

CHAPTER III

METHODOLOGY

3.1. Materials

The gases used in this research were obtained from TIG Co., Ltd.

1. Methane source gases were 15% methane in nitrogen for lean mixture and pure methane for rich mixture.
2. Air source gases were a high purity oxygen and an ultra high purity nitrogen (UHP : purity 99.999%).
3. Autosampling valve driving gas was a zero grade air.

The chemical reagents used for catalyst preparation were as followed:

1. Palladium(II)chloride (PdCl_2) was obtained from Aldrich Chemical Company, In.
2. Weakly acidic aluminum oxide (Alumina , Al_2O_3 : mesh ~150 and surface area = $182 \text{ m}^2/\text{g}$, Appendix A.) that was used as a thermal support of catalyst was obtained from Aldrich Chemical Company, Inc.
3. Concentrated hydrochloric acid (HCl : 36.5-38.0 %) used to dissolve palladium(II)chloride(PdCl_2) was obtained from J.T.Baker Inc.

3.2. Catalyst Preparation

One % palladium on alumina catalyst (surface area = $112.1 \text{ m}^2/\text{g}$, Appendix A.) was prepared by impregnation method. Impregnation method is used in preparing expensive catalysts.

Palladium metal solution was prepared by dissolving palladium(II) chloride (PdCl_2) with sufficient hydrochloric acid (HCl) to completely dissolve the salt. Alumina (Al_2O_3) support was impregnated by palladium solution and then was dried overnight at 343 K. After drying it was calcined at 1073 K for 6 hr, followed by washing with hot deionized water at 353 K. The final catalyst was dried at 343 K overnight.

3.3. Characterization

3.3.1. BET surface area

The surface area of catalyst was measured by the 5 points BET method using a Quantachrome corporation autosorb I. Before measurement, the samples were cleaned by heating under vacuum to eliminate volatile adsorbents at the surface (393 K for 12 hr.). By measuring the quantity of gas adsorbed onto or desorbed from a solid surface at 5 equilibrium vapor pressure (P/P_o) values (0.1115, 0.1615, 0.2115, 0.2615 and 0.3115) by the static volumetric method, the data were obtained by admitting or removing known adsorbate gas, nitrogen, into or out of a sample cell containing the solid adsorbent maintained at a constant temperature below critical temperature of the adsorbate, that is 77 K for nitrogen.

The adsorption data was calculated by using the Brunauer-Emmett-Teller (BET) equation.

$$1 / [W((P_o/P) - 1)] = 1 / [W_m C] + [(C-1)/(W_m C)] * P/P_o$$

W = weight of gas adsorbed at relative pressure P_o

W_m = weight of adsorbate constituting a monolayer of surface coverage

C = constant that is related to the energy of adsorption in the first adsorbed layer and magnitude of adsorbate/adsorbent interaction

$$\text{Surface area of sample} = W_m A_{\text{nitrogen}} (6.02 \times 10^{23}) / M_{w, \text{nitrogen}}$$

$$A_{\text{nitrogen}} = \text{cross-sectional area of one molecule nitrogen} \\ = 0.162 \text{ nm}^2 \text{ (at 77 K)}$$

$$M_{w, \text{nitrogen}} = \text{molecular weight of nitrogen} = 28$$

3.3.2. CHNS/O Analysis

The amount of carbon deposition (coke) was measured by using CHNS operating mode of Perkin Elmer 2400 Series II CHNS/O Analyzer. This machine employs a combustion method to convert the sample elements to simple gases (CO_2 , H_2O , N_2 and SO_2). The sample was first oxidized in a pure oxygen environment using classical reagents. Unused elements , such as halogen, are removed in the reduction zone of this equipment. The resulting gases were homogenized and controlled to exact condition of pressure, temperature and volume. The homogenized gases were passed through chromatography column for separating and were sent to the thermal conductivity detector [TCD]. The final results were in percent of carbon, nitrogen , hydrogen and sulfur in the sample.

3.4. Apparatus

The experimental apparatus used in this research is shown schematically in Figure 3.4 It consists of 3 parts : (i) gas mixing section, (ii) catalytic reactor, and (iii) analytical instrument.

