

## CHAPTER IV

### RESULTS AND DISCUSSION

The experimental data of the present study were summarized in Appendix B. And those results were plotted and described in this chapter in connection with some evidences and information derived from previously published literature. The attempt to describe the chemical reaction pathways leading to the formation of the various kinds of products were also made so as to be used as the guidelines in any further studies.

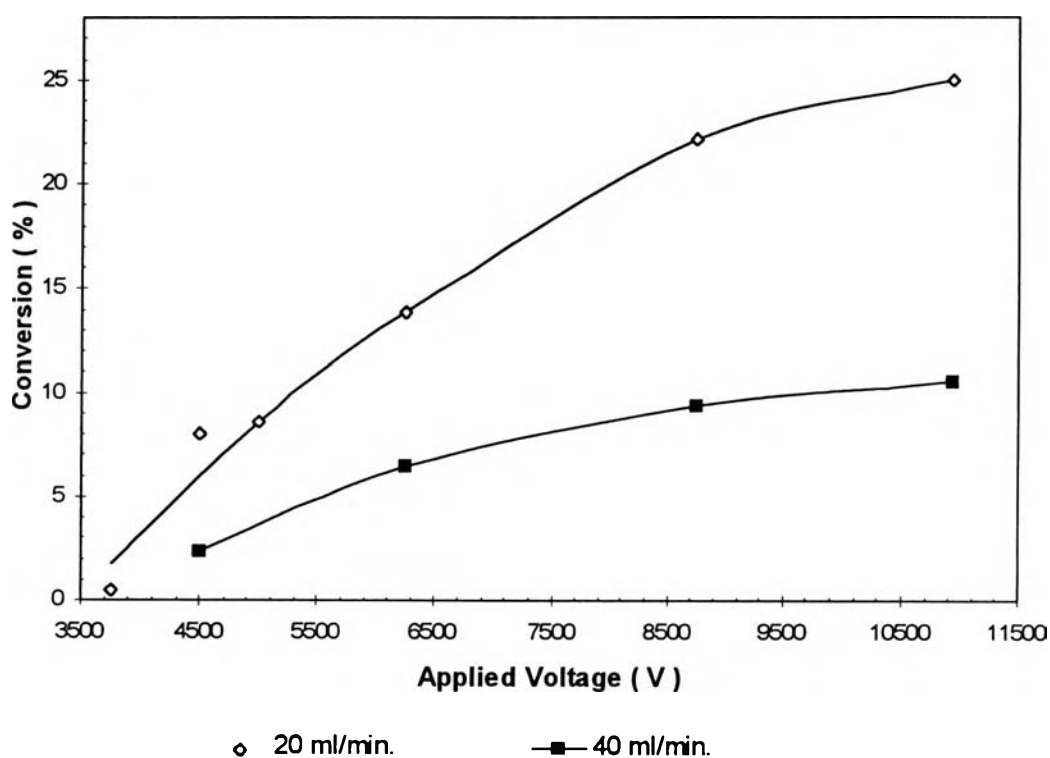
#### **4.1 Effect of applied voltage in pure methane system**

##### **4.1.1 Effect of applied voltage on methane conversion**

Figure 4.1 illustrates the effect of the applied voltage on methane conversion for two different total flow rates. It can be considered that, at either constant total flow rate used (i.e., 20 or 40 ml/min), the methane conversion was increased with increasing in voltage.

When the external voltage, and consequently its internal electric field, applied to the discharge gap was increased, the electrons that were produced inside that gap would be more accelerated and possessed much higher energy. The increase in this energy of electrons, on an average basis, resulted in higher success in breaking the bond between C and H of methane molecules and thus caused the increase in both the degree of methane dissociation and conversion. Since the energy of all of the electrons produced in the field were not equal but rather distributed corresponding to the electron energy distribution function (EEDF) described by the Boltzmann equation, then only the collisions

between those electrons that had high enough energy with the methane molecules would result in the molecular dissociation to form the active species. As can be observed from Figure 4.1, there is a tendency that the methane conversion would reach a maximum value at a very high voltage. Beyond that point, the rate of methane decomposition was equal to the rate of methane formation.



**Figure 4.1** Effect of applied voltage on methane conversion at two different total flow rates.

#### **4.1.2 Effect of applied voltage on product selectivity**

The distribution of the products for the above reactions at two different flow rates are plotted as a function of the applied voltage in Figures 4.2 and 4.3. In both cases, an increase in the voltage led to an increase in the selectivities of ethane, propane and butane at initial. Those product selectivities, however, tended to be leveled off at higher voltages.

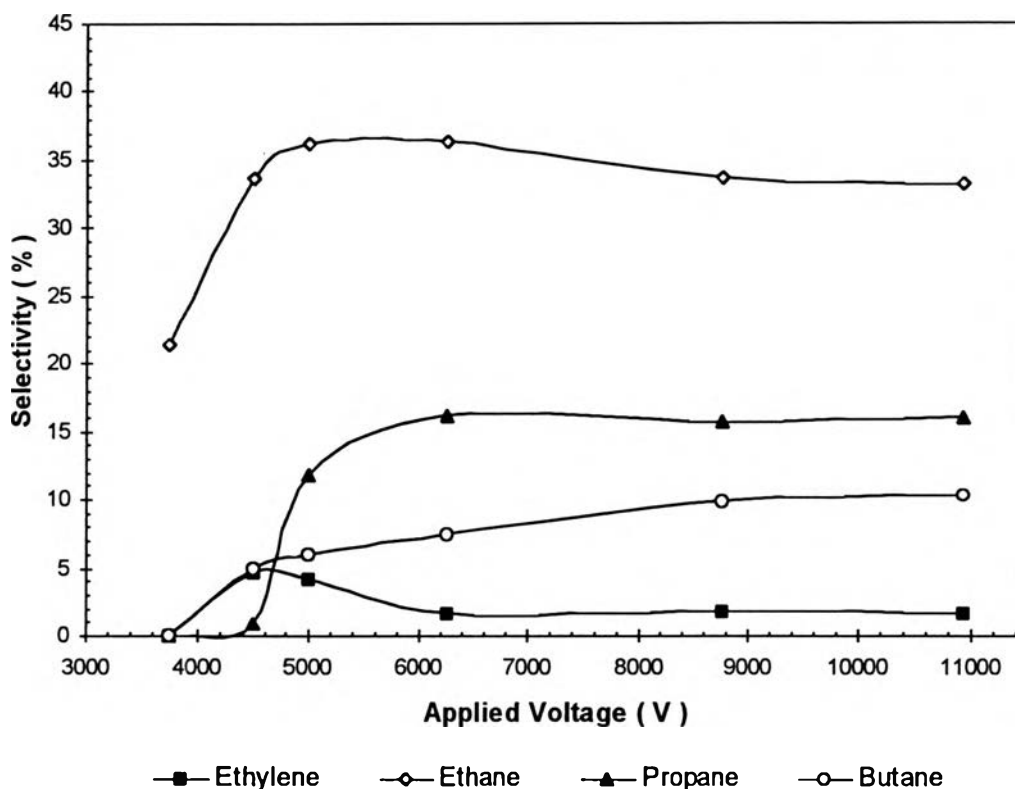
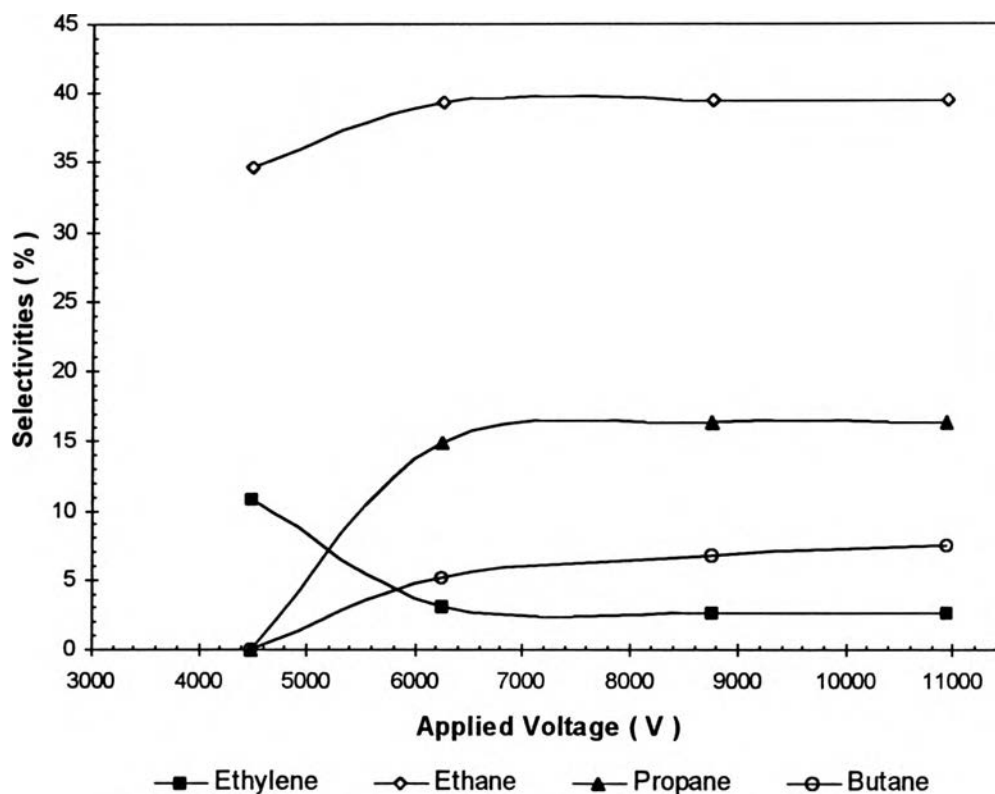


