CHAPTER III
METHODOLOGY

3.1 Materials

Reagent Gases for Reaction Experiment

Two rough-surfaced glass plates were used as dielectric barrier material. Helium (HP grade), 40 % ethylene balanced with helium, and 97 % oxygen balanced with helium used for this study were obtained from Thai Industrial Gas Co., Ltd. as follows:

3.2 Dielectric Material Characterization

In this project, rough surface glass is used as dielectric material. It is cut into the suitable size in 5.5 cm width, 17.5 cm length and 0.3 cm height that fit for DBD reactor. Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) will be used to study surface morphology and surface roughness. Moreover, the rough surface glass compositions will be provided by X-ray fluorescence (XRF).

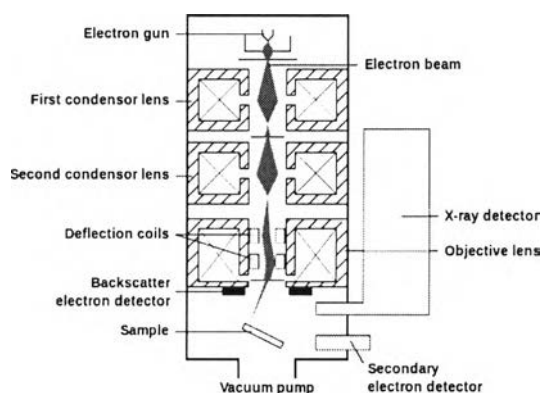### 3.2.1 Field Emission Scanning Electron Microscope (FE-SEM)

Figure 3.1 Schematics of SEM procedure. (http://en.wikipedia.org/wiki/File: Schema_MEB_(en).svg).

Field emission scanning electron microscope (FE-SEM) operated at 1 to 20 kV was employed to observe the surface structure of the rough-surfaced glass plates. The sample placed on a stub was coated by platinum (Pt) prior to being

loaded it into the microscope. An electron gun in vacuum column induced by high voltage emits an electron beam. Next, the electron beam is focused by condenser lenses or electromagnetic lenses to a point in nm and pass through deflection coils and final lens before interaction sample surface. Secondary electron, backscattered electron or X-ray is detected by detector and translated to image.

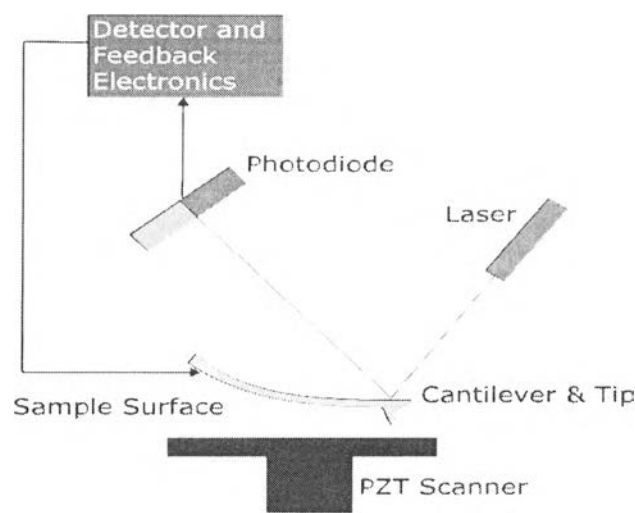### 3.2.2 Atomic Force Microscope (AFM)

Figure 3.2 Schematics of AFM procedure. (http://en.wikipedia.org/wiki/File :Atomic_force_microscope_block_diagram.svg).

Atomic Force Microscope (AFM) (XE-100 Series, Park Systems) with SPM Controller using non-contact mode, scan of 20 μm, and a scan rate of 0.1 Hz was used to observe surface roughness of the rough-surfaced glass. AFM procedure starts with cantilever with tip used to scan sample surface. The mechanical contact forces, for example, van der waals forces, capillary forces, chemical bonding, electrostatic forces, and magnetic forces, between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Afterward, the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes and detector.

