CHAPTER IV
# RESULTS AND DISCUSSION

The experimental data of the present study are given in Appendix B and the experimental results are presented comprehensively in this chapter. In addition, chemical reaction pathways are also proposed to explain how various products are formed under low temperature plasma environment.


4.1 Air/Methane System

4.1.1 Effect of Applied Voltage on the Conversions and Yields

Firstly, the experiments were carried out to investigate the effect of the applied voltage at two frequencies of 300 and 400 Hz on methane conversion and products selectivities. When the frequency was below 300 Hz, the coke was formed apparently on the electrode surface. This formation of coke resulted in the unstability of the discharge. Hence, the studied system had to be operated above 300 Hz. A methane to air ratio of 3:4.8 was selected in order to obtain a 3:1 ratio of methane to oxygen. The total flow rate was set at 100 ml/min and the gap width was fixed at 0.9 cm. The system was operated at two frequencies of 300 and 400 Hz. Figures 4.1 and 4.2 illustrate the effect of the applied voltage on partial pressures of effluent gases, which show that the partial pressures of hydrogen and carbon monoxide increase with increasing applied voltage whereas those of methane and oxygen decrease. Figures 4.1 shows that the partial pressures of hydrogen and carbon monoxide are significantly higher than those in Figure 4.2. All experimental runs were operated above 5,000 V since at the applied voltage below 5,000 V, the plasma could not exist. From Figures 4.3 and 4.4, the conversions of methane and oxygen, as well as yields of H_2 and CO, increased significantly with
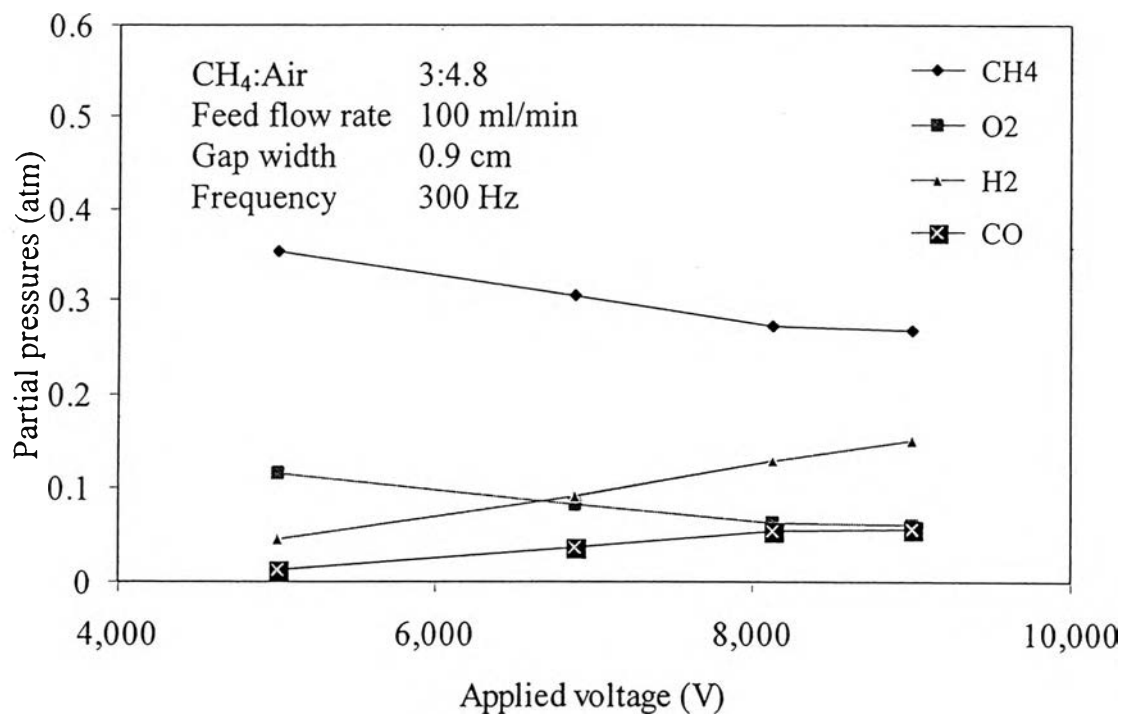
Figure 4.1 Effects of applied voltage on partial pressures of effluent gases
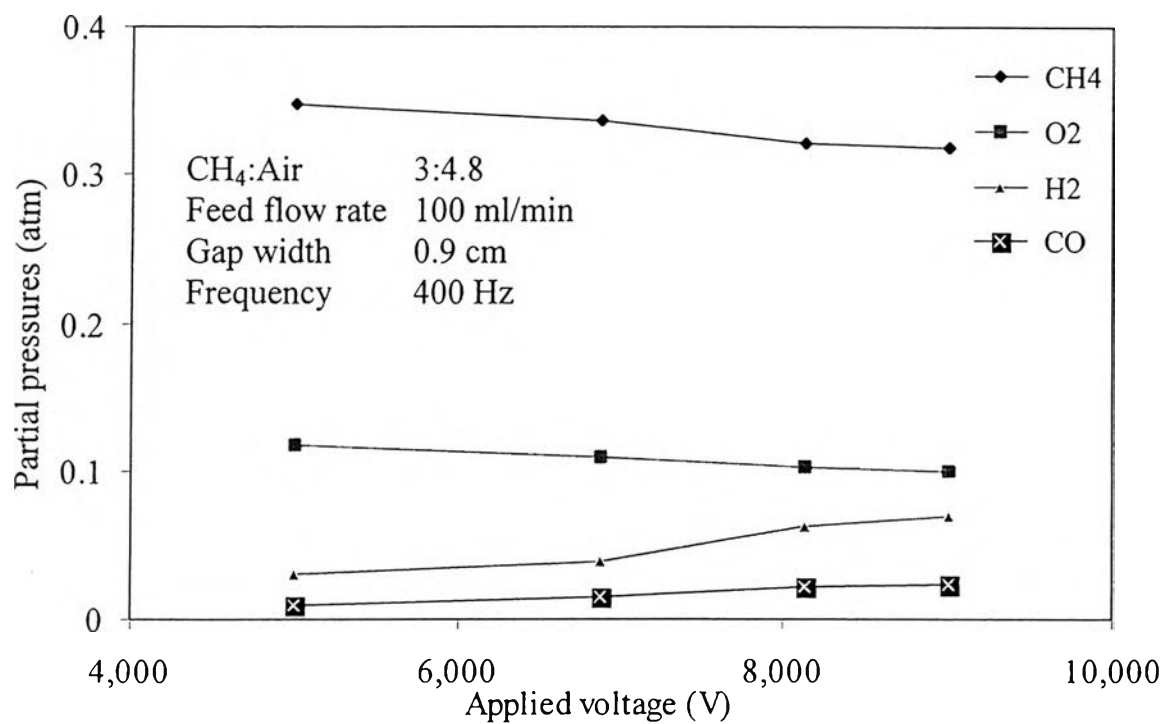
Figure 4.2 Effects of applied voltage on partial pressures of effluent gases
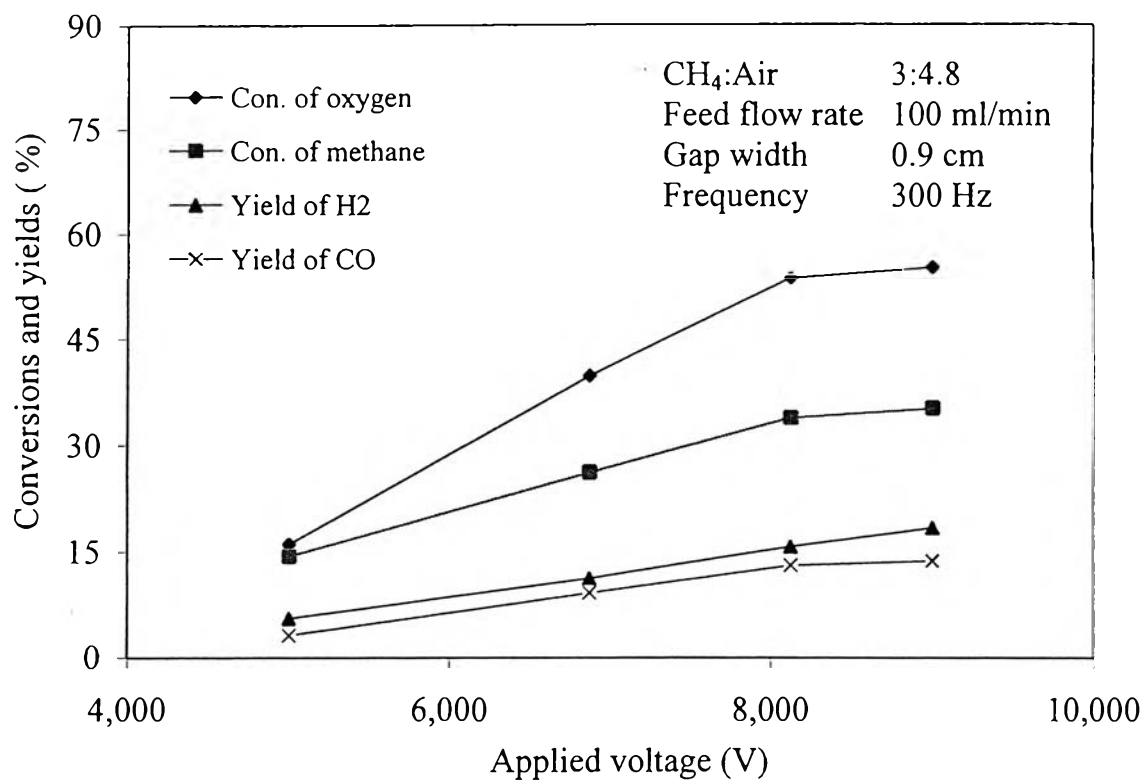
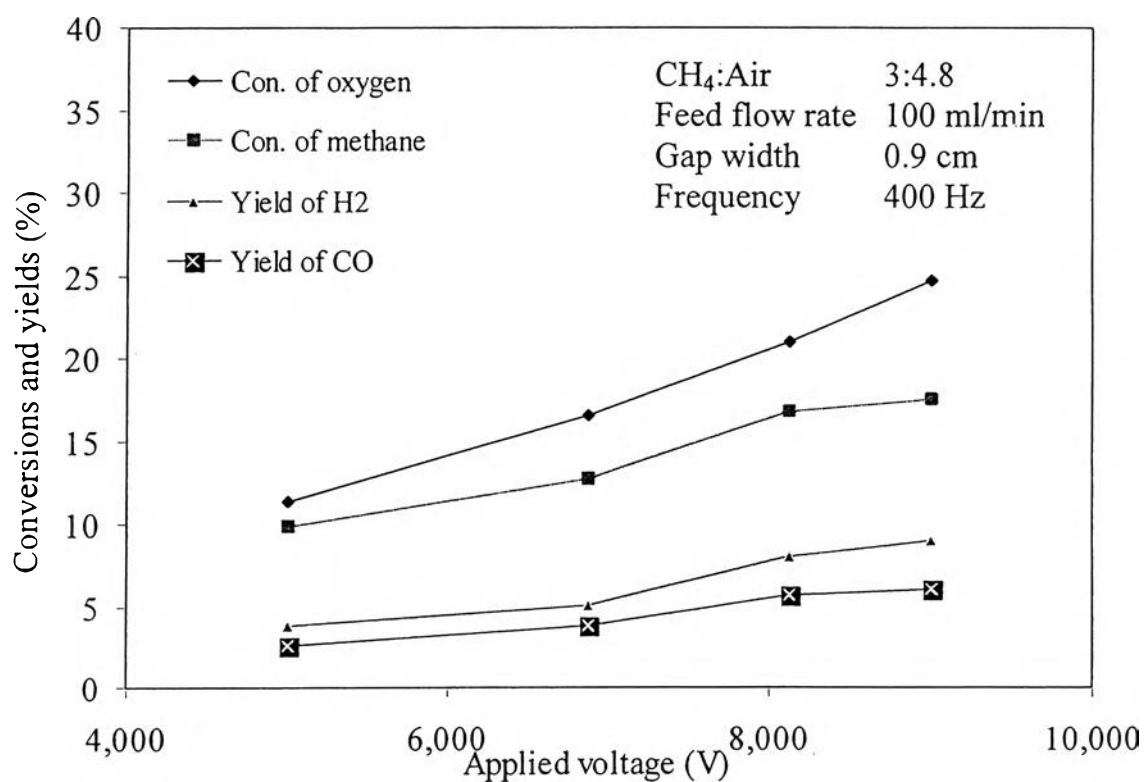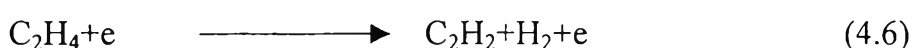**Figure 4.3** Effects of applied voltage on conversions and yields
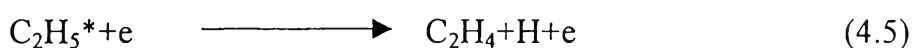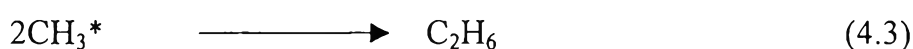

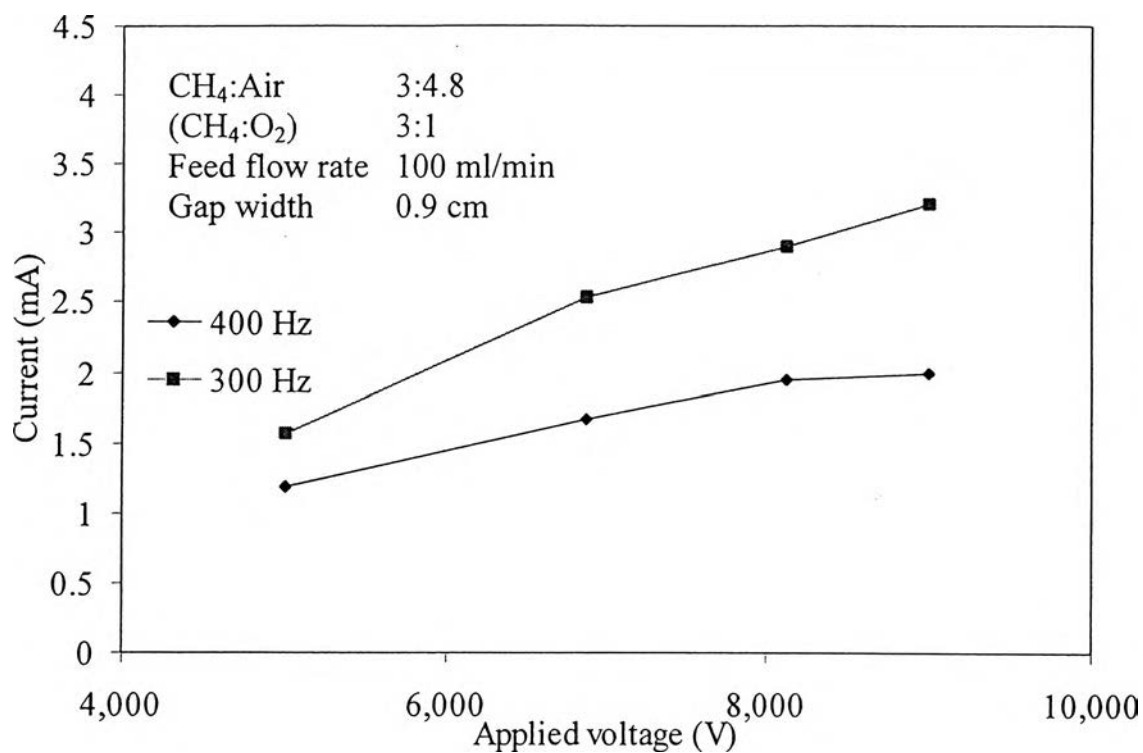**Figure 4.4** Effects of applied voltage on conversions and yields

increasing voltage. The result can be simply explained that a higher voltage means more electrons available to initiate the reactions. When the applied voltage increased beyond 8,000 V, both conversions of oxygen and methane as well as the yields of H_2 and CO seemed to level off. It indicates that an increase in voltage enhances the reactions but will reach a saturation level. This finding is similar to the previous work (Thanyachotpaiboon, 1996). It is very interesting to point out that all conversions and yields were significantly higher at the frequency of 300 Hz than those at the frequency of 400 Hz. The effect of frequency on the reaction will be discussed later.

