

## CHAPTER IV

### RESULTS AND DISCUSSION

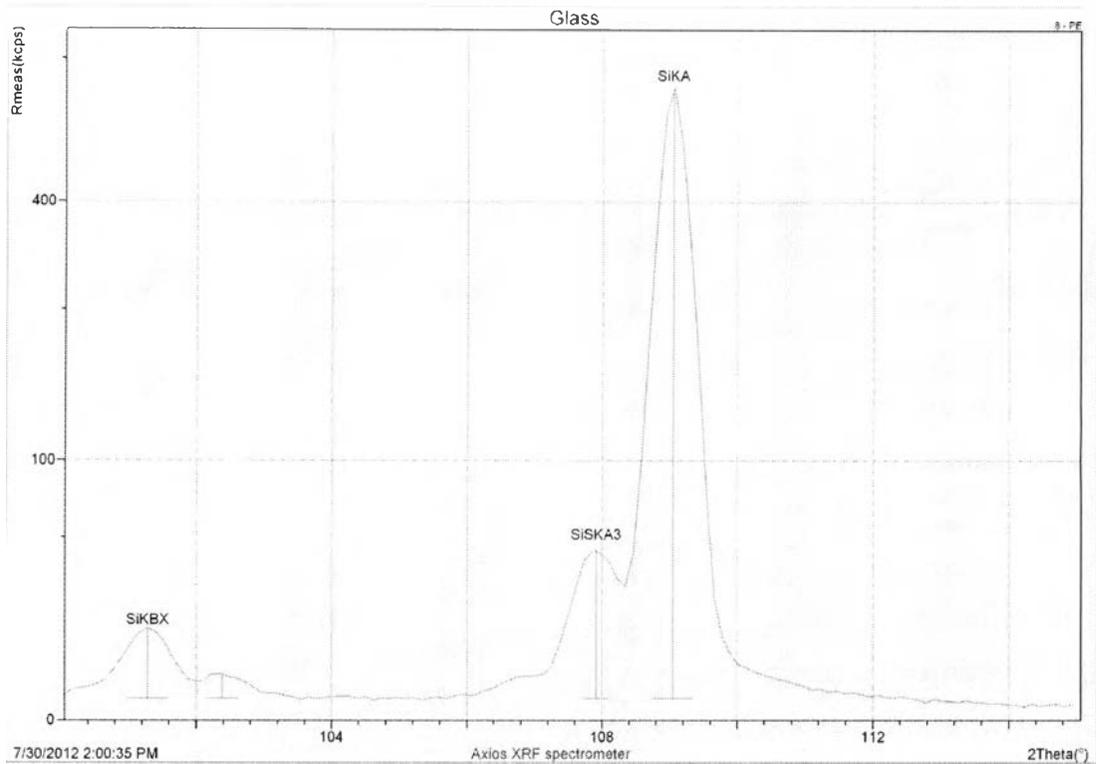
According to the previous work (Paosombat *et al.*, 2012), the smooth-surfaced glass acted as a dielectric barrier in the DBD reactor and catalyst support could be used to improve ethylene oxide product. However, the combined between DBD system and Ag catalyst supported on smooth surface support ( $\text{SiO}_2$ ) cannot enhance ethylene oxide selectivity and yield same as commercial conventional catalytic process.

In this work, two rough-surfaced glasses were employed for the ethylene epoxidation instead of the smooth-surfaced glass because electron might be get free easily from rough surface. When the smooth-surfaced glass was replaced by two rough-surfaced glasses, the area on glass increased that meant more uniform plasma or more microdischarge. The effects of operational parameters including applied voltage, input frequency,  $\text{O}_2/\text{C}_2\text{H}_4$  feed molar ratio, and  $\text{C}_2\text{H}_4$  feed position fraction were determined in order to enhance ethylene oxide (desired product) production.

#### 4.1 Dielectric Material Characterization

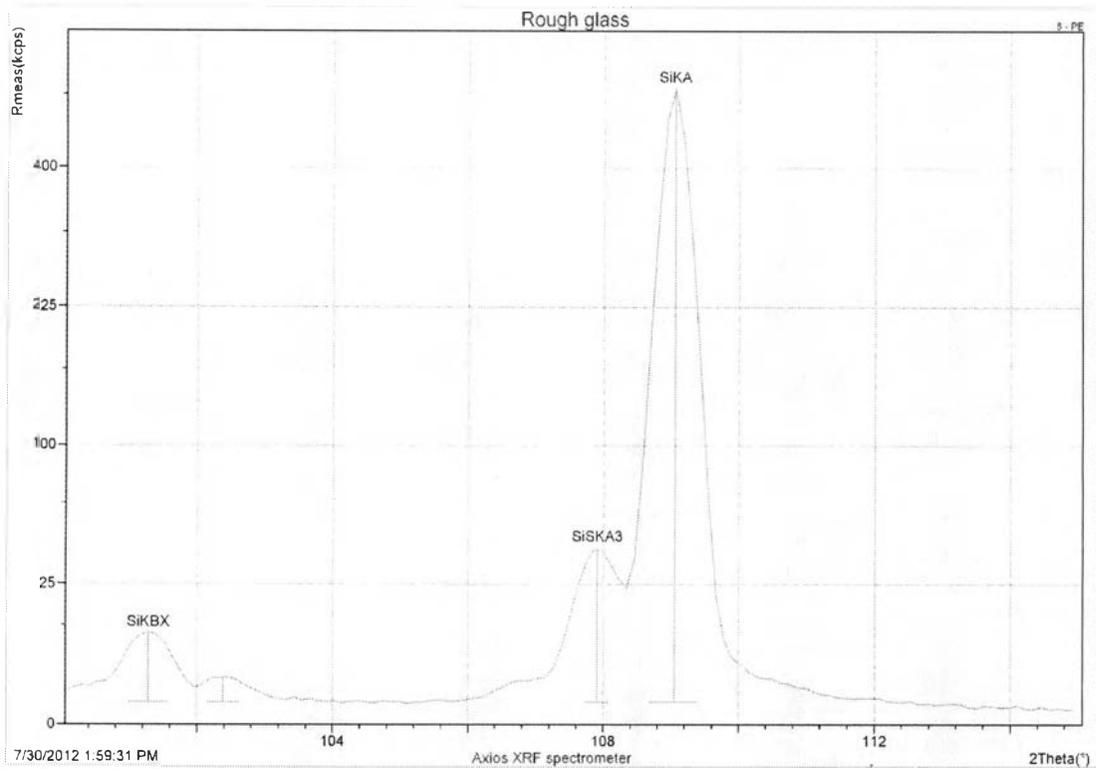
The XRF patterns of the smooth and rough-surfaced glass plates were shown in Figures 4.1 and 4.2, respectively. The compositions of rough-surfaced glass were almost similar to those of smooth-surfaced glass which mainly consisted of  $\text{SiO}_2$  (higher than 70%).

As shown in Figure 4.3, the average roughness of the rough-surfaced  $\text{SiO}_2$  was in range of 0.181-1.217  $\mu\text{m}$ , as detected by AFM. In addition, Figures 4.3 (AFM) and 4.4 (SEM) showed that the same sample provided the different roughness depending on interested position (non-homogeneous surface). Therefore, the same rough-surfaced glasses were used for varying all parameters to get the comparable results.



