

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Chemicals for Catalyst Preparation

All chemical used for catalyst preparation and analytical procedures are described as follows:

- 1) Silver nitrate AgNO_3 with 99.9% purity, supplied by RCI Labscan (Thailand) Co., Ltd., was used as silver catalyst precursor.
- 2) Triton-x-100 obtained from Sigma Alodrich Co., USA. Was used as surfactant.
- 3) Glass plate (SiO_2) was used as catalyst support.
- 4) Distilled water
- 5) Acetone

3.1.2 Reagent Gases for Reaction Experiment

All gases used for reaction were obtained from Thai Industril Gas Co., Ltd. as follow:

- 1) Helium (HP grade)
- 2) 40% ethylene balanced with helium.
- 3) 97% oxygen balanced with helium.
- 4) 10% Ethylene oxide balanced with helium.

3.2 Catalyst Preparation Procedures

The preparations method was divided into three steps which were glass plate preparation, silver nitrate aqueous solution preparation and Ag coated preparation. For the first step, glass plate was washed by distilled water followed by acetone and then dried in an oven at 100°C for 1 hour. Next, AgNO_3 were diluted with distilled water and mixed with Tritron-x-100 and after that would give the silver nitrate aqueous solution, For the last step, The treated glass plate was coated with an aqueous silver nitrate solution to achieve silver loading from 0.1 wt.%. The mixture

was then dried in an oven at 110 °C overnight. The catalysts were calcined at 550 °C for 5 h. (for determining the optimum conditions) and varied from 450 to 650 °C for 5 h. (for studying the effect of calcination temperature).

3.3 Catalyst Characterization Techniques

The characteristics of the prepared catalyst were determined with regard to their physical and chemical properties. The catalyst characterization techniques applied in this research are X-ray diffraction (XRD) and tabletop microscopy (TM 3000).

3.3.1 X-ray Diffraction (XRD)

X-ray Diffraction (XRD) analysis is generally performed based on the fact that an X-ray diffraction pattern was 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. It is also possible to make a relatively quantitative analysis by comparing the intensity of the diffraction lines. When comparing the same crystalline substance of two different samples, the higher intensity indicates the higher content.

The X-ray diffraction patterns of the prepared catalyst were obtained by using a Rigaku SmartLab diffractometer equipped with a Ni filtered CuK α radiation source ($\lambda = 1.542 \text{ \AA}$) of 40 kV and 30 mA. A catalyst sample is first pressed into a hollow of glass holder and held in place by a glass window. After that, it is scanned in the 2θ range from 20 to 90° in the continuous mode with the rate of 5°/min. The XRD results consist of peak parameters, including the centroid 2θ , the full line width at half the maximum of intensity (β), d-value, and intensity. The mean crystallite size will be calculated from the XRD data from X-ray line broadening, using the full line width at half maximum of intensity and the 2θ value and plugging them into the Debye-Scherrer equation (Cullity, 1956 and Matarić *et al.*, 1989).

$$T = K\lambda / \beta \cos\theta$$

where

- λ = The X-ray wavelength (0.1542 nm for Cu anode source);
- K = The Debye-Scherrer constant which to some degree depends on the shape of the peak (assume equal to 0.9);
- β = The full width at half maximum (FWHM) of the broadened peak;
- θ = The Bragg angle of the reflection (radian); and
- T = The mean crystallite size (nm)

This equation works well for particle sizes of less than 1,000 Å. The broadening of diffraction lines measured at half the maximum intensity (β) is corrected by using Warren's method, which is:

$$\beta^2 = \beta_M^2 - \beta_S^2$$

where

- β_M = The breadth of the diffraction line; and
- β_S = The breadth of the line from a standard.

3.3.2 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) is employed to observe the surface structure of a catalyst sample to identify the element proportion over that area and to evaluate approximately the particle size distribution. The catalyst sample placed on the stub is coated by platinum (Pt) prior to being loaded into the microscope. A beam is passed through a series of lenses to form a magnified image of a sample that is inserted in the area of the objective lens. The image from selected area is viewed through projection onto a view of screen. Because electron beams can be easily scattered by air molecules. Additionally, the electromagnetic lenses are used for focusing the electron beam.

3.4 Catalytic Activity Experiments

The experimental study of ethylene epoxidation was investigated in a parallel dielectric barrier discharge (DBD) reactor at ambient temperature and atmospheric pressure. The reactor sizes were 1.5 cm thickness \times 5.5 cm width \times 17.5 cm length for inner dimensions and 3.9 cm thickness \times 9.5 cm width \times 21.5 cm length for outer dimensions. Between the two electrodes, there were two dielectric glass plates and only one glass plate was used for loading a catalyst supported. The gap distance between the two electrodes was fixed at 7 mm (*Suttikul et al.*, 2011).

