CHAPTER III

EXPERIMENTAL AND APPARATUS

3.1 Chemicals

3.1.1 Dolomite from Southern of Thailand

3.1.2 Nickel nitrate hexahydrate

3.1.3 Ammonium carbonate

3.1.5 Cobalt nitrate

3.1.6 Hexachloroplatinic acid

3.1.7 Ferric chloride

3.1.8 Silica

3.1.9 Standard gas

3.1.10 Nitrogen gas 99.99%

3.1.11 Helium gas 99.9999%

3.1.12 Oxygen gas

3.1.13 Hydrogen gas

3.2 Apparatus

3.2.1 Experimental apparatus

The experimental set up, shown in Figure 3.1, consists of six main parts: (i) a fluidized bed reactor, (ii) biomass feeding section, (iii) steam generator and preheating section, (iv) cooling section, (v) tar collector and (vi) gas analysis section. Experiments were carried out in a fluidized bed gasifier with the height of 92 cm. and diameter of 10 cm. The cylindrical stainless steel reactor is located inside an electric furnace and controlled by electric heater. During start up, the reactor was charged with 10 g of Ni/dolomite catalyst as bed material and temperature in the catalytic bed was measured by a type K thermocouple. Biomass was continuously fed from the screw feeder with feed rate of 1.76 g/min. Steam and nitrogen was used as gasifying medium. Water was pumped into the steam generator and flowed to the reactor entrance through a preheating line. When the bed temperature reached the desired level and become steady, the gas product exited the reactor. The gas was analyzed every 3 min after the test run reaches a stable state. In this experiment, the nitrogen gas was used for fluidization.
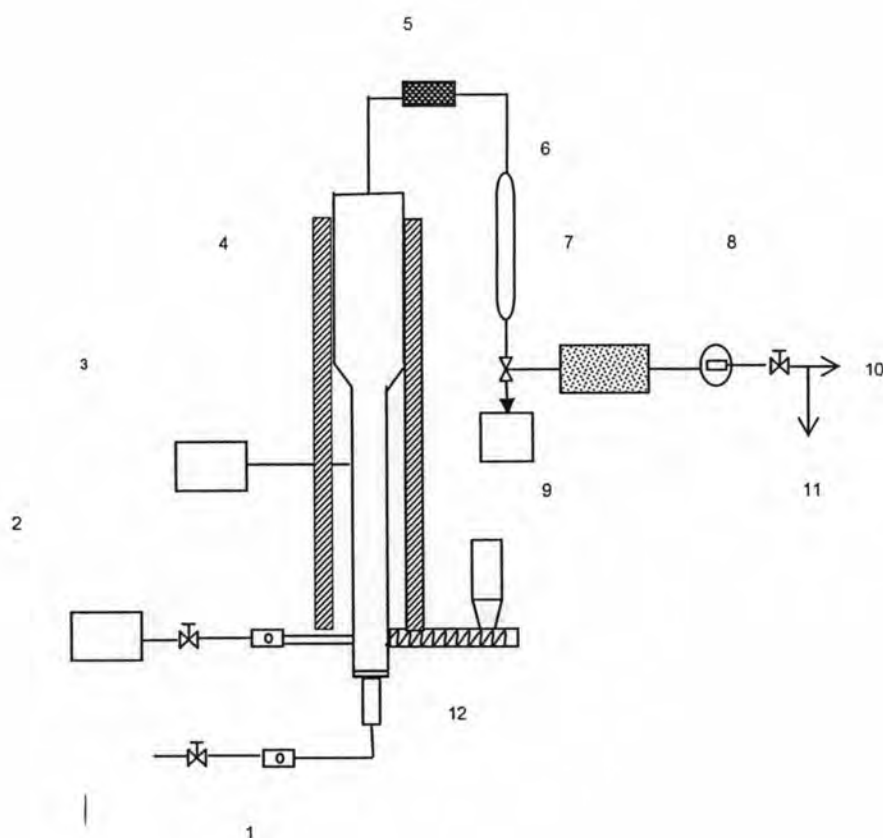
Figure 3.1 Schematic diagram of catalytic biomass gasification process (1: Flow meter; 2: Steam generator; 3: Temperature controller; 4: Tube furnace; 5: Filter; 6: Condenser; 7: Moisture trap; 8: Flow gas meter; 9: Tar trap; 10: Gas analysis; 11: Vent; 12: Biomass feed hopper)

