



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals

Catalyst preparation requires the following chemicals:

- $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Hydrogen tetrachloroaurate (III) trihydrate) Au 49.5% from Alfa AESAR.
- $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (Dihydrogen hexachloroplatinate (IV)) Pt 37.5% from Aldrich Chemical Company, Inc.
- $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Zinc nitrate hexahydrate) from Merck
- Na_2CO_3 Anhydrous (Sodium Carbonate) from APS Finechem
- $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Ferric (III) nitrate nonahydrate) from Fluka

3.1.2 Gases

Gases used in this research work are:

- 20% CO_2 in He from Praxair (Thailand) Company Limited.
- 3.00% CO in He from Thai Industrial Gases Public Co., Ltd.
- Ultra high purity (99.999%) He from Thai Industrial Gases Public Co., Ltd.
- Ultra high purity (99.999%) H_2 from Thai Industrial Gases Public Co., Ltd.
- 5% O_2 in He from Thai Industrial Gases Public Co., Ltd.

3.2 Equipment

The experiment setup is shown schematically in Figure 3.1. It can be divided into 3 main parts.

3.2.1 Gas Blending Section

The reactant gas mixture contained 1% CO , 1% O_2 and 40% H_2 with the balance being He. Each stream was passed through the micro-filter to remove particles before entering into the mass flow controllers. All reactants were sent to the

mixing chamber for mixing before going to the reactor with a total flow rate of 50 ml/min at atmospheric pressure.

3.2.2 Catalytic Reactor

The preferential oxidation of CO was conducted under atmospheric pressure in a Pyrex glass U-tube micro-reactor having an internal diameter of 6 mm. The catalyst was packed between glass wool plugs in the middle of the reactor. The temperature of catalyst bed was monitored and controlled by PID temperature controller equipped with a thermocouple (Type K).

3.2.3 Analytical Instrument

The outlet gas from the reactor was analyzed by auto-sampling in an on-line gas chromatograph equipped with a packed carbosphere (80/100 mesh) column (10 ft x 1/8 inch) and a thermal conductivity detector (TCD).

3.3 **Catalyst Preparation Procedure**

3.3.1 AuPt/A Zeolite Catalyst

AuPt/A zeolite catalyst was prepared by incipient wetness impregnation method. Commercial A zeolite was used as a catalyst support. Appropriate concentrations of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ aqueous solutions were impregnated on a catalyst support before drying in an oven at 110°C overnight and subsequently calcining in air at 500°C for 5 h with a $10^\circ\text{C min}^{-1}$ ramping rate. Prior to the reaction, the catalysts are in-situ pre-treated in the U-tube micro-reactor in a He flow at 110°C for 1 h.

3.3.2 Au/ZnO and Au/ZnO-Fe₂O₃ Catalysts

3.3.2.1 *Deposition-Precipitation Method*

The ZnO support was synthesized by the precipitation method. An aqueous solution of 1 M Na_2CO_3 was added dropwise into a 0.1 M $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution under vigorous stirring at 80°C . The mixture was kept at a pH of 8 for 1 h. Excess ions, Cl^- and NO_3^- , were eliminated by washing with warm deionized water. The precipitate was dried at 110°C overnight and calcined in air at 400°C for 4 h. Nano-size Au deposition on ZnO with a Au loading of 1% atom was prepared by the deposition-precipitation method, using 0.1 M Na_2CO_3 as a precipitating agent. An aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was heated to 80°C and ZnO was then added to

this solution. Subsequently, the pH was adjusted to 8.0 by the addition of 0.1 M Na_2CO_3 under vigorous stirring. The temperature of the slurry was maintained at this temperature for 1 h. After the deposition of Au onto the support, the precipitate was filtered and washed carefully until the disappearance of NO_3^- and Cl^- ions. The Au/ZnO catalysts were dried at 110°C overnight and calcined in air at different temperatures (300, 400, and 500°C) for 4 h. The ZnO- Fe_2O_3 support at a 5:1 Zn:Fe molar ratio was prepared by co-precipitation using aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The support was dried at 110°C overnight and then calcined at 400°C for 4 h. For Au supported on ZnO- Fe_2O_3 , the catalysts are prepared by the same method, as described previously.