Figure 4.2 Distribution of products as a function of applied voltage at a total flow rate of 20 ml/min.

From Figure 4.2, it is noticeable that when the applied voltage was increased, the ethylene selectivity was initially increased and then decreased. This might be because at higher voltage than the threshold values ( $> 4500$  V), the ethylene product starts to be decomposed into higher hydrocarbons. In this case, at higher voltage the electrons produced were expected to have higher energy and became more active in breaking the double bonds between the carbon atoms inside the ethylene molecule and then the chance of its formation decreased.



**Figure 4.3** Distribution of products as a function of applied voltage at a total flow rate of 40 ml/min.

It is very interesting to point out that, when the voltage was increased further the selectivities of all products tended to be increased at a slower rate and eventually leveled off. Since the yield is the product between the conversion and selectivity, then, even though the product selectivities were nearly unchanged beyond an extreme voltage but the methane conversion was still raised after that point. This, consequently, resulted in an increase in the yield of each product but at a slower rate.

## **4.2 Effect of residence time in pure methane system**

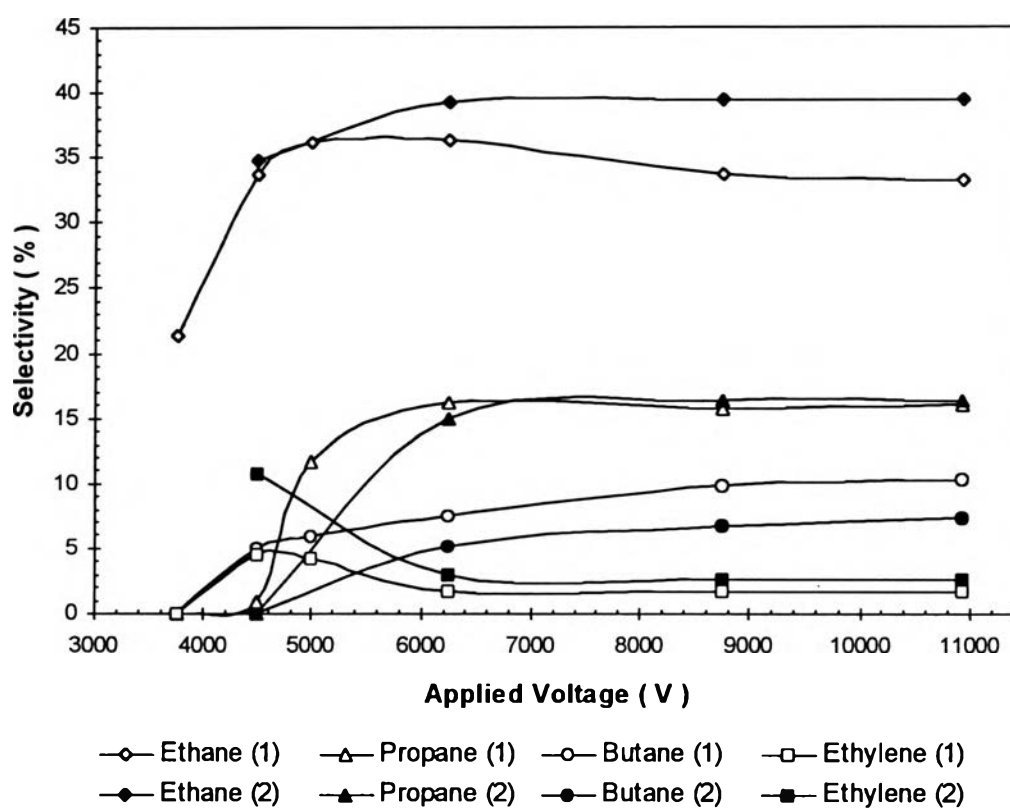
### **4.2.1 Effect of residence time on methane conversion**

From Figure 4.1, it is apparent that, for any given voltage, the percentage of methane conversion dropped drastically when the flow rate was increased. Since an increase in the total flow rate resulted in the decrease in the reaction residence time, then this plot also implies that the degree of methane conversion decreased rapidly as the exposure time of the methane molecules in the electric discharges environment was decreased. When the residence time of the reaction was decreased by increasing the flow rate, the probability that each methane molecule would have enough time to find any of those sufficiently high energetic electrons also decreased, this caused a decrease in degree of the methane dissociation and thereby its conversion. Since the effective volume of the reactor was  $231 \text{ cm}^3$ , then the residence time according to the total flow rate of 20 ml/min and 40 ml/min would be about 11.55 and 5.76 min, respectively. These very long residence times indicate that the density of those high energetic electrons produced from the reactor might not be high enough to yield considerable methane conversion at very high flow rates. Consequently, this implies that an improvement of this kind of DBD reactor should be taken into consideration for any future work.