3.2.3 X-Ray Fluorescence (XRF)

X-ray fluorescence method (XRF) used a PANalytical analysis instrument with AXIOS & SUPERQ version 4.0 systems with IQ+ program. In the analysis procedure, the scans are first searched for peaks. The found peaks are identified and analyze quantitatively using fundamental parameter. For XRF procedure in figure 3.3, X-ray generator generates primary X-ray photon to attack inner electron in K-shell of sample and this electron is removed from atom. Next, outer electron replaces the hole of removed electron and radiates secondary X-ray photon which is detected by detector. The secondary X-ray photon is the Characteristic radiation of each element.
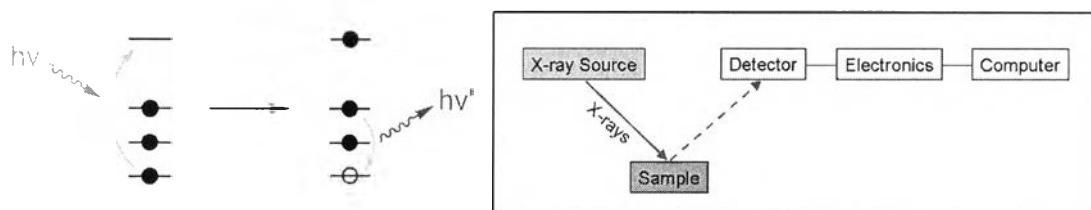

Figure 3.3 Schematics of XRF procedure. (http://en.wikipedia.org/wiki/File:X-ray_fluorescence_simple_figure.svg and http://en.wikipedia.org/wiki/File:Dmedxrfschematic.jpg).

3.3 Reaction Activity Measurement

The experimental study of ethylene epoxidation will be investigated in a parallel dielectric barrier discharge (DBD) reactor at ambient temperature and atmospheric pressure. The schematic of experimental setup for ethylene epoxidation reaction using the DBD system is shown in Figure 3.4. The reactor configuration is shown in Figure 3.5. The reactor sizes are 1.5 cm height x 5.5 cm width x 17.5 cm length for inner dimension and 4 cm height x 9.5 cm width x 21.5 cm length for outer dimension, and distance between ethylene feed positions is 3.5 cm. Between the two electrodes, there is a dielectric glass plate. The gap distance between the two glasses is fixed at 5 mm (Suttikul *et al.*, 2011).

Table 3.1 The detailed dimensions of the parallel DBD reactor

Dimension	Value
Electrode width (cm)	3
Electrode length (cm)	15
Electrode thickness (cm)	0.30
Electrode gap distance (cm)	1.1
Glass thickness (cm)	0.30
Electrode edge length (cm)	71.70
Electrode surface area (cm^2)	89.07
Reaction volume (cm^3)	22.67
Electrode edge length-to-reaction volume ratio (cm^{-2})	3.22
Electrode surface area-to-reaction volume ratio (cm^{-1})	4.00
Distant between each ethylene feed position (cm)	3.5

