CHAPTER IV
RESULTS AND DISCUSSION

4.1 Mass Transfer Limitation

Figure 4.1 shows CH_4 conversion decreases as the total flow rate increases at the power supply equal 80 watt. Normally, the increased flow rate gives the higher conversions, if there is a mass transfer limitation. But in this case, no mass transfer limitation occurs in the condition that the total flow rate is equal to 50 ml/min because as seen from Figure 4.1 the product of flow rate times the conversion actually decreases. However, the conversion normally decreases when the flow rate increases due to the less contact time. This relationship should decrease almost linearly if the heat removal effect does not occur. It may decrease more than proportionately due to the losing heat to the reactant gases. Since there were no mass transfer limitations, the total flow rate in all experiments was used at 50 ml/min.

4.2 The Effects of CO_2/CH_4 Feed Ratio

4.2.1 Water Formation Rate

At various CO_2/CH_4 feed ratio from 0.3 to 2.0, the water formation rate increases as shown in Figure 4.2. This water may come from two routes.

(i) Reverse Water Gas Shift Reaction

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad [6]$$

This reaction always gives the H_2/CO ratio less than 1.

(ii) Carbon Gasification

$$CO + H_2 \leftrightarrow C + H_2O \qquad [9]$$

The equimolar amounts of CO and H_2 are used to produce water and carbon. Then, the H_2/CO product ratio should not change by this reaction.

Thus, it is possible that the water may come from reverse water gas shift reaction only or come from both reactions simultaneously. If the water comes from both reactions, the first reaction is considered to be a dominant reaction because the production rate of CO is always higher than that of H_2 as shown in Figures 4.3-4.7.

However, the water formation decreases at CO_2/CH_4 feed ratio equal to 3.0. It might be that the large production rates of CO with the increased CO_2/CH_4 feed ratio prevents the water formation by water gas shift reaction.

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad [16]$$

4.2.2 Carbon Formation on Catalyst

At various CO_2/CH_4 feed ratio from 0.3 to 2.0, the carbon formation rate increases as shown in Figure 4.8. The carbon may come from two routes.

(i) Methane Cracking

$$CH_4 \rightarrow C + 2H_2 \qquad [7]$$

This equation shows that, the amount of H_2 should increase with the occurrence of carbon.

Table 4.1 shows that the production rate of H_2 is not proportional to the occurrence of carbon, so the carbon formation rate should not come only from methane cracking. Thus, the increased feed rate of CO_2 should effect on the carbon formation while the feed rate of CH_4 is constant.

(ii) Boudouard Reaction

$$2CO \leftrightarrow C + CO_2 \qquad [8]$$

This reaction is favored at low temperatures and the upper temperature limit of this reaction is 700°C. So, this reaction is not considered in this study because higher reaction temperatures were observed from the experiments.

Normally, the increased CO_2/CH_4 feed ratio gives the less carbon formation (Alstrup and Tavares, 1992). Due to the higher concentrations of CO_2, the carbon occurring from Boudouard reaction will be reduced.

From the observation, a yellow-white deposition occurred on the reactor wall. Gesser et al. (1994) identified the yellow-white deposition as an oxide of tungsten probably formed by the following reaction

$$W + xCO_2 \rightarrow WO_x + xCO \qquad [11]$$

Table 4.1 The average values taking from 200-700 min in time of carbon formation and production rates of H_2 and CO at various CO_2/CH_4 feed ratio; given a constant methane composition of 15% by mol in helium and a total flow rate of 50 ml/min by employing 0.236 g of tungsten

CO_2/CH_4 feed ratio	Feed Rate (μ mol/min.g)		Total Feed Rate Carbon from CH_4 and CO_2 (μ mol/min.g)	% Conversion		Unreacted (μ mol/min.g)		Production Rate (μ mol/min.g)		Carbon Formation Rate (μ mol/min.g)
	CH_4	CO_2		CH_4	CO_2	CH_4	CO_2	H_2	CO	
0.3	1312	438	1750	42	93	760	30	738	765	195
0.6	1327	845	2171	49	68	680	268	757	935	288
1.0	1387	1374	2762	65	73	491	378	1010	1427	465
2.0	1347	2729	4076	67	49	442	1390	818	1609	635
3.0	1305	3942	5247	57	33	556	2629	686	1485	576

It is possible that a fraction of CO_2 can react with tungsten resulting in tungsten oxide in the system. Less amount of CO_2 would be available to remove carbon from the catalyst surface, according to the reaction [8]. Thus, the carbon formation increases as CO_2/CH_4 feed ratios increases. Furthermore, the amount of carbon formation corresponds with the increased CO.

However, the deposited carbon decreases at CO_2/CH_4 feed ratio equal to 3.0. It might be that the large amount of produced surface H_2 from the main reaction prevents carbon deposition.

4.2.3 H_2/CO Product Ratio

The H_2/CO production ratio decreases as the CO_2/CH_4 feed ratio increases as shown in Table 4.2. This is because of the reverse water gas shift reaction. It should be noted that the suitable condition which enhances synthesis gas selectivity and prevents oxidation of products is the condition that gives the H_2/CO production ratio close to one and gives high both H_2 and CO production rates. As can be seen from Table 4.2, the suitable CO_2/CH_4 feed ratio is equal to 1.0.

Table 4.2 The average values taking from 200-700 min in time of selectivity and H_2/CO product ratio at various CO_2/CH_4 feed ratio; given a constant methane composition of 15% by mol in helium and a total flow rate of 50 ml/min by employing 0.236 g tungsten at 983 K

CO_2/CH_4 feed ratio	Selectivity*		Production Rate of (μmol/min.g)		H_2/CO product ratio
	H_2	CO	H_2	CO	
0.3	0.70	0.87	738	765	0.96
0.6	0.62	0.83	757	935	0.81
1.0	0.63	0.83	1010	1427	0.71
2.0	0.49	0.78	818	1609	0.51
3.0	0.48	0.75	686	1485	0.46

* Selectivity = mole of observed desired product
mole of theoretical desired product

Furthermore, methane conversion increases as the CO_2/CH_4 feed ratio increases as shown in Figures 4.9-4.13 due to the increased feed rate of CO_2 while the feed rate of CH_4 is constant.

4.3 The Effects of Reaction Temperature

Figures 4.14-4.17 show that the higher the reaction temperatures, the higher the CH_4 and CO_2 conversions. Since the reaction is endothermic the CH_4 and CO_2 conversions should increase when the reaction temperature increases.

At low temperatures, 863-946 K, the production rate of H_2 is always higher than that of CO as shown in Figures 4.18-4.20. Hydrogen may come from methane cracking, methane is thermally cracked to carbon and hydrogen,

$$CH_4 \rightarrow C + 2H_2 \tag{7}$$

and /or the higher hydrocarbon formation,

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \tag{16}$$

$$2CH_4 \rightarrow C_2H_4 + 2H_2 \tag{17}$$

$$2CH_4 \rightarrow C_2H_6 + H_2 \tag{18}$$

Since some traces of higher hydrocarbon formation occurred methane cracking is considered as the main source of hydrogen.

Both methane reforming and methane cracking will lead to higher H_2/CO ratios. Figures 4.14-4.16 also show that CH_4 conversion is higher than CO_2 conversion. Thus, confirming that the excess of hydrogen comes from these reactions.

Since the reverse water gas shift reaction consumes $CO_2 : H_2 = 1:1$ it should increase CO/H_2 ratio in excess CO_2. At high temperature, 983 K, the amounts of H_2 and CO are almost the same as shown in Figure 4.21. Moreover, Figure 4.22 shows that the large amount of water formation is observed at this temperature. This can be explained that the H_2 is consumed by the reverse water gas shift reaction,

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{6}$$
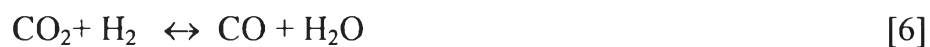
The other reaction is the desorption of hydrogen from the surface of tungsten without participating in the higher hydrocarbon formation at high temperature thus incresing the H_2/CO ratios. The amounts of CO and H_2 are the same at high temperature since both reactions appear to go on at an equal rate.

4.4 Finding the Activation Energies of H_2 and CO Formation

The activation energies were obtained from Table 4.3 which shows the production rates at various reaction temperatures by plotting the rates of H_2 and CO against the reciprocal of temperature (1/T).