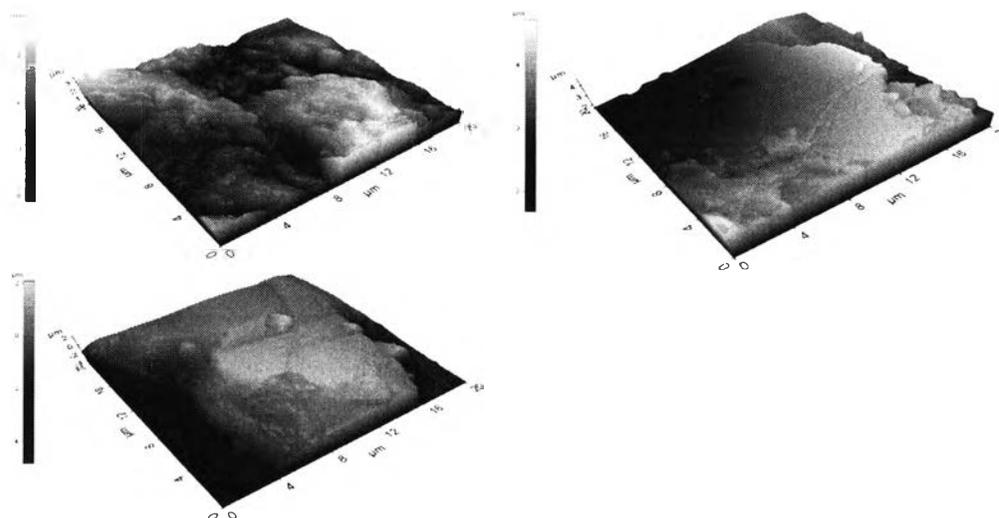
Analyte	Calibration status	Compound formula	Measured (kcps)	Used (kcps)	Concentration (%)	Calculation method
Na	Calibrated	Na2O	68.363	68.363	13.534	Calculate
Mg	Calibrated	MgO	29.157	29.157	2.860	Calculate
Al	Calibrated	Al2O3	10.647	10.647	1.002	Calculate
Si	Calibrated	SiO2	596.179	596.179	71.122	Calculate
P	Calibrated	P2O5	0.135	0.135	0.010	Calculate
S	Calibrated	SO3	2.524	2.524	0.213	Calculate
K	Calibrated	K2O	0.364	0.364	0.053	Calculate
Ca	Calibrated	CaO	64.403	64.403	10.873	Calculate
Ti	Calibrated	TiO2	0.306	0.306	0.057	Calculate
Fe	Calibrated	Fe2O3	0.783	0.783	0.129	Calculate
Zr	Calibrated	ZrO2	1.934	1.934	0.021	Calculate
Cl	Calibrated	Cl	1.512	1.512	0.127	Calculate

**Figure 4.1** XRF result from the smooth-surfaced glass.

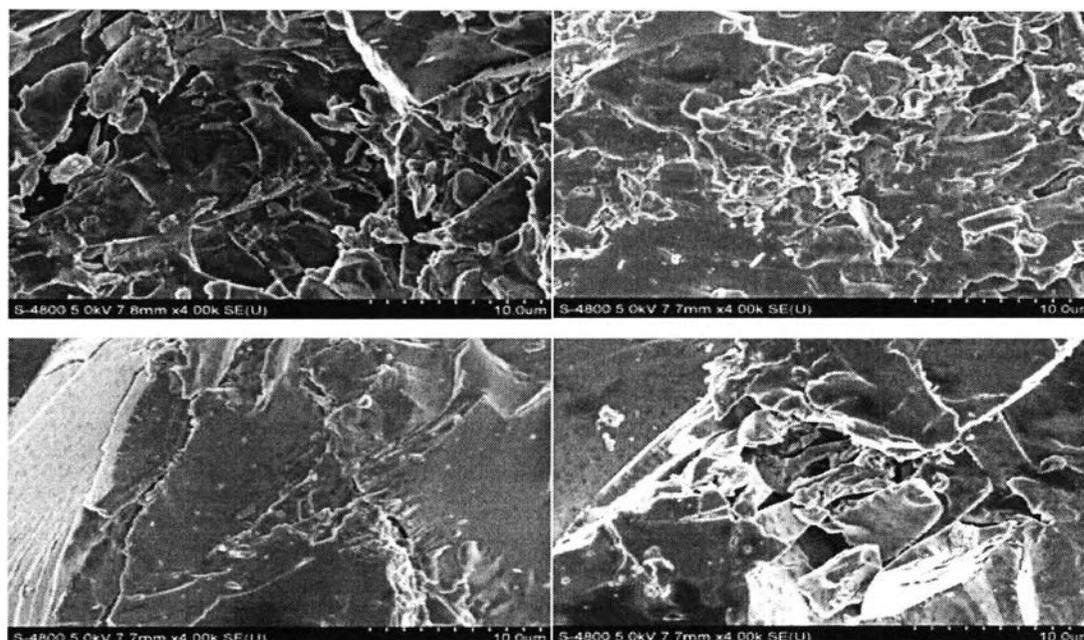


Analyte	Calibration status	Compound formula	Measured (kcps)	Used (kcps)	Concentration (%)	Calculation method
Na	Calibrated	Na2O	38.383	38.383	9.500	Calculate
Mg	Calibrated	MgO	23.074	23.074	2.658	Calculate
Al	Calibrated	Al2O3	10.050	10.050	1.114	Calculate
Si	Calibrated	SiO2	522.843	522.843	74.290	Calculate
S	Calibrated	SO3	1.828	1.828	0.190	Calculate
Ca	Calibrated	CaO	56.940	56.940	11.909	Calculate
Fe	Calibrated	Fe2O3	0.721	0.721	0.150	Calculate
Zr	Calibrated	ZrO2	2.137	2.137	0.029	Calculate
Cl	Calibrated	Cl	1.545	1.545	0.160	Calculate

**Figure 4.2** XRF result from the rough-surfaced glass.



**Figure 4.3** Surface images on the rough-surfaced glass from AFM.



**Figure 4.4** Surface images on rough glass from SEM (Accelerating voltage of 5kV, emission current of 9000 nA and Magnification of 4k).

