

# Ethylene Epoxidation in a Low-Temperature Parallel Plate Dielectric Barrier Discharge System: Effects of Ethylene Feed Position and $O_2/C_2H_4$ Feed Molar Ratio

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**Abstract**—The effects of ethylene ( $C_2H_4$ ) feed position and  $O_2/C_2H_4$  feed molar ratio on ethylene epoxidation in a parallel dielectric barrier discharge (DBD) were studied. The results showed that the ethylene feed position fraction of 0.5 and the feed molar ratio of  $O_2/C_2H_4$  of 0.2:1 gave the highest EO selectivity of 34.3% and the highest EO yield of 5.28% with low power consumptions of  $2.11 \times 10^{-16}$  Ws/molecule of ethylene converted and  $6.34 \times 10^{-16}$  Ws/molecule of EO produced when the DBD system was operated under the best conditions: an applied voltage of 19 kV, an input frequency of 500 Hz and a total feed flow rate of 50  $cm^3/min$ . The separate ethylene feed system provided much higher epoxidation activity as compared to the mixed feed system which gave EO selectivity of 15.5%, EO yield of 2.1% and the power consumption of EO produced of  $7.7 \times 10^{-16}$  Ws/molecule.

**Keywords**—Dielectric Barrier Discharge,  $C_2H_4$  Feed Position, Epoxidation, Ethylene Oxide

## I. INTRODUCTION

ETHYLENE OXIDE ( $C_2H_4O$ , EO) is a valuable chemical feedstock for many applications, including the manufacture of surfactants and detergents. The partial oxidation of ethylene to ethylene oxide, so-called ethylene epoxidation, has been of great interest in many global research works. The most widely used technique for ethylene epoxidation is catalytic processes using silver catalysts supported on low surface area alpha-alumina ( $Ag/(LSA)\alpha-Al_2O_3$ ) [1]-[4]. Some previous researches have revealed that alkali and transition metals, especially cesium (Cs) [5]-[11], copper (Cu) [12]-[15], and gold (Au) [16]-[21], can provide the improvement of the EO selectivity. However the catalytic process has to be operated at a high temperature and high pressure, leading to high energy consumption and catalyst deactivation which needs both regeneration and replacement of the deactivated catalyst. To resolve and avoid these problems, the low-temperature plasma is considered to be an alternative technique for ethylene epoxidation.

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Dielectric barrier discharge (DBD) is one kind of non-thermal plasma, which electrons on electrodes surface gain enough energy from applied voltage to overcome the potential barrier of metal surface electrodes [22]. Then, incoming reactants can be directly transformed to chemically excited or dissociated gaseous species by colliding with the energetic electrons in the plasma zone. The non-thermal plasma, in general, possesses non-equilibrium properties, either because the ion temperature is different from the electron temperature or because the velocity distribution of one of the species does not follow a Maxwell Boltzman distribution [23]-[25]. Typically, the generated excited or dissociated species have much higher reactivity than neutral species at the ground state. Moreover, the main characteristic of non-thermal plasma is that the electrons in plasma zone have a higher energy than neutral gas having a relatively low temperature near room temperature.

The objective in this work was to investigate the ethylene epoxidation performance using a dielectric barrier discharge system by initially producing oxygen active species prior to reacting with ethylene. The effects of various operating parameters, including ethylene feed position, oxygen-to-ethylene feed molar ratio, applied voltage, input frequency, and feed flow rate on the ethylene epoxidation activity were examined.

## II. EXPERIMENTAL

### A. Reagent Gases for Reaction Experiments

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.

### B. Dielectric Barrier Discharge System

The experimental study of ethylene epoxidation was 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 Fig. 1 The reactor configuration is shown in Fig. 2. 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 was a dielectric glass plate. The gap distance between the two electrodes was fixed at 7 mm [26]. The AC input of 220 V and

50 Hz was converted to DC of about 70- 80 V by a DC power supply converter. For the second step, the DC was controlled through a 500 W power amplifier, which was connected to a Instek function generator to generate waveform and to amplify voltage and frequency. The signal of the alternating current was a sinusoidal waveform. For the final step, the generated

AC was passed through an input transformer to step up an output voltage. Thereafter, the variable output was transmitted to a high voltage current by nominal factor 130 times of low side (input). An Extech series 380801 power analyzer was used to measure current, frequency, and voltage at the low side of power supply unit.

