CHAPTER IV
RESULTS AND DISCUSSION

According to the previous work (Dulyalaksananon2013), the two rough-surfaced glasses acted as a dielectric barrier in the DBD reactor provided better ethylene epoxidation reaction performance than the smooth-surface glass. However, there are several parameters which can effect on ethylene epoxidation performance, including Ag catalyst existence, different calcination temperatures, and difference oxygen source types.

In this work, two rough-surfaced glasses were employed for the ethylene epoxidation with upper coated with 0.1 wt% Ag catalyst instead of the sole plasma. The effects of operational parameters including an applied voltage, an input frequency, and a total feed flow rate were first determined in order to obtain the optimum conditions, while other parameters were fixed at a feed molar ratio of N_2O/C_2H_4 of 0.17:1, and an ethylene feed position fraction of 0.5. After that, the effects of calcination temperature as well as the effects of oxygen sources were studied for enhancing the performance of ethylene oxide

4.1 Catalyst Characterization Results

4.1.1 XRD Results

The XRD patterns of studied catalysts with various calcination temperatures shown in figure 4.1 are obviously same. All of them have highly crystalline structure. The dominant peaks at 2θ of 38°, 44°,64°, 77°, and 81° correspond to (111), (200), (220), (311), and (222) planes respectively. The most dominant peak at 38° was used to calculate the crystal size of catalyst samples. Table 4.1 shows the effect of calcination temperature on crystal size, parcel size, and ethylene epoxidation activity. The crystal size and ethylene epoxidation performance increased with increasing calcination temperature, after calcination temperature was increased higher than 550°C, the crystal size tended to decrease as same as the ethylene epoxidation activity because sintering effect and some Ag catalyst insert into glass plate layer.
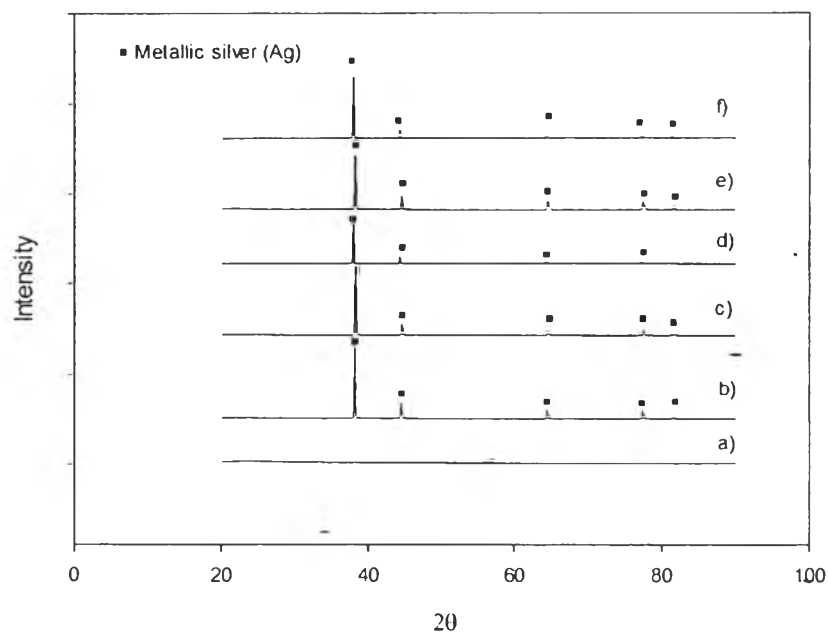
Figure 4.1 XRD patterns of rough glass coated with 0.1 wt% Ag catalyst at diferrent calcination temperatures: (a) 0 %wt Ag, (b) 450 °C, (c) 500 °C, (d) 550 °C, (e) 600°C, and f) 650°C.

Table 4.1 Crystal size of Ag catalysts, particle size and ethylene epoxidation performance at different temperatures

Calcination Temperature(°C)	Crystal Size (nm)	Particle Size (nm)	C_2H_4 Conversion (%)	N_2O Conversion (%)	EO Selectivity (%)	EO Yield (%)
450	106.25	116.96	17.21	12.10	44.55	7.67
500	110.19	188.65	18.71	22.00	47.36	8.49
550	130.09	220.81	17.68	13.38	48.87	8.58
600	75.31	239.13	18.18	19.70	43.38	7.89
650	53.22	320.40	18.49	12.68	42.96	7.95