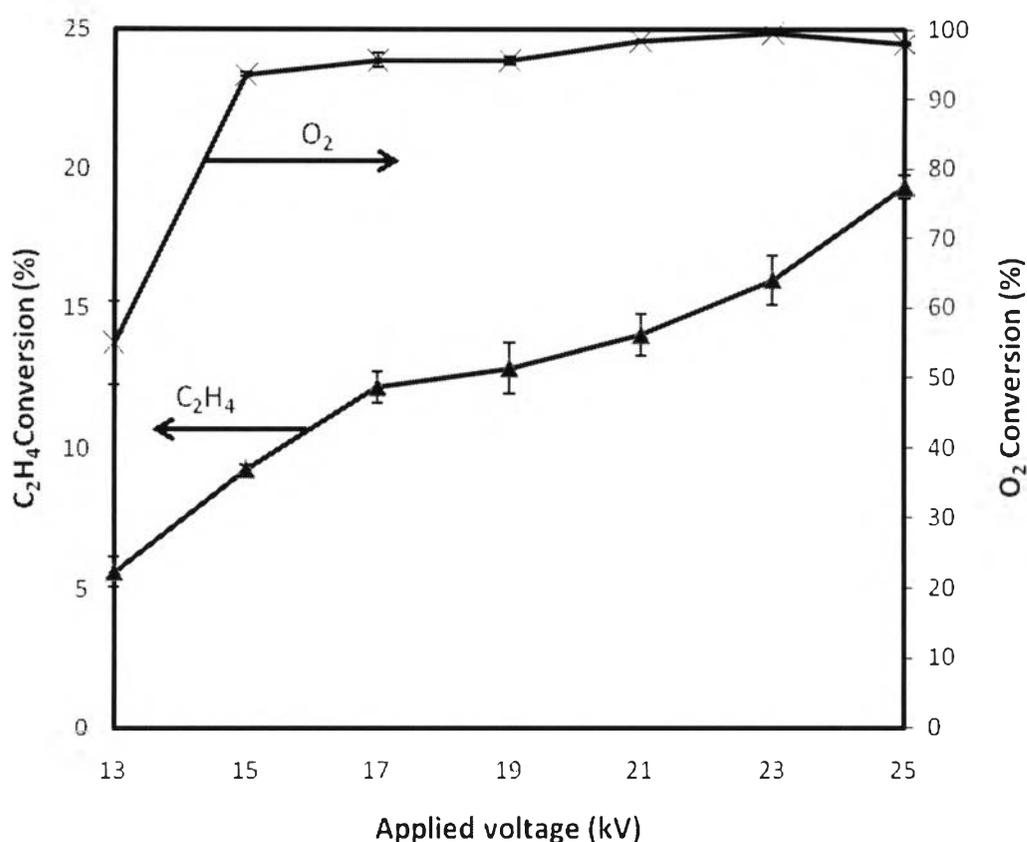
## 4.2 Reaction Activity Performance

### 4.2.1 Effect of Applied Voltage

In this study, an applied voltage was varied from 13 to 25 kV, when the other parameters were fixed at an input frequency of 500 Hz, a feed molar ratio of

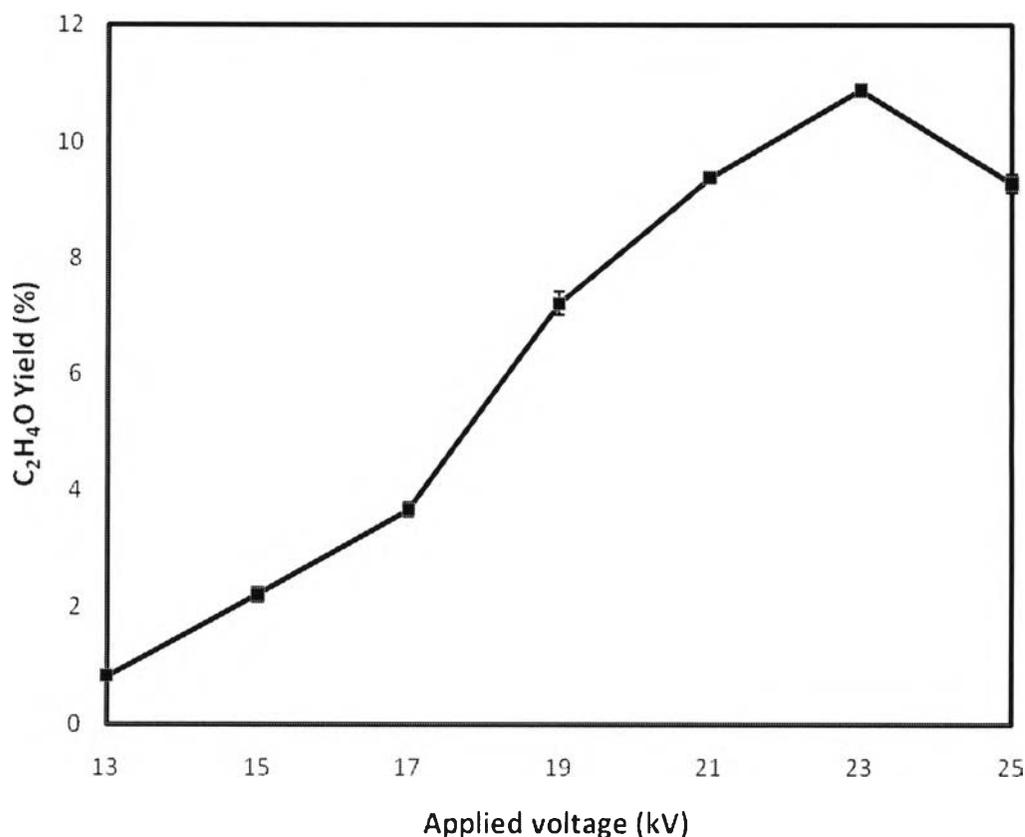
$O_2/C_2H_4$  of 0.2:1, an ethylene feed position fraction of 0.5, and a total feed flow rate of  $50\text{ cm}^3/\text{min}$ .

Figure 4.5 showed the effect of applied voltage on ethylene and oxygen conversion. Ethylene conversion dramatically increased from 5.60 to 19.35 % with increasing applied voltage from 13 to 25 kV. When applied voltage enhanced from 13 to 15 kV, oxygen conversion increased rapidly and then was nearly unchanged with increasing applied voltage over 15 kV. The maximum of oxygen conversion 99.5 % was found at applied voltage of 23 kV.



**Figure 4.5**  $C_2H_4$  and  $O_2$  conversions as a function of an applied voltage at an  $O_2/C_2H_4$  feed molar ratio of 0.2:1, an input frequency of 500 Hz, an  $C_2H_4$  feed position fraction of 0.5, and total feed flow rate of  $50\text{ cm}^3/\text{min}$ .

As shown in Figure 4.6, ethylene oxide yield enhanced obviously from 0.83 to 10.88 % with increasing applied voltage from 13 to 23 kV, and then it adversely decreased to 9.29 % with further increasing applied voltage beyond 23 kV.