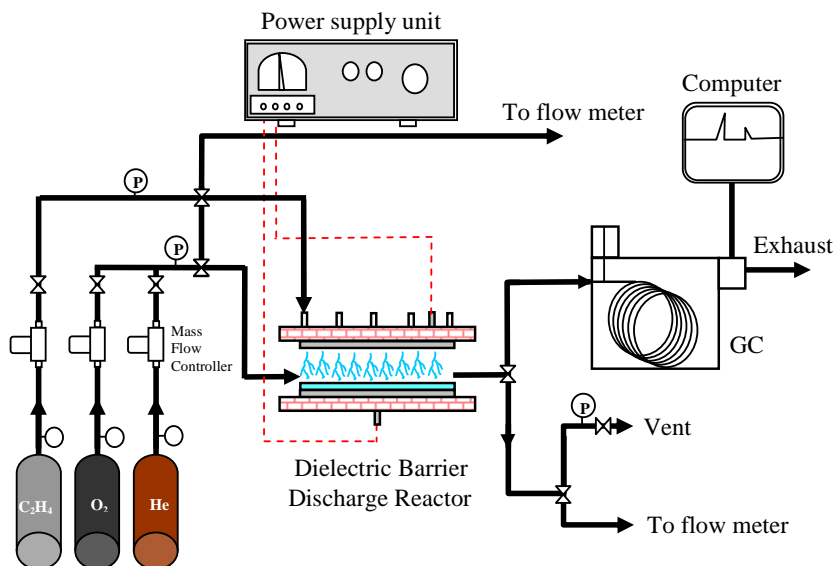


Fig. 1 Flow diagram of the dielectric barrier discharge plasma system

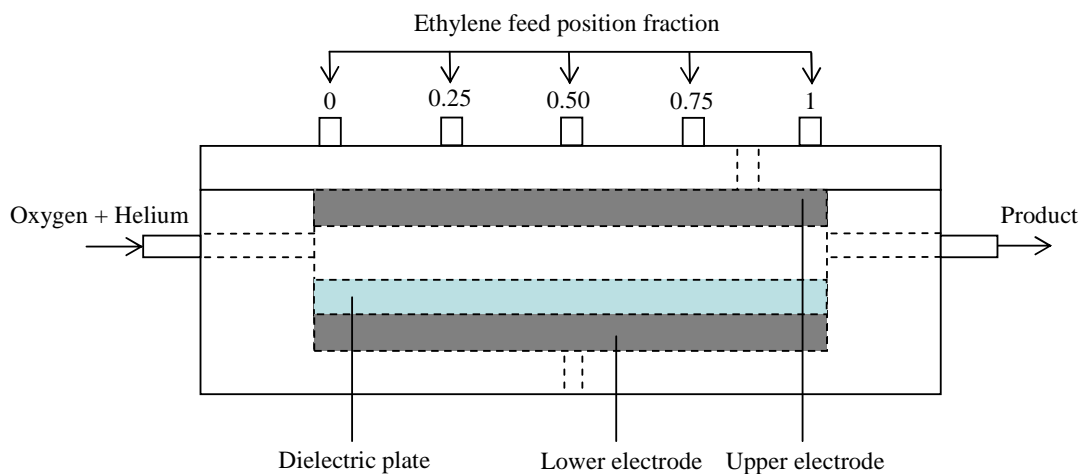


Fig. 2 Configuration of the dielectric barrier discharge reactor.

