

CHAPTER IV

RESULTS AND DISCUSSION

4.1 The effect of reaction temperature

From the experiments at temperature varied from 598-673 K. Figure 4.1 shows the relation of conversion of methane and time(min.). Because oxygen was in excess so all of methane was converted to carbon dioxide and water. The results show that the higher the reaction temperature the higher the methane conversion and that the conversion of methane decreases from the initial conversion and comes close to a steady state value. For this reason, mathematical program, Polymath version 4.0, was used to predict the steady state value by fitting the data with an exponential equation as follows :

$$\text{conversion} = \text{constant (A)} + \text{constant(B)} * \exp(-\text{constant (c)} * \text{time})$$

The steady state values of conversion obtained are shown in Table 4.1 and plotted in Figure 4.2.

Table 4.1 Steady state conversion and reaction temperature(K)

Temperature (Kelvin)	Conversion (%) at steady state
673	70.23
666	67.00
658	58.71
653	57.62
648	43.49
623	45.32
598	11.87

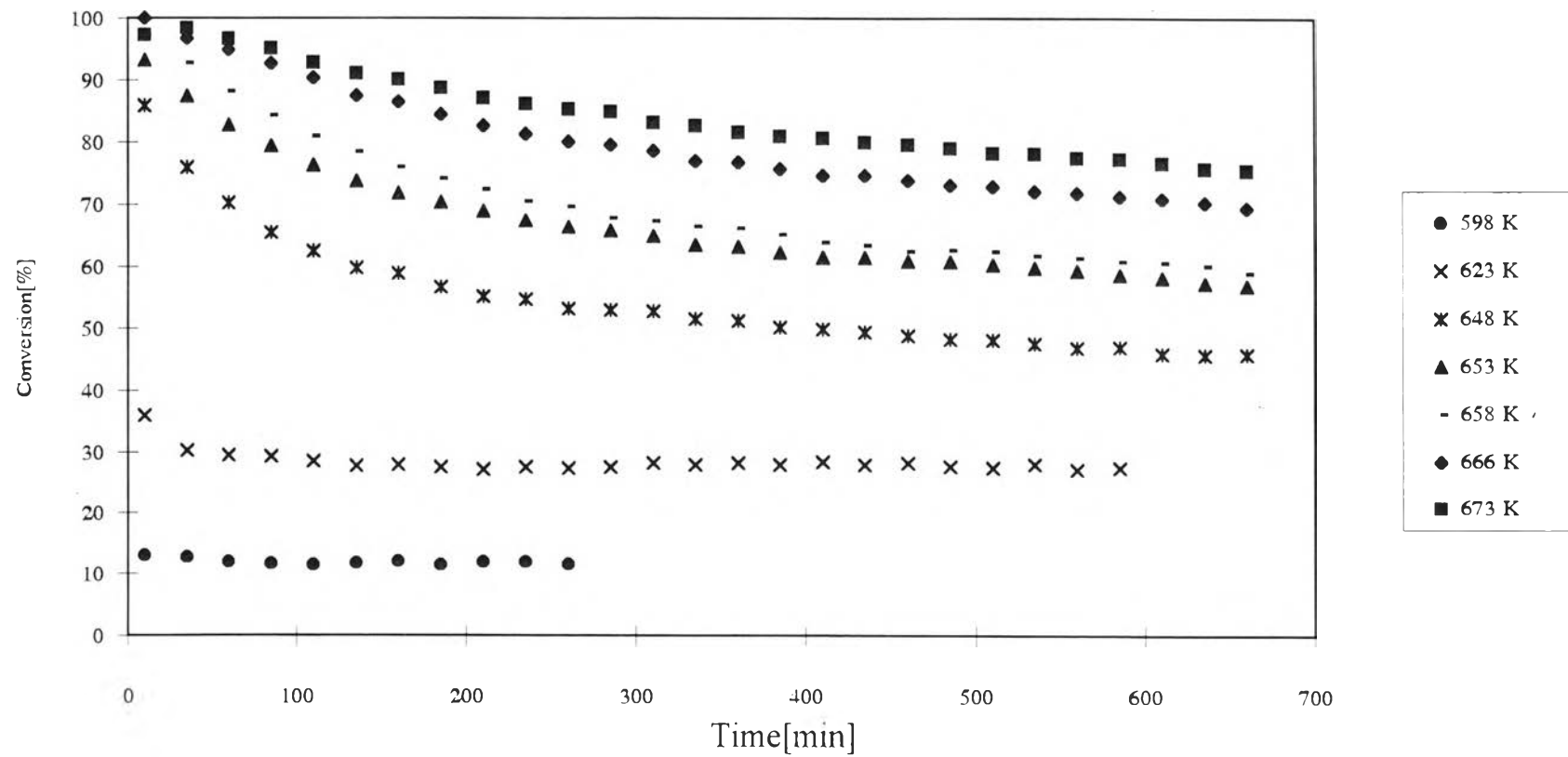


Figure 4.1 Conversion of methane with time(min) over 0.3 gram of 1% Pd on alumina, air fuel ratio =100, 598-673 K.