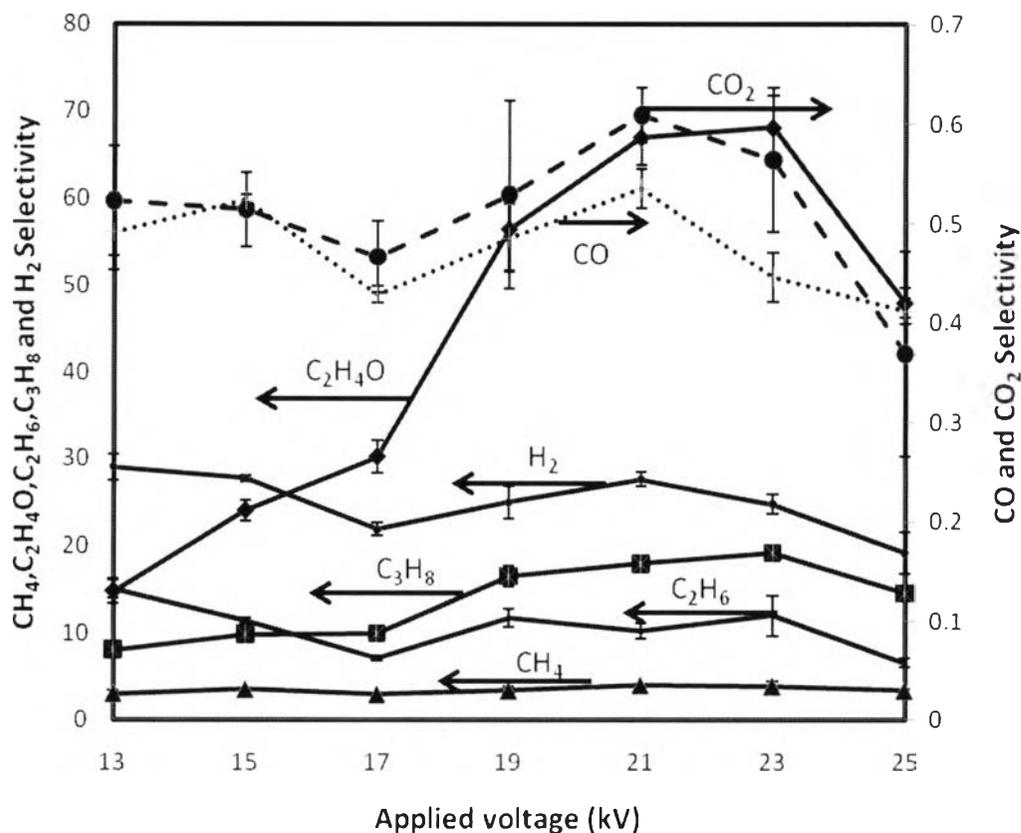
**Figure 4.6** C<sub>2</sub>H<sub>4</sub>O yield as a function of an applied voltage at an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an input frequency of 500 Hz, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

Ethylene oxide selectivity (Figure 4.7) demonstrated the same trend as ethylene oxide yield (Figure 4.6) that it increased with enhancing applied voltage to 23 kV. Ethylene oxide selectivity reached a maximum of 68.15 % when operated at applied voltage of 23 kV. Therefore, the applied voltage of 23 kV could be considered to be the optimum value for the ethylene epoxidation reaction in the DBD system using two dielectric rough glasses. Interestingly, the ethylene oxide selectivity was almost the same as compared to the previous work (Paosombat *et al.*, 2012), even though Ag catalyst was not impregnated on the rough-surfaced glass.

The CO and CO<sub>2</sub> selectivities were slightly fluctuated in range of 0.37-0.61 % and 0.41-0.54 %, respectively. The maximums of these selectivities were 0.61 and 0.54, respectively, at applied voltage of 21 kV. The maximums of H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> selectivities were 29.02 and 15.08 %, respectively, at the lowest applied

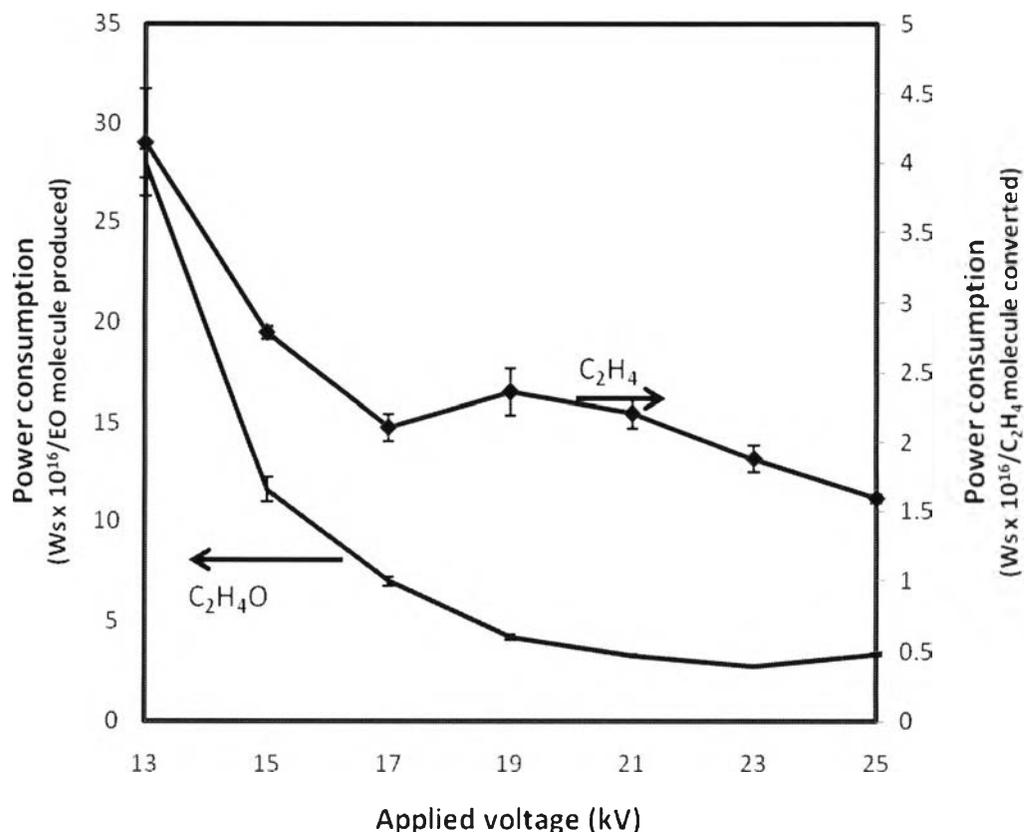
voltage of 13 kV and then, they tended to decrease with further increasing applied voltage over 13 kV. In contrast, the  $C_3H_8$  selectivity increased continuously to reach the highest  $C_3H_8$  selectivity of 19.25% at 23 kV. However, the  $C_3H_8$  selectivity decreased eminently when applied voltage increased to 25 kV whereas the  $CH_4$  selectivity was constant in the entire applied voltage range of 13-25 kV.

The results could be explained by the fact that the DBD system provided higher the amount of generated and energetic electrons with increasing applied voltage from 13 to 25 kV, leading to more opportunity of collision between  $C_2H_4$  and dissociated  $O_2$  molecules. Consequently, ethylene oxide selectivity and yield increased with increasing applied voltage up to 23 kV. However, ethylene oxide selectivity and yield decreased when applied voltage increased from 23 to 25 kV. This results from coke deposition on the glass surface, which led to reduction of all chemical reaction activities as well as ethylene epoxidation. Therefore, selectivities for  $C_2H_4O$ ,  $CH_4$  and other products including  $C_2H_6$ ,  $C_3H_8$ ,  $H_2$ ,  $CO$ , and  $CO_2$  decreased at the highest applied voltage of 25 kV.



**Figure 4.7** CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>O, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, H<sub>2</sub>, CO, and CO<sub>2</sub> selectivities as a function of an applied voltage at an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an input frequency of 500 Hz, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

The power consumption per C<sub>2</sub>H<sub>4</sub> molecule converted and ethylene oxide molecule produced are shown in Figure 4.8. Both power consumptions had the opposite trend with ethylene conversion and ethylene oxide selectivity (Figures 4.5 and 4.7) that increased with increasing applied voltage in the entire range of 13-25 kV. The minimum of the power consumption per ethylene oxide molecule converted was found at applied voltage of 23 kV. Therefore, the applied voltage of 23 kV was considered to be an optimum and was selected for further experiment because it provided the highest ethylene oxide selectivity and yield with the lowest power consumption per ethylene oxide molecule produced.



