CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

BET surface areas of commercial TiO_2 (Degussa P25), sol-gel TiO_2, and 1%Pt/sol-gel TiO_2 are 63.77, 103.1, and 103.5 m^2/g, respectively. When these catalysts are coated on glass wool, the BET surface areas of each catalyst decreases dramatically, 9.54, 1.16, and 5.23 m^2/g for Degussa P25, sol-gel TiO_2, and 1%Pt/sol-gel TiO_2 respectively. The crystal structures of the studied photocatalysts identified by XRD patterns are shown comparatively in Figure 4.1 (a), (b), and (c). The commercial TiO_2 (Degussa P25), sol-gel TiO_2, and 1%Pt/sol-gel TiO_2 show the anatase peaks observed notably at the same position of 2θ while no platinum peak at $2\theta = 40^\circ$ and 48° is present. It suggests that Pt can be well dispersed on TiO_2. From the XRD results, it indicates that the commercial TiO_2 is more crystalline than both sol-gel TiO_2 catalysts since the sol-gel TiO_2 was calcined at a relatively high temperature of 400C.

The surface morphology of the studied catalysts coated on glass wool was examined by using SEM. Figure 4.2 shows the morphology of Degussa P25, sol-gel TiO_2, and 1% Pt/sol-gel TiO_2. According to the figure, all catalysts agglomerates on the surface of the glass wool in their own crystal shape.

4.2 Effects of Frequency

4.2.1 Effect of Frequency on Benzene Conversion

Figure 4.3 shows the effect of frequency on benzene conversion at 21 kV and different stages. The conversion of benzene decreases with increasing frequency in the range of 50 to 700 Hz. The reason is that a higher frequency results in a lower current corresponding to the reduction of the number of electrons generated (Morinaga and Suzuki, 1961 and 1962) as

confirmed in Figure 4.4. Therefore, the opportunity of collision between electrons and O_2 molecules declines with reducing current. For each frequency, the conversion of benzene increases with the increase in the stage number of reactors. This is due to the residence time is increased with the increase in the stage number.

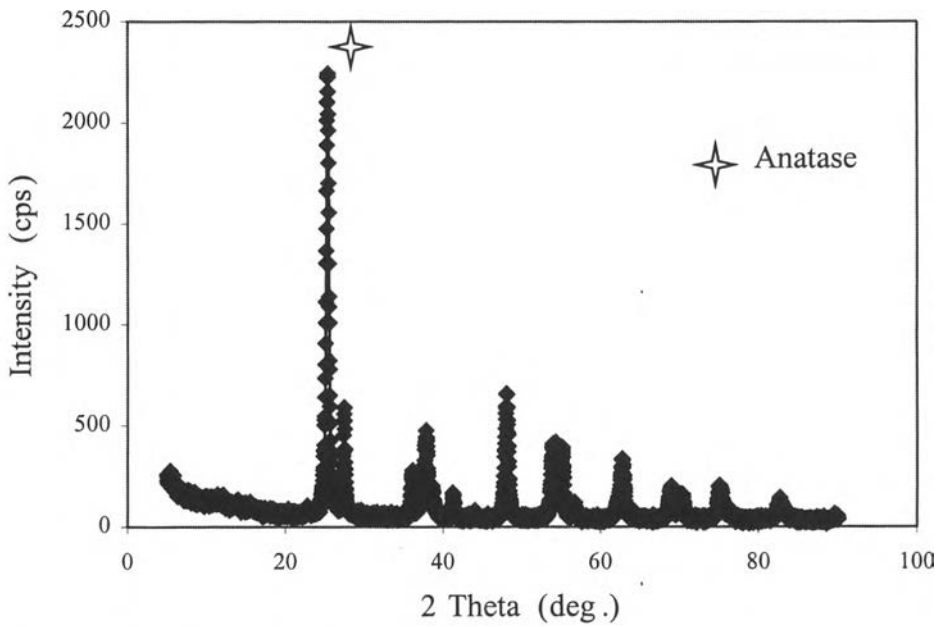

Figure 4.1 (a) XRD pattern of Degussa P25.

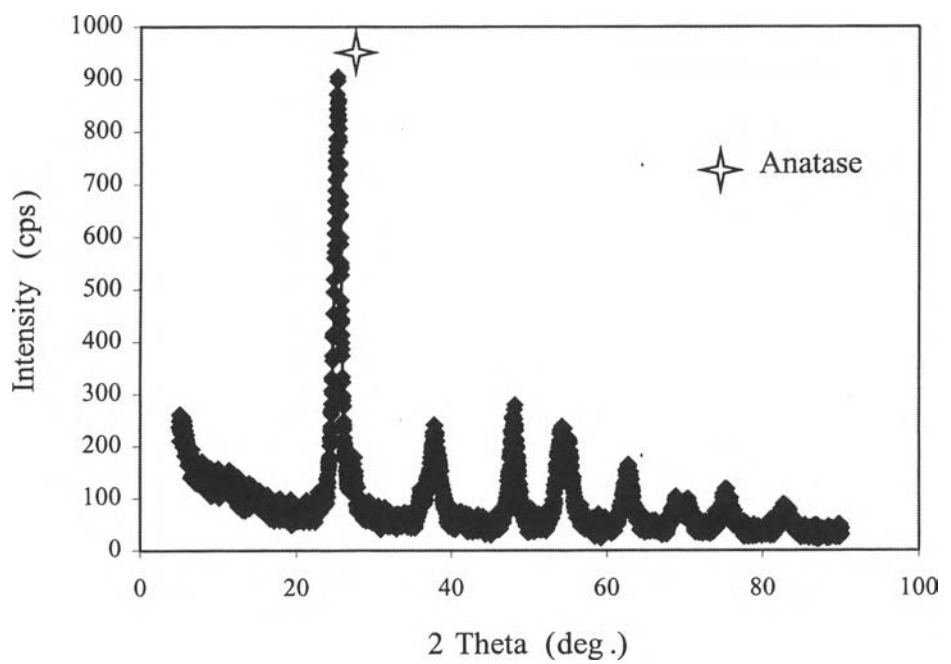

Figure 4.1 (b) XRD pattern of sol-gel TiO_2.