Table 4.3 The production rates at various reaction temperatures at a constant methane composition of 15% by mol in helium and a total flow rate of 50 ml/min by employing 0.236 g tungsten, $CO_2/CH_4 = 1$

Power Supply (Watt)	Temperature (K)	1/T (K^{-1})	Production Rate of (μmol/min.g)		ln (rate of H_2)	ln (rate of CO)
			H_2	CO		
86	631.22	0.002	207	218	5.33	5.39
90	647.17	0.002	315	430	5.75	6.06
105	706.96	0.001	754	927	6.62	6.83
110	726.90	0.001	1023	1446	6.93	7.28
120	766.76	0.001	1483	1825	7.30	7.51

The activation energies for H_2 and CO formation are nearly the same as shown in Figures 4.23 and 4.24. This indicates that H_2 and CO are primarily formed by the same reaction pathway and have the same limiting step.
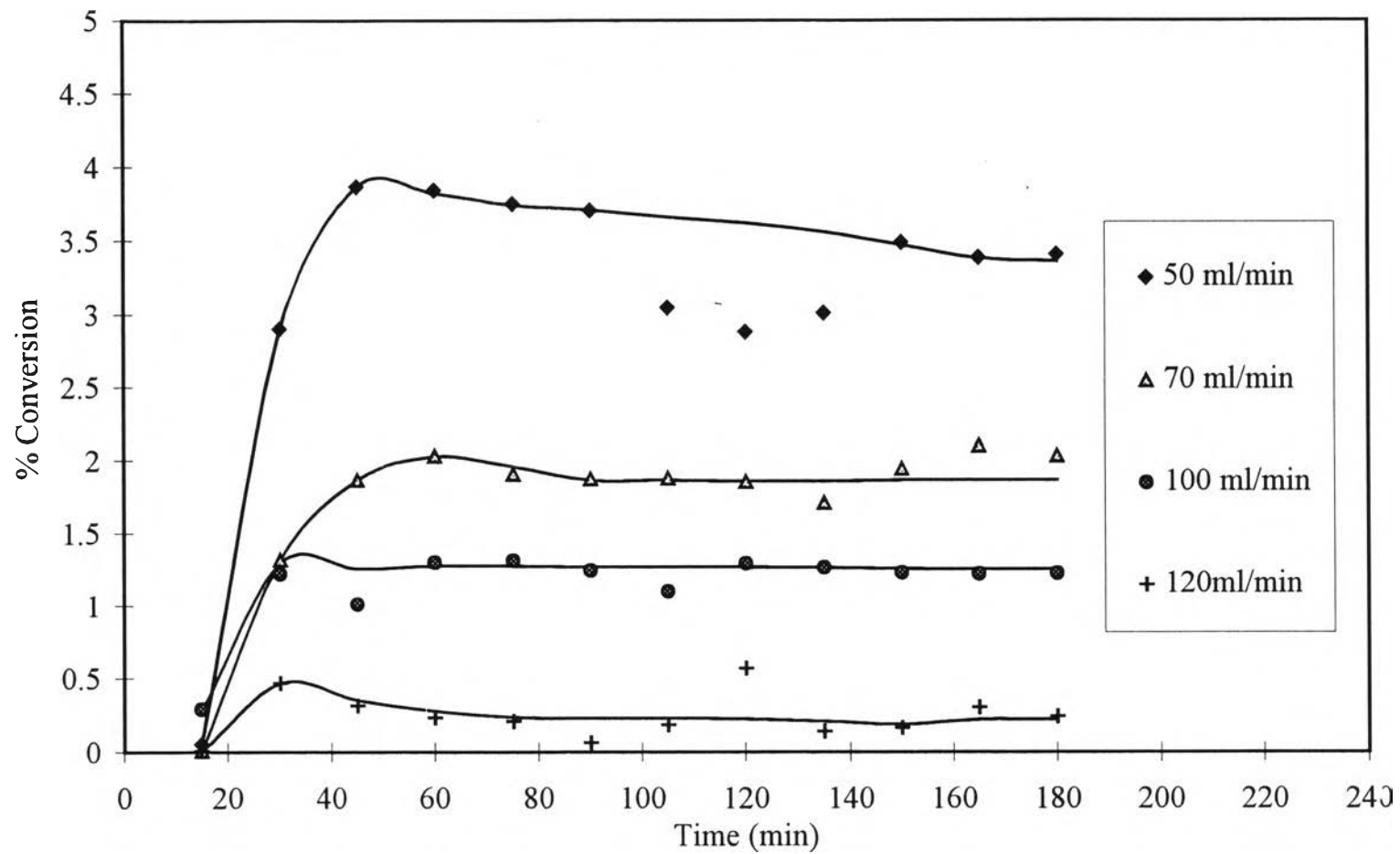
Figure 4.1 Plot of CH$_4$ conversions against flow rates, CO$_2$/CH$_4$ = 1.0, 863 K.
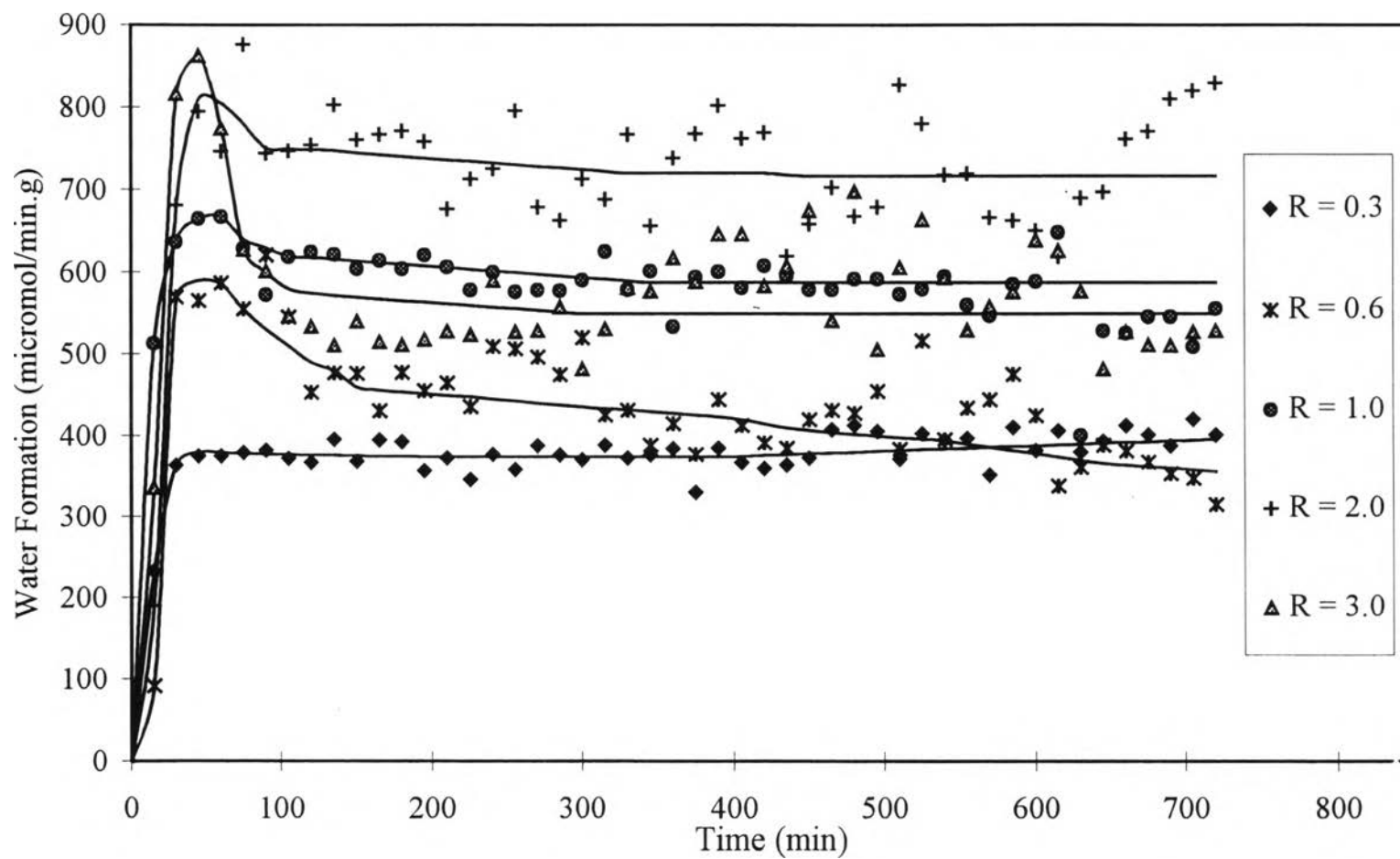
Figure 4.2 Plot of water formation rate against CO_2/CH_4 (R) ratios at the constant 15% by mol methane in helium and the total flow rate 50 ml/min by using 0.236 g tungsten, 983 K.
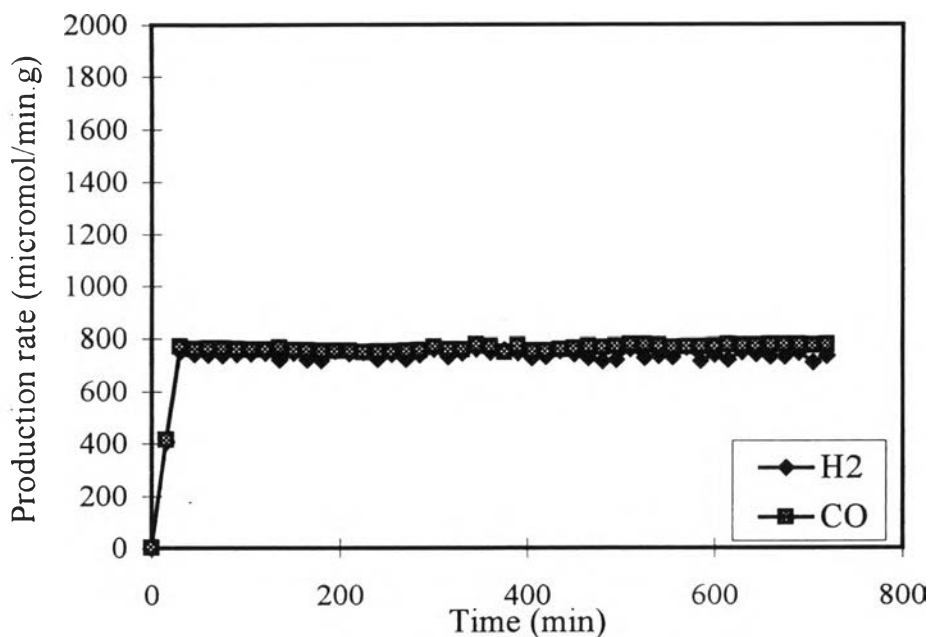
Figure 4.3 Plot of production rates of H_2 and CO at CO_2/CH_4 = 0.3; given the constant 15% by mol CH_4 and the total flow rate 50 ml/min by using 0.236 g tungsten, 983K.
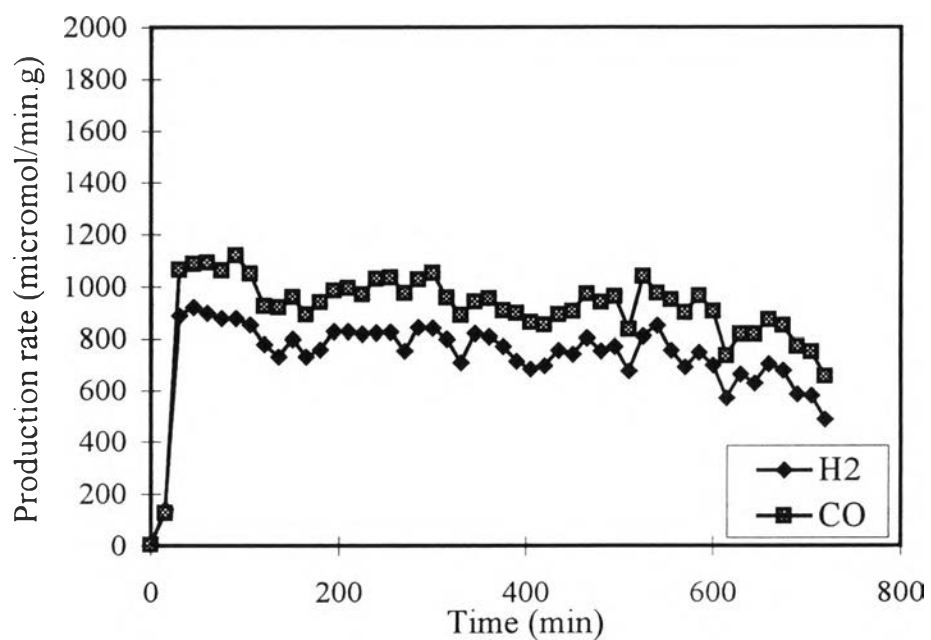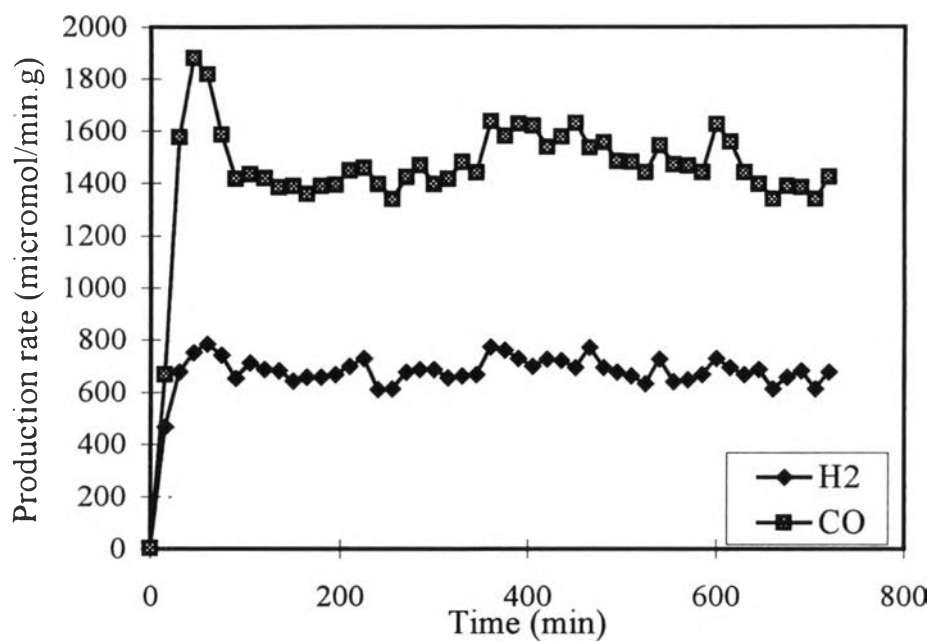

