CHAPTER III

EXPERIMENTAL

3.1. Materials and Chemicals

All materials and chemicals used in this experiment were listed as follows:

1. Methane gas 99.99 % (Thai Industrial Gases Public Co., Ltd.)
2. Hydrogen gas 99.5 % (Enviromate Co., Ltd.)
3. Nitrogen gas 99.5 % (Enviromate Co., Ltd.)
4. Distilled water
5. Anhydrous calcium chloride ($CaCl_2$ anhydrous) (Merck)
6. Nickel magnesia solid solution catalyst ($Ni_{c.03}Mg_{0.97}O$) : particle size between 20 and 40 mesh, specific area of particle being 22 m^2/g (Catalyst preparation in Appendix D)

3.2. Instruments and Apparatus

All instruments and apparatus used in this experiment were schematically shown in Figure 3.1. They consisted of six parts as follows:

1. Cylindrical fixed bed reactor
2. Temperature controller
3. Steam generator
4. Mass flow controller
5. Moisture trap
6. Gas analyzer

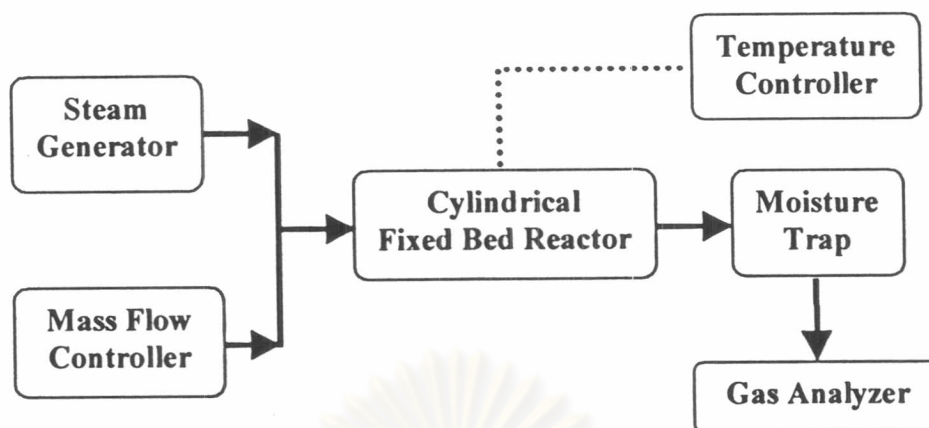In addition, flow diagram of the experiment was illustrated in Figure 3.2.

Figure 3.1. Schematic of the instruments and apparatus.

3.2.1. Cylindrical Fixed Bed Reactor

A 3-cm. I.D and 66-cm. length stainless steel reactor was employed as a cylindrical fixed bed reactor, which was shown in Figure 3.3. The screen was installed within reactor, which its size of 40 mesh. The reactor was typically loaded with nickel magnesia solid solution catalyst at which the reactant gases were fed into its bottom. It was electrically heated and controlled with a type-K thermocouple, that inserted in the center of the catalyst bed, which monitored by a temperature recorder. The leaving gases from the reactor were fed via a moisture trap.