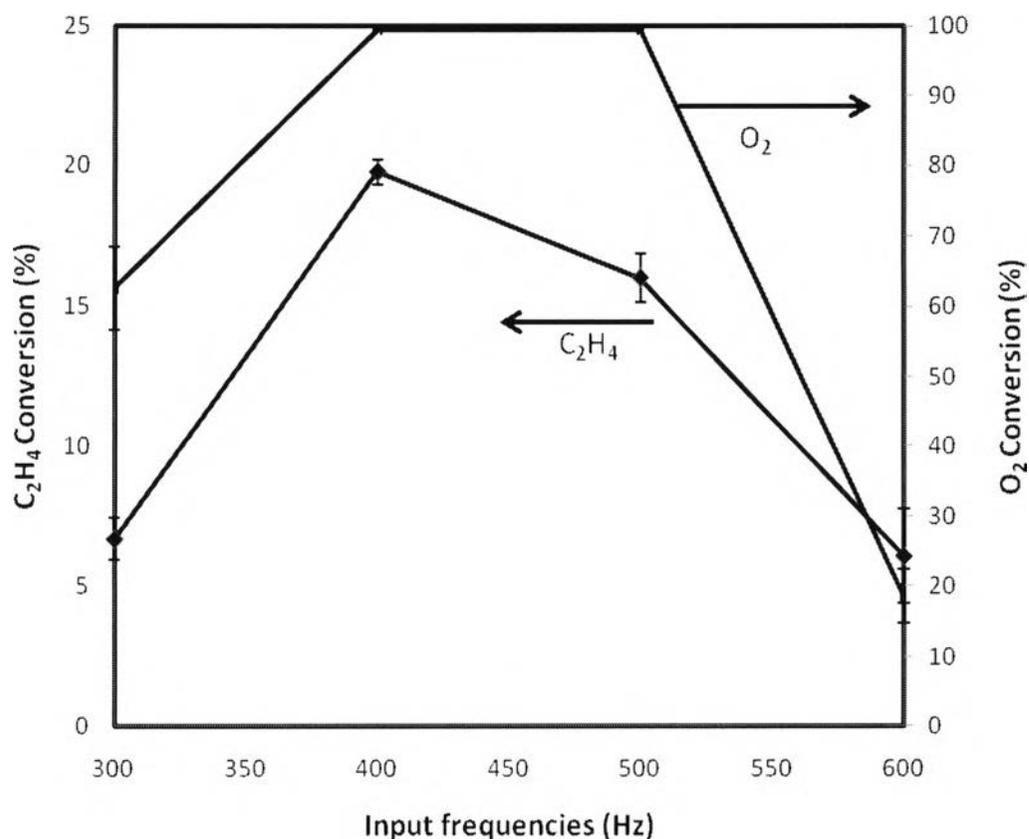
**Figure 4.8** C<sub>2</sub>H<sub>4</sub>O and C<sub>2</sub>H<sub>4</sub> power consumptions as a function of an applied voltage at an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an input frequency of 500 Hz, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

#### 4.2.2 Effect of Input Frequency

Effect of input frequency on the ethylene epoxidation performance was investigated by varying input frequency from 300 to 600 Hz. The operational parameters were fixed at an applied voltage of 23 kV, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

As shown in Figure 4.9, oxygen conversion increased to 99.53 % with increasing input frequency to 400 Hz. Then, the oxygen conversion was slightly constant until 500 Hz, and it nearly unchanged with further increasing input frequency to 500 Hz. Afterward, it rapidly decreased when input frequency enhanced over 500 Hz. Input frequency influenced the ethylene conversion as same as the oxygen conversion that increased to reach a maximum at input frequency of 400 Hz, and then decreased enormously with further increasing input frequency over 400 Hz.

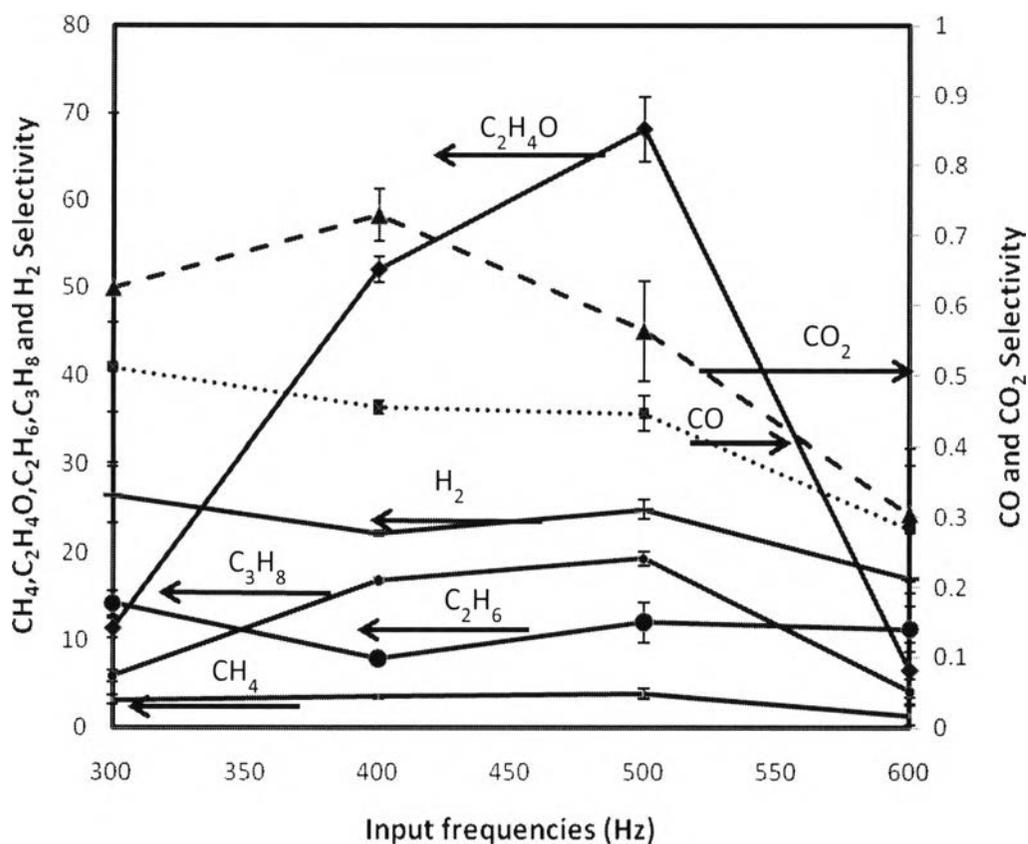
Finally, it tended to decrease. For another line, ethylene conversion was likely to increase until 19.76 % at input frequency 400 Hz and after this point the conversion decreased dramatically.