4.1.2 Surface Morphology

The SEM images of the rough glass plate supported with 0.1 wt% Ag catalysts at different calcination temperatures are shown in figure 4.2. The SEM image results support the XRD result that at calcination temperature over than 550 °C, glass plate started to deform, resulting in some Ag catalyst inserted into glass plate, moreover there was sintering effect occurred at this high calcinations temperature.
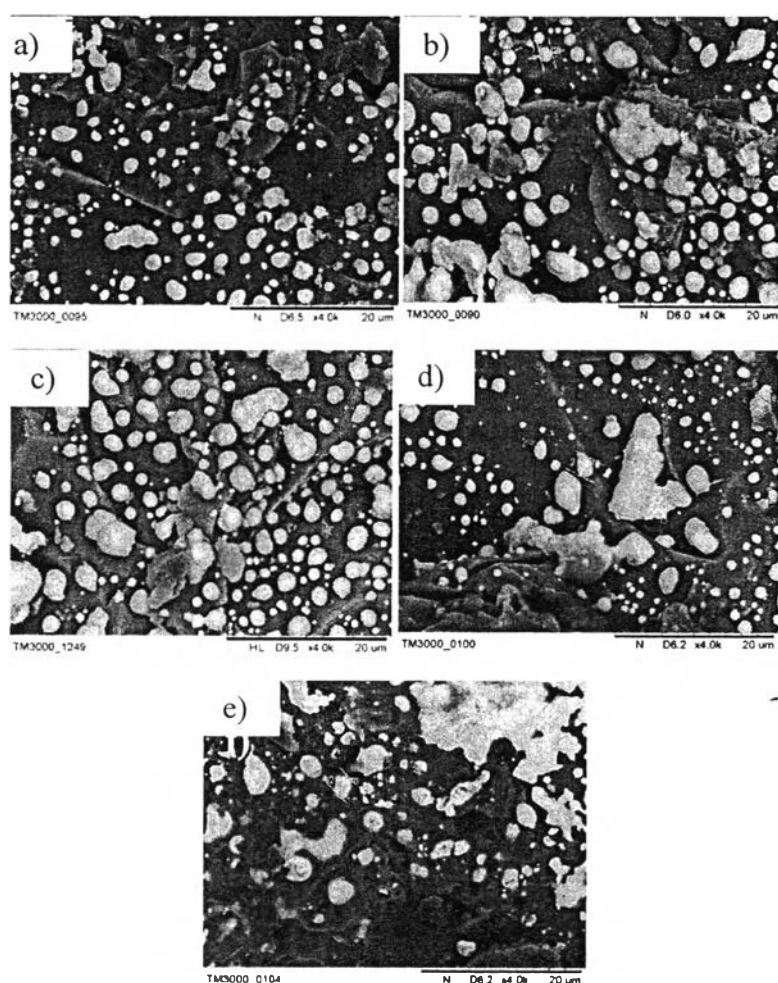

Figure 4.2 SEM images of rough glass coated with 0.1 wt% Ag catalyst at different calcination temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C, (d) 600 °C, (e) 650 °C (Accelerating voltage of 15kV and Magnification of 4k).

4.2 Reaction Activity Performance

4.2.1 Effect of Applied Voltage

In order to examine optimum condition, an applied voltage was varied from 15 to 21 kV. Since the break-down voltage or the lowest voltage (onset voltage) was found to be about 15 kV and this DBD system could not be operated at the applied voltage higher than 21 kV because the generated plasma was found to be non-uniform distribution characteristic. Thereby, the voltage of 15 to 21 kV was conducted in this experiment to investigate the effect of applied voltage. The other parameters were fixed at an input frequency of 500 Hz, a feed molar ratio of N_2O/C_2H_4 of 0.17:1, an ethylene feed position fraction of 0.5, and a total feed flow rate of 50 cm^3/min.

The effect of applied voltage on ethylene and nitrous oxide conversion is depicted in figure 4.3. The conversion of ethylene tended to increase with increasing an applied voltage. On the other hand, nitrous oxide conversion rapidly increased with increasing applied voltage from 15 to 17 kV, after that slightly remained unchanged.

As shown in Figure 4.4, ethylene oxide yield enhanced from 6.3 to 9.1% with increasing applied voltage from 15 to 17 kV, after that it slightly decreased with further increasing applied voltage beyond 17 kV, finally it adversely increased when input frequency was increased over than 19 kV.
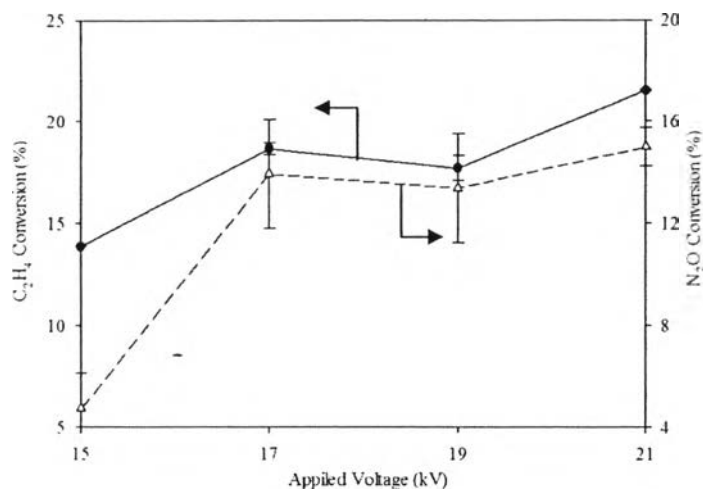
Figure 4.3 C_2H_4 and N_2O conversions in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of an applied voltage (frequency = 500 Hz, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).