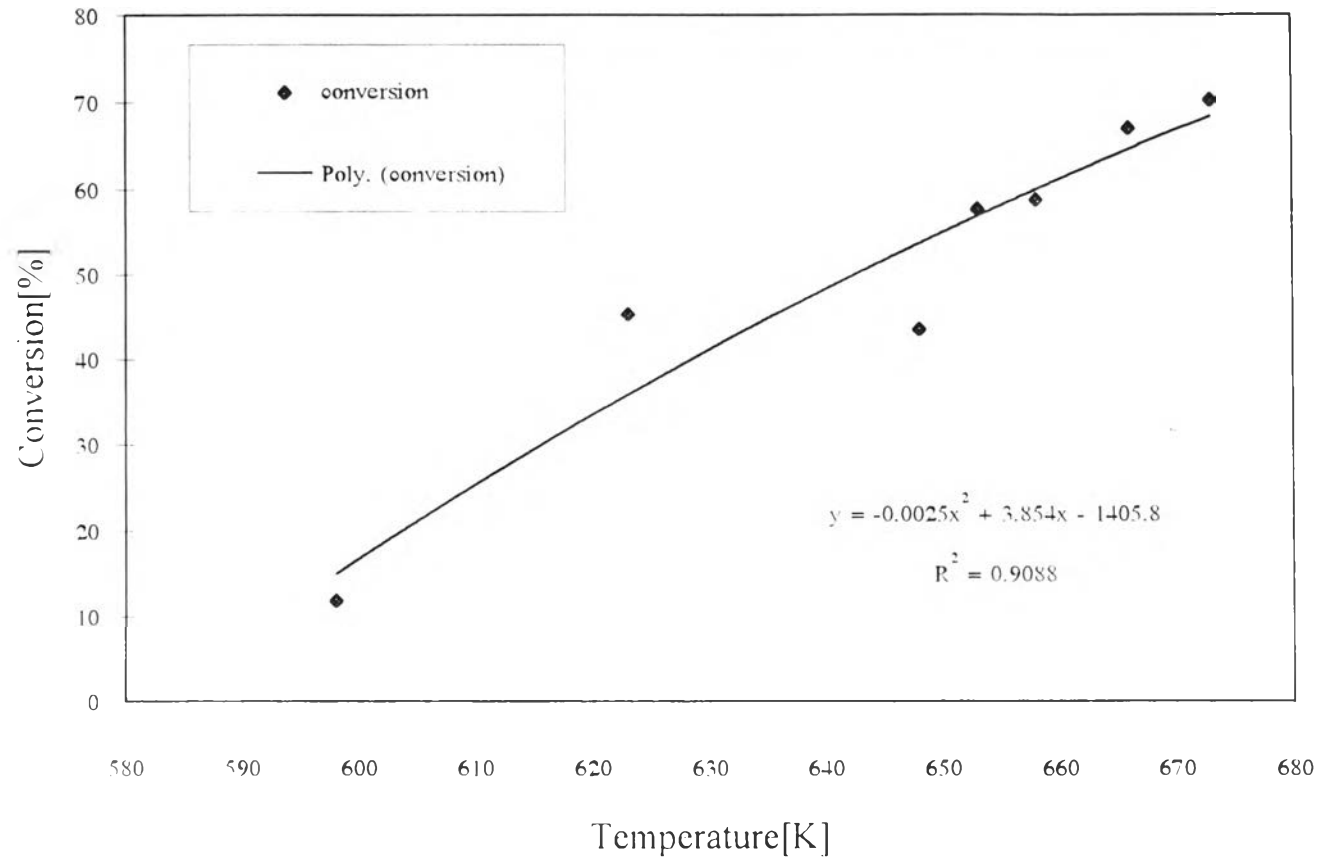


Figure 4.2 Steady state conversion of methane with reaction temperature[K] over 0.3 gram of 1% Pd on alumina, air fuel ratio = 100, 598-673 K.

By using spreadsheet program, Microsoft Excel version 5.0, to curve fit the data of Table 4.1, the following relation shown as a solid line in Figure 4.2 is obtained.

$$\text{conversion} = -0.0025(\text{temperature})^2 + 3.854(\text{temperature}) - 1405.8$$

The activation energy of the reaction is 43,537 cal/g-mol(Appendix B), that is an approximate value because it was operated at high conversion. Comparing this to activation energy that is recalculated from conversion and temperature data of Najat Mouaddib(1992) who studied methane catalytic combustion on Pd/alumina catalyst at different air-fuel ratios, it is found that the activation energy is 46,429.29 cal/g-mol at air-fuel ratio of 9.52 and 60,533.47 cal/g-mol at air-fuel ratio of 19.05 (Appendix C).

4.2 The effect of air-fuel ratio

In the case of homogeneous combustion and fuel-lean mixture, the most preferable reaction is complete combustion because there is enough oxygen for methane combustion. For fuel-rich mixture, the products are CO₂, H₂O, CO and H₂ because the lack of oxygen supplied. In the catalytic combustion at different air-fuel ratio, products of reaction depend on the range of air-fuel ratios and the selectivity of CO₂ is the parameter for studying how the non-toxic product occurs at different air-fuel ratios.

4.2.1 The effect of air-fuel ratio on the selectivity of CO₂ formation

The catalytic combustion of methane on Pd supported alumina was conducted at constant temperature(723 K), which is high enough for total combustion methane in air mixture and at varied air-fuel ratios from 3.267 to 8.540 for fuel-rich mixture and 11.365 to 14.712 for fuel-lean mixture.

For fuel-lean mixture, that is air-fuel ratios (AFR) higher than stoichiometric ratio (9.525), the mole of carbon dioxide generated equals to the mole of methane input from feed. No hydrogen and coke were produced except water as shown in Table 4.2.

Table 4.2 The concentration (% mole) of gas in the gas stream for fuel-lean mixture combustion.

AFR	CH ₄ in	O ₂ in	O ₂ out	CO ₂ out	H ₂ out
14.712	6.22	19.22	6.99	6.24	0.00
12.872	7.22	19.54	5.74	7.31	0.00
11.365	8.32	19.87	3.66	8.38	0.00

In this case we can conclude that for fuel-lean mixture, that is air-fuel ratio higher than stoichiometric ratio, the combustion reaction on the surface of palladium catalyst at 723 K was complete. The result is in agreement with of Najat Mouaddib et al., 1992.

For the fuel-rich mixture, that is air-fuel ratio lower than stoichiometric ratio, Table 4.3 and Figure 4.3 shows the concentrations (%) of major products in the exhaust gas, except water.

Table 4.3 The concentration (% mole) of gas in the gas stream for fuel-rich mixture combustion.