Figure 4.5 is a plot of the current as a function of the applied voltage at two frequencies. The current increased with increasing applied voltage. The current at the frequency of 300 Hz was remarkably higher than that at 400 Hz. This means that at lower frequency, 300 Hz, there were more number of electrons available for initiating, colliding, and reacting with gases to produce more products such as H_2, CO, acetylene, ethylene, ethane, and CO_2 when compared to what happened at the higher frequency of 400 Hz.
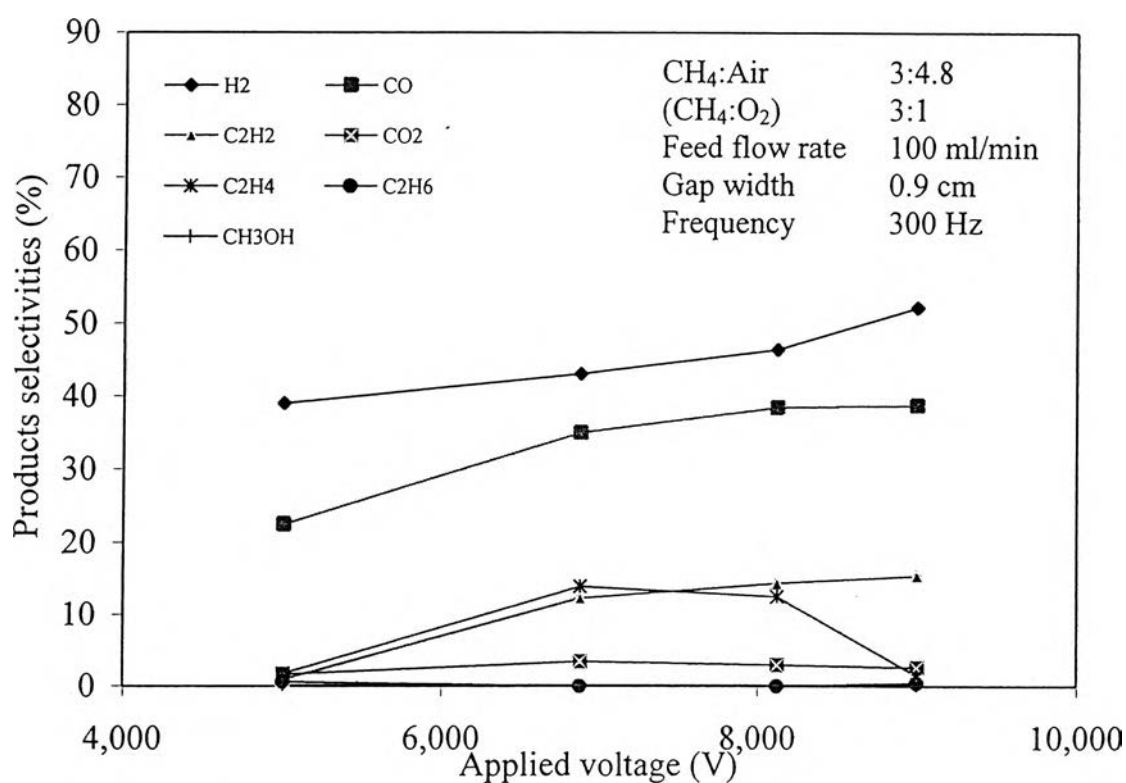
4.1.2 Effect of Applied Voltage on the Products Selectivities

The selectivities of various products versus applied voltage are shown in Figures 4.6 and 4.7. The selectivities of H_2 and CO increased substantially with increasing applied voltage since there were more number of electrons available to initiate the reactions. All possible reactions take place in the plasma as follows:

$$CH_4 + 0.5\ O_2 \longrightarrow CO + 2H_2 \quad (4.1)$$

$$CH_4 + e \longrightarrow CH_3{}^* + H + e \quad (4.2)$$

$$2CH_3{}^* \longrightarrow C_2H_6 \quad (4.3)$$

$$C_2H_6 + e \longrightarrow C_2H_5{}^* + H + e \quad (4.4)$$

$$C_2H_5{}^* + e \longrightarrow C_2H_4 + H + e \quad (4.5)$$

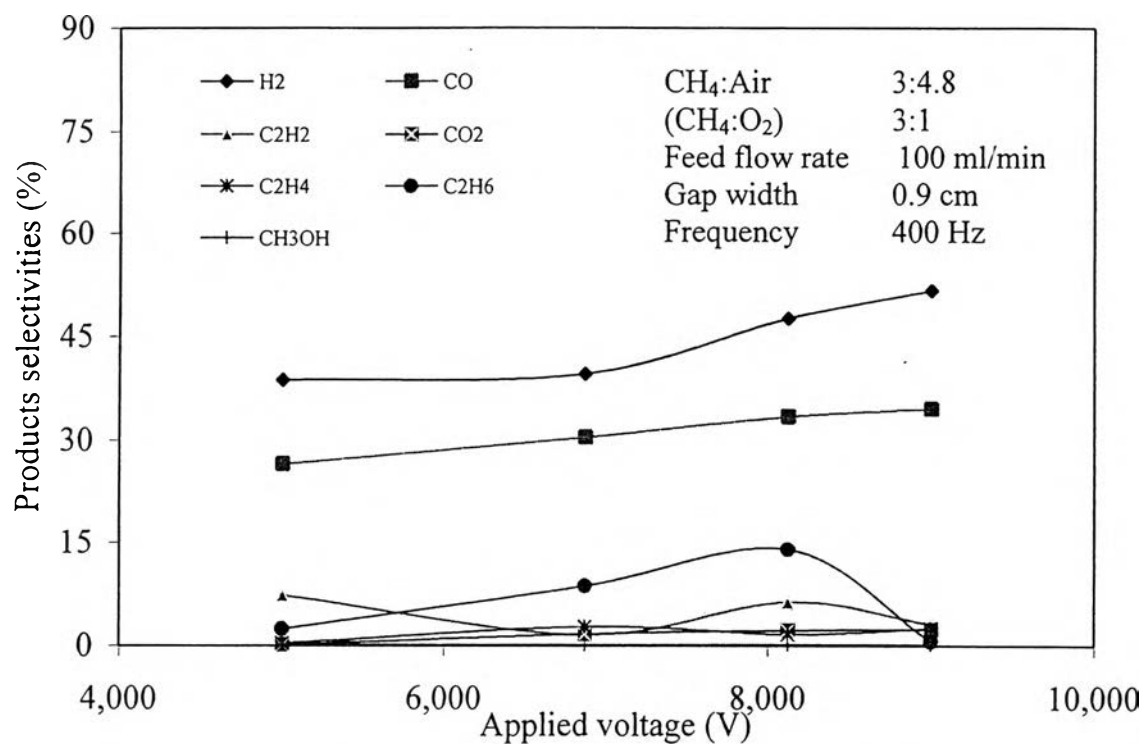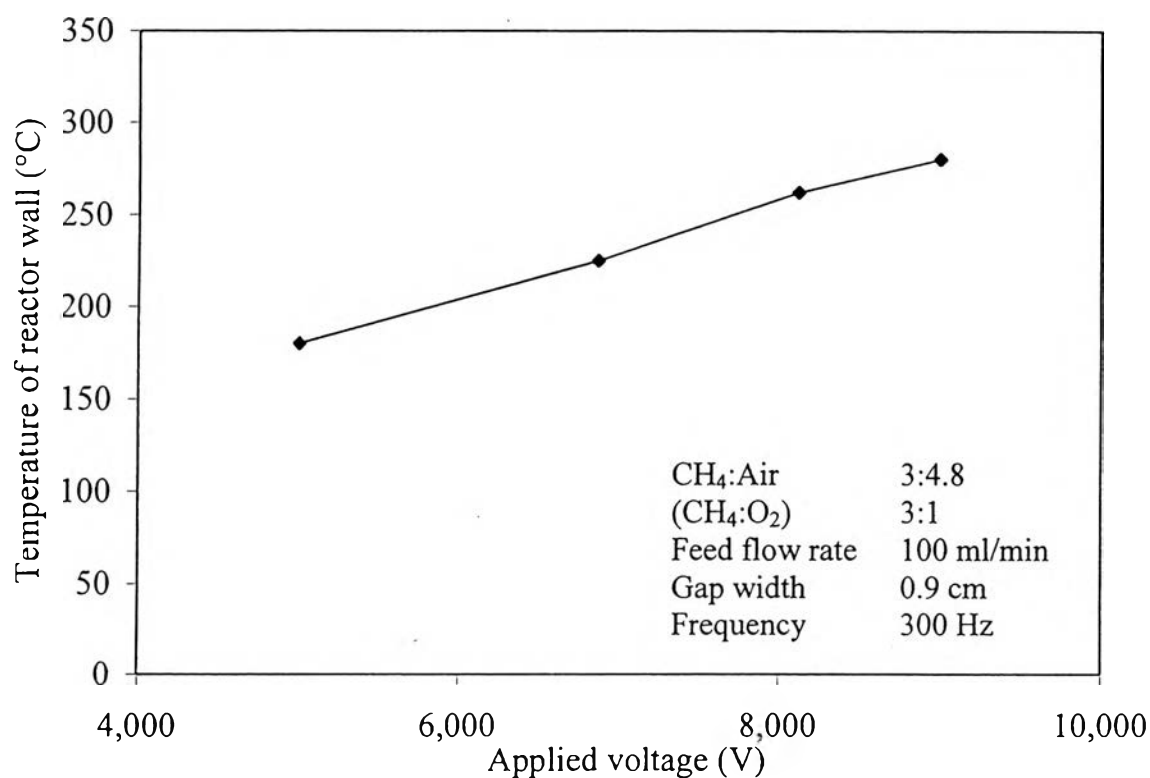$$C_2H_4 + e \longrightarrow C_2H_2 + H_2 + e \quad (4.6)$$

Figure 4.5 Relationship between applied voltage and current of the system operated at two different frequencies

Figure 4.6 Effects of applied voltage on products selectivities

Figure 4.7 Effects of applied voltage on product selectivities

Figure 4.8 Temperature of reactor wall at different voltages

There are two main reactions namely the partial oxidation to form synthesis gas and the methane coupling reaction with dehydrogenation to form C_2 hydrocarbons. As can be seen in Equation (4.1), if the partial oxidation occurs alone the ratio of CO to H_2 in the product gas should be 1:2. It can be seen clearly from Figures 4.1 and 4.2, whereas there are no C_2 products from the system operated at 5,000 V, the ratio of CO to H_2 is approximately 1:2. This evidence confirms clearly the formation of synthesis gas derived from the partial oxidation as shown in Equation (4.1).

The formation of C_2 hydrocarbons can be explained by the reactions as shown in Equations 4.2 to 4.6. The first step is the coupling reaction of methane to form ethane and then the dehydrogenation takes place to form ethylene and acetylene. The electrons break C-H bond in methane to yield CH_3^*, which will further combine with another CH_3^* to form ethane as Equation (4.3). Then ethane undergoes dehydrogenation to form ethylene and acetylene as illustrated in Equations (4.5) and (4.6) (Poonphatanapricha, 1997). The highest selectivities of hydrogen and carbon monoxide observed were found at 9,000 V. This can be explained that at this voltage there was the largest number and the highest energy of electrons available to initiate the reactions. This conclusion is also confirmed by the temperature of reactor wall as shown in Figure 4.8. An increase in the temperature is directly derived from the heat release from the reactions.