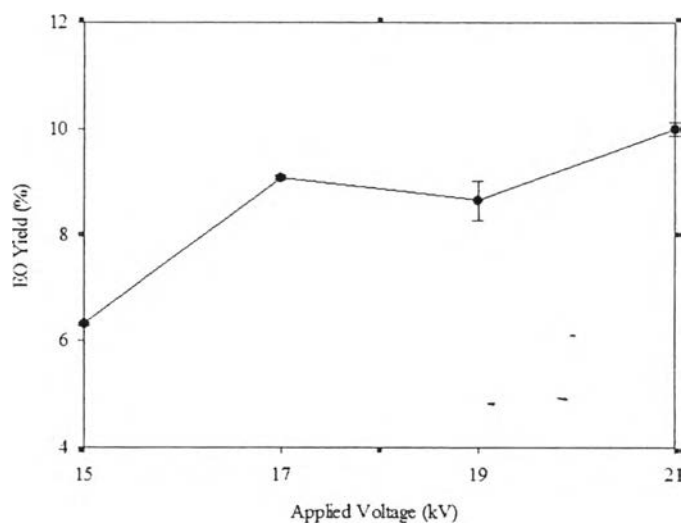**Figure 4.4** EO yield in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of an applied voltage (frequency = 500 Hz, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).

Figure 4.5 shows the product selectivities of EO, CH_4, C_2H_2, C_2H_6, C_3H_8, H_2, and CO. It demonstrated that ethylene oxide selectivity reached the maximum selectivity of 48.87% when operated at applied voltage of 19 kV.

The selectivity of C_3H_8 increased in the entire range of 15-17 kV, and then slightly decreased with increasing applied voltage from 17-21 kV, but in contrast, C_2H_6, H_2, and CH_4 selectivities remained almost unchanged with increasing applied voltage. Interestingly, the selectivity of C_2H_2 sharply decreased in the range of 15-17 kV, next its trend remained constant with further increasing applied voltage. In addition, the selectivity of CO was nearly constant and then turned to increase at input frequency over than 19 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 15 to 19 kV, leading to more opportunity of collision between C_2H_4 and dissociated oxygen. Consequently, ethylene oxide selectivity increased with increasing applied voltage up to 19 kV. However, a larger amount of active species with an increasing in applied voltage above 19 kV is likely to promote combustion reaction instead, resulting in an increasing CO selectivity and reduction in EO selectivity.

The power consumption per C_2H_4 molecule converted and ethylene oxide molecule produced are shown in figure 4.6. The power consumption per C_2H_4 molecule converted was slightly fluctuated in the range of 15-21 kV, on the other hand the power consumption per ethylene oxide molecule produced decreased in the range of 15-19 kV, and then adversely increased with increasing applied voltage over than 19 kV. Therefore, the applied voltage of 19 kV was considered to be an optimum and was selected for further experiment because it provided the highest ethylene oxide selectivity, acceptable and the lowest power consumption per ethylene oxide molecule produced, despite this condition, EO yield not as high operating at 17 kV.
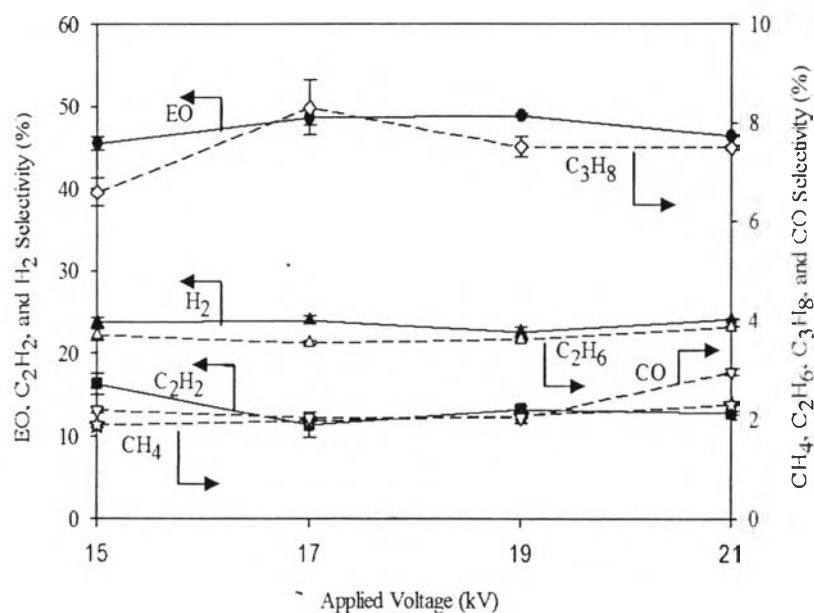
Figure 4.5 Product selectivities in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of an applied voltage (frequency = 500 Hz, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).
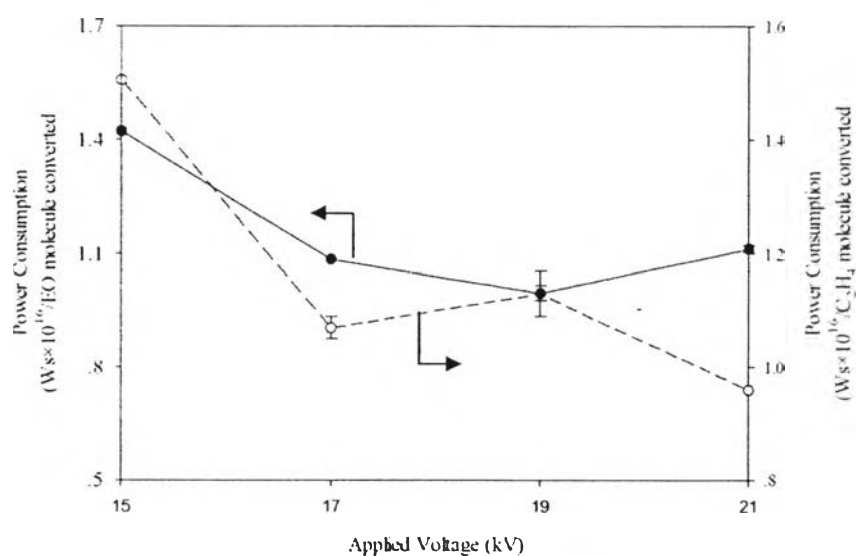