### **4.2.2 Effect of residence time on product selectivity**

Figure 4.4 shows the differences between the product selectivities of each component at two different residence times. It should be noted that the limit value for the ethane and ethylene selectivity was lower in the case of longer residence time (i.e., lower flow rate), while the butane selectivity limit was higher when the residence time was increased. However, the propane

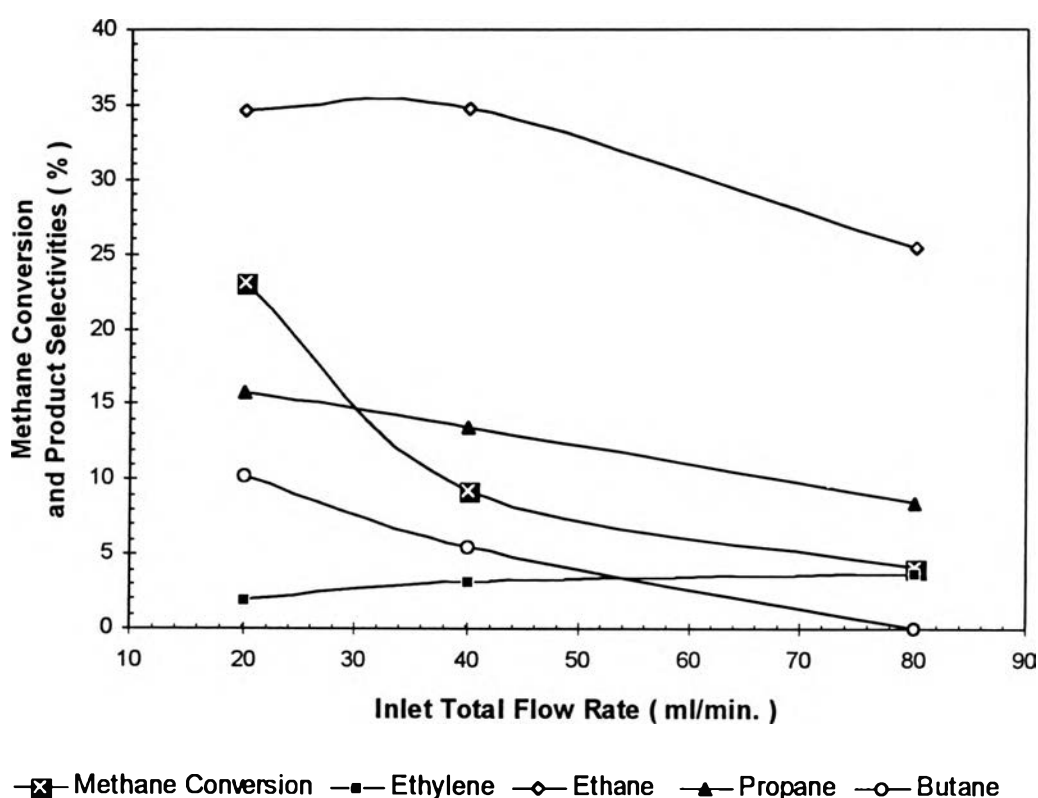
selectivity was nearly unaffected by the change in the residence time. This might lead to the hypothesis that the coupling between two  $C_2$ -hydrocarbon molecules to form  $C_4$  hydrocarbon product could be happened and its extent was also increased when the gas stream was longer exposed to the discharge environment.



**Figure 4.4** Distribution of products as a function of applied voltage at the residence times of 11.55 min (1) and 5.76 min (2), respectively.

Figure 4.5 illustrates the relationship between the methane conversion and the product selectivities for a given applied voltage at various total flow rates. As can also be observed in Figure 4.1, the methane conversion dropped dramatically when the reaction residence time was decreased. It is also found that the selectivities of all paraffin products including ethane, propane and butane decreased significantly while a slightly increase in ethylene selectivity

could be obtained as the residence time was decreased. The behaviors of the change in the propane and butane selectivities on the varied flow rate seemed to be different from those results in case of Figure 4.3. In addition, there was a somewhat large difference on the methane conversion (about 10%) between the results obtained under the same experimental conditions of 6,250 V and 20 ml/min. (See Figures 4.1 and 4.5)



**Figure 4.5** Influence of total gaseous flow rate on methane conversion and product selectivities at 6,250 V.

At this point, it was important to note that in the case of Figure 4.1, each new voltage was stepped up from the lower adjacent value after its steady state conditions had been attained. In Contrast, the methane conversion at 6,250 V derived in Figure 4.4 was resulted from an immediate increase in the voltage from the zero value. And, in Section 4.3, the effect of different voltage rising mode on the methane conversion will be further investigated. Nevertheless, it

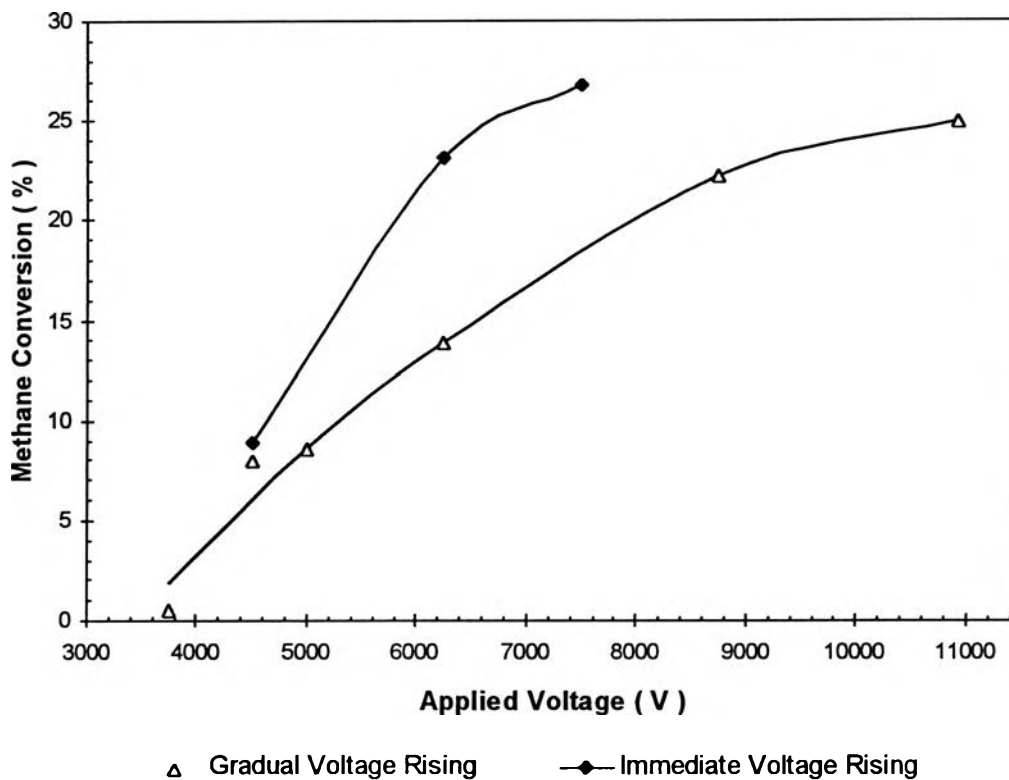
is worth to note also that the behavior of the change in the ethylene selectivity with the varied flow rate was similar to the results in Figure 4.4. This might confirmatively suggest that the ethylene molecules were destroyed at the higher flow rate where the chance of their findings with those high energetic electrons (thereby the likelihood of the breaking in C=C bond) increased.

### **4.3 Influence of different voltage rising approach**

In order to gain more information about the effect of these different voltage rising approaches, another set of experiments was conducted at the constant total flow rate of 20 ml/min by which the experimental voltage was stepped up immediately from the zero point to the desired values. In this case, after the steady state conditions had been attained at any specific voltage and the composition of the outlet stream was analyzed, the power supply was then stopped and the entire reactor system was purged with pure methane again until no other gases were left in the reactor. This step took about 2 to 6 hours to complete before a new voltage was applied at the same inlet flow rate of methane. The results from this set of experiments are shown in Figure 4.6 in comparison with the results obtained from Figure 4.1.

