CHAPTER IV
RESULTS AND DISCUSSION

All the experimental data of this present study were summarized in Appendix A. Appendix B shows the calculation procedures used in determining methane conversion and products selectivities. In this chapter, attempts are done to describe the reaction of methane with the presence of carbon dioxide under electric discharge environment.

4.1 Effect of CO_2 : CH_4 ratio

4.1.1 Effect of CO_2 : CH_4 ratio on methane conversion

Figure 4.1 shows the effect of the CO_2:CH_4 ratio on methane conversion at three different applied voltages. It was noticeable that at the CO_2 : CH_4 ratio of 2:1, the system gave the highest methane conversion, and the percentage of methane conversion decreased when the CO_2:CH_4 ratio was decreased. It is believed that under the presence of the electric discharge environment, carbon dioxide molecules are dissociated to form free radicals (i.e. O*), which are reactive species. These radicals may then be responsible for the activation of methane molecules resulting in increasing methane conversion.

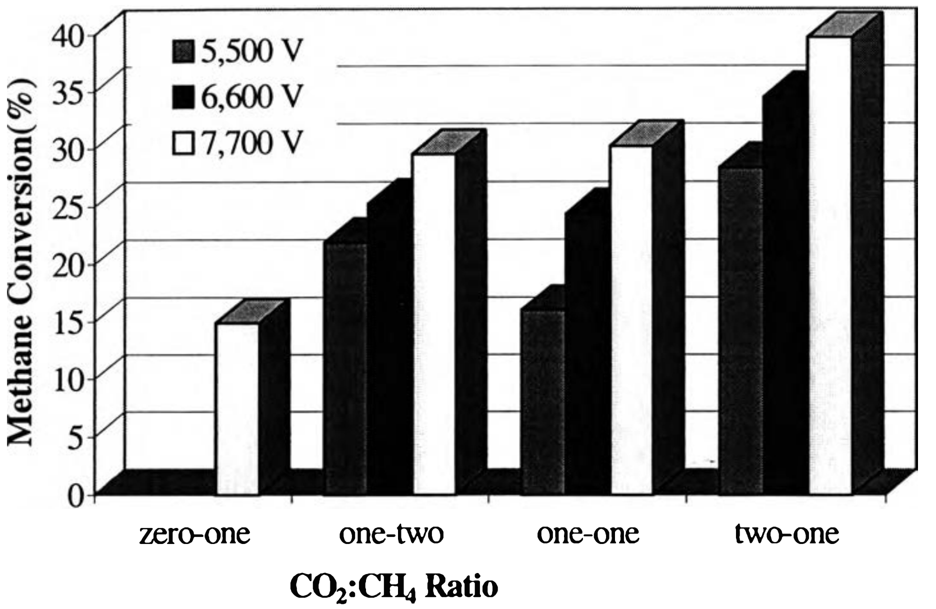


Figure 4.1 **Effect of CO_2:CH_4 ratio on methane conversion at three different applied voltages, 80% helium concentration and space time of 4 min.**

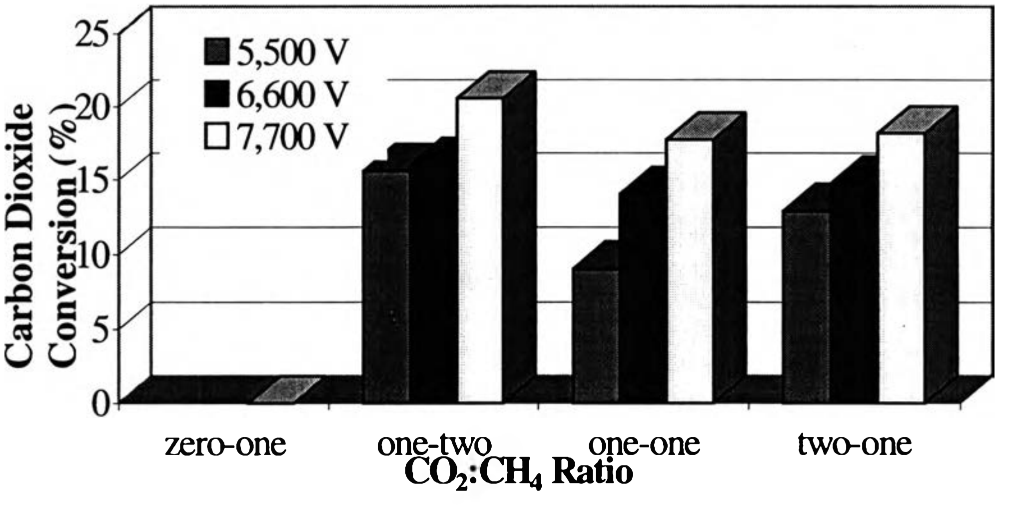


Figure 4.2 **Effect of CO_2:CH_4 ratio on carbon dioxide conversion at three different applied voltages, 80% helium concentration and space time of 4 min.**

4.1.2 Effect of CO_2 : CH_4 on carbon dioxide conversion

Figure 4.2 illustrates the effect of CO_2:CH_4 ratio on carbon dioxide conversion under three different applied voltages. It was found that at CO_2:CH_4 ratio of 1:2 gave the highest carbon dioxide conversion. This result can be explained in the same way as the effect of the ratio on methane conversion that methane molecules are dissociated under the environment of the electric discharges to form methyl radical species (CH_3*) which are very reactive. These active radicals could accelerate the carbon dioxide dissociation causing an increase in the carbon dioxide conversion. However, an increase in the CO_2 to CH_4 ratio greater than 1:2 resulted in decreasing carbon dioxide conversion. This is because carbon dioxide conversion is governed by applied voltage.

4.1.3 Effect of CO_2 : CH_4 ratio on products selectivities

Figures 4.3 - 4.8 show the effect of CO_2:CH_4 ratio on products selectivities at different applied voltage. As can be seen in Figures 4.3 to 4.5 under the absence of carbon dioxide (CO_2:CH_4 ratio of 0:1), the highest products of C_2 are obtained. An increase in the CO_2:CH_4 ratio resulted in decreasing the C_2 selectivity. This result can be explained that the formation of C_2 products are mainly derived from the thermal coupling reaction of methane. Among the C_2 hydrocarbons formed, the ethane selectivity was the highest.

Under the presence of carbon dioxide, the CO_2:CH_4 ratio of 1:2 gave the highest ethylene selectivity. This could be explained in the same way as carbon dioxide free system that the formation of hydrocarbon products are mainly derived from the thermal coupling reaction of methane. However, with increasing carbon dioxide, ethylene selectivity significantly reduced. This result can be explained that the oxygen atom from carbon dioxide was used selectively for the oxidative coupling reaction of methane, and there were less

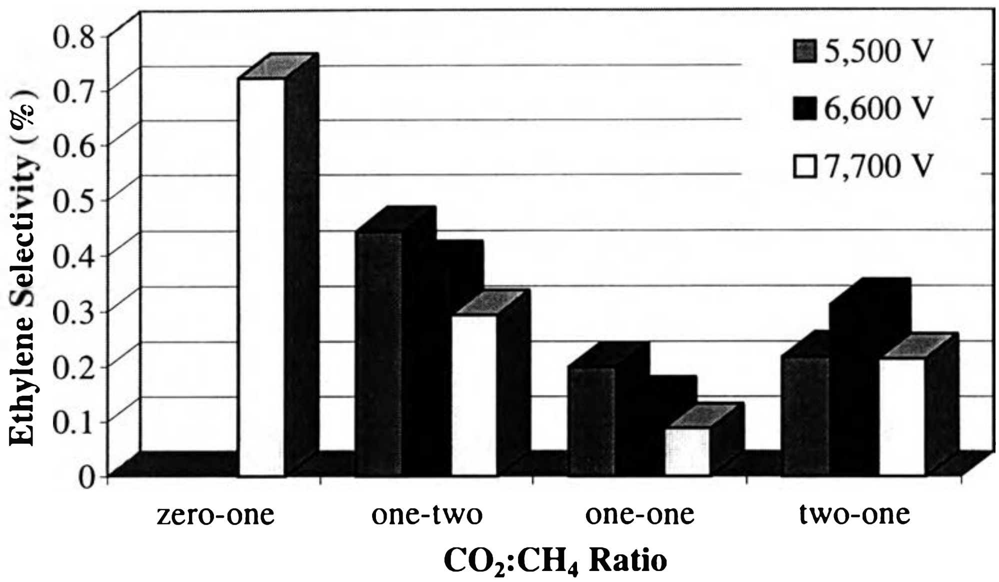


Figure 4.3 **Effect of CO_2:CH_4 ratio on ethylene selectivity at three different applied voltages, 80% helium concentration and space time of 4 min.**

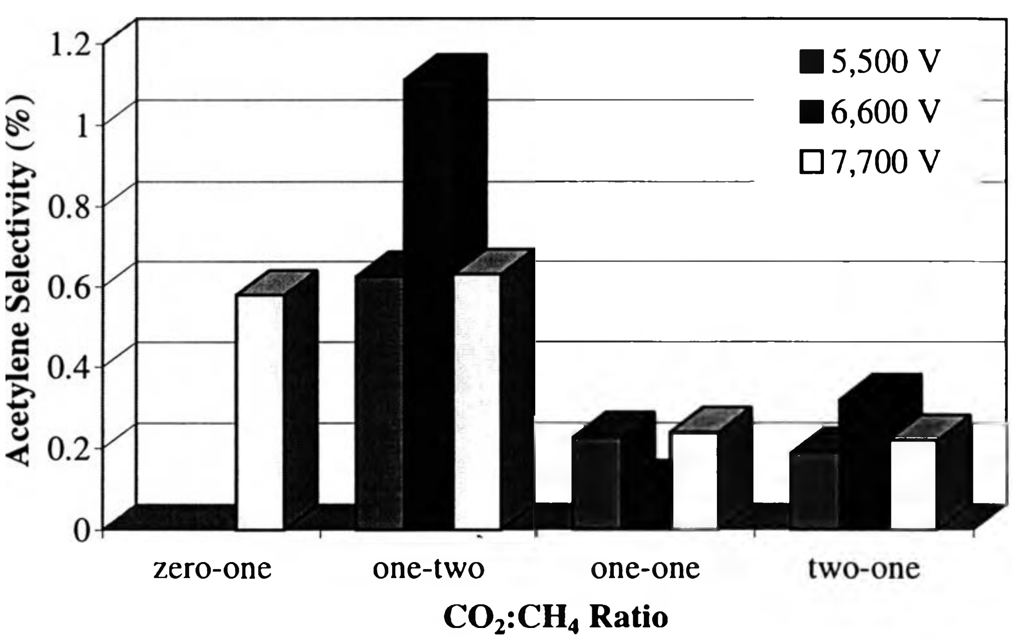


Figure 4.4 **Effect of CO_2:CH_4 ratio on acetylene selectivity at three different applied voltages, 80% helium concentration and space time of 4 min.**

methane available to form ethylene at a higher CO_2:CH_4 ratio. The acetylene and ethane selectivities can also explain in the same manner as ethylene selectivity.