Figure 4.6 EO and C_2H_4 power consumptions in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of an applied voltage (frequency = 500

Hz, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).

4.2.2 Effect of Input Frequency

Input frequency significantly affects the field strength in the plasma zone. The studied DBD system was operated in the input frequency range of 450-800 Hz. Due to at input frequency lower than 450 Hz, the plasma distribution was not fairly uniform over the whole electrode surface. Whereas, the plasma cloud exist at frequency higher than 600 Hz. Therefore, effect of input frequency on the ethylene epoxidation performance was investigated by varying input frequency from 450 to 600 Hz. Meanwhile, the other operational parameters were fixed at an applied voltage of 19 kV, a N_2O/C_2H_4 feed molar ratio of 0.17:1, an C_2H_4 feed position fraction of 0.5, and total feed flow rate of 50 cm^3/min.

The ethylene and nitrous oxide conversion are shown in figure 4.7. Ethylene conversion decreased sharply from 21.87 to 13.67% with increasing input frequency from 450 to 550 Hz, and then remained constant with further increasing input frequency. As same as ethylene conversion, nitrous oxide conversion obviously decreased from 18.51 to 13.37 % in the entire range of 450-500 Hz, then it slightly constant over input frequency of 500 Hz, finally it dramatically decreased with further increasing input frequency beyond 550 Hz.

It cloud be explained by the fact that a higher frequency result in a lower current (Figure 4.8) that correspond to the reduction of number of electrons generated (weaker field strength), leading to redaction in amount of active species for reaction.
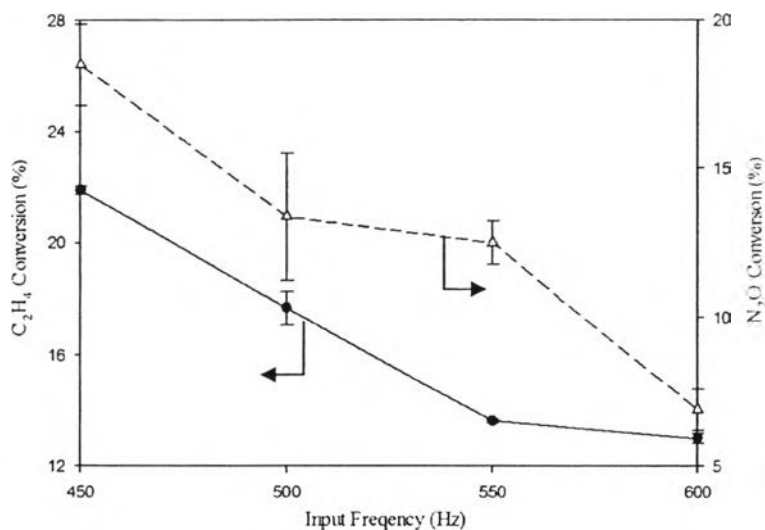
Figure 4.7 C_2H_4 and N_2O conversions in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of input frequency (voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).
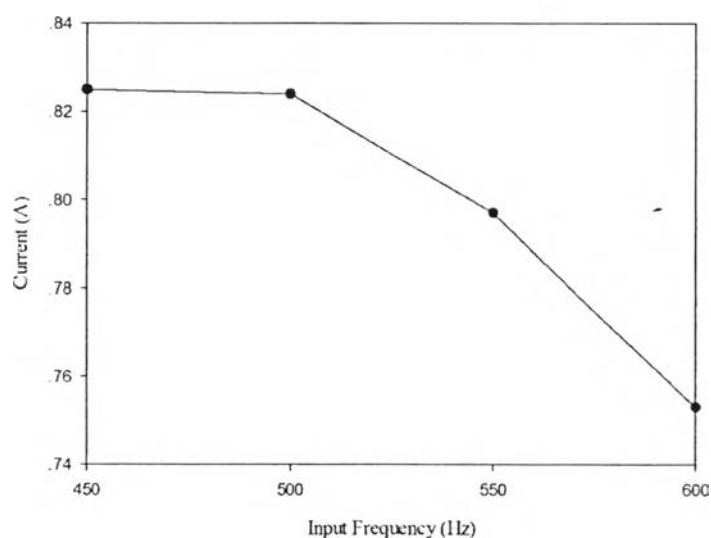

Figure 4.8 Effect of input frequency on generated current in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of input frequency (voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).