3.3.2.2 Photodeposition-Precipitation Method

ZnO and ZnO- Fe_2O_3 supports were synthesized by precipitation using aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka). The pH of solutions is adjusted to 8.0 by addition of 0.1 M Na_2CO_3 (Riedel-de Haen). After aging, washing, and drying, the precipitate was calcined at 400°C for 4 h to obtain a ZnO catalyst support. Nano-size Au deposition on synthesized supports with a Au loading of 1%atom is prepared by a photodeposition-precipitation technique under UV-vis light. ZnO is added to an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (ACROS). Subsequently, the pH is adjusted to 8.0 by addition of 0.1 M Na_2CO_3 as a precipitating agent. The suspensions were irradiated under UV-vis lamp with the power of 11 W in the photo-reactor and vigorously stirred at ambient temperature in series of 1, 3, and 5 h. The prepared catalysts were denoted as Au/ZnO-11W-1h, Au/ZnO-11W-3h, and Au/ZnO-11W-5h, respectively. Moreover, the power of UV-vis light effect was investigated which ranged from 11 to 176 W with the shortened irradiated time of 0.2 to 3 h in order to maintain the same supplied power. The prepared catalysts were denoted as Au/ZnO-11W, Au/ZnO-44W, Au/ZnO-88W, and Au/ZnO-176W, respectively.

The catalytic activities depend not only on the conditions for preparation method but also the precipitating agent. Therefore, urea (NH_2CONH_2) was used and denoted as Au/ZnO-urea. Otherwise, ZnO- Fe_2O_3 support at the Zn:Fe atomic ratio of 5:1 is prepared by co-precipitation method. The support is dried at 110°C overnight and then calcined at 400°C for 4 h. For Au supported on ZnO- Fe_2O_3 , the catalysts were prepared by the same method as mentioned above, which was denoted as Au/ZnO- Fe_2O_3 -11W-3h. The precipitate was filtered and washed carefully with deionized warm water until the disappearance of NO_3^- and Cl^- ions. Finally, the resulting solid was dried overnight. No catalyst pretreatment process was applied before all the reaction tests.