The reactant gases (ethylene, oxygen, and helium) flowing through the reactor will be controlled by a set of electronic mass flow controllers. All reactant lines have 7 µm in-line filters before passing through the mass flow controllers in order to trap any foreign particles. The reactor pressure will be controlled via a needle valve. The outlet of reactor will either be vented to the atmosphere via rubber tube exhaust or enter an on-line gas chromatograph (GC) to analyze the product gases. The moisture in the effluent gas will be removed by a water trap before entering to the on-line GC. The GC is equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). For the TCD channel, a packed column (Carboxen 1000) will be used for separating the product gases, which are hydrogen (H_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), and ethylene (C_2H_4). For FID channel, the capillary column (OV-Plot U) will be used for the analysis of ethylene oxide (EO) and other by-product gases, i.e. CH_4, C_2H_2, C_2H_6, and C_3H_8. The composition of the product gas stream will be determined by the GC every 20 min. When the system reaches steady state, an analysis of the outlet gas compositions will be performed at least three times. The experimental data under
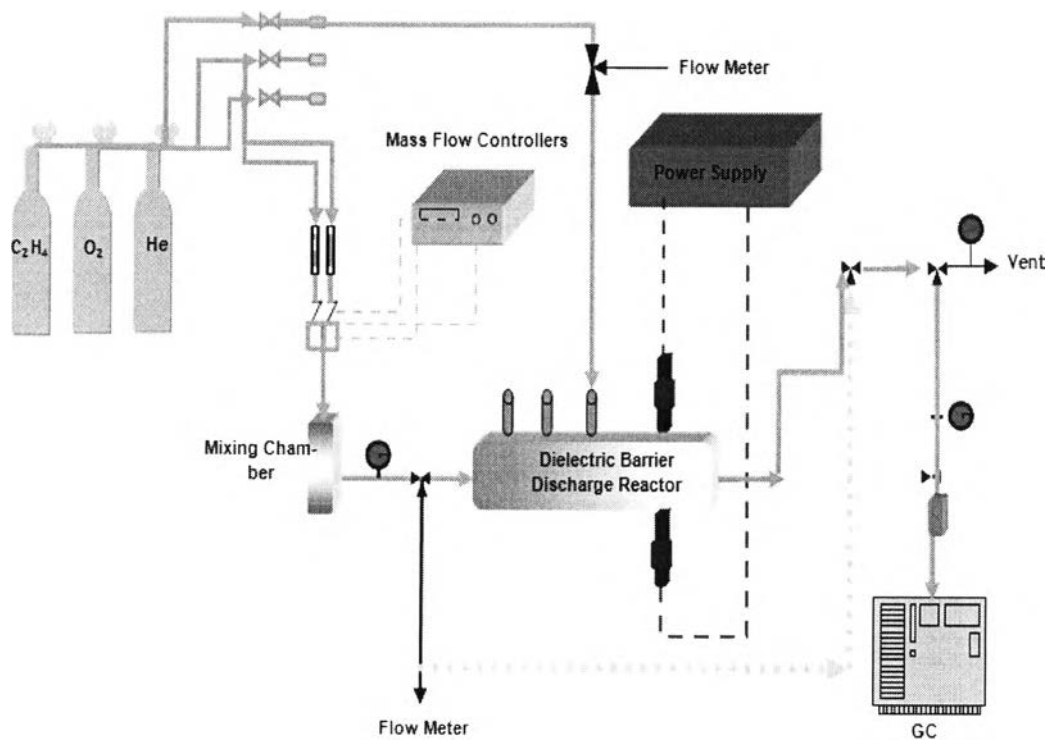
Figure 3.4 Schematics of experimental setup for ethylene epoxidation reaction using parallel DBD.
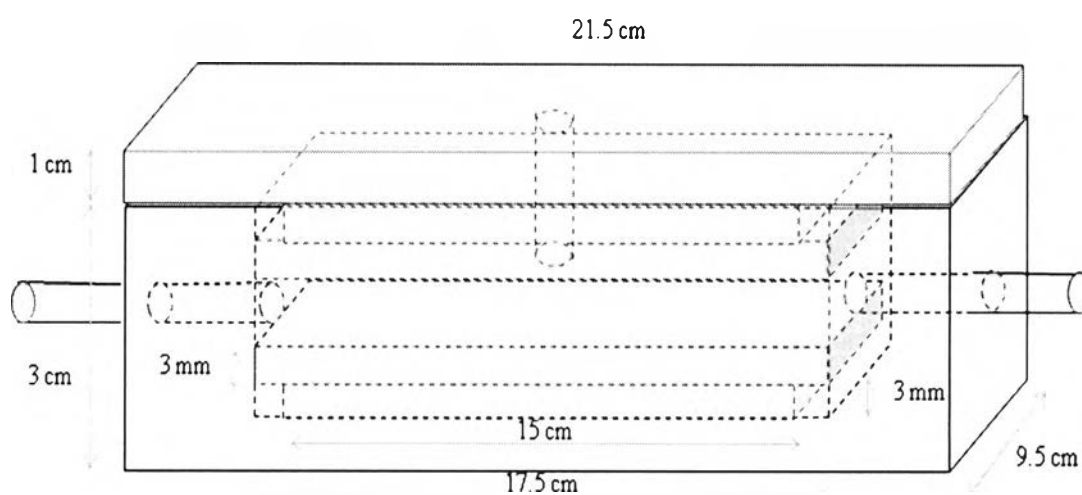

Figure 3.5 Parallel DBD reactor configurations.

The detailed dimensions of the parallel DBD reactor are given in Table 3.1.

steady state conditions will be averaged and then used to evaluate the performance of the plasma system. The GC will be operated under the following conditions:

TCD injection temperature	120 °C
FID injection temperature	150 °C
Oven temperature	40 °C for 5 min
	165°C (heating rate 10 °C/min)
Carrier gas	High purity helium
Carrier gas flow rate	30 cm^3/min (TCD channel)
	25 cm^3/min (FID channel)
Detector temperature	190 °C in TCD and 280°C for FID

To evaluate the system performance, the C_2H_4 and O_2 conversions and the selectivity for products, including EO, CO, CO_2, H_2, CH_4, C_2H_2, C_2H_6, and traces of C_3, will be considered. The conversion of both C_2H_4 and O_2 will be calculated from the following equation:

$$\% \text{ Reactant conversion} = \frac{(\text{moles of reactant in} - \text{moles of reactant out}) \times 100}{(\text{moles of reactant in})} \quad (3.1)$$

