

CHAPTER IV

RESULTS AND DISCUSSION

Appendix A shows how to calculate conversion, selectivity and yield to be used in this study. The experimental data of the present study were summarized in Appendix B and those results are plotted and described in this chapter in connection with some evidences and information derived from previously published literature. In addition, chemical reaction pathways are also proposed to explain how various products are formed under low temperature plasma environment.

4.1 The Plasma System with the Absence of Catalyst

4.1.1 Effect of Ethane Partial Pressure on Conversions and Yield

This part of experiments was carried out with varying the ethane partial pressure while all other parameters were kept constant. Figure 4.1 shows that the partial pressure of oxygen decreases slightly with increasing ethane partial pressure whereas those of ethane, methane, carbon monoxide, hydrogen, ethylene and acetylene slightly increased. The effects of ethane partial pressure on the conversions of methane, oxygen and ethane are shown in Figure 4.2. The oxygen conversion slightly increased while the methane and ethane conversions decreased as the ethane partial pressure increased. This indicates that the presence of ethane in this system is as an inhibitor to methane conversion. It was also noticeable that the ethane conversion was always higher than methane conversion. This might be due to the fact that, when higher amount of ethane was introduced into the feed, its cracking reaction to produce methane molecules might also occur. Therefore, the methane conversion seems to deteriorate in the case that ethane molecules are presented into the feed. Moreover, the single bond between the two carbon

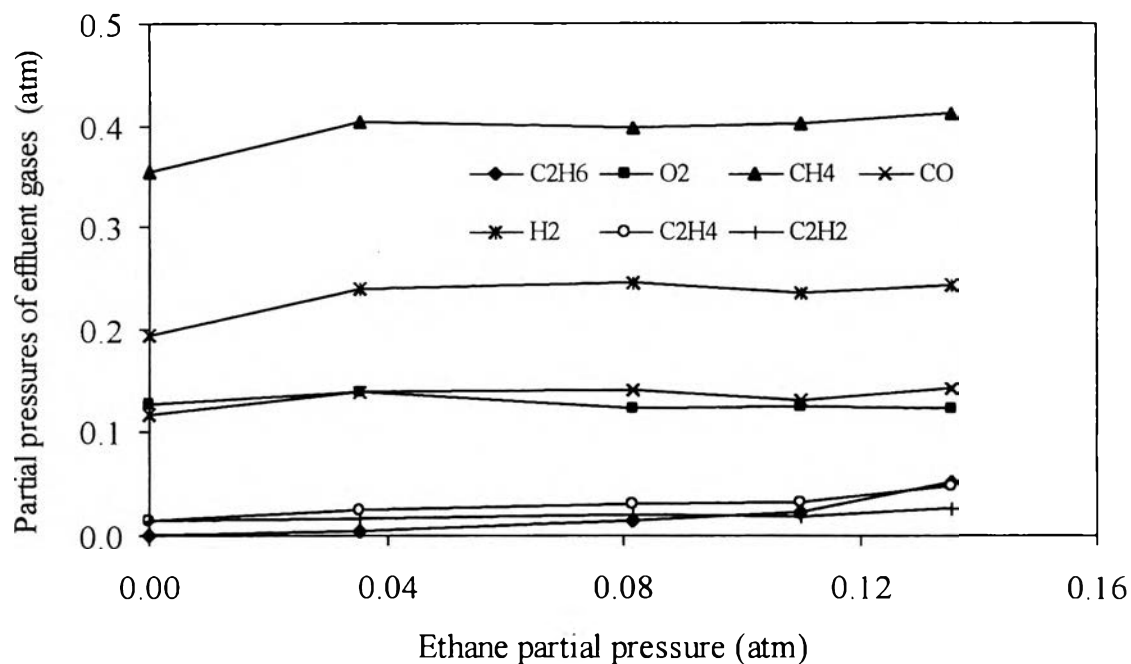


Figure 4.1 Effect of ethane partial pressure on partial pressures of effluent gases. (flow rate = 100 ml/min; applied voltage = 8,000 V; frequency = 400 Hz and gap width = 1.3 cm)

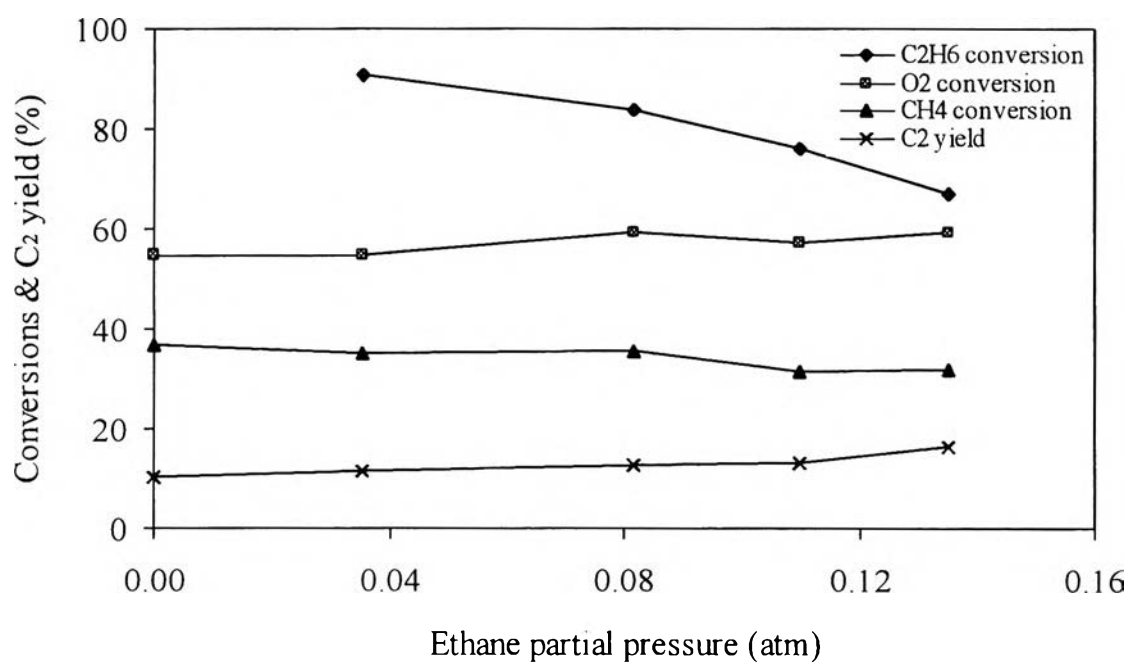


Figure 4.2 Effect of ethane partial pressure on conversions and C₂ yields. (flow rate = 100 ml/min; applied voltage = 8,000 V; frequency = 400 Hz and gap width = 1.3 cm)

atoms in the ethane molecule is relatively weak compared to the carbon-hydrogen bond in methane and can be dissociated very much easier than methane molecule. Consequently, ethane conversion is higher than methane conversion and all other experiments in this system revealed a similar behavior. In addition, the C_2 yield increased (from 10% to 16%) with increasing the ethane partial pressure in the studied range since an addition of ethane still remained mostly unreacted in the system.

4.1.2 Effect of Ethane Partial Pressure on Products Selectivities

The distribution of the products is plotted as a function of the ethane partial pressure as shown in Figure 4.3. There are two main reactions occurring in this study namely the partial oxidation of methane to form synthesis gas (CO and H_2) and the oxidative coupling of methane to form C_2 hydrocarbons (ethylene and acetylene). Interestingly, for the studied