4.1.3 Effect of Frequency on Conversions and Yields

As mentioned earlier, the AC discharge became unstable when the methane/air system was operated at frequencies below 300 Hz because carbon formation occurred on both the surfaces of electrodes and quartz tube wall. Hence, the system had to be carried out above 300 Hz. Figures 4.9 and 4.10 show that the partial pressures of hydrogen and carbon monoxide decreased with increasing frequency whereas those of methane and oxygen

increased. From Figures 4.11 and 4.12, all the conversions and yields at the applied voltage of 9,000 V were significantly higher than those at 6,500 V. The partial pressures of hydrogen and carbon monoxide at 9,000 V were significantly higher than those at 6,500 V. Figures 4.11 and 4.12 show that the conversions of methane and oxygen, as well as the yields of H_2 and CO, decrease significantly with increasing frequency at two different voltages. These findings of this study are similar to the previous work (Hill, 1997).
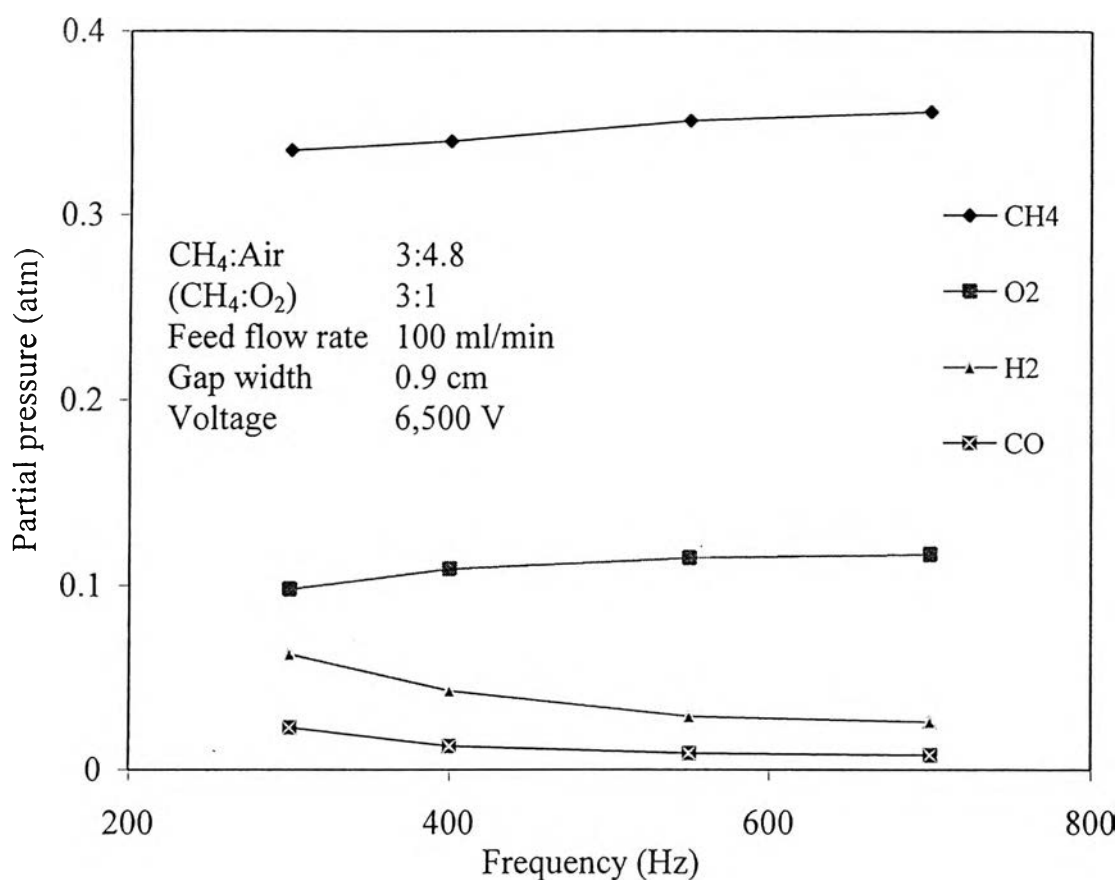
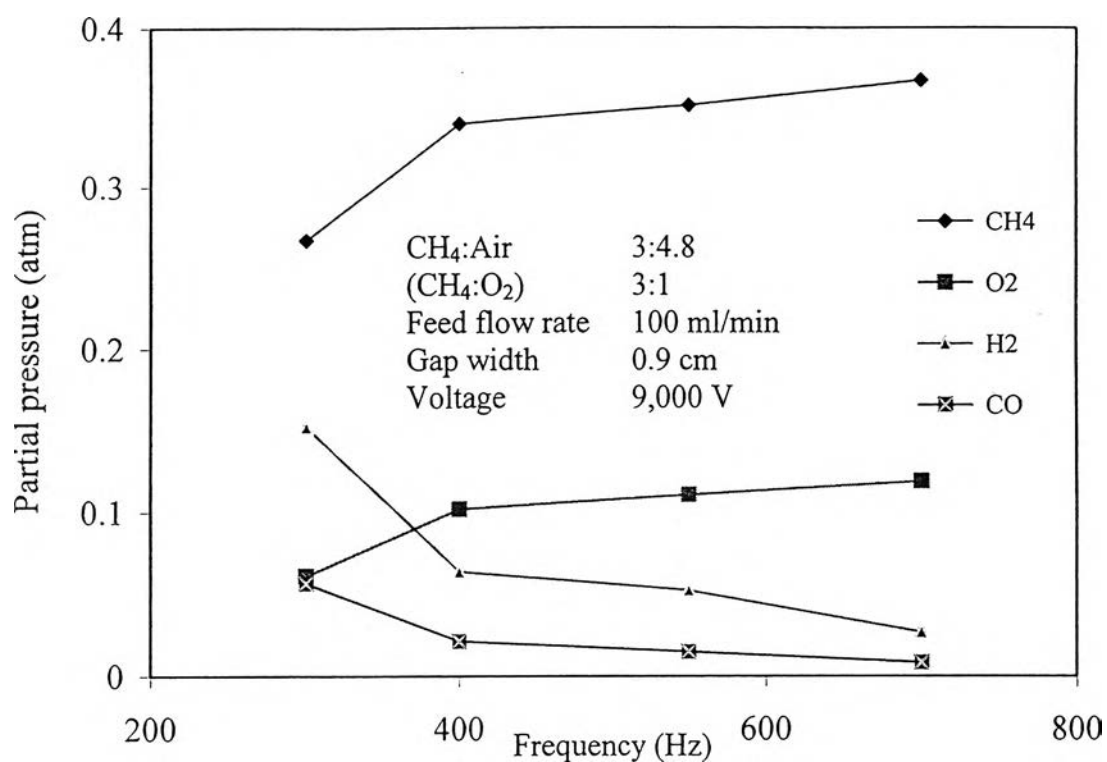**Figure 4.9** Effects of frequency on partial pressures of effluent gases

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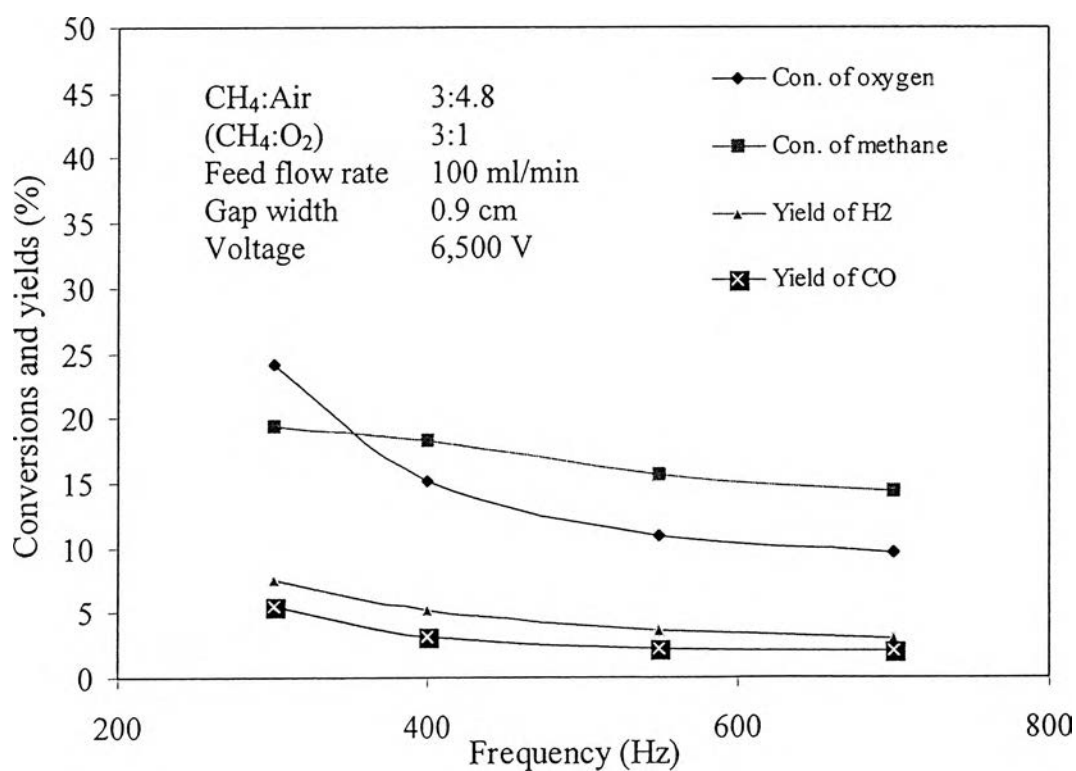**Figure 4.10** Effects of frequency on partial pressures of effluent gases

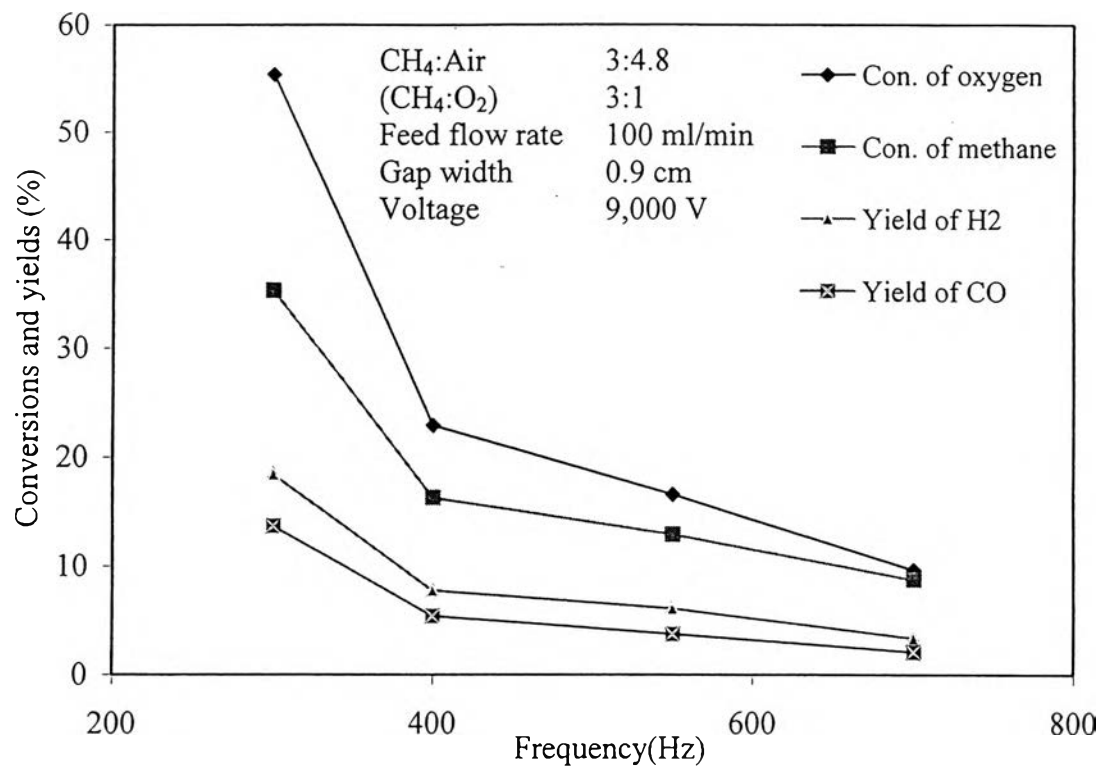**Figure 4.11** Effects of frequency on conversions and yields.

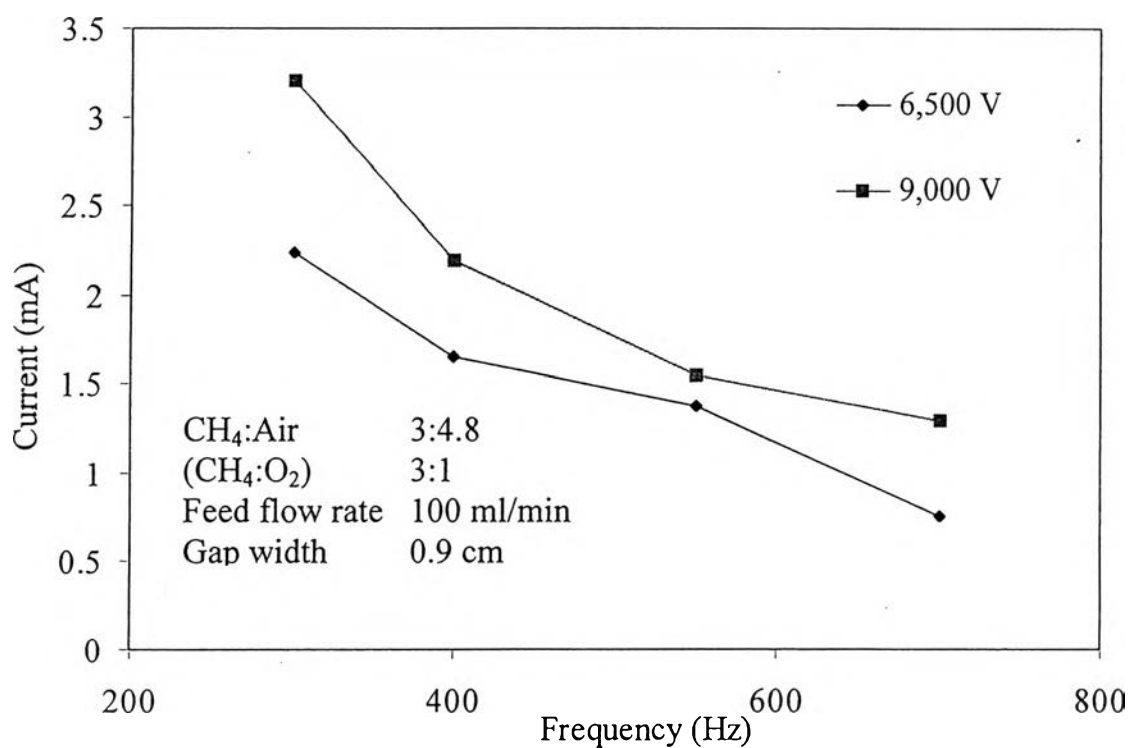**Figure 4.12** Effects on frequency on conversions and yields

Figure 4.13 Relationship between frequency at two different voltages of 6,500 and 9,000 V

The current shown in figure 4.13 decreases significantly with increasing frequency resulting in a reduction of electrons available for initialing the reaction. Thus the number of inelastic collisions decreased with decreasing current which lowered the reaction rates. As shown in Figure 4.13, the current at the applied voltage of 9,000 V is significantly higher than that at 6,500 V.