Figure 4.4 Plot of production rates of H_2 and CO at CO_2/CH_4 = 0.6; given the constant 15% by mol CH_4 and the total flow rate 50 ml/mm by using 0.236 g tungsten, 983K.
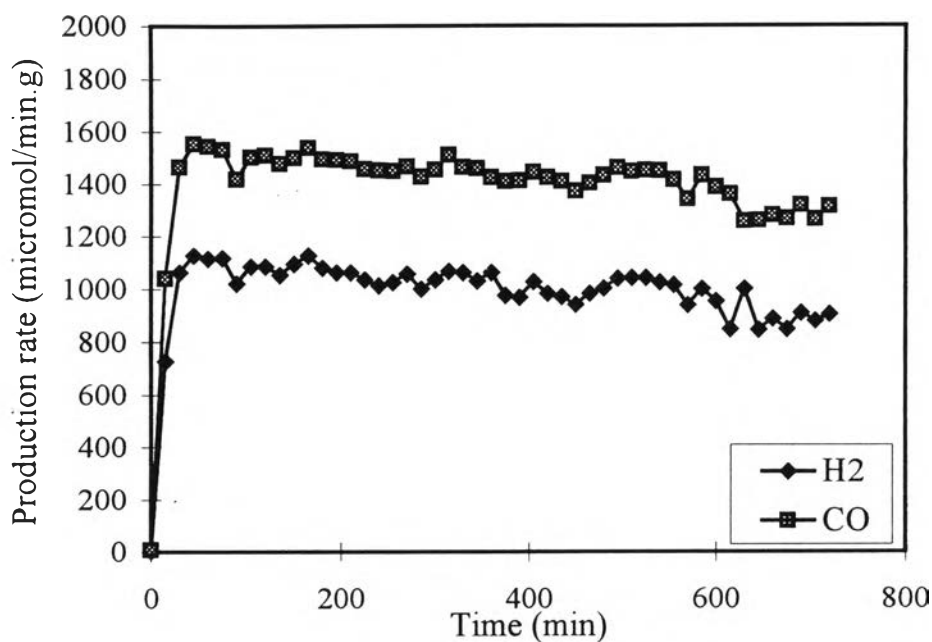
Figure 4.5 Plot of production rates of H_2 and CO at CO_2/CH_4
= 1.0; given the constant 15% by mol CH_4 and
the total flow rate 50 ml/min by usmg 0.236 g
tungsten, 983K.
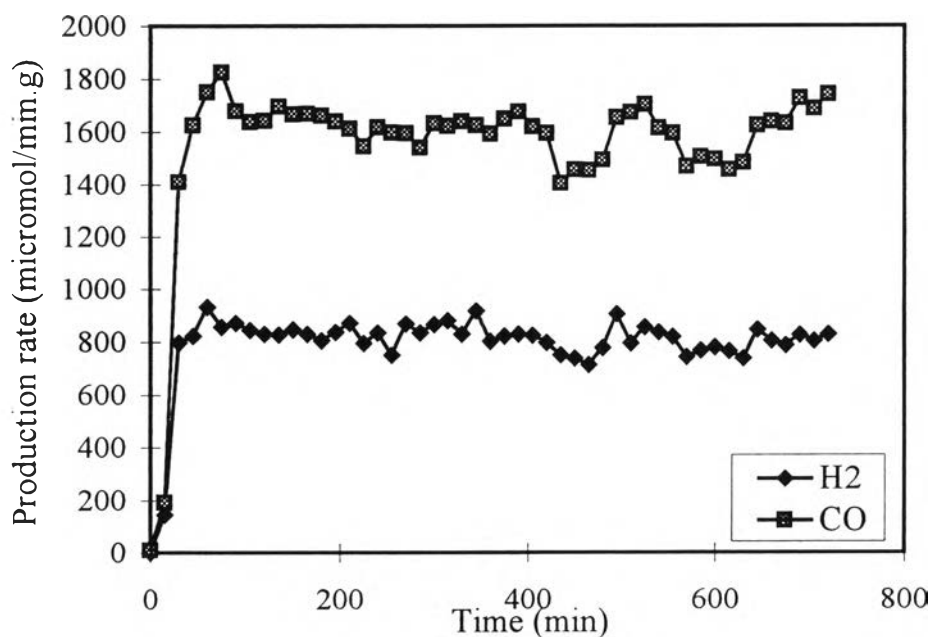
Figure 4.6 Plot of production rates of H_2 and CO at CO_2/CH_4
= 2.0; given the constant 15% by mol CH_4 and
the total flow rate 50 ml/min by using 0.236 g
tungsten, 983K.