3.2.2 Gas analysis

During reaction, the gaseous product flowed out of the reactor, passed through the cooling section, moisture trap and finally, to the gas filter for drying and cleaning. The exited gases were analyzed by an on-line gas chromatography (Model GC-2010, Shimadzu, Japan) as shown in Figure 3.2. The gas chromatography is fitted with the Unibeads C column (3mx3mm.I.D) and TCD detectors with helium and nitrogen as carriers to mainly detect H_2, CO, CO_2 and CH_4 in gaseous state. (Gas

chromatography condition: Injection temperature 100°C, Detector temperature 180°C, Column temperature 100°C, Carrier Gas flow 20 ml/min)
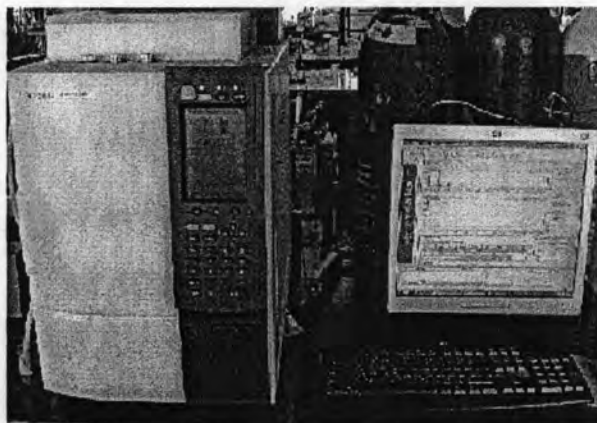

Figure 3.2 Gas Chromatography

3.3. Procedure

3.3.1 Properties of biomass

Coconut and Palm shell (Thailand) were used as the feedstock with the particle size of 0.75 mm. The properties of biomass were analyzed by proximate analysis; moisture (ASTM D3172), ash (ASTM D3174), volatile matter (ASTM D3173) and fixed carbon (ASTM D3175). The elemental analysis of biomass was measured by ultimate analysis (CHNS/O Analyzer Perkin Elmer PE 2400 Series II) as shown in Figure 3.3.

Figure 3.3 CHNS/O Analyzer Perkin Elmer PE 2400 Series II.

3.3.2 Catalyst Preparation

The 10 % of Ni/dolomite catalyst was prepared according to the precipitation method, as described by Srinakruang et al (2006). The Nickel/dolomite catalyst was prepared by precipitating 5.5 g of nickel nitrate hexahydrate with 1.8 g of ammonium carbonate in hot distilled water in the presence of dispersed calcined dolomite. The filtered catalyst was washed with hot water and dried at 120 °C over night then calcined in air at 500, 750 and 950 °C for 2 hours to study the influence of calcinations temperatures. The loading of Ni was 10% in weight and Ni loading is expressed in a weight ratio of Ni/(Ni+Dolomite). The catalysts were crushed and sieved to 20 to 40 mesh. Before use, all catalysts were reduced in H_2 at 700°C for 2 hours.

In this work, the performance of Ni-based catalyst is expected to be improved by adding small amounts of promoters containing Pt, Co and Fe to Ni/dolomite catalyst. The catalyst preparation was studied by impregnation and coprecipitation methods.

Impregnation method: The 10 g of Ni/dolomite catalyst was mixed with 0.2 g of hexachloroplatinic acid, 0.43 g of cobalt nitrate and 0.19 g of ferric chloride. Loading of metal was 1% and expressed in weight ratio of (Ni+ support). The slurry was heated at 80°C with stirring, followed by drying in a vacuum pump evaporator for 2 hours to obtain solid particles. The catalyst was dried at 120 °C over night and calcined in air at 750 °C for 2 hours (Srinakruang et al. 2006, and Li et al. 2006). The catalysts will be referred to as Ni/Pt/DM, Ni/Co/DM and Ni/Fe/DM.

Coprecipitation method: This method was prepared by precipitating nickel nitrate with aqueous solution containing 0.2 g of hexachloroplatinic acid, 0.43 g of cobalt nitrate and 0.19 g of ferric chloride and 1.8 g of ammonium carbonate in the presence of dispersed dolomite. The slurry was stirred at 60 °C and was maintained at the pH to a value of 9-10. After that, the catalyst was filtered, washed, dried at 120 °C over night and calcined in air at 750 °C for 2 hours.

