CHAPTER III
METHODOLOGY

3.1 Materials

3.1.1 Catalyst Preparation Materials

All chemicals are obtained from Fluka Co., Ltd. listed below :

- Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 . 6H_2O$) of 99% purity
- Iron (III) chloride hexahydrate, $FeCl_3 \cdot 6H_2O$ of 99% purity
- Cobalt (II) nitrate hexahydrate, $Co(NO_3)_2 \cdot 6H_2O$ of 99% purity
- Manganese (II) chloride tetrahydrate, $MnCl_2 \cdot 4H_2O$ of 99% purity
- Hexaammonium heptamolybdate tetrahydrate, $(NH_4)_6 Mo_7O_{24}4H_2O$ of 99% purity
- Sodium borohydride, $NaBH_4$ of 99% purity
- Ethanol, C_2H_5OH of 99% purity
- 1-Methoxy-2-propanol, C_2H_5OH of 99% purity

3.1.2 Gases

All gases were obtained from Thai Industrial Gas Public Co., Ltd. and listed below :

- Carbondioxide of 99.999% purity
- Helium of 99.99% purity
- Nitrogen of 99.99% purity

3.1.3 Biomass

Cellulose was obtained from Advance Agro company and Siam Pulp and Papers Co., Ltd. and were used as biomass representative.

3.2 Catalyst and Sample Preparation

3.2.1 Catalyst Preparation

Catalysts were prepared by precipitation technique. This technique is a simple way to prepare pure metal by using chemical reduction of metal ion of metal precursor solution. Five transition metals were prepared which are Fe, Ni, Co, Mn and Mo. To prepare each metal, the solid $NaBH_4$ was added to the solution of each metal precursor in a reaction vessel under an inert atmosphere of nitrogen. A vigorous gas evolution was observed instantly with the precipitation of black jellylike solid. After the gas evolution, 30 more minutes was allowed for completing the reaction and then centrifuged at 5000 rpm for 15 minutes to separate the metal particles. The precipitates were washed many times with ethanol. After washing, the precipitates were dried in a vacumm oven to achive dry metal particles.

3.2.2 Sample Preparation

The sample for gasification was prepared by mix cellulose and catalyst together. At first, cellulose was crushed to 1-2 mm and dried for overnight to remove moisture from cellulose. Then, the catalyst was mixed with dry cellulose and loaded in cylinder basket of reactor.

3.3 Catalyst Characterization

3.3.1 BET Surface Area

Brunauer-Emmet-Teller (BET) equation was applied to determine the surface area of the catalysts . This measurement is based on the physical multi-layer adsorption of the inert gas, carried out by Autosorb-1 Gas Sorption System. The liquid Nitrogen (N_2) at 77 K, which has a cross-sectional area of 16.2×10^{-20} m^2 per molecule, was used as the adsorbate. The samples were out-gassed in the flow of He at 250 ^{o}C for 8 hours before the analysis was started. The surface area was calculated from the five-point nitrogen adsorption, and the average pore volume were calculated at P/P_0 ratios close to unity.

3.3.2 X-ray Diffraction (XRD)

X-ray diffraction is based upon the fact that the X-ray diffraction pattern in unique for each crystalline substance. Thus, if an exact match can be found between the pattern of an unknown and an authentic sample, chemical identity can be assumed (Baiker, 1985). It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. Comparing the same crystalline substance of two different samples, the higher intensity shows the higher content.

A Philips X-ray diffractometer system (PW 3020) equipped with a graphite monochromator and a Cu tube for generating a CuK radiation (1.5406 Å) is used to obtain the XRD patterns. The sample is ground to a fine homogeneous powder and is held in the beam in thin-walled glass. Constructive interference may be archived with monochromatic irradiation by varying the angle of incidence (5 to 80 degrees). The digital output of the proportional X-ray detector and the goniometer angle measurements are sent to an on-line microcomputer for storage and subsequent data analysis by PC-APD version 3.5B.

Scherrer equation (Baiker, 1985) relates the mean crystallite diameter and the broadening of the X-ray diffraction lines per the expression

$$D_b = K\lambda/B_d \cos \Theta$$

where λ is wave length of the monochromatic X-ray radiation (Å)

K is the Scherrer constant whose value depends on the shape of the particle (assume equal to 1)

B_d is the angular width of the peak in the terms of $\Delta(2\Theta)$ (radian)

Θ is the glancing angle (degree)

D_b is the mean crystallite diameter (Å)

3.4 Experimental Apparatus

The experimental apparatus used in this study is schematically shown in Figure 3.1. It consists of 2 parts : (i) gas transporting section and (ii) catalytic reator.