### C. Reaction Experiments

The reactant gases (ethylene, oxygen, and helium) flowing through the reactor were controlled by a set of electronic mass flow controllers. Each reactant line had a 7  $\mu\text{m}$  in-line filter before passing through the mass flow controller in order to trap any foreign particles. The reactor pressure was controlled via a needle valve. The outlet of reactor was either vented to the atmosphere via rubber tube exhaust or entered an on-line gas chromatograph (GC) to analyze the product gases. The moisture in the effluent gas was removed by a water trap before entering to the on-line GC. The GC was equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). For the TCD channel, a packed column (Carboxen 1000) was used for separating the product gases, which were  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ . For the FID channel, a capillary column (OV-Plot U) was used for the analysis of ethylene oxide (EO),  $\text{C}_2\text{H}_4$  and other by-product gases, i.e.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$ . The composition of the product gas stream was determined by the GC every 40 min. When the system reached steady state, an analysis of the outlet gas compositions was performed at least five times. The experimental data under steady state condition was averaged and then used to evaluate the process performance of the plasma system

### D. Reaction Performance Assessment

To evaluate the system performance, the  $\text{C}_2\text{H}_4$  and  $\text{O}_2$  conversions and the selectivities for products, including EO,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and traces of  $\text{C}_3$ , were calculated. The conversions of  $\text{C}_2\text{H}_4$  and  $\text{O}_2$  were calculated from the following equation:

$$\% \text{ Reactant conversion} = 100 \times [(\text{mole of reactant in} - \text{mole of reactant out}) / \text{mole of reactant in}] \quad (1)$$

The product selectivity was calculated from the following equation:

$$\% \text{ Product selectivity} = [(\text{number of carbon or hydrogen atom in product}) \times (\text{moles of product produced})] / [(\text{number of carbon or hydrogen atom in ethylene}) \times (\text{moles of ethylene converted})] \times 100 \quad (2)$$

The ethylene oxide yield was calculated from the following equation:

$$\% \text{ Ethylene oxide yield} = (\% \text{ ethylene oxide selectivity}) \times (\% \text{ ethylene conversion}) / 100 \quad (3)$$

The power consumption was calculated in a unit of Ws per molecule of converted ethylene or per molecule of produced ethylene oxide using the following equation:

$$\text{Power consumption} = (P \times 60) / (N \times M) \quad (4)$$

where  $P$  = power (W),  $N$  = Avogadro's number =  $6.02 \times 10^{23}$  molecules/mol,  $M$  = rate of converted ethylene molecules in feed or rate of produced ethylene oxide molecules (mol/min).

## III. RESULTS AND DISCUSSION

### A. Effect of Ethylene Feed Position

The effect of ethylene ( $\text{C}_2\text{H}_4$ ) feed position was initially studied in order to obtain the most suitable position for ethylene epoxidation reaction in the low-temperature DBD system. In this study, the ethylene feed position was varied in the fraction range of 0 to 1, while the feed molar ratio of  $\text{O}_2/\text{C}_2\text{H}_4$  of 0.25:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and a total feed flow rate of 50  $\text{cm}^3/\text{min}$  were used as base conditions to operate the DBD system. The effect of ethylene feed position on the ethylene and oxygen conversion is shown in Fig. 3a, the EO selectivity and EO yield are shown in Fig. 3b and the selectivities for  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ , and  $\text{C}_3\text{H}_8$  are shown in Fig. 3c. The conversion of oxygen was almost constant with increasing ethylene feed position fraction. However, the conversion of ethylene tended to increase with increasing ethylene feed position fraction ranging from 0 to 0.5. At a higher ethylene feed position fraction, the ethylene conversion tended to decrease, and it reached a minimum at the ethylene feed position fraction of 0.75. The increase in the ethylene feed position fraction slightly affected the EO selectivity, EO yield and reactant conversions, especially in the ethylene feed position fraction range between 0 to 0.5. The EO selectivity and EO yield were found to be the highest at the ethylene feed position fraction of 0.5 and decreased with further increasing ethylene feed position fraction. Furthermore, at a highest ethylene feed position fraction of 1, the selectivity for EO was the lowest. This can be explained in that a lower ethylene feed position fraction leads to more opportunity of ethylene molecule to be cracked before colliding with  $\text{O}_2$  active species, whereas at a higher ethylene feed position fraction the ethylene has a short residence time for epoxidation reaction. The selectivities for  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$  and  $\text{CH}_4$  tended to decrease, but in contrast, the selectivity for  $\text{H}_2$  remained almost unchanged with increasing ethylene feed position. The selectivities for  $\text{CO}$  and  $\text{CO}_2$  tended to increase in the studied range of ethylene feed position fraction from 0.5 to 1. The  $\text{CO}$  selectivity increased when the ethylene feed position fraction increased, and it reached a maximum at the ethylene feed position fraction of 0.75. Fig. 3d shows the power consumptions to convert an ethylene molecule and to produce an EO molecule at different ethylene feed position fractions. The power consumption per molecule of converted ethylene reached a minimum when the ethylene feed position fraction increased up to 0.5 and rapidly increased with further increasing feed position fraction up from 0.5 to 1. However, there was a significant increase in the power consumption per molecule of produced EO with further increasing ethylene feed position fraction, especially at a feed position fraction higher than 0.5. Hence, an ethylene feed position fraction of 0.5 was therefore selected for further investigation because it provided the highest EO selectivity and yield and the lowest power consumption per molecule of EO produced.