Figure 4.7 Plot of production rates of H_2 and CO at CO_2/CH_4 = 3.0; given the constant 15% by mol CH_4 and the total flow rate 50 ml/min by using 0.236 g tungsten, 983K.
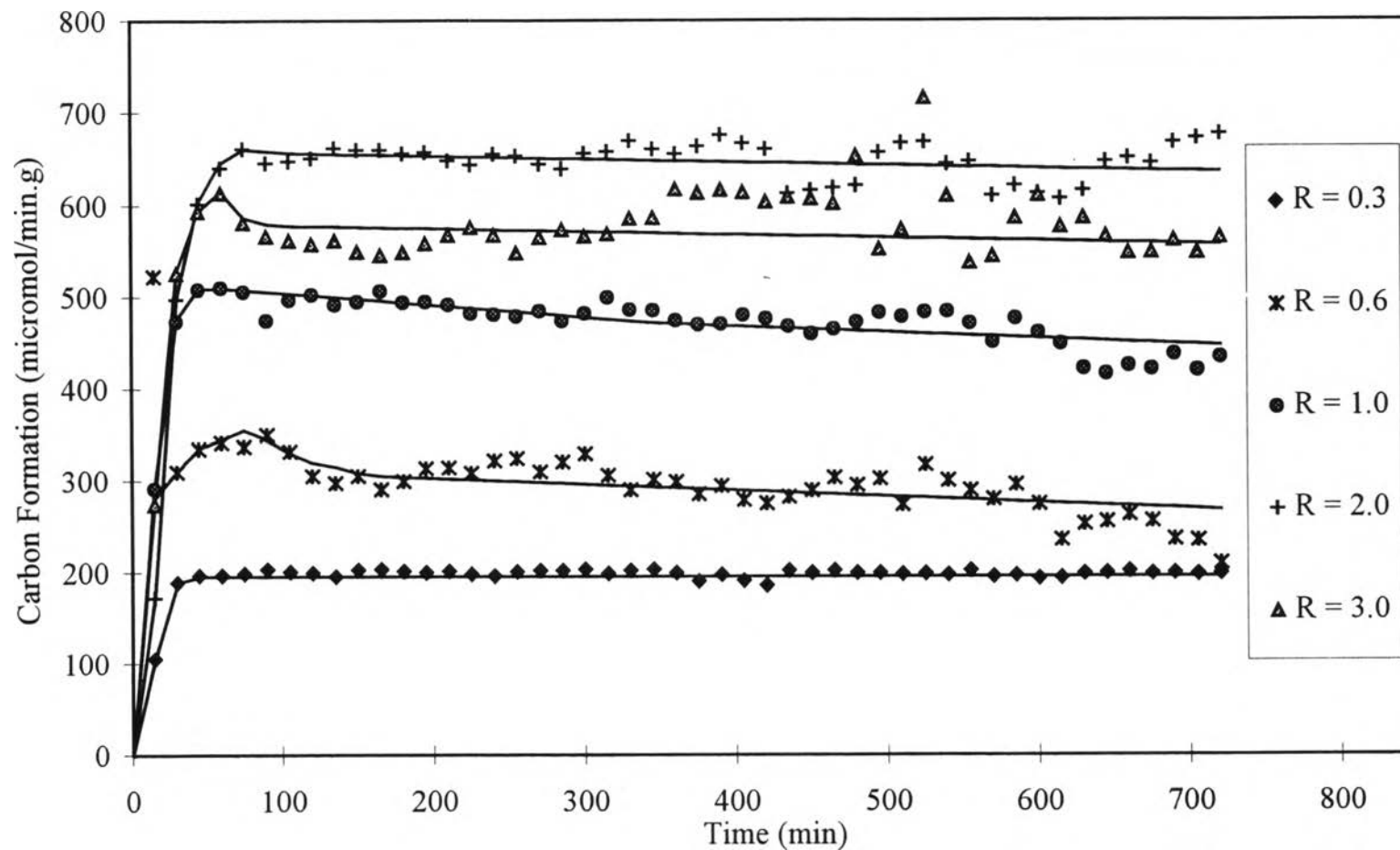
Figure 4.8 Plot of carbon formation rate against CO_2/CH_4 (R) ratios at the constant 15% by mol methane in helium and the total flow rate 50 ml/min by using 0.236 g tungsten, 983 K.
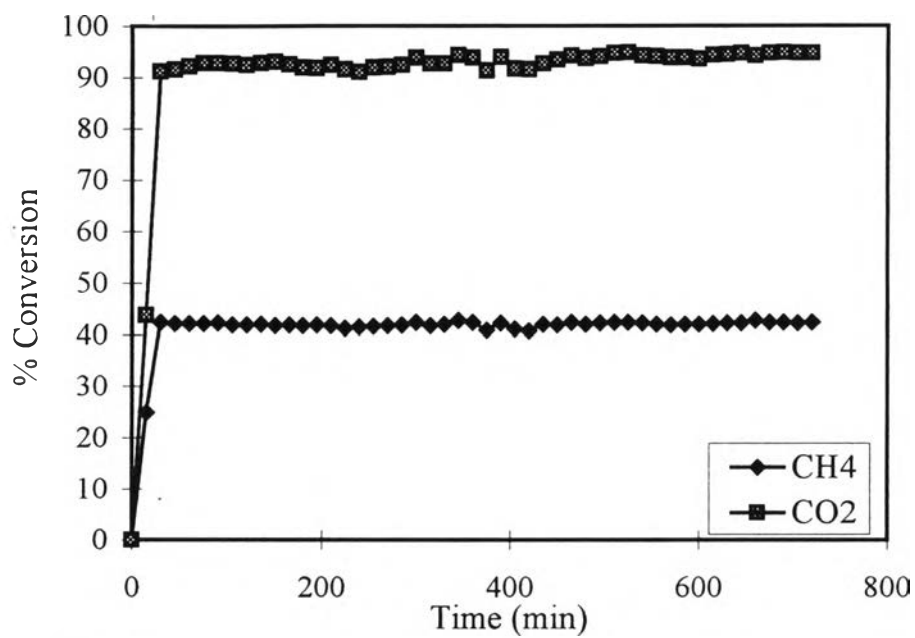
Figure 4.9 CH$_4$ and CO$_2$ conversions at CO$_2$/CH$_4$ = 0.3,
T = 983 K.
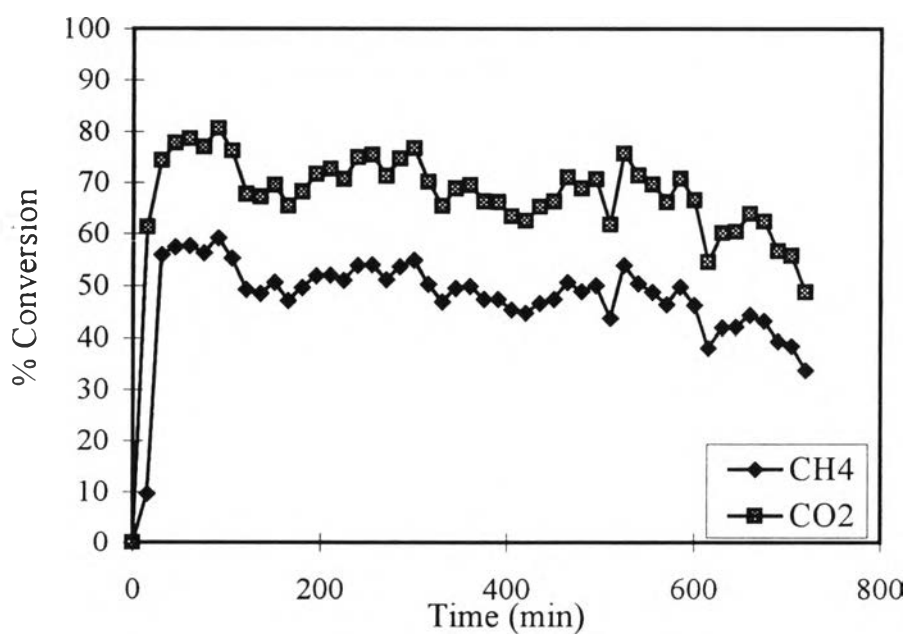
Figure 4.10 CH$_4$ and CO$_2$ conversions at CO$_2$/CH$_4$ = 0.6,
T = 983 K.
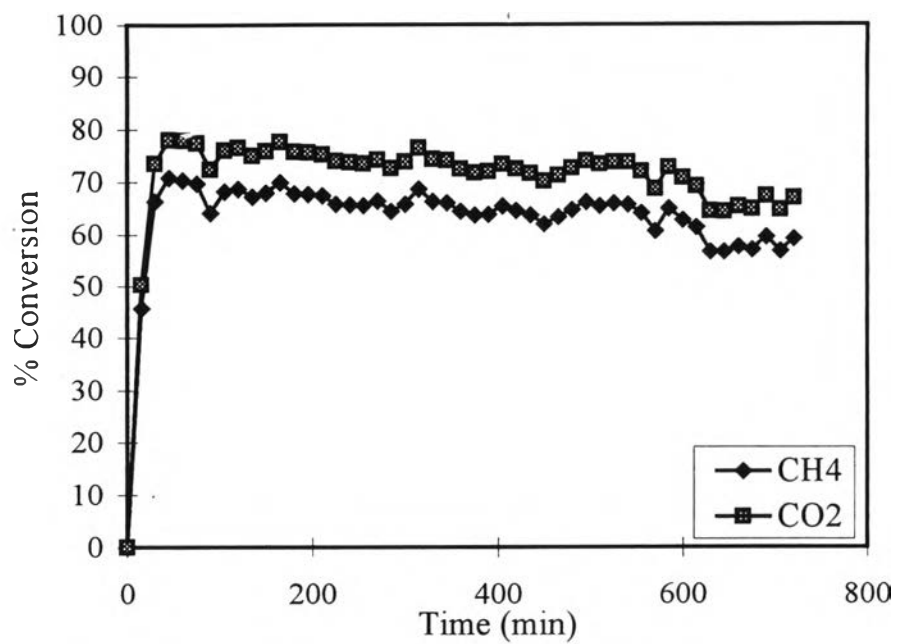
Figure 4.11 CH_4 and CO_2 conversions at $CO_2/CH_4 = 1.0$,
        T = 983 K.
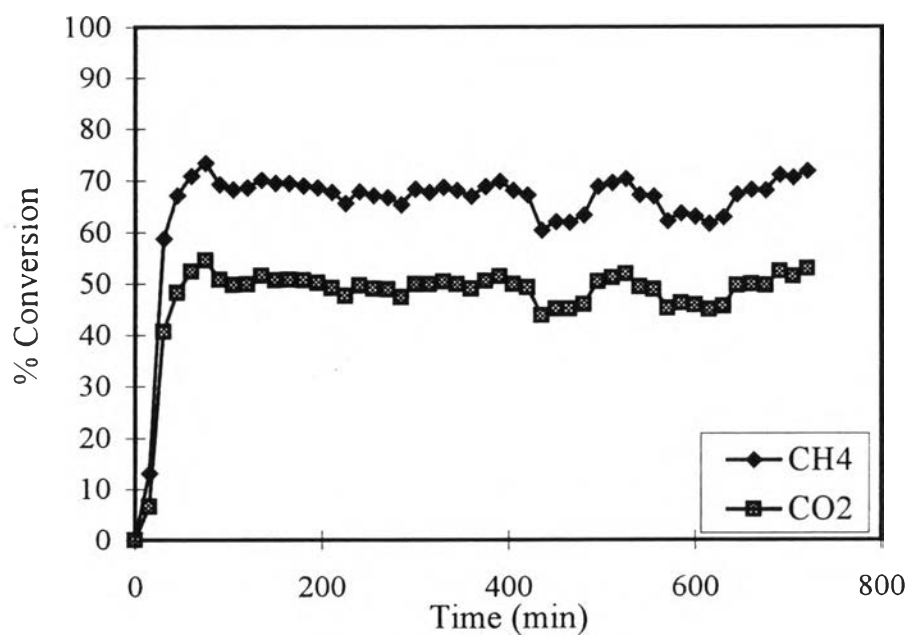
Figure 4.12 CH_4 and CO_2 conversions at $CO_2/CH_4 = 2.0$,
        T = 983 K.
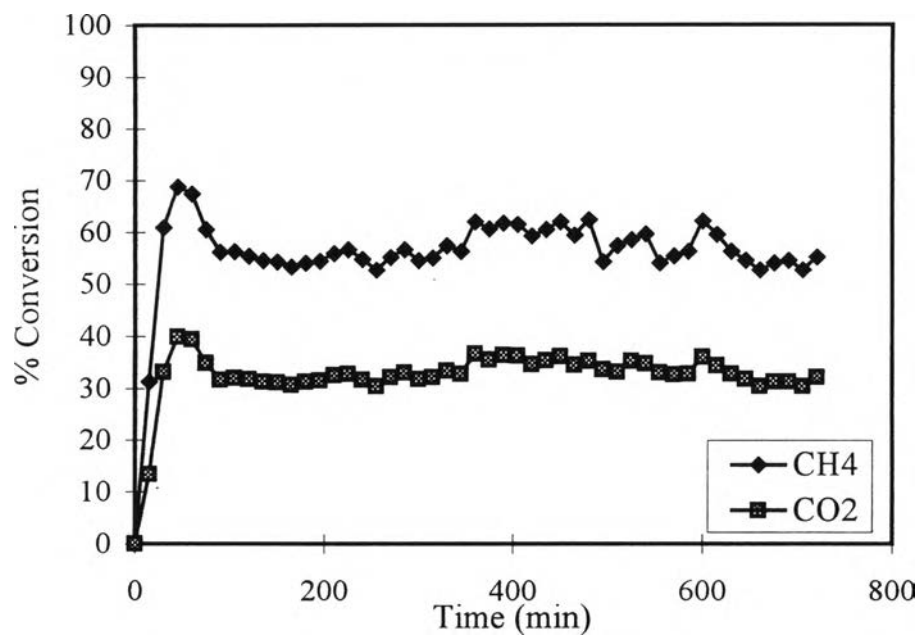