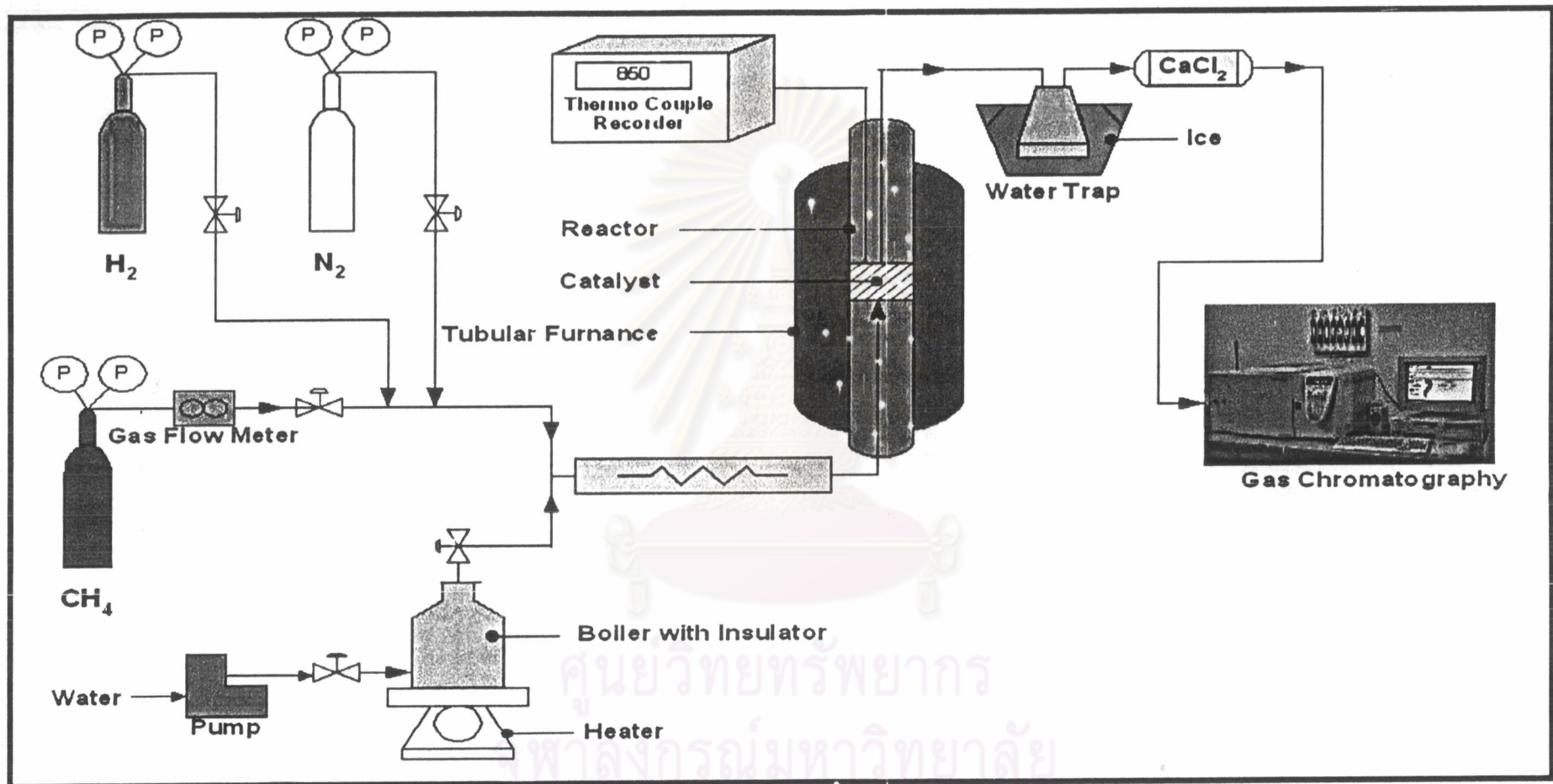**Figure 3.3.** Cylindrical fixed bed reactor.

Figure 3.2. Flow diagram of the methane steam reforming process.