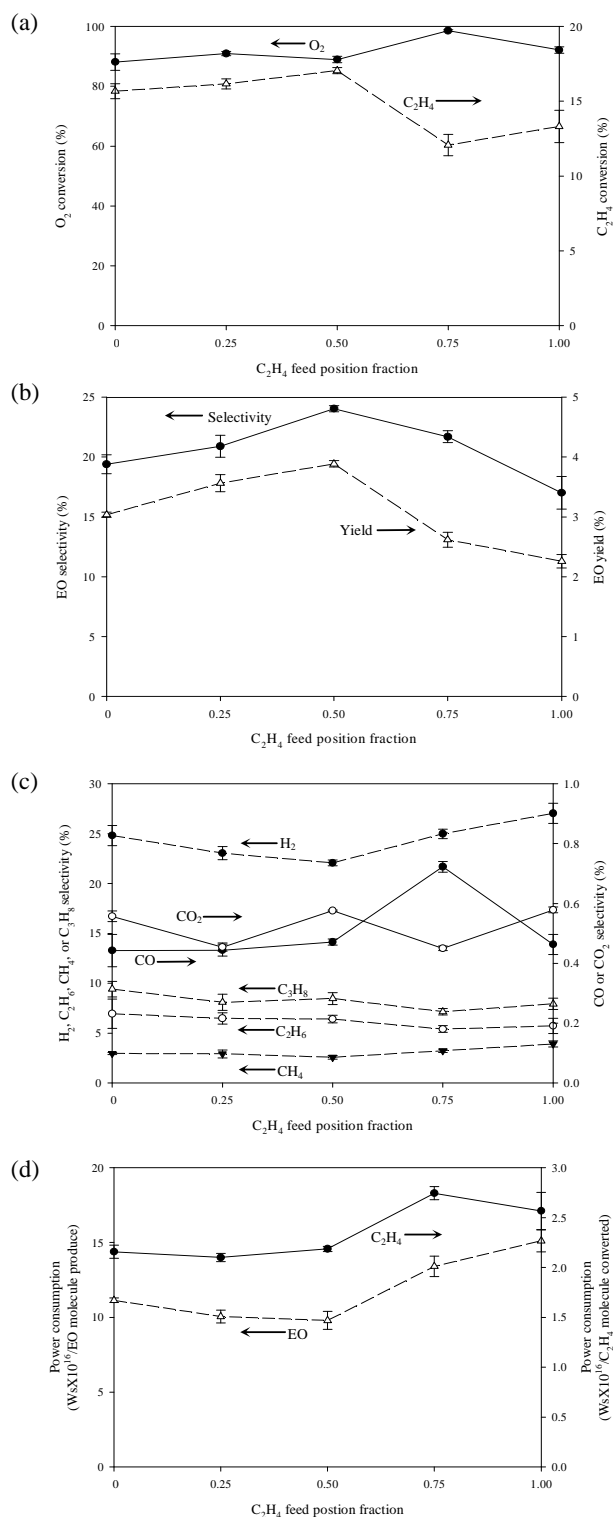


Fig. 3 (a)  $C_2H_4$  and  $O_2$  conversions, (b) EO selectivity and yield, (c) other product selectivities, and (d) power consumptions as a function of ethylene feed position fraction at an  $O_2/C_2H_4$  feed molar ratio of 0.25:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50 \text{ cm}^3/\text{min}$