Figure 4.6 illustrates the effect of CO_2:CH_4 ratio on carbon monoxide selectivity at different voltage. An increase in CO_2:CH_4 ratio resulted in increasing carbon monoxide content, which directly derived from the CO_2 conversion to CO and H_2. However, the formation of CO was reduced when the ratio of CO_2:CH_4 increased from 1:1 to 2:1. It indicates that an increase in methane becomes more available to react with CO.

As can be seen from Figure 4.7, an increase in the ratio of CH_4:CO_2 results in increasing hydrogen selectivity except at the CO_2:CH_4 ratio of 1:1. Hydrogen is produced from the coupling reaction of methane and dehydrogenation of ethane and ethylene. Hence, an increase in methane fraction leads to increase hydrogen selectivity. At the CO_2:CH_4 ratio of1:1, hydrogen selectivity became lower than the values of both higher and lower ratio of CO_2:CH_4 ratio of CO_2:CH_4. This result can be explained that most hydrogen produced is directly reacted with atomic oxygen to form water.

Figure 4.8 shows methanol selectivity at different ratios of CO_2:CH_4. Methanol selectivity increased sharply when the ratio of CO_2:CH_4 increased up to 1:1. However methanol selectivity decreased significantly as the ratios of CO_2:CH_4 increased to 2:1. The formation of methanol is form the reaction of methane and oxygen generated from carbon dioxide. Hence, methanol selectivity is governed by both carbon dioxide and methane concentrations. AT the 1:1 ratio of CO_2:CH_4, the maximum selectivity of methanol was achieved since both concentrations of methane and carbon dioxide were high.

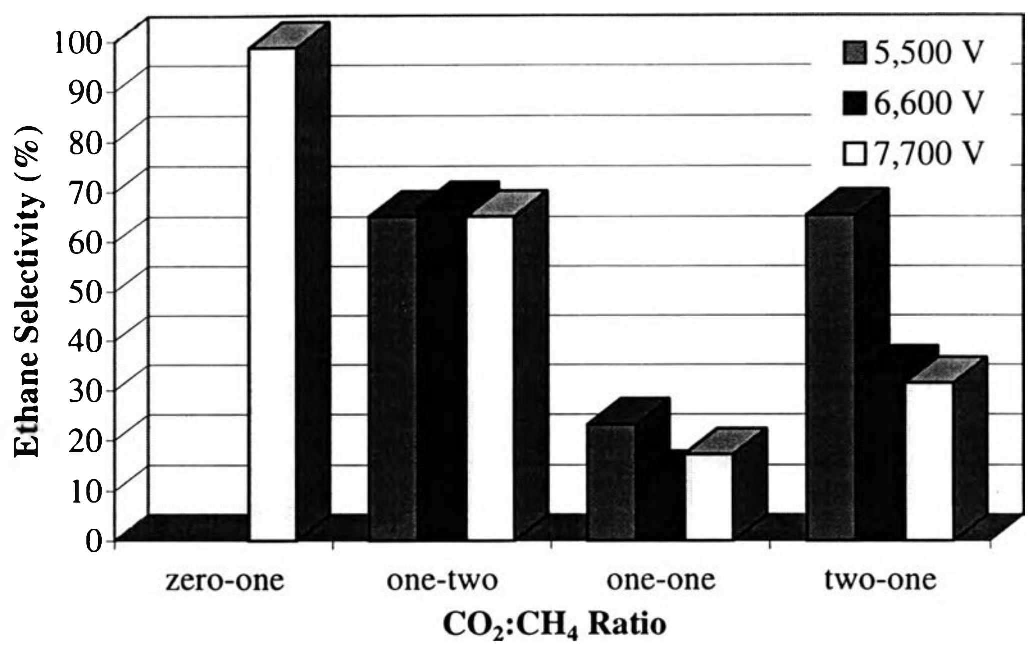


Figure 4.5 **Effect of CO_2:CH_4 ratio on ethane selectivity at three different applied voltages, 80% helium concentration and space time of 4 min.**

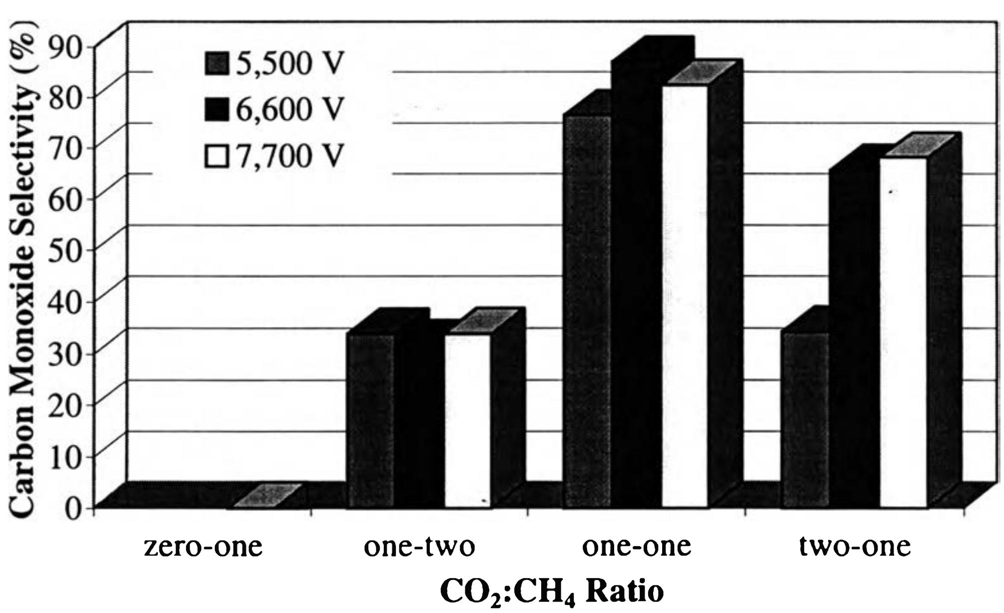


Figure 4.6 **Effect of CO_2:CH_4 ratio on carbon monoxide selectivity at three different applied voltages, 80% helium concentration and space time of 4 min.**

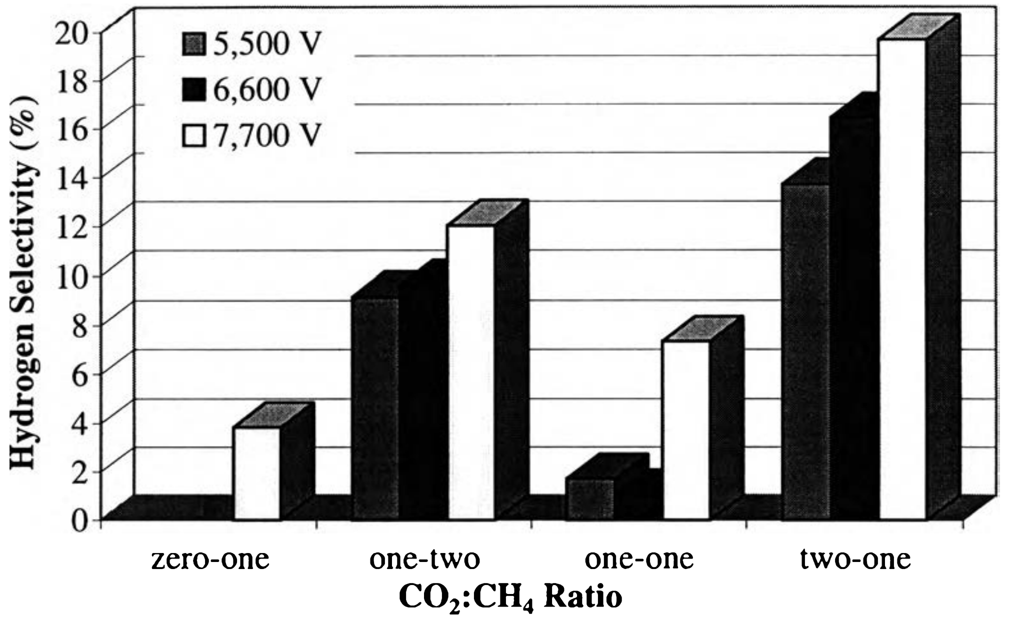


Figure 4.7 Effect of CO_2:CH_4 ratio on hydrogen selectivity at three different applied voltages, 80% helium concentration and space time of 4 min.

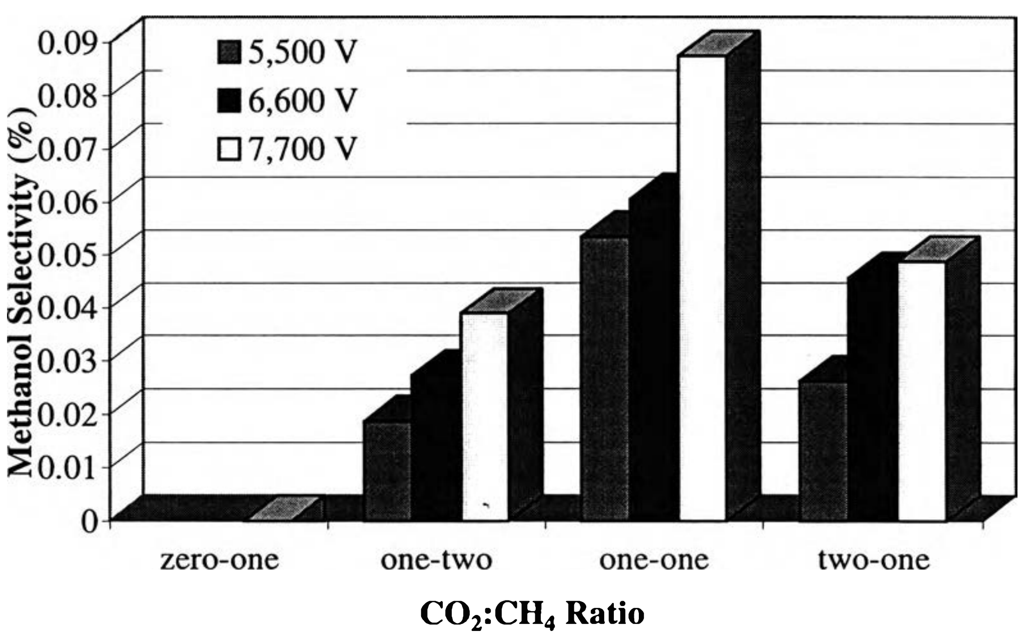


Figure 4.8 Effect of CO_2:CH_4 ratio on methanol selectivity at three different applied voltages, 80% helium concentration and space time of 4 min.