3.2.2. Temperature Controller

A temperature controller consisted of tubular furnace, type-K thermocouple and temperature recorder. The tubular furnace (CARBOLITE; Model MTF 12/38/400) controlled temperature throughout the reactor changing of electrical energy to heat for the optimum temperature as illustrated in Figure 3.4. Besides, a type-K thermocouple as illustrated in Figure 3.5 that inserted in the center of the catalyst bed could be employed as temperature of up to 1300 °C with principle of the different temperature between positive polarity and negative polarity. While the different temperature was increased, the electromotive force also increased. The signal of electromotive force from the thermocouple was transmitted to the temperature recorder (YOKOGAWA; Model 4173) as illustrated in Figure 3.6.
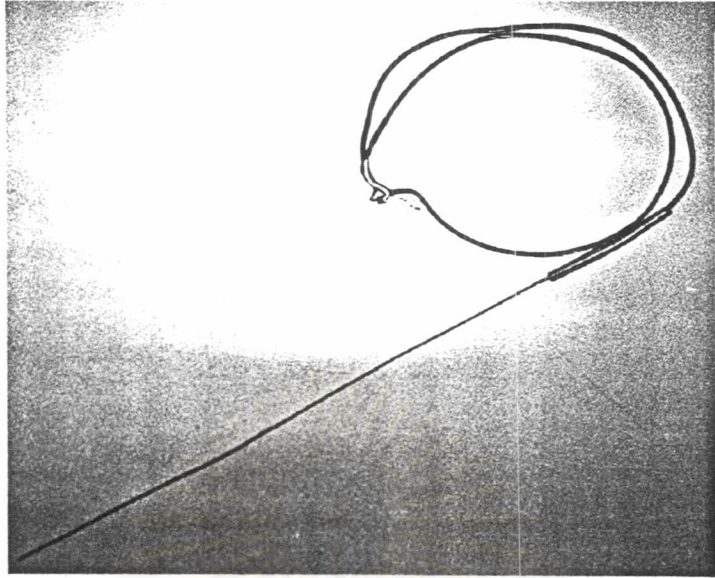

Figure 3.4. Tubular furnace.

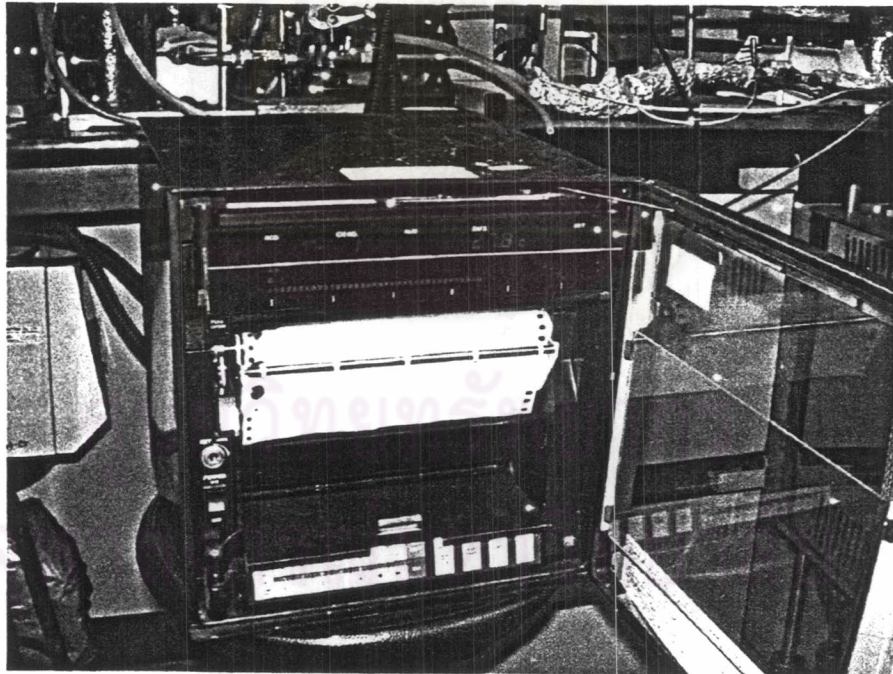**Figure 3.5.** Type-K thermocouple.

Figure 3.6. Temperature recorder.