AFR	CH ₄ inlet	CH ₄ outlet	O ₂ inlet	CO ₂ outlet	H ₂ outlet
3.267	22.873	14.816	15.690	6.957	1.072
4.136	19.314	10.578	16.776	7.112	1.354
5.252	15.528	6.347	17.126	6.390	1.759
5.997	13.850	4.367	17.442	6.536	1.715
6.161	14.031	3.986	18.125	6.848	1.554
7.037	12.010	2.682	17.749	6.887	1.421
7.226	11.674	2.305	17.714	7.230	1.801
8.540	10.606	0.619	19.021	8.709	1.298

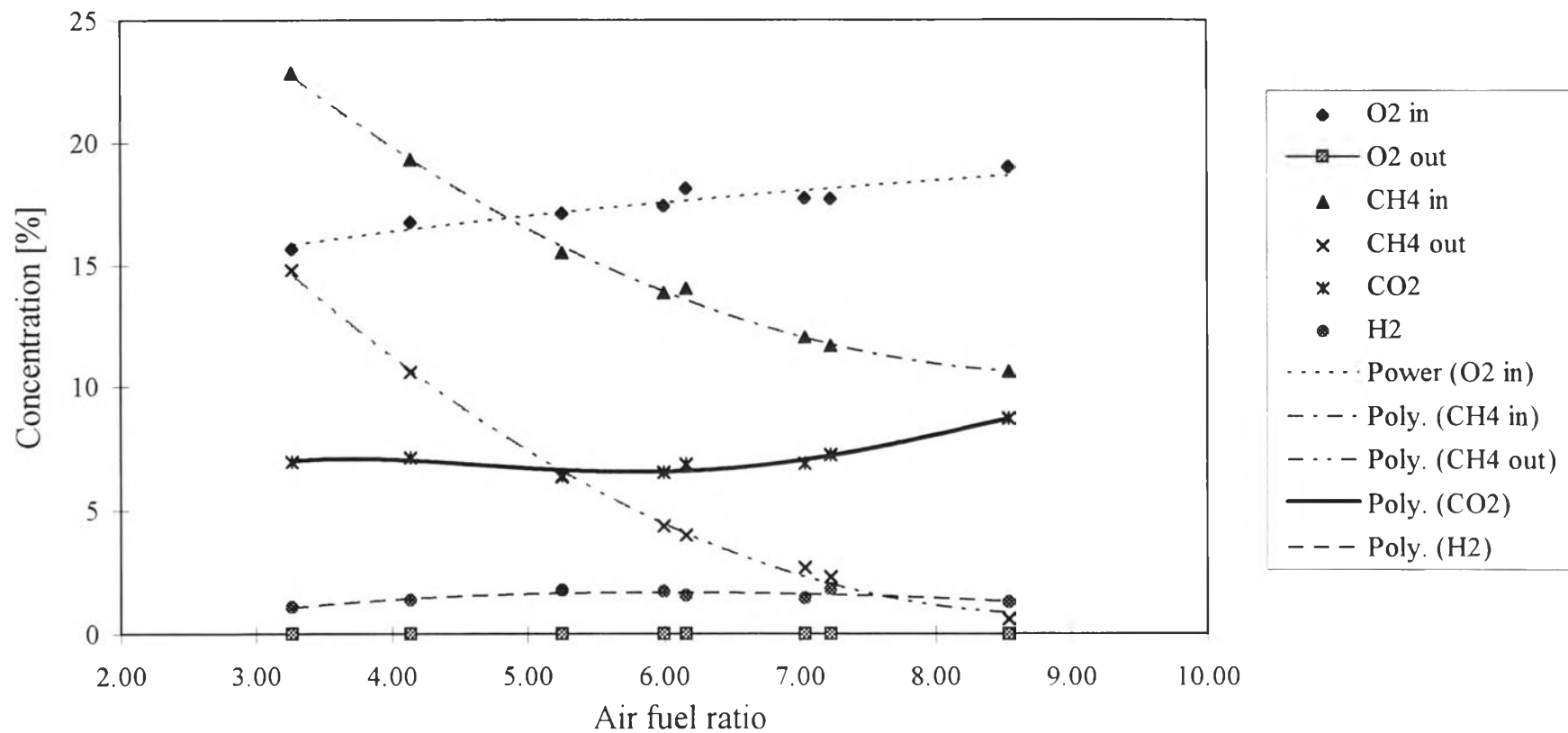


Figure 4.3 Steady state concentration of gases with air fuel ratio between 3.267-8.540 over 0.3 gram of 1% Pd on alumina, 100 % conversion of oxygen (723 K).

The concentration of CO_2 decreases more markedly with increasing air-fuel ratio. When we replot it again in terms of selectivity with respect to methane conversion, as shown in Figure 4.4, the line shows that the selectivity of methane converted to CO_2 is minimum at the air-fuel ratio around 5.8.

Comparing this to the upper limit of flammability (ULF) of methane in air mixture (15.55 % methane or air-fuel ratio = 5.43), we found that the minimum selectivity of CH_4 to CO_2 occurs at slightly higher value than the ULF, i.e. at very fuel-rich mixtures, close to the ULF.

The selectivity of CO_2 formation with continuous changing of air-fuel ratio from very fuel-lean(air-fuel ratio 29.93) to very rich(air-fuel ratio 4.58) was studied. Table 4.4 and Figure 4.5-4.6 show that the selectivity has a tendency to decrease when air-fuel ratio decreases.

Table 4.4 The concentration(% mole) of gas in the gas stream for continuous changing air-fuel ratio combustion.

AFR	CH_4 in	CH_4 out	O_2 in	CO_2 out
29.93	3.10	0.00	19.51	3.10
11.78	7.55	0.00	18.69	7.52
9.09	9.56	0.35	18.25	7.94
7.33	11.57	2.03	17.81	6.59
6.12	13.52	3.82	17.39	5.64
5.22	15.47	5.38	16.97	4.76
4.58	17.28	7.30	16.61	4.64

Comparing Figure 4.6 with Figure 4.4 one can see from that the increase of selectivity of CO_2 formation at air-fuel ratio lower than ULF does not come from catalytic combustion reaction.