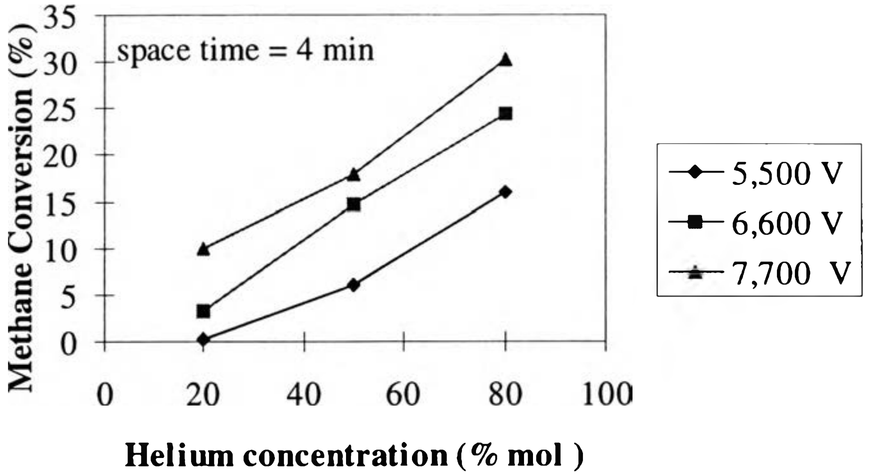
4.2 Effect of helium

4.2.1 Effect of helium on methane conversion

The effect of helium on the methane conversion at different space time (4 minutes and 6 minutes) and different voltages (5,500 V, 6,600 V, and 7,700 V) are shown in figure 4.9. With an increasing percentage of helium, methane conversion increased significantly .This result can be explained in the connection with the basic knowledge on high voltage engineering. It has been known that gas, which has higher mean free path (i.e., the average of distance that molecule can move freely between two collision), will have lower breakdown energy (i.e., the energy which make energy in electric field higher enough to cause the current theoretically infinite) because the energy that it received from electric field high enough to cause the ionization by collision. The mean free path of the helium atom is relatively high in comparison with other gaseous molecules, which means that it has higher energy to cause the ionization by collision than other molecules. So when the helium concentration was increased, the energy to cause the ionization was also increased, resulting in the methane molecular dissociation increased thus its conversion increased.

4.2.2 Effect of helium on products selectivities

Figures 4.10 to 4.15 show the effect of helium concentration on the products selectivities at different voltages, space times of 4 and 6 minutes and the CO_2:CH_4 ratio of 1:1, respectively. It was found from Figures 4.10 to 4.12 that when helium concentration was increased, the selectivity of C_2 products decrease while the selectivity of carbon monoxide and hydrogen was increased. However, the effect of helium on methanol selectivity was not significant.



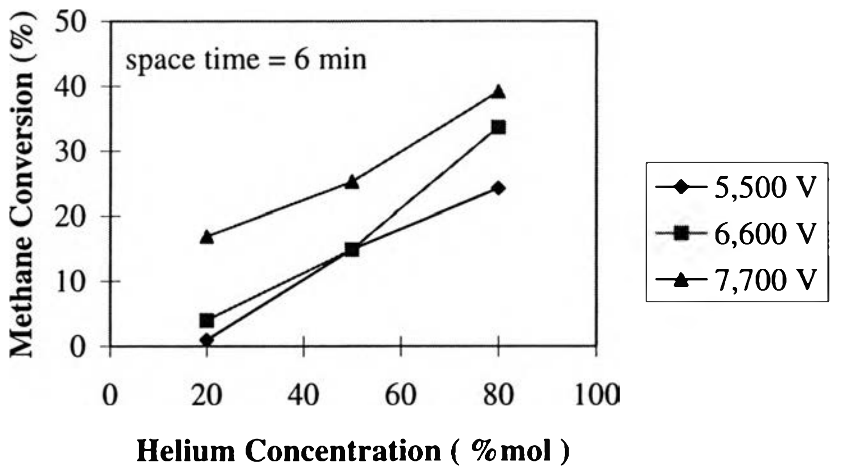


Figure 4.9 Effect of helium concentration on methane conversion at three different applied voltages, space times of 4 and 6 min and CO_2:CH_4 ratio of 1:1.

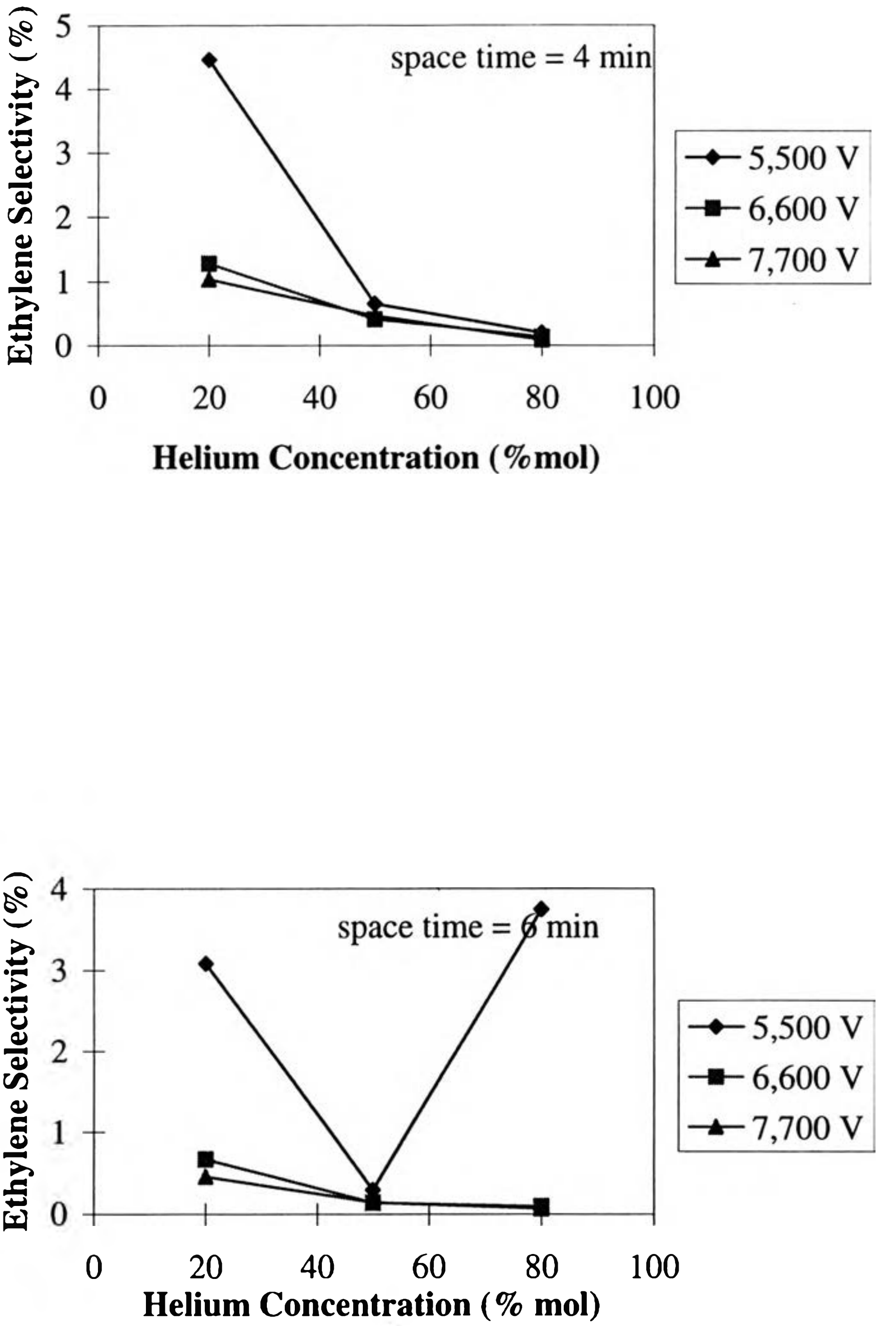
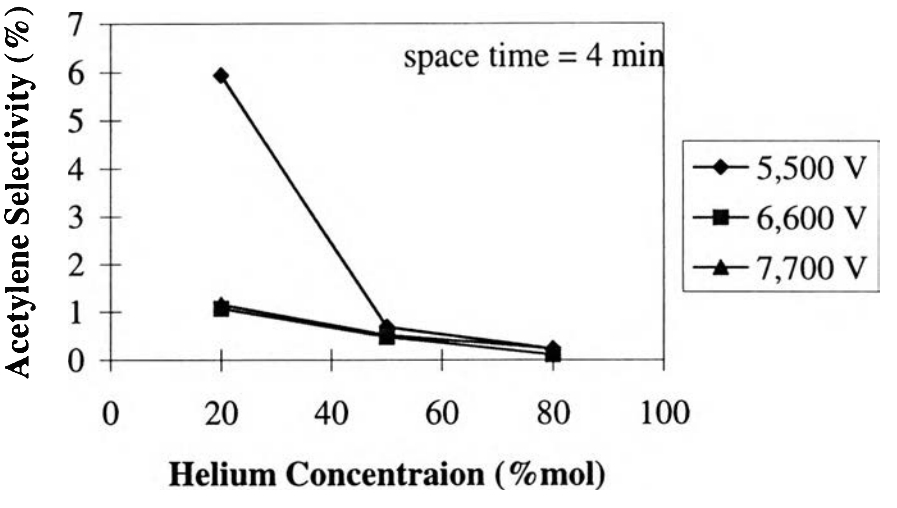


Figure 4.10 **Effect of helium concentration on ethylene selectivity at three different applied voltages space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.**



