

## CHAPTER IV

### RESULTS AND DISCUSSION

The results of this study are plotted and described in this chapter in connection with information derived from the published literature. Moreover, the results were used to derive the chemical reaction pathways and the kinetic expressions. The experimental data of this study are summarized in Appendix B.

#### **4.1 Effect of Flow rate, Voltage and The Composition of Feed**

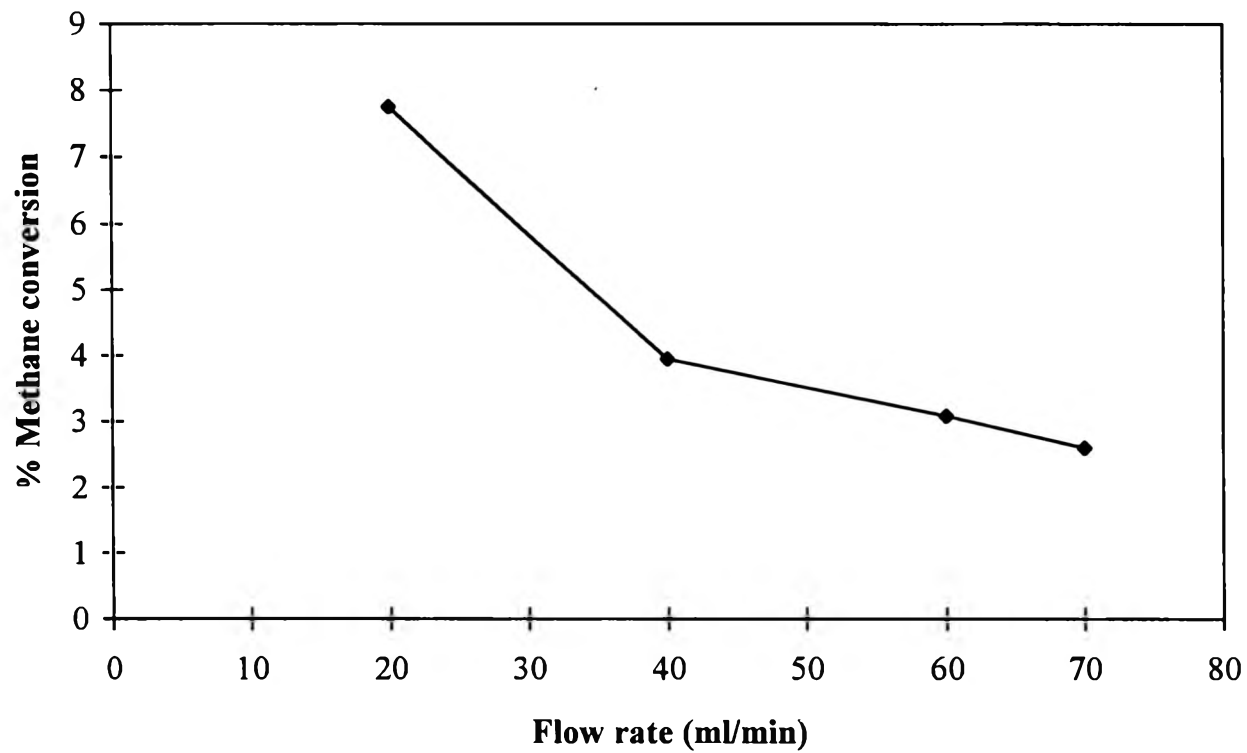
##### **4.1.1 Pure Methane System**

###### *4.1.1.1 Effect of Flow Rate on Methane Conversion*

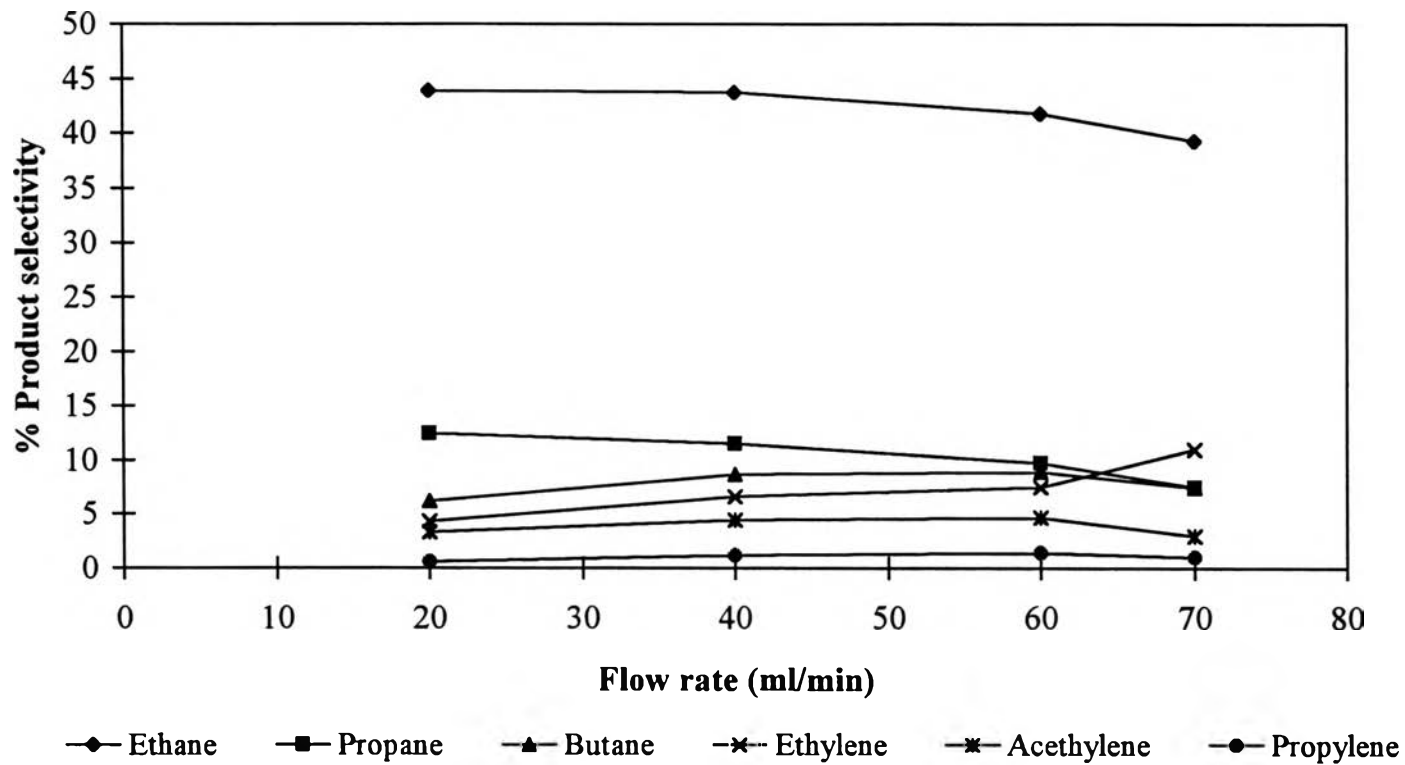
Figure 4.1 shows the effect of the flow rate on methane conversion. It can be seen that, at the applied voltage of 5,625 V, the methane conversion was decreased with increasing flow rate. When the flow rate was increased, methane would pass through the reactor faster and the contact time between the methane molecules and discharges decreased. The methane molecules would have fewer collisions to activate and break the bond between C and H, thus decreasing both the degree of methane dissociation and conversion.

###### *4.1.1.2 Effect of Flow Rate on Product Selectivity*

From Figure 4.2, it is noticeable that when the flow rate is increased, at a constant voltage of 5,625 V, the selectivities of alkane products slightly decrease while the selectivity of alkene and alkyne products increase slightly. From the highest selectivities of ethane and propane, it indicates that most



**Figure 4.1** Methane conversion at different flow rates for applied voltage of 5,625 V in pure methane system.



**Figure 4.2** Product selectivities at different flow rates for applied voltage of 5,625 V in pure methane system.

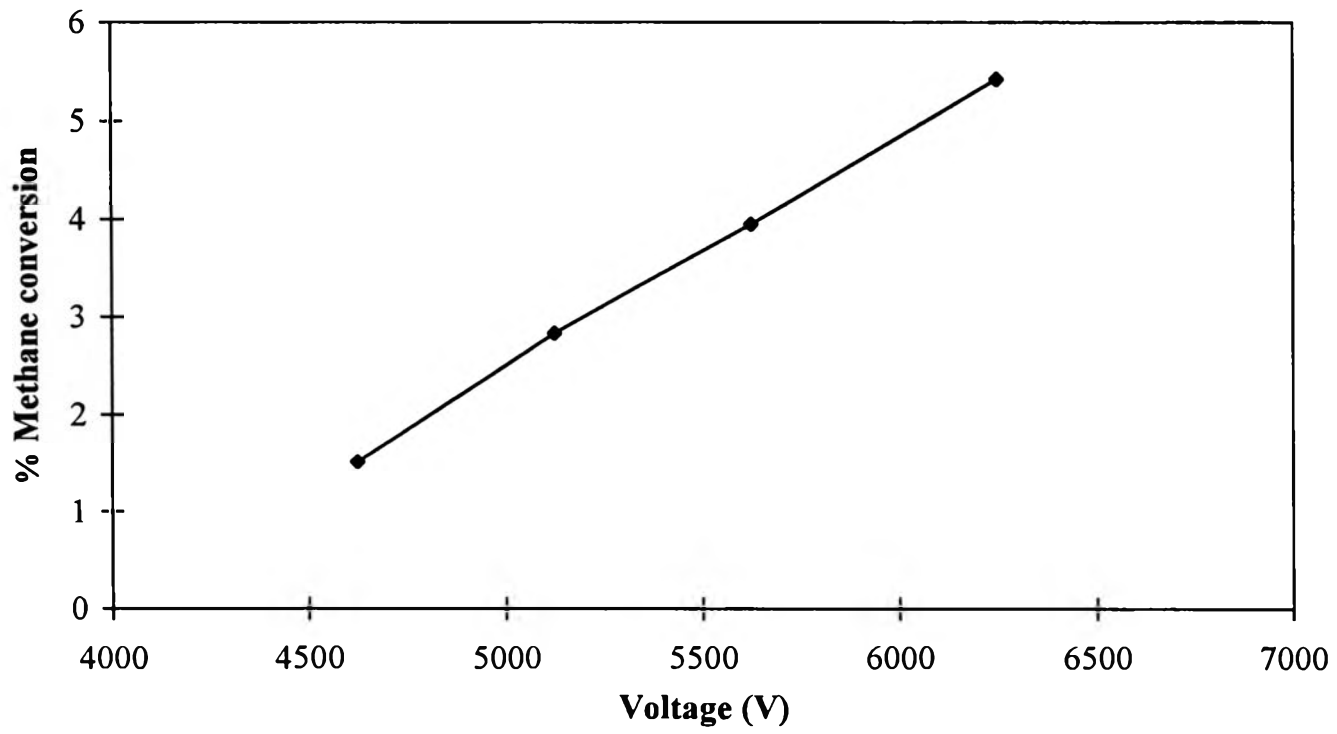
methane was coupled to form other alkanes and produced  $H_2$ . With the production of hydrogen gas in the system due to the high methane conversion, ethane and propane have less chances to dehydrogenate to alkenes and alkynes. Moreover, the less amount of the produced ethylene, acetylene and propylene, having a double bond or triple bond, would be less stable and could be hydrogenated to form ethane and propane. So, at lower flow rates (higher methane conversion), the selectivities of ethylene, acetylene and propylene decreased. The behavior of butane seems to be different from the other alkanes because the alkene predominates. This may be because butane, in this system, was not produced from methane directly, but could be produced by disproportionation.