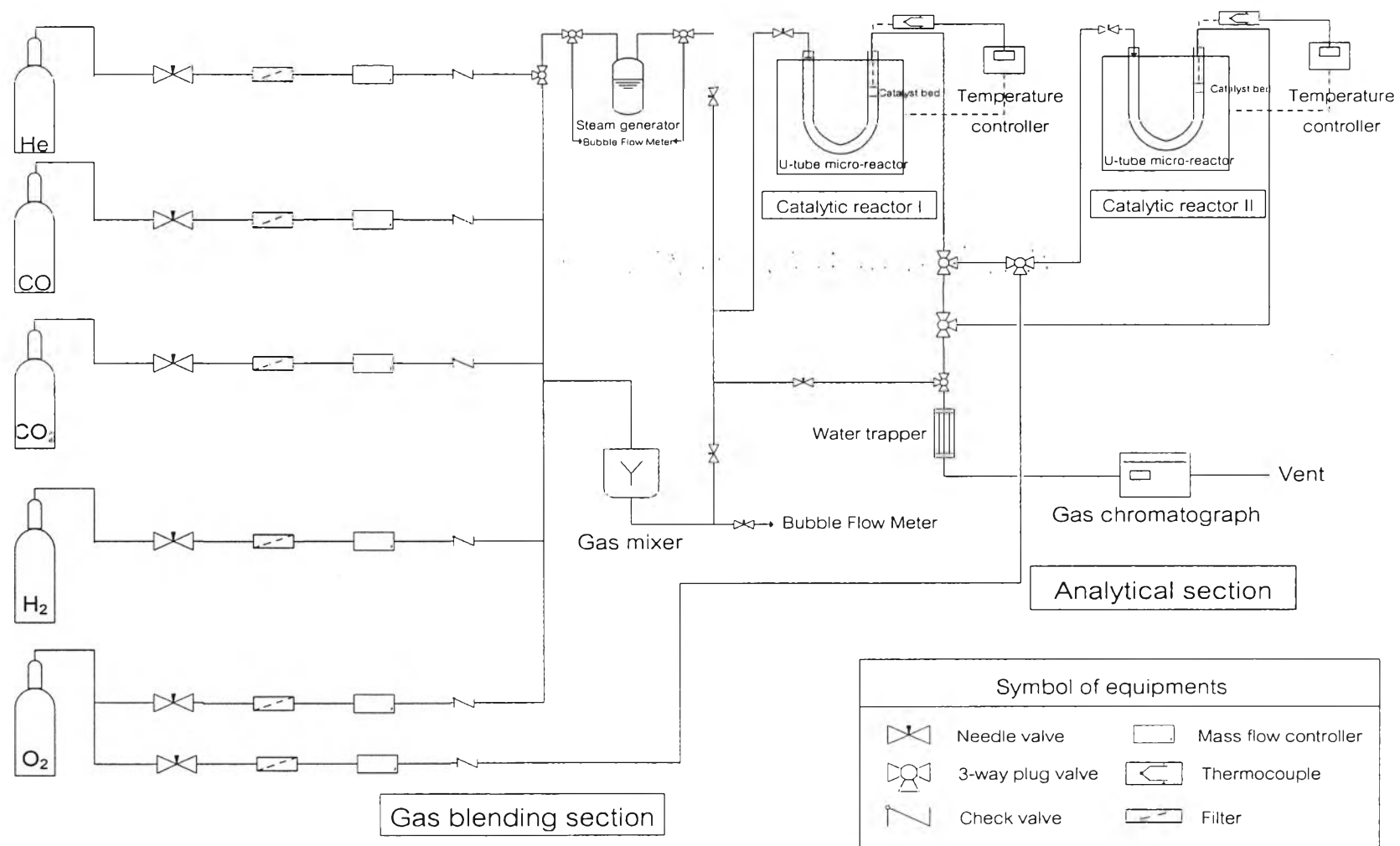


Figure 3.1 Experimental setup for preferential CO oxidation reaction using the double-stage reactor.

3.4 Catalyst Characterization

Varieties method was used to characterize the prepared catalysts to understand the effect of many parameters on the catalytic activities of the catalysts, as the followings:

3.4.1 X-ray Diffraction (XRD)

The crystallite size of the metals on the surface and the crystalline structure of the support are analyzed on a Rigaku X-ray diffractometer system (RINT-2200) with Cu tube for generating CuK_α radiation (1.5406 Å) and nickel filter, a generator voltage of 40 kV, and a generator current of 30 mA. X-ray diffraction (XRD) technique is based upon the fact that the X-ray diffraction pattern is unique for each crystalline substance. The identity of the crystalline phases can be found by matching the pattern of the unknown and standard. Additionally, the relative quantitative analysis was determined from the intensity of peak. For the same crystalline phase the higher of the peak indicates the higher content of that phase. The scan speed of $5^\circ (2\theta)/\text{min}$ with scan step of $0.02 (2\theta)$ is used for the continuous run in 20° to $80^\circ (2\theta)$ range. The goniometer parameters were took place as follows:

divergence slit: $1^\circ (2\theta)$,
 scattering slit : $1^\circ (2\theta)$,
 receiving slit : 0.3 mm.

The prepared catalysts was grounded to a fine and a homogeneous catalyst then packed in a thin-walled glass container. After that, it was placed in a sample holder. The signal was sent to an on-line computer to record and analyze. The average metal crystallite size is calculated by Scherrer's equation as shown in Equation 3.1 that shows the relationship between the crystalline thickness (D_b) and the broadening (β) of the diffraction line corresponding to the Bragg angle (θ) using wavelength (λ).

$$D_b = \frac{K \times \lambda}{B_d \times \cos(\theta)} \quad (3.1)$$

where:

D_b = mean crystallite diameter (Å),

K = Scherrer constant, 0.9,

λ = X-ray wave length (Å),

B_d = angular width of peak in term of $\Delta(2\theta)$,

θ = Bragg's angle of reflection (degree).