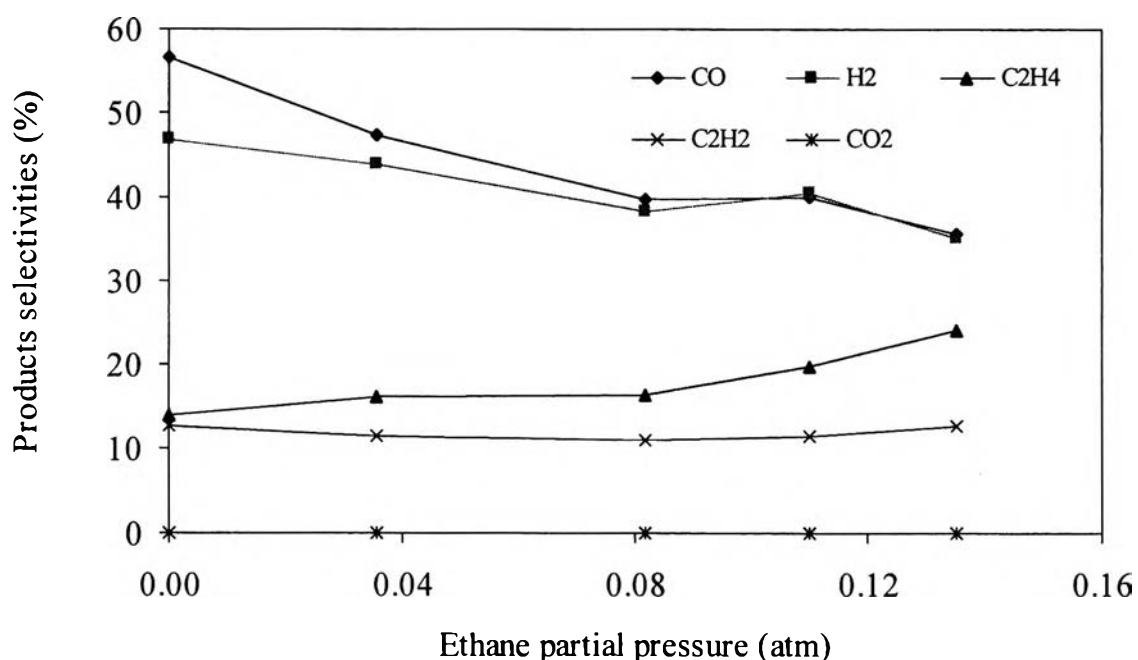
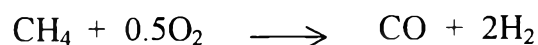


Figure 4.3 Effect of ethane partial pressure on products selectivities.

(flow rate = 100 ml/min; applied voltage = 8,000 V; frequency = 400 Hz and gap width = 1.3 cm)

conditions, no carbon dioxide was found. All possible gas discharge reactions may occur as follows (Liu *et al.*, 1996):

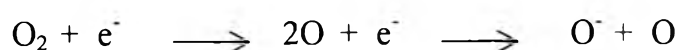
The partial oxidation of methane:



The oxidative coupling of methane consists of

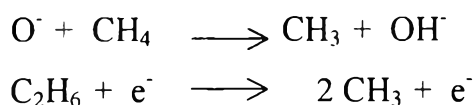
(1) O^- formation and initiation of discharge reactions

Dissociative attachment:

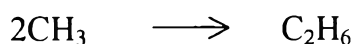


(2) Homogeneous reactions. The O^- formed by dissociative attachment reacts further as follows:

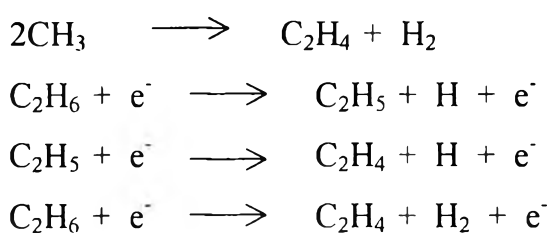
Methane radical formation:



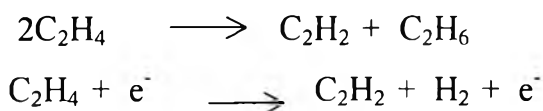
Ethane formation:



Ethylene formation:



Acetylene formation:



From the results, a parallel pathway was likely to be existed between the production of synthesis gas and the formation of C_2 hydrocarbons. At a higher ethane partial pressure, it means a higher average carbon number in the feed resulting in higher C_2 selectivities but a lower synthesis gas selectivity. The ethylene selectivity increased substantially while acetylene

selectivity slightly decreased and then increased slightly with increasing the ethane partial pressure.

A possible explanation to describe the effect of ethane partial pressure on the ethylene formation is that most of the methyl radicals (CH_3) being produced from the methane activation and the ethane cracking might be recombined and converted further into ethylene via several possible reaction pathways such as via the successive cracking of methyl radicals followed by their recombination. In another way, the abstraction of one hydrogen atom from each ethane molecule might be happened. Consequently, this leads to the formation of C_2H_5 which can be cracking again to form ethylene, C_2H_4 ; or the ethane molecules might be cracked in such a way that two hydrogen atoms are abstracted simultaneously from each ethane molecule to yield ethylene (Thanyachotpaiboon, 1996).

Furthermore, as can be seen from Figure 4.3, carbon dioxide product does not occur throughout the studied range of ethane partial pressure. All other experiments in the absence of catalyst system revealed a similar behavior. This result suggests carbon dioxide can contribute one of its two oxygen atoms to produce carbon monoxide and negatively charge oxygen by electronic dissociative attachment of CO_2 :

$$\text{CO}_2 \longrightarrow \text{CO} + \text{O}^-$$

4.1.3 Effect of Flow Rate on Conversions and Yield

Figure 4.4 shows that the partial pressures of carbon monoxide, hydrogen, ethylene and acetylene decrease with increasing the flow rate however those of methane, oxygen and ethane increase. Figure 4.5 shows the effects of the flow rate on conversions and C_2 products yield. It could be seen that, as the total flow rate increased, the methane, oxygen and ethane conversions were always lower. This finding is similar to the previous works (Hill, 1997 and Leethochawalit, 1998). The residence time was calculated from the effective volume of reactor divided by the gas flow rate. For these

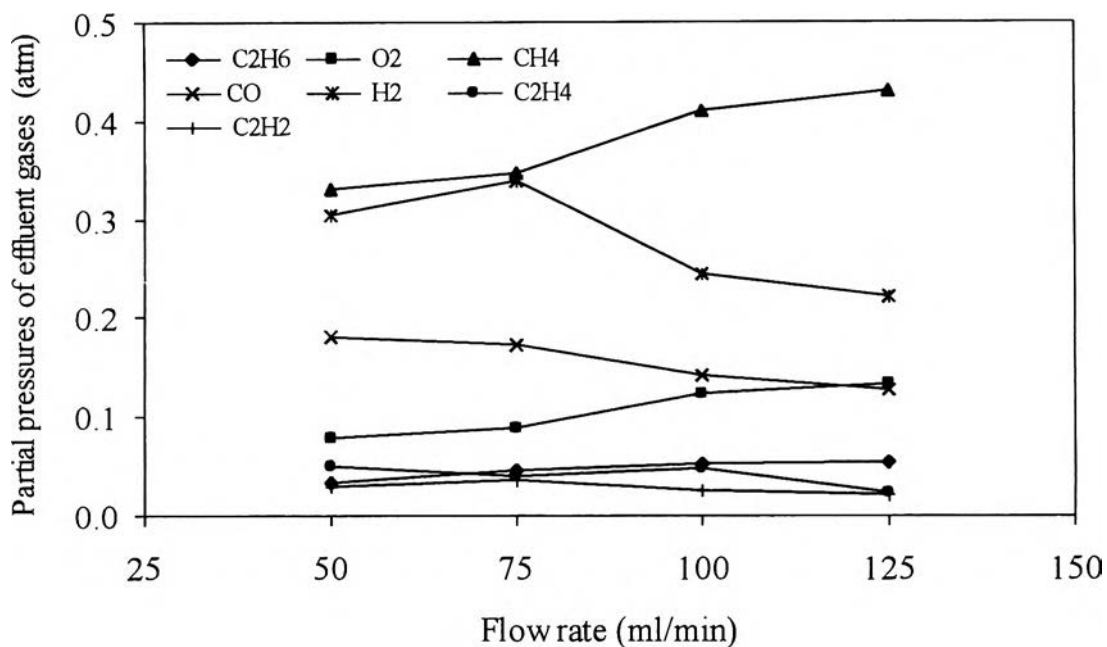


Figure 4.4 Effect of flow rate on partial pressures of effluent gases. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6 = 4:2:1$; applied voltage = 8,000 V; frequency = 400 Hz and gap width = 1.3 cm)