3.2.3. Steam Generator

A steam generator consisted of boiler and peristaltic pump. The boiler was covered with asbestos using as insulator for decreasing energy loss, which illustrated in Figure 3.7. It was continuously heated by heater in order that water became steam immediately. A distilled water was continuously fed by a peristaltic pump (Model SJ-1211 H) as illustrated in Figure 3.8 into the boiler before flowing in the reactor.
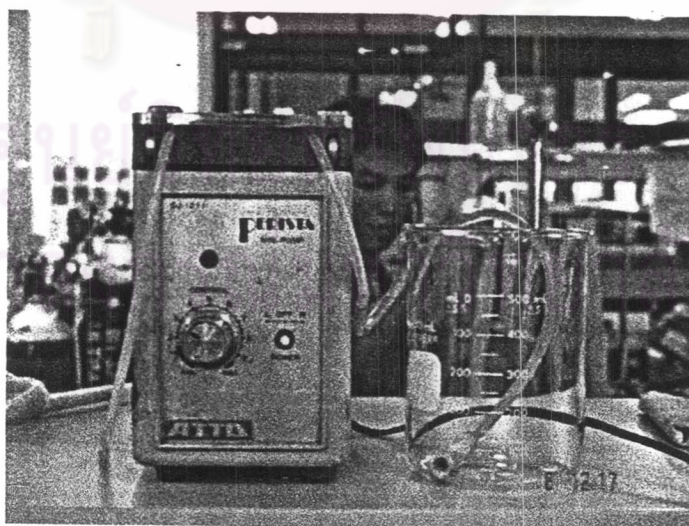

Figure 3.7. Boiler.

Figure 3.8. Peristaltic pump.

3.2.4. Mass Flow Controller

A mass flow controller (SIERRA; Model 810C-DR-13-MP; Range 0-50 SCCM; Operating Temperature Range 32-122 °F; Operating Pressure Range 100 psig /20 psig) was used to control a volumetric flow rate of methane as illustrated in Figure 3.9. Methane was continuously fed via a mass flow controller into the reactor.

Figure 3.9. Mass flow controller.

3.2.5. Moisture Trap

A 6.35-cm. O.D and 25-cm. length glass tube, which contained anhydrous calcium chloride, used as a moisture trap was illustrated in Figure 3.10. The leaving gases from the reactor were fed via a moisture trap to remove moisture before flow to the gas analyzer. Increasing moisture affected to the gas analyzer, which might be damaged.
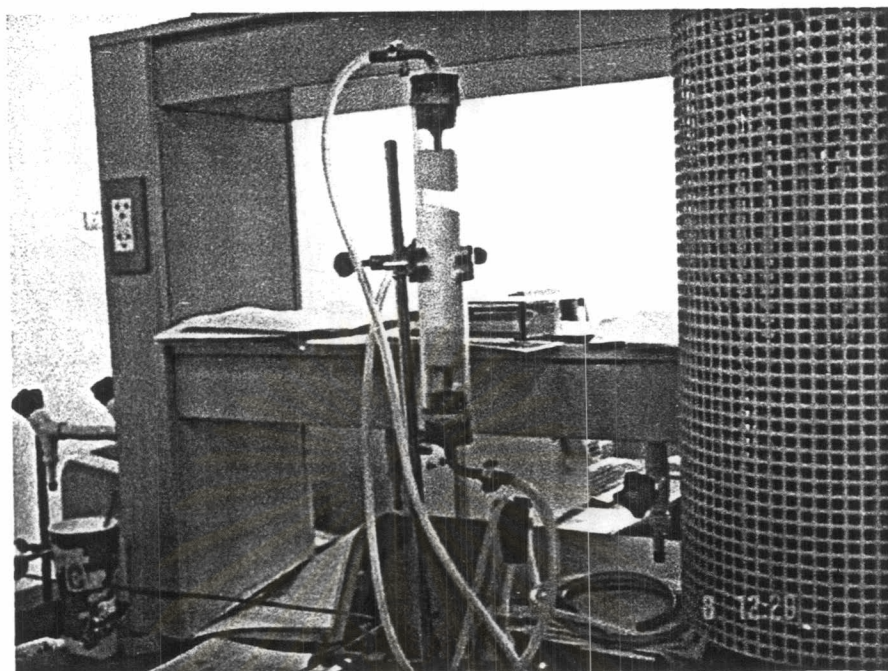
Figure 3.10. Moisture trap.