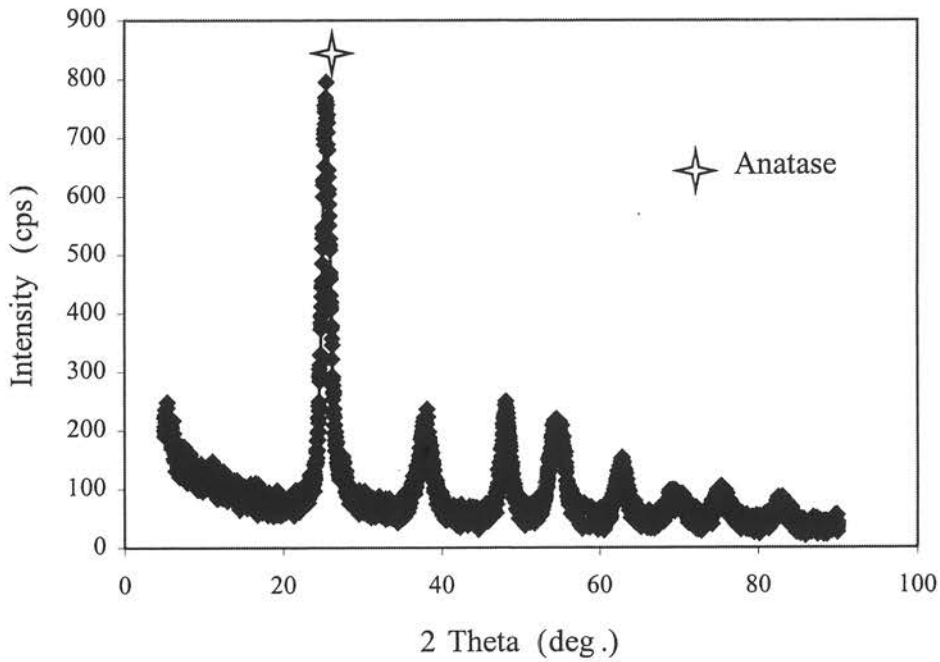

Figure 4.1 (c) XRD pattern of 1% Pt/sol-gel TiO_2.

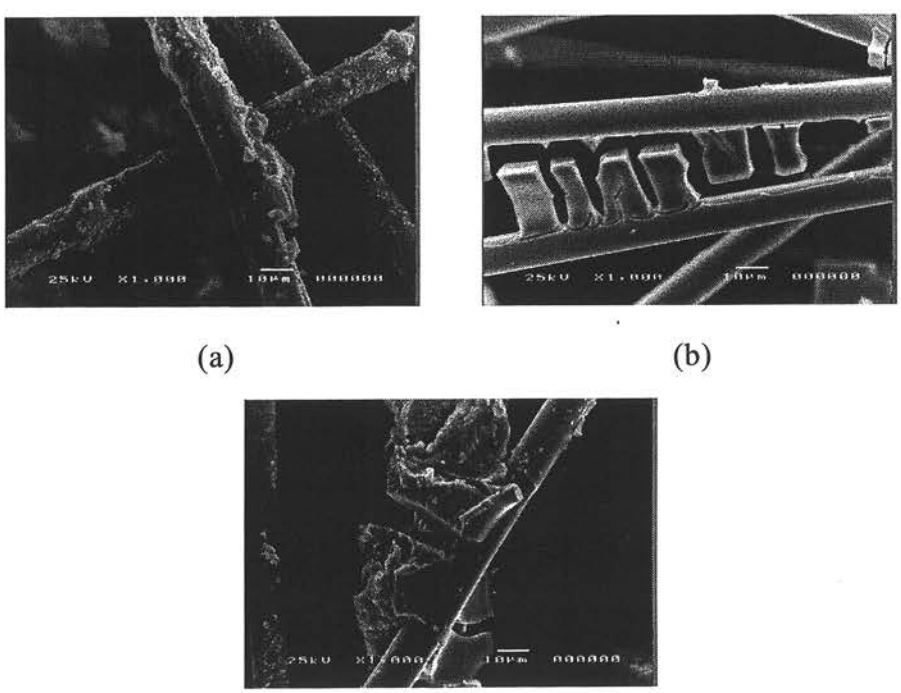

Figure 4.2 SEM micrographs of (a) Degussa P25, (b) sol-gel TiO_2, and (c) 1%Pt/sol-gel TiO_2 coated on glass wool.