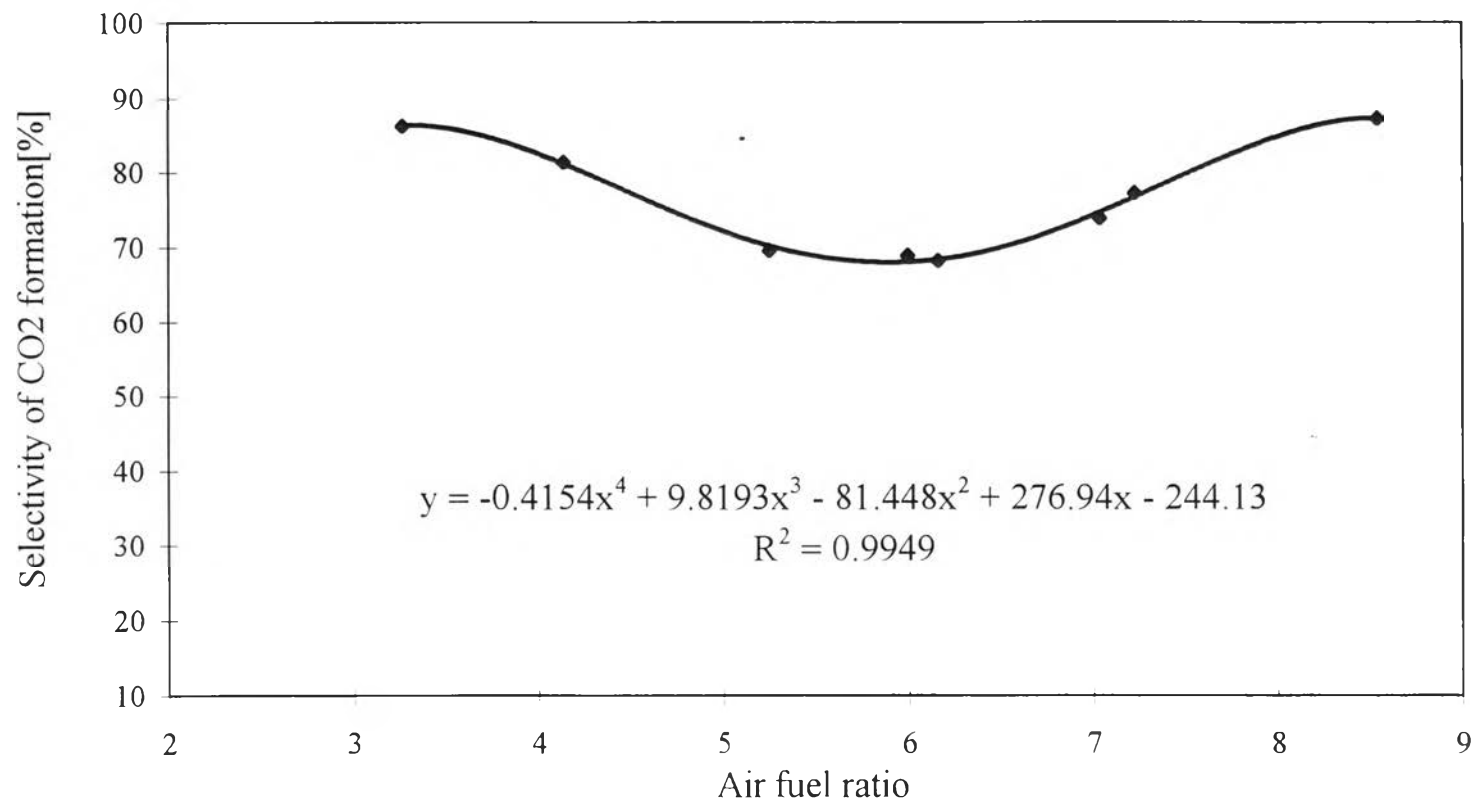


Figure 4.4 Selectivity of CO₂ formation with air fuel ratio between 3.267-8.540 over 0.3 gram of 1% Pd on alumina, 100 % conversion of oxygen (723K).