### B. Effect of $O_2/C_2H_4$ Feed Molar Ratio

To determine the influence of the feed gas composition, the  $O_2/C_2H_4$  feed molar ratio was next varied in the range of 0:1 to 0.5:1 ( $O_2$ -lean conditions), while the other operating parameters were fixed at a  $C_2H_4$  feed position fraction of 0.5 (optimum condition), an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50 \text{ cm}^3/\text{min}$ . As shown in Fig. 4a, an increase in  $O_2/C_2H_4$  feed molar ratio slightly affects the  $C_2H_4$  and  $O_2$  conversions, and the highest conversions of both reactants are obtained at an  $O_2/C_2H_4$  feed molar ratio of 0.5:1. The explanation is that an increase in the molar ratio of  $O_2/C_2H_4$  results in having more  $O_2$  available to react with ethylene molecules, leading to higher ethylene conversion and  $O_2$  conversion. The effect of the  $O_2/C_2H_4$  feed molar ratio on EO selectivity and EO yield are shown in Fig. 4b. Both of them increased with increasing  $O_2/C_2H_4$  feed molar ratio from 0.17:1 to 0.2:1 and rapidly decreased with further increasing  $O_2/C_2H_4$  feed molar ratio greater than 0.2:1, suggesting that EO can be formed dominantly under the deficient  $O_2$  condition. The highest EO selectivity and EO yield were found at an  $O_2/C_2H_4$  feed molar ratio of 0.2:1. The effect of  $O_2/C_2H_4$  feed molar ratio on the selectivities for other products is shown in Fig. 4c. The selectivities for  $H_2$ ,  $CH_4$ ,  $C_3H_8$ , and  $C_2H_6$  tended to decrease, but in contrast, the selectivities for  $CO$  and  $CO_2$  increased with increasing  $O_2/C_2H_4$  feed molar ratio, as aforementioned. Interestingly, the  $CO$  and  $CO_2$  selectivities increased when the  $O_2/C_2H_4$  feed molar ratio increased, and they reached a maximum at a  $O_2/C_2H_4$  feed molar ratio of 0.5:1. Under the studied conditions, the main products were  $CO$  and  $CO_2$  with significant amounts of EO,  $H_2$ ,  $CH_4$ ,  $C_3H_8$  and  $C_2H_6$ . The largest hydrocarbon, i.e.  $C_3H_8$ , was found in a very small fraction. The results can be explained by the fact that, both complete and partial oxidation reactions are controlled by the ratio of oxygen in the system. The decreases in the selectivities for these hydrocarbons and  $H_2$  and the increase in the selectivities for  $CO$  and  $CO_2$  with increasing oxygen fraction in feed clearly reveal that the oxidative dehydrogenation and coupling reactions unfavorably occur under  $O_2$ -rich conditions, as expected. Furthermore, at a very high  $O_2/C_2H_4$  feed molar ratio of 0.5:1, the selectivity for EO dropped to zero level since this high  $O_2/C_2H_4$  feed molar ratio induced the complete combustion to occur more favorably than the partial oxidation, as well as the epoxidation, indicating that the epoxidation reaction to produce EO is more likely to occur under  $O_2$ -lean conditions. The power consumptions required to convert  $C_2H_4$  molecule and to produce EO molecule at different  $O_2/C_2H_4$  feed molar ratios are shown in Fig. 4d. The power consumption per molecule of produced EO reached a minimum at an  $O_2/C_2H_4$  molar ratio of 0.2:1, which corresponded well with the obtained highest EO selectivity. However, the power consumption per molecule of converted  $C_2H_4$  remained almost unchanged in the  $O_2/C_2H_4$  feed molar ratio range of 0.2:1-0.25:1, but then slightly decreased with increasing  $O_2/C_2H_4$  feed molar ratio to 0.5:1, at which the lowest EO selectivity was observed.