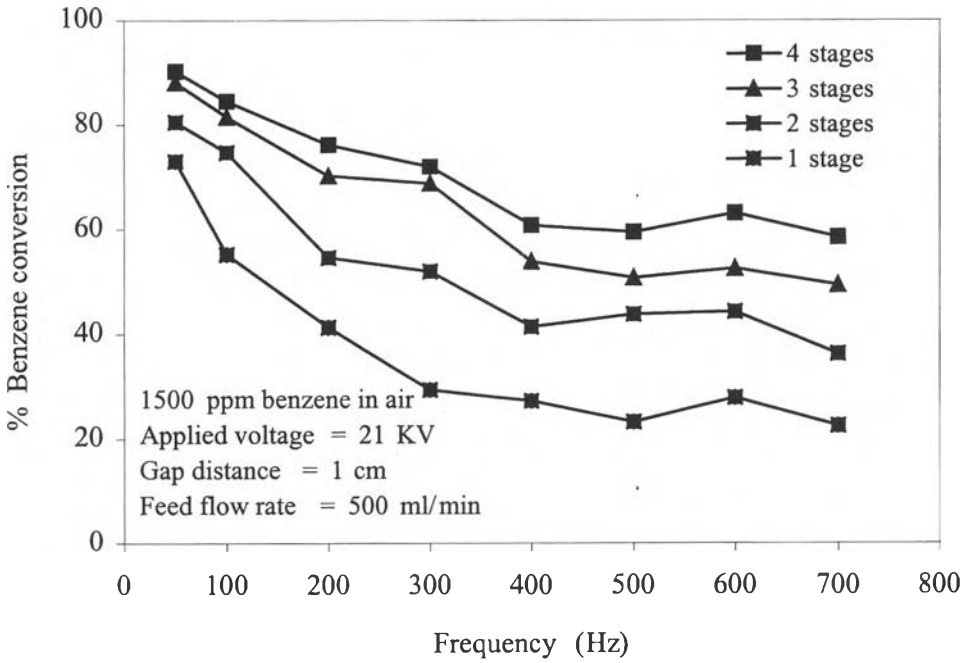

Figure 4.3 Effect of frequency on benzene conversion at different stage number of reactors at 21 kV.

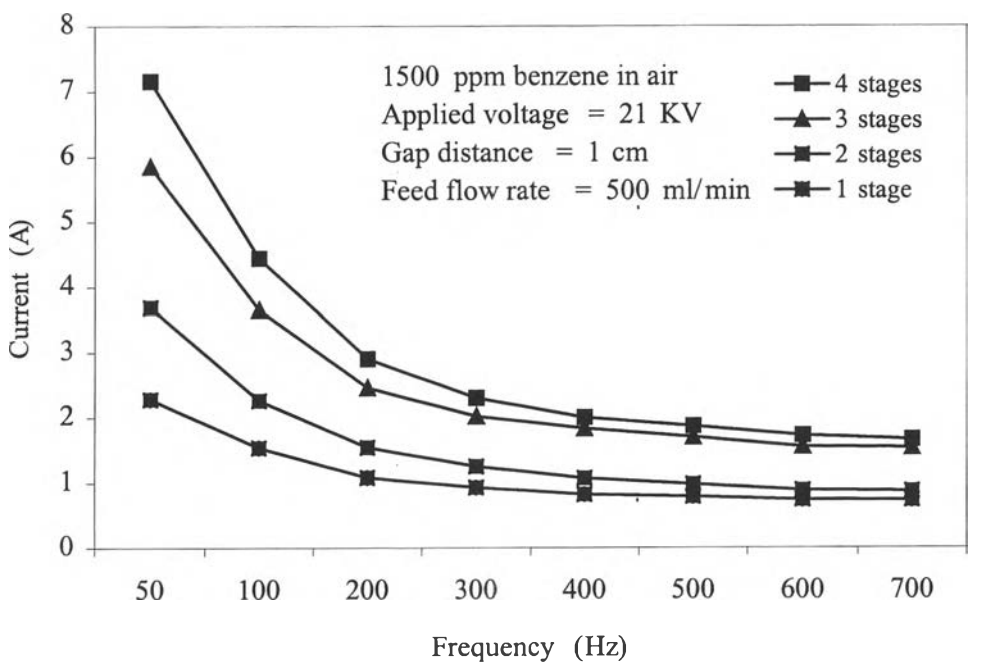

Figure 4.4 Effect of frequency on current at different stage number of reactor at 21 kV.

4.2.2 Effect of Frequency on Product Selectivity

The effects of applied frequency on CO and CO_2 selectivities are shown in Figures 4.5 and 4.6, respectively. When the frequency increases, the CO_2 selectivity decreases whereas the CO selectivity increases. As mentioned before, at lower frequency, there are a large number of electrons generated from the electrodes as shown in Figure 4.4. These electrons and O active species are accelerated to higher energy caused from the higher electric field strength. Therefore, the reaction between the O active species and CO becomes more effective leading to higher CO_2 selectivity. For any given frequency, the CO_2 selectivity also increases while CO selectivity decreases with the increase in the stage number of plasma reactors because the electrons have higher chance to break down O_2 to produce the oxygen active species.

