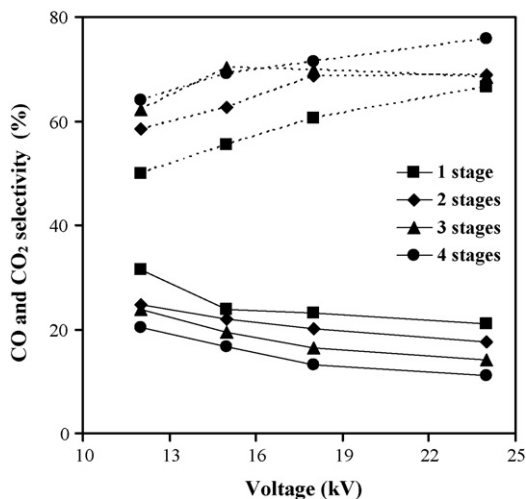


Fig. 12. Effect of applied voltage on CO and CO₂ selectivities at different stage numbers of plasma reactors (solid line: CO selectivity; dotted line: CO₂ selectivity) (initial benzene concentration in air = 1500 ppm; frequency = 300 Hz; electrode gap distance = 1 cm; feed flow rate = 500 cm³/min).

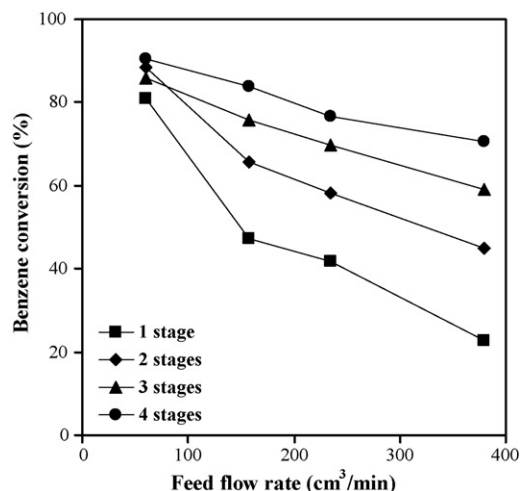


Fig. 13. Effect of feed flow rate on benzene conversion at different stage numbers of plasma reactors (initial benzene concentration in air = 1500 ppm; frequency = 500 Hz; applied voltage = 15 kV; electrode gap distance = 1 cm).

This can be plausibly explained that the increase in the applied voltage results in the increased current, as clearly verified in Fig. 11. Consequently, there are more oxygen active species available to further oxidize CO to form CO₂ molecules, leading to a higher CO₂ selectivity. For any given applied voltage, the CO selectivity decreased while the CO₂ selectivity increased when the feed gas mixture was passed through a higher stage number of plasma reactors. This is because a higher stage number of multistage plasma reactors increase the residence time of the gas inside the reaction zone.

Interestingly, the effect of applied voltage on the benzene conversion and current is much less pronounced, as compared to that of frequency. From the experimental observation, an applied voltage of 15 kV was chosen for further studies since, at this voltage, the system can provide a relatively high benzene conversion with reasonably low power consumption, as indicated by the system current shown in Fig. 11.

3.2.3. Effect of feed flow rate

Fig. 13 illustrates the effect of feed flow rate on the benzene conversion at different stage numbers of plasma reactors. For any given stage number of plasma reactors in operation, the benzene conversion decreased with increasing feed flow rate in the studied range of 60–380 cm³/min because an increase in the feed flow rate directly relates to the decrease in the residence time. For any given feed flow rate, a higher stage number of plasma reactors resulted in a higher conversion of benzene. With a decrease in the feed flow rate or an increase in the stage number of plasma reactors, electrons have a higher possibility to collide with benzene and O₂ molecules, leading to a higher conversion of both reactants.

The effects of the feed flow rate on the CO and CO₂ selectivities are shown in Fig. 14. For any given stage number of plasma reactors, the CO selectivity increased with an increasing of the feed flow rate while an opposite trend was observed for the CO₂ selectivity. A higher gas flow rate or a lower stage number of plasma reactors reduces the opportunity of collision

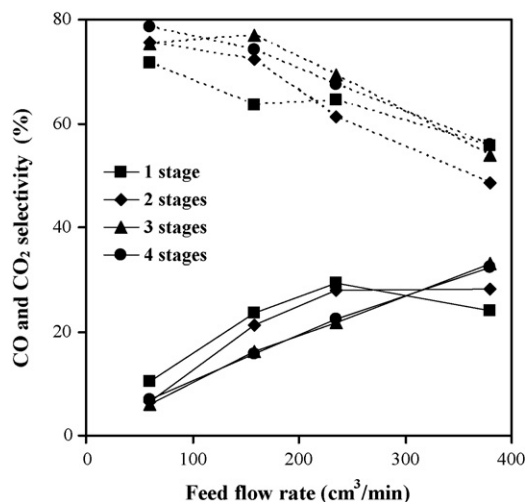


Fig. 14. Effect of feed flow rate on CO and CO₂ selectivities at different stage numbers of plasma reactors (solid line: CO selectivity; dotted line: CO₂ selectivity) (initial benzene concentration in air = 1500 ppm; frequency = 500 Hz; applied voltage = 15 kV; electrode gap distance = 1 cm).

between electrons and O₂ molecules. Thus, the oxidation of CO decreases, resulting in a lower CO₂ selectivity. Interestingly, the results of both CO and CO₂ selectivities were not consistent when the feed gas flow rate was varied as compared to the cases of both frequency and applied voltage. This is because the plasma system was operated at a very high feed flow rate corresponding to the residence time range of 0.3–2.01 s. As a result, it is not likely to obtain uniform flow patterns in the plasma system at these very short residence times.