3.2.6. Gas Analyzer

The product gases (H_2, CO, CO_2 and unconverted CH_4) via a moisture trap were analyzed by a gas chromatograph (TRACE GC 2000) as illustrated in Figure 3.11. The sampling gases were continuously fed into a gas chromatograph via rotary valve of oven and sample loop. Later, they were injected into column that each gas was separated and qualitatively analyzed by thermal conductivity detector (TCD), methanizer and flame ionization detector (FID), respectively. A thermal conductivity detector (TCD) was used as detector for determination of hydrogen and methane. For a flame ionization detector (FID), it was used as detector for determination of carbon monoxide, carbon dioxide and methane. Each gas was recorded as chromatogram profile. The operation and configuration of gas chromatograph were illustrated in Figure 3.12. For the optimum condition of gas chromatograph, it was illustrated in Table 3.1.
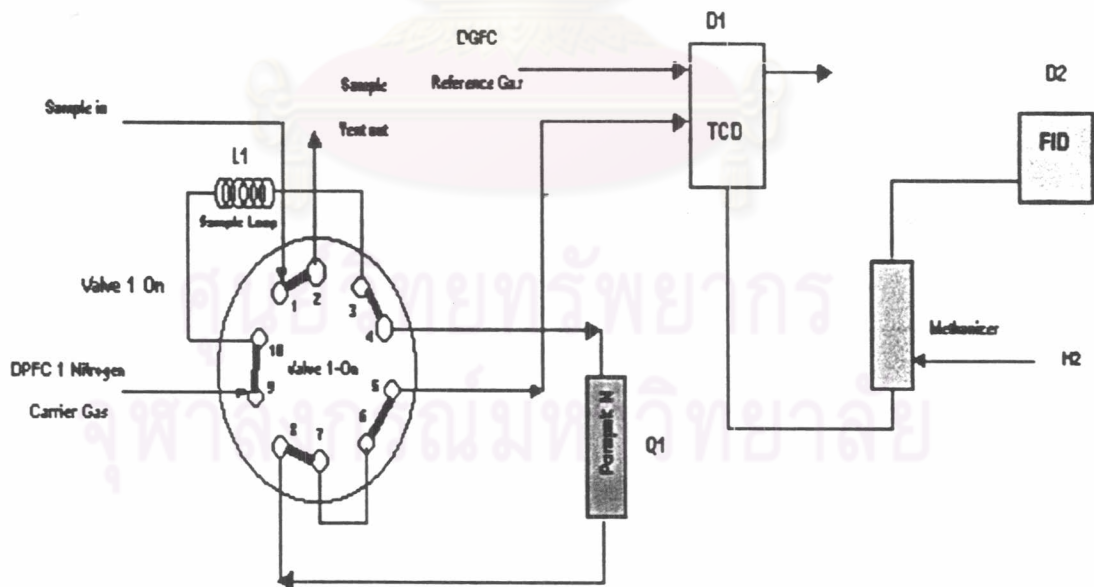
Figure 3.11. Gas chromatograph.

Figure 3.12. The operation and configuration of gas chromatograph.

Table 3.1. The optimum condition of gas chromatograph.

Component	Condition
Carrier gas and make-up gas	Nitrogen 99.99 %
Oven	Oven temperature: 40 $^{\circ}$C
	Valve oven temperature: 50 $^{\circ}$C
Injector	Injector temperature: 70 $^{\circ}$C
	Pressure: 80 kPa
	Flow rate at constant pressure: 7.2 ml/min
Column	Column type: Porapak N (packed column)
	Column length: 3 m
Methanizer	Methanizer temperature: 375 $^{\circ}$C
Thermal conductivity detector (TCD)	Block temperature: 150 $^{\circ}$C
	Transfer temperature: 120 $^{\circ}$C
	Filament temperature limit: 350 $^{\circ}$C
	Filament voltage: 10
	Flow rate of make-up gas: 10 ml/min
	Flow rate of reference gas: 50 ml/min
Flame ionization detector (FID)	Base temperature: 250 $^{\circ}$C
	Ignition threshold: 2.0 pA
	Flow rate of air: 350 ml/min
	Flow rate of hydrogen: 40 ml/min
	Flow rate of make-up gas: 30 ml/min

3.3. Experimental Procedure

3.3.1. Experimental Procedure before the Reaction

1. The specific mass of nickel magnesia solid solution catalyst was packed into the cylindrical fixed bed reactor.

2. Set temperature of tubular furnace at 600 $^{\circ}$C for reduction of catalyst with hydrogen under atmospheric pressure for 30 min and then closed valve of hydrogen.