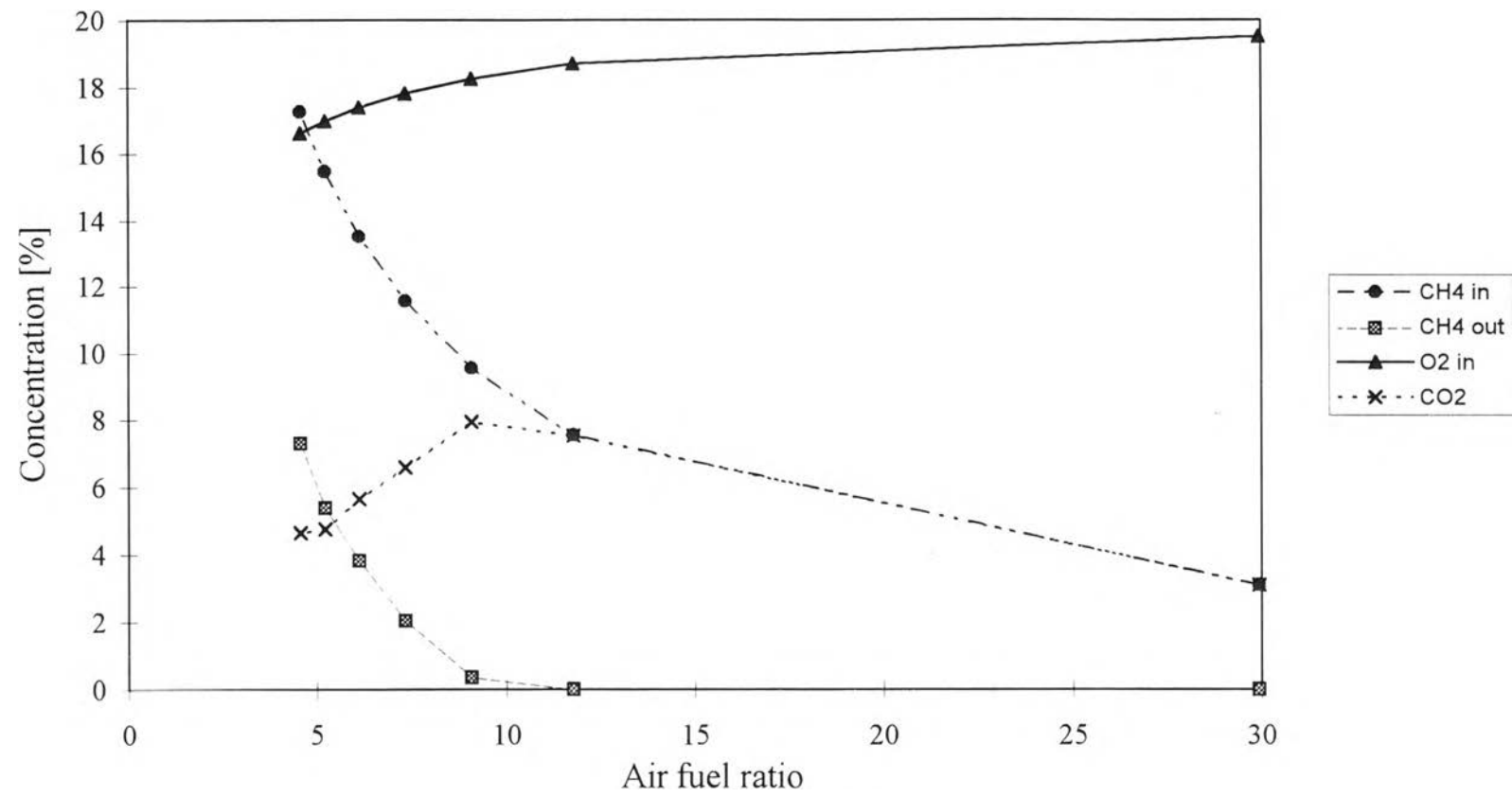


Figure 4.5 Concentration of gases with air fuel ratio between 4.58-29.93 over 0.3 gram of 1%Pd on alumina, 100% conversion of oxygen (723 K) and continuous changing of air fuel ratio .

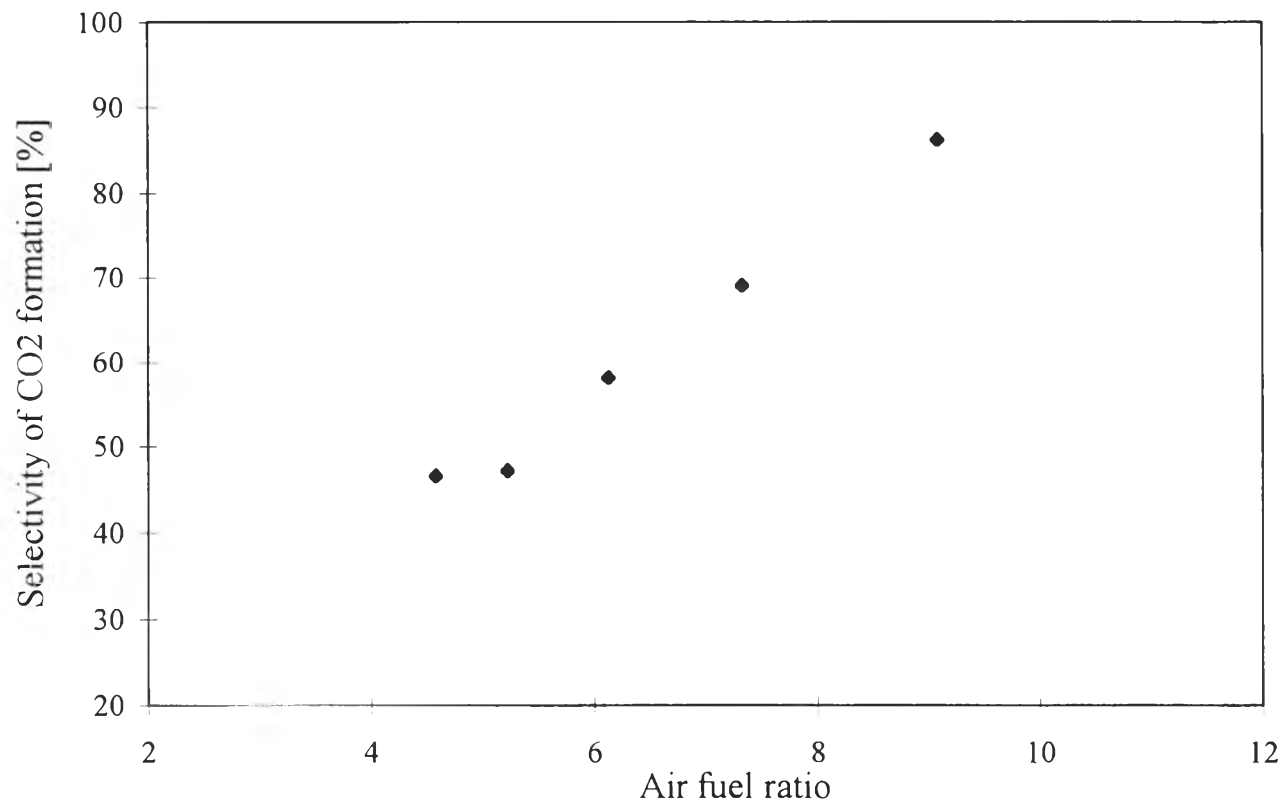


Figure 4.6 Selectivity of CO₂ formation with air fuel ratio between 4.58-29.93 over 0.3 gram of 1%Pd on alumina, 100% conversion of oxygen (723 K) and continuous changing of air fuel ratio .