#### *4.1.1.3 Effect of Applied Voltage on Methane Conversion*

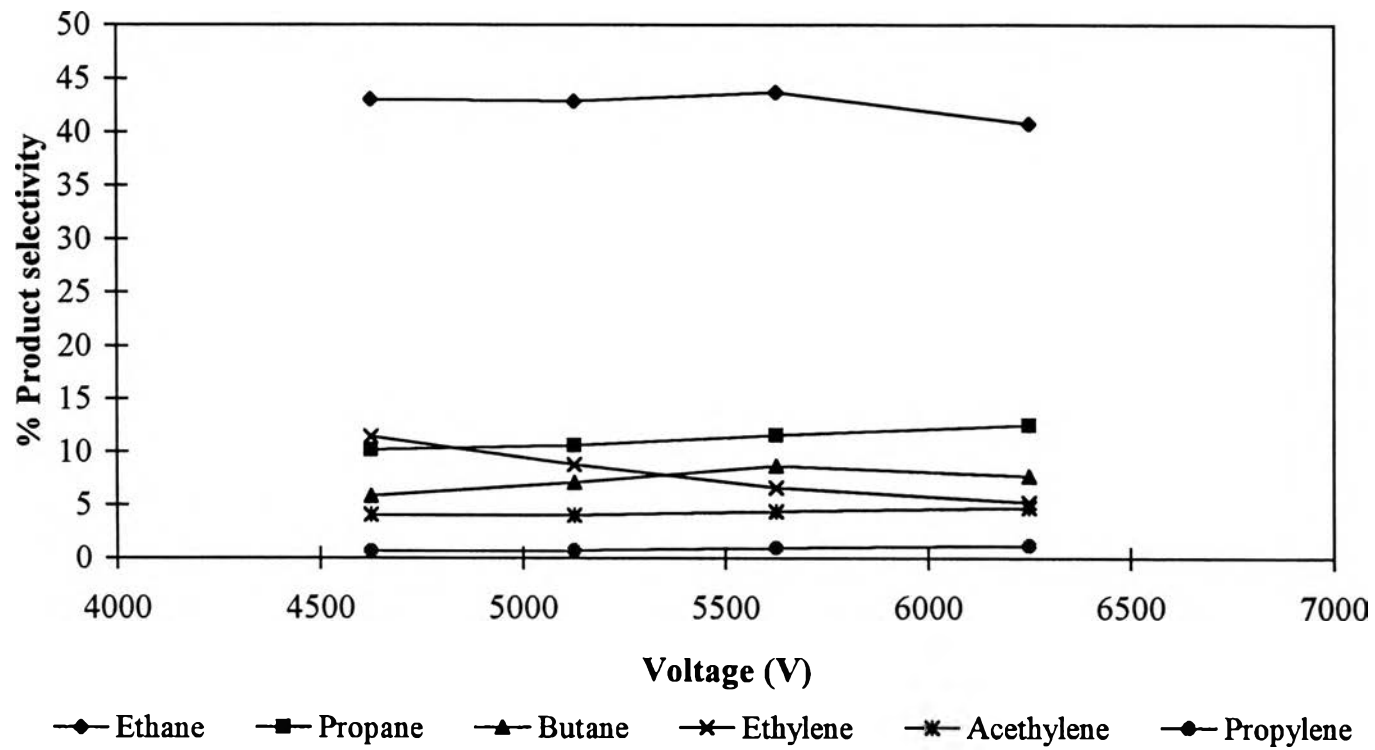
Figure 4.3 illustrates the effect of the applied voltage on methane conversion. For a given flow rate of 40 ml/min (5.757 min residence time), it was found that methane conversion increased almost linearly with increasing voltage. When the applied voltage was increased, more electrons or discharges were generated. This resulted in a higher probability for breaking the C-H bond of methane molecules and thus caused an increase in both the degrees of methane dissociation and conversion.

#### *4.1.1.4 Effect of Applied Voltage on Product Selectivity*

Figures 4.4 show that when the applied voltage was increased, the selectivities of alkene and alkyne products decreased together with an increase in alkane products. This is because the conversion of methane was higher when increased voltage and that provided higher partial pressure of hydrogen for hydrogenation reaction of alkene and alkyne to alkane.



**Figure 4.3** Methane conversion at different applied voltages for a given flow rate of 40 ml/min (5.775 min residence time) in pure methane system.



**Figure 4.4** Product selectivities at different applied voltages for a given flow rate of 40 ml/min (5.775 min residence time) in pure methane system.

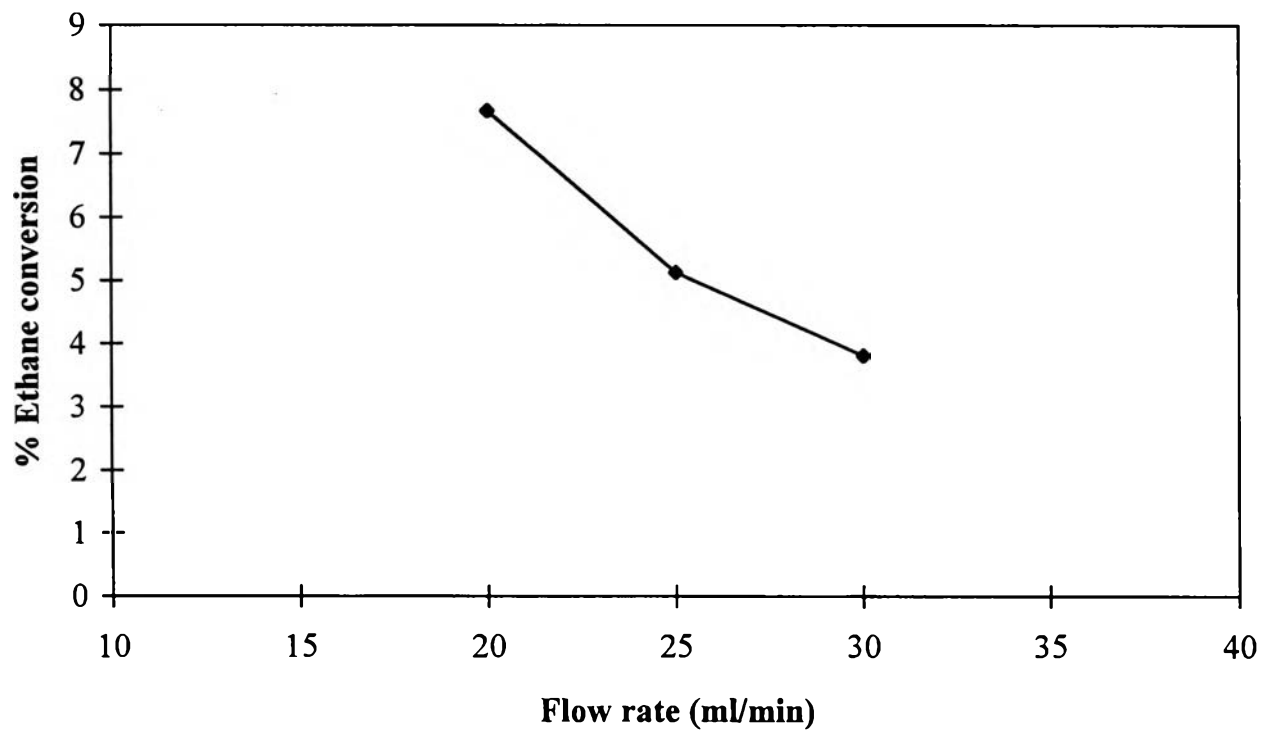
## 4.1.2 Pure Ethane System

### *4.1.2.1 Effect of Flow Rate on Ethane Conversion*

Figure 4.5 illustrates the effect of flow rate on the ethane conversion at a given voltage of 5,625 V. The results looked like those in the pure methane system; when the flow rate was increased, ethane conversion was decreased. For the same reasons, the contact time between the ethane molecules and discharges was shorter when the flow rate was higher.