**Figure 4.9** C<sub>2</sub>H<sub>4</sub> and O<sub>2</sub> conversions as a function of an input frequency at an applied voltage of 23 kV, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

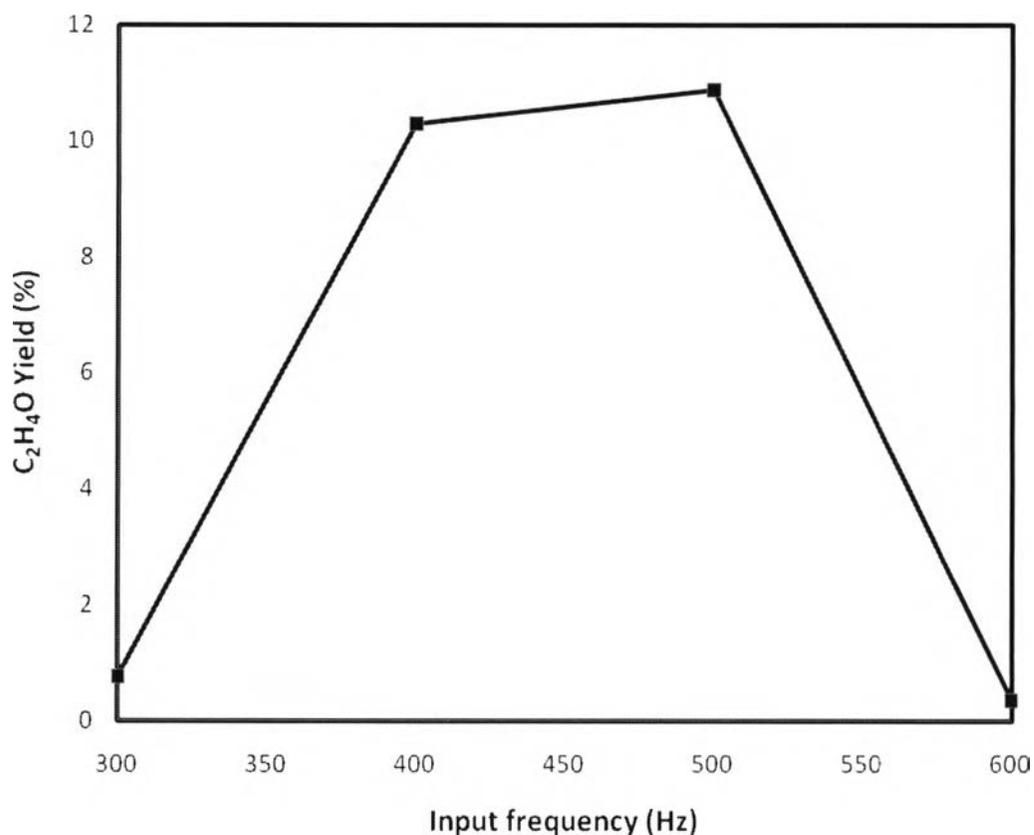
The ethylene oxide, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, and H<sub>2</sub> selectivities were found to be the highest of 68.15, 12.02, 19.25, and 24.86 %, respectively, at input frequency of 500 Hz (Figure 4.10). The CO selectivity tended to gradually decrease when input frequency increased, whereas the CH<sub>4</sub> selectivity was almost stable with increasing input frequency from 300 to 500 Hz. Moreover, effect of input frequency from Figure 4.10 could summarize that at lower frequency, plasma had higher energy leading to ethylene cracking before it reacted with oxygen. However, generated discharge was insufficient at the highest input frequency of 600 Hz to initiate all

chemical reactions including ethylene epoxidation, resulting in less ethylene oxide production.



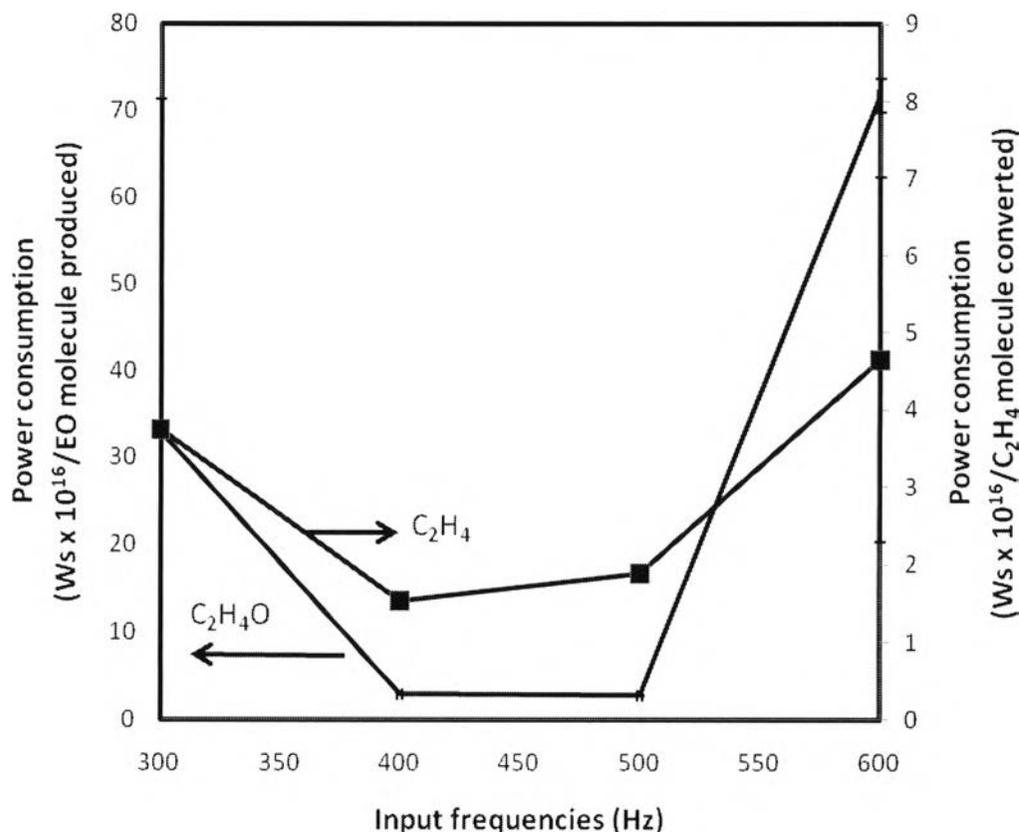
**Figure 4.10** CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>O, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, H<sub>2</sub>, CO, and CO<sub>2</sub> selectivities as a function of an input frequency at an applied voltage of 23 kV, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

The graph in Figure 4.11 encouraged Figure 4.10 that the optimum input frequency of 500 Hz was optimum for the DBD system with two rough glasses because in this point, ethylene oxide selectivity and yield were the maximum.