As can be noticed from Figure 4.6, the methane conversion is significantly different between the two distinct approaches of voltage rising technique. In the case of immediate voltage rising approach, the methane conversion could reach the magnitude as approximately high as about 30% at 7500 V whereas this would require the voltage beyond 10.5 kV in the other approach.

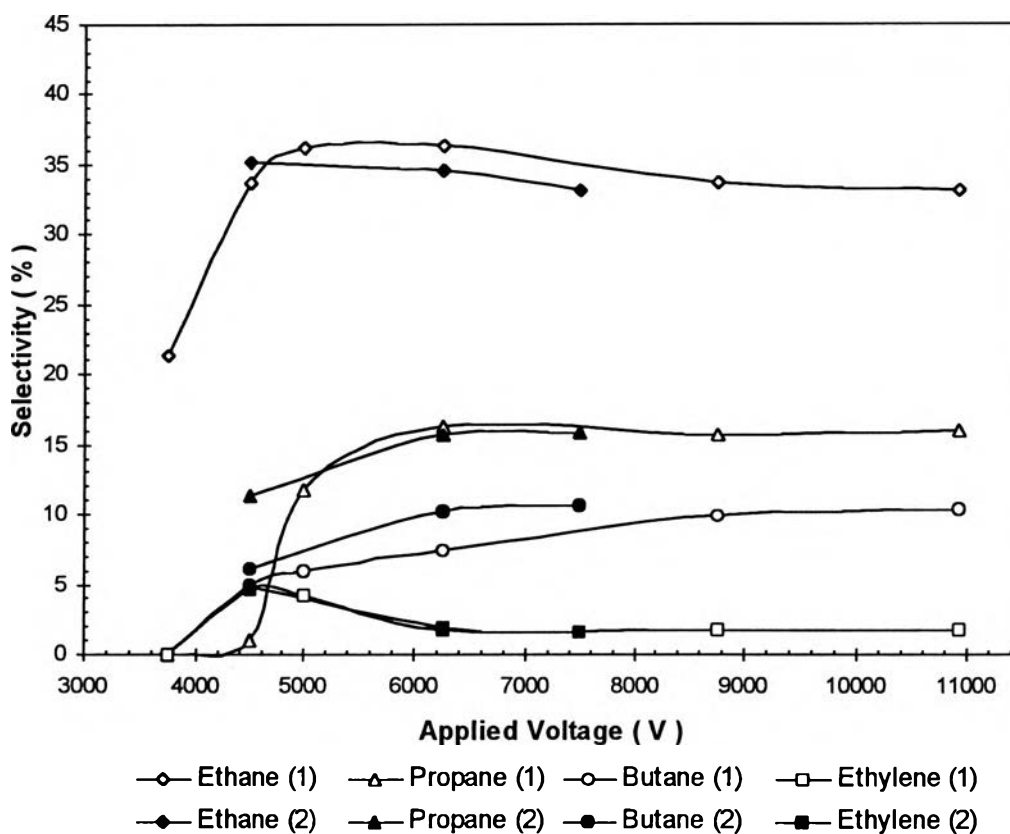




**Figure 4.6** Influence of different methods of applying voltage on methane conversion at 20 ml/min.

No informative discussion on this weird phenomena was given by any previous works. Nevertheless, it was expected that there might be something changed on the surface of either the dielectric or the metal electrode or both that could subsequently lead to the change in the behaviors of the charged particles generations and destruction within the discharge gaps. Hereafter, it is strongly recommended to investigate this point further in order to gain some more qualitative understanding.

Figure 4.7 compares the differences in the product selectivities between these two distinct approaches. It is found, however, that there were no obvious differences in each pair of these product selectivities.



**Figure 4.7** Influence of different methods of applying voltage on product selectivities at 20 ml/min.

(1) - Gradual Voltage Rising

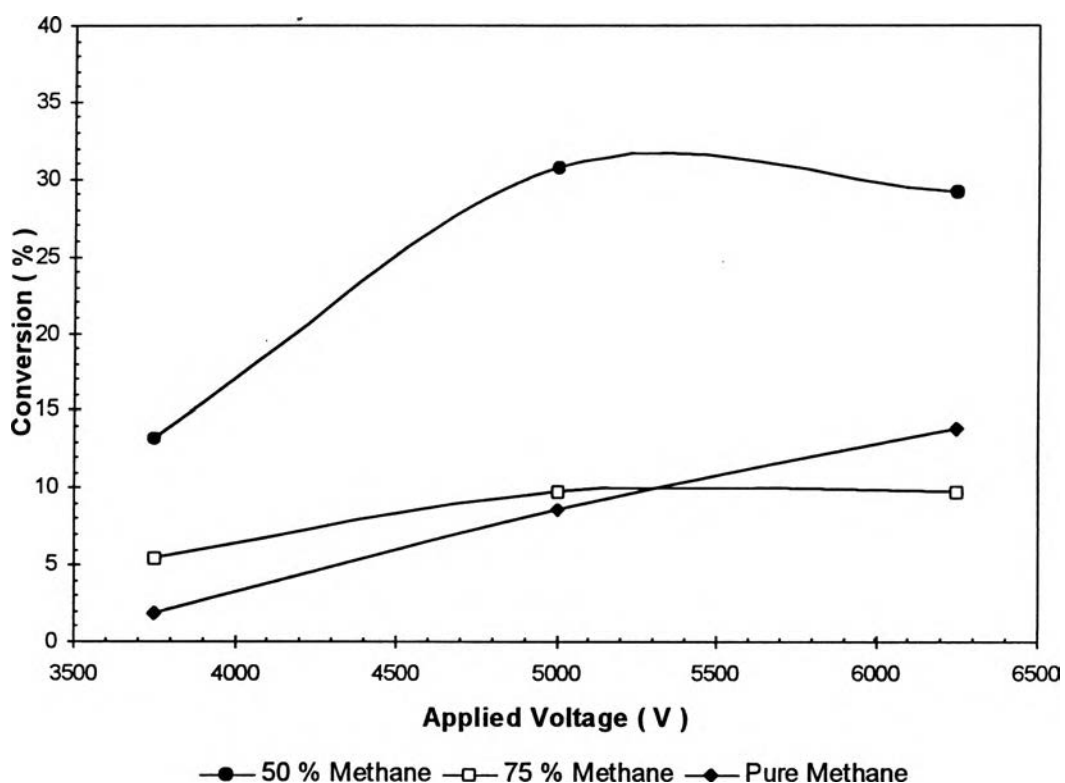
(2) - Immediate Voltage Rising

#### **4.4 Effect of helium on methane reaction**

##### **4.4.1 Effect of helium on methane conversion**

Figure 4.8 illustrates the influence of the helium molecule on the methane reaction at different voltages. All of these experimental parts were conducted at the total flow rate of 20 ml/min using gradual voltage rising technique. It was found that, in the case 50% methane ( $\text{CH}_4/\text{He} = 1:1$ ) present in the feed mixture, the methane conversion was greatly enhanced. However,

for the feed mixture of 25 % He and 75 % CH<sub>4</sub>, the methane conversion was slightly greater at the applied voltage below 5300 V and lower at the applied voltage above 5300 V in comparison with the case of pure methane inlet system. If the helium molecule really exhibits no interactive effects with the discharges environment, it should serve only as the function of the diluent for blocking any couplings between two active species; such as two CH<sub>3</sub><sup>•</sup> radicals, to form higher hydrocarbon products rather than to enhance in the methane conversion. This, therefore, leads to a conclusion that the helium molecules may have some interactions with methane under the electric discharges environment and does not behave only as the inert molecules or the diluents as that generally found in any thermal reactions.