4.1.4 Effect of Frequency on Products Selectivities

From Figures 4.14 and 4.15, both selectivities of hydrogen and carbon monoxide decrease with increasing frequency. Obviously, the highest product selectivities of H_2 and CO were achieved at the lowest frequency of 300 Hz. This can be explained that at this frequency, there was the largest number and the highest energy of electrons available to initiate the partial oxidation of methane to from synthesis gas as described in Equation 4.1. The selectivities of hydrogen and carbon monoxide in Figure 4.15 were significantly higher than those in Figure 4.14. The temperature of reactor wall at the applied voltage of 9,000 V as shown in Figure 4.16 decreased with increasing frequency. The explanation is that less number of electrons and ions dissipated as heat decreased, thus resulting in fewer exothermic reactions.
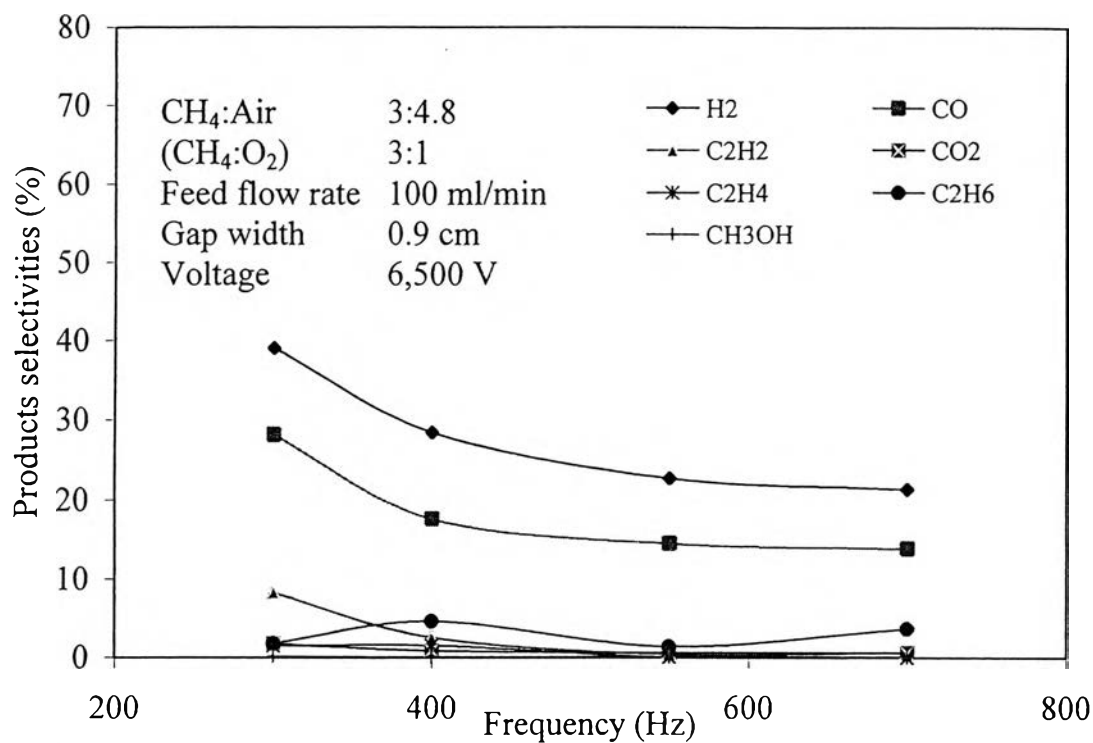
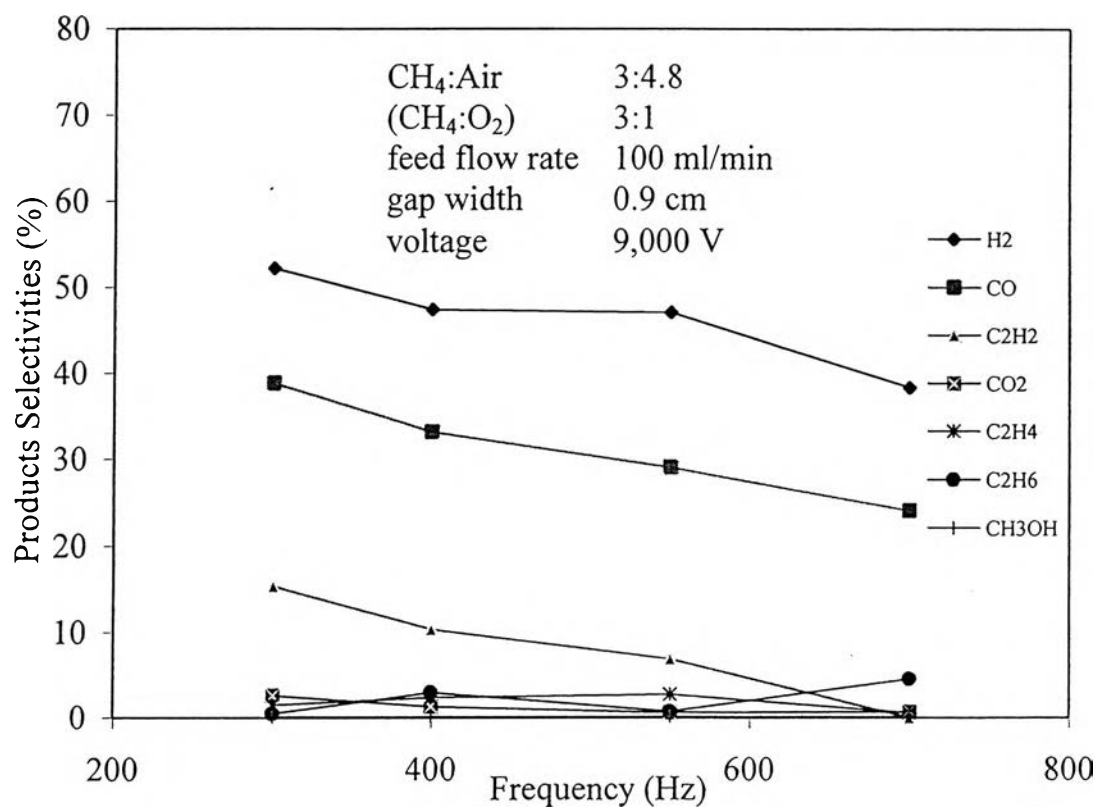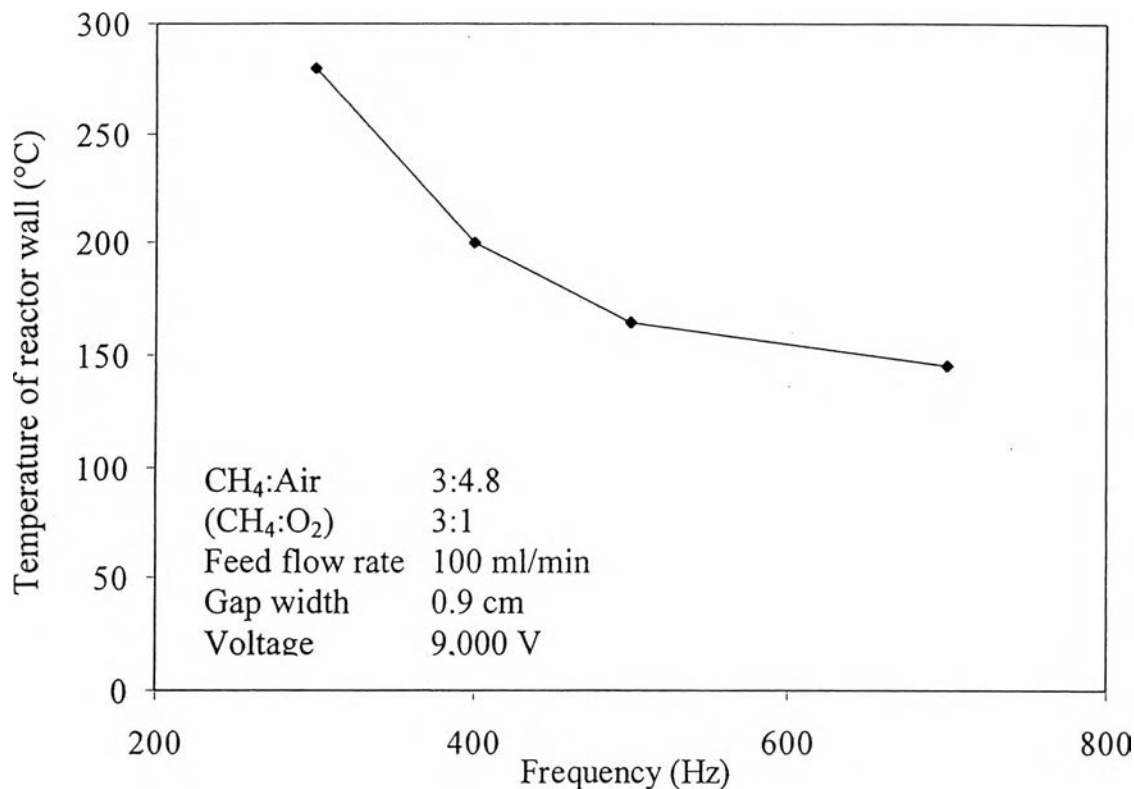**Figure 4.14** Effects of frequency on products selectivities

**Figure 4.15** Effects of frequency on the products selectivities

Figure 4.16 Temperature of reactor wall at different frequency

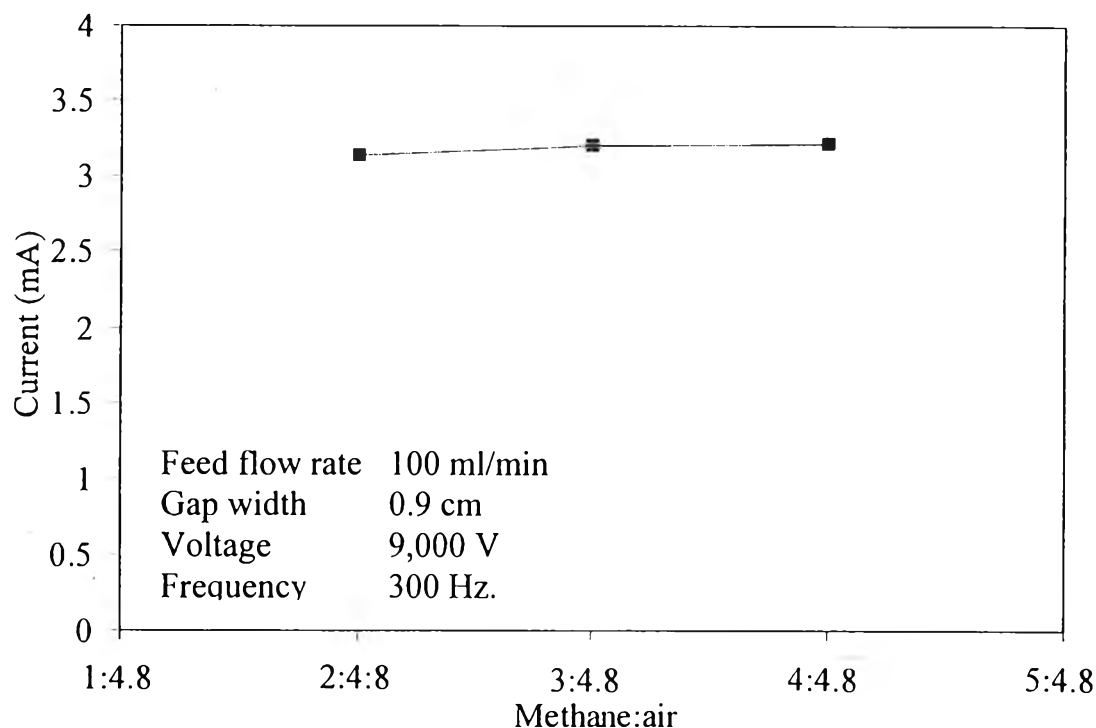4.1.5 Effect of Methane/Air Ratio on Conversions and Yields

