CHAPTER III

METHODOLOGY

3.1 Materials and Equipment

3.1.1 Chemicals

- $Ni(NO_3)_2 \cdot 6H_2O$ precursor (AR grade)
- gamma-Al_2O_3 (AR grade)
- Distillated water
- Simulated natural gas (CH_4:C_2H_6:C_3H_8:CO_2 molar ratio of

70:5:5:20)

- Oxygen (HP grade)

Note: All gases were provided from Linde (Thailand) PLC.

3.1.2 Equipments

- Surface Area Analyzer, Quantachrome / Autosorb-1
- Scanning Electron Microscopy, TM3000
- X-ray Diffractometer, Rigaku / DMAX 2200 HV
- X-ray Photoelectron Spectroscopy
- Temperature program oxidation
- Atomic Absorption Spectroscopy, Varian / SpectrAA 300

3.2 Experimental Procedures

3.2.1 The Experimental System

All experiments were performed by using a corona discharge reactor which was operated at atmospheric pressure and ambient temperature (25-27 °C). The reactor was an 20-centimeter-long quartz tube with an outer diameter of 10 mm and an inner diameter of 8 mm. Plasma was generated between pin and plate electrodes which were located at the center of the reactor. For the combination of plasma and catalysts, the catalysts were placed on a glass wool in order to prevent the falling down of the catalyst pellets with a packed-bed height of 5 mm. The power for generating plasma was alternating current power 220 V and 50Hz which was adjusted by a

function generator, whereas the sinudoidal waveform is monitored by an oscillo-scope. The system schematic was shown in Figure 3.1 and reactor with a catalyst was shown in Figure 3.2.
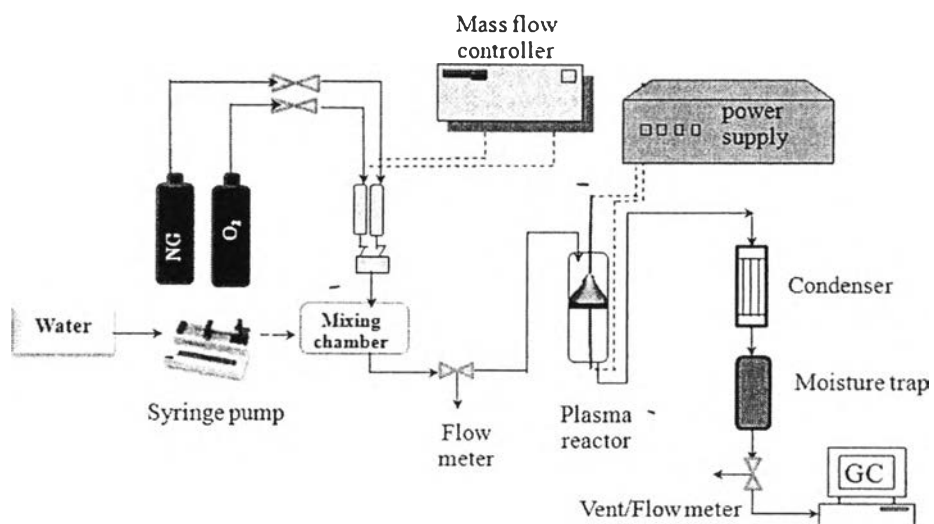
Figure 3.1 System schematic.
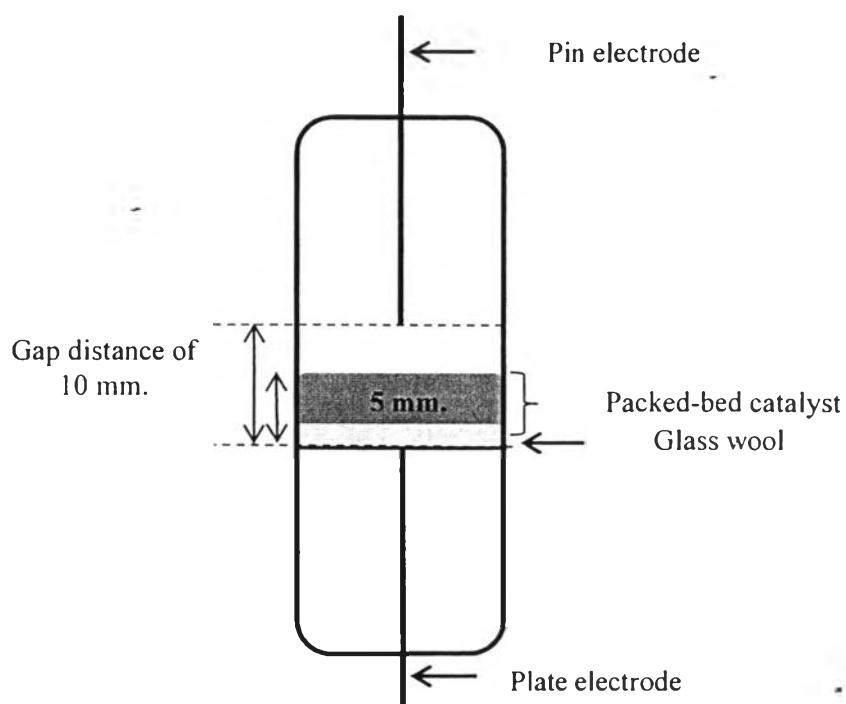
Figure 3.2 Schematic of corona discharge.