Because water is a combustion product and at the temperature range studied (673-873 K), it is possible that methane or carbon monoxide reacts with water, as in the following reactions :

Methane steam reforming reaction.



$$\Delta H = 206 \text{ kJ/mol}$$

Water-gas shift reaction.



$$\Delta H = -41 \text{ kJ/mol}$$

There is a possibility that these two reactions can take place, up to a certain extent, which depends on their equilibrium constants, as shown in Fig 4.7.

At 723 K(450 °C), the methane steam reforming reaction is less favourable than the water gas shift reaction. At low air-fuel ratio around ULF, after all oxygen is consumed, it is possible that the water gas shift reaction occurs, more to the reverse direction, and decrease the selectivity of methane to CO₂. However, at still lower air-fuel ratio than ULF, which is more fuel rich, there is high content of water in the gas stream. In this case, it will support the forward water-gas shift reaction that helps to increase the selectivity of CO₂ formation as shown in the result. The result is also in agreement with that of Najat Mouaddib et al., 1992.

By comparing the rate of reaction, that is recalculated from the conversion data of Najat Mouadibb et al., 1992. The rate of reaction on 1.93% Pd on alumina at air-fuel ratio 4.76 and temperature 723 K, equals to 55 moles of CH₄ converted per hr per mole of Pd, while in this work the rate of reaction

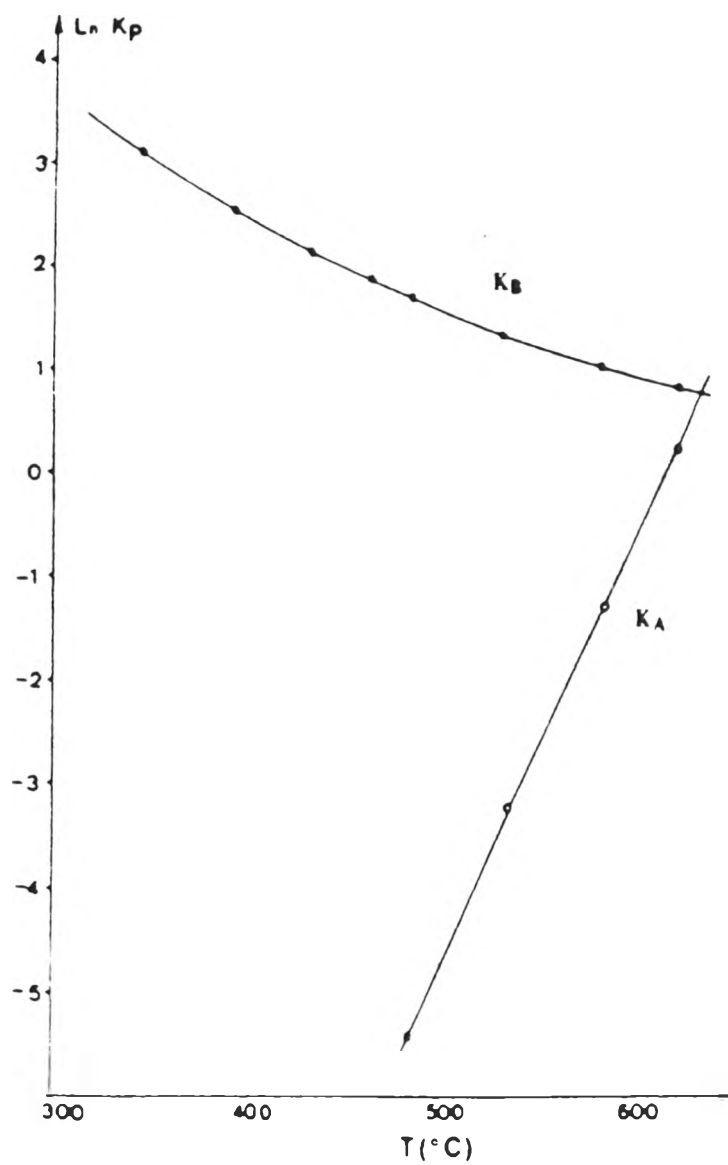


Figure 4.7 Equilibrium constant K_A (methane steam reforming) and K_B (water-gas shift reaction) as a function of temperature

on 1% Pd on alumina at the same temperature and mixture composition is much higher at 400 mole of CH_4 converted per hr per mole of Pd. It is possible to be the effect of Pd loading. The excess Pd loading as in the work of Najat Mouadibb et al. may lead to the higher particle size and a lot of Pd molecule inside that is not used.

For the fuel-lean mixture, the only products found were CO_2 and H_2O , so the topic to investigate is the effect of air-fuel ratio on conversion at the same temperature (673 K).

4.2.2 Methane conversion at constant temperature

The effect of air-fuel ratio on conversion was studied by the experiments at constant temperature (673 K) and varied air-fuel ratio from 10 to 100.

The conversion of methane catalytic combustion on palladium at constant temperature (673 K) is shown in Figure 4.8-4.9. Figure 4.8 is the plot between conversion and time of CH_4 -air mixtures within but close to the lower limit of flammability (LLF) i.e. 4.36 % of methane or 21.94:1 air-fuel ratio. One can see from this plot that the closer the mixture is to the LLF, the lower the conversion.

Figure 4.9 is the similar plot between conversion and time of CH_4 -air mixtures which are close to but outside the LLF i.e. at air-fuel ratios higher than 21.94. One can see that the more the ratios depart from the LLF, the higher the methane conversion.