Figure 4.13 CH_4 and CO_2 conversions at $CO_2/CH_4 = 3.0$,
T = 983 K.
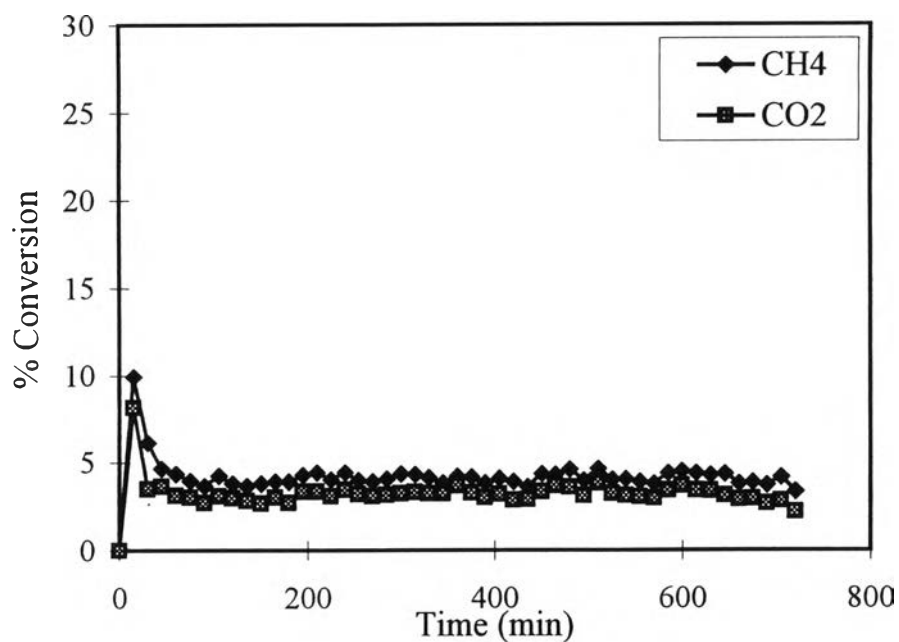
Figure 4.14 CH_4 and CO_2 conversions at $CO_2/CH_4 = 1.0$,
power supply = 80 watt (T = 863 K).
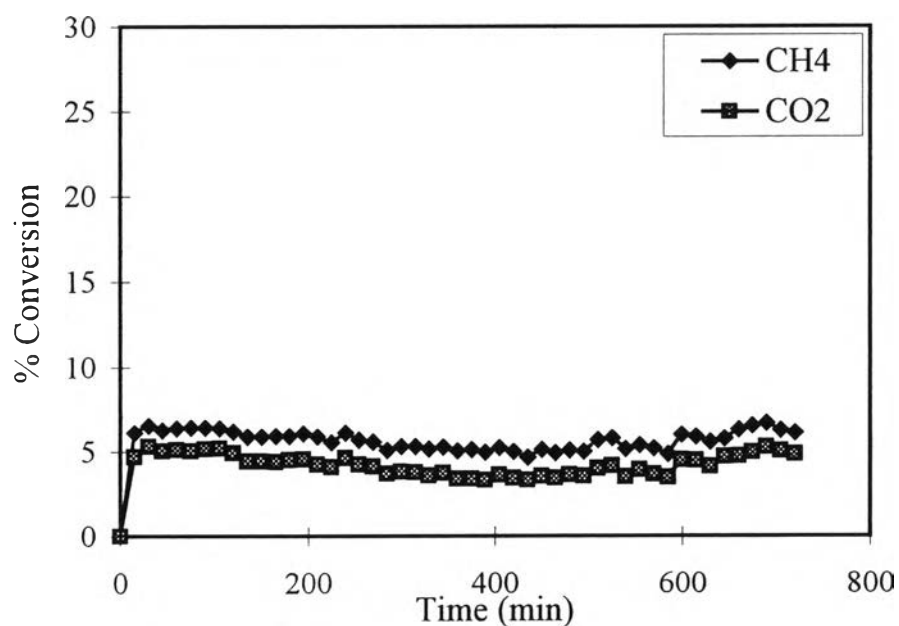
Figure 4.15 CH_4 and CO_2 conversions at $CO_2/CH_4 = 1.0$,
power supply = 90 watt (T = 903 K).
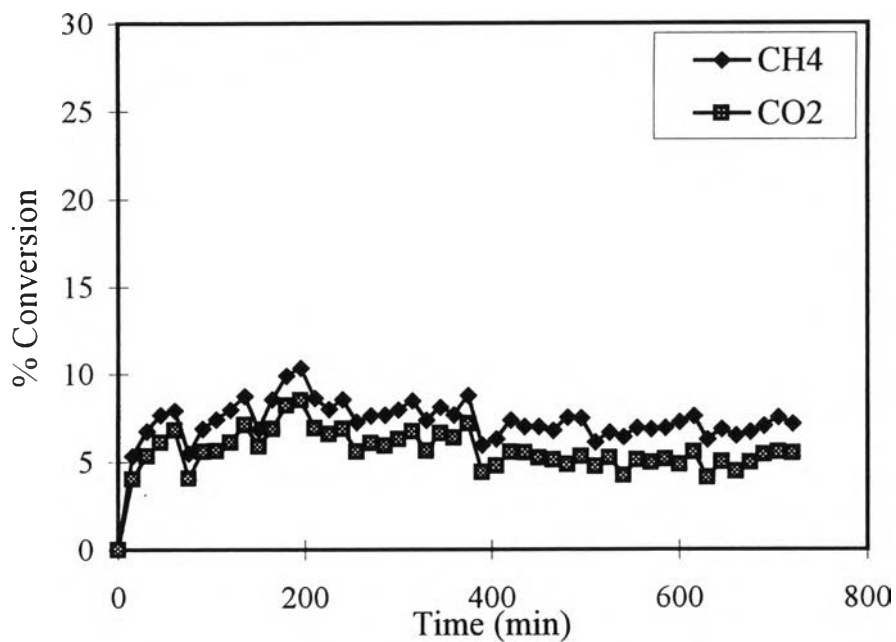
Figure 4.16 CH_4 and CO_2 conversions at $CO_2/CH_4 = 1.0$,
power supply = 100 watt (T = 946 K).
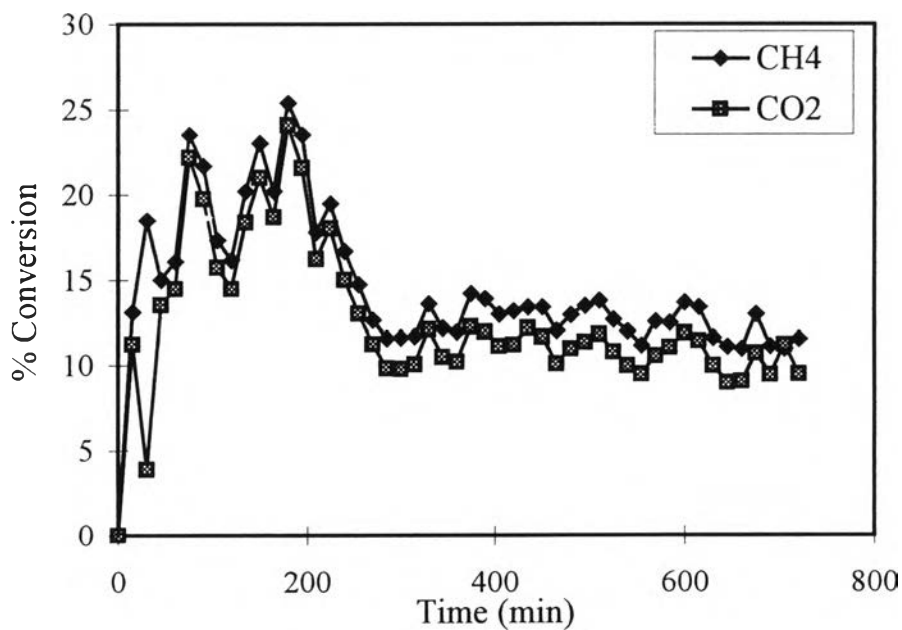
Figure 4.17 CH_4 and CO_2 conversions at $CO_2/CH_4 = 1.0$,
power supply = 110 watt (T = 983 K).
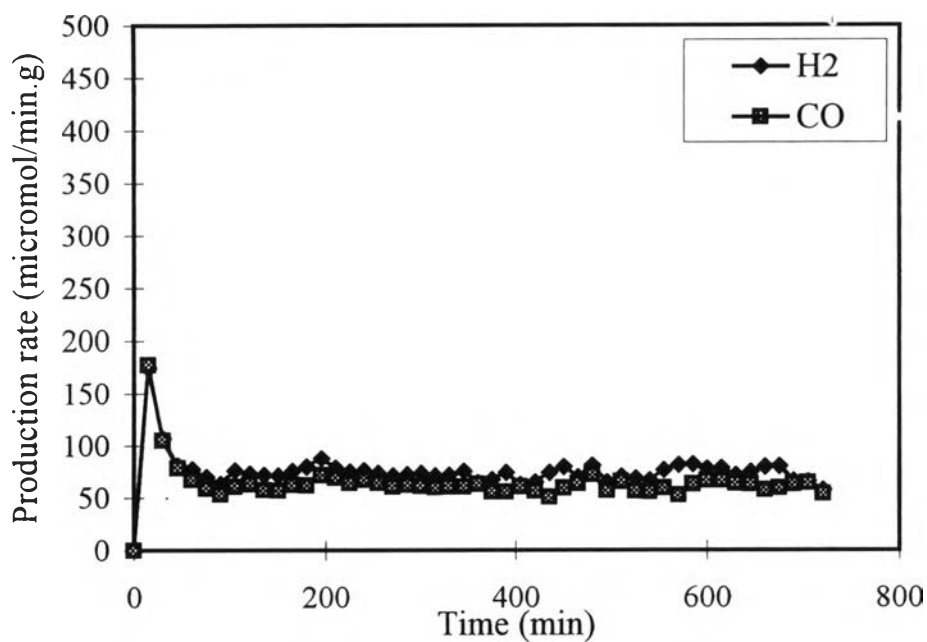
Figure 4.18 Plot of production rates of H_2 and CO using power
supply = 80 W(T = 863 K); given the constant 15%
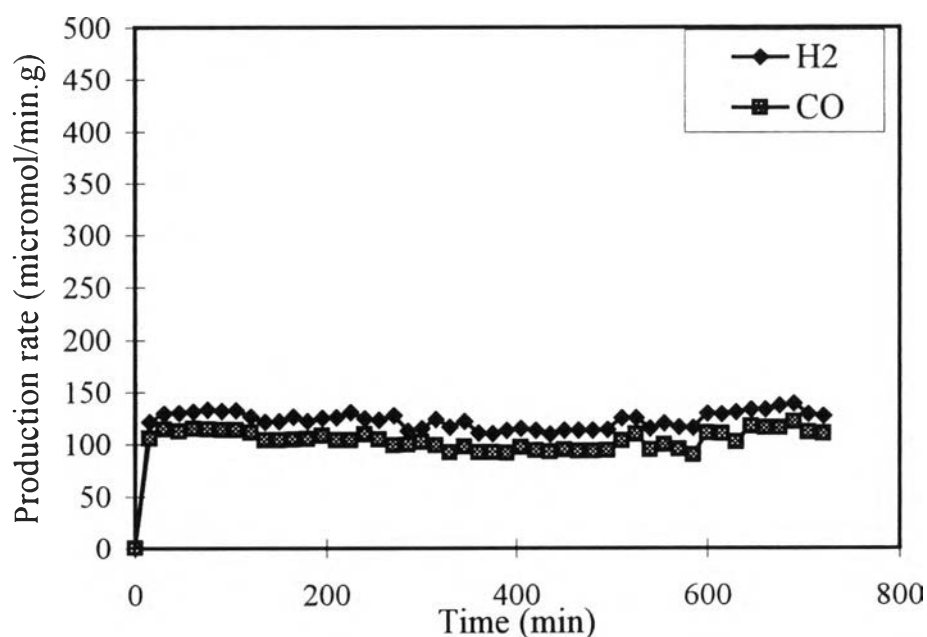by mol CH_4 and the total flow rate 50 ml/min by
using 0.236 g tungsten, CO_2/CH_4 = 1.0.