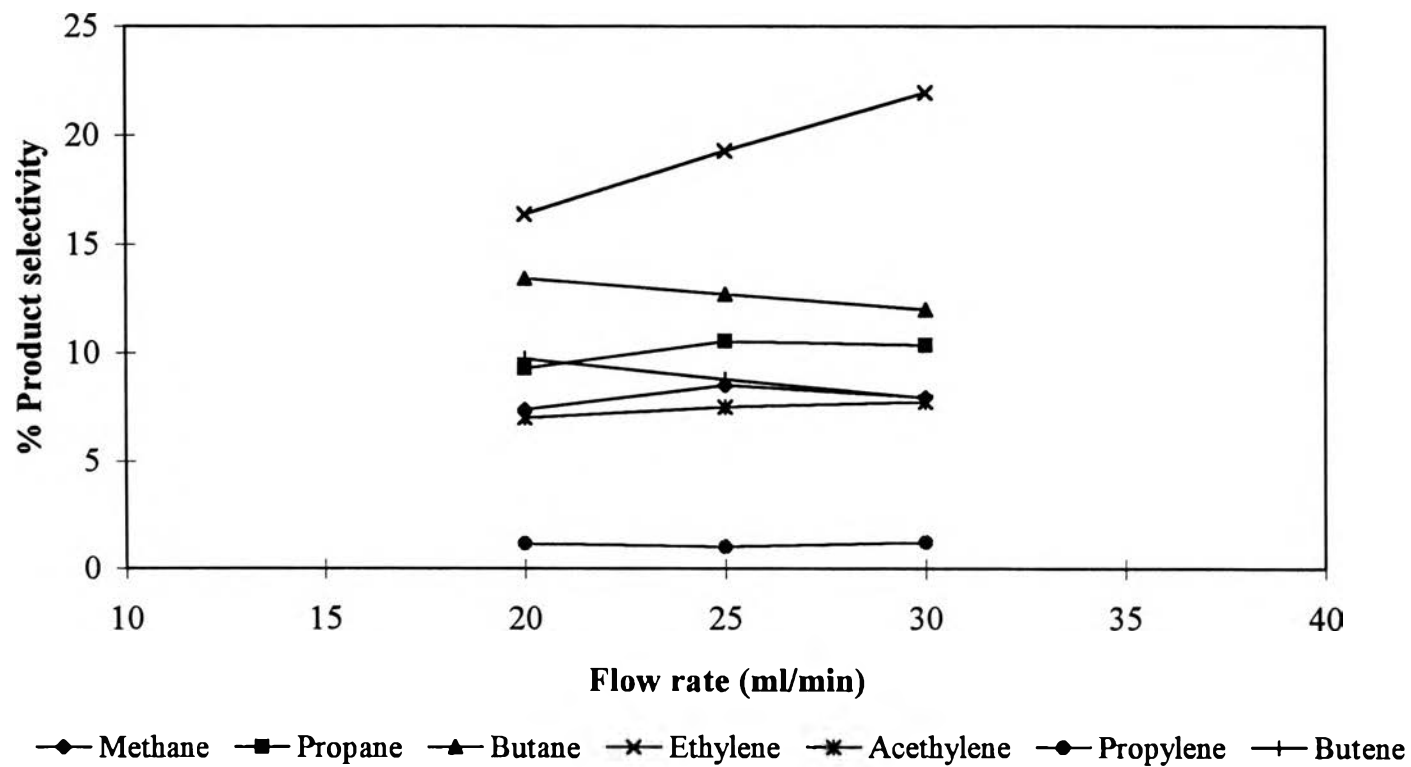
### *4.1.2.2 Effect of Flow Rate on Product Selectivity*

In these experiments, a limitation of the maximum flow rate occurred because the ethane gas tank (including the regulator) could not provide a constant high flow rates. This resulted in a short-range of lower operational flow rates to be used in the experiment. As can be seen from Figure 4.6 ethylene and butane had the first and second highest selectivities, respectively. This indicates that ethylene and butane were the primary products that were produced from ethane. This results leads to a conclusion that, in this system, the dehydrogenation of ethane to ethylene is faster than the coupling of ethane to form butane, especially in higher flow rates that had lower ethane conversion. Hydrogen from dehydrogenation would break C-C bonds of ethane to produce methane and this allows coupling with ethane to produce propane. The selectivities of alkene and alkyne decreased slightly with a decrease in the flow rate. This is because ethane conversion was higher and provided more H<sub>2</sub> to facilitate these hydrogenation step. This is the same reason as in the pure methane system.



**Figure 4.5** Ethane conversion at different flow rates for applied voltage of 5,625 V in pure ethane system.





**Figure 4.6** Product selectivities at different flow rates for applied voltage of 5,625 V in pure ethane system.

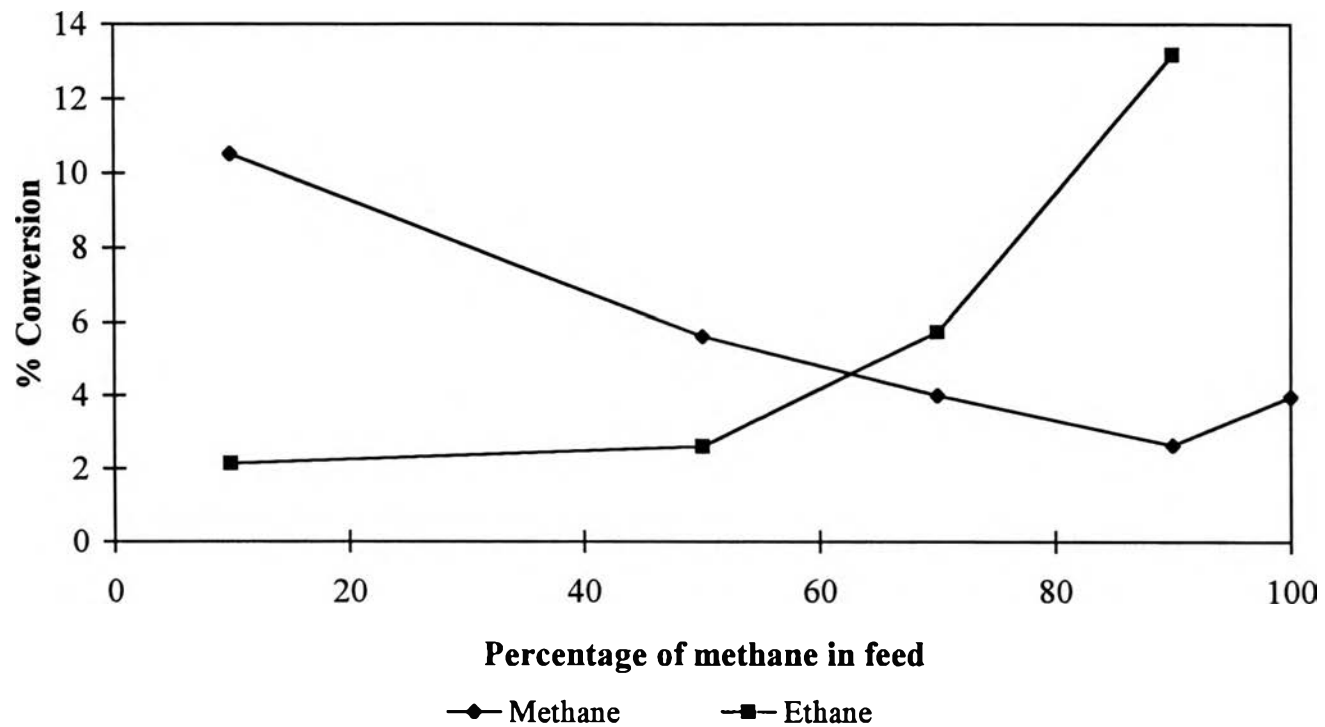
### 4.1.3 Methane-Ethane System

#### 4.1.3.1 *Effect of Ethane on Methane Conversion*

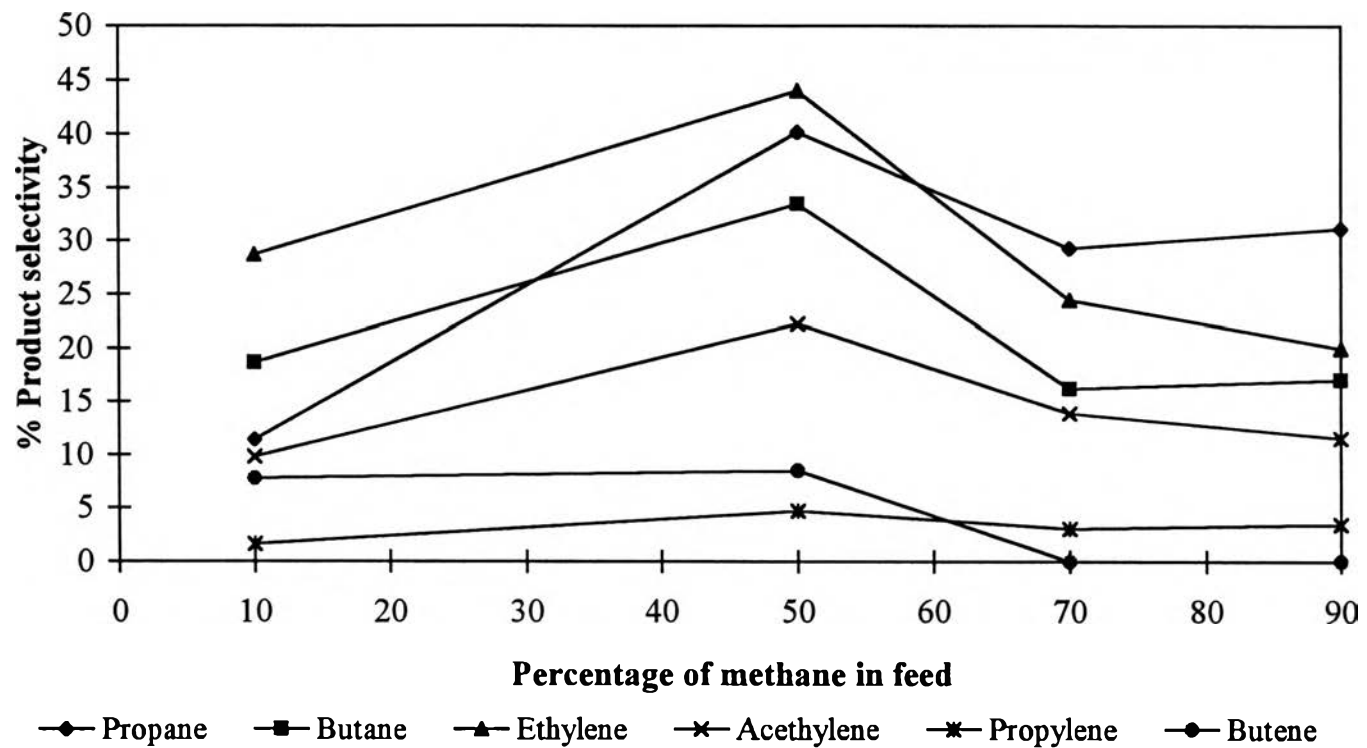
The effect of ethane concentration on the methane conversion at constant voltage and flow rate (5,625 V, 40 ml/min) is shown in Figure 4.7. With increasing percentage of ethane (10-100%), methane conversion increased almost linearly. This might be because ethane molecules activated are more effective than electrons in activating methane molecules. These results suggest that the more ethane in the feed, the better the methane conversion can be obtained. On the other hand, the activated molecules of methane can also activate ethane and help ethane to have a more conversion. As observed in the figure, when compared to the pure methane system, at a percentage of ethane below 20%, the methane conversion is lower than the pure methane system. This might be because ethane could decompose to methane and make net methane conversion lower.

#### 4.1.3.2 *Effect of Feed Ethane Fraction on Product Selectivity*

From Figure 4.8, the ratio of methane to ethane equal to 1:1 provides the highest products selectivities with ethylene and propane as the main products. At this point, all products can be produced from both ethane and methane in significant amounts. These products selectivities become twice the selectivities as obtained from both of the pure methane system and the pure ethane system. For this reason, the graph of the selectivities looks like a triangle. For the high methane side, propane, was the primary product as a result of a main reaction of methane and ethylene coupling. For the high ethane side, ethylene was the primary product.



**Figure 4.7** Conversions of methane and ethane at different feed methane contents for applied voltage of 5,625 V and 40 ml/min flow rate (5.775 min residence time) in methane-ethane system.