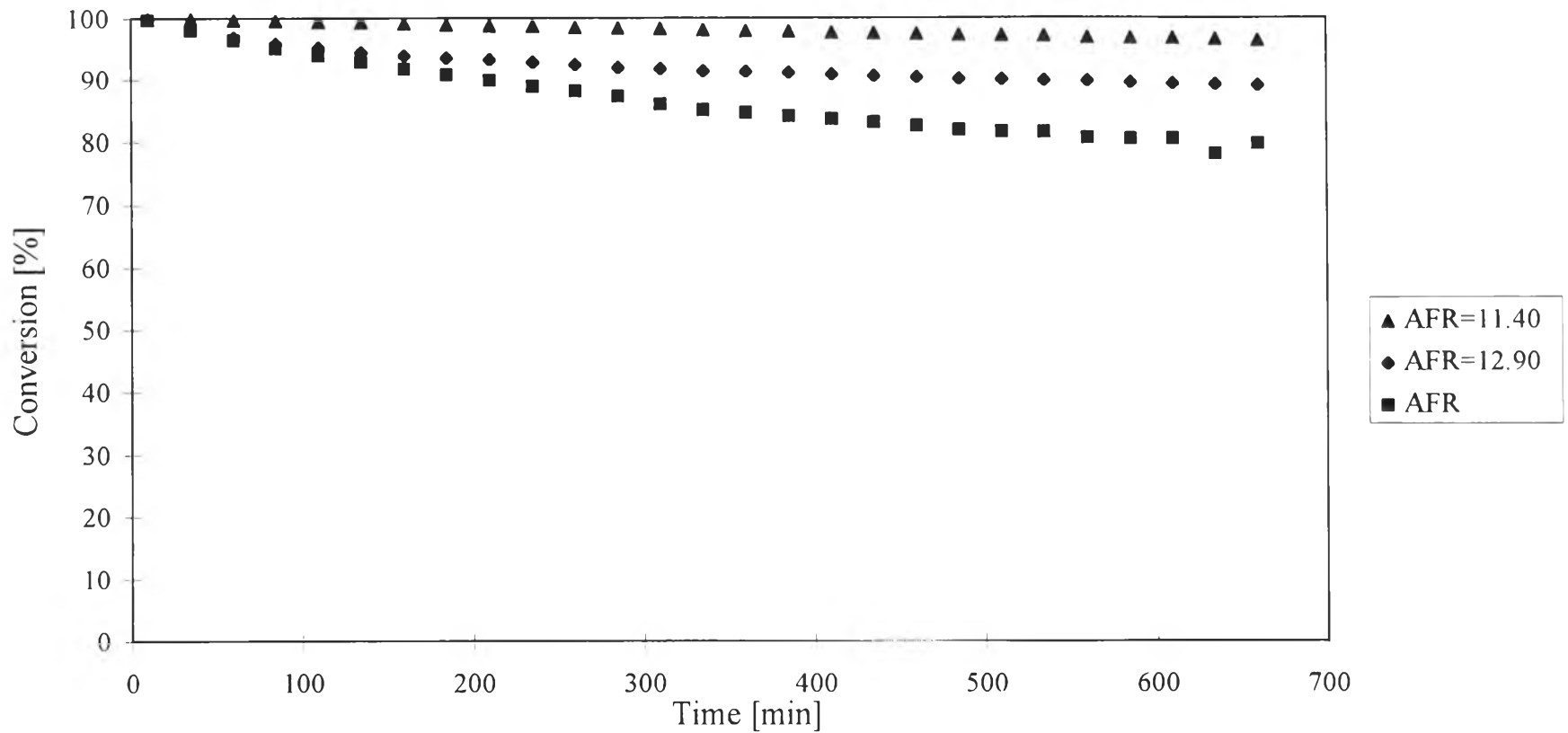


Figure 4.8 Conversion of methane with time[min] over 0.3 gram of 1%Pd on alumina, at constant reaction temperature [673 K] and fuel-lean mixture within LLF.