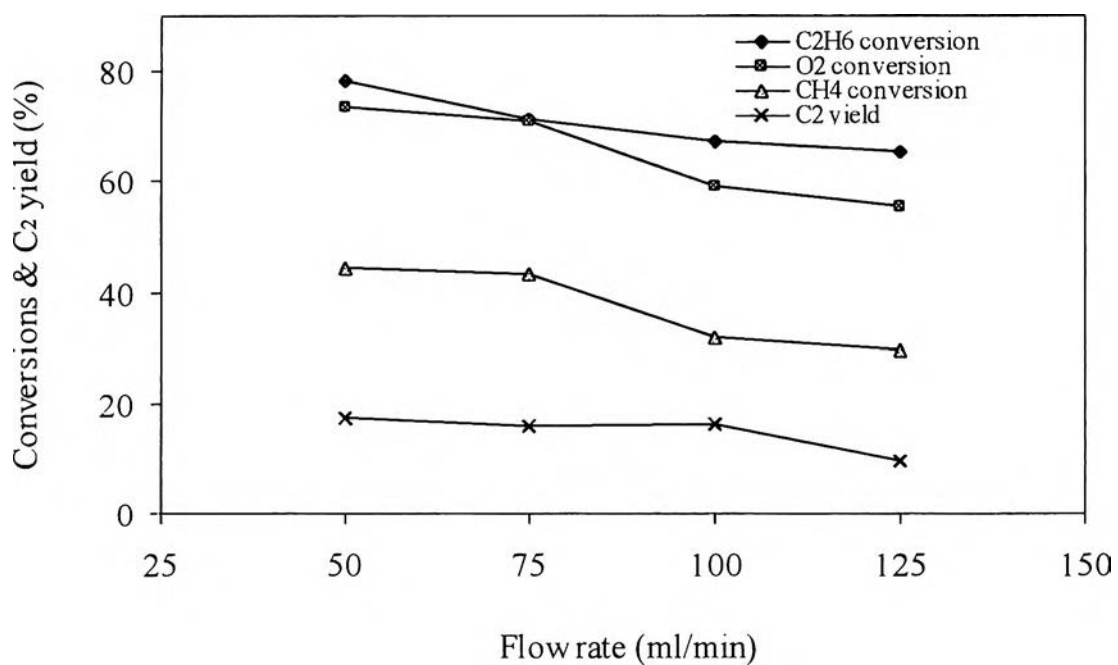


Figure 4.5 Effect of flow rate on conversions and C₂ yields. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6 = 4:2:1$; applied voltage = 8,000 V; frequency = 400 Hz and gap width = 1.3 cm)

experiments, the residence times were 0.78, 0.52, 0.39 and 0.31 s for the flow rates of 50, 75, 100 and 125 ml/min, respectively. An increase in the total flow rate corresponded to a lower residence time and so the reactant gases would pass through the reactor faster. All reactant molecules would have less probability to be collided to activate and break the chemical bonds of the reactant molecule by the electrons generated between the two electrodes so that the rates of all reactions decreased. This caused a decrease in degree of the dissociation and thereby their conversions. The C_2 yield remained fairly constant (about 16%) over most of the flow rate range, but finally decreased to less than 10% at 125 ml/min.

4.1.4 Effect of Flow Rate on Products Selectivities

Figure 4.6 shows the effect of the total flow rate on the products selectivities. For the system operated at 8,000 V and 400 Hz, a increase in the flow rate resulted in initially increasing then decreasing the

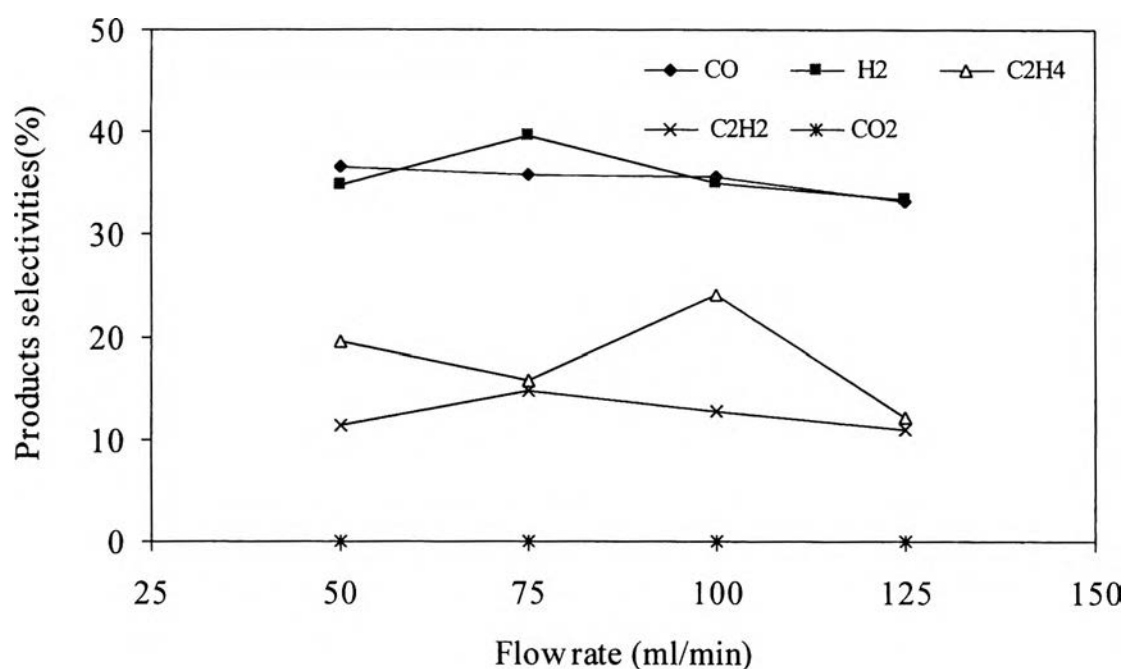


Figure 4.6 Effect of flow rate on products selectivities. ($CH_4:O_2:C_2H_6 = 4:2:1$; applied voltage = 8,000 V; frequency = 400 Hz and gap width = 1.3 cm)

selectivities of hydrogen and acetylene while the selectivity of ethylene initially decreased then increased significantly and decreased dramatically again. The results indicated that the selectivities of the desired products (ethylene and acetylene) were much lower than that of the synthesis gas product. It is very interesting to point out that under the studied conditions, the formation of carbon dioxide was negligible.

4.1.5 Effect of Frequency on Conversions and Yield

In order to investigate the effect of the frequency, the system was operated at a constant applied voltage of 8,000 V. When the system was operated at the frequency below 400 Hz, the coke formed apparently on the electrode surface. This formation of coke resulted in the instability of the discharge. Hence, the studied system had to be operated above 400 Hz. Figure 4.7 shows that the partial pressures of carbon monoxide, hydrogen and

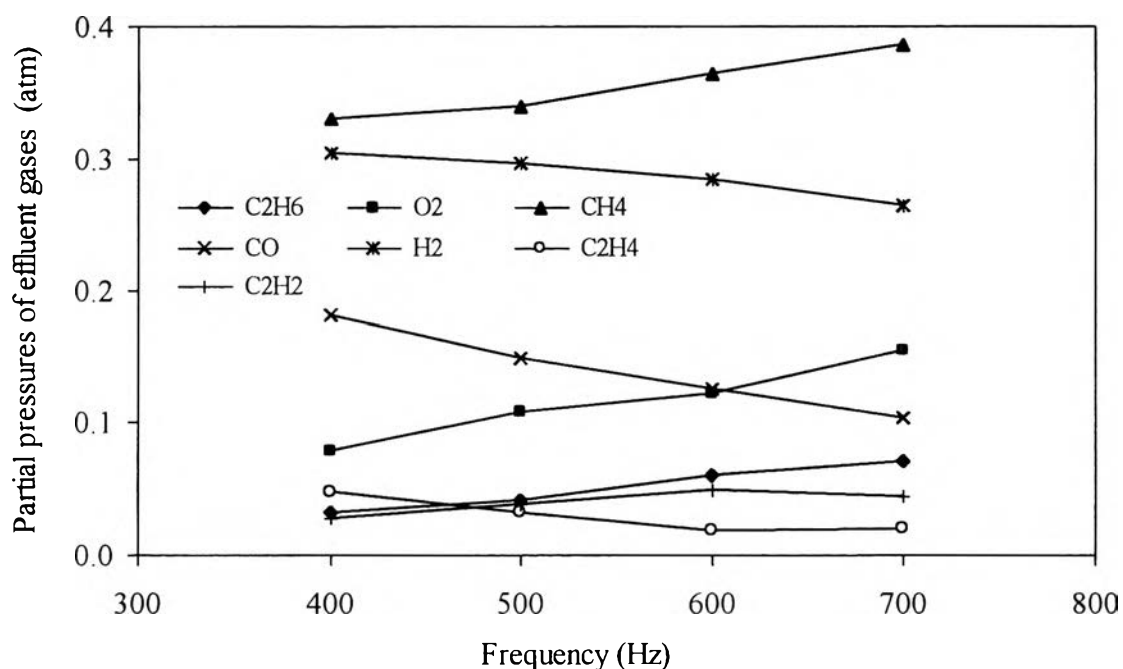


Figure 4.7 Effect of frequency on partial pressures of effluent gases. (CH₄:O₂:C₂H₆ = 4:2:1; applied voltage = 8,000 V; flow rate = 50 ml/min and gap width = 1.3 cm)

ethylene decrease with increasing frequency whereas those of methane, oxygen, ethane and acetylene increase. As can be noticed from Figure 4.8, all the conversions decrease significantly with increasing frequency. Interestingly, it was found experimentally that the conversion of ethane was significantly higher than that of methane for the whole range of the studied frequency as a result of methane molecule more stable than ethane molecule. These findings in this study are similar to the previous works (Hill, 1997). As shown in Figure 4.9, the current decreases significantly with increasing frequency resulting in a reduction of electrons available for initiating the reactions. Thus the number of collisions decreased with decreasing current which lowered the reaction rates. In addition, C₂ yield decreased from 17.42% to 14.04% with increasing frequency from 400 Hz to 700 Hz.