3. After reduction of catalyst, hydrogen was removed to outside with nitrogen under the same condition and then closed valve of nitrogen.

3.3.2. Operation of the Reaction Procedure

1. Set up reaction temperature of tubular furnace for the reaction.
2. Distilled water, which already adjusted its flow rate, was continuously fed by a peristaltic pump into the boiler in order that water became steam immediately.
3. Methane was adjusted its flow rate with a mass flow controller and continuously fed immediately into the reactor.
4. When the reaction between methane and steam was at steady state, the sampling gases were analyzed by a gas chromatograph.
5. The used catalyst was regenerated to employ in next experiment.

3.4. The Influence of Operating Parameters on the Performance of Reaction at Atmospheric Pressure and Determination of Kinetics of the Reaction

3.4.1. Reaction in Case of Excess Steam

In this part, the effect of temperature and methane feed rate on methane conversion was investigated and the rate equation of reaction was determined. The studied condition was as follows, the temperature, from 700-850 °C and the excess steam to methane ratio was operated. The methane feed rate was varied from 6.0×10^{-5} to 6.0×10^{-4} mole/min. The steam feed rate was controlled at 0.15 mole/min. The catalyst weight was fixed at 2 g.

3.4.2. Reaction in Case of Non-Excess Steam

1. The effect of steam to methane ratio, from 2.0 to 8.0 on methane conversion was investigated at 850 °C, methane feed rate from 6.0×10^{-5} to 5.1×10^{-4} mole/min, steam feed rate from 1.0×10^{-4} to 4.1×10^{-3} mole/min and catalyst weight of 2 g.

2. The rate equation of reaction was determined the following reaction conditions. The temperature was varied from 700-850 °C. The steam to methane ratio was varied from 2.0, 4.0, 6.0 and 8.0. The methane feed rate was varied from 1.0×10^{-3} to 1.25×10^{-3} mole/min. The steam feed rate was varied from 2.0×10^{-3} to 1.0×10^{-2} mole/min. The catalyst weight was fixed at 2 g. (Note: the order of reaction was calculated by multiple linear regression method.)

3.4.3. The Effect of Catalyst Weight

The effect of catalyst weight on the methane conversion, product gas composition and hydrogen to carbon monoxide ratio was investigated in this experiment. The catalyst weight was varied from 2, 5, 8 and 10 g. The experiment was achieved at 850 °C, excess steam to methane ratio, methane feed rate of 1.27×10^{-4} mole/min and steam feed rate of 0.15 mole/min. Each experiment must be achieved at equilibrium.

3.5. Reaction Mechanism and Determination of Rate Equation by Langmuir-Hinshelwood Model

In this part, the mechanism of reaction was investigated and the rate equation of reaction was determined. The temperature was operated at 850 °C. The steam to methane ratio was varied from 2.0, 4.0, 6.0, 8.0 and excess. The methane feed rate was varied from 6.0×10^{-5} to 5.1×10^{-4} mole/min. The steam feed rate was varied from 1.27×10^{-4} to 0.15 mole/min. The catalyst weight was fixed at 2 g.

3.6. The Influence of Diffusion on the Rate of Reaction

In this part, the effect of diffusion on the rate of reaction was investigated with using the criteria of Weisz and Prater. The experiment was performed at 850 °C, steam to methane ratio from 2.0 to excess, methane feed rate from 6.0×10^{-5} to 5.1×10^{-4} mole/min, steam feed rate from 1.0×10^{-4} to 0.15 mole/min and catalyst weight of 2 g.

3.7. Determination of Thermodynamics Model of Reaction

In this part, the thermodynamics model of reaction was determined by comparing product gas composition from the experiment with thermodynamics equilibrium at various temperatures. The experiment was performed at 700-850 °C, steam to methane ratio of 4.0, methane feed rate from 1.27×10^{-4} to 1.46×10^{-4} mole/min, steam feed rate from 5.07×10^{-4} to 5.86×10^{-4} mole/min and catalyst weight of 5 g.