This part of experiments was carried out with varying the methane to air ratio while all other parameters were kept constant. Figure 4.17 shows that the partial pressures of hydrogen and carbon monoxide decreased significantly with increasing methane partial pressure whereas those of methane and oxygen increased. Figure 4.18 illustrates that not only the methane and oxygen conversions but also the yields of H_2 and CO decrease remarkably when the methane partial pressure increases. This finding is similar to the previous works (Hill, 1997 and Sutthiruangwong, 1999). Figure 4.19 show that the current is approximately constant for the entire ratios of methane to air. This implies that the number of electrons available to initiate the reactions was approximately the same for different methane to air ratios.
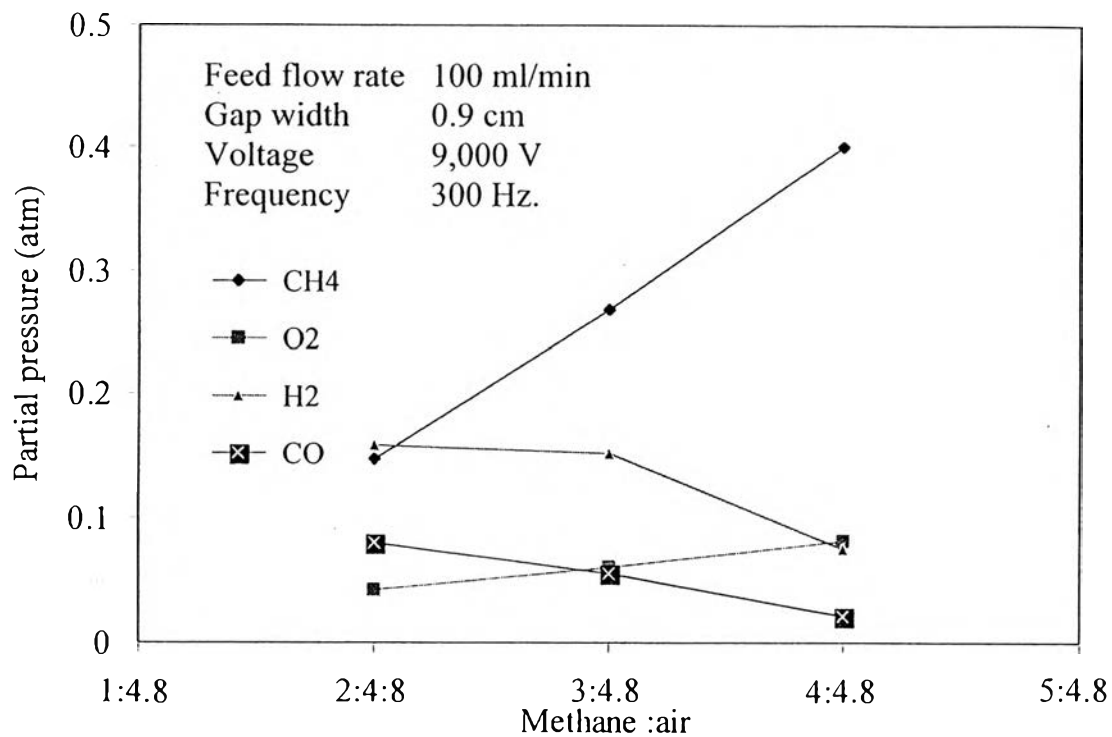
Figure 4.17 Effects of methane to air ratio on partial pressures of effluent gases
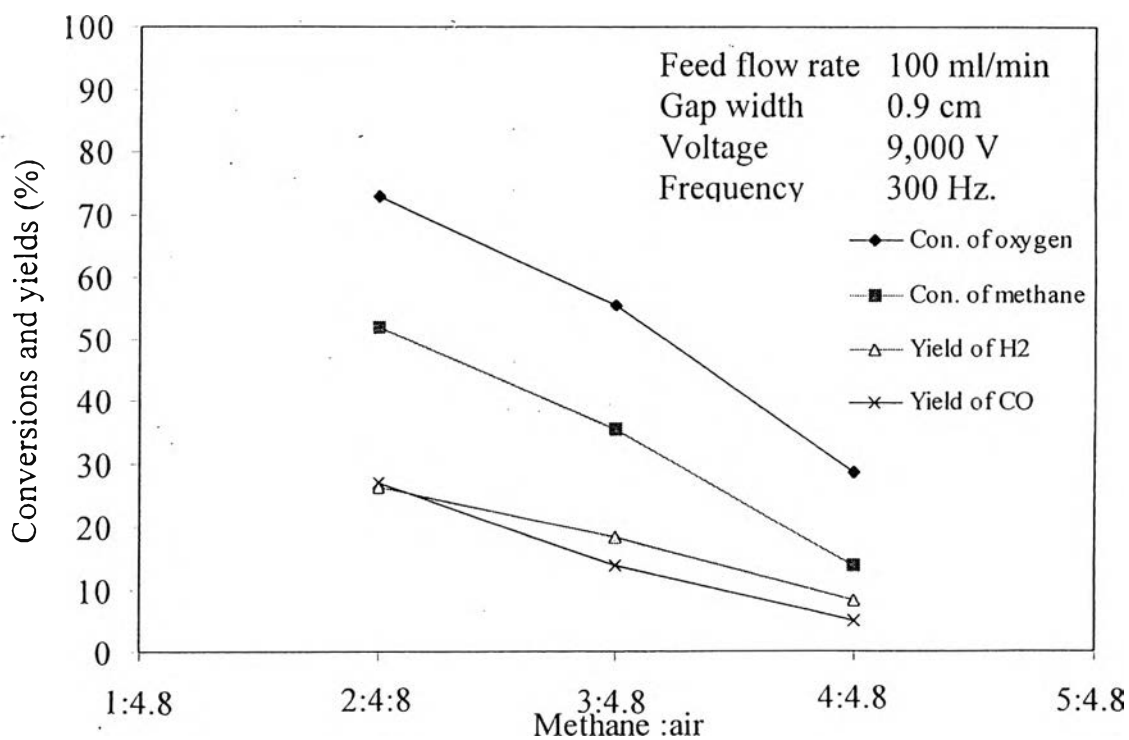
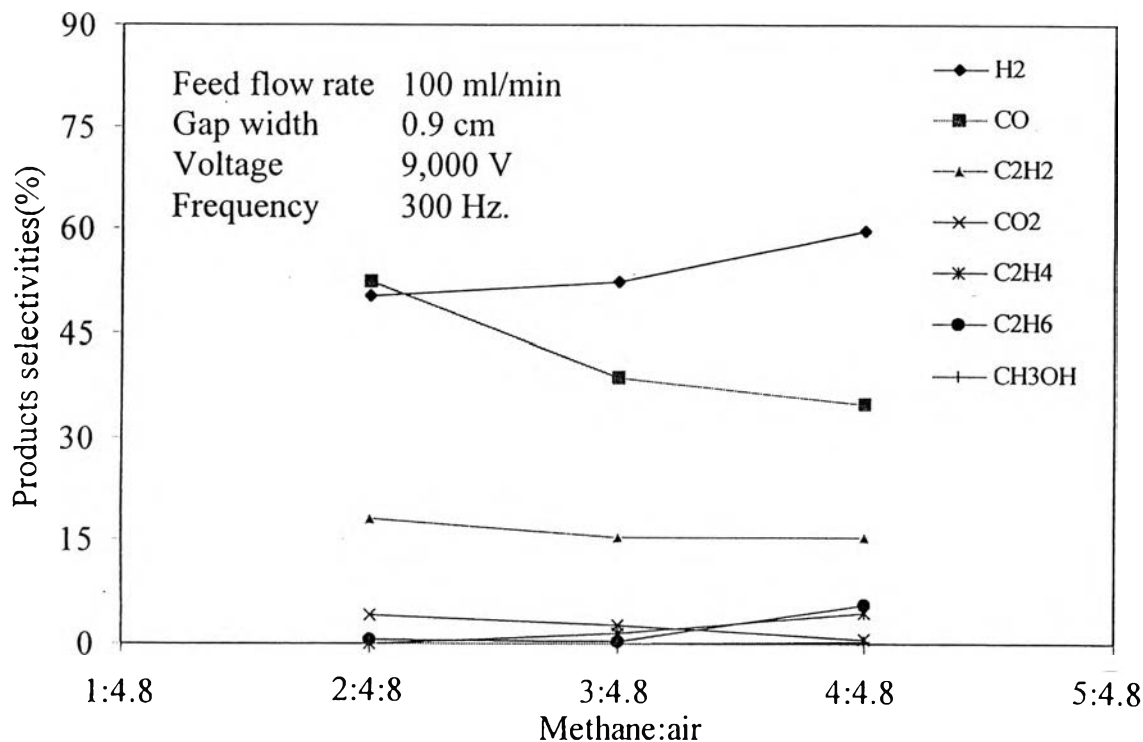**Figure 4.18** Effects of methane to air ratio on conversions and yields

Figure 4.19 Relationship between methane to air ratio and current under the studied conditions

4.1.6 Effect of Methane/Air Ratio on the Products Selectivities

Figure 4.20 shows that only the selectivity of hydrogen increases slightly while CO selectivity decreases significantly with increasing methane partial pressure. This is due to the fact that there is higher probability of electrons and ions to break the C-H bond on methane molecules and thus ethane and ethylene were produced as shown in Equations 4.2 through 4.5. In addition, acetylene was also produced by coupling and dehydrogenation reaction according to Equation 4.6.

Interestingly, an increase in the methane to air ratio resulted in decreasing CO selectivity. This result can be explained that a higher ratio of methane to air gave a lower oxygen available to oxidize methane to carbon monoxide.

Figure 4.20 Effects of methane to air ratio on the products selectivities

4.1.7 Effect of Flow Rate on Conversions and Yields

From Figure 4.21 shows that partial pressures of hydrogen and carbon monoxide decrease slightly with increasing the flow rate however those of methane and oxygen increase slightly. From Figure 4.22, it is apparent that both methane and oxygen conversions, including yields of H_2 and CO, dropped significantly with increasing the flow rate. This finding is similar to the previous works (Hill, 1997 and Leethochawalit, 1998). The retention time was calculated from the volume of effective space divided by the gas flow rate. In this experiment, increasing the total flow rate resulted in decreasing the retention time of reaction. Figure 4.22 also implies that the degree of methane conversion decreases as the exposure time of the methane molecules in the electric discharge environment decreases. When the flow rate increased, the contact time simply decreased resulting in the less change of methane molecules to be contacted with electrons. This resulted in a decrease in the rate of methane conversion, and all products selectivities.
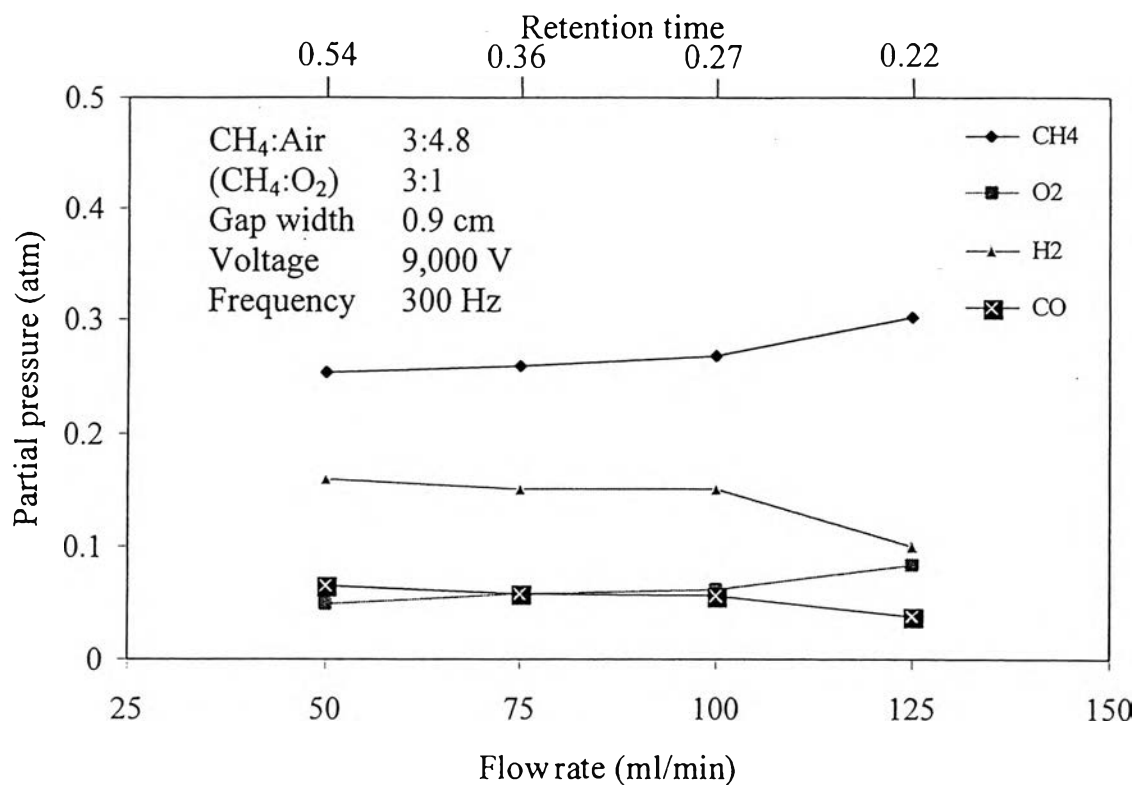
Figure 4.21 Effect of flow rate on partial pressures of effluent gases
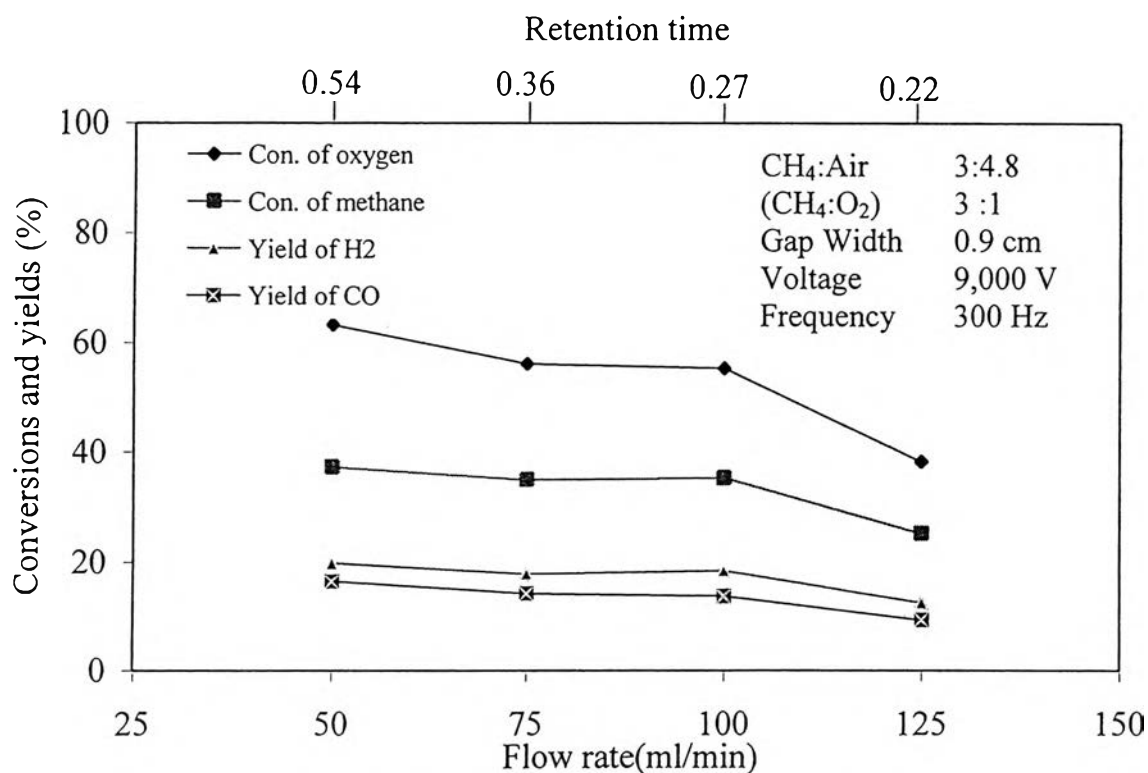

Figure 4.22 Effect of flow rate on conversions and yields

Likewise, this phenomenon maybe mentioned as the same explanation applied for oxygen conversion.