3.4.1 Gas Transporting Section

This section was used for transporting gases to a desired concentration and flow rate before it was fed into the catalytic reactor. Carbon dioxide, steam or both of them were used as the gasifying agents in the experiments. Helium was used as carrier gas for steam which was produced from steam generator. Brooks mass flow controllers were used to control the flow rate of carbon dioxide and helium to attain the exact vale of desired concentration.

3.4.2 Catalytic Reactor

The catalytic reactor made of stainless steel. A 10 mm inside diameter cylinder basket was connected at the top of reactor tube. The mixture of cellulose and catalyst in weight ratio 5:1 was put between quartz wool at the middle of cylinder basket and placed in a tubular furnace equipped with a temperature controller. The temperature controller which connected to a K-type thermocouple was placed into the reactor with one end touching on the sample in order to measure the sample bed temperature. The variation of temperature was $\pm$ 5 ^{o}C.

3.5 Product Analysis

3.5.1 Mass Spectrometer (MS)

A Balzers Omnistar mass spectrometer with an ion source of electron impact at 70 eV was employed for qualitative analysis of gas products from gasification. The qualitative identification of possible products was performed comparing sample mass spectrum with NIST database reference mass spectrum.

3.5.2 Gas Chromatography (GC)

The product gases which are H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 were analyzed by a Shimatzu gas chromatograph using a Carbonplot capillary column. All product gases were analyzed with a thermal conductivity detector (TCD). Each cycle of GC analysis required about 35 minutes to complete before the next injection can start. The GC conditions used in this study were summarized as follows:

Injector Temperature :	185 °C
Oven Temperature :	120 °C
Detector Temperature :	150 °C
Carrier Gas : He (99.99 %)	
Carrier Gas Flow Rate :	28 ml/min

3.5.3 Gas Chromatography/Mass Spectroscopy (GC/MS)

The liquid product obtained from gasification was analyzed by TraceGC/PolarizQ MS (ThermoFinnigan). The capillary column DB-5 MS was used and the compounds were identified by MS (15-500 a.m.u., 70 eV). The qualitative identification of compounds was performed comparing sample mass spectrum with NIST database reference mass spectrum.

3.6 Experimental Procedures

At first, the sample was placed in the cylinder basket and purge with He at for 15 minutes in order to remove air and oxygen in reactor. This method was used in all of the experiments. The concentration of reactant gases were checked by using a by-pass line to a GC to meet the desired concentration before feeding the reactant gases to the reactor.

3.6.1 Catalyst Screening

Six samples which are blank sample (pure cellulose) and 5 samples with catalysts, Fe, Ni, Mn, Co, and Mo were tested by Mass Spectrometer. In each

batch, the sample was heated under 100 % of CO_2 with flow rate 100 ml/min. The heating rate is 10 °C/min from room temperature to 900 °C, when temperature reaches to 900 °C. The reaction will be operated under isothermal process at 900 °C for 45 minutes. The effluent gases were on-line detected by MS. The relative intensity of mass of H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 of each catalyst were compared.

3.6.2 CO_2 Gasification

The 100 % of carbon dioxide with flow rate of 100 ml/min was fixed for all experiments. After loading sample in reactor, the system was stared by feed CO_2 at desired level and reactor temperature was ramped from room temperature to desired temperatures which are 600, 700, 800 and 900 °C within 10 minutes. When temperature go to desired temperature it will be switched to isothermal process at this temperature for 45 minutes. The effluent gases were collected in gas collector. After finishing isothermal process, the collected gases were analyzed by sampling the collected gases at injection port of gas collector then inject the sampling gas to GC. Product gas composition, gas yield, liquid yield and char yield were investigated.

3.6.3 Steam Gasification

In this test, steam was used as gasifying agent instead CO_2. The desired steam flow rate was 100 ml/min. After loading sample in reactor, the system was purged with helium gas for about 10 min. The furnace and steam generator were then turned on. When the reactor temperature reached 150 °C, the syringe pump was started and the flow was adjusted at the desired level. Each sample was ramped from room temperature to desired temperature which are 600, 700 and 800 °C within 10 minutes. When temperature go to desired temperature it will be switch to isothermal process at this temperature for 45 minutes. The effluent gases were collected in gas collector. After finishing isothermal process, the collected gases were analyzed by sampling the collected gases at injection port of gas collector then inject the sampling gas to GC. Product gas composition, gas yield, liquid yield and char yield were investigated.