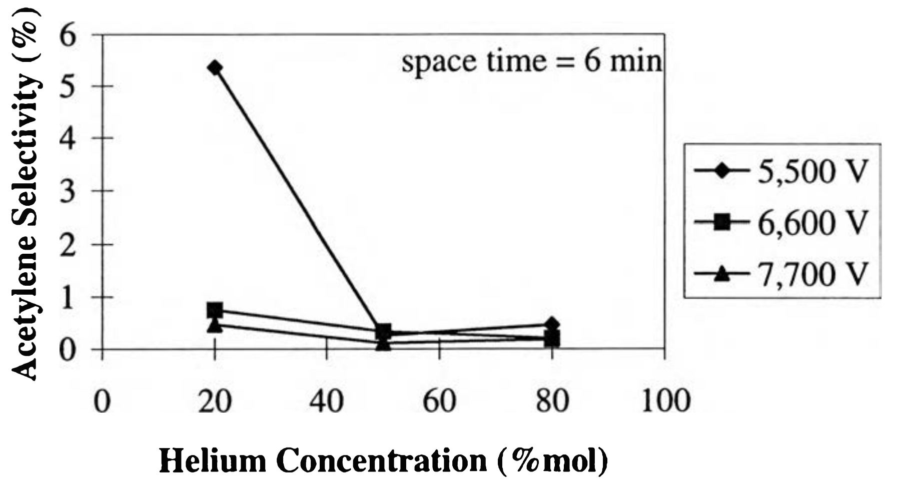
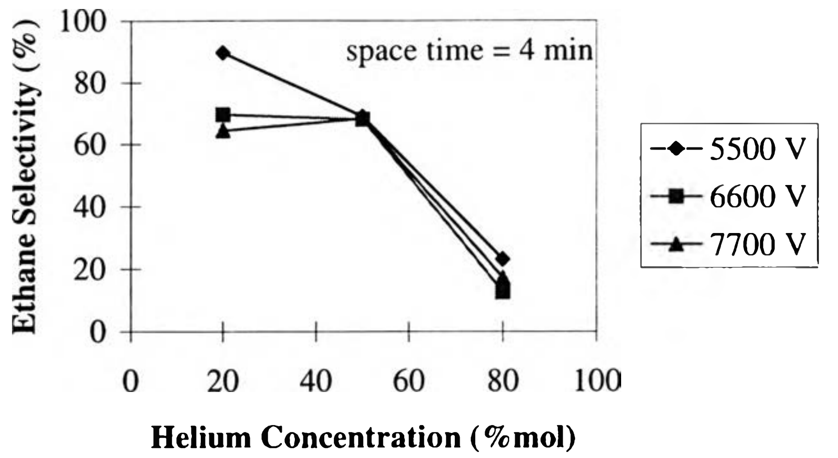


Figure 4.11 **Effect of helium concentration on acetylene selectivity at three different applied voltages space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.**



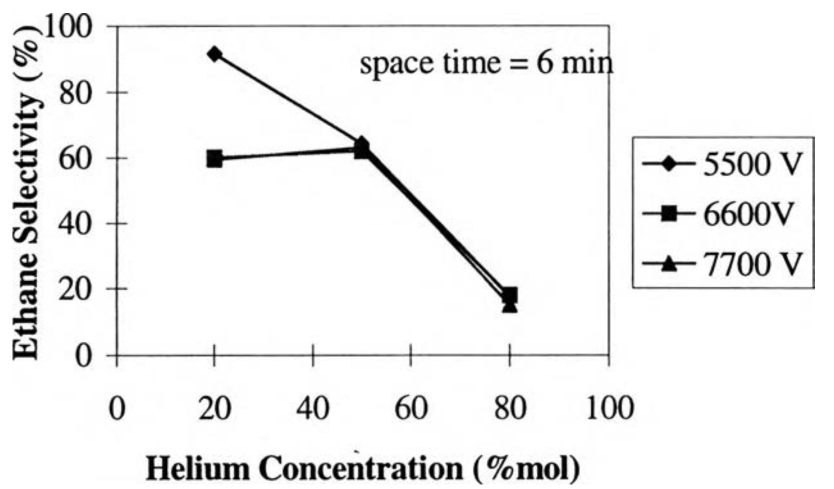
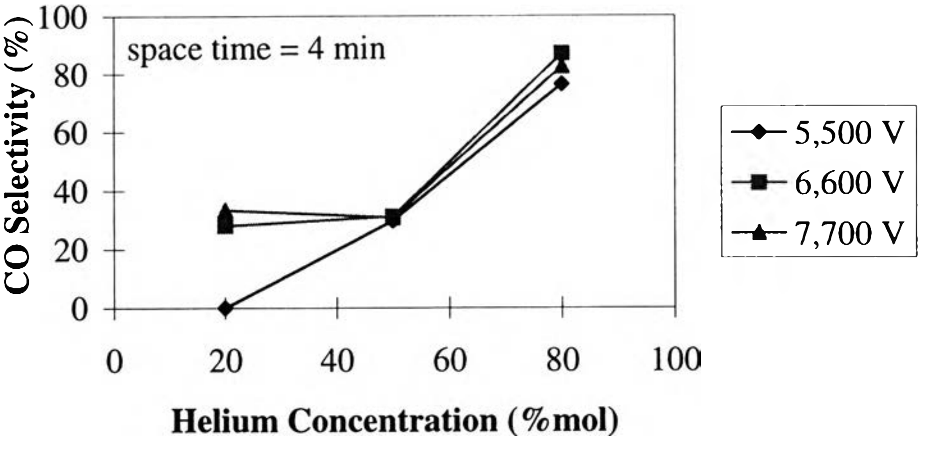


Figure 4.12 Effect of helium concentration on ethane selectivity at three different applied voltages space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.



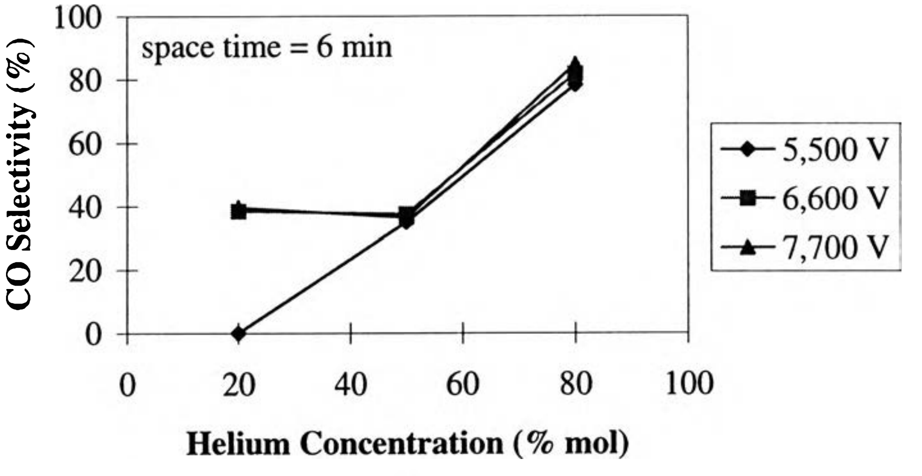
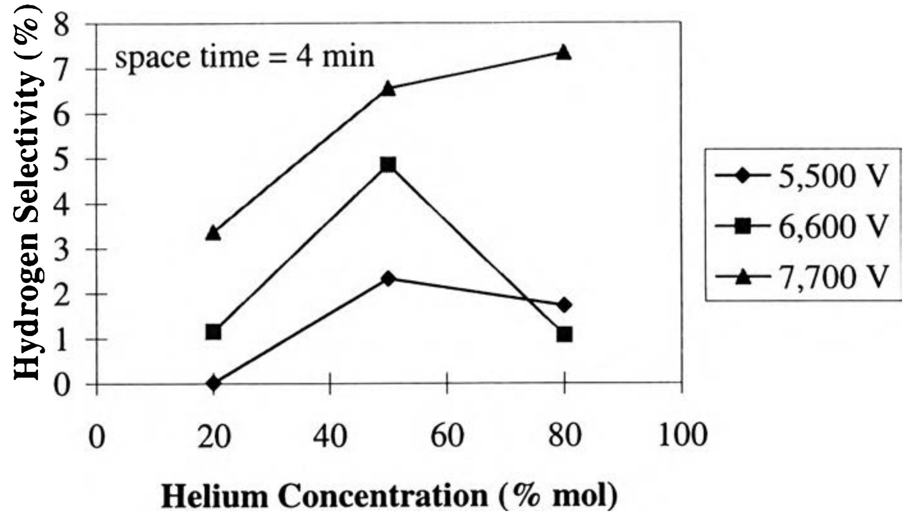


Figure 4.13 **Effect of helium concentration on carbon monoxide selectivity at three different applied voltages, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.**



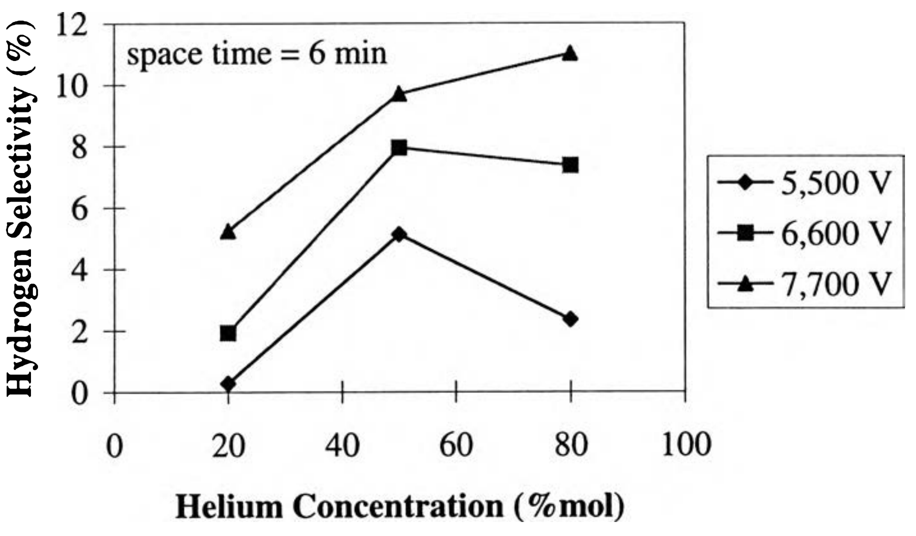


Figure 4.14 Effect of helium concentration on hydrogen selectivity at three different applied voltages, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.