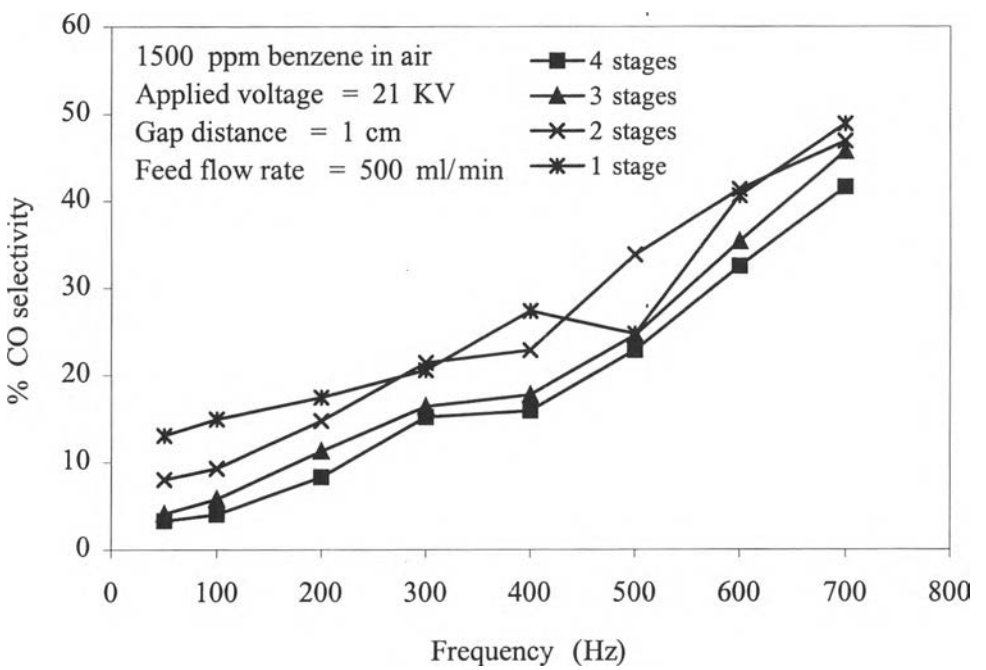

Figure 4.5 Effect of frequency on CO selectivity at different stage number of reactors at 21 kV.

When 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 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 reduce the amount of current needed to maintain the discharge (Hill, 1997). In addition, the alternating behavior has been proven effectively in eliminating contaminant accumulation on the electrodes resulting in increasing conversions as compared to DC discharge (Liu *et al.*, 1996). Although the power is constant, the effect of frequency on the conversion and selectivity comes from the space charge (electrons, radicals, and ions) and characteristics of the discharge.

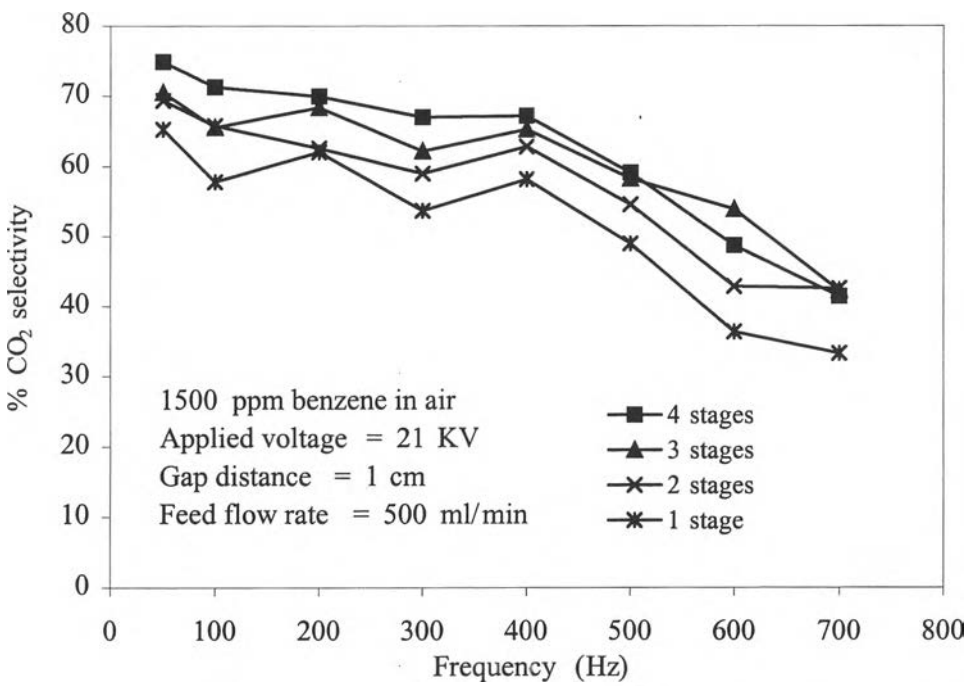

Figure 4.6 Effect of frequency on CO_2 selectivity at different stage number of reactors at 21 kV.

The effect of frequency on power consumption to break down each benzene molecule is shown in Figure 4.7. From the figure, the optimum power is obtained with the frequency in the range of 200 – 700 Hz. Since lower frequency results in a large number of electrons generated leading to higher power consumption. On the other hand, a higher frequency corresponds to the reduction of electrons generated from electrodes leading to lowering

benzene decomposition. To achieve both a minimum power consumption and a relatively high benzene conversion, 300 Hz was selected for further experiments. In addition, the amounts of by-products at 300 Hz were not detected at a significant level by the GC.

It has been also reported that other hydrocarbon (C_1-C_2) by-products from the aromatic decomposition in a packed-bed plasma reactor are detected with very low levels (Ogata *et al.*, 2002 and Suhr *et al.*, 1979). However, coke deposit was observed at the surface of the pin and plate electrodes. It can be concluded that, under the optimum frequency of 200-500 Hz, CO and CO_2 are the main products of the system.