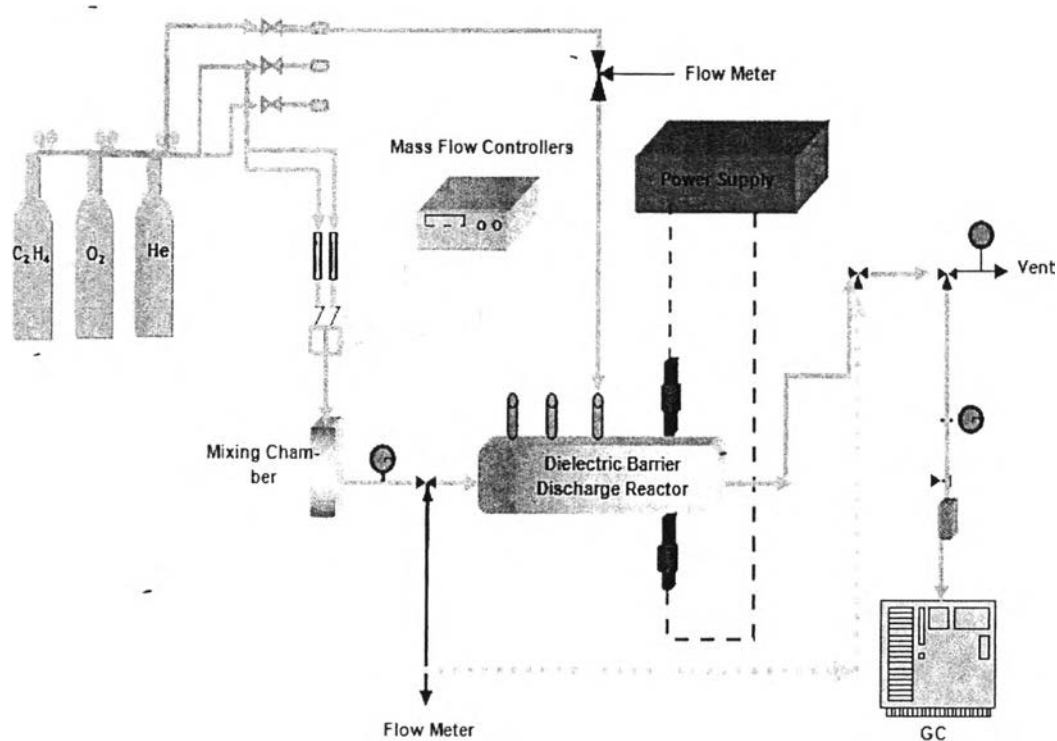


Figure 3.1 Schematics of experimental setup for ethylene epoxidation reaction using parallel DBD.

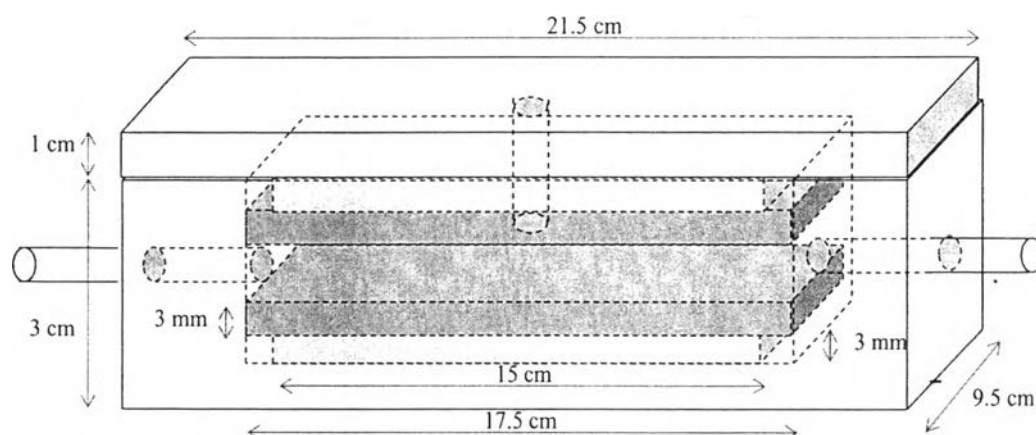


Figure 3.2 Parallel DBD reactor configurations.