The product selectivity will be calculated from the following equation:

$$\% \text{ Product selectivity} = \frac{[(\text{number of C or H atom in product}) (\text{moles of product produced})] \times 100}{[(\text{number of carbon or hydrogen atom in ethylene}) (\text{moles of ethylene converted})]} \quad (3.2)$$

The ethylene oxide yield will be calculated from the following equation:

$$\% \text{ Ethylene oxide yield} = (\% \text{ ethylene conversion}) \times (\% \text{ ethylene oxide selectivity}) / 100 \quad (3.3)$$

To determine the energy efficiency of the plasma system, the specific power consumption will be calculated in a unit of Ws per molecule of converted ethylene or per molecule of produced ethylene oxide using the following equation:

Specific power consumption = $\dfrac{P \times 60}{N \times M}$ (3.4)

Where P = Power (W)

N = Avogadro's number = 6.02×10^{23} molecules/mol

M = Rate of converted ethylene molecules in feed or rate of produced ethylene oxide molecules (mol/min).

3.4 Power Supply Unit

The block diagram of the power supply unit is shown in Figure 3.6. For the first step, the AC input of 220 V and 50 Hz will be converted to DC of about 70-80 V by a DC power supply converter. For the second step, the DC will be supplied through a 500 Watt power amplifier, which is connected to the Instek function generator to generate waveform and to amplify voltage and frequency. The signal of alternating current is a sinusoidal waveform. For the final step, the amplified AC will pass through the input transformer to convert to 230 V AC. Thereafter, the variable output will be transmitted to a high voltage current by nominal factor 130 times of low side (input). An Extech® series 380801 power analyzer will be used to measure current, frequency, and voltage at the low side of the power supply unit.
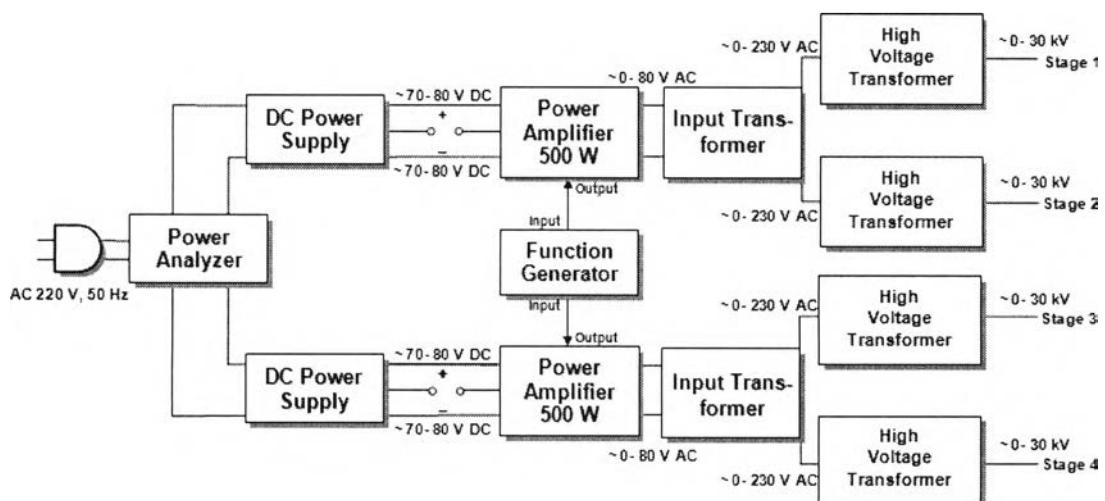

Figure 3.6 Block diagram of the power supply unit.

3.5 Experiment Procedures

The main objective of this research is to investigate the DBD plasma system with two dielectric rough-surfaced glasses for improving the efficiency of ethylene epoxidation to form ethylene oxide.

The effects of various operating parameters, including an applied voltage, an input frequency, an O_2/C_2H_4 feed molar ratio, and an ethylene feed position will then be examined.

The experimental conditions will be as follows:

Applied voltage	13-25 kV
Input frequency	300-600 Hz
O_2/C_2H_4 molar ratio	0.17:1-1:1
Ethylene feed position fraction	0.375-0.625
Feed flow rate	50 cm^3/min
Electrode gap distance	11 mm