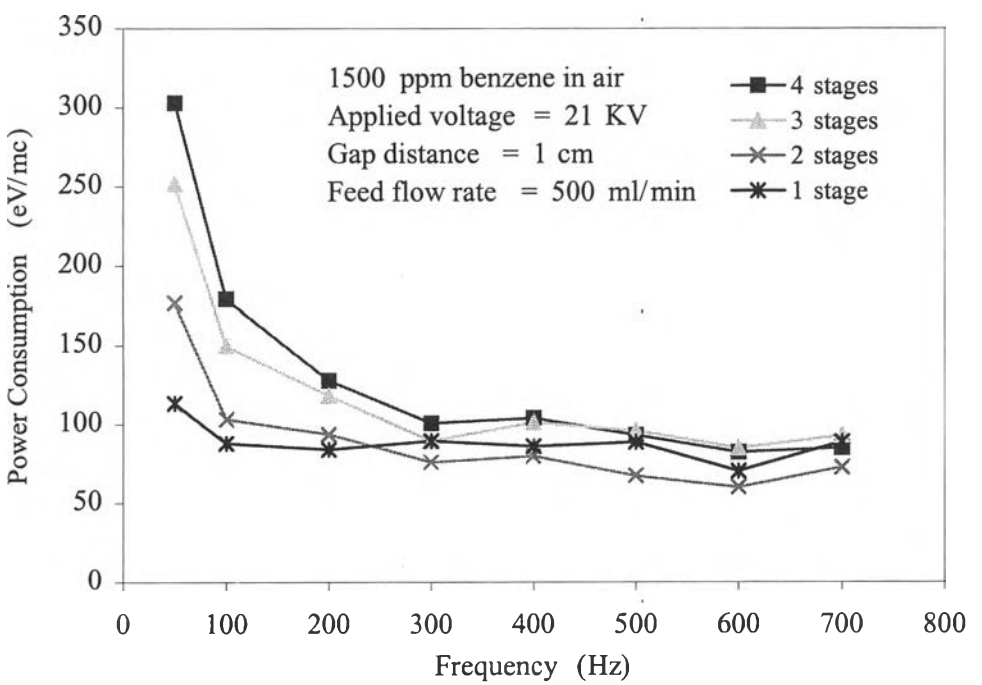

Figure 4.7 Effect of frequency on power consumption of benzene at different stage number of reactors at 21 kV.

4.3 Effects of Applied Voltage

4.3.1 Effect on Benzene Conversion

Figure 4.8 shows the effect of applied voltage on benzene conversion. The conversion of benzene increases with the increase in the applied voltage in the range of 12 to 24 kV, which is in contrast with the effect

of frequency. The reason is that a higher voltage results in higher electric field strength as shown in Figure 4.9, raising average electron energy, which sequentially increases the conversion. Morinaga and Suzuki (1962) also found that, with a fixed geometry, the quantity of electricity transferred between electrodes increases as the applied voltage increases. Kang *et al.* (2002) also concluded that a decrease in applied voltage resulted in lowering toluene decomposition. An increase in the stage number of reactors in operation increases the conversion of benzene because of a longer residence time leading to higher chance of electrons to break down benzene molecules.

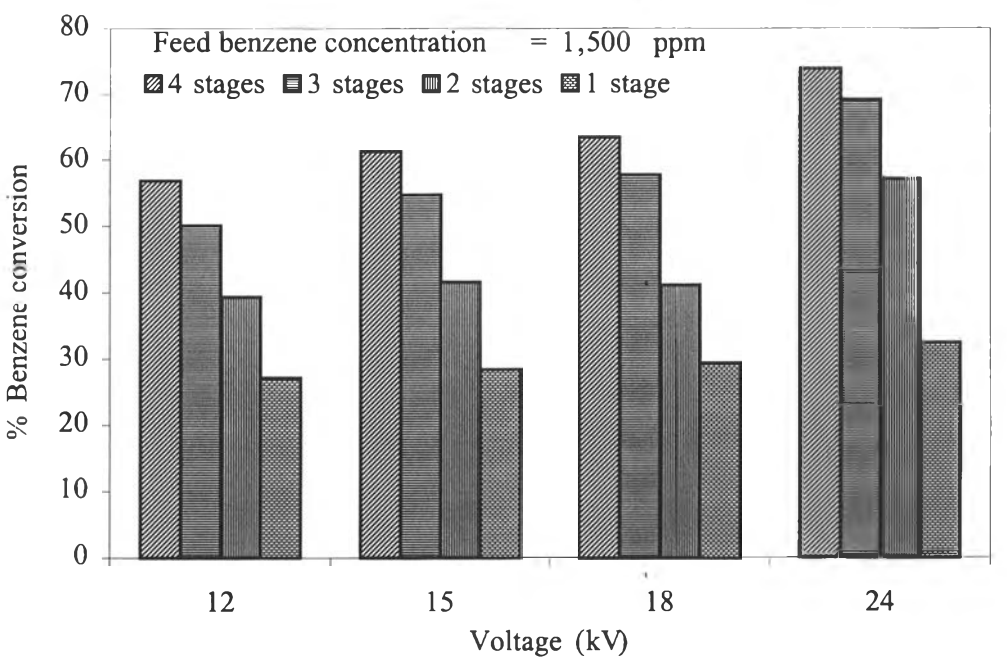

Figure 4.8 Effect of applied voltage on benzene conversion at different stage number of reactors at a feed flow rate of 500 ml/min, 300 Hz, and a gap distance of 1 cm.

4.3.2 Effect on Product Selectivity

The effects of applied voltage on CO and CO_2 selectivity are shown in Figures 4.10 and 4.11, respectively. As the applied voltage increases, the CO_2 selectivity increases whereas the CO selectivity decreases. This is because the increase in the voltage results in the increased current as shown in

Figure 4.11. As a result, there are more oxygen active species available to oxidize CO molecules leading to higher CO_2 selectivity. For any given applied voltage, the CO selectivity decreases while the CO_2 selectivity increases when the gas mixture is passed through a higher stage number of the plasma reactors. The reason is that a higher number of multi-stage plasma reactors increases the residence time of the gas. Consequently, the oxidation reaction increases.

In this study, an applied voltage 15 kV was selected for further experiments since, at this voltage, the system can provide a relatively high benzene conversion with reasonably low power consumption.