4.1.6 Effect of Frequency on Products Selectivities

The effect of the frequency on products selectivities is illustrated in Figure 4.10. As the frequency increased, the selectivity of carbon monoxide dramatically decreased while the hydrogen selectivity slightly increased. Interestingly, the acetylene selectivity initially increased then leveled off, and the ethylene selectivity continuously decreased then increased slightly with increasing the frequency. It is very interesting to point out that an increase of the dehydrogenation reaction of ethylene to acetylene formation increased with increasing the frequency therefore a dramatic rise in acetylene selectivity was obtained as the frequency increased. As be expected, carbon dioxide did not form throughout the studied range of frequency. The result indicates that under the insufficient oxygen, methane can be oxidized to form carbon monoxide and hydrogen.

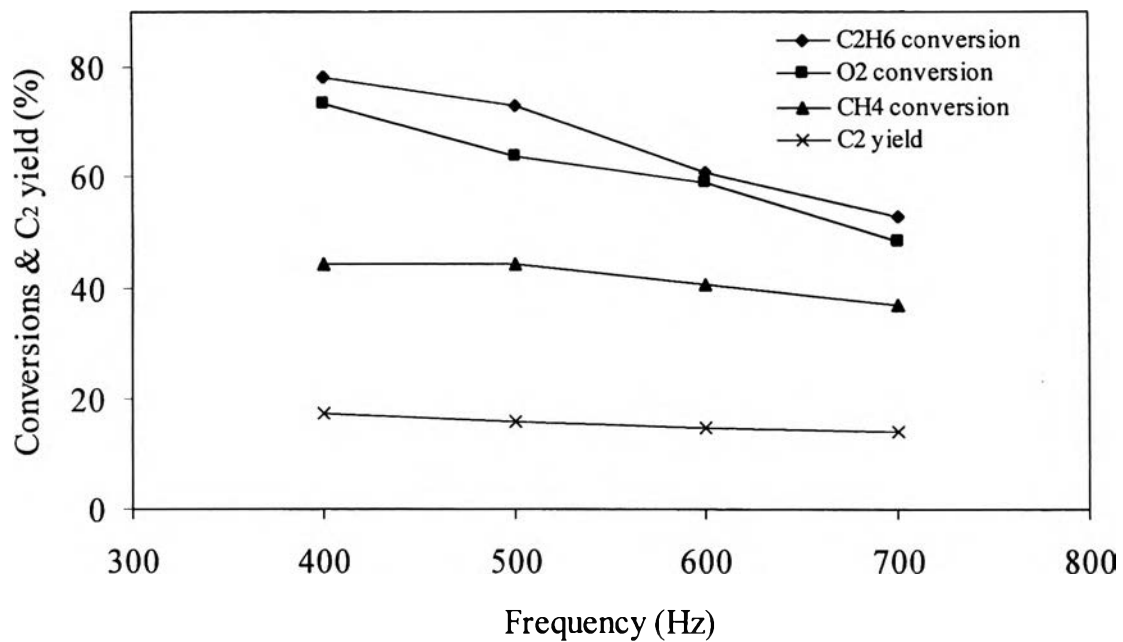


Figure 4.8 Effect of frequency on conversions and products yields. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6 = 4:2:1$; applied voltage = 8,000 V; flow rate = 50 ml/min and gap width = 1.3 cm)

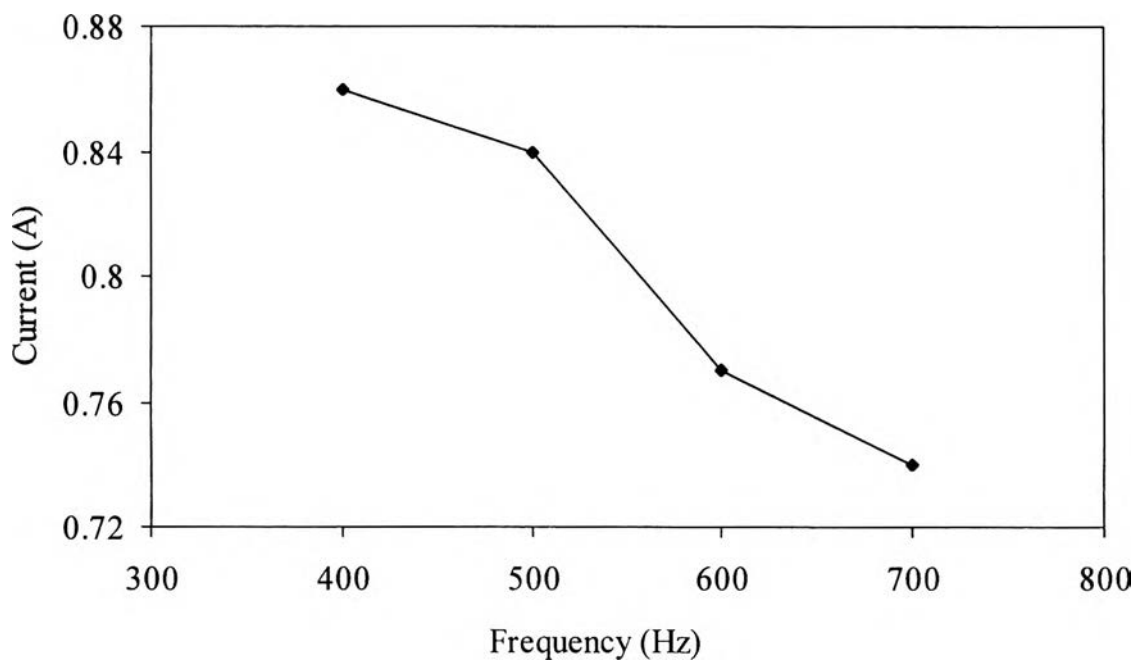


Figure 4.9 Effect of frequency on current. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6 = 4:2:1$; applied voltage = 8,000 V; flow rate = 50 ml/min and gap width = 1.3 cm)

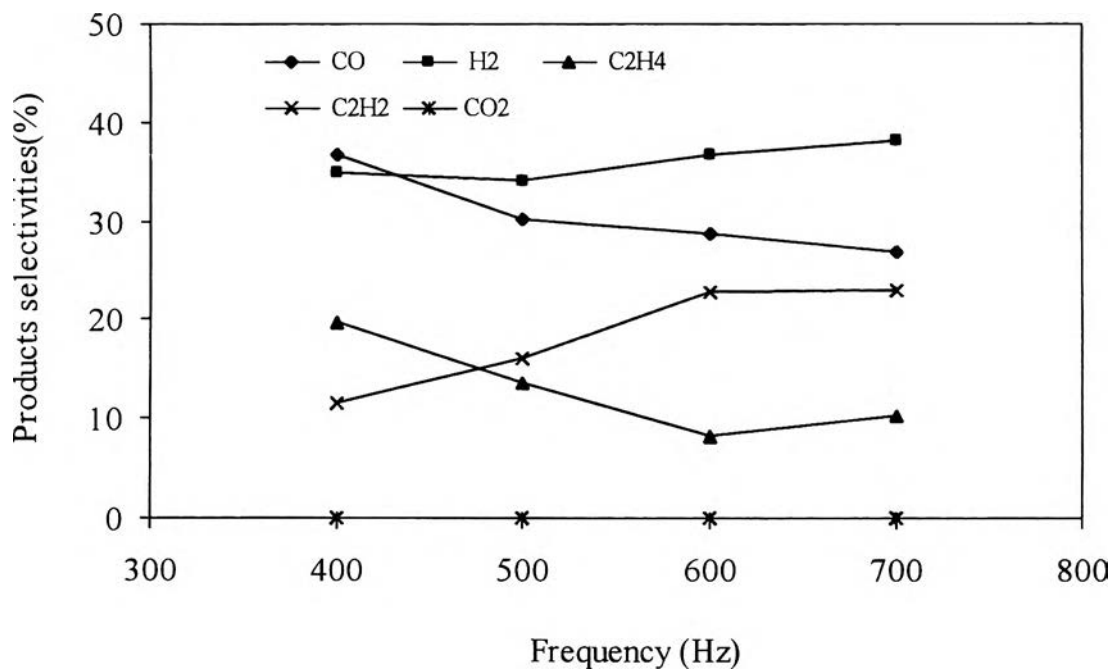


Figure 4.10 Effect of frequency on products selectivities. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6=4:2:1$; applied voltage= 8,000 V; flow rate= 50 ml/min and gap width= 1.3 cm)

