

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

- Methane of 99.99% purity obtained from Thai Industrial Gas Public Co., Ltd. was used as a reactant gas.
- Carbon dioxide of 99.999% purity obtained from Thai Industrial Gas Public Co., Ltd. was used as a reactant gas.
- Helium of 99.999% purity obtained from Thai Industrial Gas Public Co., Ltd. was used as a dilute gas and a carrier gas in Gas Chromatograph.
- Hydrogen of 99.999% purity obtained from Thai Industrial Gas Public Co., Ltd. was used for catalyst pretreatment.
- Carbon monoxide of 1%, carbon dioxide of 1%, methane of 1%, ethane of 1%, ethylene of 1% and acetylene of 1% in nitrogen (Scotty II Standard Gases) obtained from Ligand Scientific Co., Ltd. was used as standard gases.
- Carbon monoxide of 10% in helium obtained from Ligand Scientific Co., Ltd. was used as a standard gas.
- Zero-graded air obtained from Thai Industrial Gas Public Co., Ltd. was used for driving the auto-sampling valve.

3.2 Catalyst

The tungsten wire of 99.95% (metals basis) purity and 0.25 mm in diameter was used as a catalyst. The length of the wire for each experiment was approximately 25 cm. It was coiled for shortening its length in order to be fitted into the reactor used (see Sec.3.3.2) in which the coiled tungsten was tentatively 1/8 inch in inside diameter.

3.3 Apparatus

The experimental apparatus used in this study is schematically shown in Figure3.1. It consists of 3 parts: (i) gas mixing section, (ii) catalytic reactor, and (iii) gas analytical instrument.

3.3.1 Gas Mixing Section

This section was used for blending gases to a desired concentration and flow rate before it was sent to the catalytic reactor. Methane, carbon dioxide and helium were used as the reactant gases in this experiment without any further purification. All gases were passed through 7 micron stainless steel filters for removing the small particles. Sierra mass flow controllers (Model 904C-PE-II-PM) were used to control the flow rate of each gas to reach the exact value of desired concentration. In this report we give the concentration in terms of CO₂/CH₄ ratio that based on percentage mole basis.