3.4.2 Transmission Electron Microscopy (TEM)

TEM was employed for investigating the average particle size of metals and identifying the microstructure of the prepared catalysts, such as metals dispersion, and the crystalline size of the metals on the support. Catalysts were prepared in thin form appropriate for TEM that it was dispersed in pure water and a drop of the suspension was deposited on a copper grid. TEM was carried out on a JEM 2010 operating at an accelerating voltage of 200 kV in bright field mode. A beam was passed through a series of lenses to form a magnified image of a sample that has been inserted in the area of the objective lens. The image from selected area was viewed through projection onto a viewing screen. However, electron beams are easily scattered by air molecules and TEM columns must be kept under high vacuum. Additionally, the electromagnetic lenses were used for focus the electron beam. The average Au size diameter (d_{TEM}) was calculated from the following formula: $d_{TEM} = \Sigma(n_i d_i) / n_i$ where n_i is the number of Au particles of diameter d_i .

3.4.3 Temperature Programmed Reduction Technique (TPR)

Temperature-Programmed Reduction (TPR) was employed for evaluating the number and quantity of the reducible species present in the prepared catalyst and the temperature at which the reduction itself takes place as a function of the temperature. The gas used for analysis is a mixture of reactive gas with an inert gas, as hydrogen in nitrogen at 5.32%. The prepared catalyst sample was submitted to a linear increase of temperature and to a constant flow of the gas mixture. The reaction generally starts at room temperature. At a certain temperature, the reaction speed becomes considerable and the hydrogen consumption can be monitored through the TCD detector. The signal integration allows calculating the quantity of

hydrogen consumed and the number of reacting sites. The TPR analysis also allows checking the presence of different states of oxidation of the contained metals.

3.4.4 Surface Area Measurement (BET)

One of the most essential properties of a heterogeneous catalyst is its surface area because the reaction takes place over the catalyst surface. The surface area, total pore volume and average pore size diameter of all prepared catalyst samples was determined by Brunauer-Emmet-Teller (BET) method using Sorptomatic 1990. N₂ gas was used as the adsorbate at liquid N₂ temperature (-196°C). A sample was outgassed by heating under vacuum at 300°C for 6 hours in order to eliminate adsorbed species on the surface before measurement. The results were analyzed by Autosorb Anygas Software Version 2.1, which were calculated using the BET equation as shown in Equation 3.2.

$$\frac{1}{W\left(\frac{P}{P_0} - 1\right)} = \frac{1}{W_m C} + \frac{(C-1) P}{W_m C P_0} \quad (3.2)$$

where:

W = weight of gas adsorbed at relative pressure P₀

W_m = weight of adsorbate constituting a monolayer of surface coverage

P = pressure of gas

P₀ = saturated vapour pressure of the liquid at the operating temperature

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

The surface area can be calculated by Equation 3.3.

$$A = \frac{W_m A_{nitrogen} \times 6.02 \times 10^{23}}{M_{w,nitrogen}} \quad (3.3)$$

where:

A = Surface area of sample

A_{nitrogen} = Cross-section area of one molecule nitrogen (0.162 nm^2 at -196°C)

$M_{\text{w,nitrogen}}$ = molecular weight of nitrogen (28 g/g-mol).

3.4.5 H₂ Pulse Chemisorption

A H₂ pulse chemisorption analysis determines mean particle size and percent metal dispersion by applying measured pulses of H₂ gas to the prepared catalysts. The H₂ gas chemically reacts with each active site until they have all reacted. Once the active sites have totally reacted, the discretely injected N₂ gas volumes emerge from the sample tube uncharged. The amount of H₂ gas chemisorbed is difference between the total amount of reactant gas injected and the amount that did not react with the active sites of the prepared catalysts. The size of each pulse of H₂ gas is determined by the loop on an electrically operated valve. Ten loops of different sizes are provided with the analyzer.

3.4.6 Inductively Coupled Plasma (ICP)

Elemental analyses were carried out in a Perkin-Elmer Optima 4300 DV inductively coupled plasma – optical emission spectrometer (ICP-OES) that detects the traces metal in prepared catalysts it can detect a wide range of elements with a sensitivity in the ppb range. An ICP requires that the elements which are to be analyzed be in solution. A liquid is nebulized and then vaporized with in the Argon plasma. The atoms and ions contained in the plasma vapour are excited into a state of radiated light (photon) emission. The radiation emitted can be passed to the spectrometer optic, where it is dispersed into its spectral components. From the specific wavelengths emit by each element. The radiation intensity, which is proportional to the concentration of the element in the sample, is recalculated internally from a stored set of calibration curves and can be shown directly as percent or measured concentration.