**Figure 4.8** Product selectivities at different feed methane contents for applied voltage of 5,625 V and 40 ml/min flow rate (5.775 min residence time) in methane-ethane system.

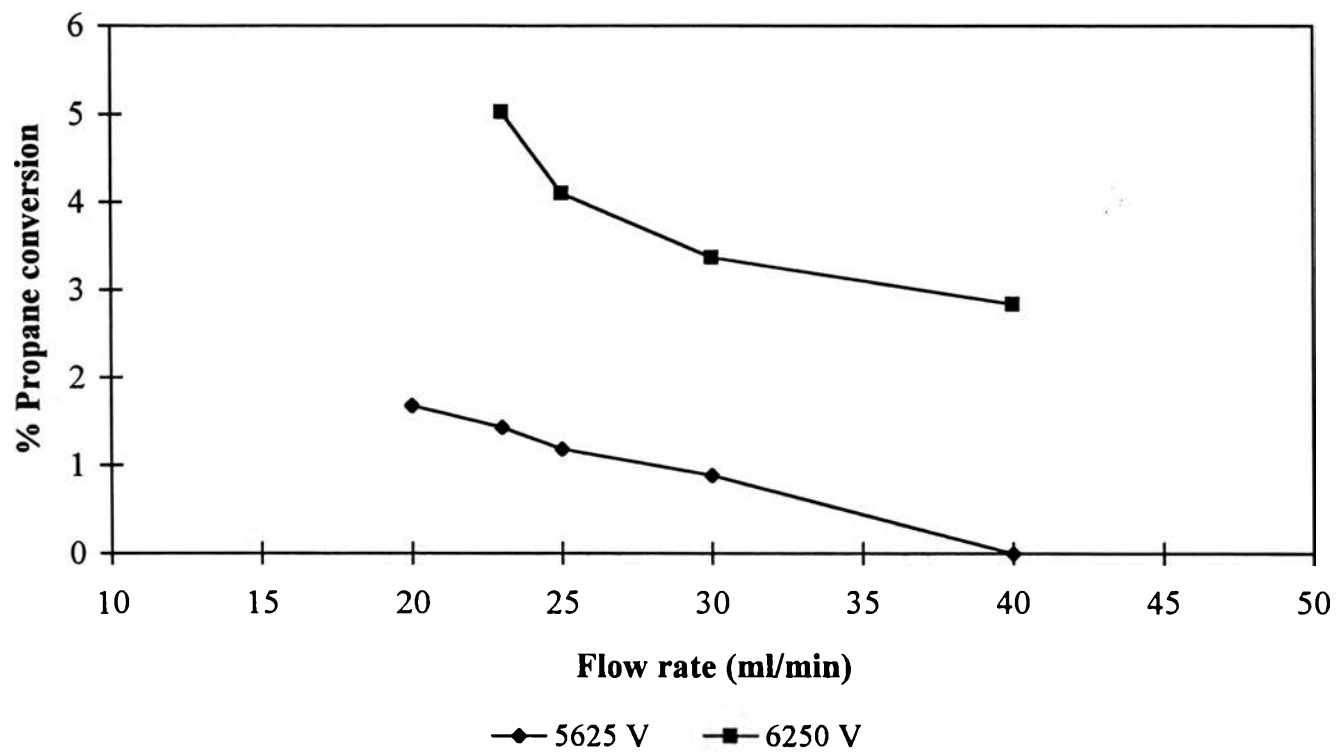
#### 4.1.4 Pure Propane System

##### *4.4.1 Effect of Flow Rate and Voltage on Propane Conversion*

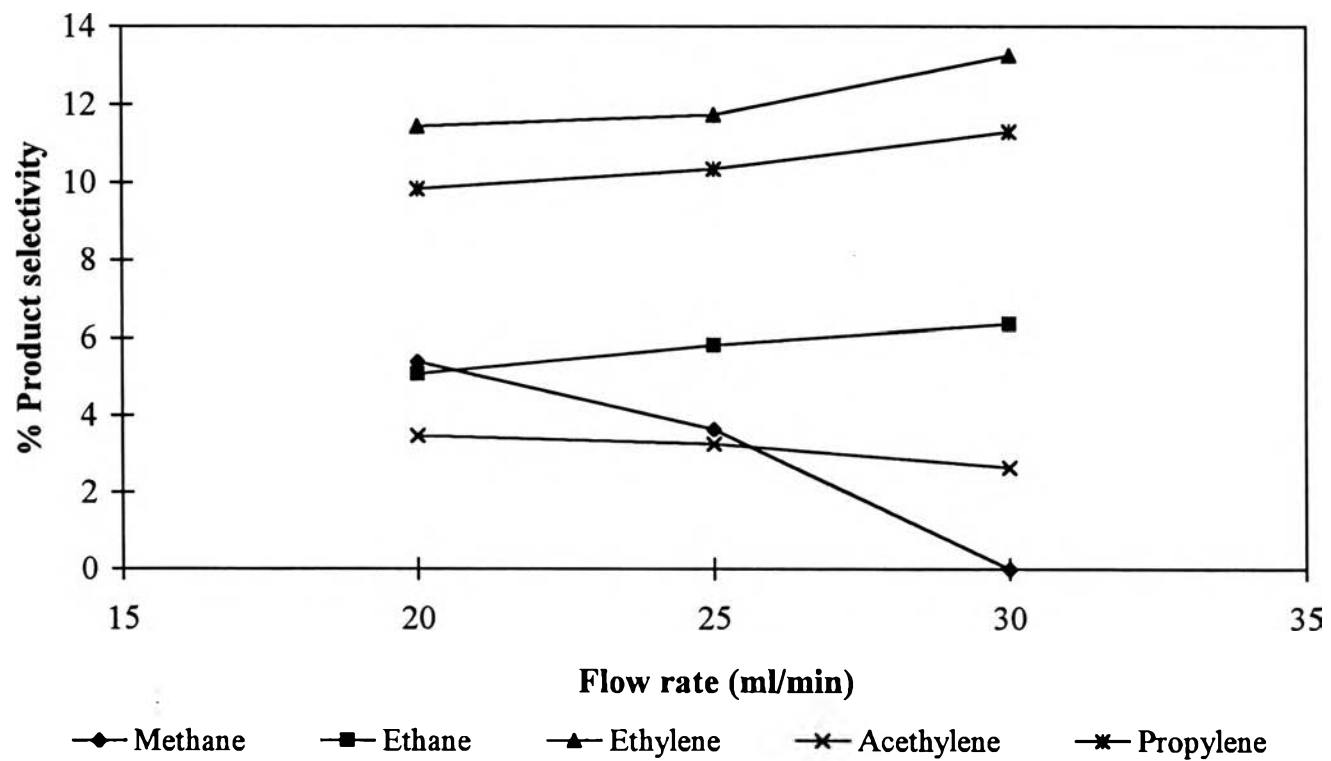
The effects of flow rate and voltage on propane conversion is shown in Figure 4.9. In comparison with both pure methane and pure ethane systems, the similar results occurred when increasing the voltage or when decreasing the flow rate, propane conversion increased remarkably. It is noticeable that in this system, propane conversion was much lower when compared to other systems. This shown that, at the lower voltage, propane itself was not activated as well to convert to other products.

##### *4.4.2 Effect of Flow Rate on Product Selectivity*

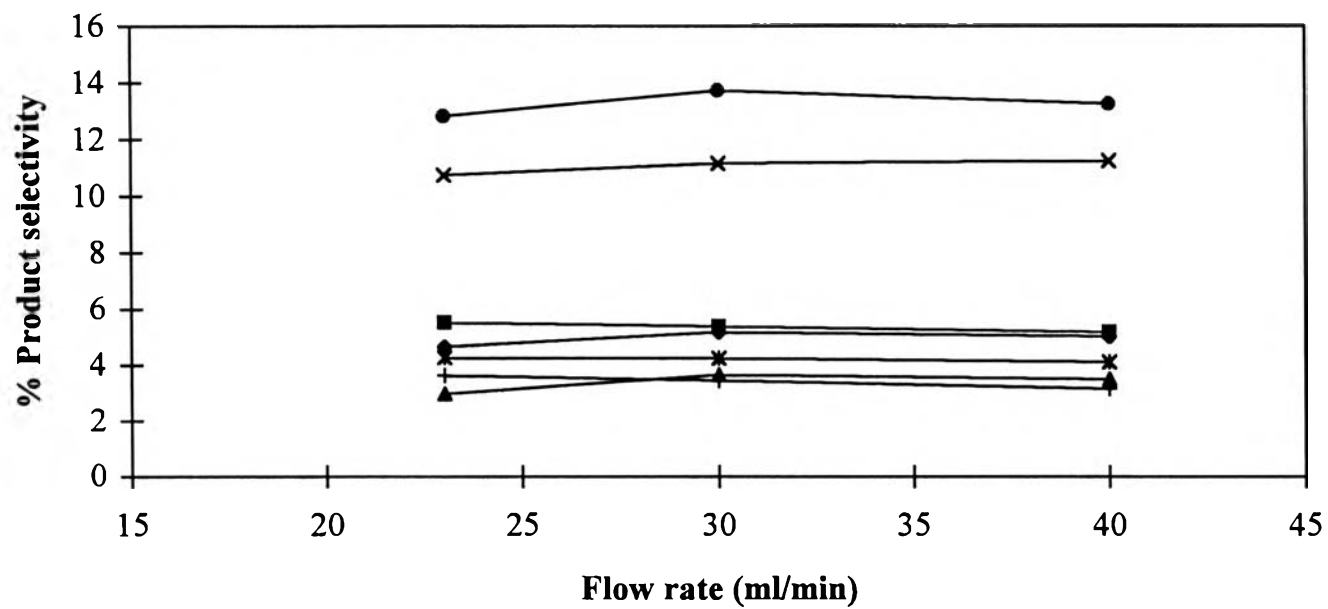
Figures 4.10 and 4.11 show the effect of flow rate on product selectivities at two constant voltages (5,625 and 6,250 V), respectively. For the lower voltage, ethylene had the highest selectivity followed by propylene. In fact, propylene was the primary product produced from propane dehydrogenation. The H<sub>2</sub> produced from that reaction allows reactions breaking a C-C bond of propane, to form methane and ethane. With a lower conversion of propane, when increasing the flow rate, H<sub>2</sub> from dehydrogenation reactions were not enough for alkane formation. So that ethyl radicals will dehydrogenate further to become ethylene when methyl radicals are formed ethane. Moreover, with less hydrogen gas in the system, propylene can react further to become other products such as acetylene. Under these conditions ethylene has the highest selectivity. With an increase in flow rate, the propane conversion decreased and the selectivities of the products changed slightly except for methane. It decreased significantly when the flow rate was increased. With the previous discussion, less H<sub>2</sub> because of less conversion,