All products selectivities are summarized in figure 4.9. The ethylene oxide selectivity increased when the input frequency increased from 450 to 500 Hz, then the selectivity of ethylene oxide decreased with further increasing input frequency over than 500 Hz. In contrast to the ethylene oxide selectivity, H_2 selectivity slightly constant for all input frequency. For the selectivity of C_3H_8, it sharply increase with increasing input frequency in the range of 450 to 550 Hz, next tended to constant after increasing input frequency over than 550 Hz. In case of CH_4, C_2H_6, and CO selectivities, they tended to decease and then increased with increasing input frequency over than 550 Hz. A possible explanation is that at higher input frequency, the generated current and input power are lower, leading to the reduction of the number of electrons generated (weaker field strength). Therefore, it can cause a decrease in the amount of active species for reaction, including ethylene epoxidation reaction, resulting in decreasing ethylene oxide selectivity as mention before. On the other hand, lower frequency, plasma has higher energy resulting in ethylene cracking before it reacts with oxygen, moreover it predominantly causes hydrocarbon combustion and dehydrogenation instead of ethylene epoxidation reaction (Suttikul *et al.*, 2012).
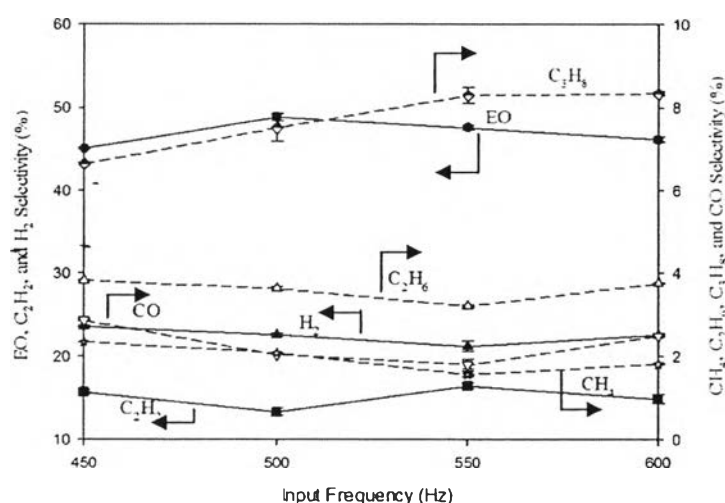

Figure 4.9 Product selectivity in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of input frequency (voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).

The trend line in figure 4.10 indicates that the dominant value of ethylene oxide yield was obtained at input frequency of 450 Hz, after that sharply decreased with further increasing an input frequency more than 450 Hz.
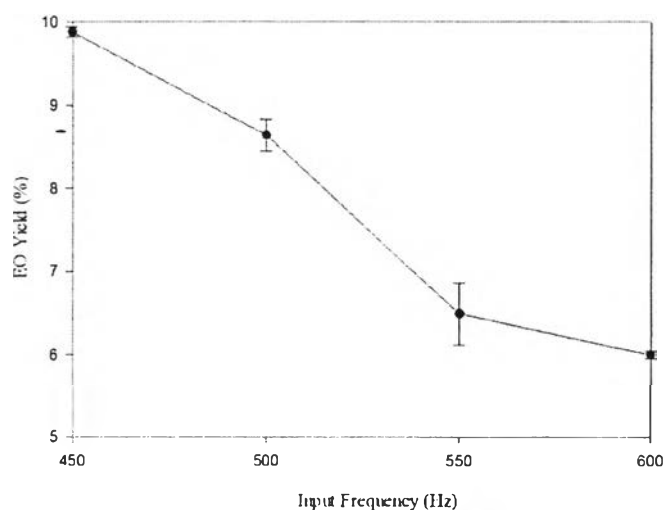

Figure 4.10 EO yield in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of input frequency (voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).