**Figure 4.8** Effect of feeding methane-to-helium ratio on methane conversion at different voltages.

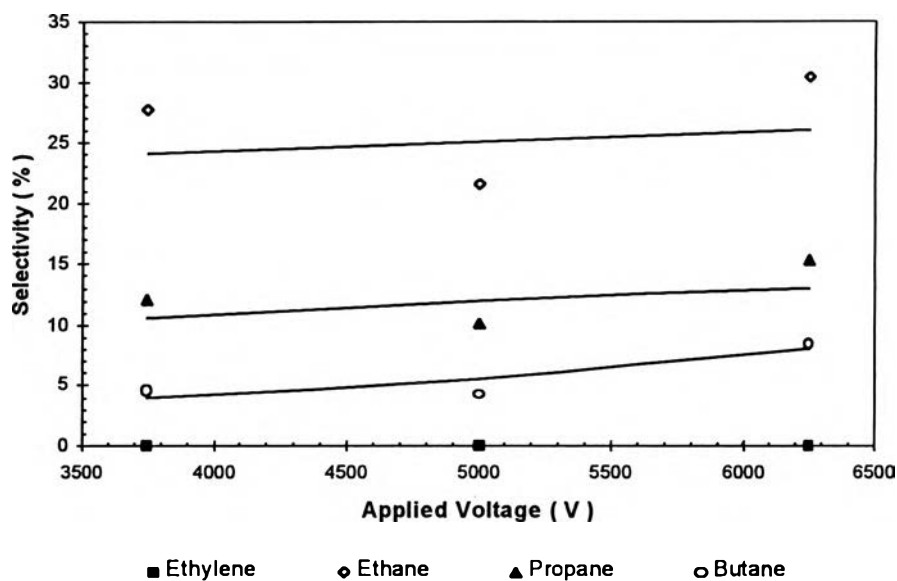
(flow rate = 20 ml/min, residence time = 11.55 min)

Furthermore, it is found that the helium content in the feed can significantly affect the degree of methane conversion. It is observed in the latter case on the same plot that when only 25 % of He was present in the feed (i.e., in the case of  $\text{CH}_4/\text{He} = 3:1$ ), its synergistic effect is nearly offset by its diluent effect. In this case, the methane conversion was found to be relatively the same as that was obtained when only pure methane had been fed into the reactor.

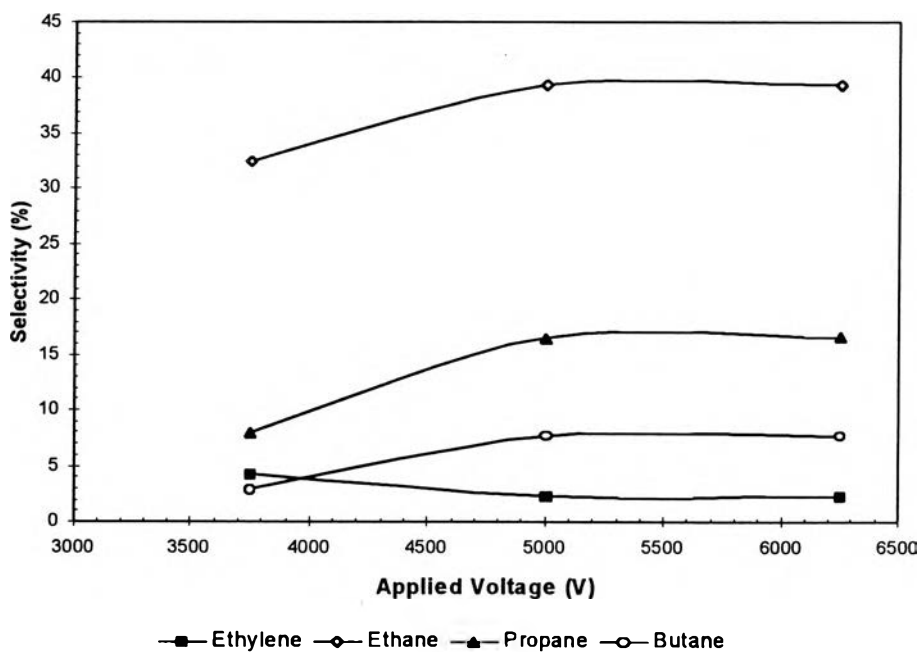
The synergistic effect of helium atoms on the methane reaction may be explained in connection with the basic knowledge on the plasma chemistry. It has been known that, under high voltage electric field, the gas that has higher mean free path will be much easier to cause the electrical breakdown (i.e., the phenomenon that occurs when the degree of the gases ionization in the discharge gap is extremely high until large amounts of electric current can be allowed to flow between the gap). Since the mean free path of the helium atom is relatively higher than that of the methane molecule, then it is likely that the helium is much easier to be activated by the dielectric-barrier discharges produced in the discharge gap. Therefore, it can exhibit some synergistic effects.

#### **4.4.2 Effect of helium on product selectivities**

Figures 4.9 and 4.10 show the distribution of the product compositions at different voltages when helium content in the feed is 50 % and 25 %, respectively. It was found from both figures that the difference in each pair of the selectivities of an individual product was not significant. However, in the case that only 25 % of helium was participated in the feed, its products distribution behaved much like those distributions obtained in the case of pure methane feeding.



**Figure 4.9** Distribution of products as a function of applied voltage  
(total flow rate = 20 ml/min; CH<sub>4</sub>/He ratio in the feed = 1:1).

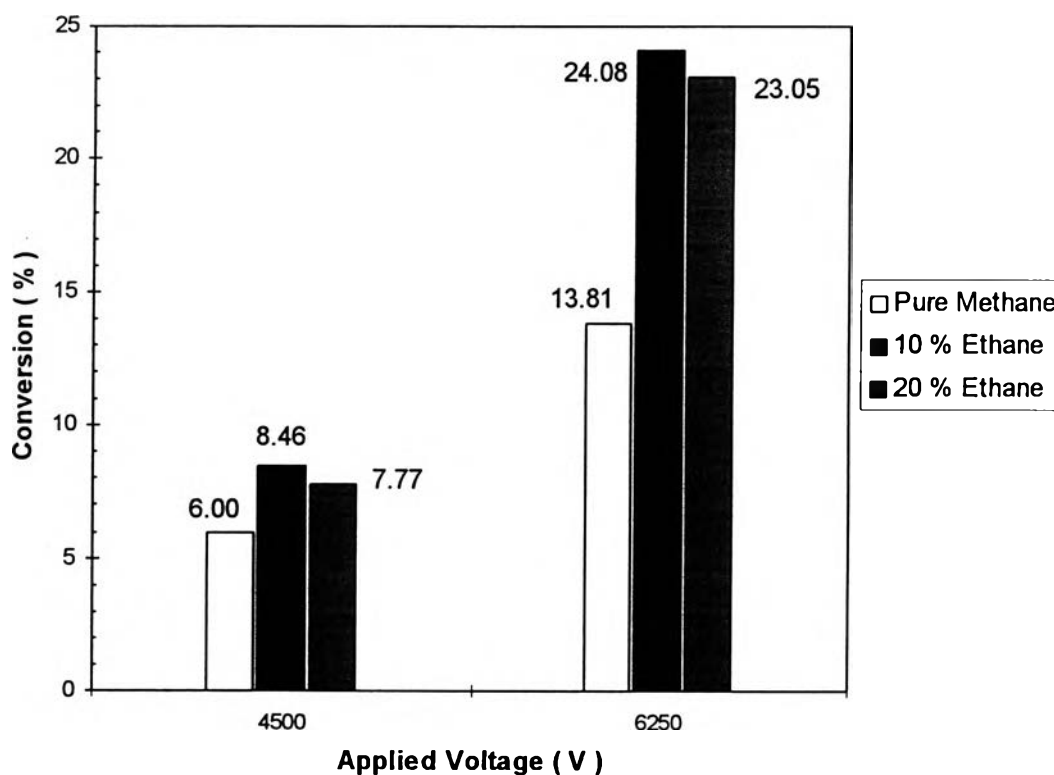


**Figure 4.10** Distribution of products as a function of applied voltage  
(total flow rate = 20 ml/min; CH<sub>4</sub>/He ratio in the feed = 3:1).