**Figure 4.9** Propane conversion at different flow rates for two different applied voltages in pure propane system.



**Figure 4.10** Product selectivities at different flow rates for applied voltage of 5,625 V in pure propane system.



● Methane    ■ Ethane    ▲ Butane    × Ethylene    \* Acetylene    ● Propylene    + Butene

**Figure 4.11** Product selectivities at different flow rates for applied voltage of 6,250 V in pure propane system.



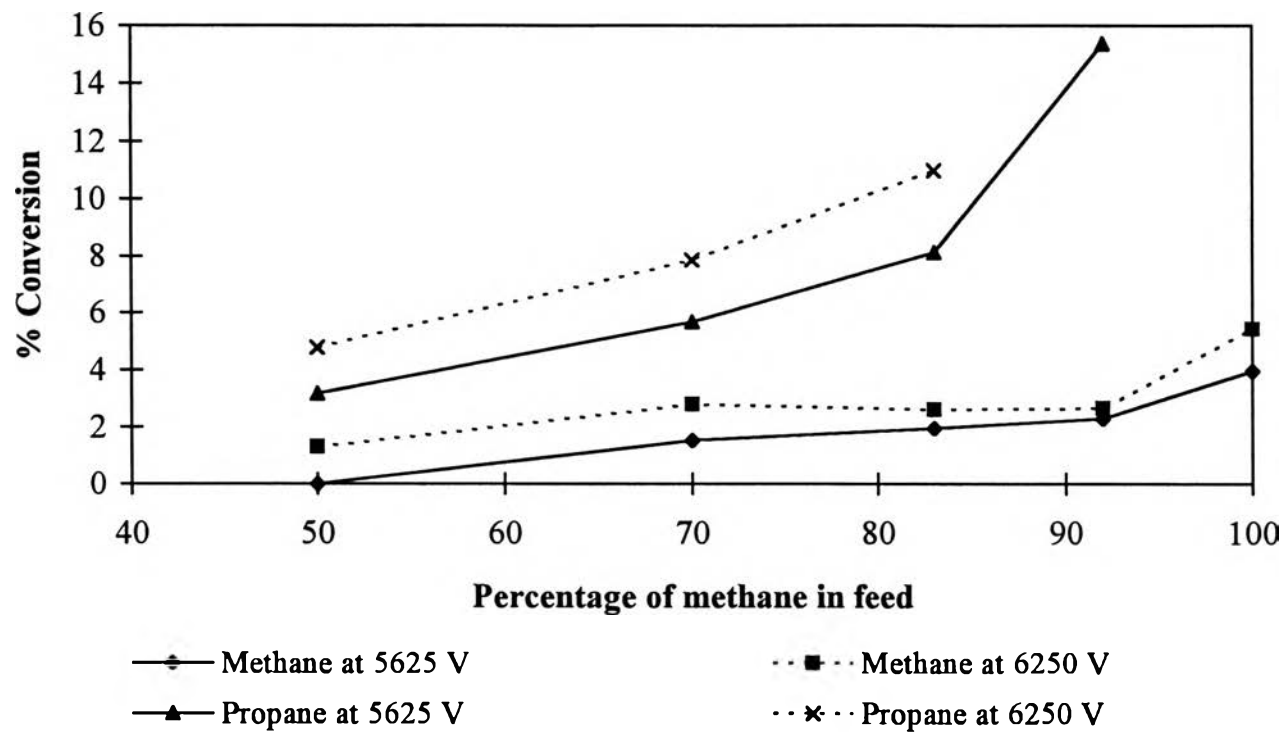
favors ethane formation over dehydrogenation. This made the selectivity of ethane higher.

For the higher voltage, the conversion was higher and provided a higher H<sub>2</sub> partial pressure in the system. Propylene became a main product that had the highest selectivity followed by ethylene. This indicates that under the studied conditions, the dehydrogenation of propane played a major role in the system in comparison with the other reactions. The product selectivities had few changes over the range of the studied flow rates. It is noticeable that, at this voltage, butane and butene were higher.

#### 4.1.5 Methane-Propane System

##### *4.1.5.1 Effect of Methane to Propane Ratio on Conversion*

The effect of propane concentration on the methane conversion at constant flow rate (40 ml/min) for two different voltages (5,625, 6,250 V) is shown in Figure 4.12. With increasing percentage of propane, under 30%, at 5,625 V, methane conversion decreased significantly. If the percentage of propane was further increased, methane was no longer “converted”. This indicates that the presence of propane in the methane system is as an “inhibitor”. When the percentage of propane increased, methane produced from propane increased and made the net methane conversion lower. At higher than 30% propane, the rate of methane conversion was less than the rate of methane production from propane and this gives a net production of methane. With an increase in voltage to 6,250 V, the conversion of methane increased slightly with an increase in percentage of propane under 30%. This indicates that, at this voltage, more discharges activated methane to have a higher conversion. Nevertheless, more activated propane would also activate methane to have a more conversion. When the percentage of propane was increased



**Figure 4.12** Conversions of methane and propane at different feed methane contents for 40 ml/min flow rate (5.775 min residence time) and two different applied voltages in methane-propane system.

(above 30%), the results were the same as at 5,625 V. This suggests that at a high enough voltage, more propane in the feed might enhance methane conversion in a similar fashion to the methane-ethane system.

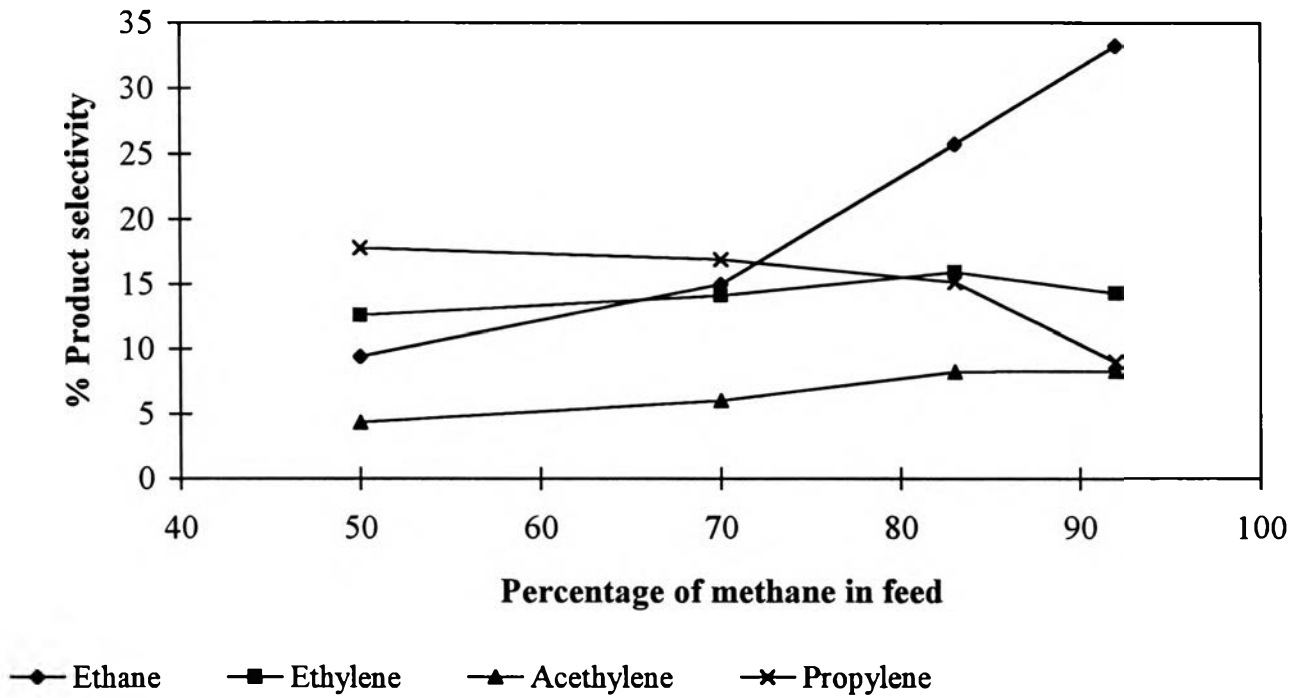
For propane conversion, the figure shows that with increasing percentages of methane, propane conversion was increased for both voltages. Similarly, many excited methane molecules might activate propane better than the electrons of the discharges. And the more methane in the feed, the better the propane conversion could be obtained.

#### *4.1.5.2 Effect of Methane to Propane Ratio on Product Selectivity*

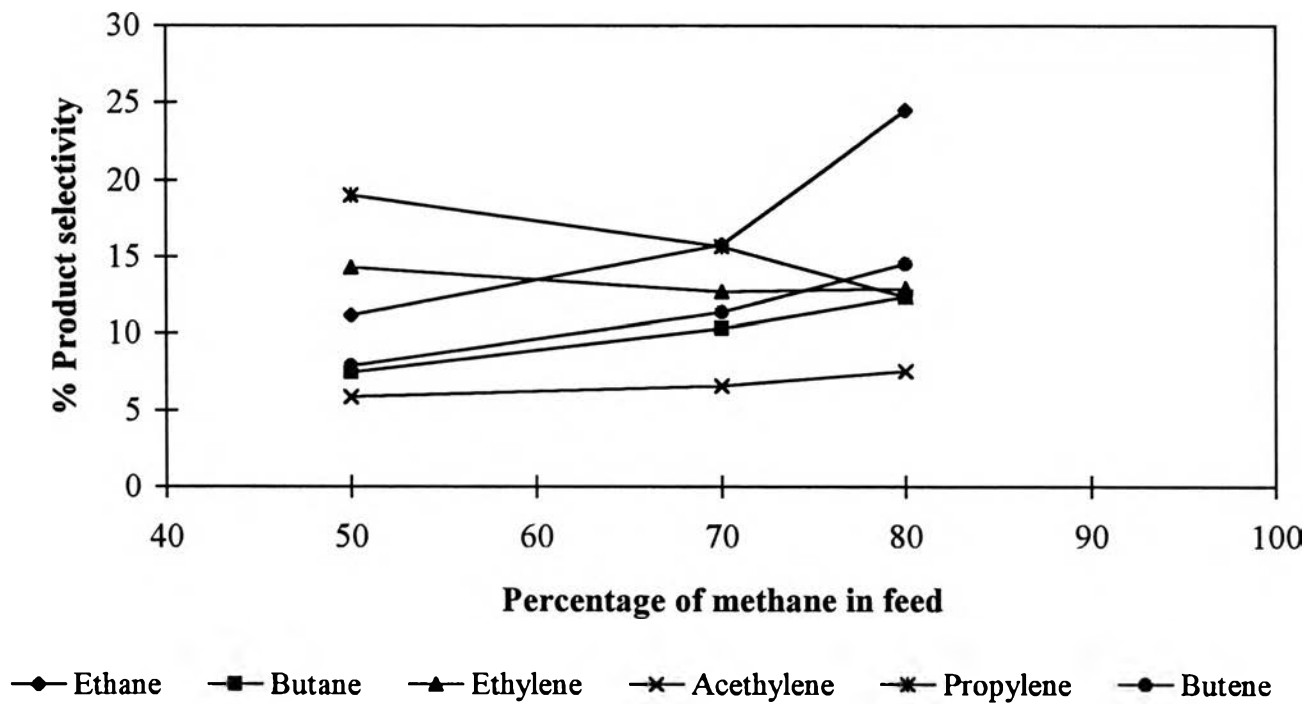
Figures 4.13 and 4.14 show the effect of propane concentration on product selectivities at two different voltages, 5,625 and 6,250 V, respectively. It is shown that the selectivity of ethane was increased drastically with increasing percentage of methane in the feed. This indicates that at these conditions, the formation of ethane depends on methane as described in the pure methane system. On the other hand, the selectivity of propylene increased with increasing percentage of propane in the feed. This indicates that propylene was produced from propane by the dehydrogenation mechanism as described in the pure propane system.

