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 were 63.77, 103.1, and 103.5 m^2/g, respectively. The crystal structures of the studied photocatalysts identified by XRD patterns are shown comparatively in Figure 4.1. The commercial TiO_2 (Degussa P25), sol-gel TiO_2, and 1%Pt/ sol-gel TiO_2 show the anatase peaks observed prominently at the same position of 2θ whereas no peaks of platinum at $2\theta = 40^\circ$ and 48° were observed. It suggests that Pt can be dispersed well 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 very low temperature of 400°C. Moreover, the surface morphology of the studied catalysts coated on glass wool was also examined by using a scanning electron microscope (SEM). Figure 4.2 shows the topography of Degussa P25, sol-gel TiO_2, and 1% Pt/ sol-gel TiO_2. According to the figure, the surface characteristics of sol-gel TiO_2 and 1%Pt/ sol-gel TiO_2 prepared by the sol-gel method are smoother than Degussa P25.

4.2 Effects of Frequency

4.2.1 Effect on Ethylene and Oxygen Conversions

Figures 4.3 and 4.4 show the effects of frequency on C_2H_4 and O_2 conversions, respectively. The conversions of C_2H_4 and O_2 decreased with increasing frequency in the range of 50 to 700 Hz. The explanation is that a higher frequency results in lower current that corresponds to the reduction of the number of electrons generated (Morinaga and Suzuki, 1961 and 1962) as confirmed in Figure 4.5. Consequently, the opportunity of collision between electrons and O_2 molecules decreases. At each frequency, the conversions of C_2H_4 and O_2 increased as an increase in the stage number of reactors. This is because the residence time is increased with increasing the stage number.

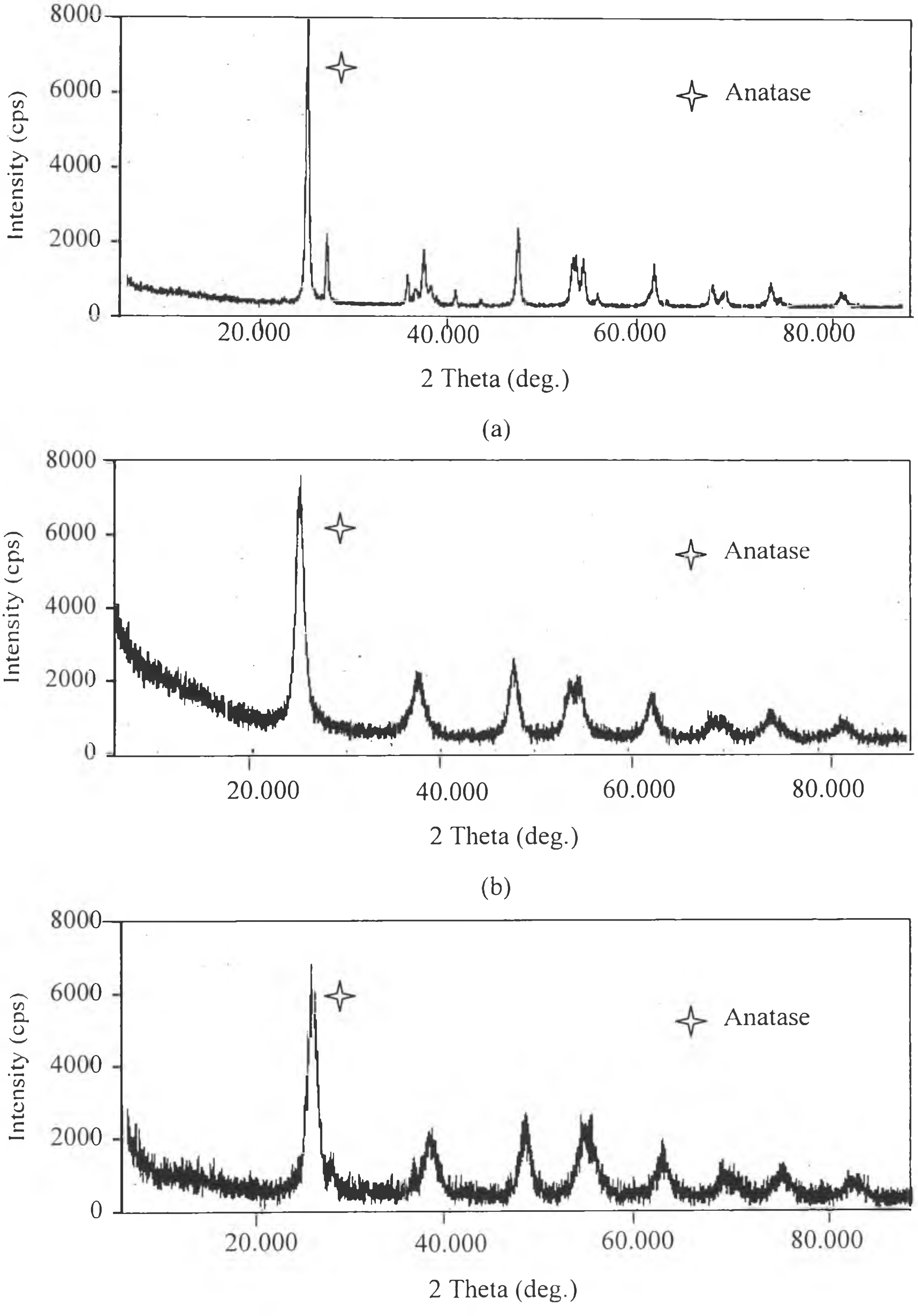
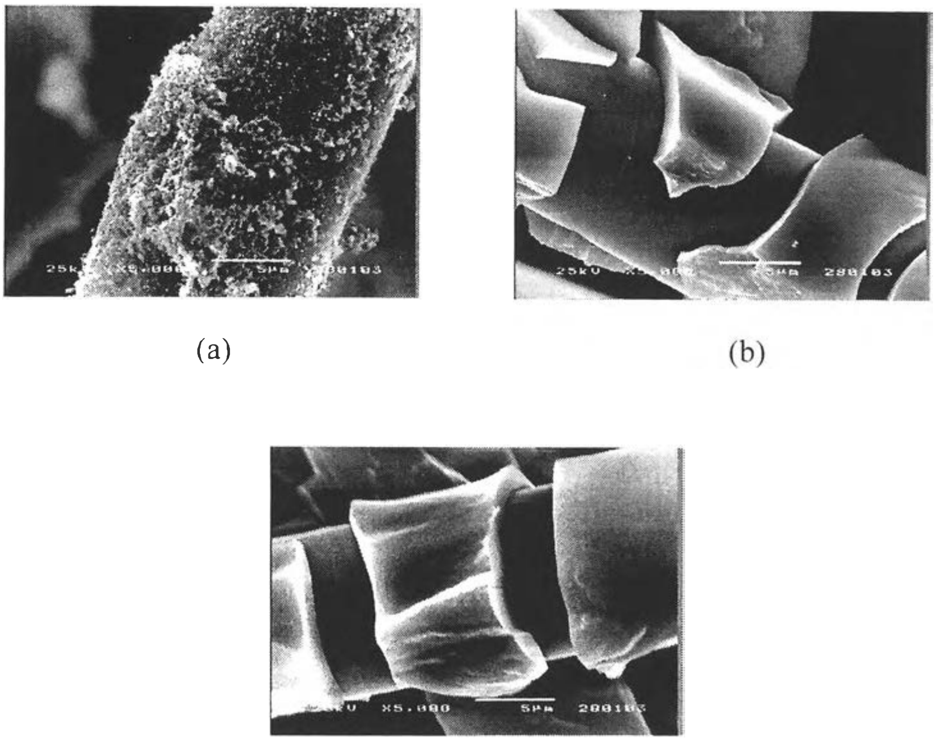


Figure 4.1 XRD patterns of (a) Degussa P25, (b) sol-gel TiO_2, (c) 1%Pt/ sol-gel TiO_2.