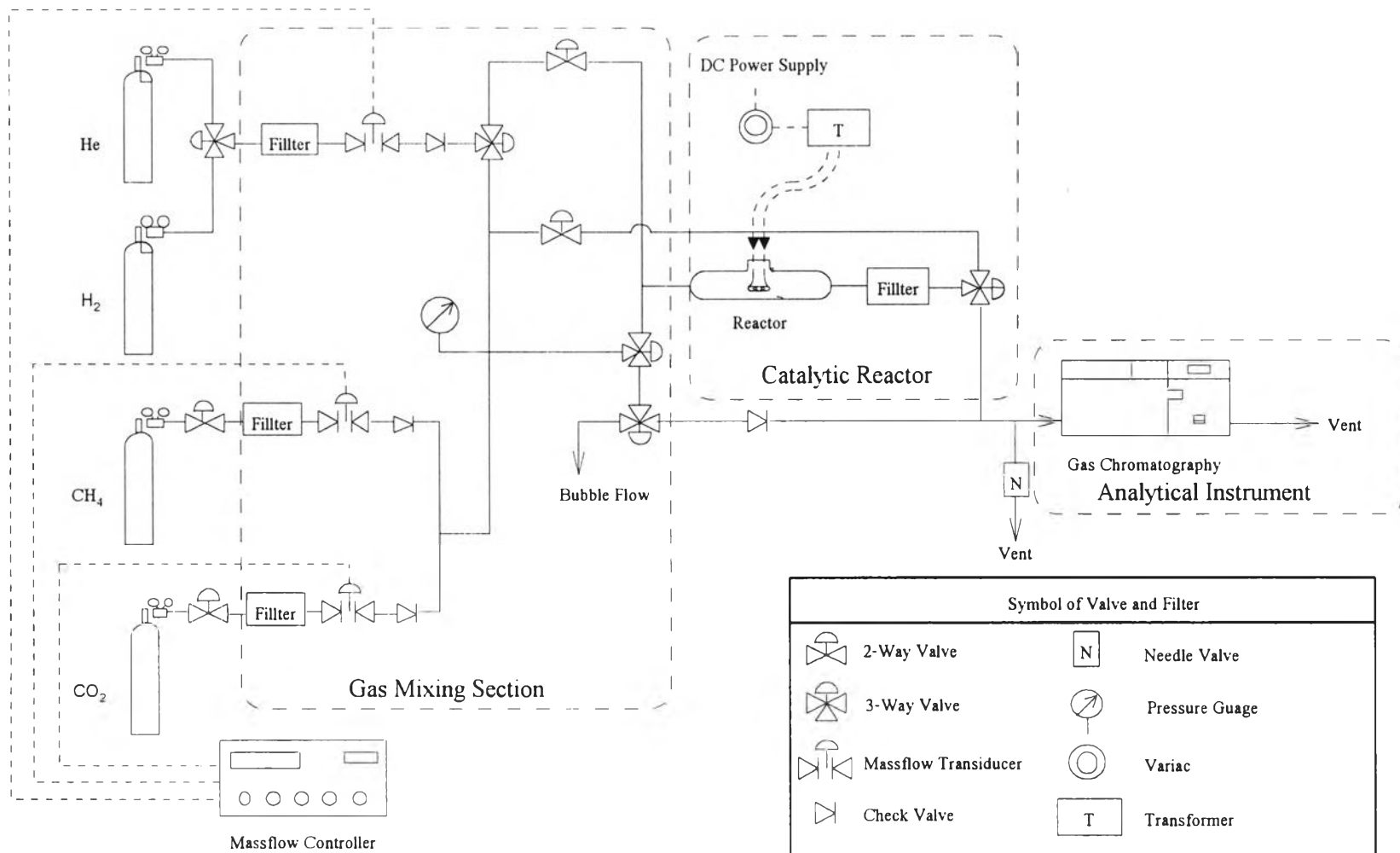


Figure 3.1 Schematic flow diagram.

3.3.2 Catalytic Reactor

Reactant gases were sent to the 2 inch-inside-diameter horizontal reactor. The tungsten coil positioned in the center of the reactor was heated by passing an DC current through it. The temperature of the wire was controlled by keeping the power of transformer constant, and an optical pyrometer was used to determine the average temperature of the wire. The temperature difference along the wire was approximately 20 °C.

3.3.3 Analytical Instrument

Product gases leaving the reactor were analyzed by Perkin-Elmer “Autosystem” Gas Chromatograph (GC). Two packed columns were used for GC separation: HayeSep DB for analysis of H₂, CO, CH₄, CO₂, C₂H₂, C₂H₄ and C₂H₆ with thermal conductivity detector (TCD); HayeSep T for analysis of methanol with flame ionization detector (FID). The 10-port valve was used in this research for injection of the same sample into separate column simultaneously.

Each cycle of GC analysis required about 15 minutes to complete before the next injection could be started. The GC conditions used for this research were summarized as follows:

| | |
|------------------------|--------------|
| Injector Temperature: | 110 °C |
| Oven Temperature: | 120 °C |
| Detector Temperature: | 160 °C |
| Carrier Gas: | He (99.999%) |
| Carrier Gas Flow Rate: | 30 ml/min |

3.4 Experimental Section

The coiled tungsten was pretreated at 130 watts power (about 800 °C) in hydrogen for 45 minutes and was cooled down in hydrogen for 30 minutes. After that the reactor was flushed with helium for 30 minutes. The total flow rate of each step was 50 ml/min. The concentrations of reactant gases were checked by using a bypass line to a GC to meet the desired concentration before feeding the reactant gases to the reactor.

3.4.1 Mass Transfer Limitation

The study of catalyst structure activity relationship for the purpose of catalyst improvements requires that the catalyzed chemical reaction is rate determining (no transport limitation, no gas phase reaction), and that the same reaction step remains rate determining over the temperature range studied. A major concern in the investigation of heterogeneously catalyzed gas phase reactions is that of transport phenomena, which usually tend to become rate determining at high temperatures. As the reforming reaction proceeds at high temperatures, reaction conditions have been carefully chosen to exclude such effects.

A stoichiometric feed composition of $\text{CH}_4/\text{CO}_2 = 1$ was used in this experimental part with the variation of total flow rate of reactant gases: 50, 70, 100 and 120 ml/min. The power supply was fixed at 80 watt (about 590 °C) and the initial concentration of CH_4 was 15 mole percent in all experiments. The CH_4 conversions were plotted as a function of total flow rate of reactant gases. The minimum flow rate necessary for no mass transfer limitation was determined.

3.4.2 The Effects of CO₂/CH₄ Feed Ratio

The variation of CO₂/CH₄ feed ratios: 0.3, 0.6, 1.0, 2.0 and 3.0 were studied by keeping the power of transformer constant at 110 watt (about 710 °C). The total flow rate was 50 ml/min by keeping the constant CH₄ concentration which was equal to 15% mol. Not only CH₄ and CO₂ conversions but also the production rates of H₂ and CO were plotted as a function of CO₂/CH₄ feed ratios. The surface carbon formed and water formation were also calculated from making a mass balance on carbon and hydrogen respectively.

3.4.3 The Effects of Reaction Temperature

In this experimental part, the suitable CO₂/CH₄ feed ratio and the total flow rate of reactant gases excluding diffusional limitations were used. The reaction temperature was varied by changing the power input to the wire: 80 watt, 90 watt, 100 watt and 110 watt. Both CH₄ and CO₂ conversions, and the production rates of H₂ and CO were plotted as a function of reaction temperature.

3.4.4 Finding the Activation Energies of H₂ and CO Formation

A stoichiometric feed composition of CH₄/CO₂ = 1 and the total flow rate was 50 ml/min. The variations of power supply that gave 3-5 percent conversion, 5-10 percent conversion, 20-30 percent conversion, 40-50 percent conversion and 80-100 percent conversion were investigated. The rates of H₂ and CO formation were plotted as a function of temperature. Then the activation energies of H₂ and CO formation were obtained.