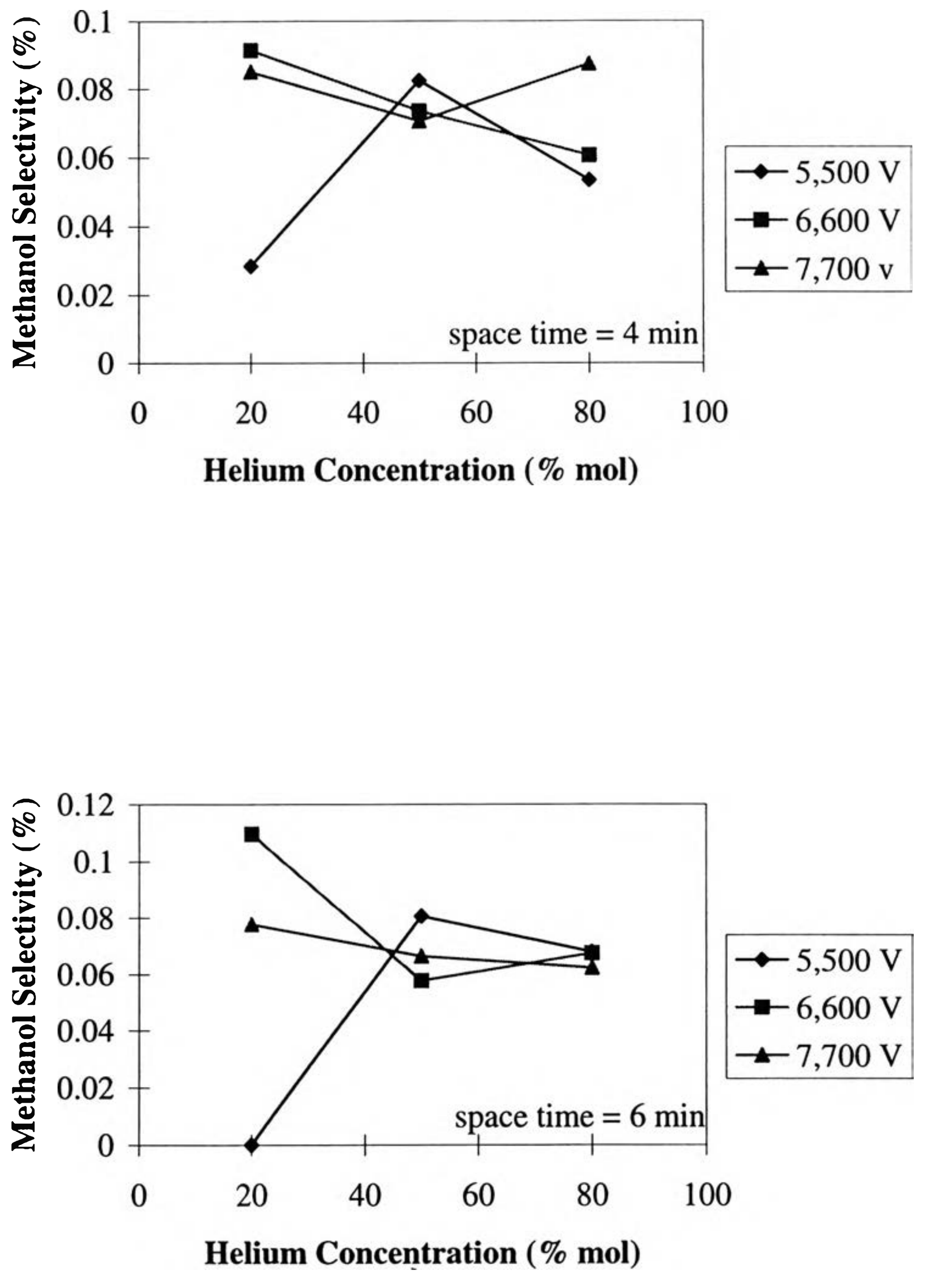


Figure 4.15 Effect of helium concentration on methanol selectivity at three different applied voltages, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.

From Figure 4.10, an increase in helium concentration led to an decrease in the selectivity of ethylene. This might lead to the hypothesis that the helium molecule has higher energy than other gaseous molecules to cause the ionization by collision due to its higher mean free path and this property could enhance reactions under electric discharge. At higher helium concentration there are more higher energetic species, resulted in higher success in breaking the bond inside the ethylene molecule thus the chance of its formation decrease. This reason could be apply in case of acetylene and ethane selectivities, that the selectivity also decrease as increase in helium concentration.

In contrast to the hydrogen and carbon monoxide selectivity in Figures 4.13-4.14, an increase in helium concentration led to an increase in the selectivity of hydrogen and carbon monoxide. These results could be explained in a similar manner as in the case of C_2 products selectivities that the higher energetic species resulted in higher activation and higher success in breaking the molecular bonding. When the helium concentration is increased, these species are, therefore, responsible for an increase in decomposition of carbon dioxide and hydrocarbons to form carbon monoxide and hydrogen respectively.

4.3 Effect of applied voltage

4.3.1 Effect of applied voltage on methane conversion

Figure 4.16 illustrates the effect of the applied voltage on methane conversion for three different helium concentrations and at 4 and 6 min space time. It could be seen that, at any given helium concentration (i.e., 20 %, 50 % and 80 % of helium in feed),the methane conversion was increased with

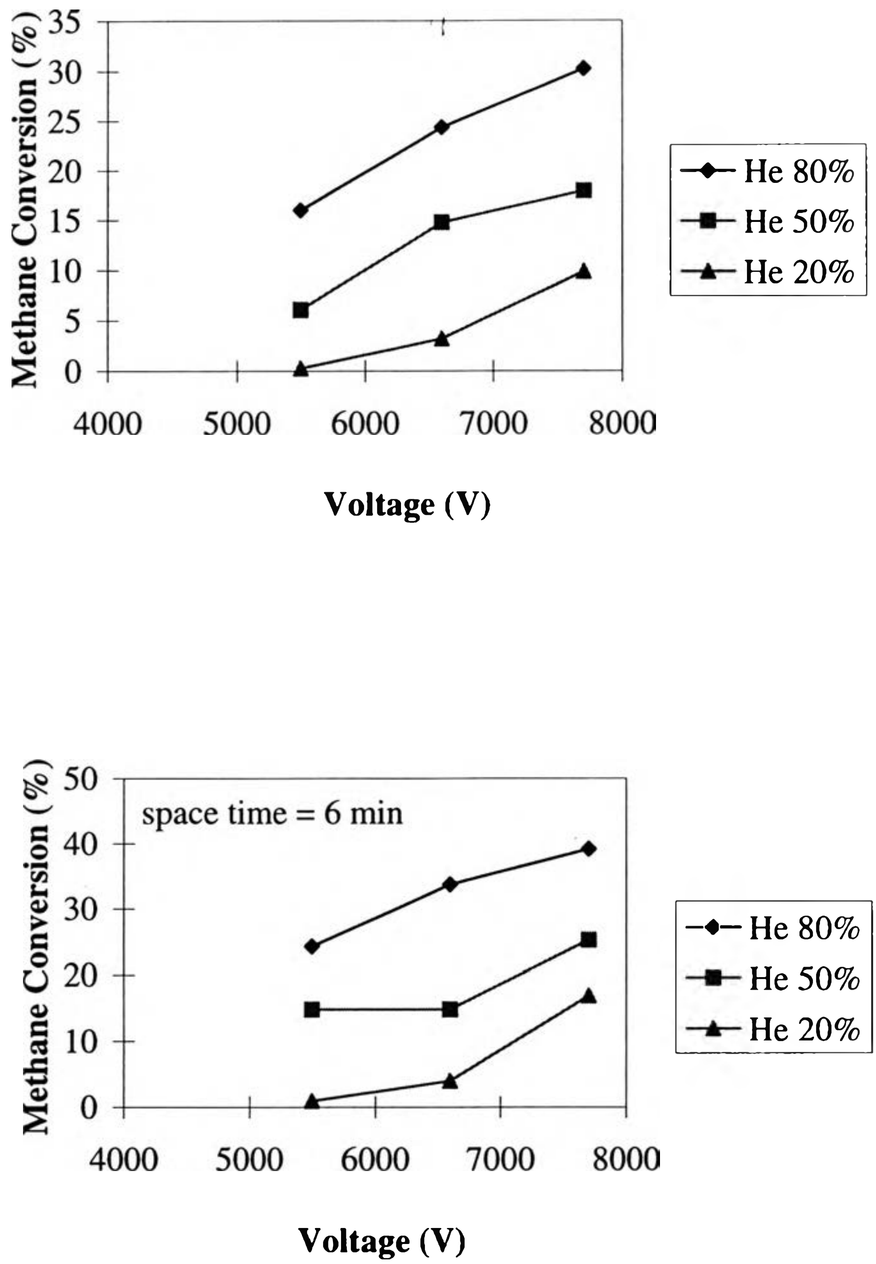


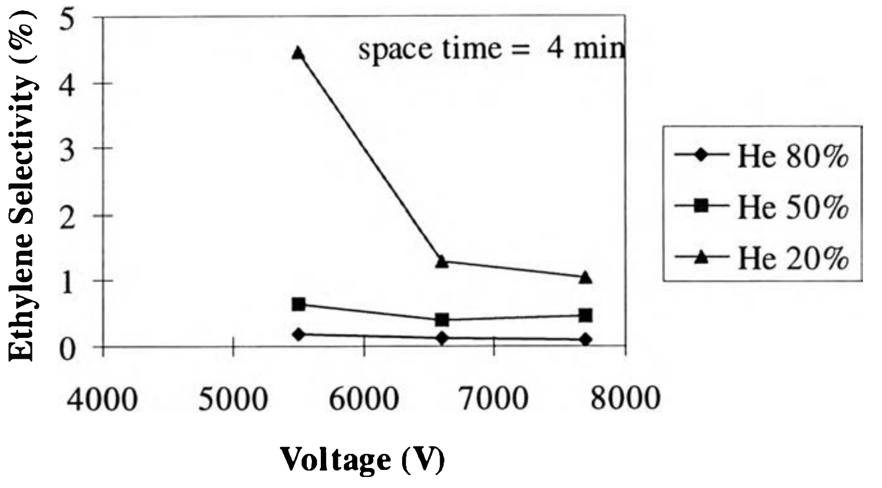
Figure 4.16 **Effect of applied voltage on methane conversion at three different helium concentration, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.**

increasing in voltage. When the applied voltage is increased, its internal electric field is also increased. The electrons in the field are more generated both from the field emission (i.e. the process of liberating an electron from solids) and collision ionization. These electrons and other gaseous molecules are more accelerated by electric field and possessed much higher energy , resulting in increasing the methane molecular energy to overcome its dissociation energy. It causes an increase in the degree of methane dissociation and thus the methane conversion increases.

4.3.2 Effect of applied voltage on products selectivities

The effect of applied voltage on products selectivities at space time of 4 minutes and 6 minutes and three different helium concentrations are shown in Figures 4.17 to 4.22 . As can be seen from Figure 4.17, for a given space time, an increase in voltage results in decreasing ethylene selectivity. Acetylene selectivity was also decreased as increasing voltage. As can be seen from Figure 4.19, it is not clear whether an increase in the applied voltage does not affects ethane selectivity. An increase in voltage led to decreases in the selectivities of ethylene and acetylene. This can be explained that at higher voltage the ethylene and acetylene start to decompose. At higher voltage, electrons are expected to have higher energy and become more active in breaking the bond in ethylene and acetylene.