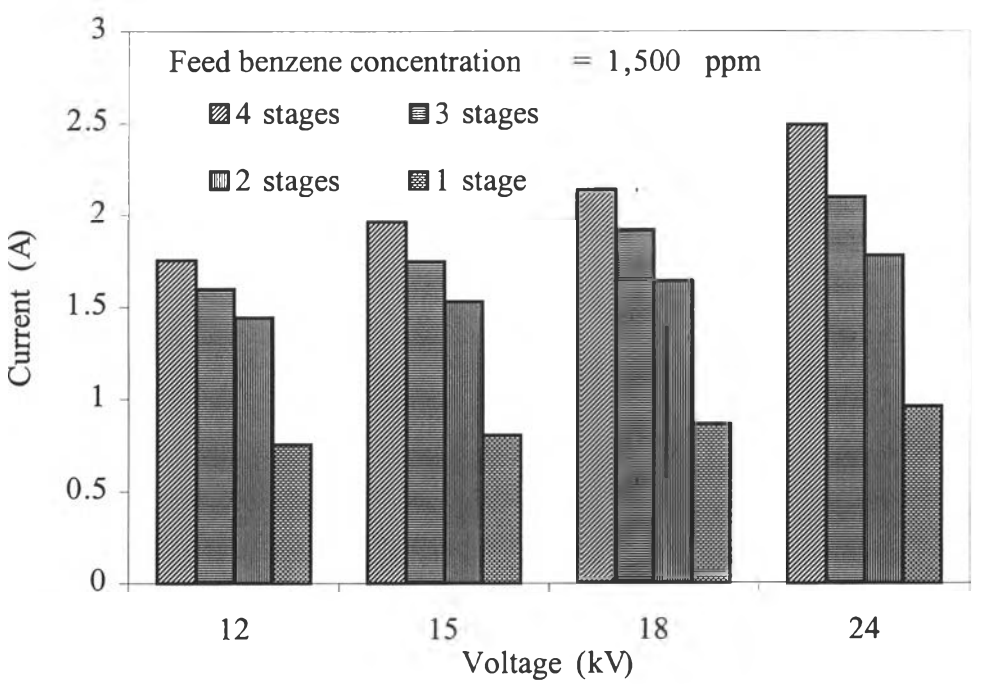

Figure 4.9 Effect of applied voltage on current at different stage number of reactors at a feed flow rate of 500 ml/min, 300 Hz, and a gap distance of 1 cm.

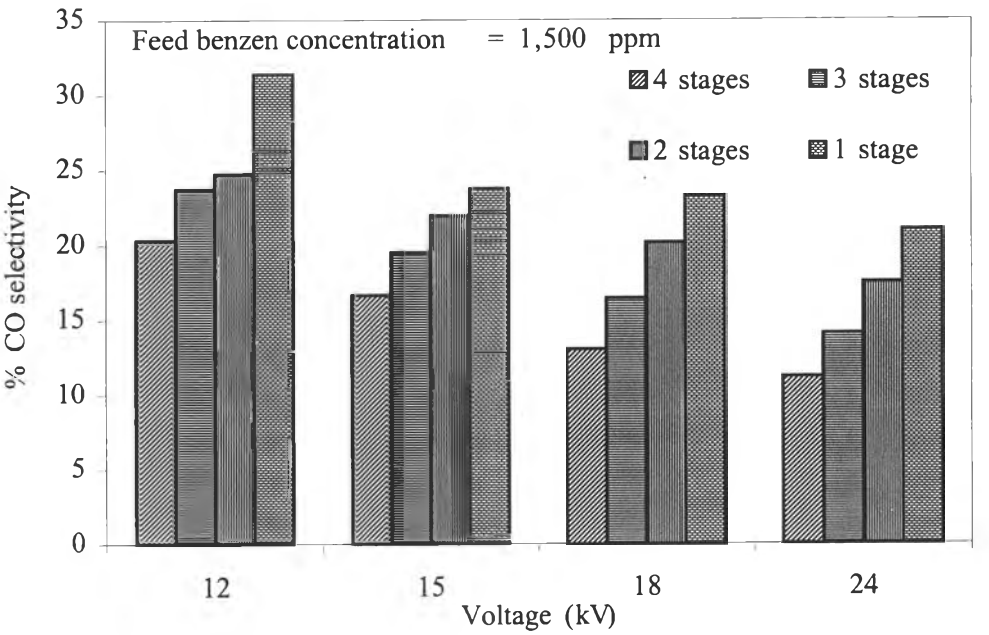

Figure 4.10 Effect of applied voltage on CO selectivity at different stage number of reactors at feed flow rate of 500 ml/min, 300 Hz, and a gap distance of 1 cm.

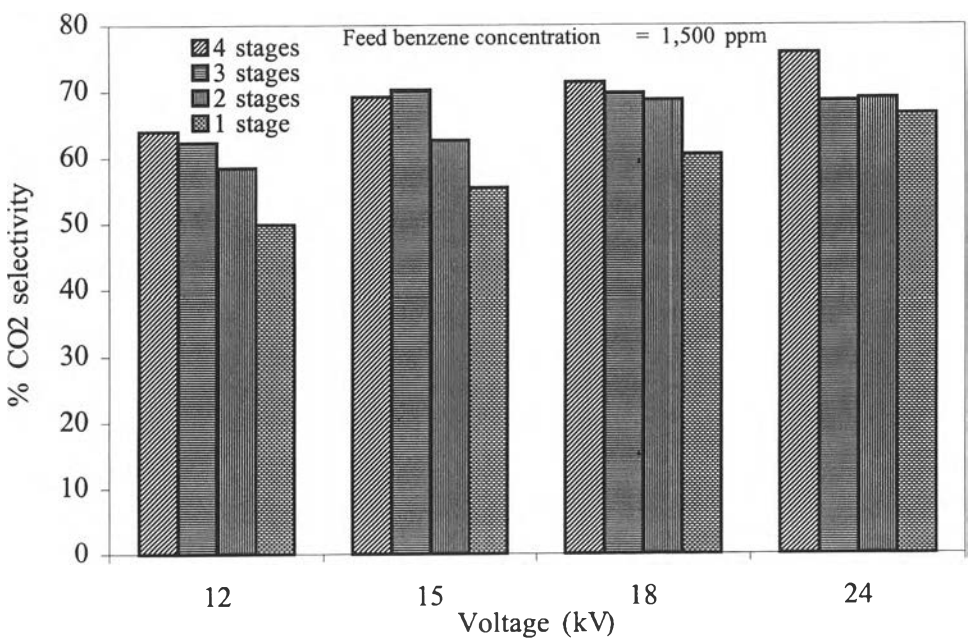

Figure 4.11 Effect of applied voltage on CO_2 selectivity at different stage number of reactors at feed flow rate of 500 ml/min, 300 Hz, and a gap distance of 1 cm.