4.1.7 Effect of Applied Voltage on Conversions and Yield

The experiments were carried out to investigate the effect of the applied voltage on methane conversion and products selectivities. A methane to oxygen to ethane ratio of 4:2:1 was selected in this experiment. The total flow rate was set at 50 ml/min and the gap width was fixed at 1.3 cm. All experiments were operated above 5,500 V and at a fixed frequency of 500 Hz since at the applied voltage below 5,500 V, the plasma could not exist. Figure 4.11 illustrates the effect of the applied voltage on the partial pressures of the effluent gases. It was found that the partial pressures of carbon monoxide, hydrogen and ethylene increased slightly with increasing the applied voltage whereas those of methane, oxygen, ethane and acetylene decreased slightly. Figure 4.12 illustrates the effect of applied voltage on conversions and C_2 yield. It was found that methane and ethane conversions increased significantly with increasing voltage. When the external voltage, and consequently the internal electric field, applied across the discharge gap

increased, the density of high-energy electrons within the gap increased leading to increases in both methane and ethane conversions. Figure 4.13 shows the increment in current with increasing voltage. The increment in the number of electrons discharged may lead to a higher probability of breaking the bond between the carbon and hydrogen in the methane and ethane molecule and thus increase both the degree of dissociation and conversion (Thayachotpaiboon, 1996). The trends shown in Figure 4.12 support this conclusion. The marked increase in oxygen conversion observed can be explained with similar logic as that for methane and ethane conversion. As the figure shows, C₂ yield increased from 12.82% to 15.83% with increasing voltage from 5,500 V to 8,000 V.

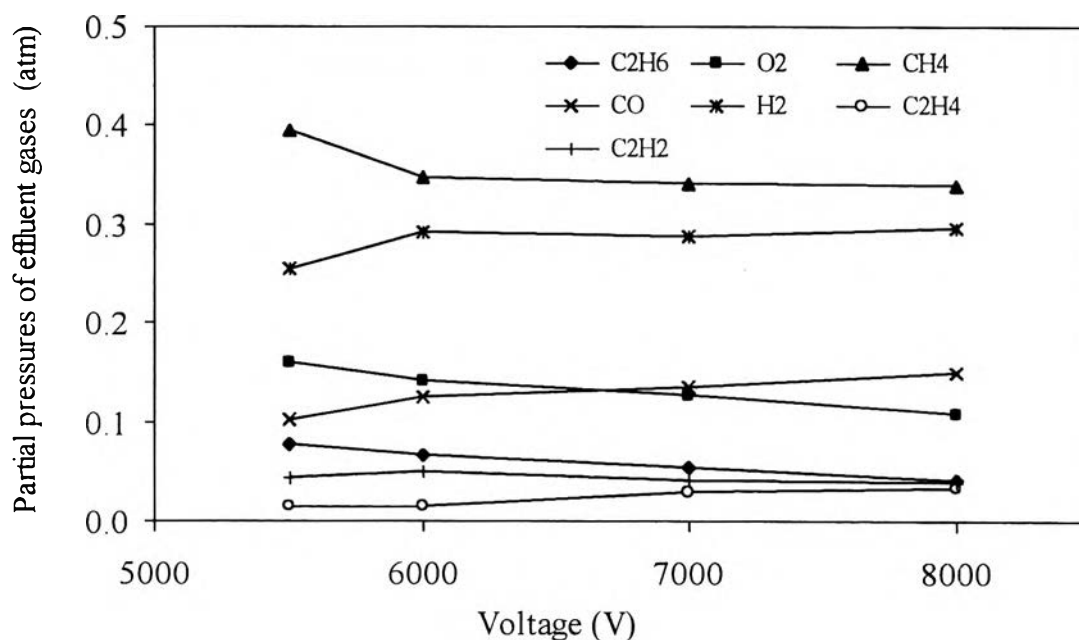


Figure 4.11 Effect of voltage on partial pressures of effluent gases. (CH₄:O₂:C₂H₆= 4:2:1; frequency= 500 Hz; flow rate= 50 ml/min and gap width= 1.3 cm)

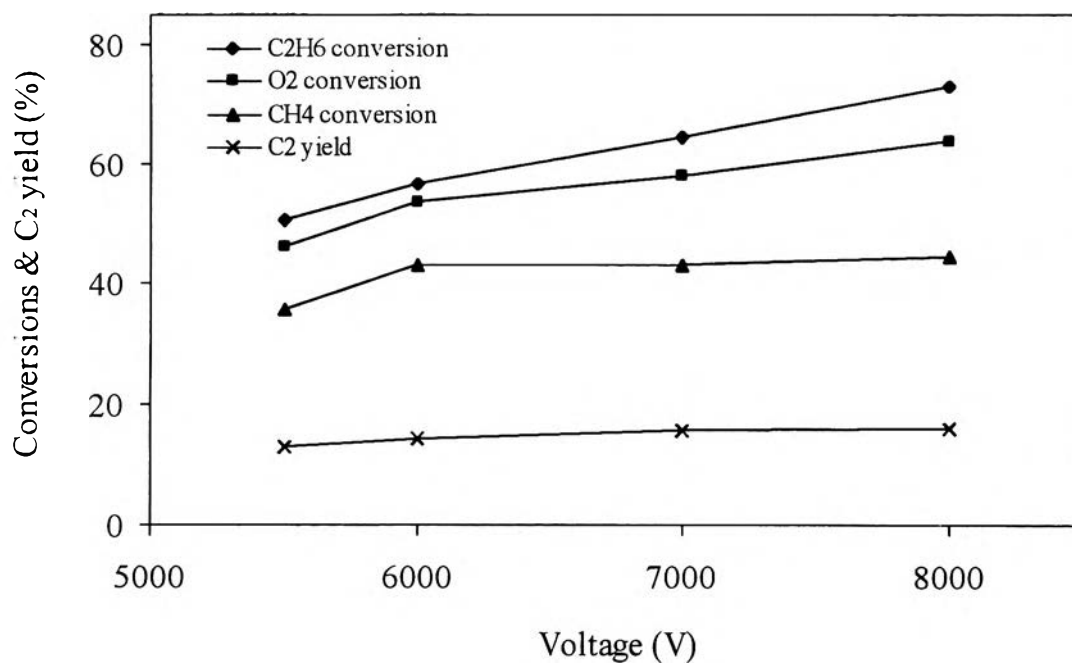


Figure 4.12 Effect of voltage on conversions and yield. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6 = 4:2:1$; frequency = 500 Hz; flow rate = 50 ml/min and gap width = 1.3 cm)

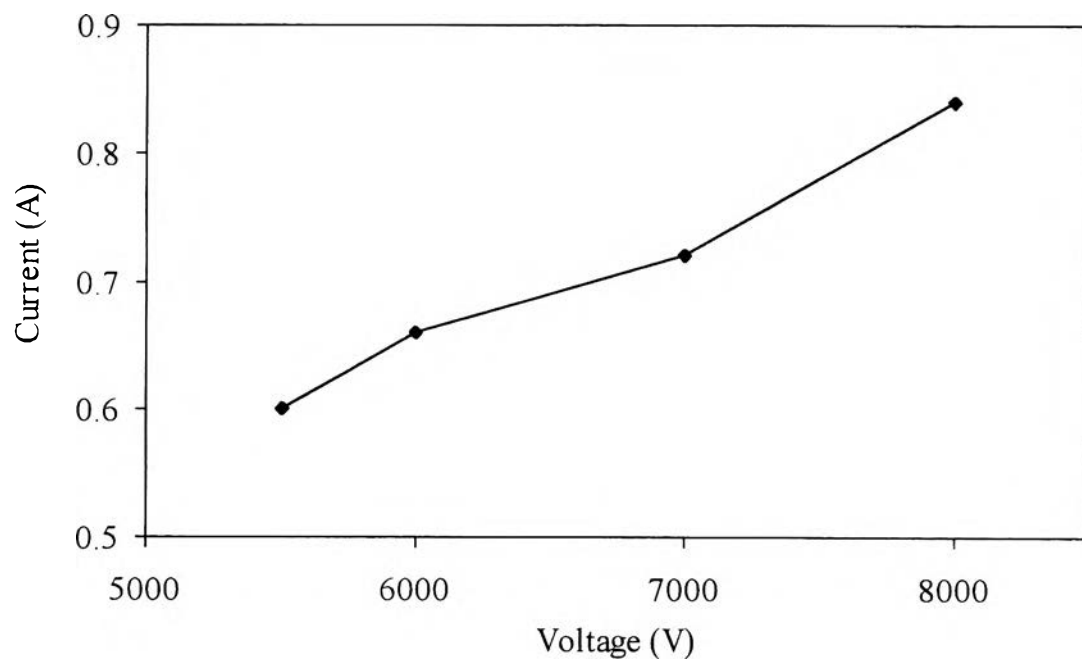


Figure 4.13 Effect of voltage on current. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6 = 4:2:1$; frequency = 500 Hz; flow rate = 50 ml/min; gap width = 1.3 cm)