## 4.5 Effect of ethane on methane reaction

### 4.5.1 Effect of ethane on methane conversion

The effect of ethane concentration on the methane conversion at different voltages is shown in Figure 4.11. Two values of the relative amount of ethane were subjected into this study, the first was 10% ethane in the mixture (i.e.,  $\text{CH}_4/\text{C}_2\text{H}_6 = 9:1$ ) and the other was 20% ethane in the feed ( $\text{CH}_4/\text{C}_2\text{H}_6 = 4:1$ ). In addition, at the individual ratio of methane to ethane, two magnitudes of voltage were investigated using the gradual voltage rising technique.



**Figure 4.11** Effect of ethane concentration on methane conversion at two different applied voltages.

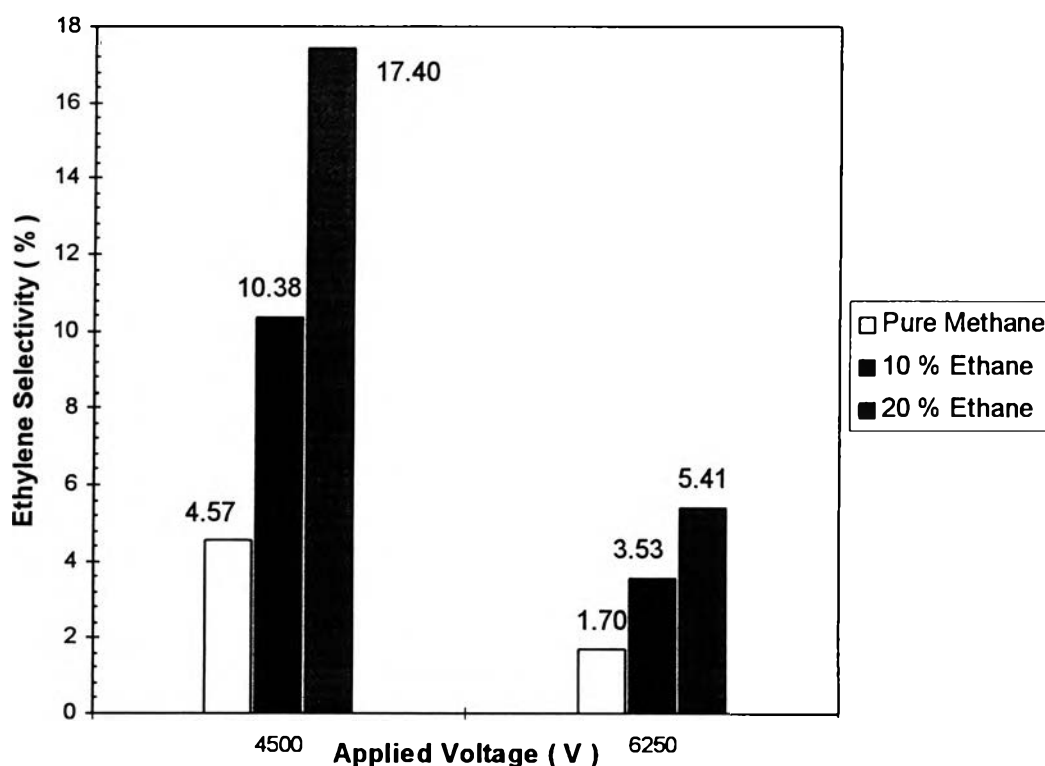
From this figure, it is very interesting to point out that the presence of the ethane molecules into the methane feed remarkably enhanced the methane conversion compared to the case of pure methane feeding system. However, as the  $\text{CH}_4/\text{C}_2\text{H}_6$  ratio continued to increase, it is discovered that the percent methane conversion was dropped slightly. This might be due to the fact that, when higher ratio of ethane to methane was introduced in the feed, the methane partial pressure would be decreased and, finally, a decrease in methane conversion was resulted. Moreover, when higher amount of ethane was introduced into the feed, its cracking reaction to produce methane molecules might also be occurred (as that could also be happened in the case of pyrolysis reaction). Therefore, the methane conversion seemed to deteriorate in the case that too much ethane molecule were presented into the feed.

While the voltage was increased, it was found that the methane conversion was also increased when compared at the same feeding  $\text{CH}_4/\text{C}_2\text{H}_6$  ratio. This result could be explained in a similar manner as in the case of pure methane reaction that the higher energetic electrons must be transited between two discharge surfaces (i.e., the dielectric and the metal electrode surface) when the voltage is increased, these electrons are, therefore, responsible for an increase in the methane conversion.

Since the single bond between two carbon atoms in the ethane molecule is very weak and can be dissociated very much easier than the bond between the carbon and hydrogen atoms. Therefore, it might be possible that the ethane molecules were cracked under the presence of the electric discharges to form methyl radicals species ( $\text{CH}_3\cdot$ ) which are very reactive. These radicals may then be responsible for the activation of the feeding methane molecules and hence increased the methane conversion.

Nevertheless, it was already shown so far that, within the voltage range of 4,500 to 6,250 V, the C-H bonds in the methane molecules could be dissociated, this implied that the bonds between C and H atoms in the “ethane” molecules might also be broken upon the collisions with the high energetic electrons. As a result, two distinguish active species including ethyl radicals ( $C_2H_5\cdot$ ) and hydrogen radicals ( $H\cdot$ ) could be produced. And these radicals might actually be the primary cause of an increase in the methane conversion. Consequently, the extensive quantitative data must be obtained before any conclusions about the exact chemical pathways leading to this phenomena can be postulated.