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

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)	0.70
Glass thickness (cm)	0.20
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 is 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 is controlled via a needle valve. The outlet of reactor is 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 is 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 HP plot Molesive 19096 (P_MS6) is 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) is used for the analysis of ethylene oxide (EO) and other by-product gases, i.e. CH_4 , C_2H_6 , and C_3H_8 . The composition of the product gas stream is determined by the GC every 20 min. When the system reaches steady state, an analysis of the outlet gas compositions is performed at least three times. The experimental data under steady state conditions is averaged and then used to evaluate the performance of the plasma system. The GC is operated under the following conditions:

TCD injection temperature	150 °C
FID injection temperature	150 °C
Oven temperature	50 °C for 5 min 165°C (heating rate 25°C/min)
Carrier gas	High purity helium
Carrier gas flow rate	12 cm^3/min (TCD channel) 15 cm^3/min (FID channel)
Detector temperature	250°C in TCD and 300°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_6 , and traces of C_3 , is considered. The conversion of either C_2H_4 or O_2 is calculated from the following equation:

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

The product selectivity is calculated from the following equation:

$$\% \text{ Product selectivity} = \frac{[(\text{number of carbon or hydrogen atom in product}) (\text{moles of product produced})] \times 100}{[(\text{number of carbon or hydrogen atom in ethylene}) (\text{Total moles of products produced})]}$$

The ethylene oxide yield is calculated from the following equation:

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

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

$$\text{Specific power consumption} = \frac{P \times 60}{N \times M}$$

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).

3.5 Power Supply Unit

The block diagram of the power supply unit is shown in Figure 3.3. For the first step, the AC input of 220 V and 50 Hz is converted to DC of about 70-80 V by a DC power supply converter. For the second step, the DC is 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 is pass through

the input transformer to convert to 230 V AC. Thereafter, the variable output is transmitted to a high voltage current by nominal factor 130 times of low side (input). An Extech® series 380801 power analyzer is used to measure current, frequency, and voltage at the low side of the power supply unit.

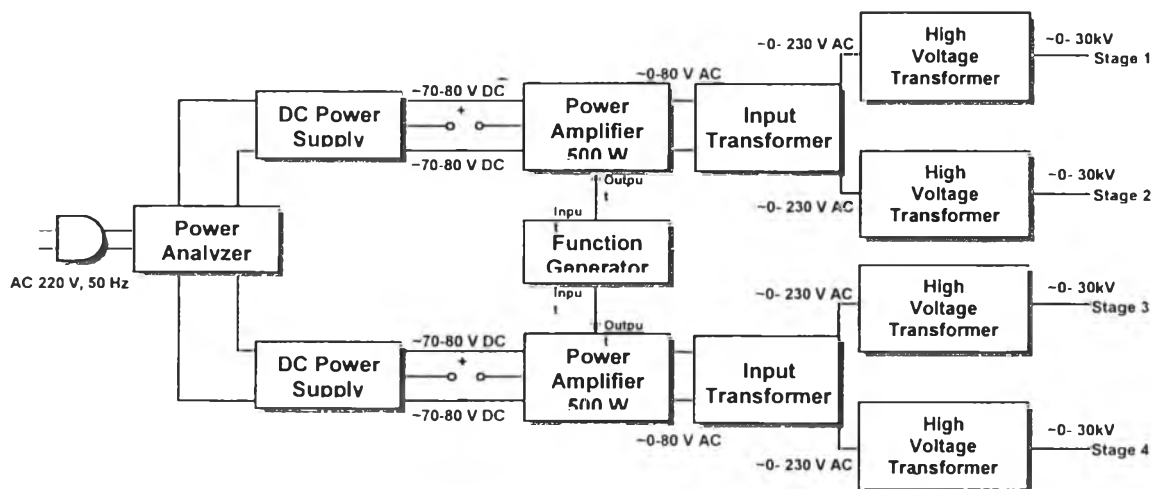


Figure 3.3Block diagram of the power supply unit.

3.6 Experiment Procedures

The main objective of this research is to determine the optimum conditions including an applied voltage, an input frequency, total feed flow rate and calcination temperature for the ethylene epoxidation. And comparison effect of using different oxygen source.

The effect of ethylene feed position is first investigated. The effects of various operating parameters, including the existence of Ag catalyst on SiO₂ supported, oxygen sources/ethylene feed molar ratio, applied voltage, input frequency, and feed flow rate, is further examined. The experimental conditions as follows:

Ethylene feed position fraction:	0.5
wt% of Ag loading:	0.1%
N ₂ O/C ₂ H ₄ molar ratio:	0.1:1-1:1

O ₂ /C ₂ H ₄ molar ratio:	0.1:1-1:1
Applied voltage:	15-21 kV
Input frequency:	450-650 Hz
Feed flow rate:	30-50 cm ³ /min
Electrode gap distance:	7 mm
Calcination Temperature	450-650 °C