4.1.8 Effect of Flow Rate on Products Selectivities

Figure 4.23 shows the effect of the flow rate on the products selectivities when the system is operated at 9000 V and 300 Hz. An increase in the flow rate resulted in decreasing the selectivities of hydrogen, carbon monoxide and ethylene while the selectivities of acetylene and carbon dioxide were relatively constant with increasing the flow rate. Under the studied conditions, the selectivities of both ethane and methanol were extremely low. The results indicated that the partial oxidiation of methane to hydrogen and carbon dioxide was the main reaction.The coupling reaction following with dehygrogenation also appeared significantly. The current is approximately constant throughout all flow rates as indicated in Figure 4.24. This constant current is similar to the previous works (Hill, 1997). According to Paschen's Law, the breakdown voltage necessary to initiate a discharge is a function of the inner-electrode gap distance and pressure (Grill, 1994). Paschen's law predicts that the current will remain constant with increasing flow rate, which is supported by the results from this experiment.
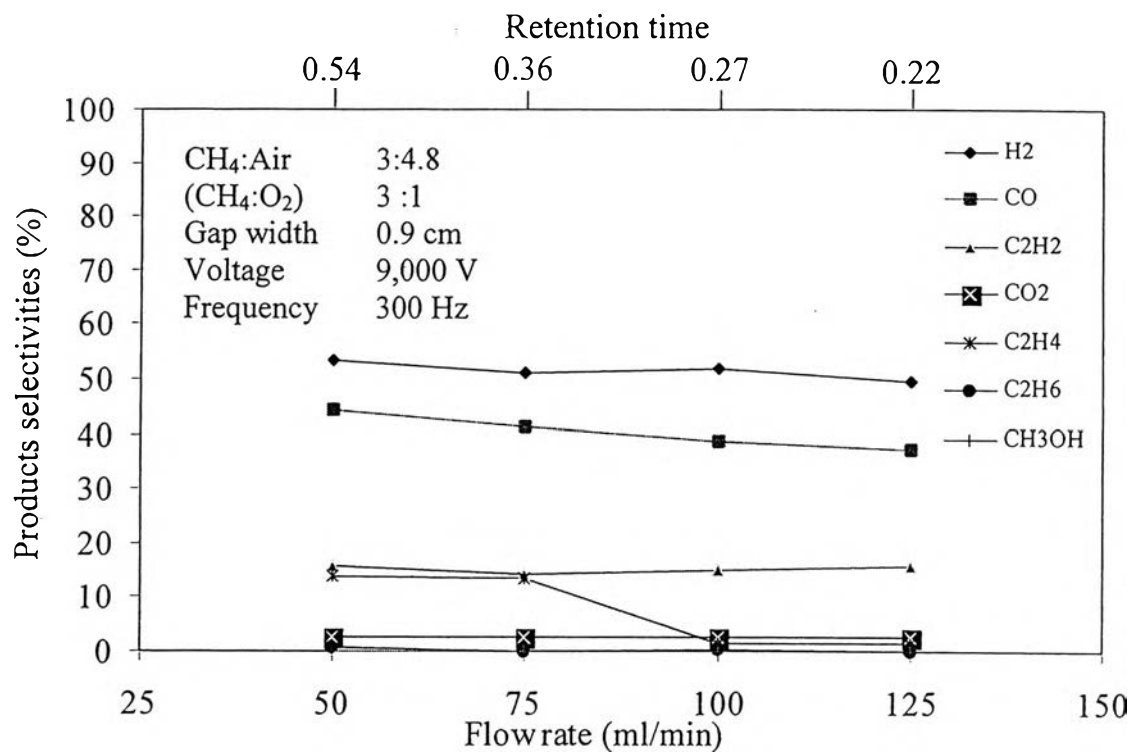
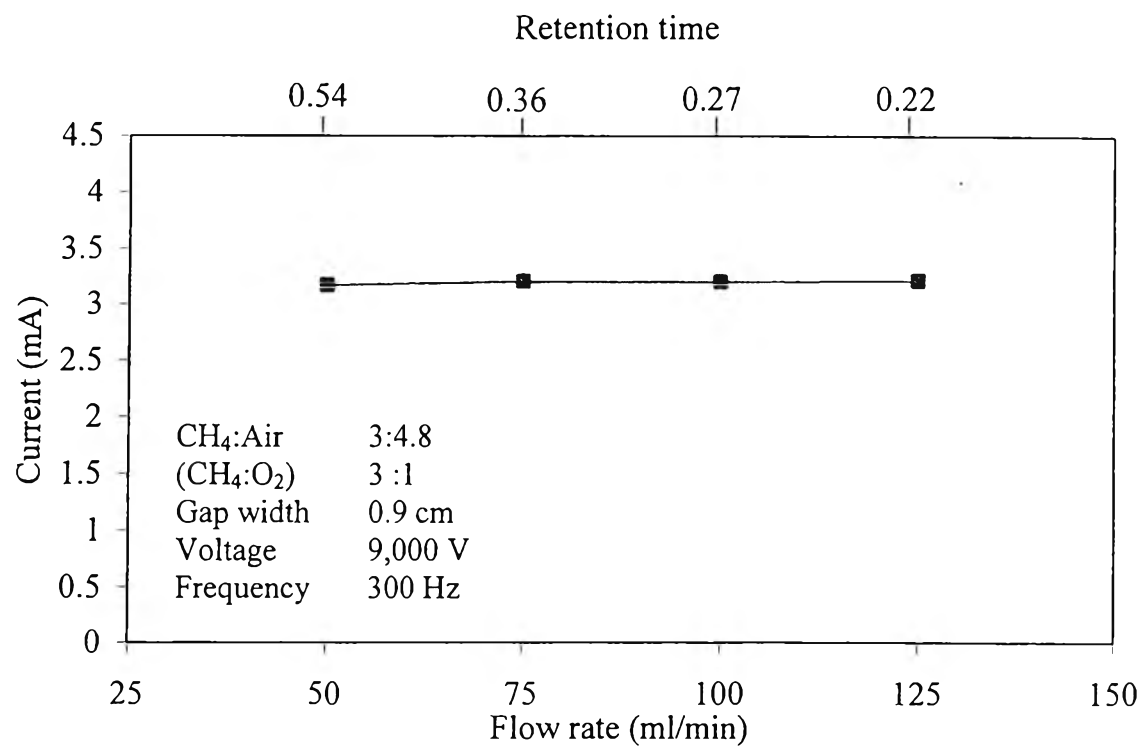**Figure 4.23** Effects of flow rate on products selectivities

Figure 4.24 Relationship between flow rate and current

4.1.9 Effect of Gap Width on Conversions and Yields

The minimum voltage required to initiate the discharge increased with increasing gap width. The breakdown voltage at 9,000 V was the lowest operating voltage for the reaction at the gap width of 1.9 cm. In this experiment, the gap width was varied from 0.7 to 1.9 cm at a constant flow rate of 100 ml/min. Interestingly, at the gap width below 0.7 cm, there was carbon filament formation at all frequencies. The residence times of each gap width were 0.84 for 0.7 cm, 1.10 for 0.9 cm, 1.81 for 1.5 cm and 2.29 for 1.9 cm. Figure 4.25 shows that partial pressures of H_2 and CO gradually decrease with increasing the gap width. Figure 4.26 illustrates that as the gap width increases, the methane and oxygen conversions also increases whereas the yields of H_2 and CO decrease. This finding is similar to the previous work conducted by Hill, (1997). A larger gap width increases the residence time or gives more time for reaction. This will increase the chance for inelastic collisions and therefore more reactions were occurred. The electric field strength decreased with increasing the gap width, which mean electrons had lower energy with increasing gap width. The residence time was more significant than the electric field strength.
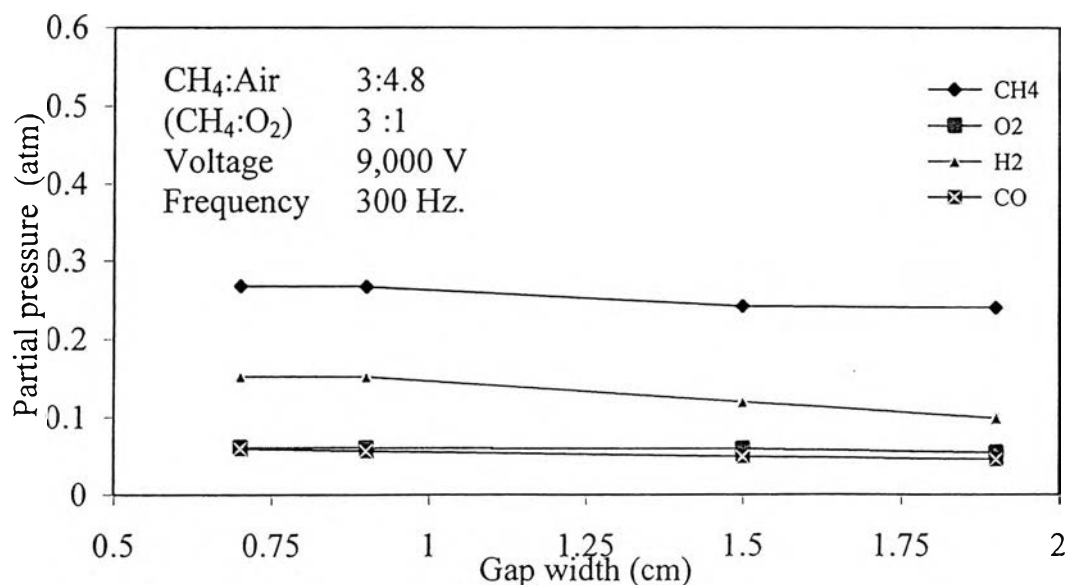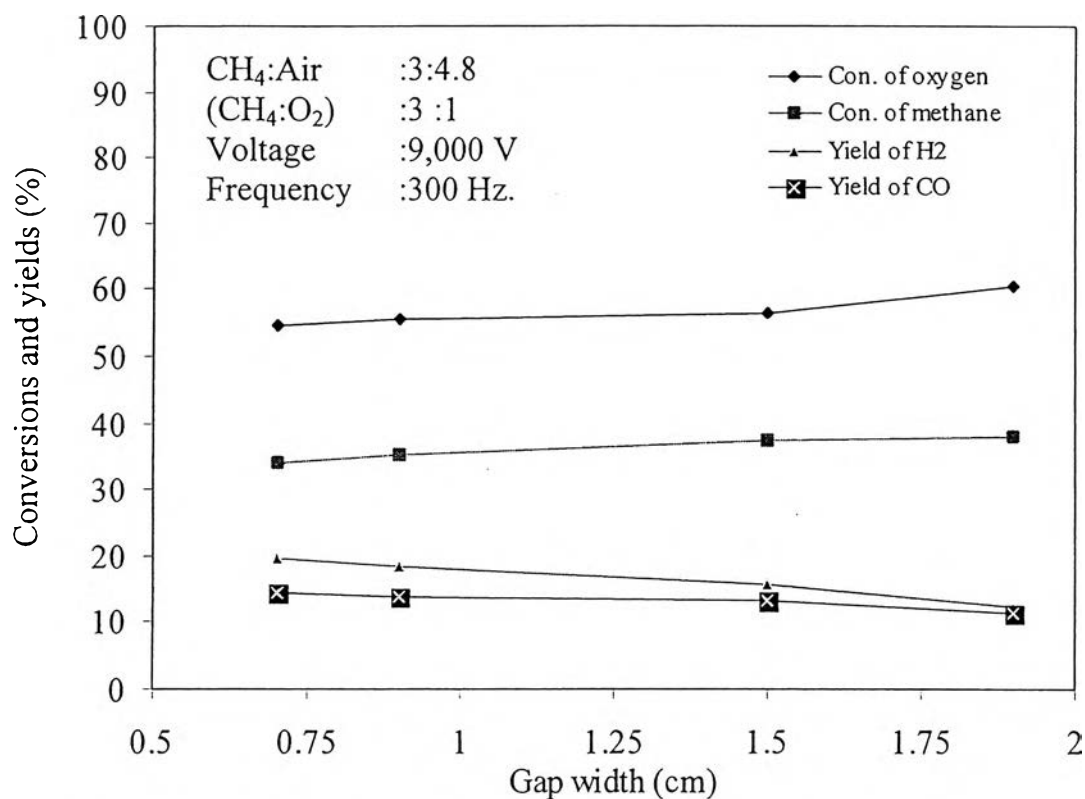