#### 4.5.2 Effect of ethane on ethylene formation



**Figure 4.12** Effect of the ethane concentration on ethylene selectivity at two different applied voltages.



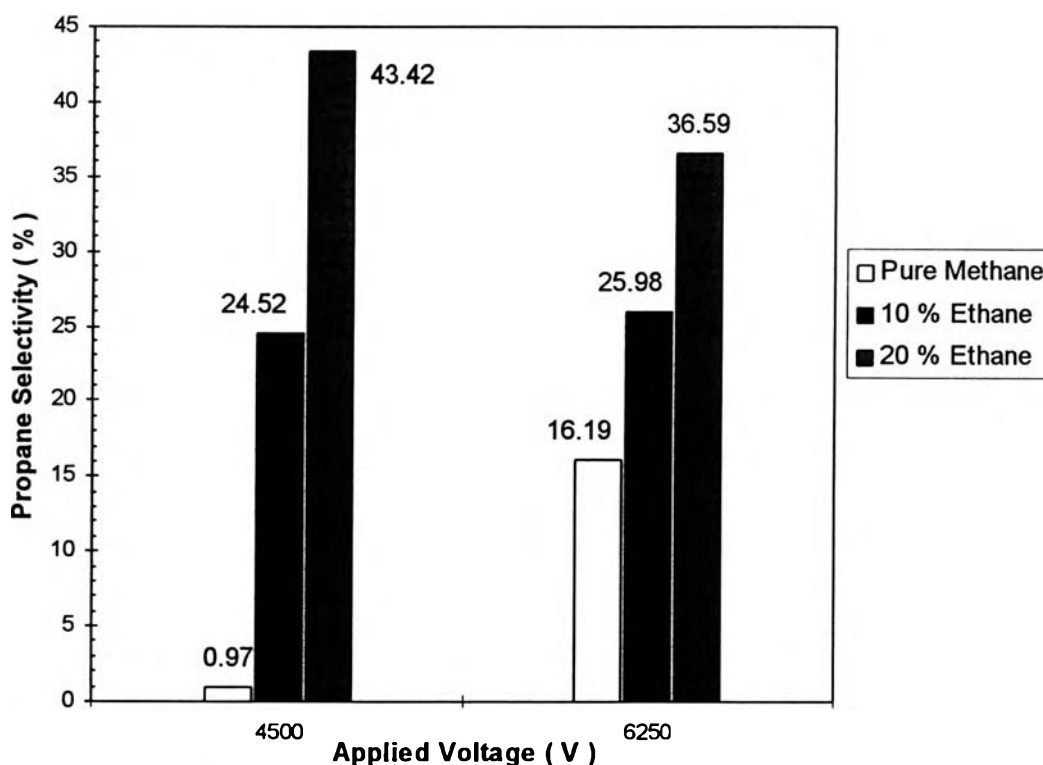
The effect of the ethane concentrations on the ethylene formation is shown in Figure 4.12. Again, this selectivity was illustrated in comparison with the result obtained in Figure 4.2. With the presence of ethane into the feeding mixture, the effect of voltage on the ethylene selectivity was quite explicit. At any given voltage, when the relative amount of ethane (i.e.,  $C_2H_6/CH_4$  ratio) was increased in the feed, the ethylene selectivity was accordingly increased. This indicates that the ethylene molecules being formed were likely to be produced directly by the cracking of ethane molecules. And when the voltage was increased, the ethylene selectivity was significantly decreased. This is probably due to the further reactions of the ethylene molecules to form other hydrocarbons.

A possible explanation to describe the effect of ethane on the ethylene formation is that most of the methyl radicals being produced from the ethane cracking might be recombined and converted further into ethylene via several possible reaction pathways such as via the successive cracking of  $CH_3^\bullet$  radicals into  $CH_2^\bullet$  followed by their recombination. In another way, the abstraction of one hydrogen atom from each ethane molecule might be happened. And this led to the formation of  $C_2H_5^\bullet$  which could be cracked 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 in order to produce ethylene.

#### **4.5.3 Effect of ethane on propane formation**

Figure 4.13 illustrates the effect of ethane concentration on the propane selectivity in comparison to the result from the case of pure methane feeding system. It was found that the effect of the applied voltage on the propane formation depended on the relative  $CH_4/C_2H_6$  ratio. In the case that the amount

of methane was much richer than the ethane (i.e., when no ethane or 10% ethane was present), the voltage of this range helped increase in the propane selectivity. When the concentration of ethane was double to 20%, the propane selectivity was slightly decreased. Furthermore, there was an explicit observation that the presence of ethane in both cases greatly enhanced the propane selectivity when compared to the case of pure methane feeding system. Although it is possible that the ethane molecules could be decomposed into  $C_1$  radicals, but the probability for any three of those  $C_1$  radicals to suddenly come closer to one another and attach among themselves to form  $C_3$  hydrocarbon (e.g., propane) should be much less than the opportunity that a  $C_2$  species, either  $C_2$  radical or a stable  $C_2$ -hydrocarbon, would come into contact with a  $C_1$  species and then form propane.



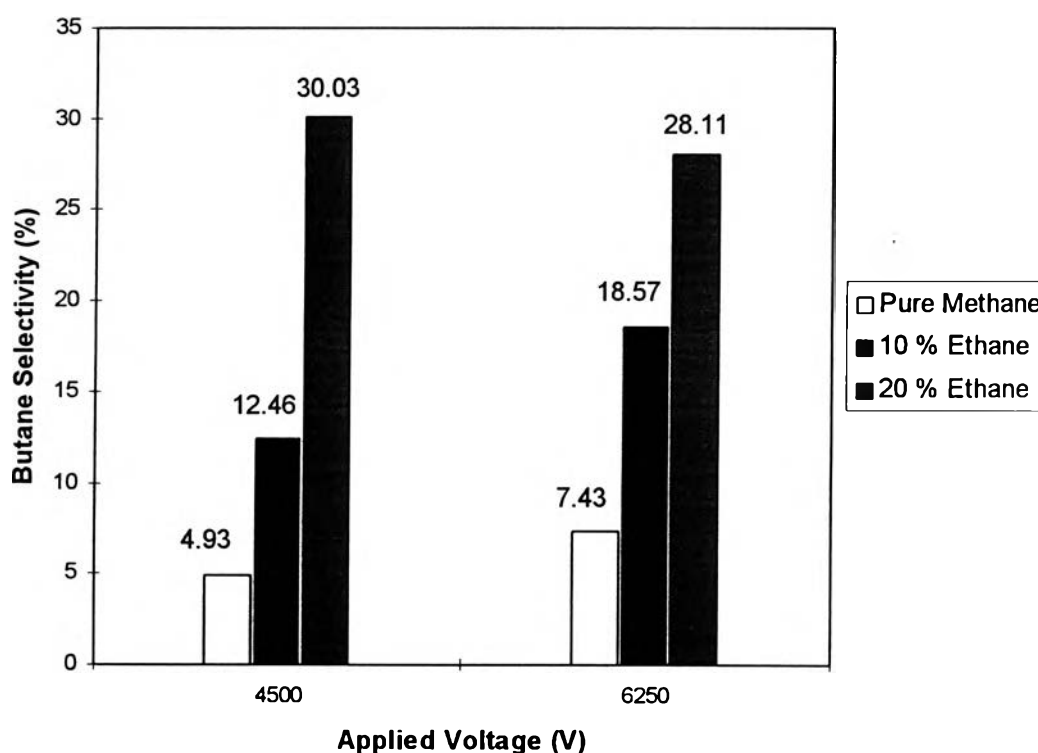
**Figure 4.13** Effect of ethane concentration on propane selectivity at two different applied voltages.

As can be seen from both Figures 4.12 and 4.13, it can be hypothesized that the ethane molecules should mostly be cracked into  $C_2$  radicals species

first and then these radicals could either form ethylene or attach with the  $C_1$  species to form propane.

#### 4.5.4 Effect of ethane on butane formation

Figure 4.14 shows a plot of butane selectivity at different levels of ethane concentration. As the concentration of ethane in the feed was increased, a significant increase in butane selectivity could be obtained.