4.1.8 Effect of Applied Voltage on Products Selectivities

Figure 4.14 shows the effect of the applied voltage on the products selectivities. The results indicated that the synthesis gas (hydrogen and carbon monoxide) was the main product. As be mentioned before, carbon dioxide did not form throughout the studied range of applied voltage because of insufficient amount of oxygen in the feed mixture. Carbon monoxide selectivity continuously increased while the hydrogen selectivity decreased slightly with increasing the applied voltage. The selectivity of ethylene molecule increased while the selectivity of acetylene produced decreased when the applied voltage increased. From the results, it indicated that some methane molecules were coupled to form ethylene as well as dehydrogenation of ethane. Ethylene produced could be dehydrogenated to form acetylene. However, under the system having a high partial pressure of hydrogen could facilitate hydrogenation reaction of acetylene to form ethylene therefore hydrogen selectivity decreased with higher voltage.

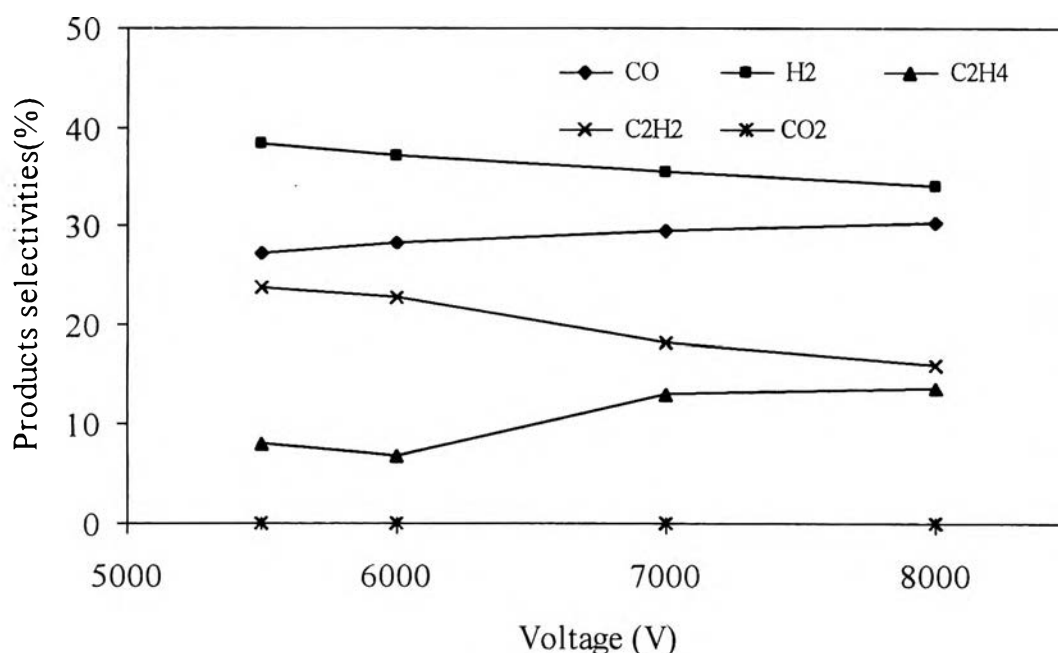


Figure 4.14 Effect of voltage on products selectivities. ($\text{CH}_4:\text{O}_2:\text{C}_2\text{H}_6 = 4:2:1$; Frequency = 500 Hz; flow rate = 50 ml/min and gap width = 1.3 cm)

4.2 The Plasma System with the Presence of Catalyst

4.2.1 Effect of Frequency on Conversions and Yield over 1% Pt/KL

The effect of frequency over 1% Pt/KL system under the corona discharges environment was studied. The catalytic plasma system was operated with the feed gas having a methane to oxygen to ethane ratio of 4:2:1 at the total flow rate of 50 ml/min and the applied voltage of 8,000 V. Figure 4.15 shows that the partial pressures of carbon monoxide, hydrogen, ethylene and acetylene decreases with increasing frequency whereas those of ethane, methane and oxygen increases. Figures 4.16 shows the effect of the frequency on conversions and yield in 1% Pt/KL system. It was found that an increase in the frequency led to decreases in methane and ethane conversions. These results are similar to those of the plasma system with the absence of catalyst as mentioned before. It is very interesting to point out that the addition of

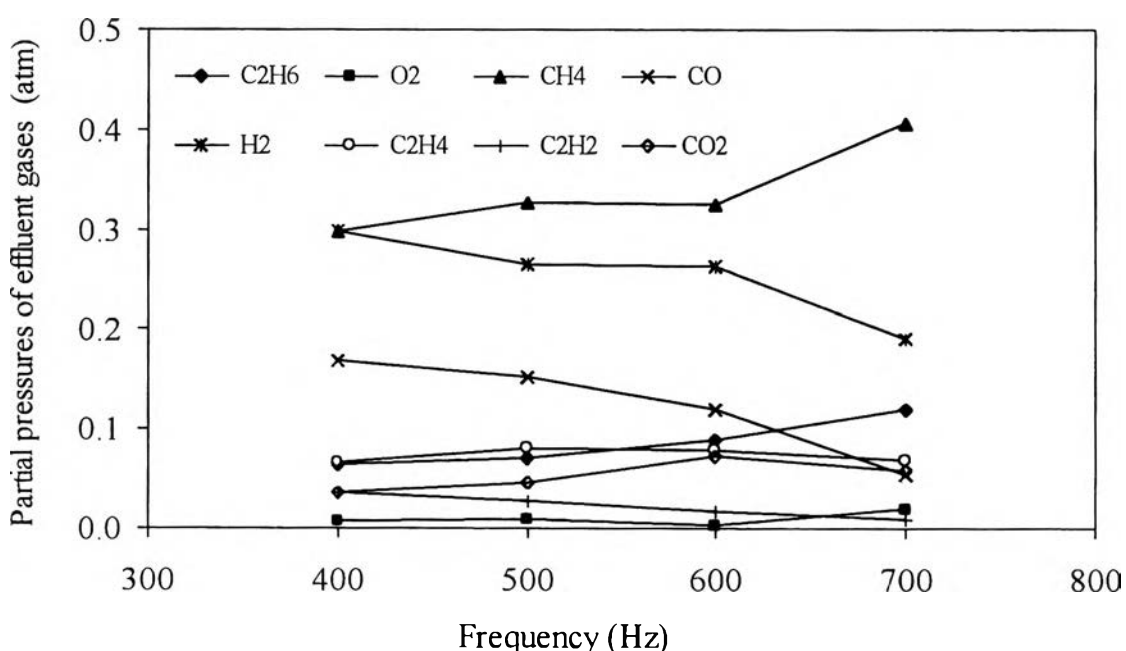


Figure 4.15 Effect of frequency on partial pressures of effluent gases over 1% Pt/KL system. (CH₄:O₂:C₂H₆ ratio = 4:2:1; applied voltage = 8,000 V; flow rate = 50 ml/min; gap width = 1.3 cm)

1% Pt/KL remarkably enhanced the oxygen conversion. The oxygen conversion was extremely high, greater than 93% and nearly independent of this frequency change. This might be the Pt supported with KL promoted the oxygen dissociation, so that it led to an increase in the oxygen conversion.