From these two figures, it can be pointed out that no maximum in the selectivities of all the products was observed, unlike the methane-ethane system. This might be because in the methane-ethane system, both ethane and methane could be converted to form all of the products. But in this case, propane did not seem to produce all of the products. This conclusion can be drawn from the fact that most product selectivities increased with an increase in methane concentration, except propylene for reasons described above.

Butane and butene were found in the system only when higher voltage was used. Their selectivities increased with increasing methane percentage in



**Figure 4.13** Product selectivities at different feed methane contents for applied voltage of 5,625 V and 40 ml/min flow rate (5.775 min residence time) in methane-propane system.



**Figure 4.14** Product selectivities at different feed methane contents for applied voltage of 6,250 V and 40 ml/min flow rate (5.775 min residence time) in methane-propane system.

the feed. This indicates that butane and butene would be produced from ethane that was formed from methane or propane, better than from methane reacting with propane. For these reasons, at the lower voltage and at the higher concentration of methane, the methane conversion was higher and produced more  $H_2$  from coupling of methane to form ethane. This made ethane less likely to dehydrogenate to suitable activated molecules for producing butane and butene. There are the same results as those obtained in the pure methane system.

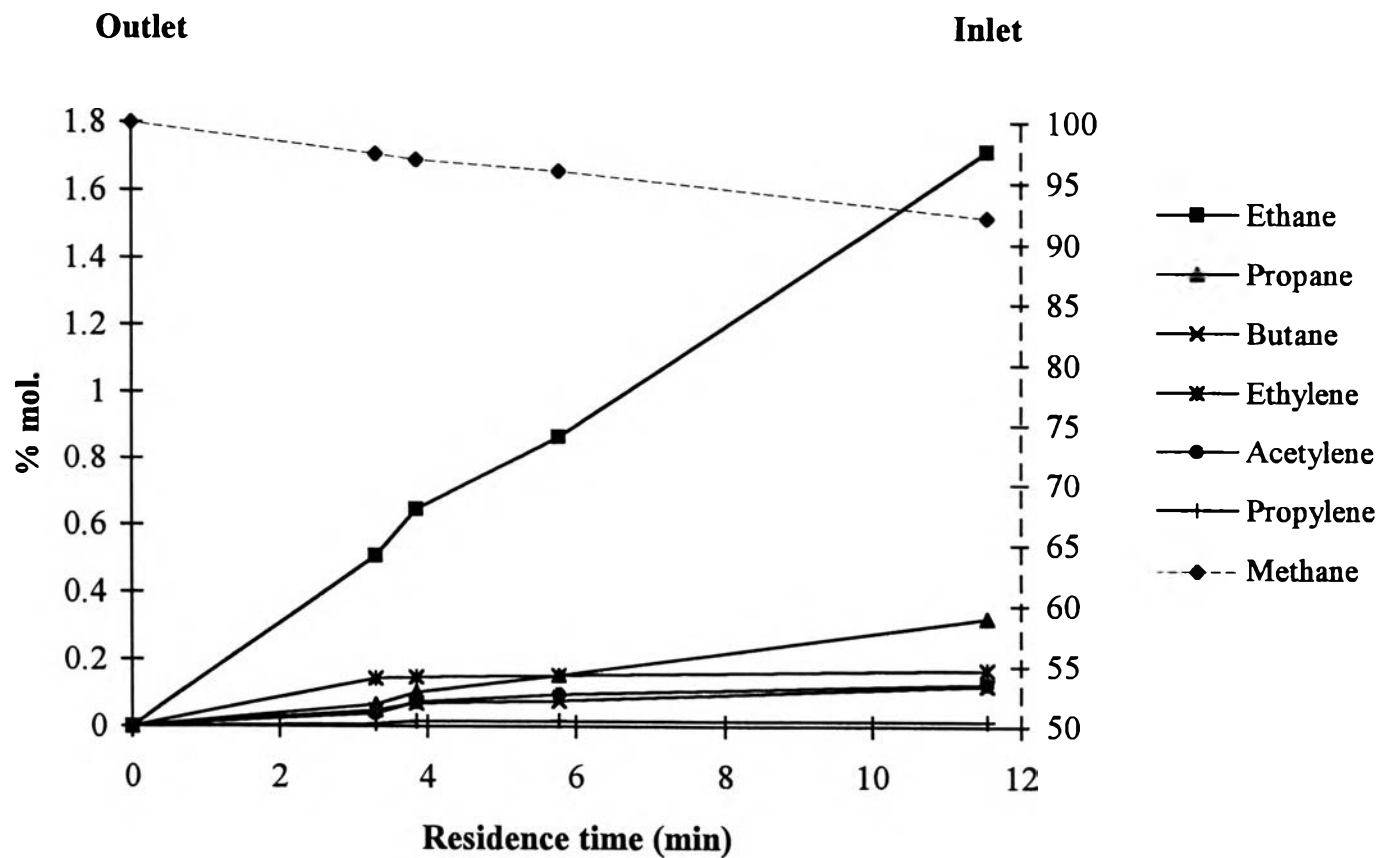
## 4.2 Kinetics of Reactions

### 4.2.1 Reaction Mechanisms in Studied Systems

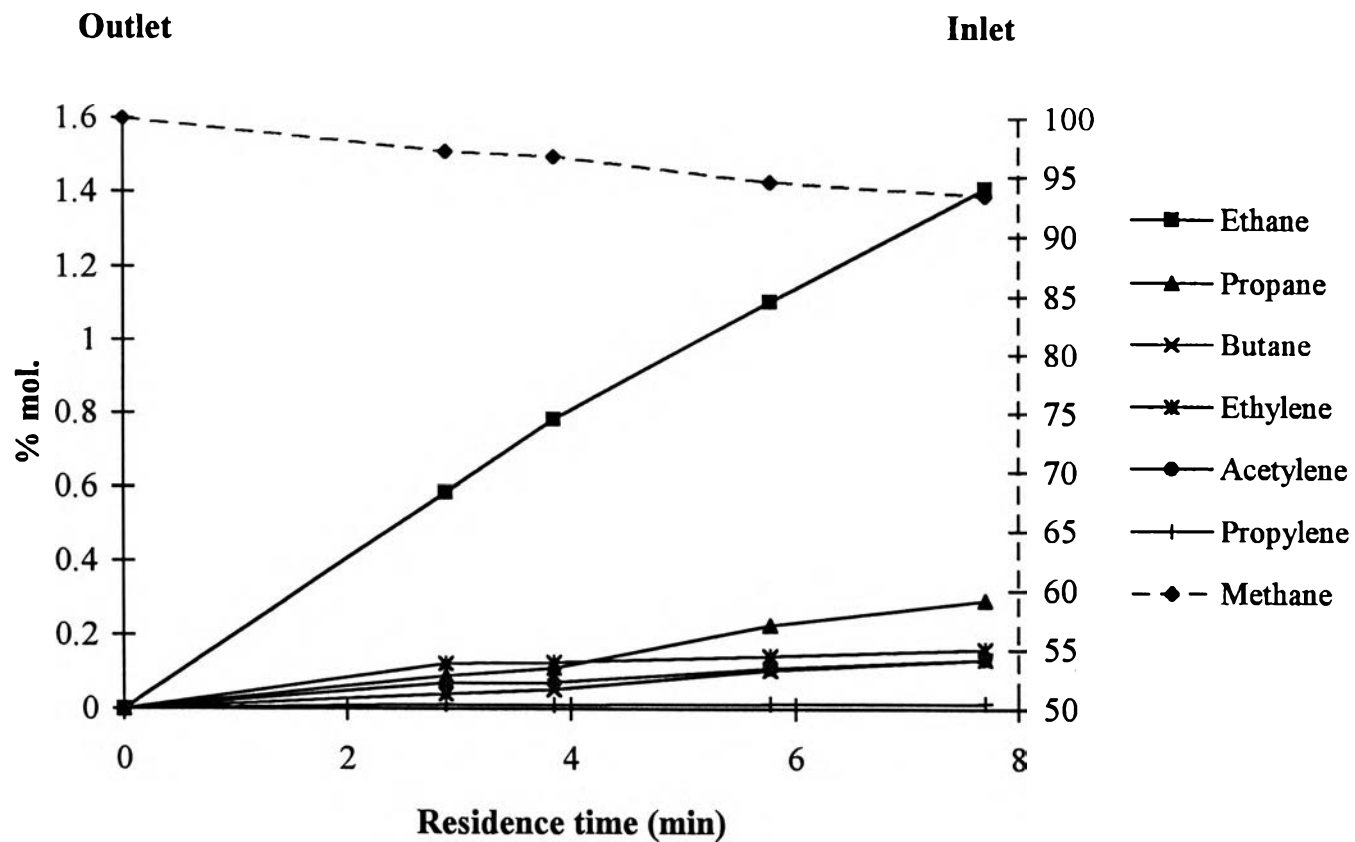
From chapter 2, many mechanisms reactions were suggested in general conditions. For each studied system, mechanisms would be different from each other because of the effect of the composition of the feed.