Figure 4.19 Plot of production rates of H_2 and CO using power
supply = 90 W(T = 903 K); given the constant 15%
by mol CH_4 and the total flow rate 50 ml/min by
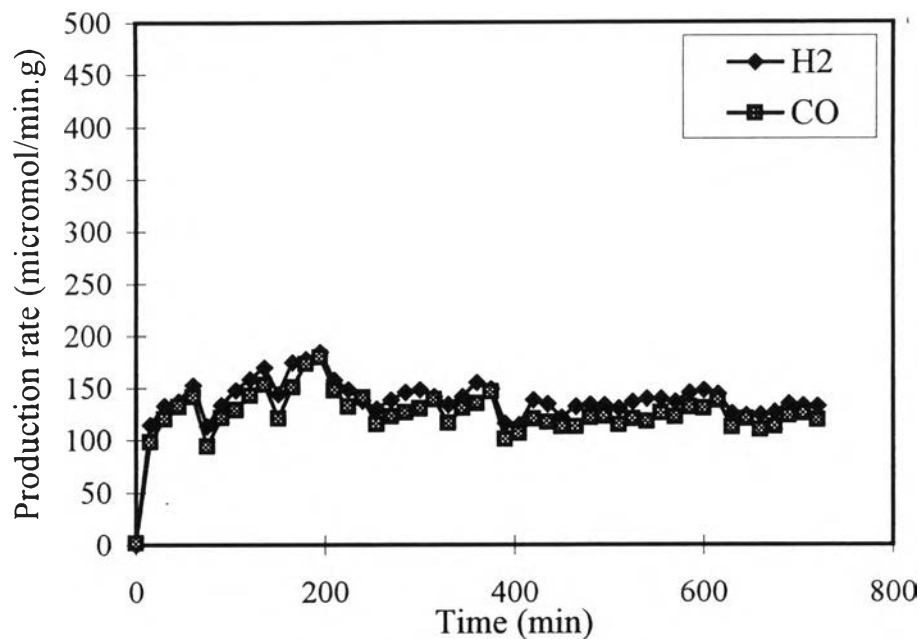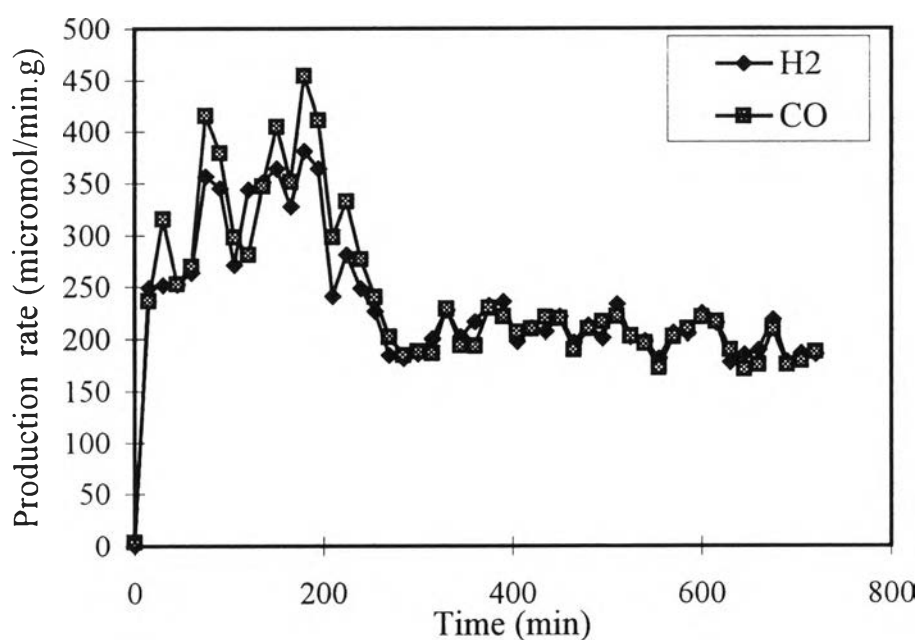using 0.236 g tungsten, CO_2/CH_4 = 1.0.