3.5 Catalytic Activity Measurement

3.5.1 Single-stage Process

The reaction was carried out in a fixed-bed U-tube micro-reactor by packing with 100 mg of the catalyst (80–120 mesh). For AuPt/A zeolite catalyst, helium gas was used to flush out the remaining water at 110°C for 1 h and the catalyst bed was cooled down to room temperature before being heated to the desired reaction temperature.

3.5.2 Double-stage Process

The preferential catalytic reactors were serially connected, as shown in Figure 3.1. The reaction in each stage was carried out in a fixed bed U-tube micro-reactor by packing each equally with 50 mg of the catalyst. The catalytic activity and process performance were investigated at various temperatures in the range of 50–300°C. Each stage has its own O₂ supply and a temperature controller to control the reaction temperature. An amount of O₂ entering each stage was varied at the split ratios of 20:80, 40:60, 50:50, 60:40 and 80:20. The effluent from the first reactor was passed directly to the second reactor.

3.5.3 Fuel Processing System

The fuel processing system, consisting of two major units in series i.e. evaporators, methanol steam reformer reactor, and double-stage preferential CO oxidation reactors, was constructed (Figure 3.2) to observe the catalytic activities in the real reformat. The methanol steam reforming generates hydrogen fuel. After evaporation of the fuel, a methanol-water mixture, the methanol reacts with water in the reformer over the prepared catalysts to produce H₂, CO₂ and CO. The products coming out from the methanol steam reformer was passed directly through the double-stage PROX reactors to eliminate trace amounts of carbon monoxide in the H₂-rich stream to an acceptable level (<10 ppm), by oxidation with O₂ over the prepared catalysts.

The effluent gas from the reactors was analyzed by auto-sampling in an on-line gas chromatograph using He as the carrier gas.

The methanol conversion, hydrogen yield, hydrogen selectivity, carbon monoxide selectivity and carbon dioxide selectivity from the methanol steam reformer are calculated by Equations 3.4 - 3.8.

$$X = \frac{CO + CO_2 + CH_4}{MeOH_{(in)}} \cdot 100\% \quad (3.4)$$

where

X = methanol conversion (%)

$MeOH_{(in)}$ = mole of methanol inlet

$$Y_{H_2} = X * S_{H_2} \quad (3.5)$$

where

$$S_{H_2} = \frac{H_2}{H_2 + CH_4 + CO + CO_2} \cdot 100\% \quad (3.6)$$

$$S_{CO} = \frac{CO}{H_2 + CH_4 + CO + CO_2} \cdot 100\% \quad (3.7)$$

$$S_{CO_2} = \frac{CO_2}{H_2 + CH_4 + CO + CO_2} \cdot 100\% \quad (3.8)$$

where

Y_{H_2} = H₂ yield (%)

S_{H_2} = hydrogen selectivity (%)

S_{CO} = carbon monoxide selectivity (%)

S_{CO_2} = carbon dioxide selectivity (%)

H_2 = mole of hydrogen in the product stream

CO = mole of carbon monoxide in the product stream

CO_2 = mole of carbon dioxide in the product stream

CH_4 = mole of carbon methane in the product stream

For PROX performance, the CO conversion and O₂ conversion are calculated based on the consumption of reactant gases along the preferential CO oxidation reaction. The CO selectivity was defined by the O₂ consumption for the desired CO oxidation reaction over the total O₂ consumption.

$$X_{CO} = \frac{[CO]_o - [CO]}{[CO]_o} \times 100 \quad (3.9)$$

$$X_{O_2} = \frac{[O_2]_o - [O_2]}{[O_2]_o} \times 100 \quad (3.10)$$

$$S = \frac{[O_2]_{CO}}{[O_2]_{CO} + [O_2]_{H_2}} \times 100 \quad (3.11)$$

where:

X = CO conversion (%),

S = selectivity (%),

[CO]_o = concentration of CO in the reactant gas,

[CO] = concentration of CO in the product gas,

[O₂]_o = concentration of O₂ in the reactant gas,

[O₂] = concentration of O₂ in the product gas,

[O₂]_{CO} = amount of O₂ for CO oxidation and

[O₂]_{H₂} = amount of O₂ for H₂ oxidation.