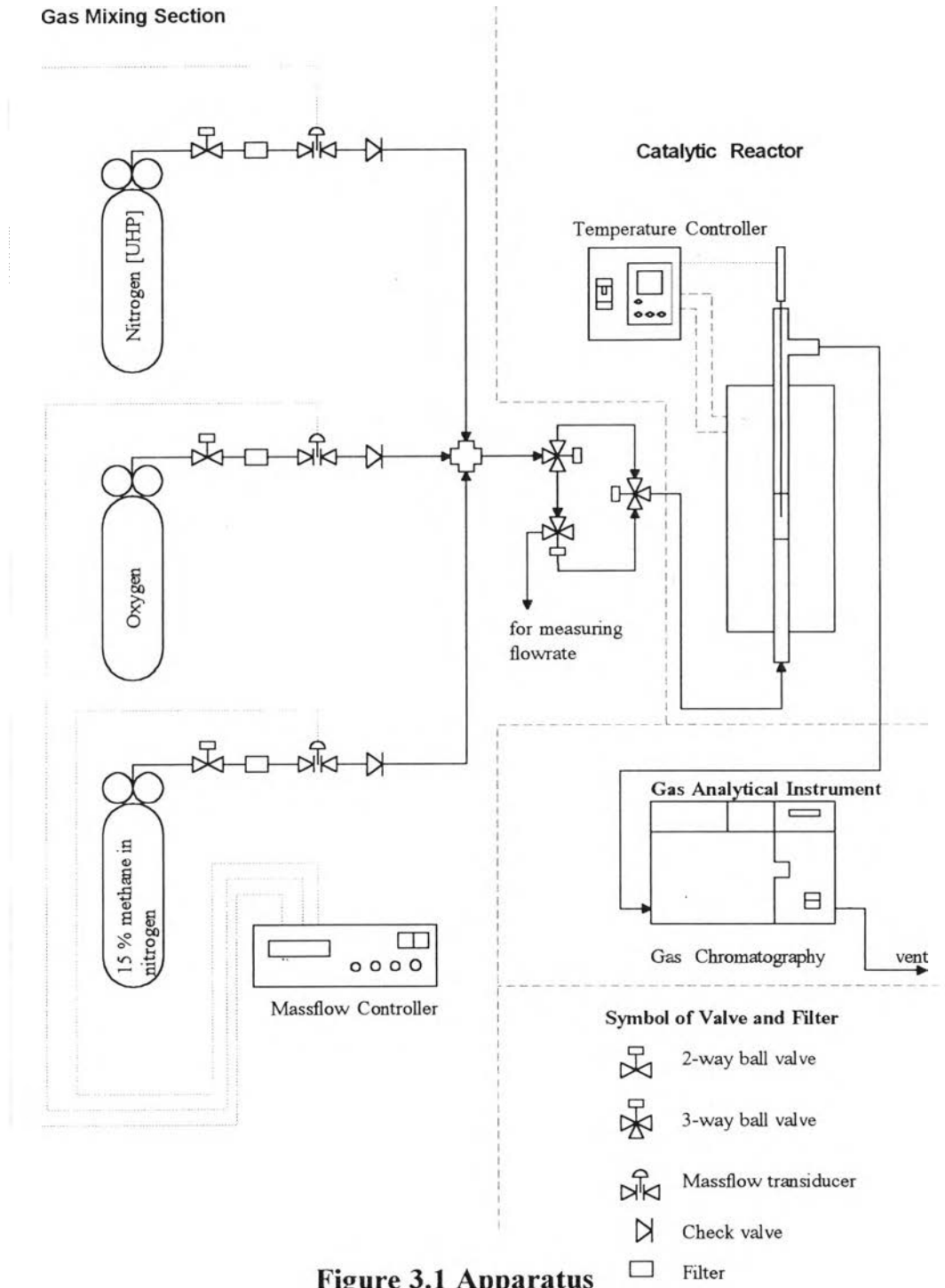


Figure 3.1 Apparatus

3.4.1. Gas Mixing Section

This section was for blending gases to a desired concentration and flowrate before it was sent to the catalytic reactor. Methane, oxygen and nitrogen were the reactant gases in this experiment. All gases were passed through the 7 micron stainless steel filter for removing the small particle in the gas. Sierra mass flow controllers (Model 904C-PE-II-PM) were used to control amount of each gas to reach the exact value of desired concentration. In this research the concentration was in terms of air-fuel ratio that based on volumetric basis or percentage basis, and flowrate in unit of ml/min.