**Figure 4.11** C<sub>2</sub>H<sub>4</sub>O yield as a function of an input frequency at an applied voltage of 23 kV, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

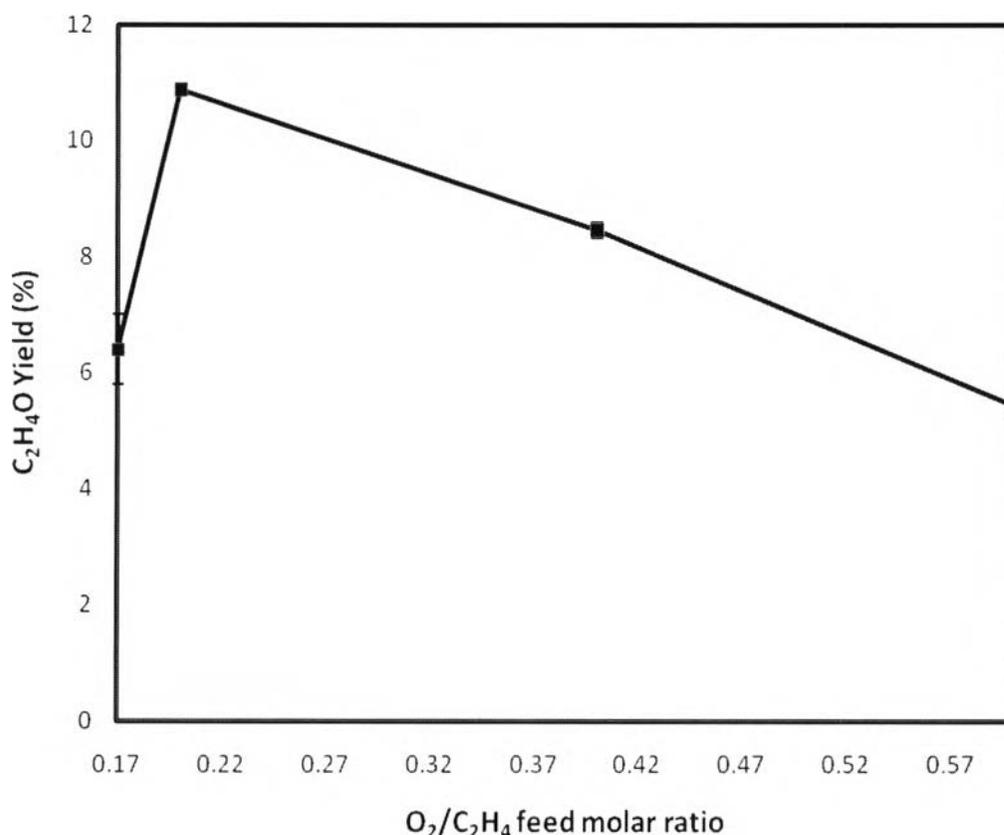
Ethylene oxide power consumption in Figure 4.12 supported with its selectivity and yield in Figures 4.10 and 4.11 since if the higher ethylene oxide occurred, the lower energy consumption became. In the same way, if the higher ethylene converted, the lower energy consumption became.



**Figure 4.12** C<sub>2</sub>H<sub>4</sub>O and C<sub>2</sub>H<sub>4</sub> power consumption as a function of an input frequency at an applied voltage of 23 kV, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

#### 4.2.3 Effect of O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> Feed Molar Ratio

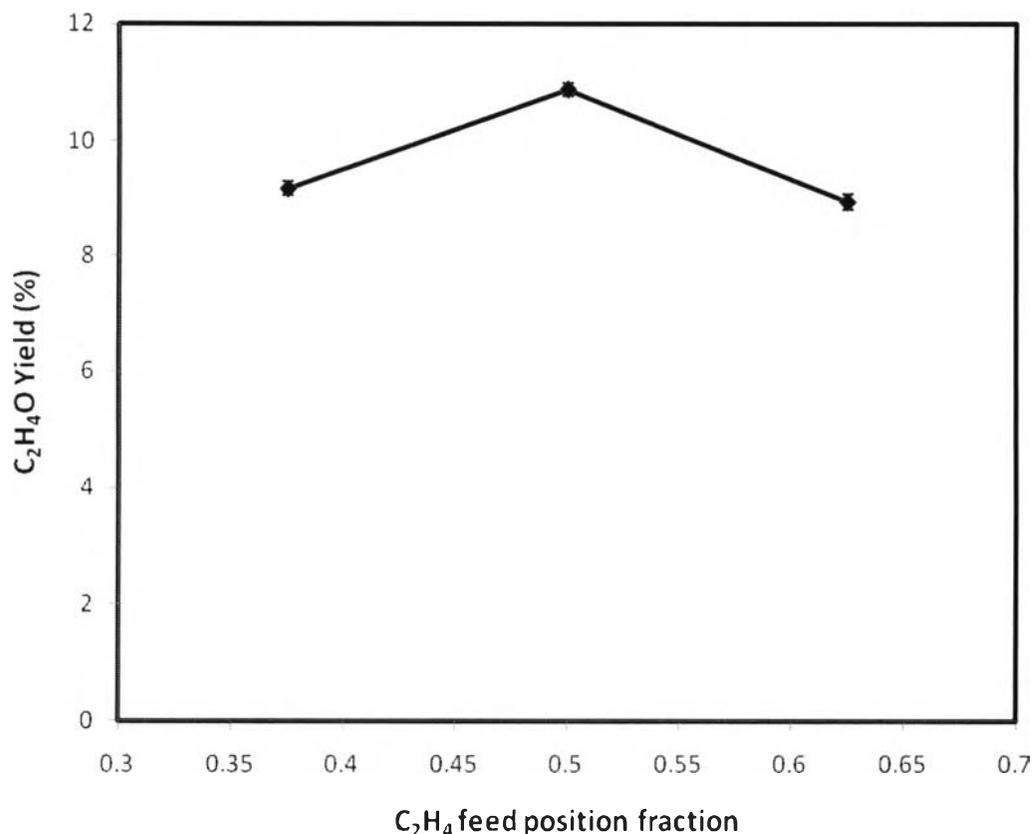
The applied voltage and input frequency optimums were 23 kV and 500 Hz, respectively, used for providing the optimum O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio. As shown in Figure 4.13, ethylene oxide yield was the maximum at O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2. This result supported with previous work (Paosombat *et al.*, 2012) that both complete and partial oxidation reactions were controlled by the ratio of oxygen in the system. The higher O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2 led to generate the complete combustion more than the partial oxidation that was epoxidation reaction, therefore, ethylene oxide was more favorable O<sub>2</sub>-lean condition than O<sub>2</sub>-rich condition. In contrast, the lower O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2 resulted in insufficient O<sub>2</sub> to occur the reaction.



**Figure 4.13** C<sub>2</sub>H<sub>4</sub>O yield as a function of an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio at an applied voltage of 23 kV, an input frequency of 500 Hz, an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5, and total feed flow rate of 50 cm<sup>3</sup>/min.