(a)

(b)

(c)

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

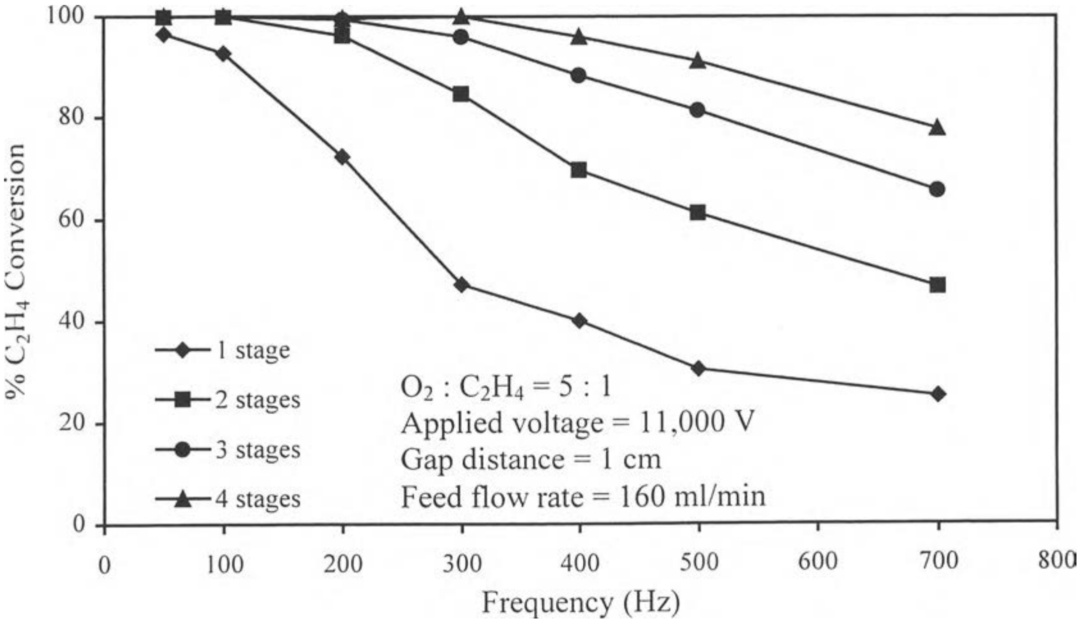


Figure 4.3 Effect of frequency on C_2H_4 conversion at different stage number of reactors.

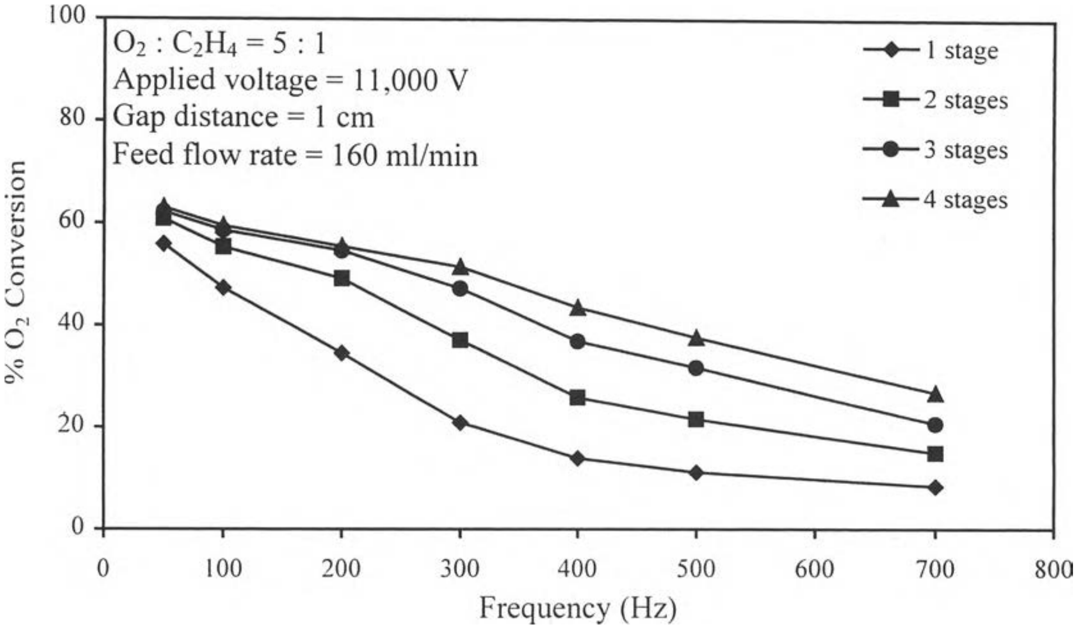


Figure 4.4 Effect of frequency on O_2 conversion at different stage number of reactors.

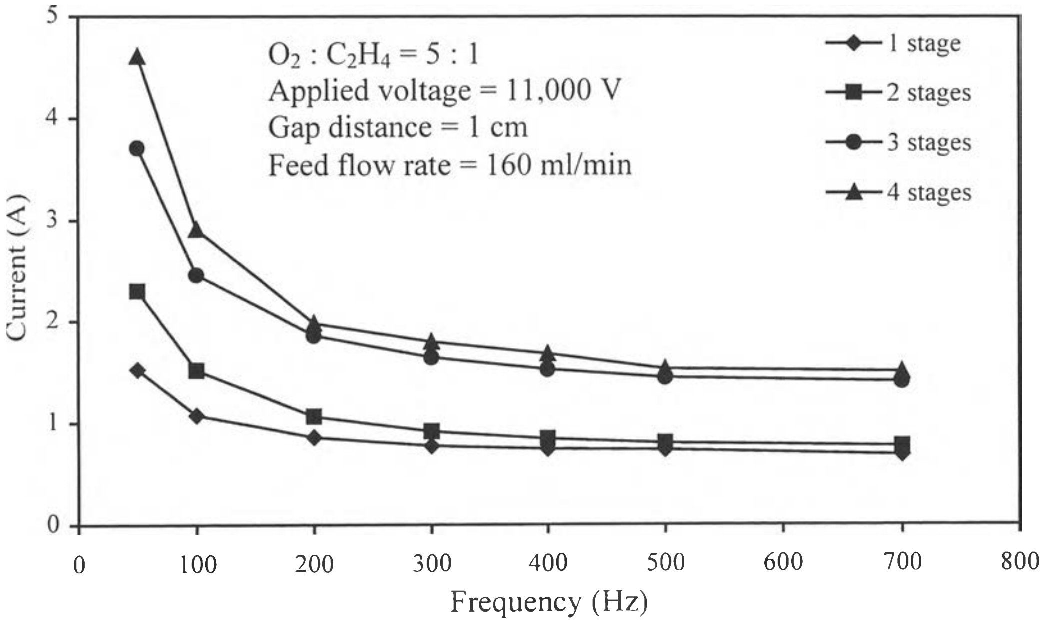


Figure 4.5 Effect of frequency on current at different stage number of reactors.

4.2.2 Effect on Product Selectivities

The effects of applied frequency on CO and CO_2 selectivities are shown in Figures 4.6 and 4.7, respectively. When the frequency increased, the CO_2 selectivity decreased whereas the CO selectivity increased. As mentioned before, at a lower frequency, there is a larger number of electrons generated from the electrodes as it shown in Figure 4.5. These electrons and O active species are accelerated to have higher energy resulted from higher electric field strength. Consequently, the reaction between the O active species and CO becomes more effective leading to a higher CO_2 selectivity. For any given frequency, the CO_2 selectivity also increased while CO selectivity decreased with increasing stage number of plasma reactors because the electrons have more chances to break down O_2 to produce the oxygen active species.

As 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

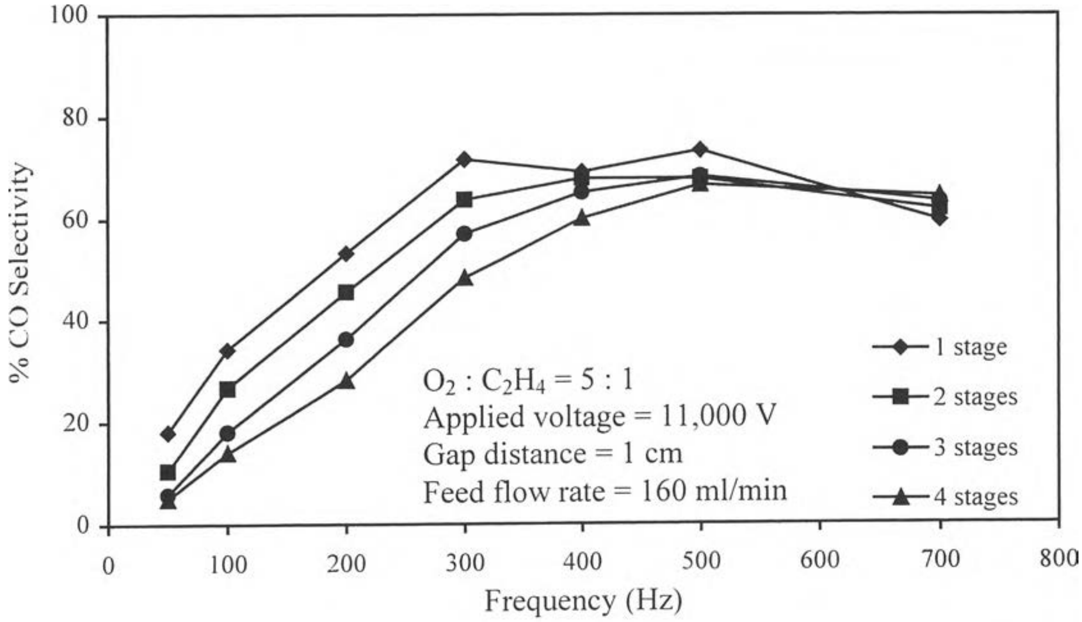


Figure 4.6 Effect of frequency on CO selectivity at different stage number of reactors.