#### 4.2.1.1 *Pure methane system*

Figure 4.15 shows that ethane has the highest amount, so that, most methyl radicals, that came from reaction 2.1, would react to form ethane via reaction 2.6. Then ethane was activated to form ethyl radicals and reacted further to other products. It seemed that most ethyl radicals would react with methyl radicals to form propane via reaction 2.7. It is difficult to specify the reaction for other products that could occur from other species. Ethylene and propylene seemed to be constant at high residence time. This indicates that they reached an “equilibrium” from reactions 2.9, 2.10 and 2.11 for ethylene and reactions 2.14 and 2.15 for propylene. When comparing this figure with Figure 4.16, that operated at higher voltage, methyl radicals would be increased and made other products increase also. But the increased voltage



**Figure 4.15** Composition of inlet and outlet gases at different residence time of pure methane system operated at 5,625 V.



**Figure 4.16** Composition of inlet and outlet gases at different residence time of pure methane system operated at 6,250 V.



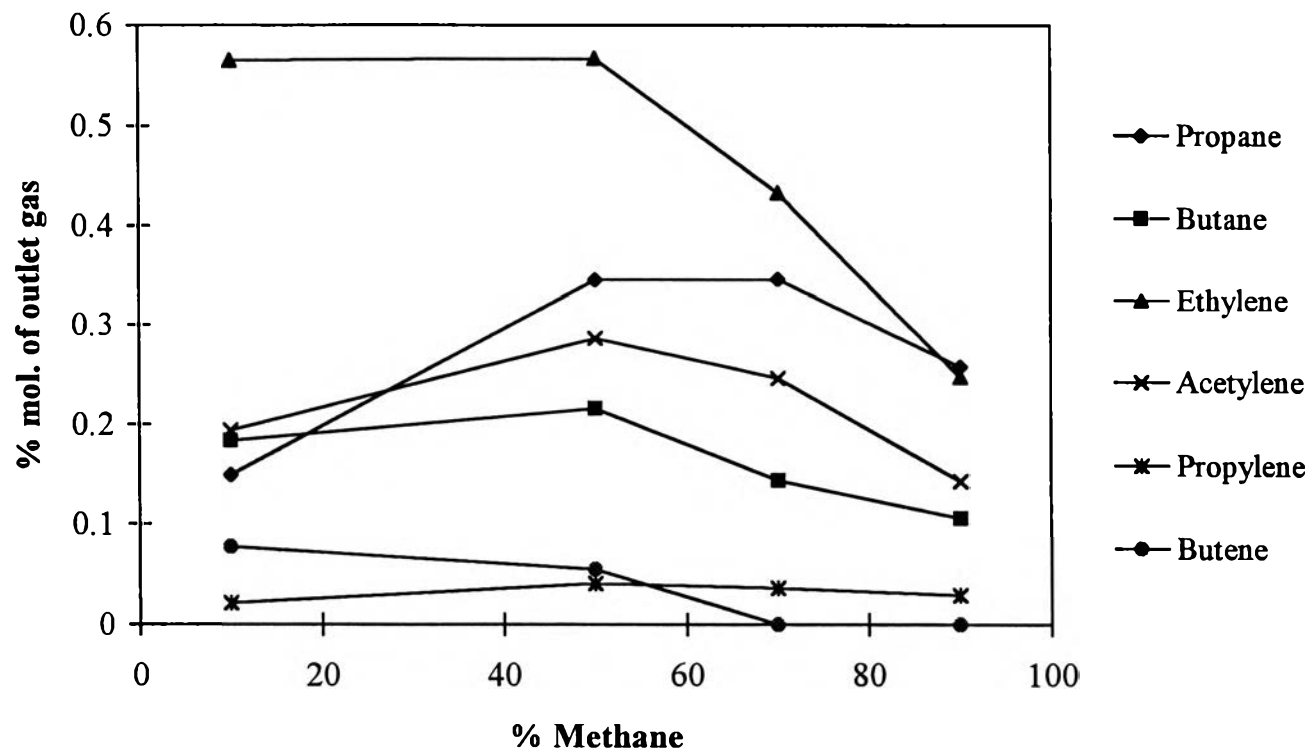
made the reactions producing ethylene and propylene less because of higher  $H_2$  in the system produced from C-C bond formation. So, the amount of both these products would be decreased with increased voltage.

#### *4.2.1.2 Methane-ethane system*

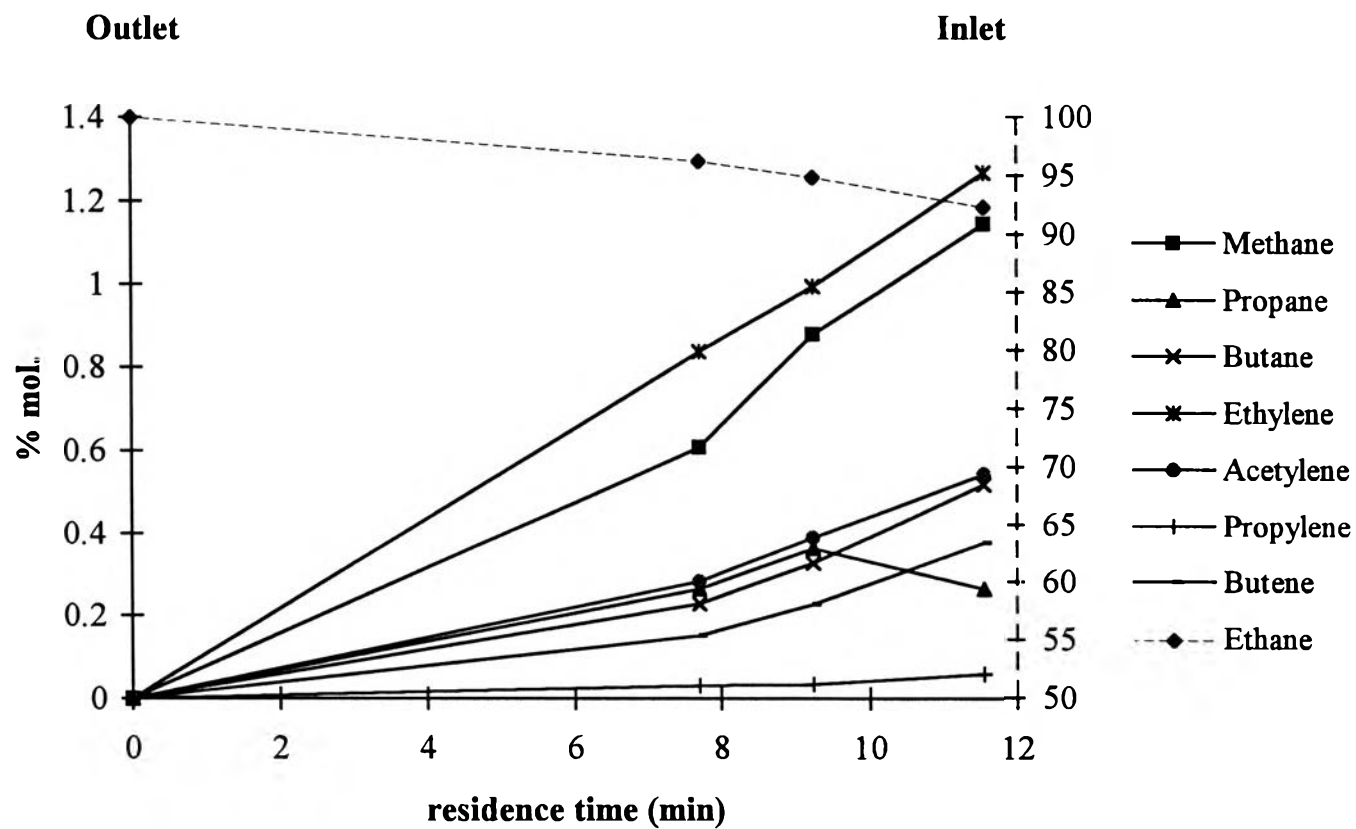
The relation between percentage of methane and percentage of products is shown in Figure 4.17. When increasing the methane in the feed, ethylene decreased significantly. This indicates that ethylene could be produced from reactions 2.8 and 2.9 more than from reactions 2.10 and 2.11. Propane could be produced from high methane concentration more than from high ethane concentration in the feed. From reaction 2.7, it indicates that methane could react to ethane first and then to propane more than from ethane cracking itself to form methane and then reacting with ethane to form propane. Propylene seemed to follow propane, on the other hand, butane, butene and acetylene seemed to be produced from ethane more than from methane because chain building (C-C formation) is less pronounced and more in balance with cracking reactions (C-C breaking). The former is an  $H_2$  producer, inhibiting olefins; while the latter is an  $H_2$  user, creating a more suitable environment for olefins formation.

#### *4.2.1.3 Pure ethane system*

Figure 4.18 illustrates that, in this system, dehydrogenation (reactions 2.2 and 2.9) is faster than cracking (reaction 2.6). So, ethylene was produced much more than propane. The other interesting point was, at high residence time, propane seemed to decrease and propylene appeared in a significant amount. This shows that, at high residence time, reaction 2.15 is more pronounced than any other reactions in producing propylene.



**Figure 4.17** Composition of outlet gas at different methane content in feed of methane-ethane system operated at 5,625 V and 40 ml/min flow rate (5.775 min residence time).



**Figure 4.18** Composition of inlet and outlet gases at different residence time of pure ethane system operated at 5,625 V.