At the lowest feed flow rate, some by-products (C₁–C₂ hydrocarbons) were detected at insignificant levels, indicating that all hydrocarbon intermediate products are oxidized almost completely under the studied conditions. It should be mentioned here that the system current did not alter significantly with feed

flow rate. Hence, the power consumption is not an important factor to determine the optimum feed flow rate. Regarding the aspect of air pollution control, the highest benzene conversion should be used to choose the optimum feed flow rate. Therefore, a feed flow rate of 60 cm³/min (a total residence time = 2.01 s) was selected for further experiments in order to determine the effect of the presence of catalysts.

3.2.4. Effect of the presence of catalysts

Table 1 summarizes the effect of the presence of different catalysts coated on glass wool on the benzene conversion and the product selectivities. It was apparent that all the catalysts (commercial TiO₂, sol-gel TiO₂, and 1% Pt/sol-gel TiO₂) enhanced the benzene conversion by 8% with one stage of plasma reactor and by 2% with two stages in operation. Even though the same effect was not observed at a significant level with a stage number of plasma reactors greater than two, the operation at a higher stage number plays an important role on the product selectivities. The results imply that the energy released from the plasma can excite TiO₂, leading to the oxidation and reduction reactions on the TiO₂ surface. TiO₂ as a reducible oxide can enhance the oxidation reaction on its surface.

With four stages of plasma reactors, the presence of either the sol-gel TiO₂ or the commercial TiO₂ was found to improve the CO₂ selectivity by 6–10% and to worsen the CO selectivity by 3–4%. This can be explained by the fact that TiO₂ contributes to the acceleration of the superoxide radical anion (O₂^{•-}) formation and consequently inhibits the recombination process and increases the catalytic activity [18]. The formation of the superoxide radical anion in the presence of the TiO₂ catalyst is believed to be very effective for further CO oxidation to form CO₂. The addition of Pt on sol-gel TiO₂ did not enhance the benzene conversion and the product selectivities. In comparisons among all studied catalysts, the sol-gel TiO₂ is the best catalyst, since it provided the highest CO₂ selectivity. This

Table 1
Effect of different catalysts in the four-stage corona discharge system for benzene oxidation

Type of catalyst	Stage	Benzene conversion (%)	Selectivity (%)	
			CO	CO ₂
No catalyst	1	81.1	8.0	54.2
	2	89.3	4.2	64.2
	3	91.9	4.1	66.9
	4	91.7	5.7	70.5
Commercial TiO ₂	1	91.1	10.1	57.5
	2	91.7	4.2	67.2
	3	92.7	2.8	68.5
	4	92.3	2.1	76.7
Sol-gel TiO ₂	1	89.2	7.8	67.4
	2	91.5	5.8	77.5
	3	91.6	3.1	80.6
	4	91.7	2.6	81.0
1% Pt/sol-gel TiO ₂	1	87.5	4.3	68.1
	2	91.8	0.9	77.2
	3	100	1.6	74.5
	4	91.6	2.1	80.4

Feed flow rate = 60 cm³/min; initial benzene concentration = 1500 ppm; frequency = 500 Hz; applied voltage = 15 kV; electrode gap distance = 1 cm.

is because the sol–gel TiO₂ has a higher surface area than the commercial TiO₂.

4. Conclusions

The benzene decomposition efficiency decreased substantially with increasing frequency, since at a higher frequency the current was lowered, leading to the reduction of the number of electrons generated. A higher applied voltage increased the benzene conversion as well as the CO₂ selectivity since the system current was increased with increasing applied voltage. A higher feed flow rate decreased both benzene conversion and CO₂ selectivity because of decreasing residence time. It was found that benzene was predominantly removed by the plasma, with an insignificant effect from the presence of catalysts. The presence of a small amount of TiO₂ (commercial or sol–gel) could enhance the CO oxidation, leading to a higher CO₂ selectivity. The multistage plasma reactor with TiO₂ catalyst used in this study has demonstrated a promising potential for VOC removal with a very short residence time, in the range of seconds. For real applications, we recommend the use of a multistage plasma system with two or three plasma reactors in series. And, sol–gel TiO₂ should be packed in the reactor to enhance the CO oxidation. The system should be operated at a much longer residence time (e.g. 4–6 s), as compared to that of 2.01 s of the present study, to ensure the complete removal of benzene.

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