Figures 4.20 and 4.21 show an opposite effect of voltage on hydrogen and carbon monoxide selectivities. An increase in voltage led to an increase in the selectivities of hydrogen and carbon monoxide. The decomposition of hydrocarbon and carbon dioxide are increased with increasing voltage due to higher electrons energy to break the chemical bonds. Hence, either hydrogen and carbon monoxide selectivities increased.



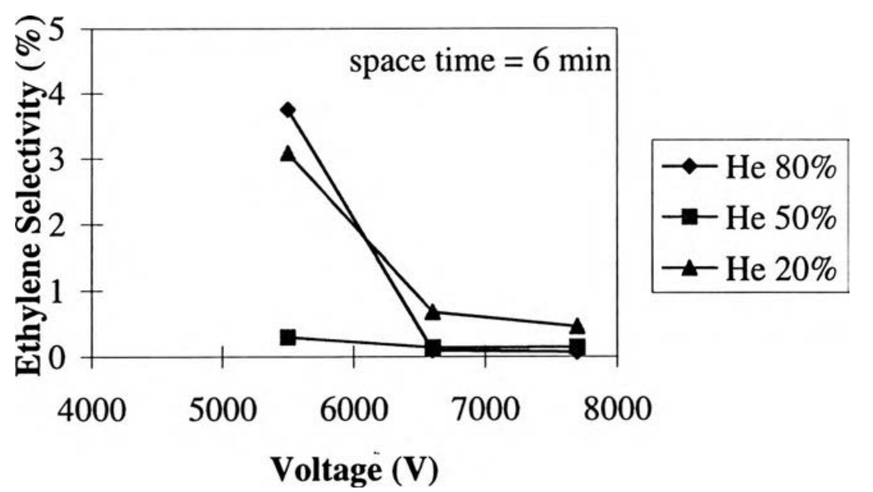


Figure 4.17 Effect of applied voltage on ethylene selectivity at three different helium concentration, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.

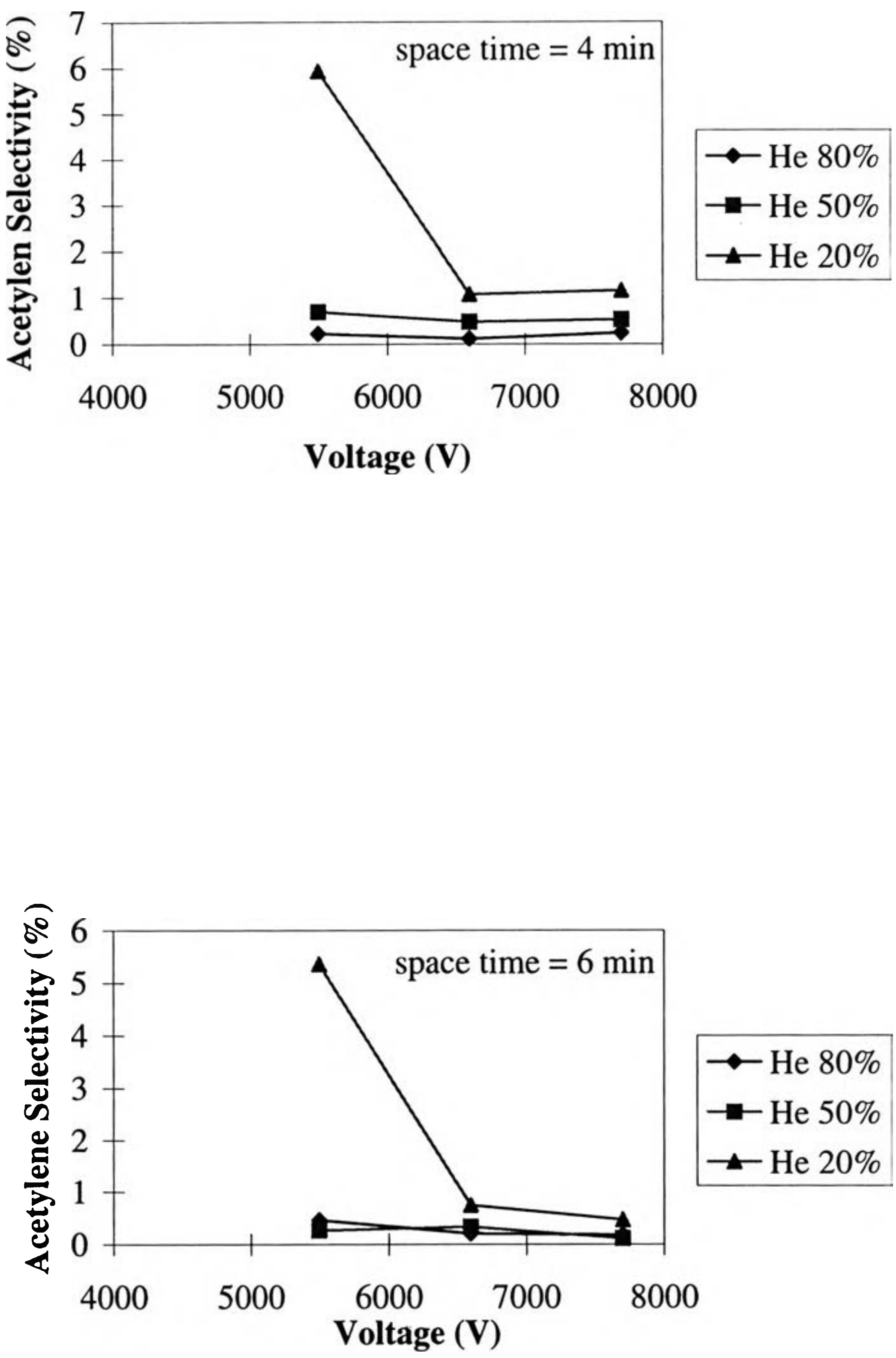
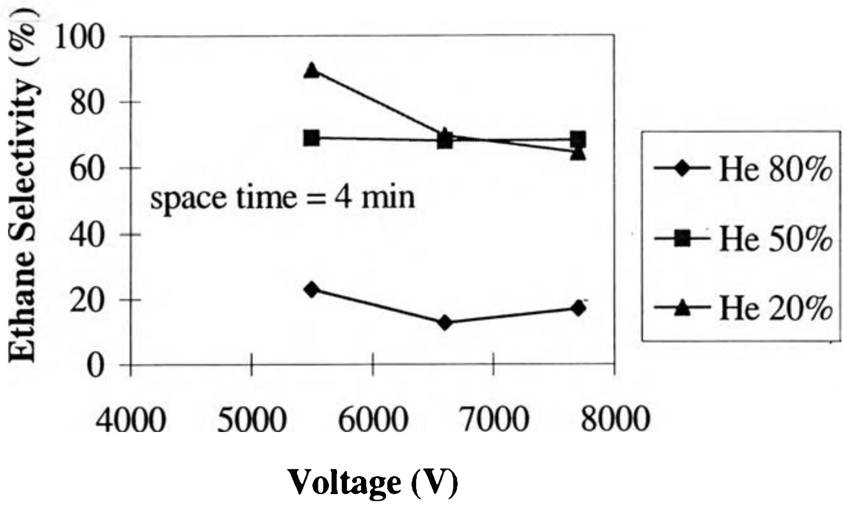


Figure 4.18 Effect of applied voltage on acetylene selectivity at three different helium concentration, space timees of 4 and 6 min and CO_2:CH_4 ratio of 1:1.



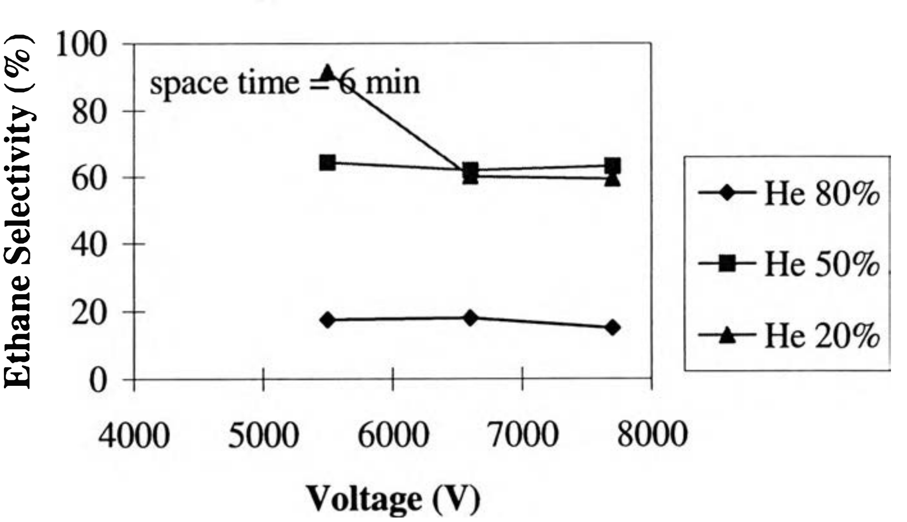
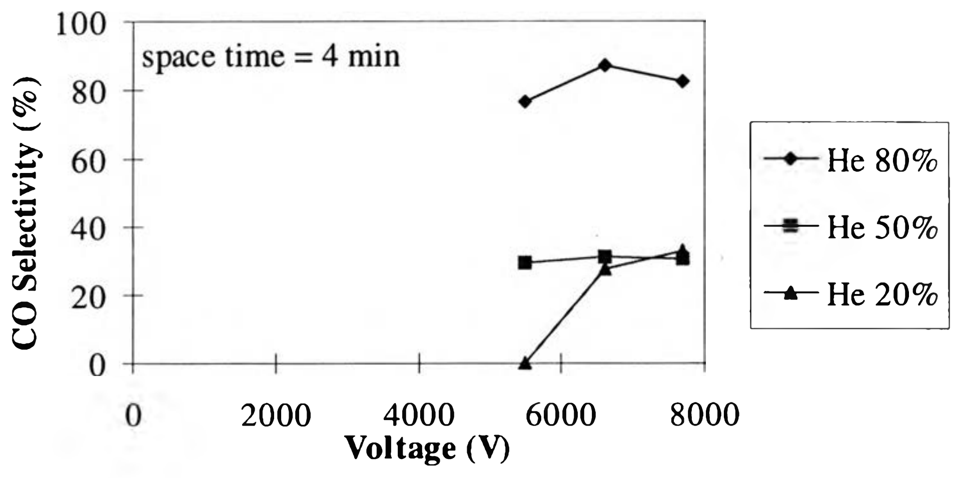


Figure 4.19 **Effect of applied voltage on ethane selectivity at three different helium concentration space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.**