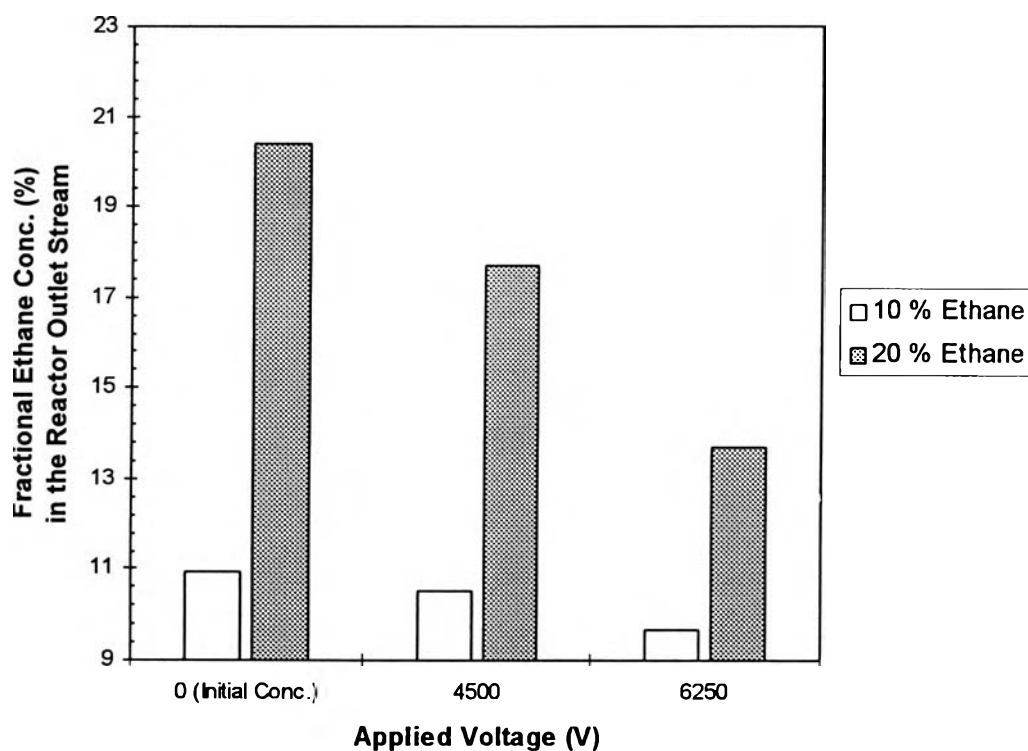


**Figure 4.14** Effect of ethane concentration on butane selectivity at two different applied voltages.

The previous hypothesis that most of the ethane molecules were cracked into  $C_2$  radicals could also be used to describe an increase in this butane selectivity. Because when those  $C_2$  radicals were produced, they would

not only bond with the  $C_1$  radicals to form propane but they might combine among themselves to form  $C_4$ -hydrocarbons like butane as well.

Also, it is interesting to point out that, even though the unsaturated  $C_3$ -hydrocarbon (i.e., propylene) had never been detected in any of all those previous runs, but the formation of some unsaturated  $C_4$ -hydrocarbons could be observed from many GC chromatograms. This suggests that the degree of hydrogen abstraction from  $C_2$  species could be greater than 1. And so, those  $C_2$  radicals might recombine among themselves to form the unsaturated  $C_4$  products.

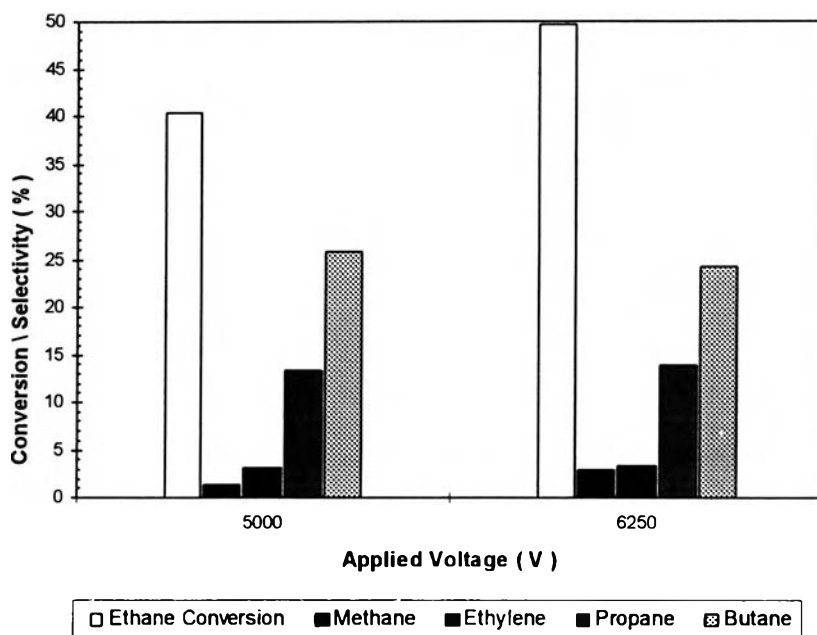


**Figure 4.15** Variation in outlet ethane concentration at different applied voltages.

Figure 4.15 shows the dependence of ethane concentration in the reactor outlet stream as a function of the applied voltage when the inlet ethane concentration was kept constant at 10% and 20% by volume. A remarkable decrease in the ethane concentration took place when the applied voltage was

increased. And this implies that some ethane was consumed by the reactions to form other hydrocarbons.

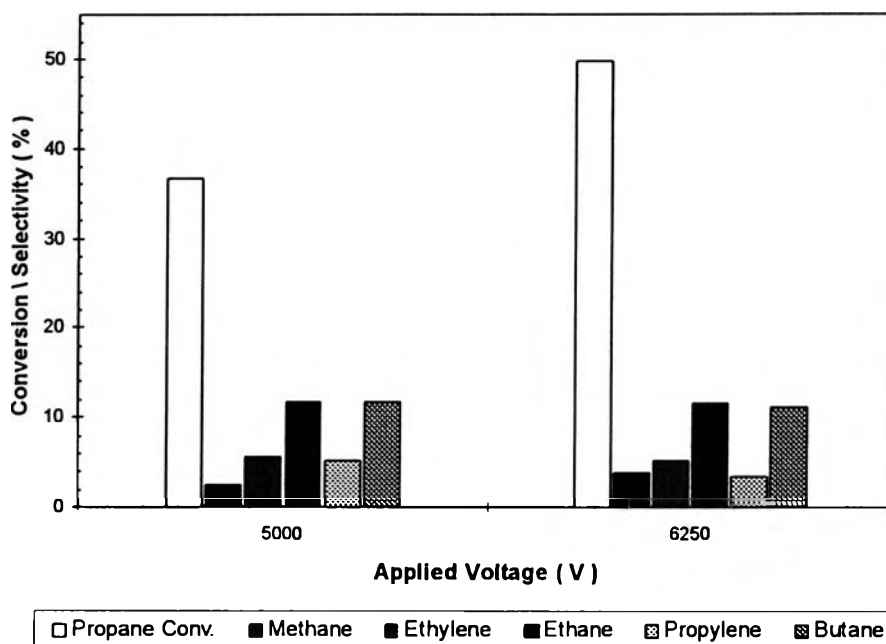
#### 4.6 Reaction of ethane-helium system and propane-helium system



**Figure 4.16** Effect of applied voltage on ethane conversion and product selectivities (total flow rate = 20 ml/min, 20% ethane in helium).

The reactions of ethane-helium and propane-helium system under the electric discharges environment were also studied. Figures 4.16 and 4.17 show the effect of the applied voltage on the ethane conversion and propane conversion at 20 ml/min, respectively. The feeding mixtures in both cases consisted of 80 % He and 20 % ethane or propane. For the case of the ethane-helium system, a small fraction of ethane was converted into methane and ethylene while most of ethane was reacted to form propane and butane. It was found that an increase in the applied voltage resulted in a slight increase in the

methane and ethylene formation while the propane and butane selectivities were nearly unaffected.



**Figure 4.17** Effect of applied voltage on propane conversion and product selectivities (total flow rate = 20 ml/min, 20% propane in helium).

The experimental study with 20% propane and 80% helium in the feed was the only experiment that some traces of propylene could be detected. This reaction system produced a very high product distribution. The result indicates that a significant fraction of propane was cracked to form lower hydrocarbons such as methane, ethylene, ethane and propylene. And an increase of the applied voltage led to an increase in propane conversion while the product selectivities were nearly independent of this voltage change.