Figure 4.25 Effects of gap width on partial pressure of effluent gases

Figure 4.26 Effects of gap width on conversions and yields

4.1.10 Effect of Gap Width on Products Selectivities

As be seen from Figure 4.27, when the gap width increases, the selectivities of H_2 and CO in decrease, corresponding to the yields of H_2 and CO as shown in Figure 4.26. The decreasing selectivities of H_2 and CO resulted from a lower number of electrons available for initiating reactions with increasing the gap width, which corresponds to the decreasing current as shown in Figure 4.28. An increase in the resistance between the electrode gap was obtained with increasing the gap width.
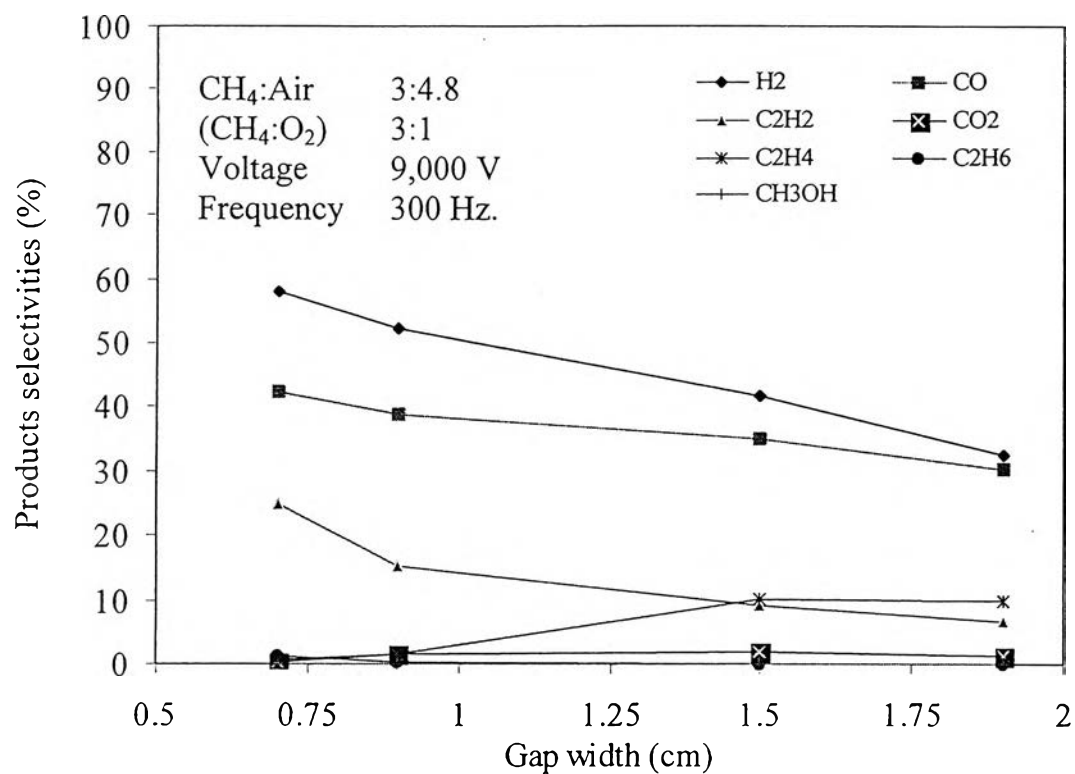
Figure 4.27 Effect of gap width on products selectivities
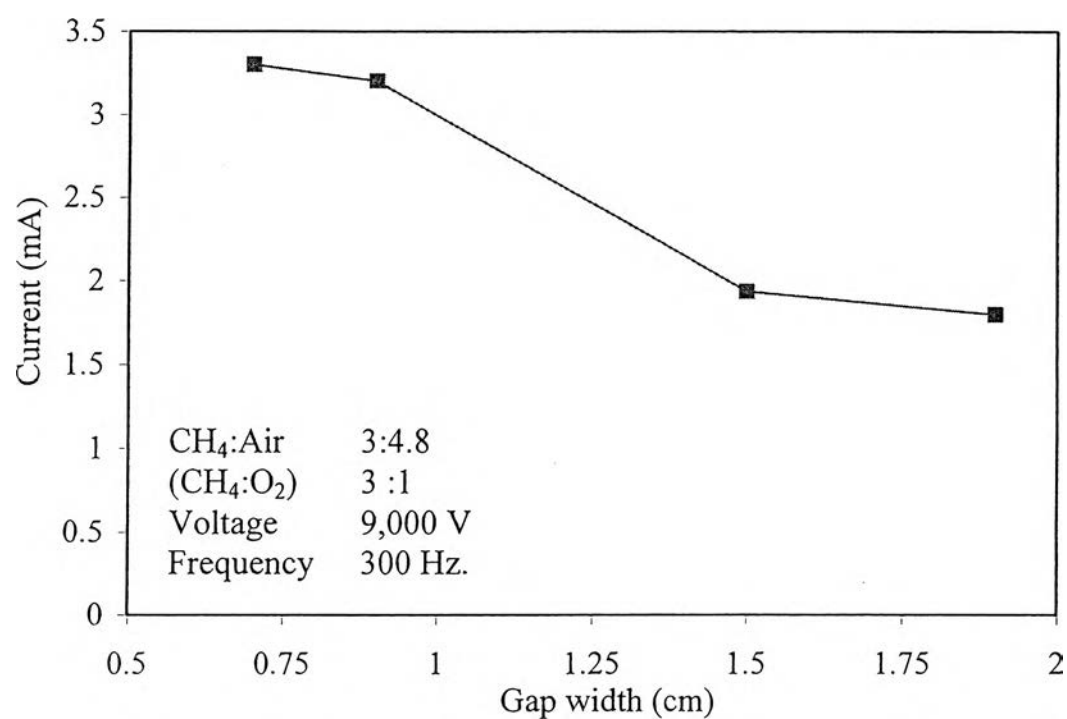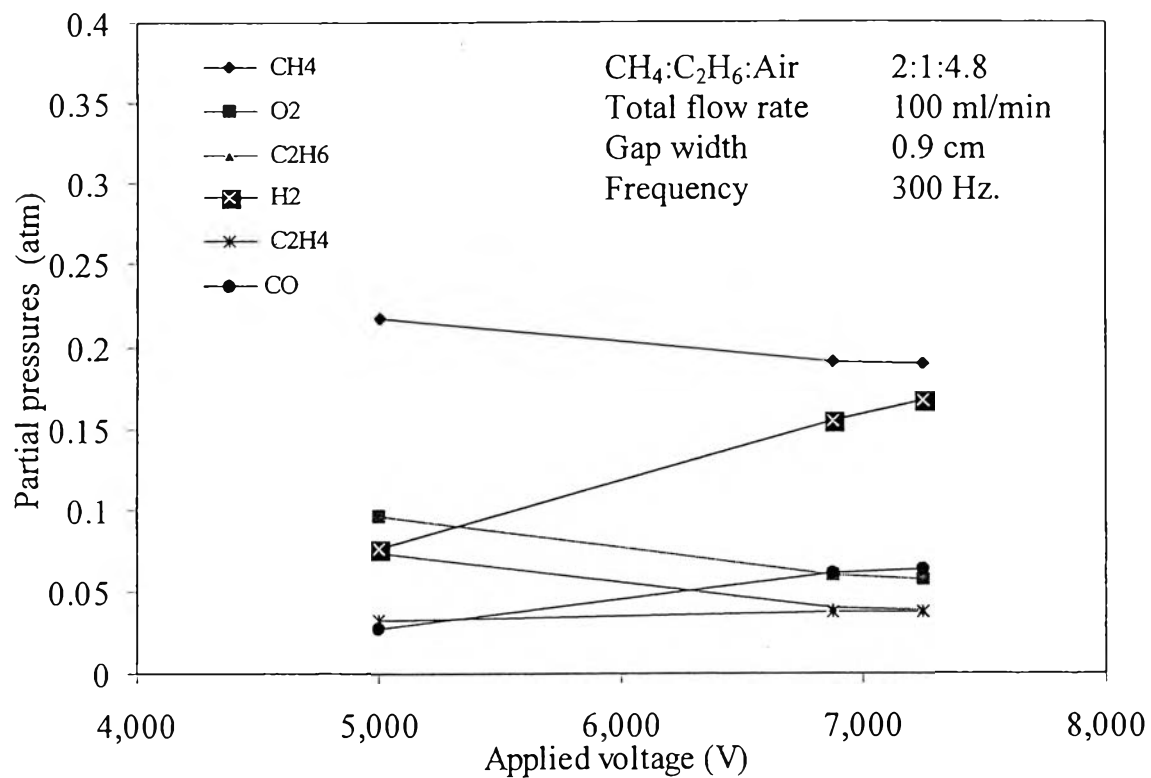

Figure 4.28 Relationship between gap width and current

4.2 Air/Methane/Ethane System

4.2.1 Effect of Applied Voltage on Conversions

The experiment was operated at a ratio of $CH_4:C_2H_6:air$ equal to 2:1:4.8, a total flow rate of 100 ml/min, the gap width of 0.9 cm, and the frequency of 300 Hz. Beyond the voltage of 7,250 V at the frequency of 300 Hz, the reaction was unstable because of carbon filament formation at electrodes and tube. Therefore, the experiment was run in the range of 5,000 to 7,250 V. Figure 4.29 illustrates that the partial pressures of hydrogen, carbon monoxide, and ethylene increase with increasing applied voltage whereas those of methane, oxygen and ethane decrease. From Figure 4.30 shows that oxygen and ethane conversions increased with applied voltage. However, methane conversion increase and is then almost constant from the applied voltage increasing from 6,875 to 7,250 V. This can be explained that ethane could decompose to methane especially at higher voltage, which made overall methane conversion constant. Figure 4.31 illustrates that the current increased significantly with increasing voltage, giving a larger number of electrons available to initiate the reactions as a result of higher oxygen and ethane conversions.
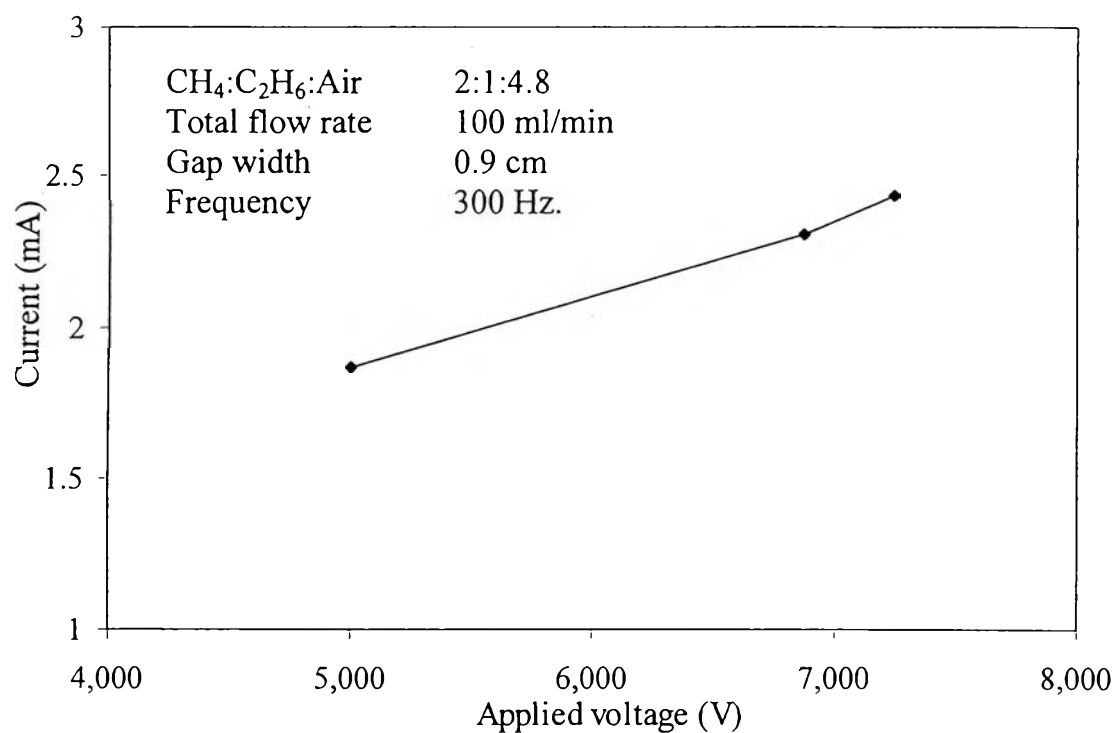
Figure 4.29 Effects of applied voltage on partial pressure of effluent gases
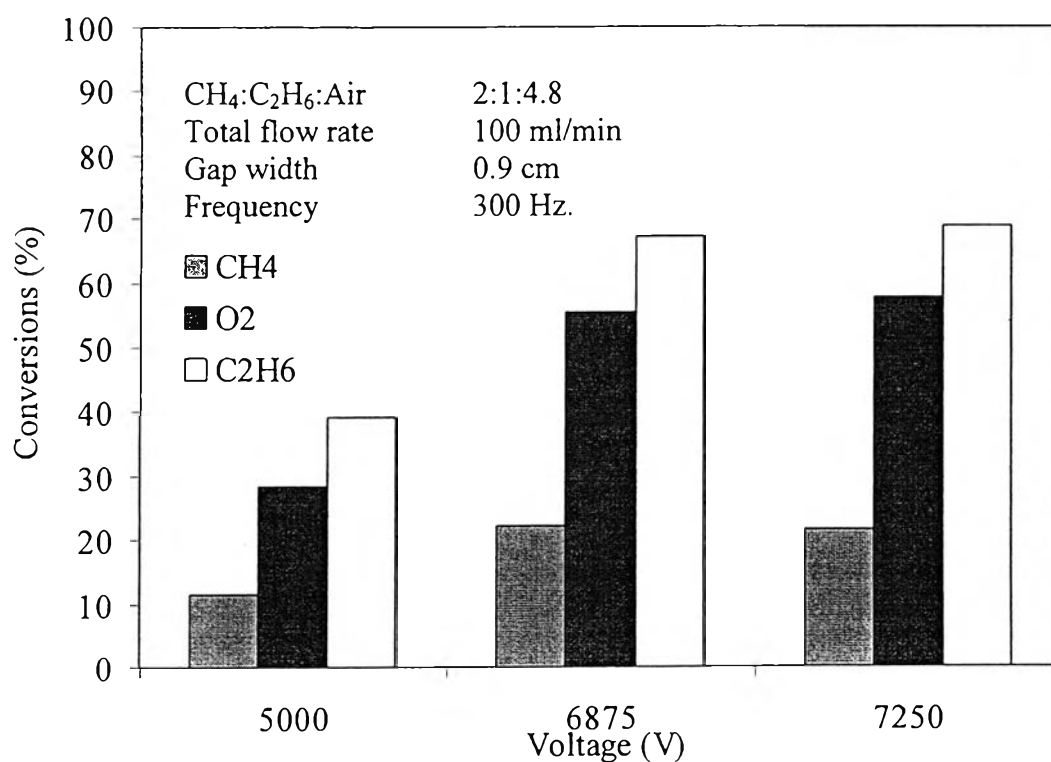
Figure 4.30 Effects of applied voltage on the conversions of the methane and air under presence of ethane

Figure 4.31 Relationship between applied voltage and current under presence of ethane