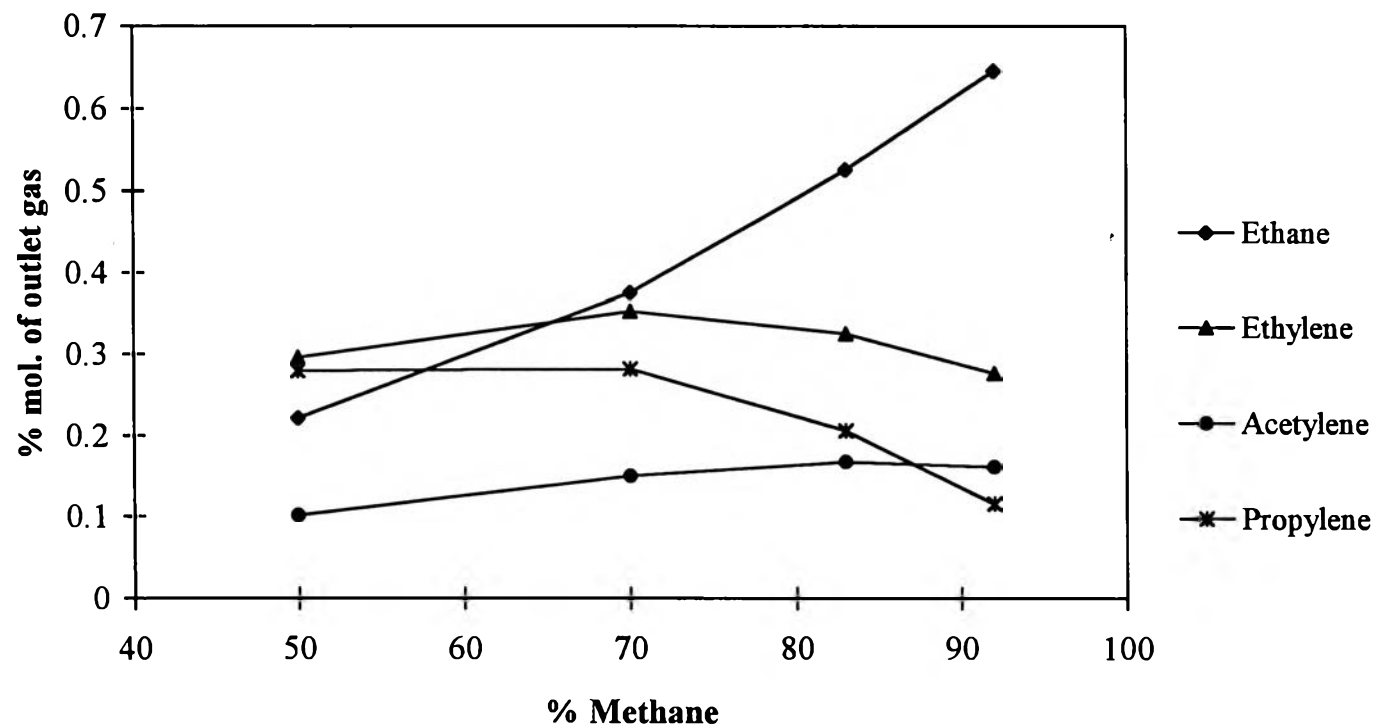
#### *4.2.1.4 Methane-propane system*

Figure 4.19 shows that ethane could be produced from reaction 2.6 faster than reaction 2.7. For propylene, reaction 2.15 seems faster than reaction 2.14 with high propane concentration in the feed. With less propane in the feed, reaction 2.14 became more significant. With reactions 2.12 and 2.13, ethylene was decreased because of less H<sub>2</sub> in the system, dehydrogenation to form acetylene occurred remarkably with increasing percentages of methane in the feed. Moreover, most ethylene was lost because most methyl radicals in reaction 2.10 reacted to form ethane (reverse reaction 2.6) instead of ethylene. When comparing this system with the methane-ethane system, at the same voltage, it is shown that butane can be produced via reaction 2.19 better than reaction 2.18. Butene also acts like butane, implying reaction 2.19 is better than reaction 2.24.

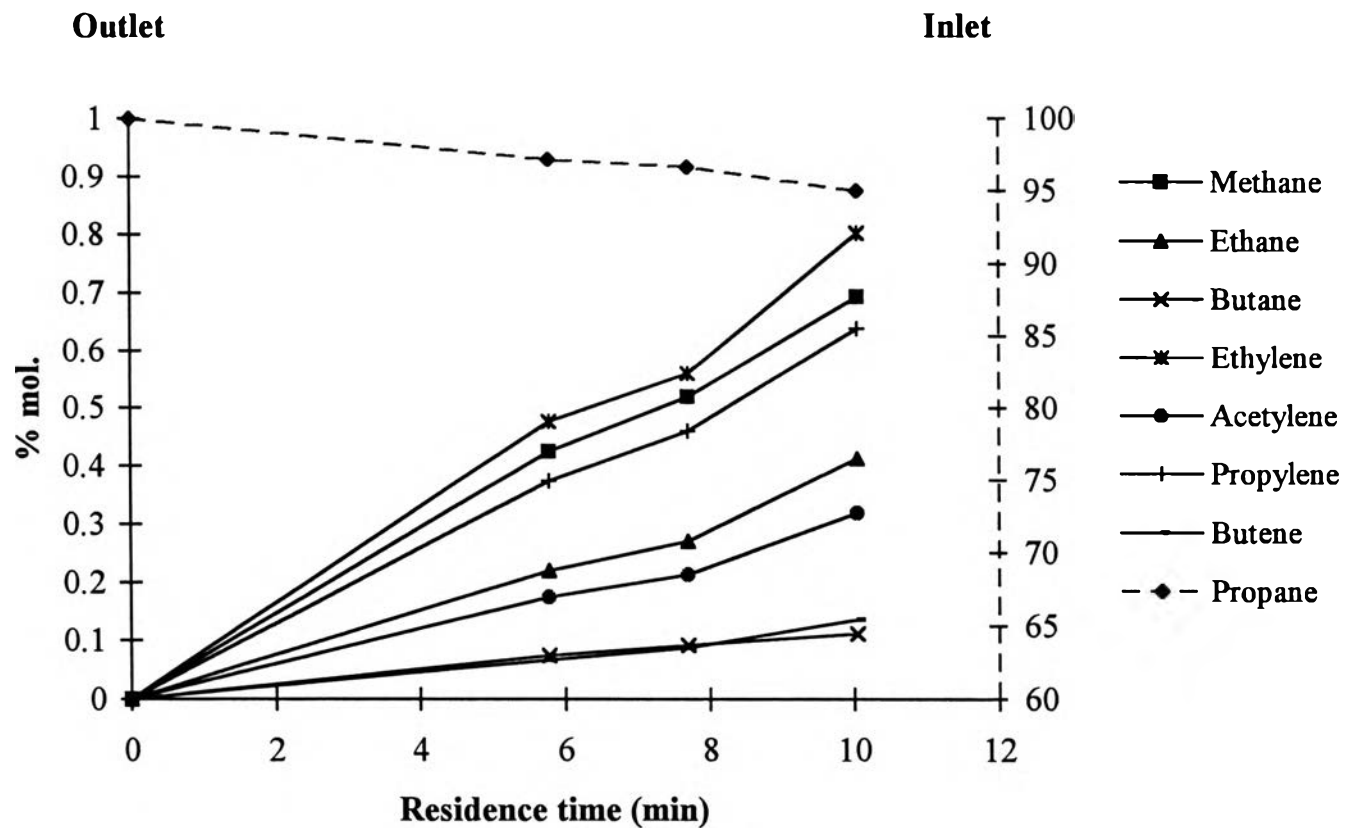
#### *4.2.1.5 Pure propane system*

From Figure 4.20, reaction 2.7 appeared to be faster than reaction 2.3, and reaction 2.1 and 2.9 were better than reactions 2.2 and 2.19. This made the percentage of ethylene and methane greater than that of propylene. Another point is that butene seemed to occur more than butane. From reaction 2.19, it is shown that the system had less H<sub>2</sub> molecules creating a better environment for olefins formation.

In this study, the experiments were not designed for calculating rates of these reactions so that these results only suggested the reactions that may occur.



**Figure 4.19** Composition of outlet gas at different methane content in feed of methane-propane system operated at 5,625 V and 40 ml/min flow rate (5.775 min residence time).



**Figure 4.20** Composition of inlet and outlet gases at different residence time of pure propane system operated at 6,250 V.

## 4.2.2 Determination of Reaction Rates

### 4.2.2.1 Differential Analysis

From chapter 2, using the solver in the Excel program, the parameters were obtained. Table 4.1 shows the calculated values of the kinetic constants of both methane-ethane and methane-propane systems.

**Table 4.1** Differential analysis results of methane-ethane and methane-propane system

System	$k_i$	$a_i$	$b_i$	$r^2$
<b>Methane-Ethane System</b>				
RCH <sub>4</sub>	0.000085	0.57	0.29	0.9868
RC <sub>2</sub> H <sub>6</sub>	0.000050	0.17	0.38	0.9971
<b>Methane-Propane System</b>				
RCH <sub>4</sub>	0.000022	0.87	-0.20	0.9908
RC <sub>3</sub> H <sub>8</sub>	0.000030	-0.21	0.17	0.8819

From this table, methane had a stronger influence on the rate of methane conversion. The fits for both cases were quite good although the reactions did not follow the first order kinetics.

Since the volume of the reactor was large, the residence times for all experiments were quite high to be considered a differential reactor. Thus the assumption of differential conditions may not be valid in some systems that have conversion more than 10%. Due to this, it was decided to apply a plug flow model for this reaction system.

### 4.2.2.2 Plug Flow Model

With the previous equations in chapter 2, using regression analysis from Excel program, we could find the rate for the methane-propane system, the

pure methane system, the pure ethane system and the pure propane system as show in Table 4.2.

**Table 4.2** Calculated values of rate expression of studied systems

System	Rate expression	r <sup>2</sup>
Pure Methane	$\left(-\frac{dP_{\text{CH}_4}}{dt}\right) = 0.0073 P_{\text{CH}_4}^{0.47}$	0.9829
Pure Ethane	$\left(-\frac{dP_{\text{C}_2\text{H}_6}}{dt}\right) = 0.006 P_{\text{C}_2\text{H}_6}^{0.71}$	0.9953
Pure Propane	$\left(-\frac{dP_{\text{C}_3\text{H}_8}}{dt}\right) = 0.00134 P_{\text{C}_3\text{H}_8}^{0.5}$	0.9990
Methane-Ethane	$\left(-\frac{dP_{\text{CH}_4}}{dt}\right) = 0.0019 P_{\text{CH}_4}^{0.75} P_{\text{C}_2\text{H}_6}^{-0.2}$	0.9937
	$\left(-\frac{dP_{\text{C}_2\text{H}_6}}{dt}\right) = 0.0172 P_{\text{CH}_4}^{0.35} P_{\text{C}_2\text{H}_6}^{0.89}$	0.9520
Methane-Propane	$\left(-\frac{dP_{\text{CH}_4}}{dt}\right) = 0.0029 P_{\text{CH}_4}^{0.4} P_{\text{C}_3\text{H}_8}^{0.26}$	0.9930
	$\left(-\frac{dP_{\text{C}_3\text{H}_8}}{dt}\right) = 0.0085 P_{\text{CH}_4}^{0.31} P_{\text{C}_3\text{H}_8}^{0.4}$	0.9827

The reaction orders, for the partial pressure of all reactants, are low for the conversion rates. The methane conversion rate increases slightly with an increase in the partial pressure of both reactants, respectively. Thus to increase the rate significantly, the values of the rate constants will have to be increased. Since the applied voltage directly initiate the reaction to occur, an increase in the voltage will lead to an increase in the rate constants. For the pure methane system, when the voltage was increased, the rate equation was recalculated with the same order to find new rate constant.

$$\left(-\frac{dP_{\text{CH}_4}}{d\tau}\right) = 0.009 P_{\text{CH}_4}^{0.47}, \quad r^2 = 0.9940$$

This supports the previous discussion in that rate constant increased from 0.0073 to 0.009 when the voltage was increased from 5,625 to 6,250 V.