The experiments were divided into 3 steps which are partial oxidation, combination of steam reforming with partial oxidation and combination of plasma and catalysis. In each step, the reactant gases were firstly detected by online gas chromatography until the feed compositions remained constant.

3.2.1.1 Partial Oxidation Experiments

The reactant gases which were the simulated natural gas and pure O_2 were introduced into the system with the hydrocarbons to oxygen molar ratio of 2:1. Each flow was controlled by mass flow controllers which supplied by ÄALBORG. Each reactant gas passed a stainless steel filter with 7 μm in order to trap any impurities. Then, the reactant gases were mixed in a mixing chamber and introduced into the plasma reactor.

3.2.1.2 Combined Partial Oxidation with Steam Reforming Experiments

The steam was prepared by vaporized water at a controlled temperature of 120 °C. The water flow rate was controlled by a syringe pump. The steam was mixed with simulated natural gas and oxygen in the mixing chamber before being introduced into the plasma reactor. In order to prevent the condensation of water in the feed line, the temperature of stainless tube from syringe pump to the reactor was maintained at 120 °C by using a heating tape.

3.2.1.3 Combined of Plasma with Catalytic Experiments

The conditions in this step were used from the optimum condition from the previous step. The activity tests were performed by using Ni/Al_2O_3 catalysts with different weight percentages. All reactant gases and steam flowed through the packed bed under plasma environment.

After the reactions, the effluent gas samples passed though condensation in order to trap any liquid product and were analyzed by an on-line gas chromatograph (HP 5890) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The quantitative analysis of the percent volumes of all gaseous components was carried out by correlating their peak area responses from the GC chromatograms. The gas chromatograph was equipped with a 10-port valve in order to separate the gas sample into two parts with independent sample loops. The first part was flow through a Carboxen 1000 column with the TCD. The

second part was fed into a PLOT Al$_2$O$_3$"S" column connected with the FID. The GC conditions were summarized as follows:

Injector type:	Automatic sampling valve (programmable)
Injection temperature:	120 °C
Oven temperature:	Initial temperature 40 °C, ramp up at 70 °C/min to 100 °C followed by ramping up again at 30 °C/min to 190 °C and then hold for 17 min
Detectors:	Thermal conductivity detector (TCD) and flame ionization detector (FID)
Detector temperature:	190 °C
GC columns:	Carboxen 1000 (15' x 1/8') and PLOT Al$_2$O$_3$ "S" (30 m x 0.53 mm)
Carrier gas:	High purity helium (99.995%)
Carrier gas flow rates:	35 cm^3/min for Carboxen 1000 column and 105 cm^3/min for PLOT Al$_2$O$_3$ "S" column