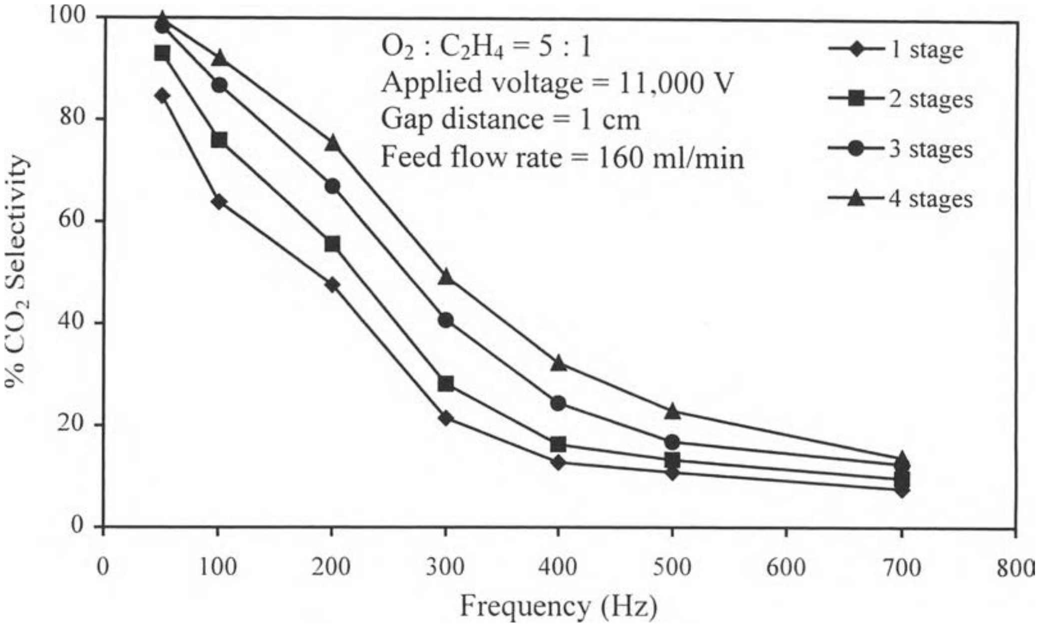


Figure 4.7 Effect of frequency on CO_2 selectivity at different stage number of reactors.

decrease the amount of current needed to sustain the discharge (Hill, 1997). Moreover, 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). The effect of frequency on the conversions and selectivities is from the space charge (electrons and ions) characteristics of the discharge, even though the power is constant.

The effect of frequency on power consumption to break down each C_2H_4 molecule is shown in Figure 4.8. As can be seen from Figure 4.8, the optimum power is obtained with the frequency in the range of 200 – 500 Hz. Since a lower frequency results in a larger number of electrons generated leading to higher power consumption. On the other hand, a higher frequency corresponds to reduce electrons generated form electrodes leading to reducing C_2H_4 decomposition. To obtain the minimum power consumption as well as to have a relatively high C_2H_4 conversion, 200 Hz was selected for next experiments. In addition, the amounts of by-products at 200 Hz are lower than at higher frequencies as shown in Table 4.1.

Interestingly, other hydrocarbon products were found very low in the studied range of frequency except large amounts of hydrocarbons were produced at high frequency (greater than 400 Hz). It can be concluded that under the optimum frequency of 200 Hz, CO and CO_2 are mainly end products of the system. From the viewpoint of air pollution control, it is reasonable to discuss comprehensively our experiment results on selectivities of CO and CO_2.

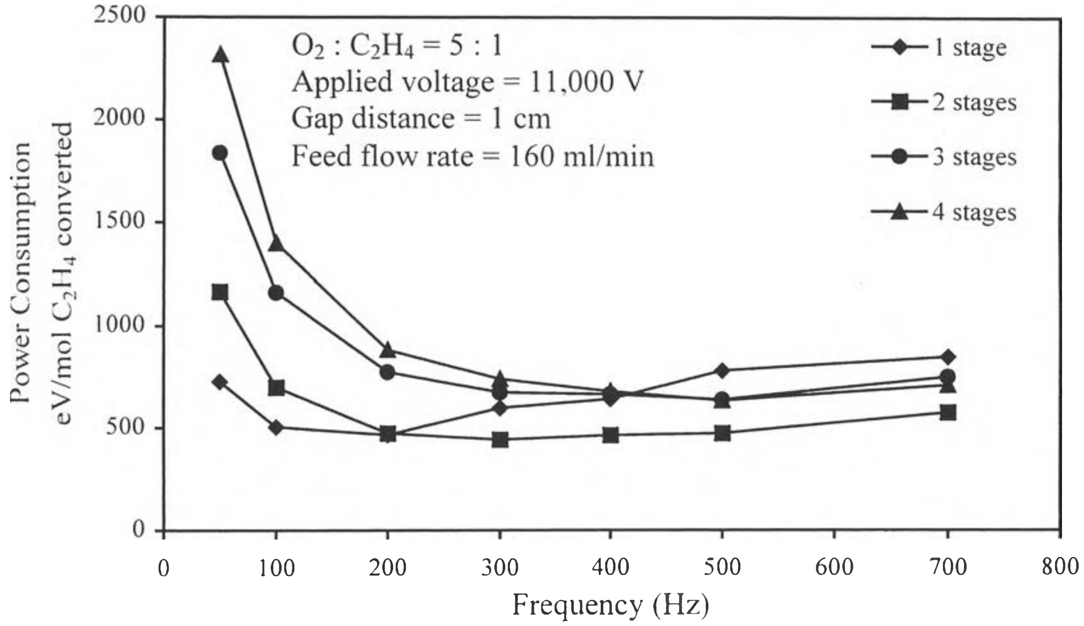


Figure 4.8 Effect of frequency on power consumption of C_2H_4 at different stage number of reactors.

4.3 Effects of Applied Voltage

As be known, it is not possible to measure the voltage across the electrodes of the reactor (high side voltage) because of its non-equilibrium in nature. The low side voltage was measured instead and then the high side voltage was calculated by multiplying with a factor of 130.

4.3.1 Effect on Ethylene and Oxygen Conversions

Figures 4.9 and 4.10 show the effects of applied voltage on C_2H_4 and O_2 conversions, respectively. The conversions of C_2H_4 and O_2 increased with increasing

Table 4.1 Effect of frequency on by-product selectivities at feed flow rate 160 ml/min, 11,000 V, and a gap distance of 1 cm with different stage number of reactors

Types of by-products	% Selectivities						
	Frequency, Hz						
	50	100	200	300	400	500	700
1 Stage							
H_2	U	U	U	U	U	12.52	15.53
CH_4	0.16	U	U	0.27	1.24	1.54	2.45
C_2H_2	0.13	U	0.26	U	0.16	0.47	0.16
C_2H_6	0.06	U	U	U	U	1.01	0.15
2 Stages							
H_2	U	U	U	U	15.03	9.12	17.76
CH_4	U	U	U	0.94	1.62	2.42	2.61
C_2H_2	0.06	U	0.13	0.06	U	0.23	U
C_2H_6	0.20	U	0.11	0.05	0.13	U	U
3 Stages							
H_2	U	U	U	U	5.94	14.57	17.80
CH_4	0.09	U	0.16	0.16	1.43	2.26	2.69
C_2H_2	U	0.08	0.11	0.12	0.02	0.11	0.09
C_2H_6	0.59	U	0.34	U	1.41	U	U
4 Stages							
H_2	U	U	U	U	U	37.48	U
CH_4	U	0.03	U	U	0.98	1.63	1.12
C_2H_2	U	0.04	0.48	U	U	U	0.14
C_2H_6	U	0.10	0.25	U	U	U	0.12

U = undetectable due to lower than detected limit

applied voltage in the range of 9,000 to 15,000 V, which is in contrast with the effect of frequency. The explanation is that a higher voltage results in higher electric field strength as shown in Figure 4.11, promoting higher average electron energy, which in turn increases the conversions. Morinaga and Suzuki (1962) also found that, with a fixed geometry, the quantity of electricity transferred between electrodes increased as the applied voltage increased. An increase in the stage number of reactors in operation resulted in increasing both conversions of ethylene and oxygen since the system had a longer residence time leading to electrons having more chance to break down C_2H_4 and O_2 molecules.