Figure 4.20 Plot of production rates of H_2 and CO using power
supply = 100 W(T = 946 K); given the constant
15% by mol CH_4 and the total flow rate 50 ml/min
by using 0.236 g tungsten, CO_2/CH_4 = 1.0.

Figure 4.21 Plot of production rates of H_2 and CO using power
supply = 110 W(T = 983 K); given the constant
15% by mol CH_4 and the total flow rate 50 ml/min
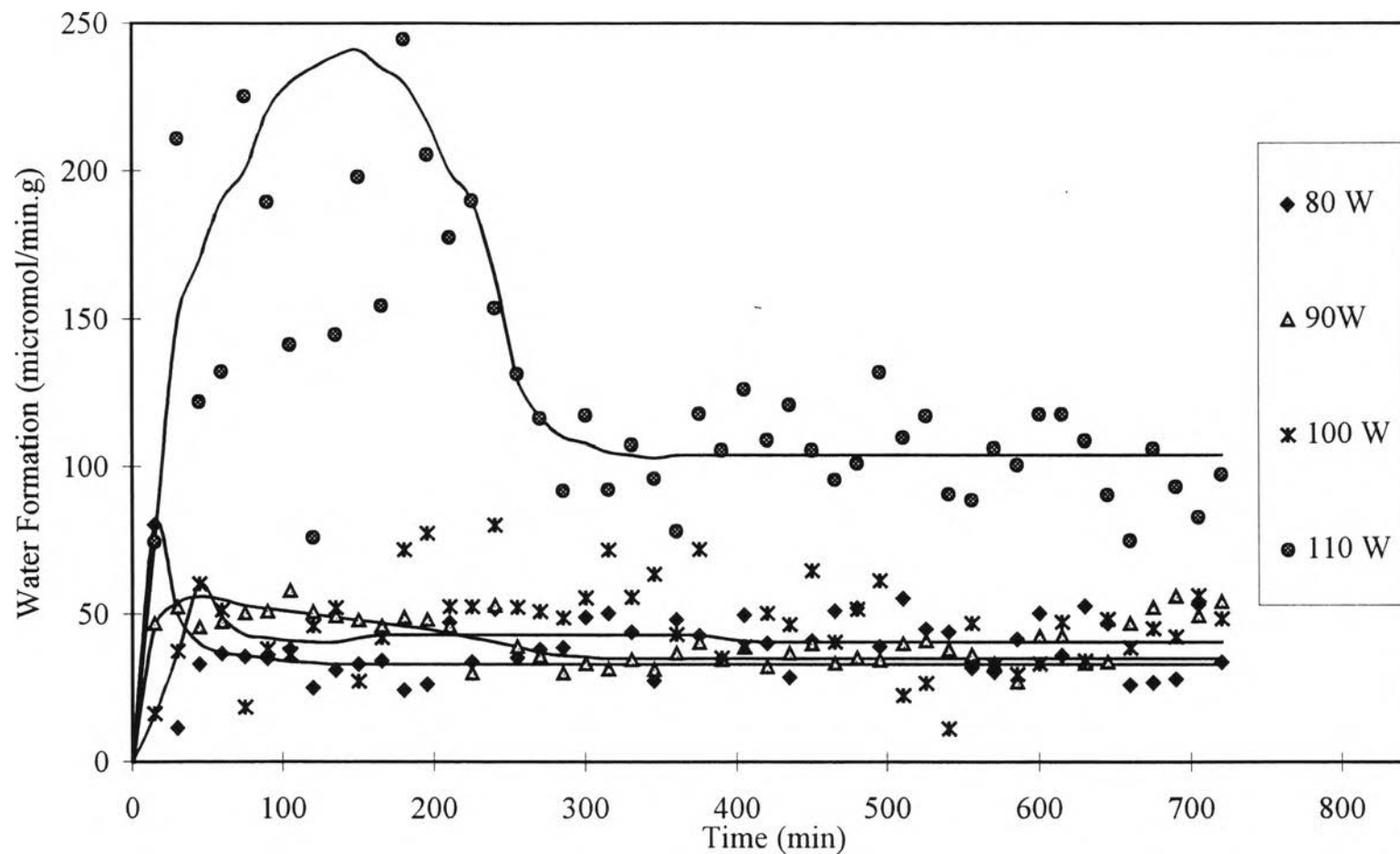by using 0.236 g tungsten, CO_2/CH_4 = 1.0.