## 4.2.2 Effect of Applied Voltage on Products Selectivities

Figure 4.32 shows that the selectivities of H_2 and CO increase with increasing the applied voltage, conversely with that of C_2H_4. The highest selectivity of C_2H_4 was obtained at the lowest voltage of 5,000 V, and then decreased with increasing voltage. This implied that C_2H_4 had the tendency to dissociate to H_2 and C_2H_2 with increasing the applied voltage as shown in Equation 4.6.
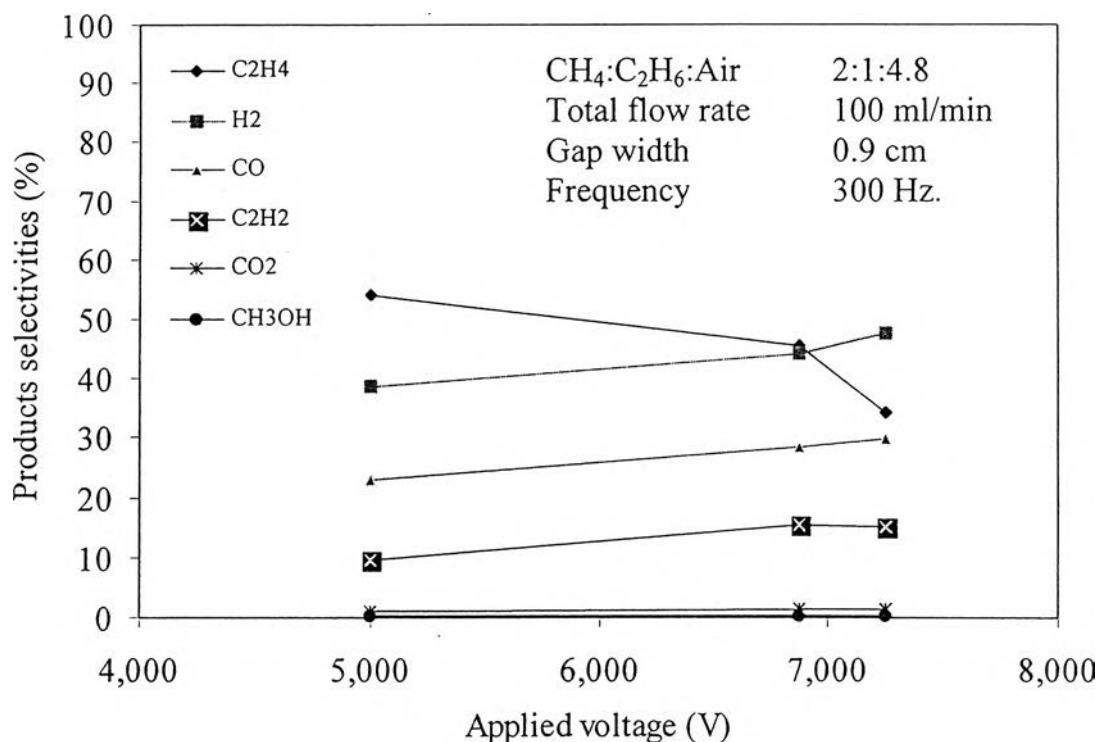
Figure 4.32 Effects of applied voltage on the products selectivities under presence of ethane

### 4.2.3 Effect of Frequency on Conversions

Figure 4.33 illustrates that the partial pressures of hydrogen, carbon monoxide, and ethylene decrease with increasing frequency, whereas those of methane, oxygen and ethane increase. Figure 4.34 illustrates that methane, oxygen and ethane conversions decreased significantly with increasing frequency. On the other hand, an increase in frequency results in a lower number of electrons as observed from the current in Figure 4.35. The current decreased significantly with increasing frequency and thereby decreased all conversions. This can be explained that there were a lower number of electrons available to initiate the reactions.
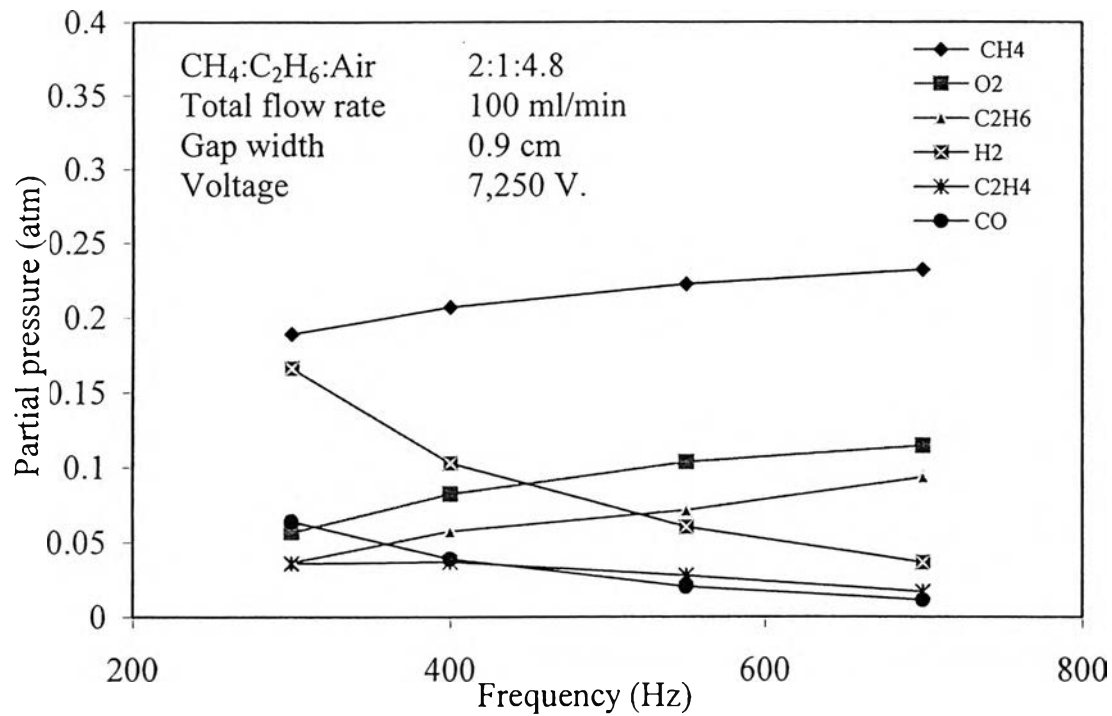
Figure 4.33 Effects of frequency on partial pressures of effluent gases under presence of ethane
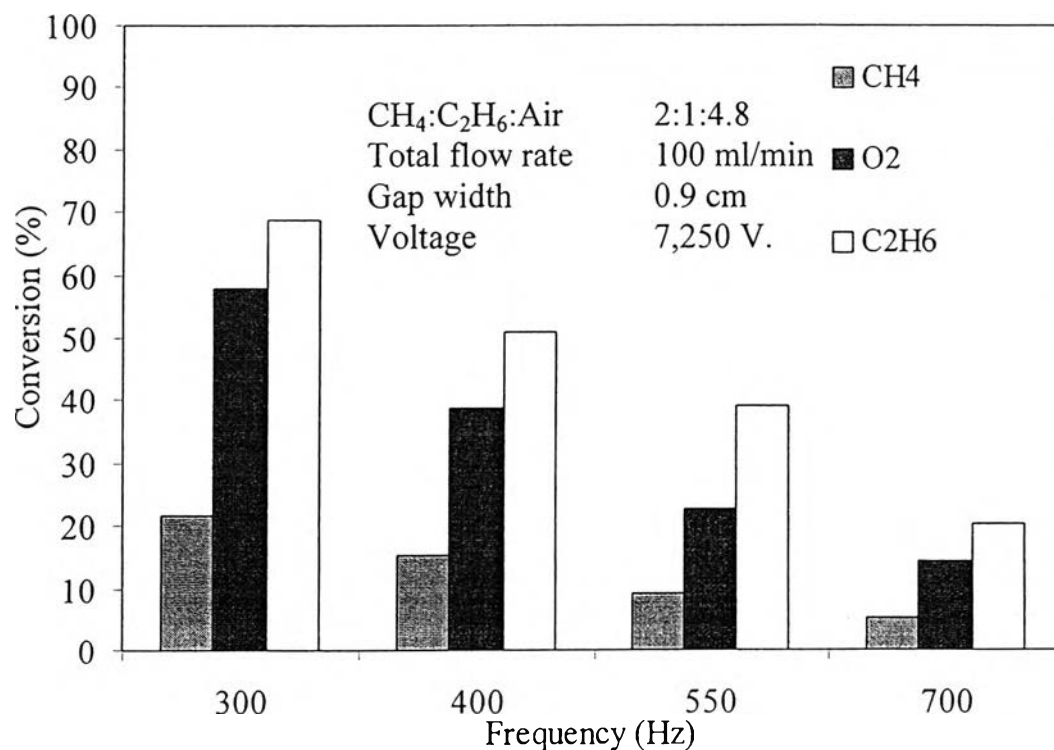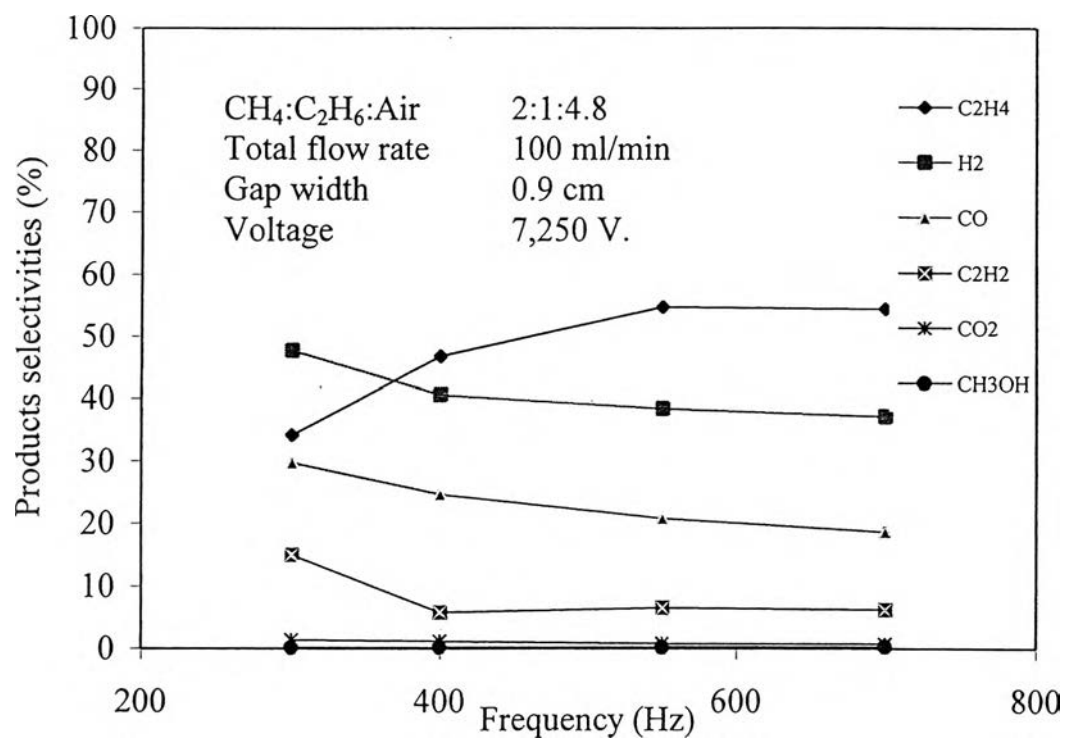

Figure 4.34 Effects of frequency on the conversions under the presence of ethane
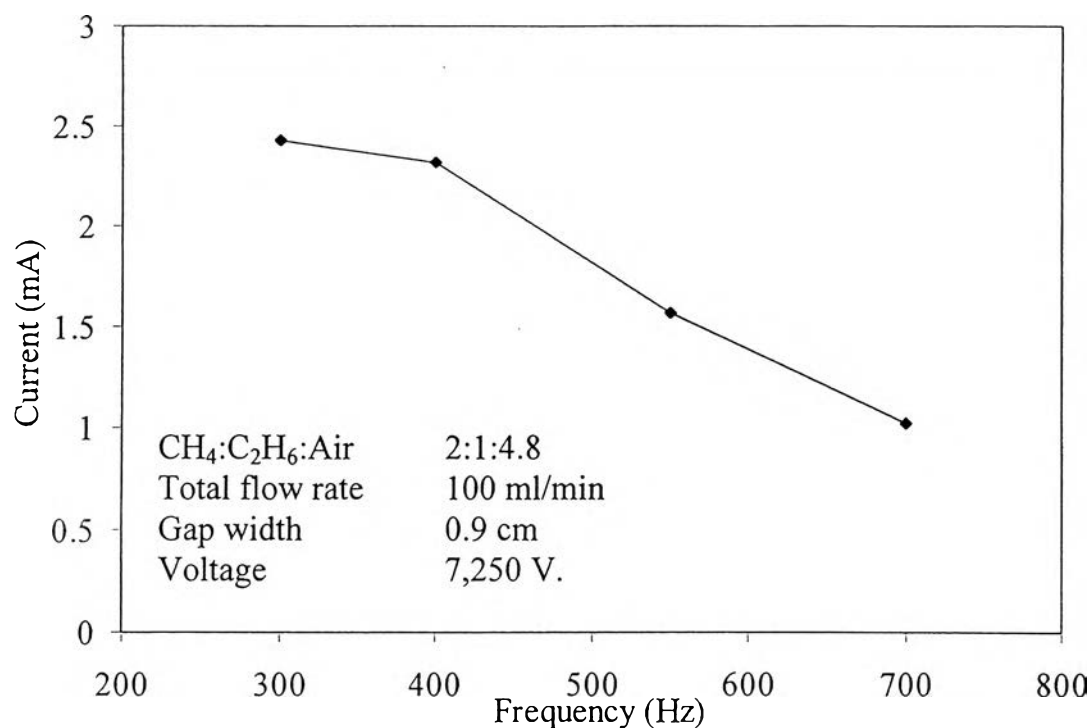
Figure 4.35 Relationship between frequency and current under the presence of ethane

4.2.4 Effect of Frequency on Products Selectivities

Most of producst selectivities as shown in Figure 4.36 have the tendency to decline with increasing frequency except the selectivity of C_2H_4, of which the lowest was at the frequency of 300 Hz, but was higher at higher frequency since the C_2H_4 was difficult to dissociate to C_2H_2 and H_2 with increasing frequency. Also, the highest selectivities of H_2 and CO were at 300 Hz and decline with increasing frequency. This can be explained that there were a lower number of electrons available to initiate the reactions as shown in Equation 4.6.

Figure 4.36 Effects of frequency on the products selectivities under the presence of ethane