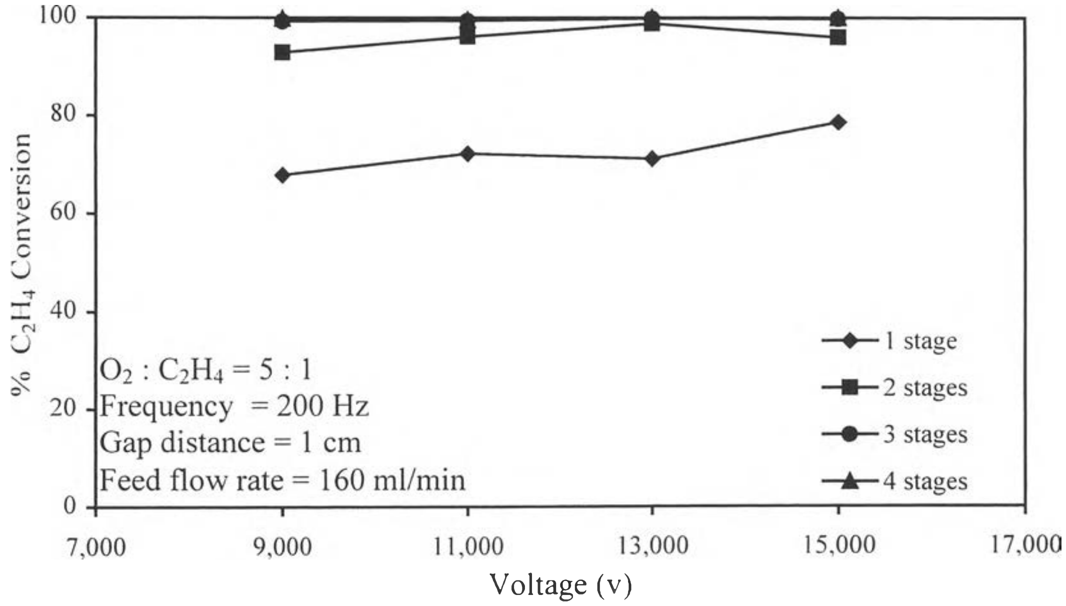


Figure 4.9 Effect of applied voltage on C_2H_4 conversion at different stage number of reactors.

4.3.2 Effect on Product Selectivities

The effects of applied voltage on CO and CO_2 selectivities are shown in Figures 4.12 and 4.13, respectively. As the applied voltage increased, the CO_2 selectivity increased whereas the CO selectivity decreased. This is because increasing voltage results in increasing 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 decreased while the CO_2 selectivity increased when the gas mixture was passed through a higher stage number of plasma reactors. The reason is that a higher number of multi-stage plasma reactors increases the residence time of the gases. Consequently, the oxidation reaction increases.

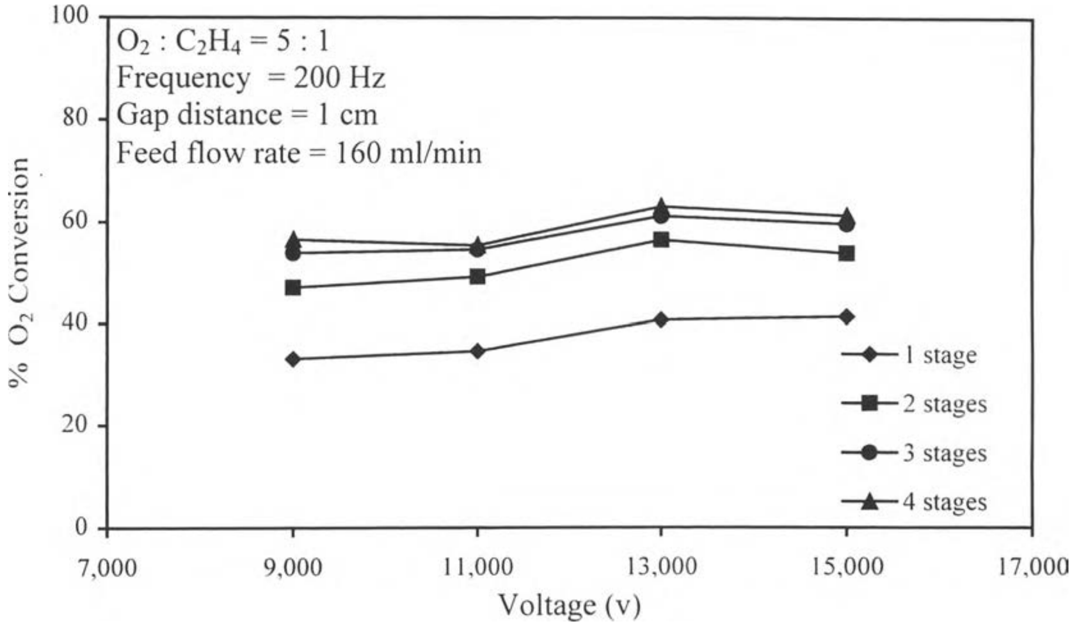


Figure 4.10 Effect of applied voltage on O_2 conversion at different stage number of reactors.

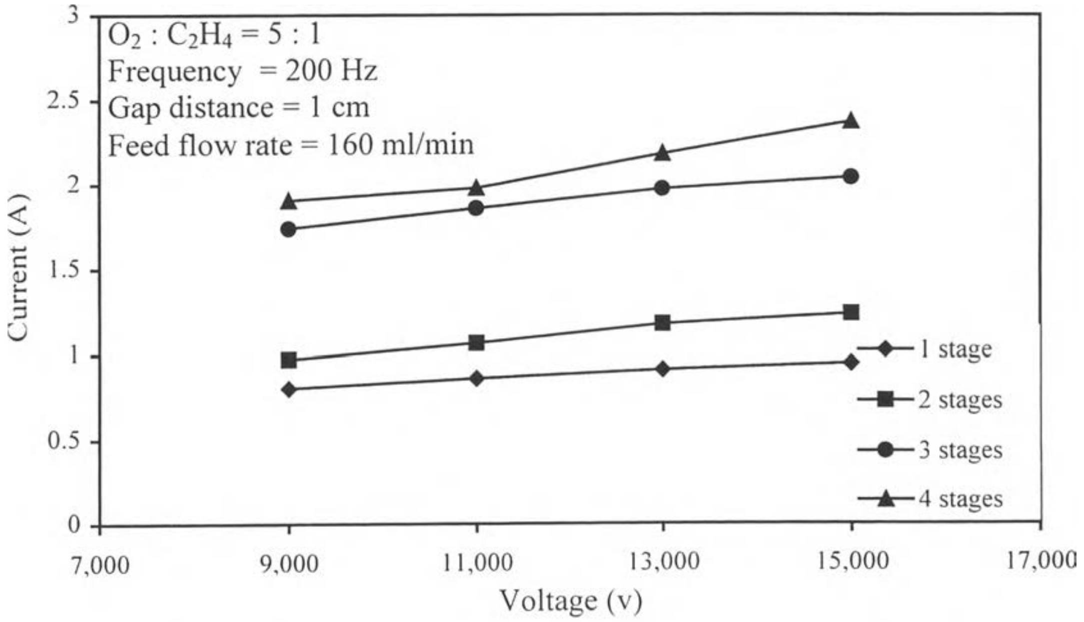


Figure 4.11 Effect of applied voltage on current at different stage number of reactors.

In this study, 11,000 V was selected for next experiments because a higher applied voltage than 11,000 V resulted in higher by-product selectivities (see Table 4.2). Even though the system at 9,000 V had less by-product selectivities than at 11,000 V but the C_2H_4 conversion was lower than at 11,000 V.