Figure 4.22 Plot of water formation rate against temperatures at the constant 15 % by mol methane in helium and the total flow rate 50 ml/min by using 0.236 g tungsten, $CO_2/CH_4 = 1.0$.
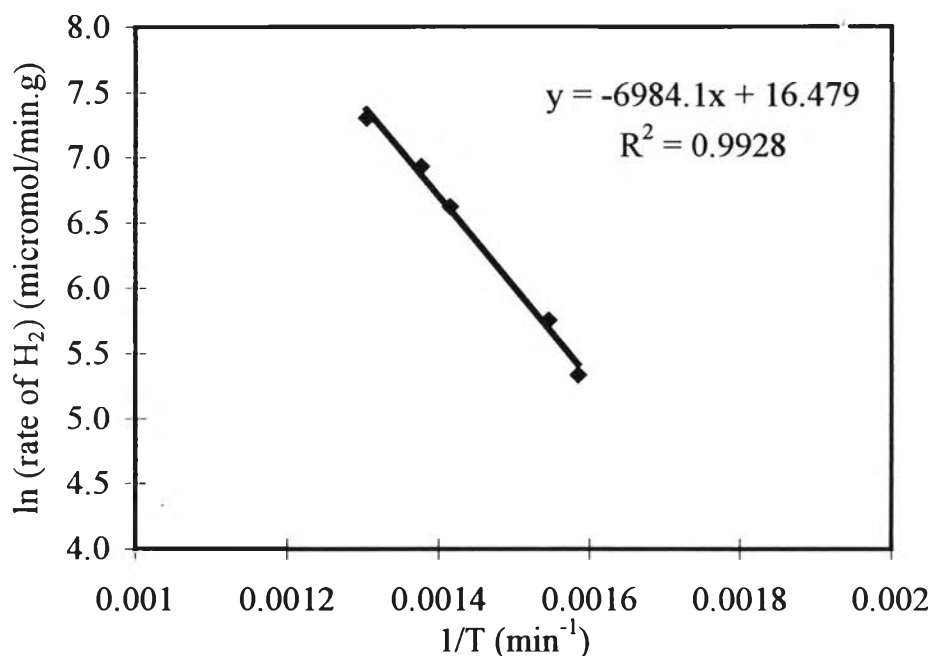
Figure 4.23 Arrhenius plot of H_2 formation for tungsten wire at the constant 15% by mol methane in helium and the total flow rate 50 ml/min by using 0.236 g tungsten, $CO_2/CH_4 = 1.0$.
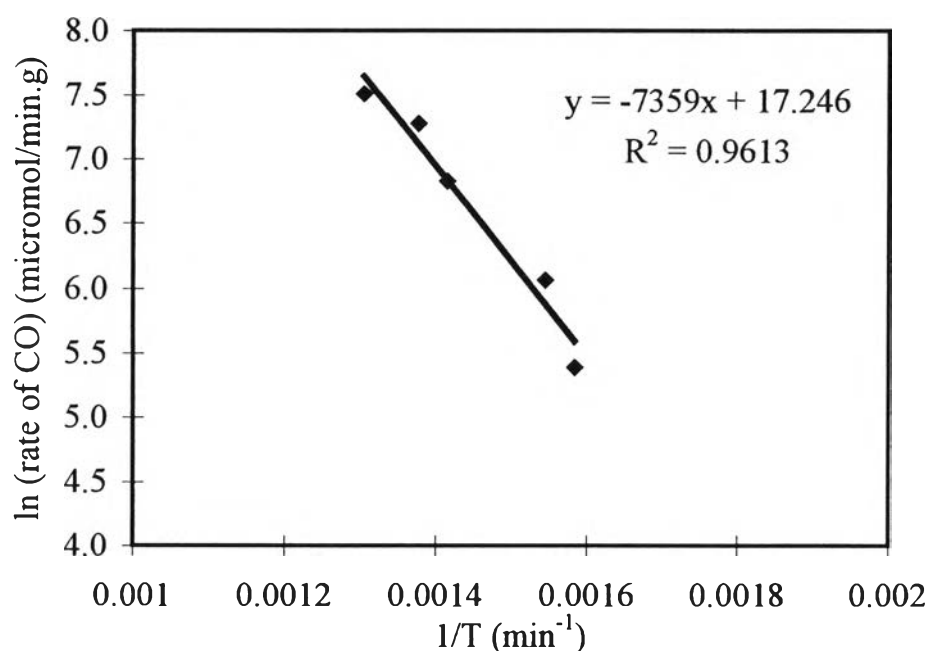

Figure 4.24 Arrhenius plot of CO formation for tungsten wire at the constant 15% by mol methane in helium and the total flow rate 50 ml/min by using 0.236 g tungsten, $CO_2/CH_4 = 1.0$.