3.4.2. Catalytic Reactor

Reactant gases were sent to the T-shape 1/4 inch diameter quartz reactor at the bottom end. Gases were oxidized by catalyst at the middle of reactor and the product gases flowed out at the top end. At the other top end a 25 inch type-K thermocouple was fixed for measuring the temperature of catalyst bed. The signal from the thermocouple was sent to the Yokogawa temperature controller model UT 37 that was used to control catalyst bed temperature for achieving a constant operating temperature. Heat was generated by a heating coil in the heater and was insulated by refinery brick.

3.4.3. Gas Analytical Instrument

This is the final section of the apparatus. Product gases from the reactor were analyzed by Perkin Elmer Autosystem gas chromatograph. Gases were sampled by the 100 microlitre Arnel autosampling valve (6-port valve) and were injected into the column at 413 K. The 30 ft. Hayesep DB chromatography column was used for separating all gases. A thermal

conductivity detector (TCD) at 413 K was used. The results were analyzed by the Therbochrome Program in PC.

The calibration standard gases were : methane and oxygen as the reactants; carbon dioxide, hydrogen, ethylene and ethane as the products. Carbon monoxide could not be detected because of the overlapping effect with nitrogen peak, which was used as the carrier gas.

3.5. Experimental Section

This experiment was investigated by using 0.3 gram of 1% Pd on alumina catalyst. In the experiment, the catalyst was heated up to the desired constant temperature at the rate of 15 K/min and maintained at that temperature for 5 minutes. The catalyst was oxidized “ in situ ” under oxygen for 30 minutes and then was cleaned by passing nitrogen for 10 minutes. Methane was passed through the bed first for 10 minutes then nitrogen, followed by oxygen at desired flowrate. The total flowrate of this test is 100 ml/min. The composition of outlet gases were continuously measured at 25 min. interval by the G.C. After reaching steady state, the flame was extinguished and the reactor was let to cool down. The catalyst was analyzed for carbon deposition (coke) that may be generated during the operation.

3.5.1 The effect of reaction temperature

In this test, the desired constant feed composition is 1% methane balance air mixture (air-fuel ratio = 100) and 100 ml/min of gas flowrate. The temperature in these tests was varied from 598 to 673 K.

The conversion of methane was calculated by

$$\text{conversion} = [\text{CH}_4 \text{ in feed} - \text{CH}_4 \text{ in product}] / \text{CH}_4 \text{ in feed.}$$

Finally, the relation between conversion and temperature were determined by plotting both values on the X-Y diagram and fitting them with a mathematical model.

3.5.2. The effect of air to fuel ratio

In this experiment, air-fuel ratio is varied in the wide range (from fuel-rich to fuel-lean), so the effect of air-fuel ratio was separated into 2 parts. For the fuel-rich mixture and around stoichiometric ratio, the product distribution at 100 % conversion of a limiting reactant, i.e. oxygen, was investigated. In fuel-lean mixture, there is enough oxygen for combustion so the conversion of methane at constant temperature and various air-fuel ratio was investigated.

a.) Product distribution under rich and lean operation condition testing.

The criterion of this part was 100 % conversion of a limiting reactant. In the fuel-rich mixture operating condition, methane was in excess and the limiting reactant was oxygen. On the other hand for fuel-lean mixture condition, methane was the limiting reactant. Air-fuel ratio for the fuel-lean mixture operation was varied from 11.365, 12.872 and 14.712. For the rich mixture operation, it was varied from 3.267 to 8.540. The stoichiometric air-fuel ratio is 9.524.

b.) Methane conversion at constant temperature testing

In this test, the effects were measured at the constant temperature of 673 K. The air to fuel ratio was varied from 11.40 to 94.63. The steady state conversion was determined in the same way as in the previous part using a mathematical program to fit the data.