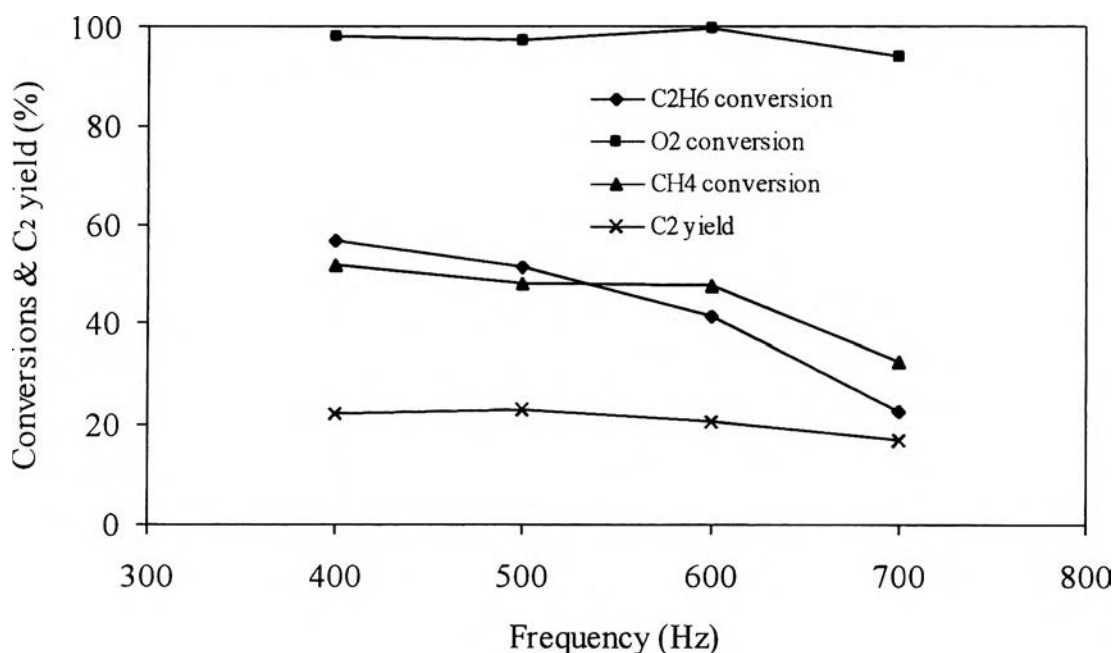


Figure 4.16 Effect of frequency on conversions and C₂ yields over 1% Pt/KL system. (CH₄:O₂:C₂H₆ ratio = 4:2:1; applied voltage = 8,000 V; flow rate = 50 ml/min and gap width = 1.3 cm)

4.2.2 Effect of Frequency on Products Selectivities over 1% Pt/KL

The effect of frequency on products selectivities over 1%Pt/KL was illustrated in Figure 4.17. The results indicate that 1% Pt/KL zeolite catalyst was more selective for ethylene formation than the plasma system without 1% Pt/KL zeolite. The ethylene selectivities dramatically increased while the acetylene selectivity decreased with increasing frequency. Again, under the high partial pressure of hydrogen, hydrogenation reaction of acetylene to ethylene is more dominant than dehydrogenation reaction of ethylene to acetylene. It is very interesting to point out that carbon dioxide was

observed in this 1% Pt/KL system. The selectivity of carbon dioxide increased significantly while the selectivity of carbon monoxide decreased dramatically when the frequency increased. It can be explained that oxygen conversion was extremely high in the 1% Pt/KL system because of the active and excited species of oxygen such as O^- from dissociative attachment on the catalyst surface. This large number of active oxygen ions could then further combine with CO to form CO_2 .

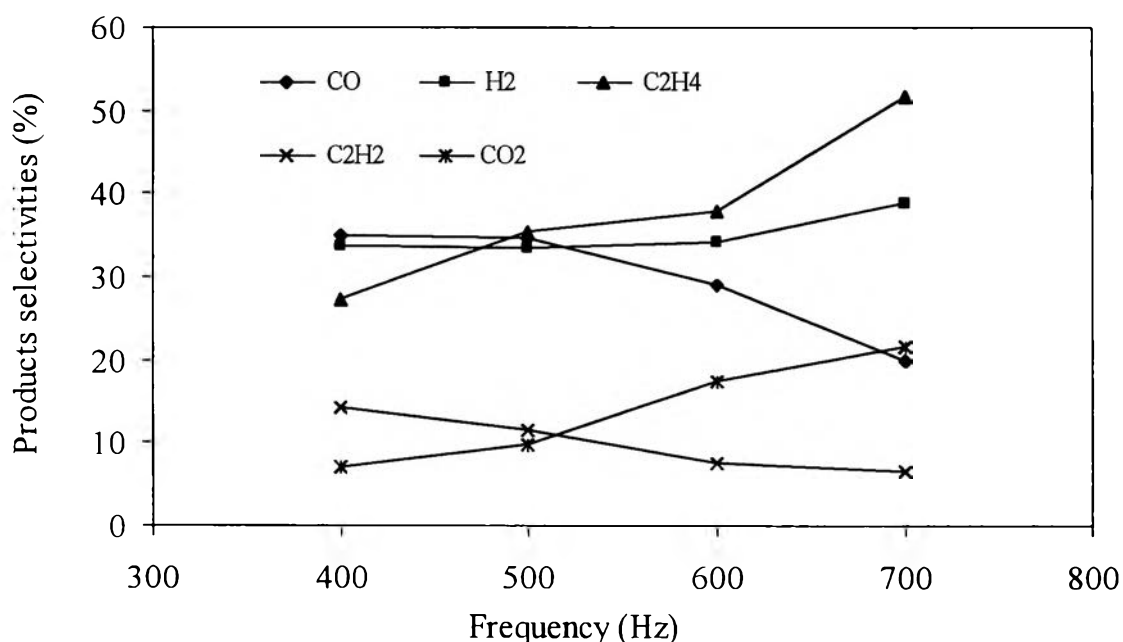


Figure 4.17 Effect of frequency on products selectivities over 1% Pt/KL system. ($CH_4:O_2:C_2H_6$ ratio = 4:2:1; applied voltage= 8,000 V and flow rate= 50 ml/min).

4.2.3 Effect of Voltage on Conversions and Yield over 1% Pt/KL

Figure 4.18 illustrates the effect of the applied voltage on partial pressures of effluent gases. The partial pressures of carbon monoxide, hydrogen, ethylene and acetylene increased with increasing the applied voltage whereas those of methane, oxygen and ethane decreased. The effect of applied voltage on conversions and yield in the 1% Pt/KL system is illustrated

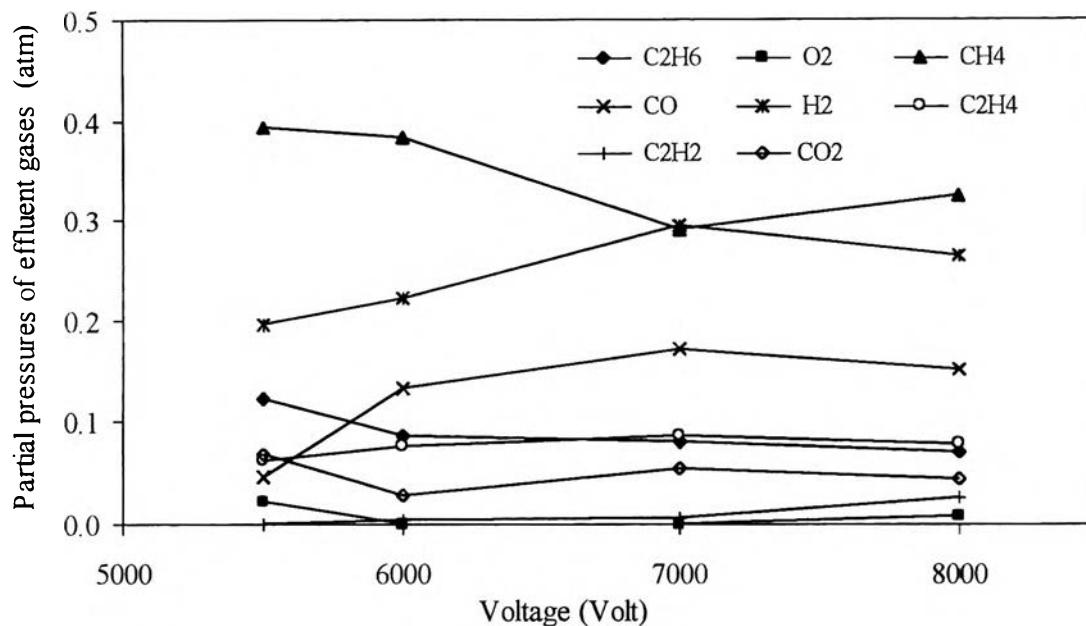


Figure 4.18 Effect of voltage on partial pressures of effluent gases over 1% Pt/KL system. (CH₄:O₂:C₂H₆ ratio = 4:2:1; frequency = 500 Hz and flow rate = 50 ml/min)