3.2.2 Power Supply Unit

The diagram of the power supply was shown in Figure 3.3. In the first step, the AC input of 220 V and 50 Hz was converted to DC of about 70-80 V by a DC power supply converter. Then, the DC was supplied passing a 500 W of power amplifier which was connected to the function generator in order to turning to AC with a sinusoidal waveform and different frequencies. The function generator are also controlled the output voltage and frequency. Finally, the outlet voltage was stepped up by using a high voltage transformer. The voltage and current at the low voltage side were measured instead of those at the high voltage side by using a power analyzer. The high side voltage and current were there by calculated by multiplying and dividing by a factor of 130, respectively.
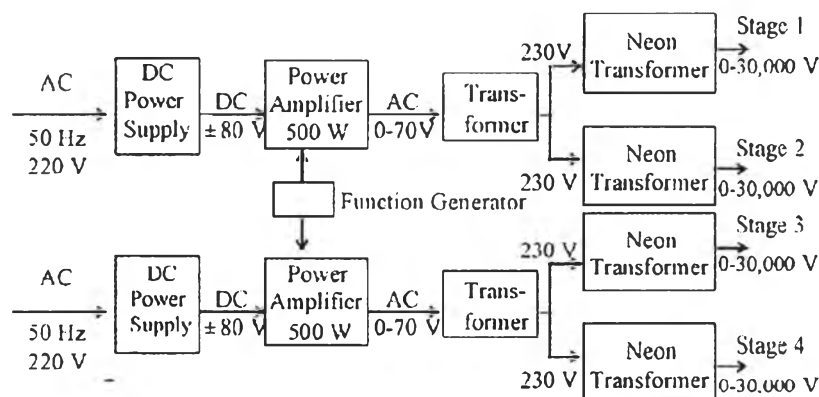
Fig.3.3 Schematic of power supply system.

3.2.3 Studied Conditions

3.2.3.1 Partial Oxidation Experiments

At this step, the important parameters were studied in order to find the optimum conditions which were following as:

Input voltage	6.7-21 kV
Frequency	300-600 Hz
Flow rate	50-150 cm^3/min

3.2.3.2 Combination Partial Oxidation and Steam Reforming Experiments

At this step, the effects of steam were studied with varying of 5, 10, 15, 20 mol% of steam which the operating conditions were kept from the first step.

3.2.3.3 Combination Plasma and Catalytic Experiments

At this step, the effects of catalyst were studied with varying of wt% Ni loading of 5, 7, 10 wt% and without loading. The operating conditions were kept from the second step.

3.2.4 Reaction Performance Evaluation

The plasma system performance was evaluated from reactant conversions, product selectivities, yields, and power consumption. Each of reactant conversion was defined as:

$$\% \text{ Reactant conversion} = \frac{(\text{Moles of reactant in} - \text{Moles of reactant out}) \times (100)}{\text{Moles of reactant in}} \qquad (4)$$

The selectivity was evaluated base on the dry basis of the mol of that gas product to total gas products, as stated in equation. 5. The percentages of coke formed can be calculated from the difference between the total reactant conversions and total C-containing products, as given in equation 6.

$$\% \text{ Selectivity} \qquad = \frac{[P_i]}{\Sigma[P_i]} \times 100 \qquad (5)$$

$$\% \text{ Coke} \qquad = \frac{\Sigma[R_i] \, C_{Ri} - \Sigma[P_i] \, C_{Pi}}{\Sigma[P_i]C_{pi}} \times 100 \qquad (6)$$

Where   [P]   =   Moles of product in the outlet gas stream

         [R]   =   Moles of each reactant in the feed stream

         C_P =   Number of carbon atoms in a product molecule

         C_R =   Number of carbon atom in a reactant molecule

The yields of various products are calculated by using the following equations:

$$\% \text{ H}_2 \text{ yield} = \frac{[\Sigma(\% \text{ CH}_4, \%\text{C}_2\text{H}_6, \%\text{C}_3\text{H}_8 \text{ conversions})][\% \text{ H}_2 \text{ selectivity}]}{(100)} \qquad (7)$$

$$\% \text{ CO yield} = \frac{[\Sigma(\% \text{ CH}_4, \%\text{C}_2\text{H}_6, \%\text{C}_3\text{H}_8, \%\text{CO}_2 \text{ conversions})][\% \text{ CO selectivity}]}{(100)} \qquad (8)$$

$\% \text{ C}_2\text{H}_4$ hydrocarbon yield

$$= \frac{[\Sigma(\%\text{CH}_4, \%\text{C}_2\text{H}_6, \%\text{C}_3\text{H}_8, \%\text{CO}_2 \text{ conversions})][\%\text{C}_2\text{H}_4 \text{ selectivity})]}{(100)} \qquad (9)$$

$\% \text{ C}_3\text{H}_6$ hydrocarbon yield

$$= \frac{[\Sigma(\%\text{CH}_4, \%\text{C}_2\text{H}_6, \%\text{C}_3\text{H}_8, \%\text{CO}_2 \text{ conversions})][\%\text{C}_3\text{H}_6 \text{ selectivity})]}{(100)} \qquad (10)$$