#### 4.2.4 Effect of C<sub>2</sub>H<sub>4</sub> Feed Position Fraction

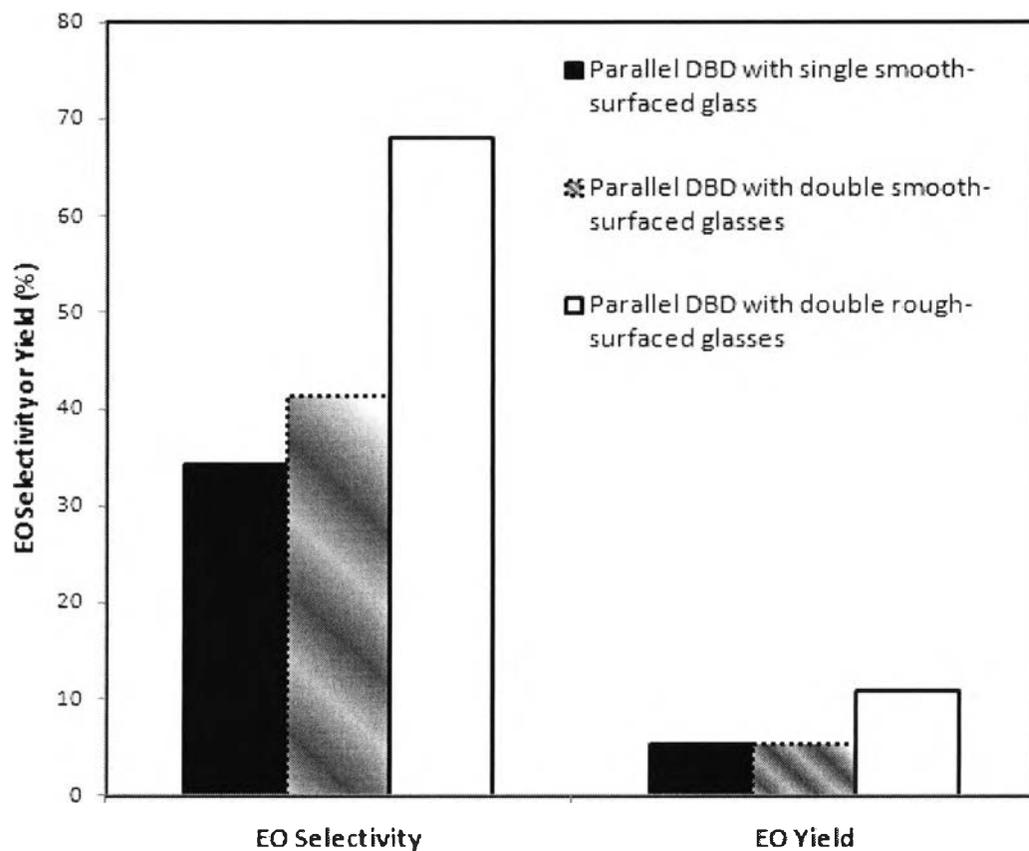
Effect of C<sub>2</sub>H<sub>4</sub> feed position was found by using fixed the optimum condition from previous results. The result showed that at an C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5 provided the highest ethylene oxide yield that it supported previous work (Paosombat *et al.*, 2012). A lower C<sub>2</sub>H<sub>4</sub> feed position fraction of 0.5 resulted in more residence time of ethylene in DBD reactor, resulting in it more opportunity of ethylene cracking. Moreover, at a higher C<sub>2</sub>H<sub>4</sub> feed position of 0.5, the ethylene has a short residence time for epoxidation reaction.



**Figure 4.14** C<sub>2</sub>H<sub>4</sub>O yield as a function of an C<sub>2</sub>H<sub>4</sub> feed position fraction at an applied voltage of 23 kV, an input frequency of 500 Hz, an O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> feed molar ratio of 0.2:1, and total feed flow rate of 50 cm<sup>3</sup>/min.

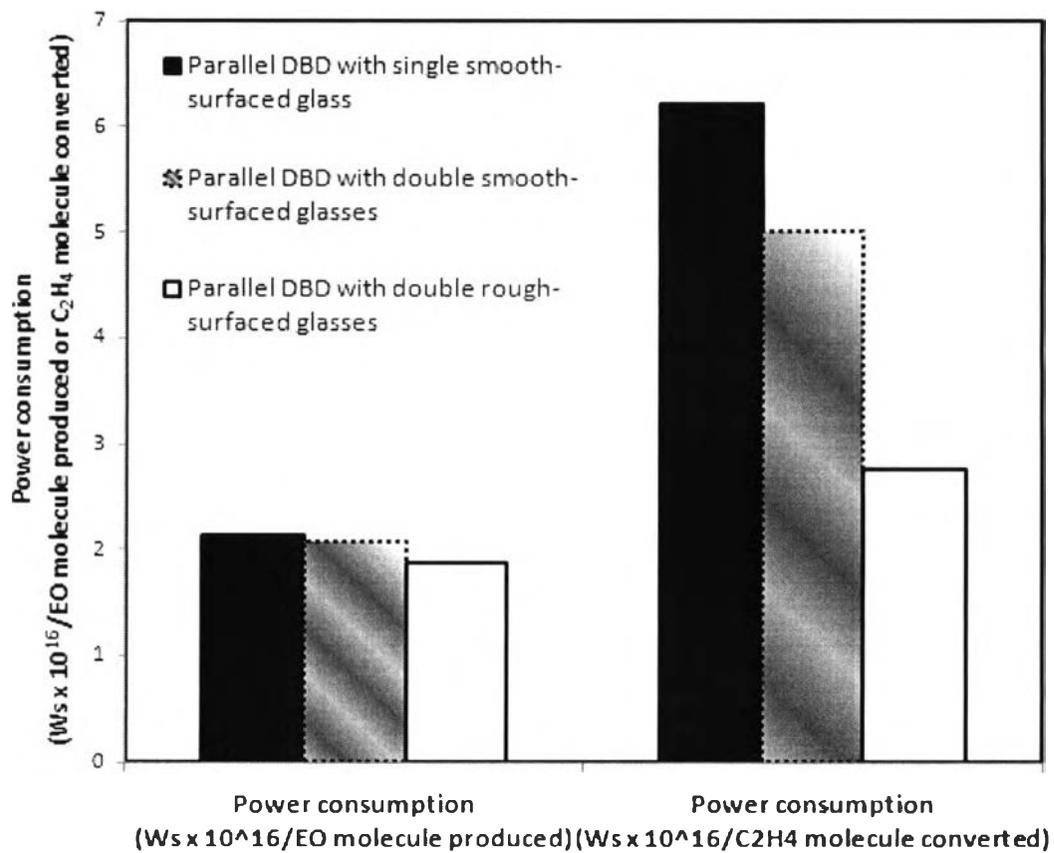
### 4.3 Glass Plate Activity Comparison

Surface roughness and a number of glasses had an significant effect on ethylene oxide selectivity. The DBD reactor using one smooth-surfaced glass provided the ethylene oxide selectivity of 34.32 %, while the DBD using two smooth-surfaced glasses improved the selectivity to 41.27 % at the same condition as the previous work. In this research, changing two smooth-surfaced glasses to two rough-surfaced glasses, the selectivity increased to 68.15 % whereas provided the highest ethylene oxide selectivity by using the new conditions. From this result, ethylene oxide selectivity was 2 times higher than that of the previous work. Moreover, ethylene oxide yield tended to increase the same as the selectivity when changing a number and types of glasses (Figure 4.15).



**Figure 4.15** Comparisons of EO selectivity and yield of DBD system with single and double glass plates.

Figure 4.16 showed the results supported Figure 4.15 since when this system generated more ethylene oxide, the power consumption of produced ethylene oxide and converted ethylene should decrease. From both results (Figures 4.15 and 4.16), it could be concluded that surface roughness and adding more than one plate provided better generated ethylene oxide performance than smooth surface because it might be easier to generate uniform microdischarge plasma, leading to dissociated oxygen had suitable energy for epoxidation reaction.



**Figure 4.16** Comparisons of power consumption of produced EO and converted ethylene in DBD system with single and double glass plates.