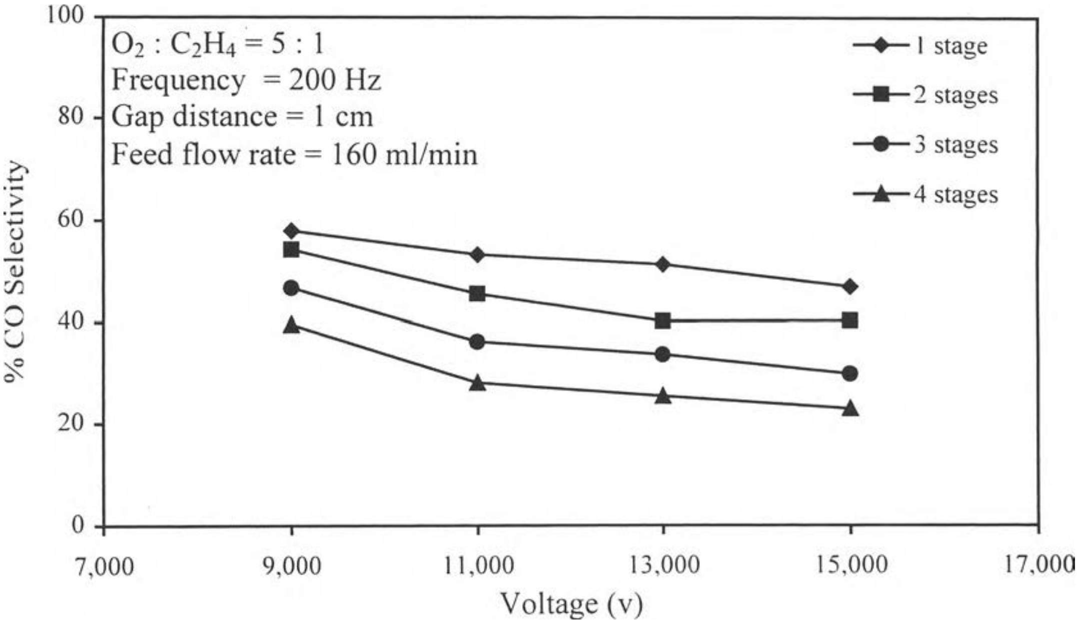


Figure 4.12 Effect of applied voltage on CO selectivity at different stage number of reactors.

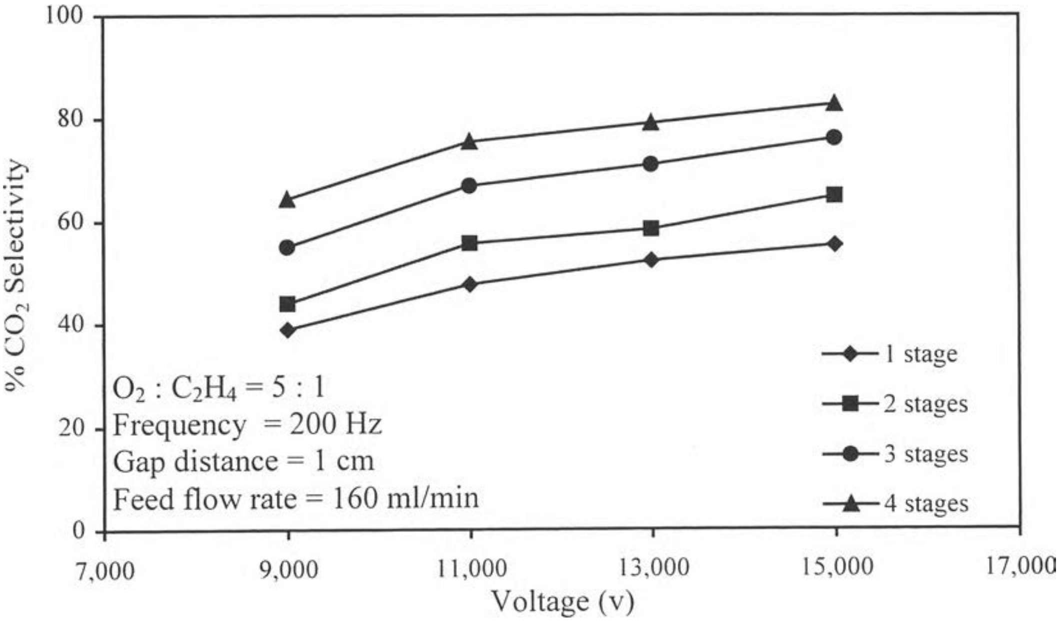


Figure 4.13 Effect of applied voltage on CO_2 selectivity at different stage number of reactors.

Table 4.2 Effect of applied voltage on by-product selectivities at feed flow rate 160 ml/min, 200 Hz, and a gap distance of 1 cm with different stage number of reactors

Types of by-products	% Selectivities			
	Applied Voltage, V			
	9000	11,000	13,000	15,000
1 Stage				
H_2	U	U	U	U
CH_4	U	U	0.29	U
C_2H_2	U	0.26	0.09	0.25
C_2H_6	U	U	U	0.15
2 Stages				
H_2	U	U	U	U
CH_4	0.36	U	0.10	U
C_2H_2	U	0.13	0.52	U
C_2H_6	U	0.11	0.65	0.06
3 Stages				
H_2	U	U	U	U
CH_4	0.08	0.19	U	U
C_2H_2	U	0.11	0.01	0.09
C_2H_6	U	0.34	0.08	0.03
4 Stages				
H_2	U	U	U	U
CH_4	0.14	U	U	U
C_2H_2	U	0.48	0.23	U
C_2H_6	U	0.25	0.08	0.08

U = undetectable due to lower than detected limit

4.4 Effects of Feed Flow Rate

4.4.1 Effect on Ethylene and Oxygen Conversions

Figures 4.14 and 4.15 illustrate the effects of feed flow rate on C_2H_4 and O_2 conversions, respectively. For either a single or two-stage system, both C_2H_4 and O_2 conversions decreased with increasing the feed flow rate in the studied range of 40 to 240 ml/min because an increase in the feed flow rate corresponds to a decrease in the residence time. For any given feed flow rate, a higher stage number of plasma reactors in use resulted in higher conversions of both C_2H_4 and O_2. With a decrease in the feed flow rate or an increase in the stage number of plasma reactors in operation, electrons have more possibility to collide with C_2H_4 and O_2 molecules leading to higher conversions of both reactants.

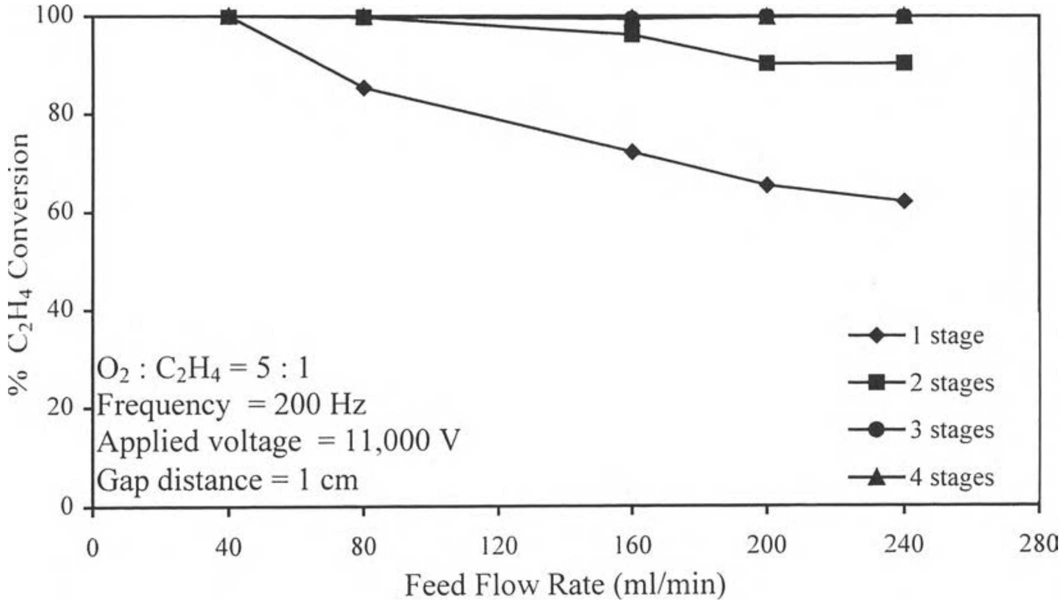


Figure 4.14 Effect of feed flow rate on the C_2H_4 conversion at different stage numbers of reactors.

4.4.2 Effect on Product Selectivities

The effects of feed flow rate on CO and CO_2 selectivities are shown in Figures 4.16 and 4.17, respectively. For any given stage number, the CO selectivity increased 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.