4.4 Effects of Feed Flow Rate

4.4.1 Effect on Benzene Conversion

A Figures 4.12 illustrates the effects of the feed flow rate on benzene conversion. For all of the stage numbers in operation, benzene conversion decreases with increasing the feed flow rate in the studied range of 60 to 380 ml/min because an increase in the feed flow rate corresponds to a decrease in the residence time. For any given feed flow rates, a higher stage number of plasma reactors in use results in higher conversion of benzene. With a decrease in the feed flow rate or an increase in the stage number of plasma reactors in operation, electrons have higher possibility to collide with benzene and O_2 molecules leading to higher conversion of both reactants.

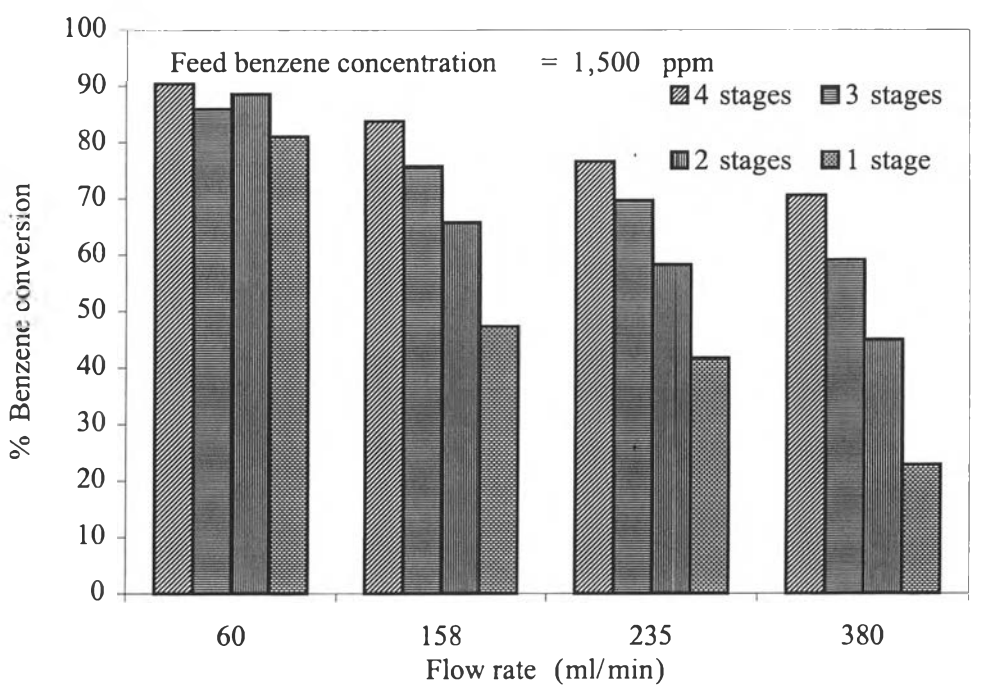

Figure 4.12 Effect of feed flow rate on benzene conversion at different stage number of reactors at 15 kV, 500 Hz, and a gap- distance of 1 cm.

4.4.2 Effect on Product Selectivity

The effects of feed flow rate on CO and CO_2 selectivity are shown in Figures 4.13 and 4.14, respectively. For any given stage number, the CO selectivity increases with increasing the feed flow rate while the opposite trend was observed for the CO_2 selectivity. A higher gas flow rate or a lower of stage number reduces the opportunity of collision between electrons and O_2 molecules. Therefore, the oxidation of CO is reduced resulting in lower CO_2 formation.

At the lowest feed flow rate, some by-products (C_1-C_2 hydrocarbons) were detected at an insignificant level and almost complete benzene conversion was observed. Thus, a range of the feed flow rate of 60-158 ml/min was selected for further study in order to determine the other effects such as stage number and the presence of photocatalyst.