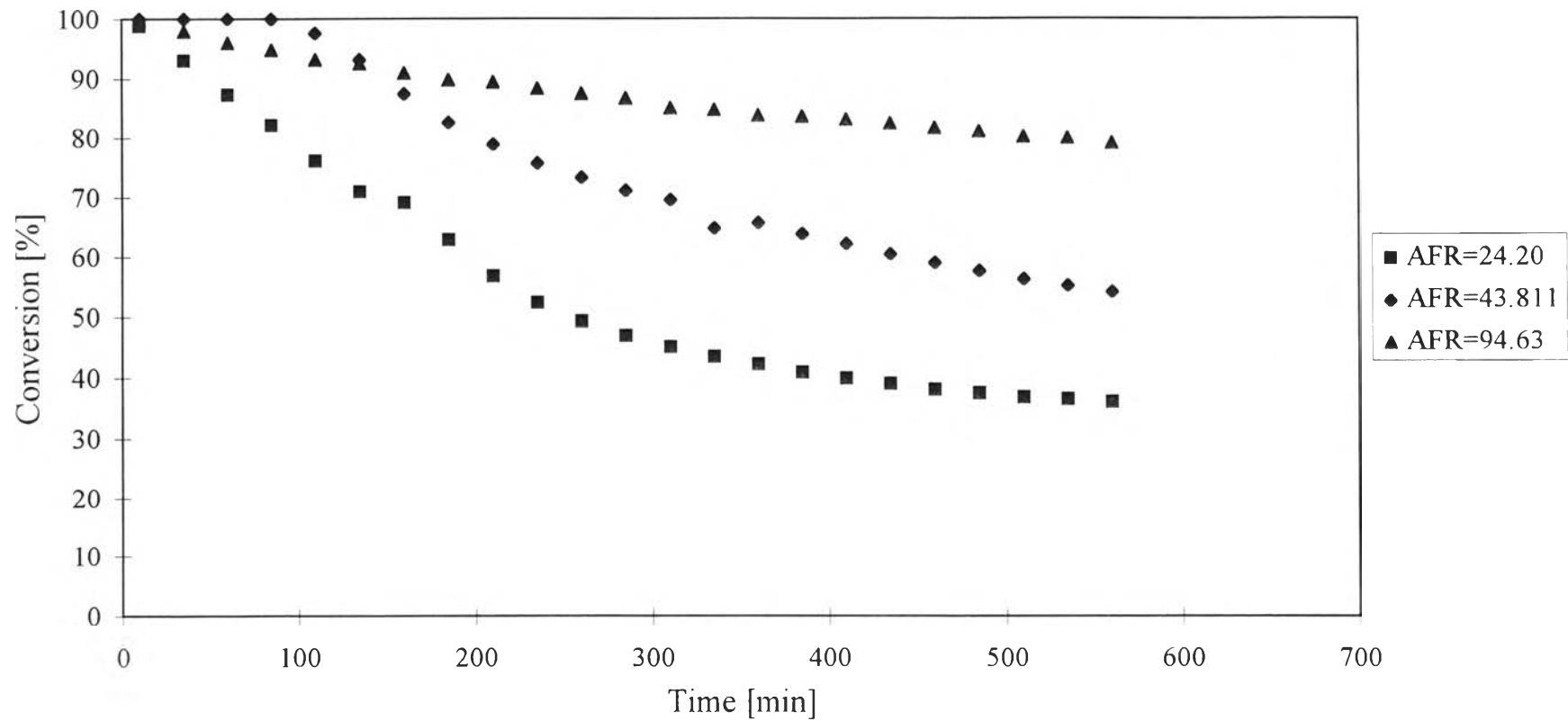


Figure 4.9 Conversion of methane with time[min] over 0.3 gram of 1%Pd on alumina, at constant reaction temperature [673 K] and fuel-lean mixture outside LLF.

Combining the two plots together, as shown in Figure 4.10, one can see that there is a tendency that the conversion reaches a minimum at and around the lower limit of flammability that is an air-fuel ratio of 21.94. The decrease in the conversion at air-fuel ratios lower than LLF is very fast compared to the increase of conversion at air-fuel ratios higher than LLF.

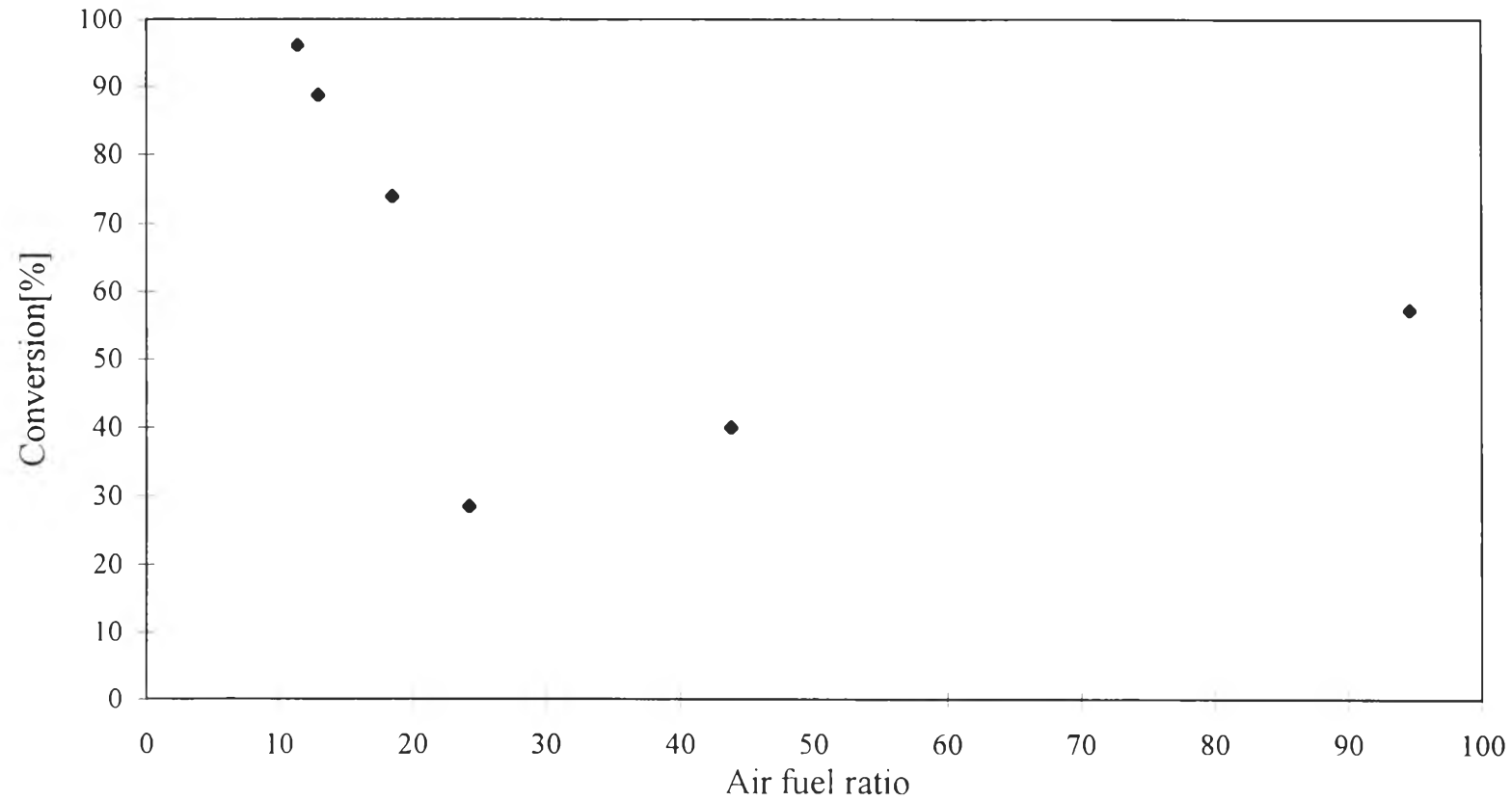


Figure 4.10 Steady state conversion of methane with air fuel ratio over 0.3 gram of 1%Pd on alumina, at constant reaction temperature [673 K] and fuel-lean mixture outside the LLF.