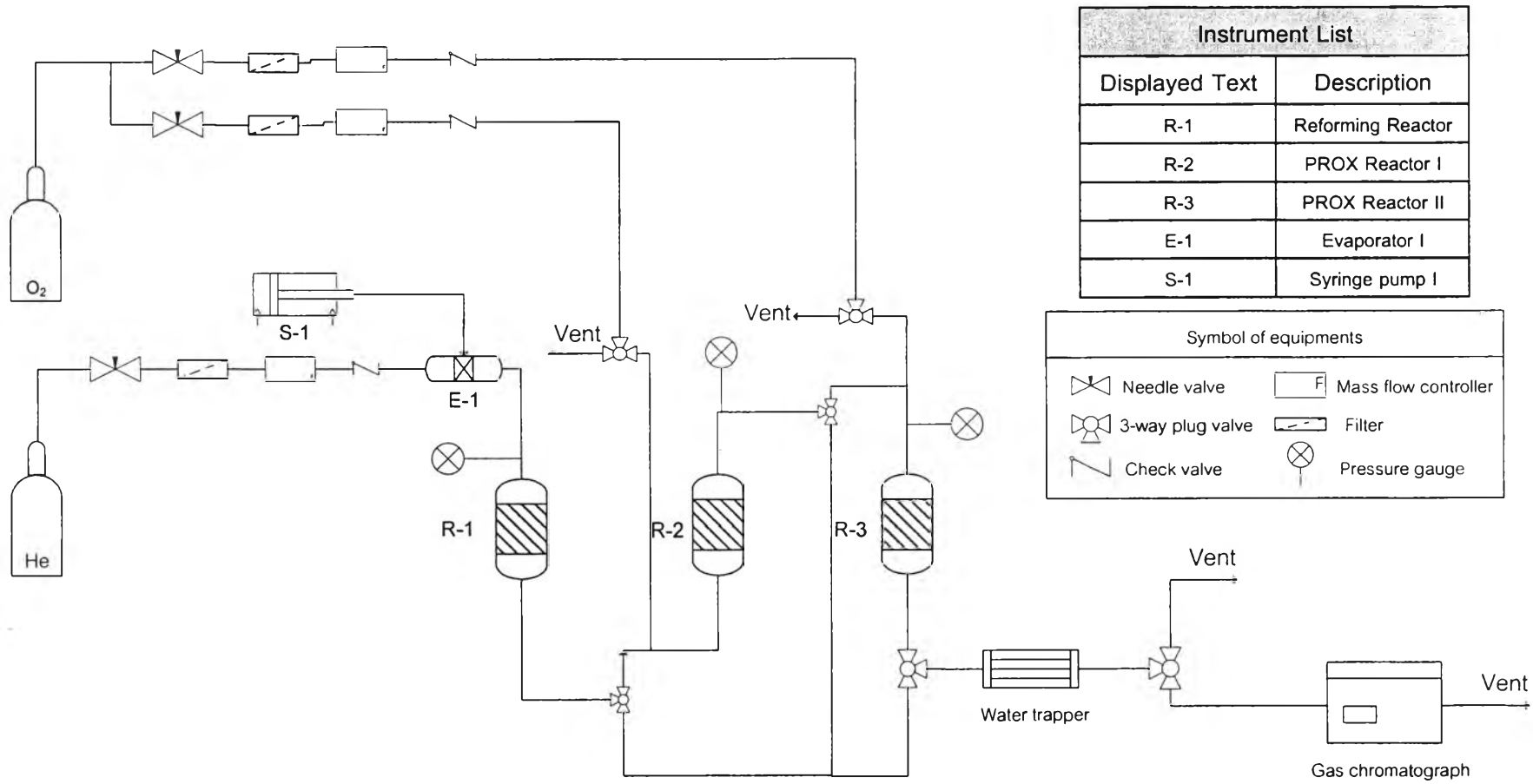


Figure 3.2 Schematic of fuel processor testing system.