$\% \text{ C}_4\text{H}_{10}$ hydrocarbon yield

$$= \frac{[\Sigma(\%\text{CH}_4, \%\text{C}_2\text{H}_6, \%\text{C}_3\text{H}_8, \%\text{CO}_2 \text{ conversions})][\%\text{C}_4\text{H}_{10} \text{ selectivity})]}{(100)} \qquad (11)$$

The power consumption is calculated in a unit of eV per C-containing reactant molecule converted and per H_2 molecule produced by using the following equation:

$$\text{Power consumption (eV)} \qquad = \frac{P \times 60}{N \times M \times (1.602 \times 10^{-19})} \qquad (12)$$

Where   P =   Power measured at the low voltage side of the power supply unit (W)

N =   Avogadro's number (6.02×10^{23} molecule g mole^{-1})

M =   rate of converted carbon and the rate of produced H_2 molecules

(g mole min^{-1})

The residence time was calculated based on the reaction volume of corona reactor divided by the feed flow rate. The reaction volume was estimated from the appearance in a cone shape of corona plasma.

3.2.5 Catalyst Preparation

Ni catalysts were prepared by incipient wetness impregnation by using $Ni(NO_3)_2 \cdot 6H_2O$ as a precursor and gamma Al_2O_3 as a support. Ni precursors were firstly impregnated on the support with different wt% including with 5, 7, 10 wt%. After impregnation, catalysts were dried at 110 °C and calcined in air at 500 °C for 4 hours. Catalysts were crushed and sieved at 20-40 mesh before using in activity testing.

3.2.6 Characterization of Ni Catalysts

The characterization equipments consisted of Surface Area Analyzer, Scanning Electron Microscopy, X-ray Diffractometer, X-ray Photoelectron Spectroscopy, Temperature Program Oxidation and Atomic Absorption Spectroscopy.

3.2.6.1 Surface Area Analyzer

The surface area of the catalysts was determined to examine the effect of plasma on the catalyst. Surface area measurement was carried out by using Quantachrome Corporation Autosorb-1. The catalyst sample was first out gassed to removes the humidity and volatile absorbents that adsorbed on surface under vacuum at 280 °C over night before starting the analysis with 24 points BET.

3.2.6.2 X-ray Diffractometer

XRD is performed by using a Rigaku Dmax X-ray diffraction, RINT-2200 with Cu tube for generating CuKα equipped with a Ni filtered CuKα radiation source (λ = 1.542$\mathring{A}$) of 40 kV and 30 mV. An exact pattern match can be found between the unknown and the authentic sample, so chemical identity can be assumed. X-ray diffraction patterns of all catalyst samples were

obtained. Catalyst samples were pressed into a hollow of glass holder and held in the machine. Then, samples were scanned in the 2θ range from $10°$ to $80°$ in the continuous mode with the rate $5°$/min. XRD pattern would be used to characterize crystalline of fresh and spent catalysts.

3.2.6.3 X-ray Photoelectron Spectroscopy

XPS technique was used to characterize species of Ni both fresh and spent catalysts. XPS was performed by using monochromatic Al source and pass energy at 20 and 160 for narrow and wide scan, respectively.

3.2.6.4 Temperature Program Oxidation

The coke formation on the spent catalysts was investigated by TPO technique. TPO were performed in a continuous flow of 2 %O_2 balanced in He with the linear increasing of temperature at the rate of 10 °C/min. The spent catalysts were packed in a 1/4" quartz tube. Coke on the spent catalysts was firstly burning with oxygen to from CO_2 and H_2O. After coke burning, H_2O was trapped by absorbent and CO_2 was continuing to methanator with 15 wt% of Ni/Al_2O_3 to form CH_4 which would be detected by FID detector to evaluate the coke formation.

3.2.6.5 Atomic Absorption Spectroscopy

The actual percentage of metal loading was evaluated by AAS. 0.1 g of Ni catalyst was digested in hydrochloric, nitric and hydrofluoric acid solution of 6 ml, and then solution was heated at 50 °C. After the digestion, all sample solutions were diluted in to the range of Ni absorbance (2-7 ppm.) and analyzed by Atomic Absorption Spectroscopy. The Ni standard with 1000 ppm was used for providing the calibration curve.

3.2.6.6 Scanning Electron Microscopy

Low vacuum SEM were used to study the surface morphology of the fresh and spent catalyst. The samples were firstly dried in order to trap the humidity out, then the samples were place on a stub with carbon tape and coated by Platinum. SEM created the picture by catching the signal from back scattering electrons with voltage of 15 kV and magnification of 10k.