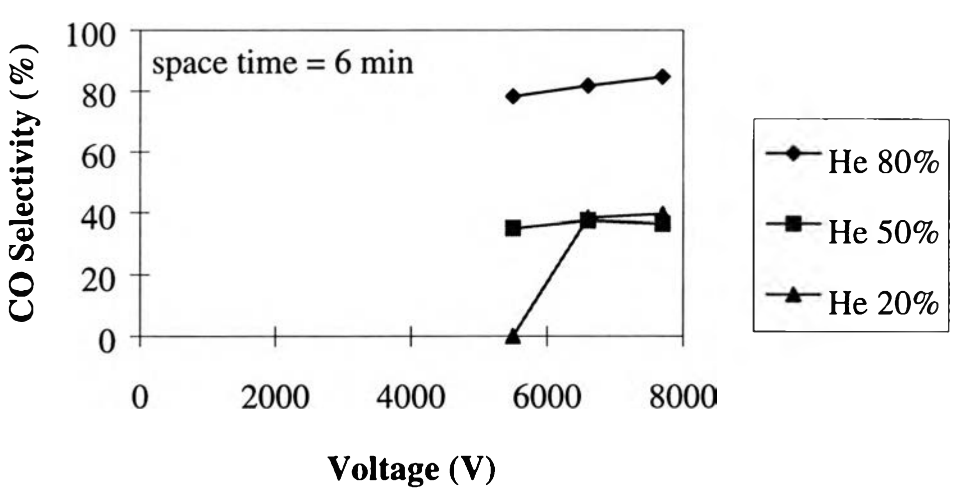
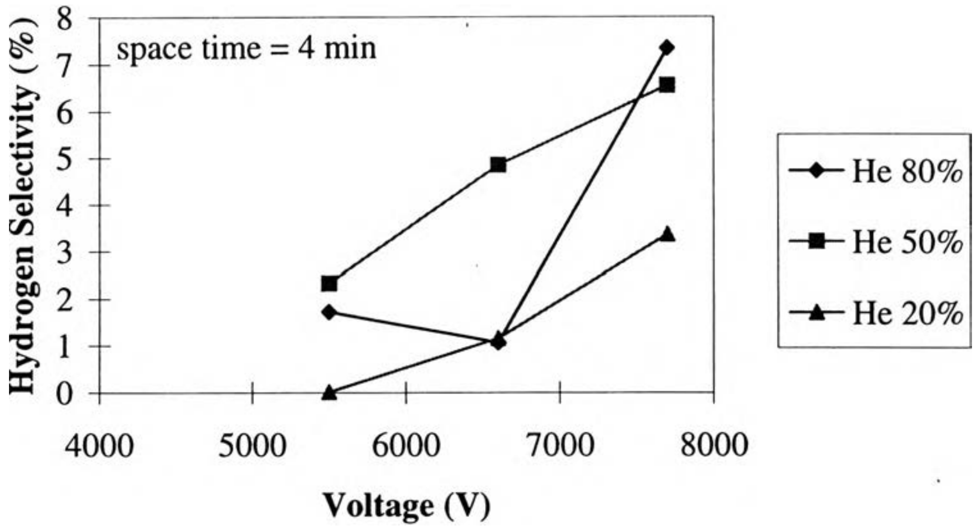


Figure 4.20 Effect of applied voltage on carbon monoxide selectivity at three different helium concentration, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.



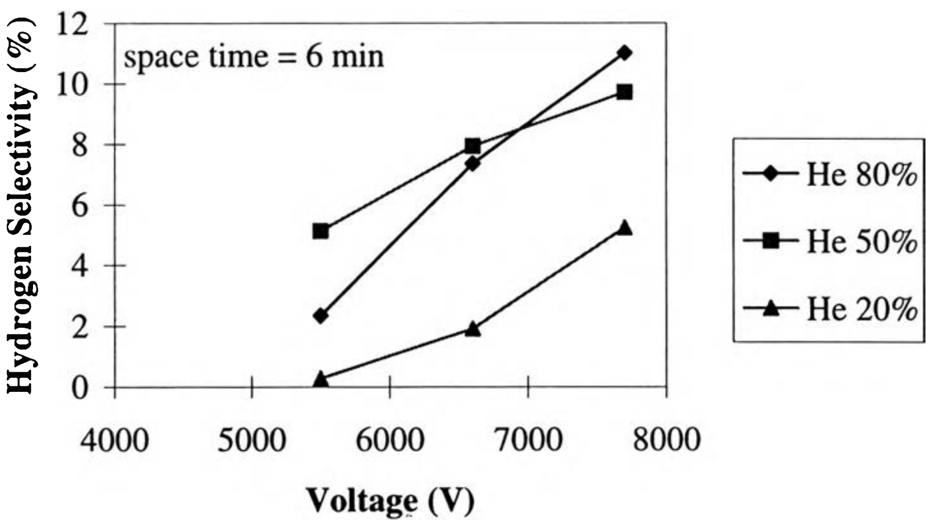
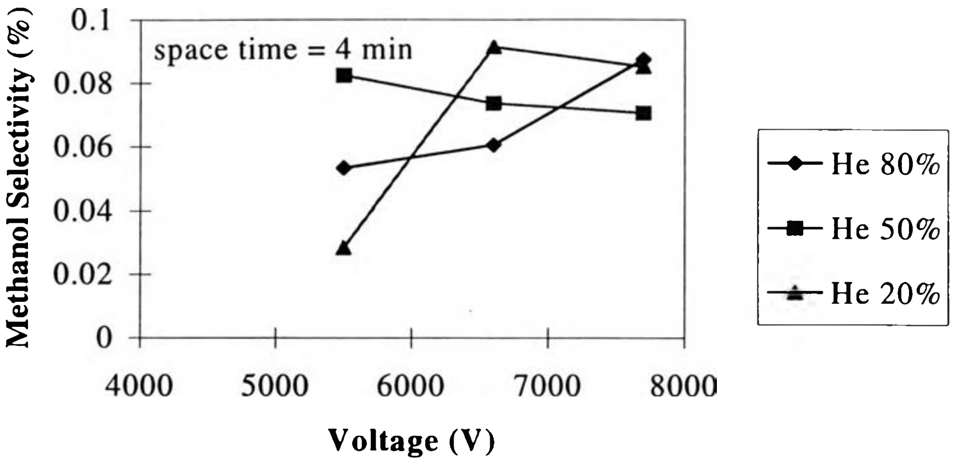


Figure 4.21 Effect of applied voltage on hydrogen selectivity at three different helium concentration, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.



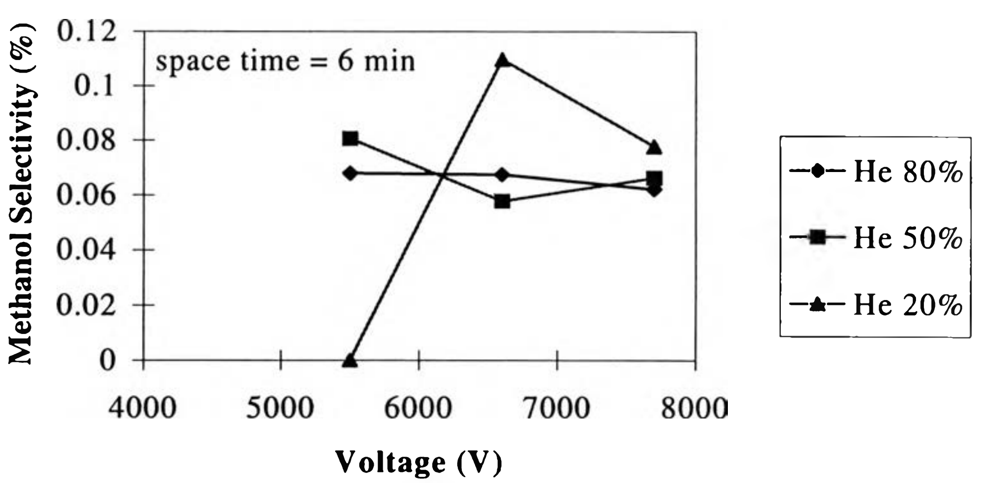


Figure 4.22 Effect of voltage on methanol selectivity at three different applied voltages, space time of 4 and 6 min and CO_2:CH_4 ratio of 1:1.

4.4 Effect of space time

4.4.1 Effect of space time on methane conversion

Figure 4.23 Shows the effect of space time on methane conversion. It is apparent that at helium concentration used (50 % helium in total feed) and different applied voltage, the methane conversion was increased with increasing space time.

When space time was increased, the time of each methane molecule to find and collide with any high enough energetic species also increase, this caused an increase in methane molecular energy and, thereby, increase in degree of methane dissociation and conversion.

4.4.2 Effect of space time on products selectivities

The effect of space time on products selectivity at helium concentration of 50% and three different voltage applied are shown in Figure 4.24 - 4.29. It seen that when the space time was increased the selectivity of C_2 products decreased while the selectivity of carbon monoxide and hydrogen increased.

Figures 4.24-4.26 exhibited that an increase in space time led to an decrease in the selectivity of C_2 products . This might explain that at higher space time the C_2 products molecules start to decompose. Since at higher space time, there were more chance of molecules to find and collide with any sufficiently high energetic species, causing an increase in energy of C_2 product molecules. Thus, corresponding to the decrease in C_2 selectivity. On the other hand, Figures 4.27-4.28 show that the selectivity of carbon monoxide and hydrogen decrease with the increasing of space time. As a result from the dissociated of carbon dioxide and methane at sufficient high energy .

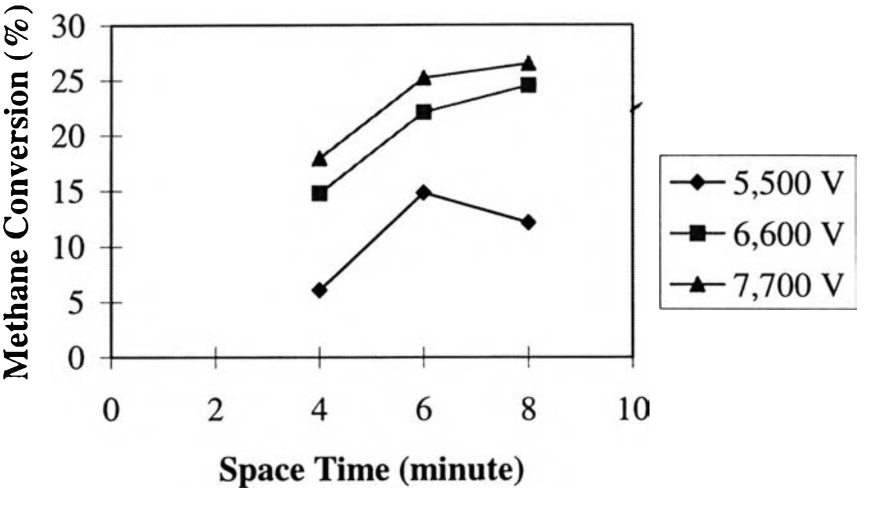


Figure 4.23 Effect of space time on methane conversion at three different applied voltages, 50% helium concentration and CO_2:CH_4 ratio of 1:1.