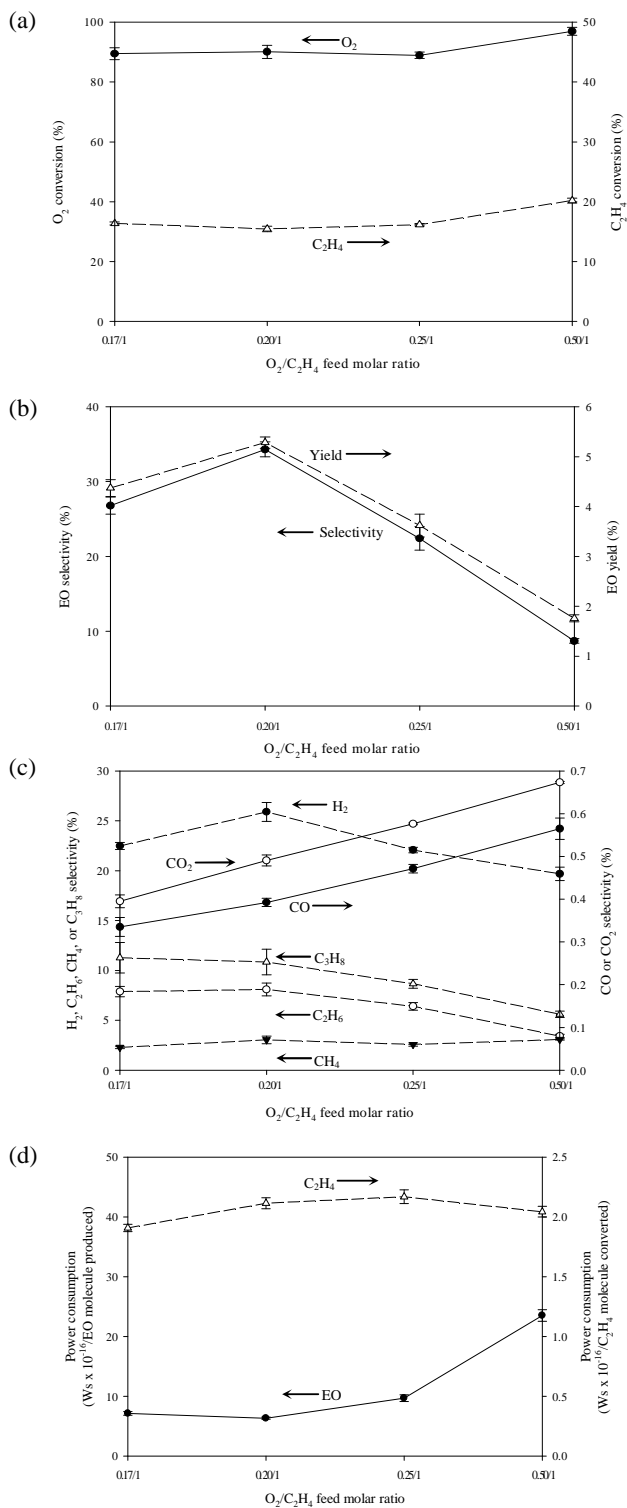


Fig. 4 (a)  $C_2H_4$  and  $O_2$  conversions, (b) EO selectivity and yield, (c) other product selectivities, and (d) power consumptions as a function of  $O_2/C_2H_4$  feed molar ratio at an ethylene feed position fraction of 0.5, an applied voltage of 19 kV, an input frequency of 500 Hz, and total feed flow rate of  $50 \text{ cm}^3/\text{min}$

#### IV. CONCLUSIONS

The epoxidation reaction of ethylene was investigated in the low-temperature DBD plasma system at different ethylene feed position fractions and feed molar ratios of  $O_2/C_2H_4$ . The highest EO selectivity of 34.3% and the highest EO yield of 5.28% were obtained when the DBD was operated at an ethylene feed position fraction of 0.5, an  $O_2/C_2H_4$  feed molar ratio of 0.2:1, an applied voltage of 19 kV, an input frequency of 500 Hz, and a total feed flow rate of  $50 \text{ cm}^3/\text{min}$ . At these best conditions, the power consumptions to break down each  $C_2H_4$  molecule and to create an EO molecule were found to be  $2.11 \times 10^{-16} \text{ W}$ /molecule of  $C_2H_4$  converted and  $6.34 \times 10^{-16} \text{ W}$ /molecule of EO produced.

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