As shown in figure 4.11, the power consumptions required to convert ethylene molecule tended to increase with increasing input frequency until reaching the maximum value at input frequency of 550 Hz. Meanwhile, ethylene oxide power consumption per ethylene oxide molecule produced decreased and reached the minimum at input frequency of 500 Hz, and then adversely increased with further increasing input frequency. Because at 500 Hz input frequency provided the highest ethylene oxide selectivity and the lowest power consumption to produce ethylene oxide, even though the EO yield not as high as when operating at input frequency 450 Hz, operating at low frequency, plasmas have high energy and non-uniform that could destroy the reactor. Hence, an input frequency of 500 Hz was selected to the optimum condition for further studying.
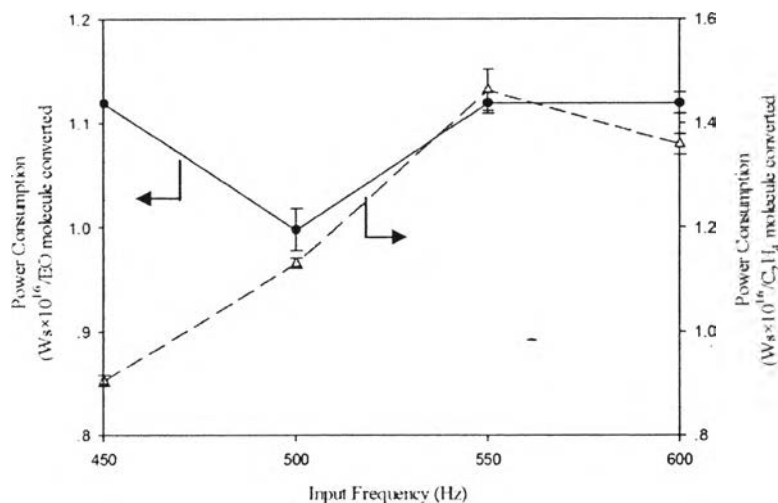
Figure 4.11 EO and C_2H_4 power consumptions in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of input frequency (voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, C_2H_4 feed position fraction of 0.5, and feed flow rate = 50 cm^3/min).

4.2.3 Effect of Total Feed Flow Rate

The feed flow rate plays a significant role on the residence time of gas molecules within the plasma zone, affecting the performance of the plasma system. The experiment was examined by varying total feed flow rate from 30 to 60 cm^3/min. The total feed flow rate 30 cm^3/min was minimum value since at total feed flow rate below this level, the N_2O flow rate cannot be adjusted due to the limitation of mass flow controller. The other operational parameters were fixed at an applied voltage of 19 kV, an input frequency of 500 Hz, a N_2O/C_2H_4 feed molar ratio of 0.17:1, and an C_2H_4 feed position fraction of 0.5.

Figure 4.12 illustrates the effect of total flow rate on the C_2H_4 and N_2O conversions. Both conversion of ethylene and nitrous oxide obviously decreased with increasing the total feed flow rate. Since an increasing in the feed flow rate can cause the residence time in the reaction reduced, resulting in having a shorter contact time of gas molecules to collide with electrons.
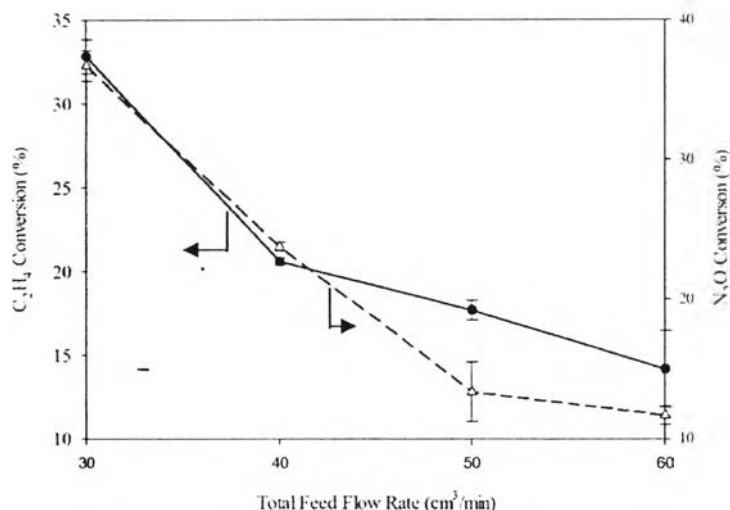
Figure 4.12 C_2H_4 and N_2O conversions in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of total feed flow rate (frequency = 500 Hz, voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, and C_2H_4 feed position fraction of 0.5).