3.6.4 Liquid Product Characterization

The liquid obtained from the condensed vapor of gasification products at temperature around -5 °C. To identify the components in these products, GC/MS is utilized to analyze these samples. The sample liquid were filtered and injected to sampling port. The qualitative identification of compounds was performed comparing sample mass spectrum with NIST database reference mass spectrum.

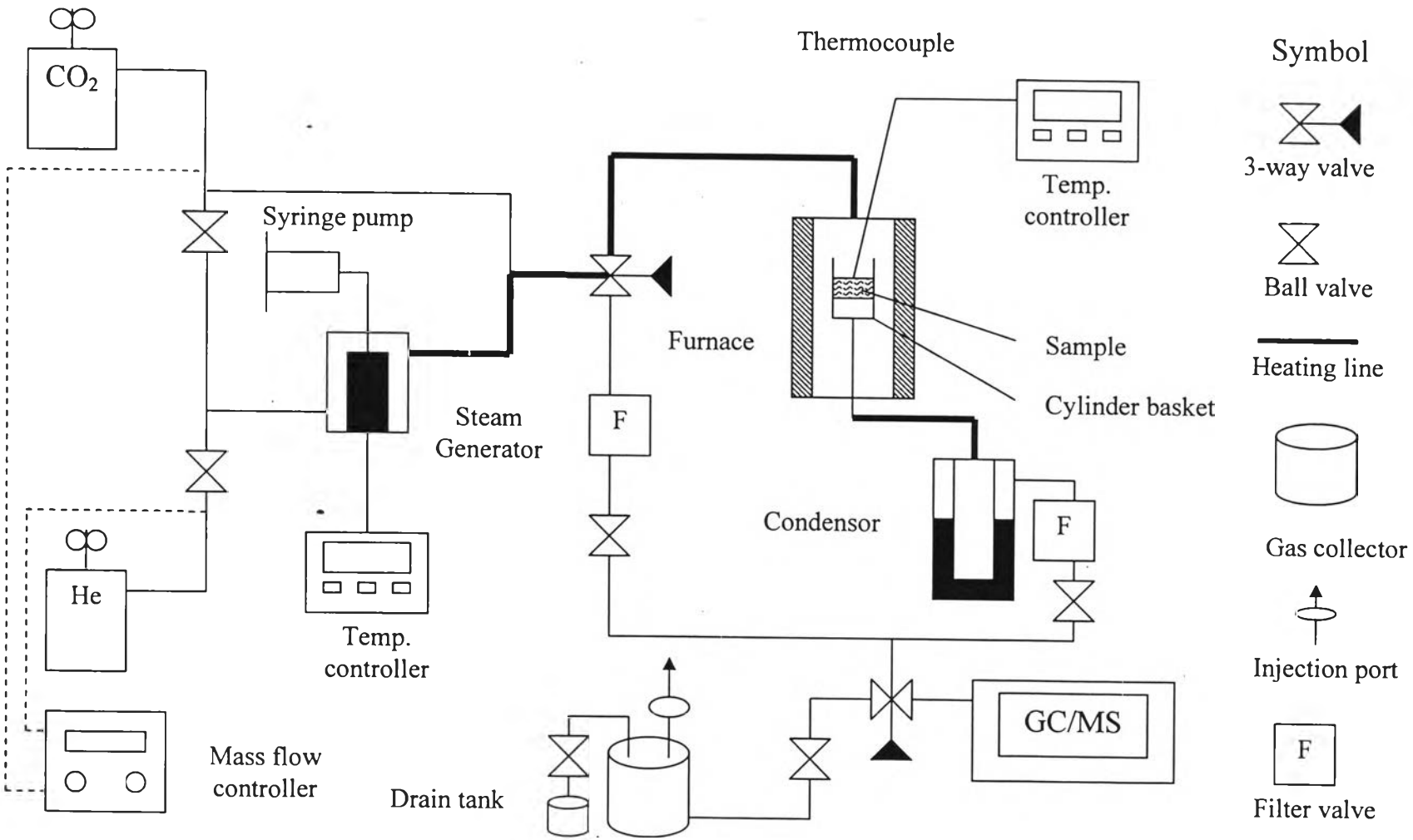

Figure 3.1 Schematic of experimental apparatus.