3.4. Catalyst characterization

3.4.1 BET surface area

The Catalyst surface area was measured by Brunauer-Emmett-Teller (BET) method. The BET analysis is the standard method for determining surface areas from nitrogen adsorption isotherms by using surface area and porosity analyzer (Model ASAP 2020 Micromeritic) as shown in Figure 3.4. Porosity and (BET) surface analysis define surface area, pore size and pore size distribution, and void structure of solid material. Surface area is an important factor in determining the activity of catalysts and adsorbents.
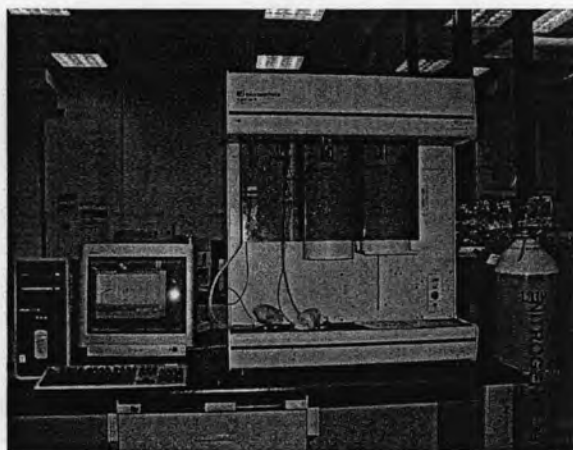
Figure 3.4 Surface area and porosity analyzer (Model ASAP 2020 Micromeritic)

3.4.2 Elemental distribution

Elementary analysis of catalyst was measured by using the Energy dispersive x-ray fluorescence spectrometer (EDX) and implementing the X-ray fluorescence analysis. X-ray fluorescence (XRF) is the emission of characteristic secondary (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays as shown in Figure 3.5. The phenomenon is widely used for elemental analysis and chemical analysis.
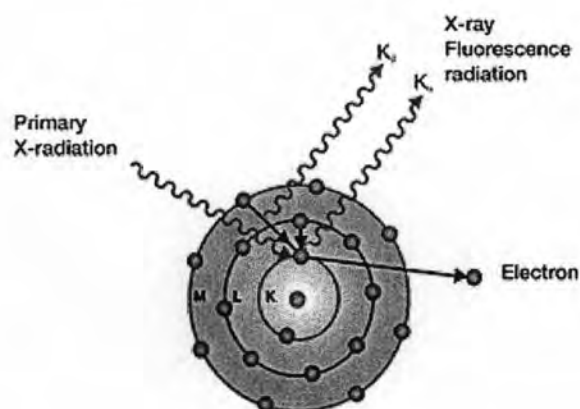
Figure 3.5 X-ray fluorescence spectrometry (XRF)

3.4.3 Chemisorption

Metallic surface area of catalyst was measured by H_2 adsorption. The chemisorption experiment was carried out in Micromeritics Autochem II 2920 as shown in Figure 3.6. Chemisorption analyzer can determine catalytic properties such as percentage of metal dispersion, active metal surface area, acid strength, and surface acidity, distribution of strength of active sites, BET surface area, and more.
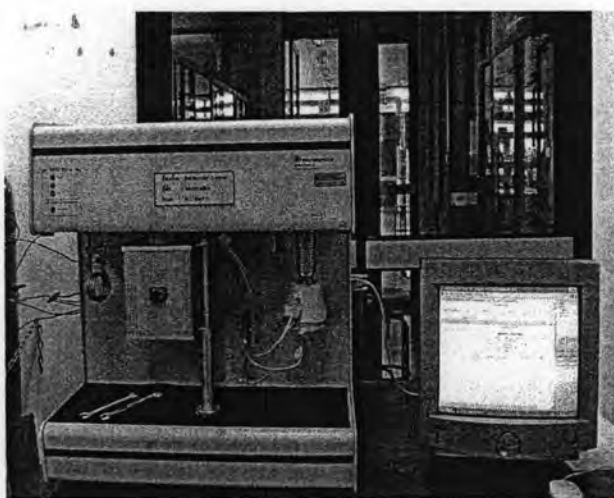