As illustrated in figure 4.13, when increasing feed flow rate over than $50 cm^3/min$ the selectivity of ethylene oxide decreased. This is because at feed flow rate higher than $50 cm^3/min$, the opportunity of collision between electrons/oxygen active species and reactant/intermediate molecules for partial oxidation is reduced. But for other products, C_2H_6, CH_4, and CO selectivities remained almost invariant. For other products, including the selectivities of C_3H_8 and C_2H_2 were found to fluctuate over all total flow rate range. Interestingly, the H_2 The selectivity firstly decreased in the range of 30 – 40 cm^3/min, then tended to increase with further increasing flow rate results display that hydrogenation, cracking, and further second reactions occurred instead of ethylene epoxidation reaction when operating at flow rate higher than $50 cm^3/min$, leading to reduction in ethylene oxide slectivity. By the way, when the collision opportunity was the highest at the lowest total feed flow rate 30 cm^3/min (the longest residence time), resulting in high selectivities of CO and H_2 but low EO and C_2H_2 selectivities. These results consistent with the previous work (Suttikul *et al.* 2012).
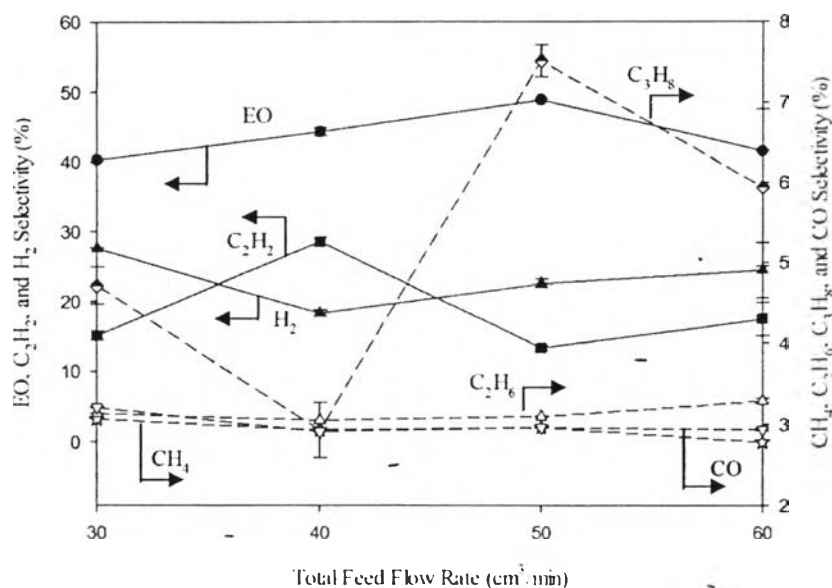
Figure 4.13 Product selectivities in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of total feed flow rate (frequency = 500 Hz, voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, and C_2H_4 feed position fraction of 0.5).

Corresponding to figure 4.12 and 4.13, the ethylene oxide yield rapidly decreased, next slightly increased, and finally extremely decreased because of at the highest total feed rate, the residence time is the shortest, resulting to lowest conversion as mention above.

To choose the optimum condition, there are several effects need to be concerned including EO yield, power consumption, and importantly selectivity value. Here, the highest of EO yield was obtain at feed flow rate 30 cm^3/min but this condition also provided the highest energy consumption per ethylene oxide molecule produced (figure 4.15) and the lowest ethylene oxide selectivity (figure 4.13), so it better to use flow rate at 50cm^3/min because of at this flow rate, EO selectivity was the highest and power consumption was lower.
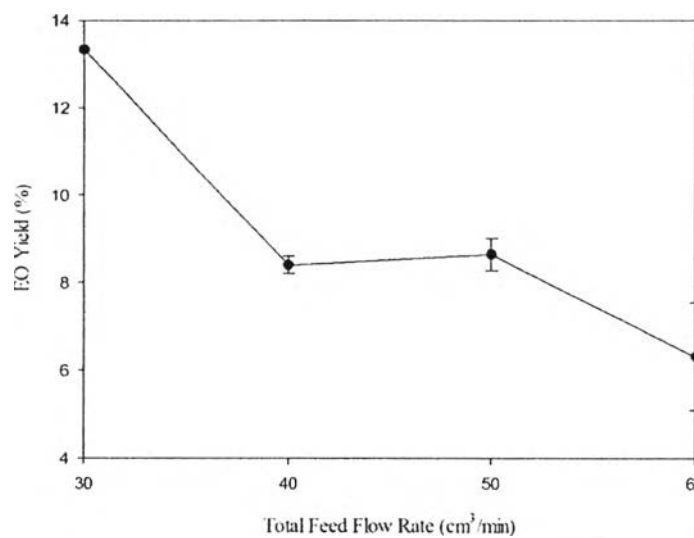
Figure 4.14 EO yield in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of total feed flow rate (frequency = 500 Hz, voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, and C_2H_4 feed position fraction of 0.5).
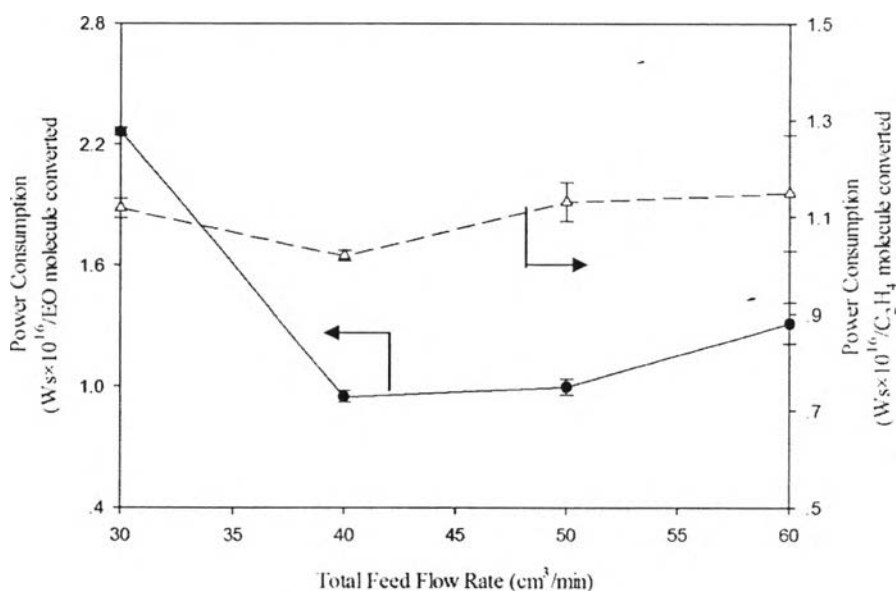