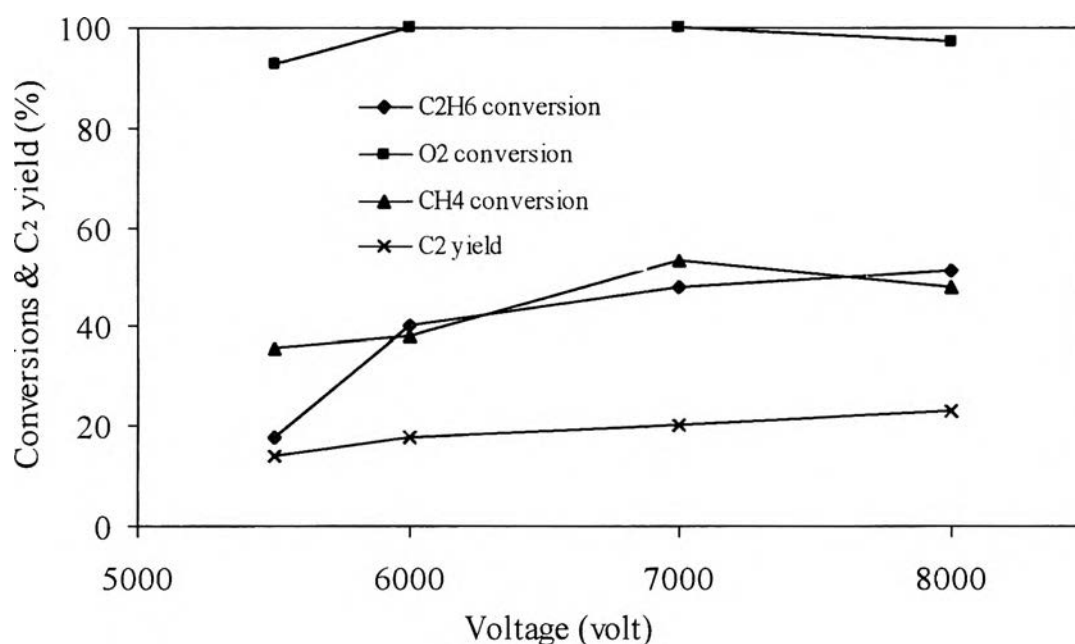


Figure 4.19 Effect of voltage on conversions and C₂ yields over 1% Pt/KL system. (CH₄:O₂:C₂H₆ ratio = 4:2:1; frequency= 500 Hz and Flow rate= 50 ml/min)

in Figure 4.19. It was found that under the studied conditions, the oxygen conversion was very high (greater than 92%) and nearly unaffected with the voltage change. These results confirm that Pt supported KL zeolite enhanced oxygen dissociation. Both methane and ethane conversions increased with increasing applied voltage. This result could be explained in a similar manner as in the case of non-catalytic system.

4.2.4 Effect of Voltage on Products Selectivities over 1% Pt/KL

Figure 4.20 shows the effect of the applied voltage on products selectivities in the 1% Pt/KL system. It is very interesting to point out that the presence of Pt/KL zeolite catalyst remarkably enhanced the ethylene product. This reaction system gave a very high ethylene selectivity while acetylene was lower as compared to the non-catalytic system. The ethylene selectivity decreased gradually while acetylene selectivity increased slightly with increasing voltage. These results led to a conclusion that, in these studied conditions, the rate of dehydrogenation of ethylene to form acetylene is lower than the rate of hydrogenation of acetylene to form ethylene because of the high partial pressure of hydrogen in the system. Moreover, ethane added could be dehydrogenated to form ethylene. Therefore, both selectivity and partial pressure of ethylene were much higher than those of acetylene. As the applied voltage increased, carbon monoxide selectivity increased significantly and then decreased slightly while carbon dioxide selectivity initially decreased dramatically and then slightly increased. This result could be explained in a similar manner as in the study of frequency effect.

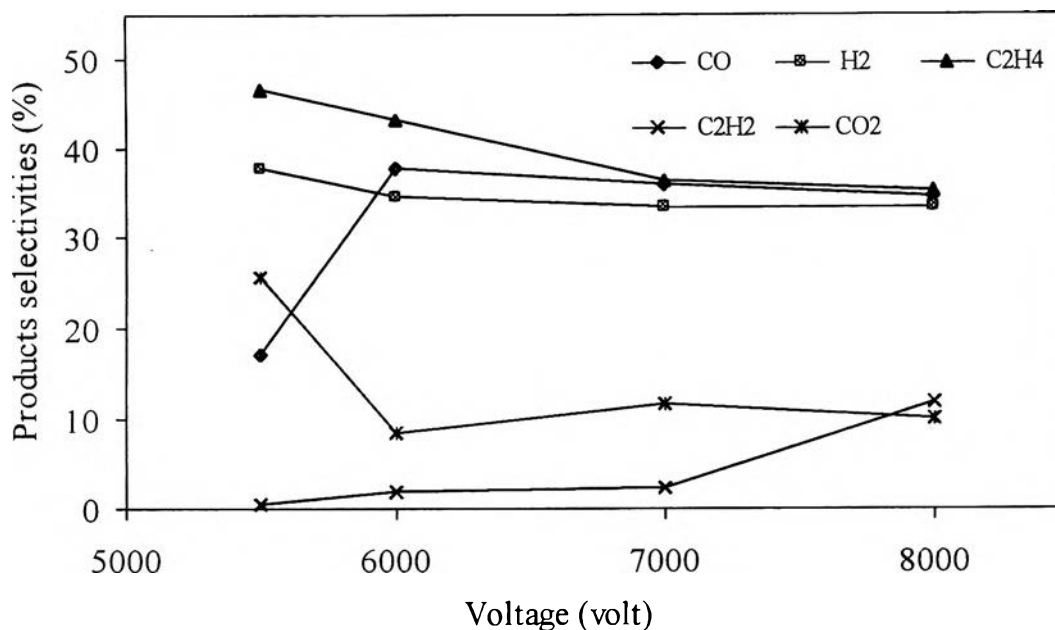


Figure 4.20 Effect of voltage on products selectivities over 1% Pt/KL system. (CH₄:O₂:C₂H₆ ratio = 4:2:1; frequency = 500 Hz and flow rate = 50 ml/min)

4.2.5 Plasma Catalytic Oxidative Conversion of Methane over Different Zeolites

The experiments were carried out to investigate the plasma catalytic oxidative conversion of methane over different zeolites. 1% Pt/NaX and 1% Pt/NaOH treated Y zeolites could not be operated above 6,000 V since the catalysts moved and then attached with the electrode rod, the plasma could not exist. Hence, these two zeolites were only tested at 6,000 V in order to compare with 1% Pt/KL and non-catalytic systems. Tables 4.1 and 4.2 presents the experimental results on conversions, C₂ yield and products selectivities over three different zeolites and without catalyst. 1% Pt/NaOH treated Y led to more significant methane and ethane conversions, while the highest oxygen conversion (greater than 99%) was obtained with 1% Pt/KL and 1% Pt/NaX. The zeolite most selective for ethylene formation was 1% Pt/KL. The lowest selectivity for ethylene was found with 1% Pt/NaOH treated Y. The absence of catalyst was observed to be effective in maximizing

the acetylene selectivity while no acetylene was produced in 1% Pt/NaX system. Furthermore for both systems with 1% Pt/NaOH treated Y and the absence of catalyst, the carbon dioxide selectivity became zero.

Any previous works gave no informative discussion on these results. Hereafter, it is strongly recommended to investigate this point further in order to gain some more qualitative understanding.

Table 4.1 Comparison of non-catalytic and catalytic plasma systems over different zeolites on conversions and yield at CH₄:O₂:C₂H₆ ratio = 4:2:1; applied voltage = 6,000 V; flow rate = 50 ml/min; gap width = 1.3 cm and frequency = 500 Hz.

system	CH ₄ conversion	O ₂ conversion	C ₂ H ₆ conversion	C ₂ yield
no catalyst	43.16	53.35	56.63	14.07
1% Pt/KL	37.97	99.81	40.25	17.42
1% Pt/NaX	37.69	99.96	14.63	7.64
1% Pt/NaOH treated Y	64.52	78.26	79.78	17.65

Table 4.2 Comparison of non-catalytic and catalytic plasma systems over different zeolites on products selectivities at CH₄:O₂:C₂H₆ ratio = 4:2:1; applied voltage = 6,000 V; flow rate = 50 ml/min; gap width = 1.3 cm and frequency = 500 Hz.

system	CO selectivity	H ₂ selectivity	C ₂ H ₄ selectivity	C ₂ H ₂ selectivity	CO ₂ selectivity
no catalyst	28.13	36.99	6.79	22.72	0
1% Pt/KL	37.76	34.56	43.22	1.8	8.29
1% Pt/NaX	23.79	46.81	25.43	0	50.43
1% Pt/NaOH treated Y	26.77	32.42	5.77	19.6	0