Figure 3.6 Micromeritics Autochem II 2920

3.4.4 X-ray diffraction

Phase analysis of catalyst was carried out by X-ray diffractometer (XRD) as shown in Figure 3.7 with monochormatized CuKα radiation, at 30 kV and 30 mA. The 2θ range between 10° and 70° was scanned at the rate of 0.02° per minute.
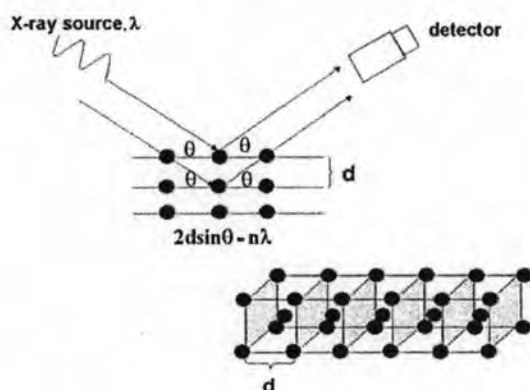
Figure 3.7 X-ray diffraction (XRD)

3.4.5 Scanning electron microscopy

The morphology of catalyst was carried out by Scanning electron microscopy (SEM) shown in Figure 3.8 (a) and Transmission electron microscopy (TEM) shown in Figure 3.8 (b). The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through an ultra thin specimen, interacting with the specimen as it passes through it. An image is formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen, a fluorescent screen in most TEMs, plus a monitor, or on a layer of photographic film, or to be detected by a sensor such as a CCD camera.
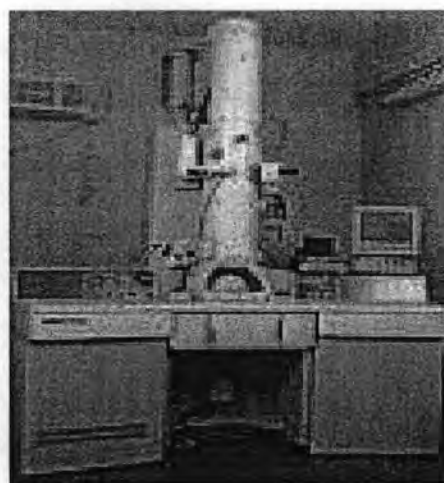
(a)   (b)

Figure 3.8 (a) Scanning electron microscopy (b) Transmission electron microscopy

3.4.6 Measurement of coke deposition on catalyst

The primary source of deactivation of a catalyst may be the formation of coke deposition on the catalyst. This can be determined by calculate the weight loss of the catalyst (Formation of coke deposits = weight loss of the catalyst after combustion by air divided by grams of catalyst sample used). The measurement of coke deposition on catalyst by combustion was investigated by thermogravimetric analysis (TGA). TG/DTA was carried out in Thermal analyzer model Pyris Diamon PerkinElmer (Figure 3.9) to evaluate the amount of carbon deposition on the catalyst after the reaction. TGA profile was collected between 40 to $1000^{\circ}C$ under air flow rate of 50 ml/min and heat rate of 10 K/min. Sample weight was about 10 mg.

Figure 3.9 Thermal analyzer (model Pyris Diamon Perkin Elmer)

3.4.7 Gas chromatography/mass spectroscopy (GC-MS)

The gas chromatography/mass spectroscopy (GC-MS) analysis was performed using Shimadzu Model GC-MS 2000 (Figure 3.10). The following chromatographic conditions were used: 30 m × 0.25 mm ID fused silica capillary column coated with 0.1 µm DB-1 Column. The GC oven program was 40°C (5 min) to 290°C (23 min) at a rate of 15 °C/min. Helium was the carrier gas. Mass spectra were obtained under E1 conditions at 70 eV. Compound identifications were made based upon comparison to mass spectra and relative retention times of authentic standards.
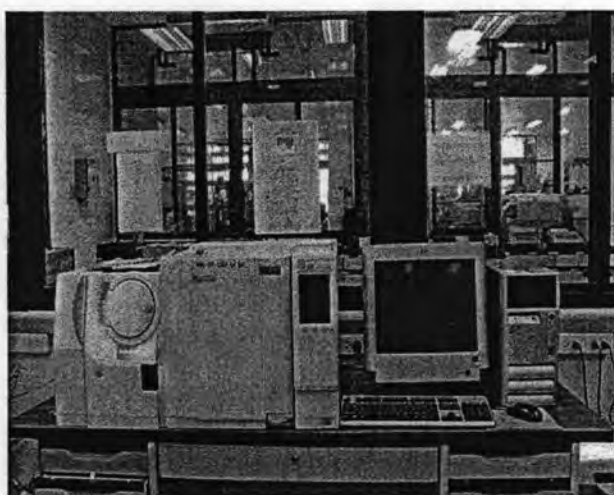

Figure 3.10 Gas chromatography/Mass spectroscopy (model GC- MS 2000)