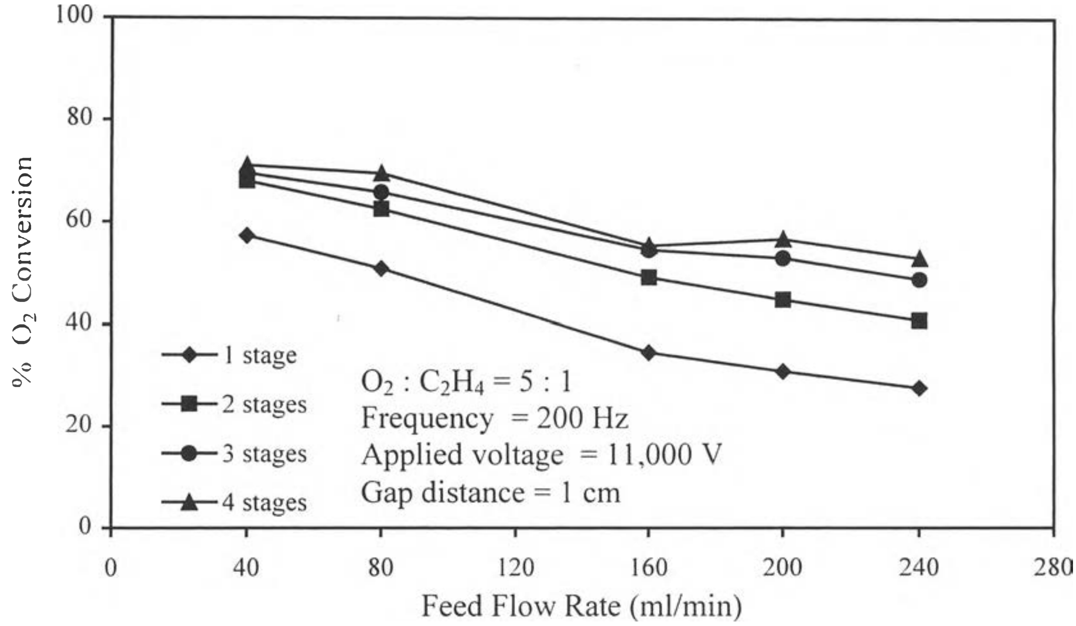


Figure 4.15 Effect of feed flow rate on O_2 conversion at different stage numbers of reactors.

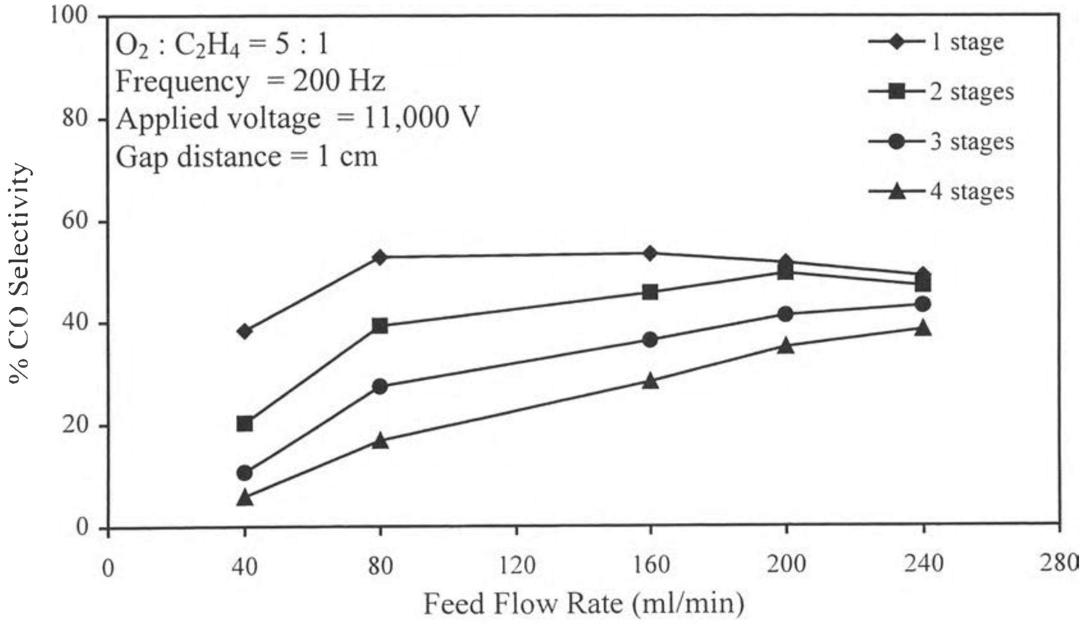


Figure 4.16 Effect of feed flow rate on CO selectivity at different stage numbers of reactors.

As shown in Table 4.3, an increase in feed flow rate results in increasing byproduct selectivities. Interestingly, at the lowest feed flow rate of 40 ml/min, by-products were not found and the complete C_2H_4 conversion was observed (see Figure 4.14). Thus, a feed flow rate of 160 ml/min was selected for further study in order to determine the other effects such as stage number and the presence of photocatalyst.

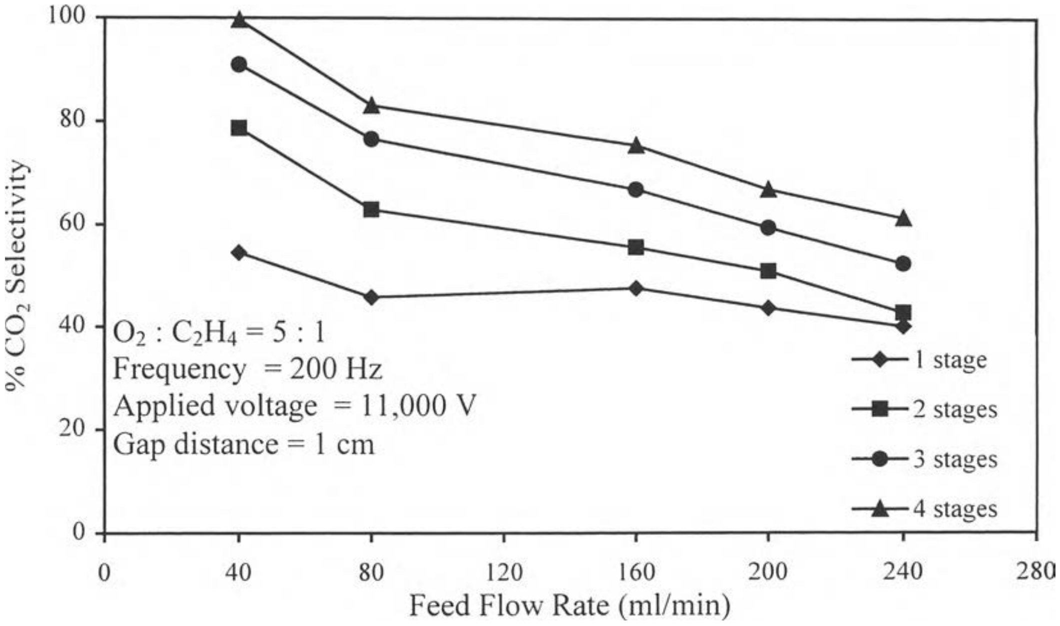


Figure 4.17 Effect of feed flow rate on CO_2 selectivity at different stage numbers of reactors.

4.5 Effects of Stage Number of Plasma Reactors

4.5.1 Effect on Ethylene and Oxygen Conversions

Figure 4.18 shows the effect of stage number of plasma reactors on the C_2H_4 conversion. Under the studied conditions, complete conversion of C_2H_4 was observed at two residence times of 1 and 0.75 sec. As expected, at the lowest residence time of 0.38 sec, the conversion of C_2H_4 increased with increasing number of stage. As seen from Figure 4.19, for any given residence time, an increase in stage number seems not to affect the oxygen conversion. The result can be explained that the system was operated under the excess oxygen environment.

Table 4.3 Effect of feed flow rate on by-product selectivities at 11,000 V, 200 Hz, and a gap distance of 1 cm with different stage numbers of reactors

Types of by-products	% Selectivities				
	Feed Flow Rate, ml/min				
	40	80	160	200	240
1 Stage					
H_2	U	U	U	U	U
CH_4	U	0.22	U	0.65	0.19
C_2H_2	U	0.39	0.26	0.45	U
C_2H_6	U	0.39	U	0.24	0.25
2 Stages					
H_2	U	U	U	U	U
CH_4	U	0.03	U	0.05	0.38
C_2H_2	U	0.10	0.13	0.13	0.19
C_2H_6	U	0.38	0.11	0.07	0.39
3 Stages					
H_2	U	U	U	U	U
CH_4	U	0.05	0.19	U	0.03
C_2H_2	U	0.19	0.11	0.19	0.28
C_2H_6	U	0.18	0.34	0.51	0.27
4 Stages					
H_2	U	U	U	U	U
CH_4	U	0.17	U	U	0.09
C_2H_2	U	U	0.48	0.05	U
C_2H_6	U	0.19	0.25	0.02	0.18