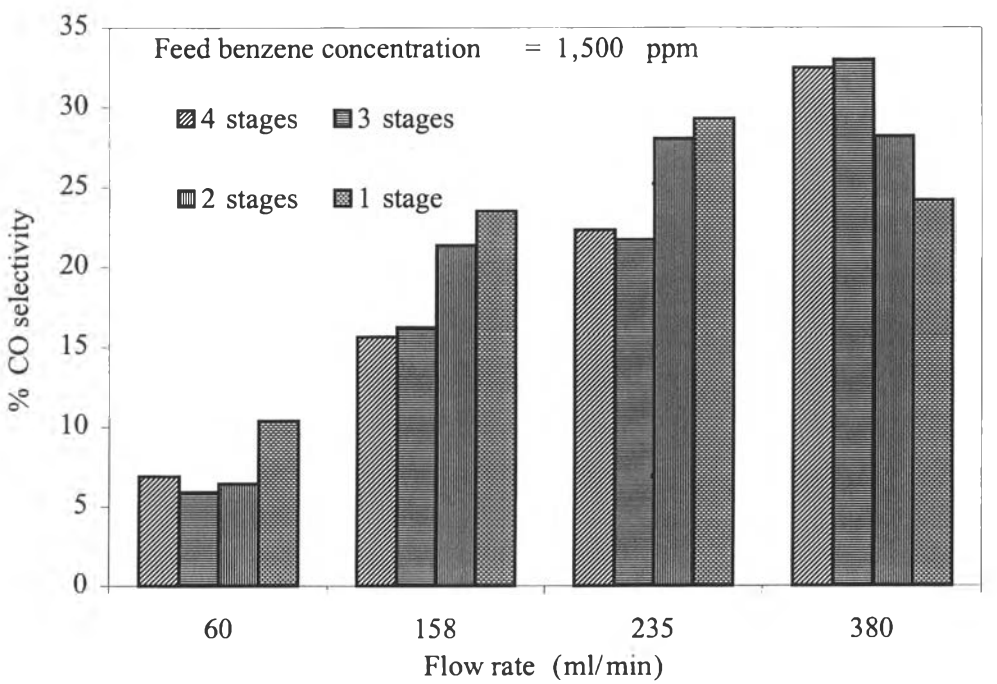

Figure 4.13 Effect of feed flow rate on CO selectivity at different stage number of reactors at 15 kV, 500 Hz, and a gap distance of 1 cm.

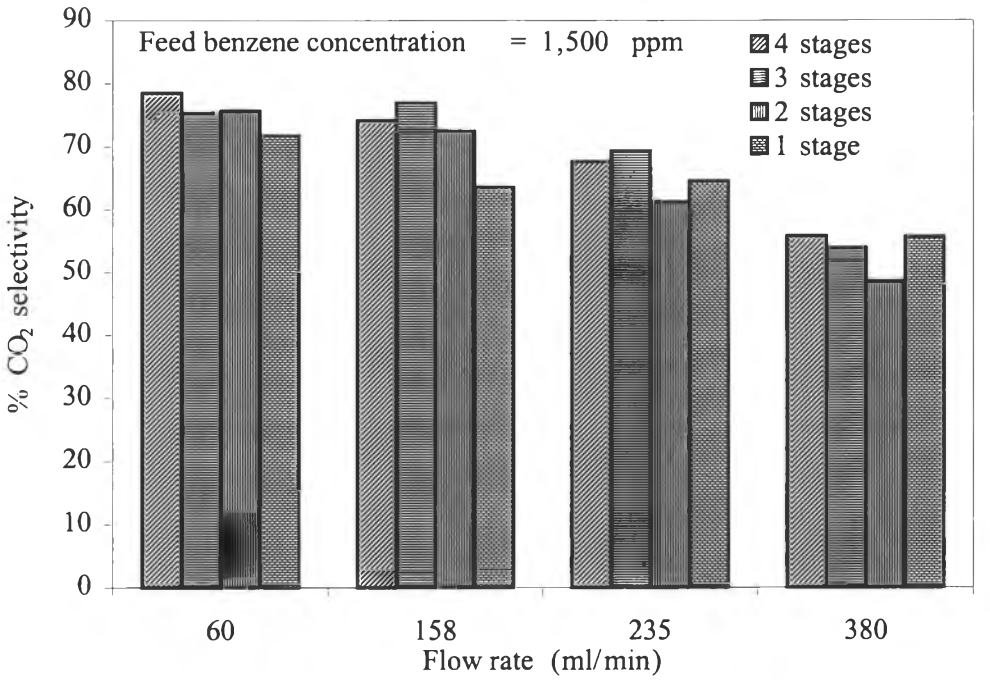

Figure 4.14 Effect of feed flow rate on CO_2 selectivity at different stage number of reactors at 15 kV, 500 Hz, and a gap distance of 1 cm.

4.5 Effect of the Presence of Different Photocatalysts

4.5.1 Effect on Benzene Conversion

Table 4.1 shows the effects of the presence of different photacatalysts coated on glass wool on benzene conversion and its product selectivity. It appears that all the catalysts (Degussa P25, sol-gel TiO_2 and 1%Pt/sol-gel TiO_2) increase the benzene conversion by 8% with 1 stage in operation and by 2 % with 2 stages in operation. Even though the same effect was not observed in a significant level with a stage number in operation higher than 2, the operation in higher stage number of plasma reactor plays an important role on the selectivity. The results imply that the energy released from the plasma can excite TiO_2 leading to the oxidation and reduction reactions on the TiO_2 surface.

4.5.2 Effect on Product Selectivity

During the plasma generation, there is energy that can activate TiO_2; therefore, the catalyst may help the oxidation of benzene. With 4 stages in operation, the presence of either sol-gel TiO_2 or the commercial TiO_2 (Degussa P25) increases the CO_2 selectivity by 6-10% and decreases the CO selectivity by 3-4%. It can be explained that TiO_2 attributes to the acceleration of superoxide radical anion formation, $O_2^{\bullet -}$, and consequently decreases the recombination process and enhance the catalytic activity (Blazkova *et al.*, 1998).

From these results, it can be concluded that benzene is dominantly removed by the plasma discharge whereas only insignificant effect from catalysis was observed. Although the amount of catalyst loaded on the glass wool is small, the combination effect only affects the selectivities of CO and CO_2. The multistage plasma reactor used in this study did demonstrated that the presence of photocatalyst could enhance both benzene conversion and CO_2 selectivity.

Tables 4.1 Effect of photocatalysts coated on glass wool at the flow rate of 60 ml/min, 500 Hz, 15,000 V, and a gap distance of 1 cm

Types of catalyst	Stage(s)	% Conversion	% Selectivity	
		Benzene	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
Degussa P25	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