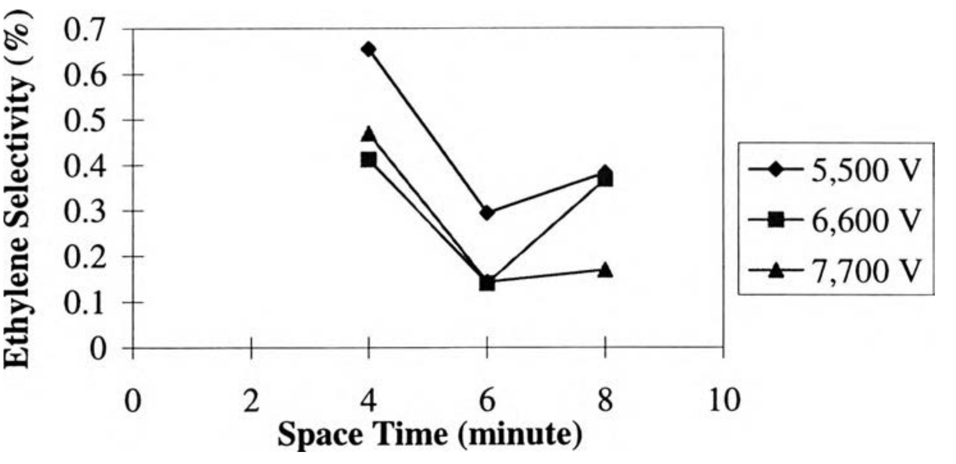


Figure 4.24 Effect of space time on ethylene selectivity at three different applied voltages, 50% helium concentration and CO_2:CH_4 ratio of 1:1.

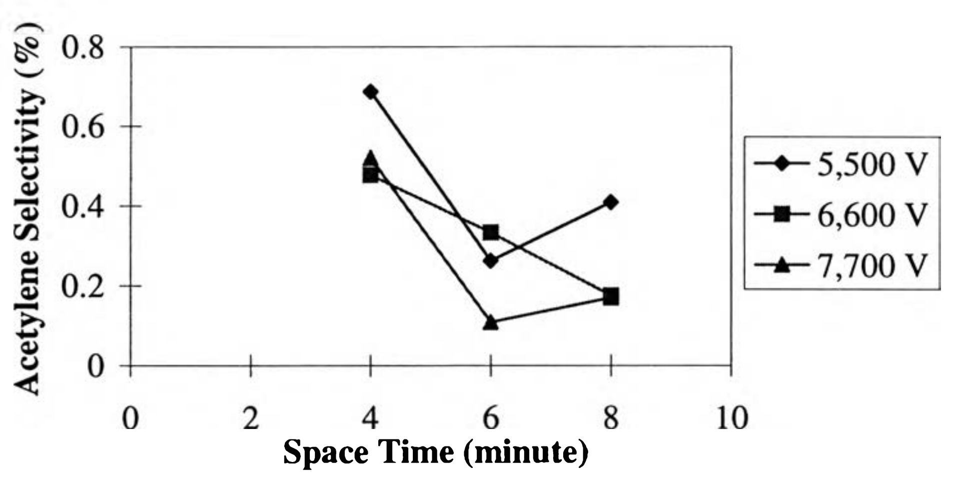


Figure 4.25 Effect of space time on acetylene selectivity at three different applied voltages, 50% helium concentration and CO_2:CH_4 ratio of 1:1.

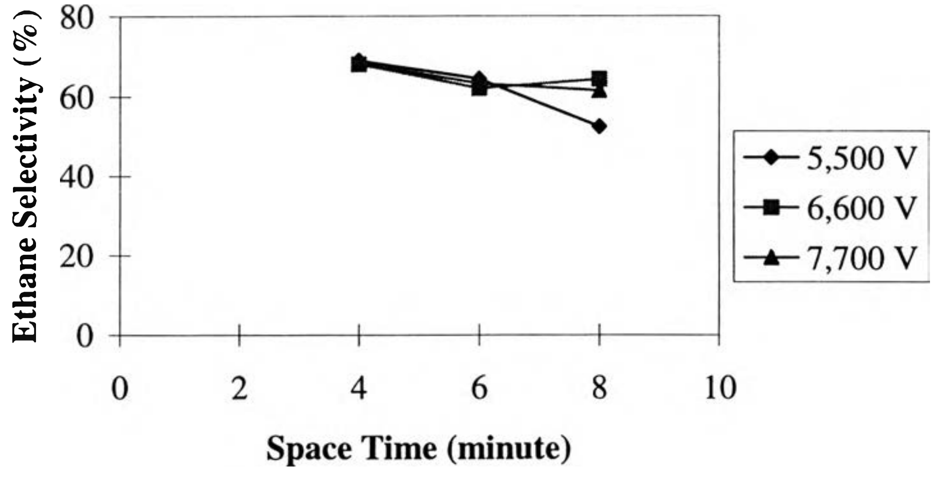


Figure 4.26 **Effect of space time on ethane selectivity at three different applied voltages, 50% helium concentration and CO_2:CH_4 ratio of 1:1.**

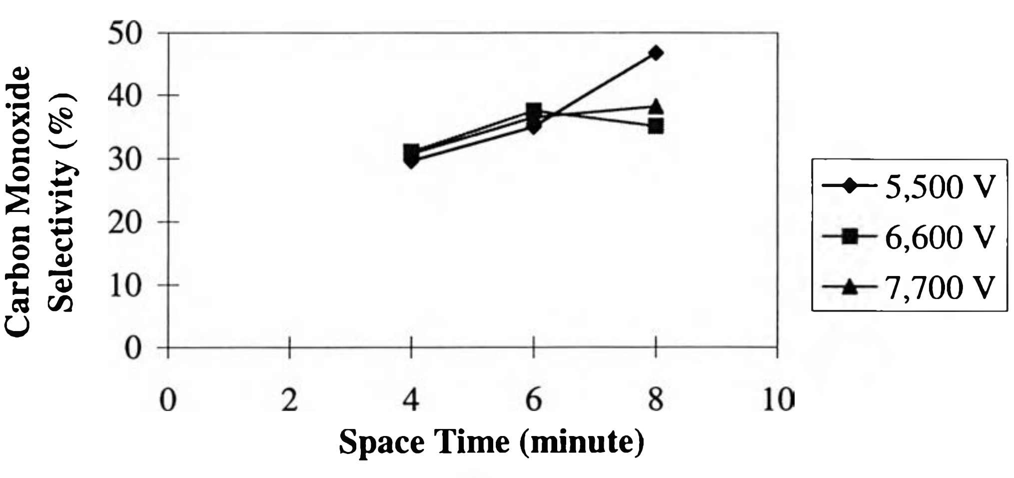


Figure 4.27 **Effect of space time on carbon monoxide selectivity at three different applied voltages, 50% helium concentration and CO_2:CH_4 ratio of 1:1.**

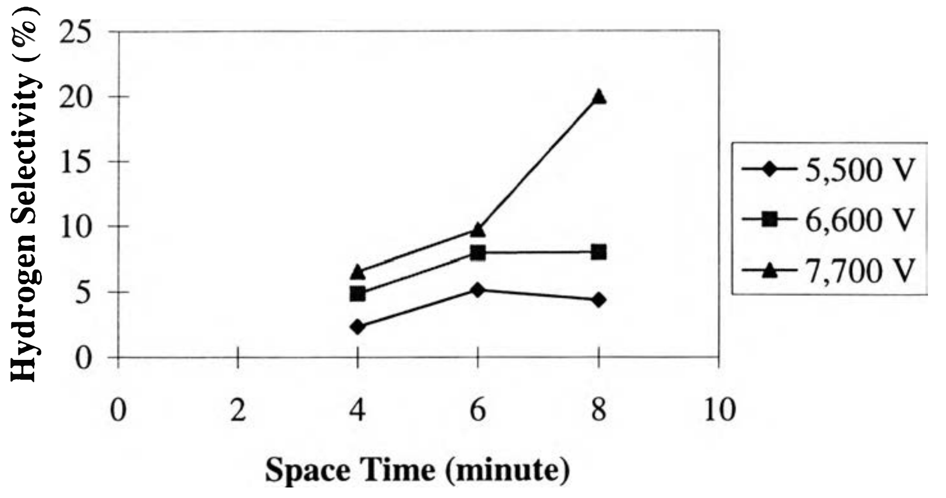


Figure 4.28 Effect of space time on hydrogen selectivity at three different applied voltages, 50% helium concentration and CO_2:CH_4 ratio of 1:1.

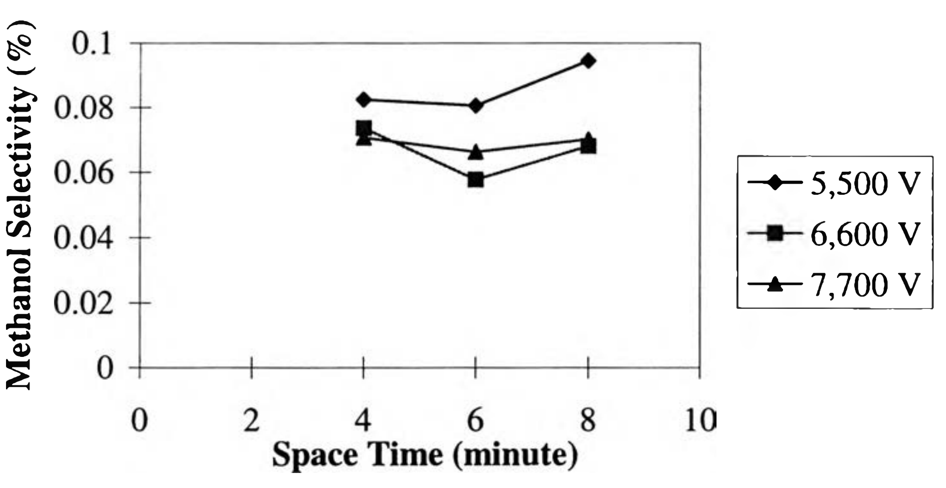


Figure 4.29 Effect of space time on methanol selectivity at three different applied voltages, 50% helium concentration and CO_2:CH_4 ratio of 1:1.