U = undetectable due to lower than detected limit

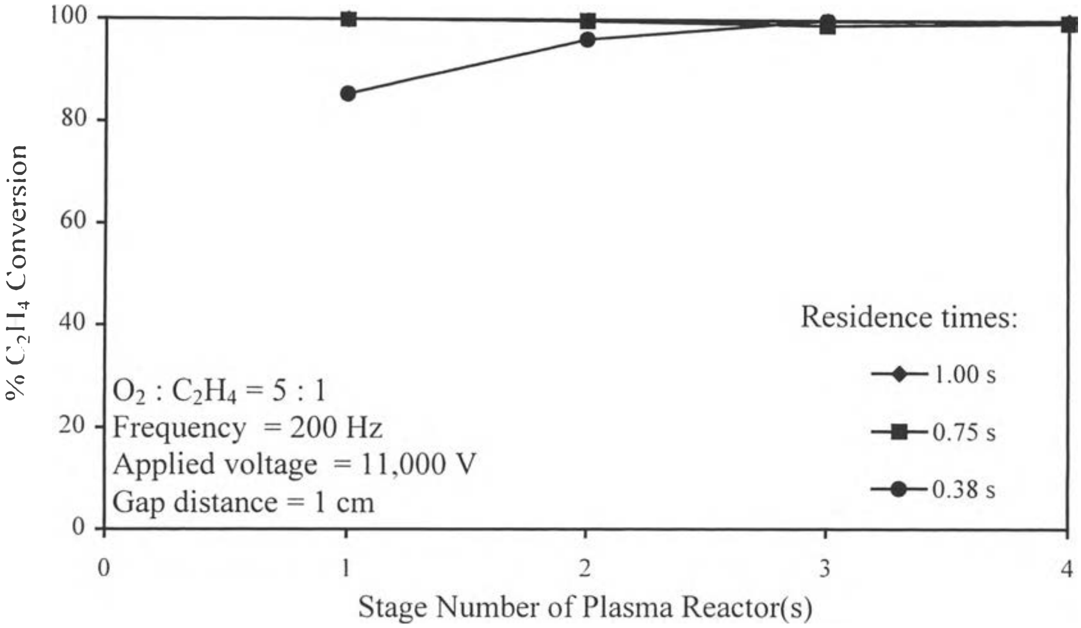


Figure 4.18 Effect of stage number on C_2H_4 conversion with different residence time.

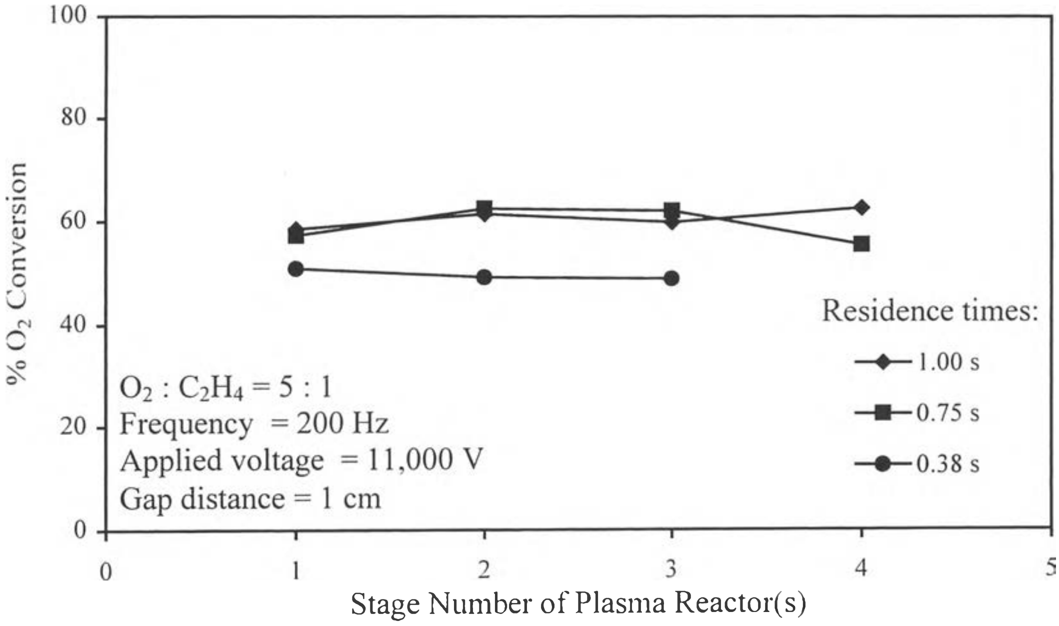


Figure 4.19 Effect of stage number on O_2 conversion with different residence time.

4.5.2 Effect on Product Selectivities

The effects of the stage number on the CO and CO_2 selectivities are shown in Figures 4.20 and 4.21, respectively. For any given residence time, as the stage number of the plasma reactors increased, the CO_2 selectivity increased whereas the CO selectivity decreased. It can be explained that a higher stage number can enhance the collision between electrons and O_2 molecules; therefore, the oxidation of CO is increased resulting in the higher CO_2 formation.

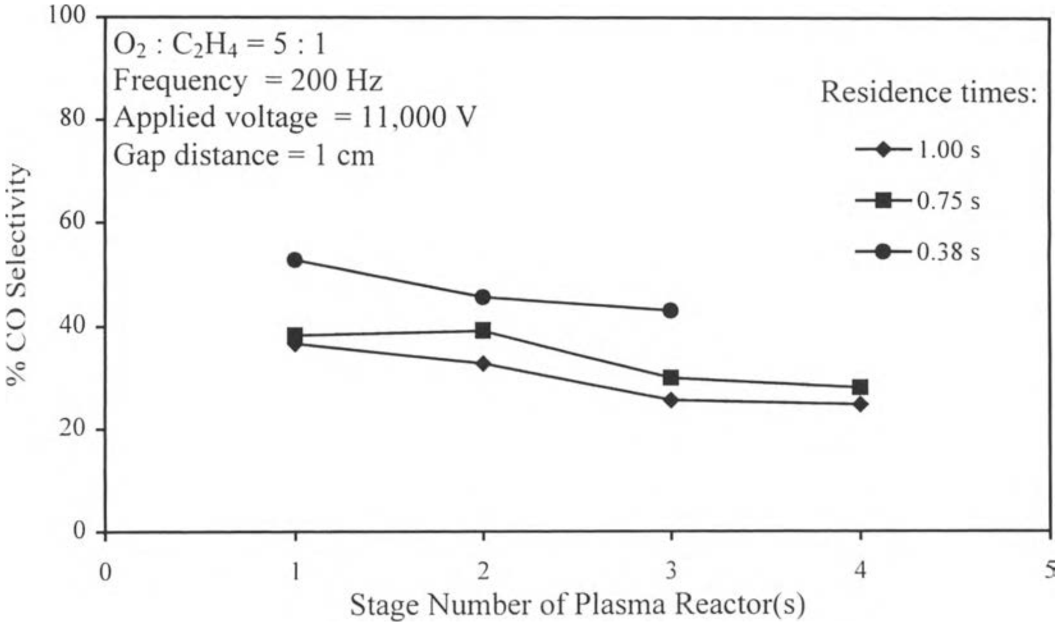


Figure 4.20 Effect of stage number on CO selectivity with different residence time.

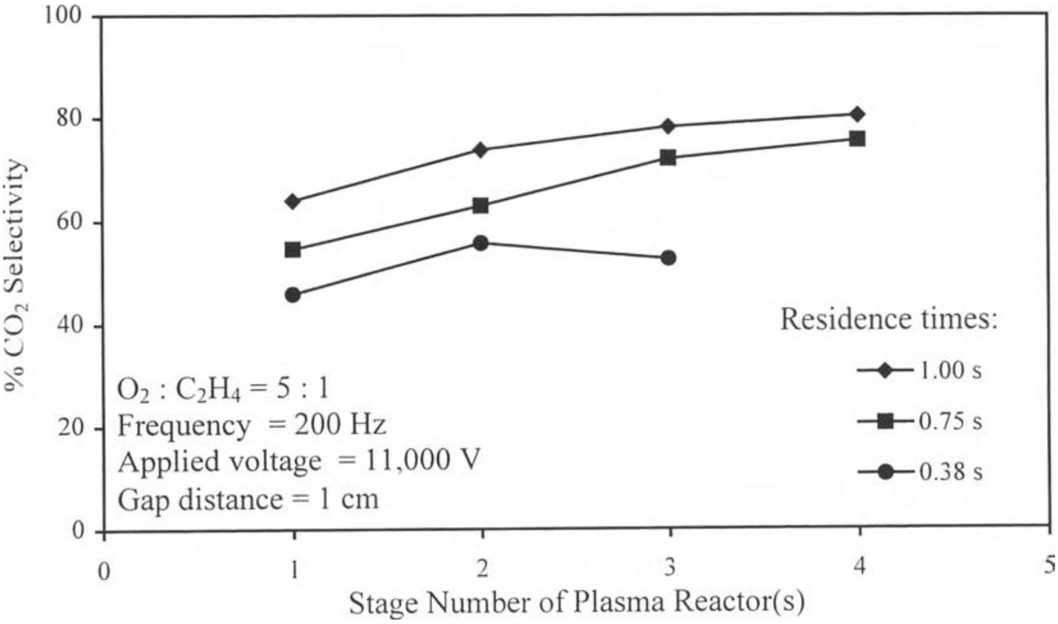


Figure 4.21 Effect of stage number on CO_2 selectivity with different residence time.

4.6 Effect of the Presence of Different Photocatalysts

4.6.1 Glass Ring Support

4.6.1.1 Effect on Ethylene and Oxygen Conversions

Table 4.4 shows the effect of two types of TiO_2 coated on glass ring on C_2H_4 and O_2 conversions. It appears that both Degussa P25 and Sol-Gel TiO_2 did not significantly enhance both C_2H_4 and O_2 conversions, which are consistant to the results reported that by Harndumrongsak *et al.* (2002).

4.6.1.2 Effect on Product Selectivities

As can be seen from Table 4.4, both CO and CO_2 selectivities are not affected by the presence of either Degussa P25 or sol-gel TiO_2. The result of the present study is different from the previous work (Harndumrongsak *et al.*, 2002), in which glass wool was used instead of a glass ring. From the previous work, the addition of TiO_2 increased the CO_2 selectivity from 58 to 71 % at the power of 3.5 W and decreased the CO selectivity. A possible explanation is that the glass ring used has less surface area than the glass wool. With the low surface area of the glass ring, it had to be coated eight times to obtain the same amount of TiO_2 on the glass wool. As a result, a multilayer of TiO_2 was formed on the glass ring. On the contrary, the glass wool only required one coating for the same amount of TiO_2 to deposit. It has been known that an external thin layer of TiO_2 exposed to light can initiate redox reaction. That is why the TiO_2-coated glass ring did not have the same effect on the selectivity as the glass wool. Another reason could be the location of the glass ring, which was far from the plasma zone so the light generated from plasma could not activate the catalyst effectively.

4.6.2 Glass Wool Support

4.6.2.1 Effect on Ethylene and Oxygen Conversions

Table 4.5 shows the effects of the presence of different photocatalysts coated on glass wool on conversions and product selectivities. As compared to the absence of photocatalyst, all of Degussa P25, sol-gel TiO_2 and 1%Pt/sol-gel TiO_2 significantly increased the C_2H_4 conversion by 20% and 10% with 1 and 2 stages in operation, respectively. However, the same effect was not observed when higher than two stages were used since the ethylene conversion on all catalysts approached 100%. The presence of all studied photocatalysts appeared to increase the O_2 conversion in a following order: 1%Pt/sol-gel TiO_2 >sol-gel TiO_2 >Degussa P25 for any given stage number. The results imply that the energy released from the plasma will excite TiO_2 to create the energy band gap of conductance band and valance band leading to the oxidation and reduction reactions on the TiO_2 surface.

Table 4.4 Effect of Photocatalysts coated on glass ring at flow rate 160 ml/min, 11,000 V, a gap distance of 1 cm, and weight of photocatalyst of 0.008 g

Stage (s)	Frequency = 200 Hz				Frequency = 50 Hz			
	% Conversion		% Selectivity		% Conversion		% Selectivity	
	O_2	C_2H_4	CO	CO_2	O_2	C_2H_4	CO	CO_2
No catalyst								
1	30	61	29	42	45	82	13	86
2	44	87	54	49	56	98	14	90
3	52	98	45	60	59	100	8	96
4	56	100	34	71	60	100	6	98
Degussa P25								
1	28	58	56	38	45	79	13	85
2	43	85	54	44	61	98	14	87
3	51	98	45	54	64	100	8	94
4	56	100	36	64	65	100	6	96
Sol-Gel TiO_2								
1	28	58	59	42	53	87	13	88
2	42	86	54	46	60	93	11	90
3	51	97	46	56	62	100	7	93
4	55	100	36	67	62	100	6	94

4.6.2.2 Effect on Product Selectivities

During plasma generation, it also releases the energy that can activate TiO_2; therefore, the catalyst can promote more complete oxidation of C_2H_4. The presence of either sol-gel TiO_2 or the commercial TiO_2 (Degussa P25) increased the CO_2 selectivity by 4-7%, but decreased the CO selectivity by 6%. With 1%Pt loaded on sol-gel TiO_2, the CO_2 selectivity increased significantly about 10-17%. Since Pt on TiO_2 attributes to the acceleration of superoxide radical anion, $O_2^{\bullet -}$, formation and consequently decreases the recombination process leading to enhance the catalytic activity (Blazkova *et al.*, 1998).

Tables 4.5 Effect of Photocatalyst coated on glass wool at flow rate 160 ml/min, 200 Hz, 9,000 V, a gap distance of 1 cm, and weight of photocatalyst 0.008 g

Types of catalyst	Stage(s)	% Conversion		% Selectivity	
		C_2H_4	O_2	CO	CO_2
No catalyst	1	47	22	70	29
	2	80	37	61	35
	3	95	47	52	46
	4	99	52	43	56
Degussa P25	1	67	30	58	36
	2	90	43	56	42
	3	98	50	48	51
	4	99	53	41	60
Sol-Gel TiO_2	1	68	33	57	38
	2	90	44	55	43
	3	99	50	48	51
	4	99	54	41	60
1% Pt/Sol-Gel TiO_2	1	68	35	56	46
	2	90	46	55	46
	3	98	53	46	56
	4	99	57	35	70

During plasma generation, it is believed to generate UV light. Under the studied conditions of frequency 200 Hz, voltage 9,000 V, and a gap distance of 1 cm, the UV intensity generated from the first-stage reactor was measured to be about 0.012 μW/cm^2 or 3.3943 μW by using a UV meter as shown in Figure 4.22. As compared to the input power of 97 W, the UV intensity was considerably small. However, the UV light meter is only to measure the light intensity in UV range but the energy released from plasma has also in various wavelengths. In addition to UV, shorter wavelengths can also initiate the photocatalytic reaction. From the results, it can be concluded that ethylene is dominantly decomposed by plasma while a minor effect from photocatalysis was observed.

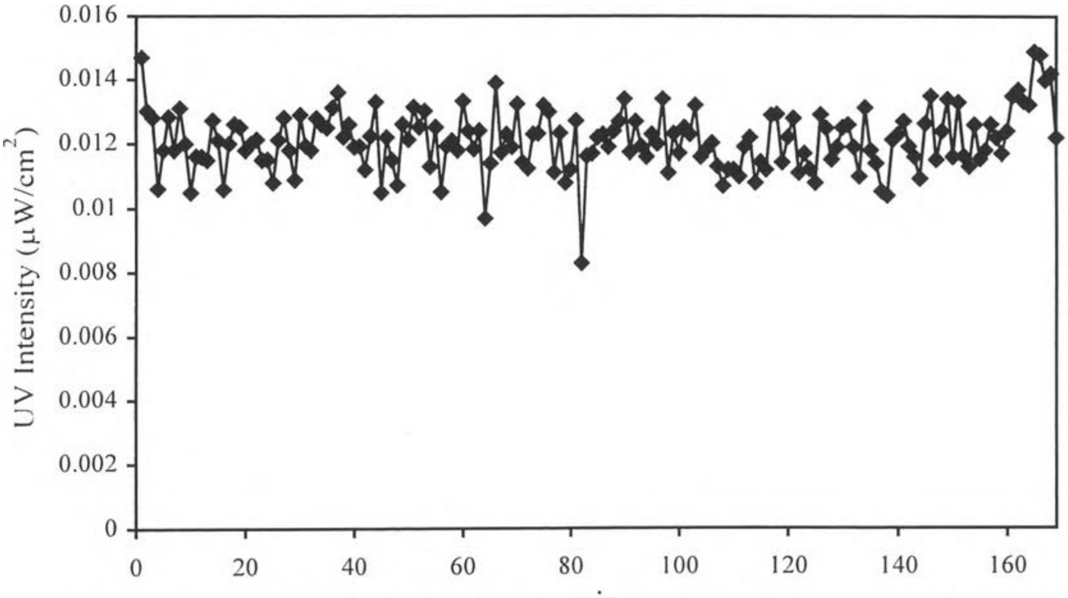


Figure 4.22 The UV light intensity generated from the first-stage plasma reactor operated at a feed flow rate 160 ml/min, 200 Hz, 9,000 V, and a gap distance of 1 cm.