Figure 4.15 EO and C_2H_4 power consumptions in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of total feed flow rate (frequency = 500 Hz, voltage = 19 kV, N_2O/C_2H_4 feed molar ratio = 0.17:1, and C_2H_4 feed position fraction of 0.5).

4.2.4 Effect of Calcination Temperatures

The effect of calcination temperatures on ethylene epoxidation performance was investigated by varying the temperatures from 450 to 650 °C. As shown in the figure 4.16, ethylene oxide selectivity increased with increasing calcination temperature until reaching the maximum of ethylene oxide selectivity of 48.87% at calcinaton temperature of 550°C, and then it turned to decrease with increasing calcinaton temperature over than 550°C. Furthermore, at this calcinaton temperature (550°C), it was also provided the highest of ethylene oxide yield because the largest of crystal size, good particle size distribution, and highly dispersed of Ag catalyst on surface were achieved when used this calcination temperature.
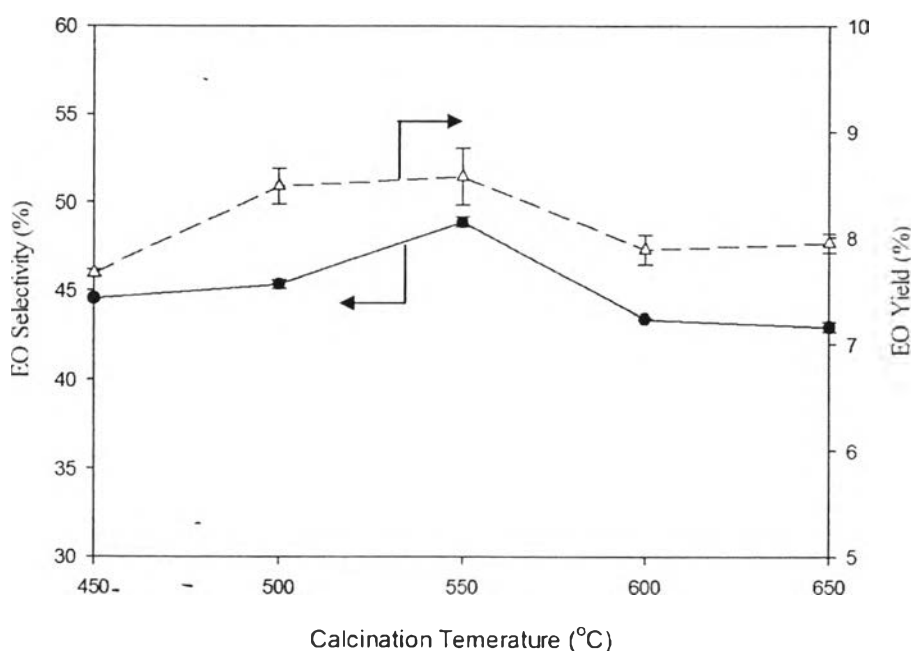

Figure 4.16 C_2H_4O selectivity and yield in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of calcination temperature (voltage = 19 kV, frequency = 500 Hz, a N_2O/C_2H_4 feed molar ratio of 0.17:1, an C_2H_4 feed position fraction of 0.5, and total feed flow rate of 50 cm^3/min).

4.2.5 Effect of Oxygen Sources

Effect of oxygen source on ethylene epoxidation performance was studied by comparing different oxidants (nitrous oxide and oxygen).The oxygen sources were firstly varied oxygen source/C_2H_4feed molar ratio at their own optimum conditions from previous results, after that the ethylene epoxidation performance was compared at their optimum feed molar ratio value. Figure 4.17 shows the effect of a used of molecular oxygen as oxygen source. The result shows that the ethylene oxide selectivity rapidly decreased with increasing O_2/C_2H_4 feed molar ratio and nearly reaching zero at the O_2/C_2H_4 feed molar ratio of 0.5, moreover the selectivity tended to nearly unchanged with further increasing O_2/C_2H_4 feed molar ratio over than 0.5.

The explanation is that at higher O_2/C_2H_4 feed molar ratio the reaction favor to combustion reaction and high amount of coke deposit on catalyst surface, leading to decrease in the ethylene oxide selectivity.

Figure 4.17 EO selectivity in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of an O_2/C_2H_4 feed molar ratio (voltage = 19 kV, frequency = 500 Hz, an C_2H_4 feed position fraction = 0.5, and total feed flow rate = 50 cm^3/min).

As shown in figure 4.18, ethylene oxide selectivity increased to the maximum of 48.87% at N_2O/C_2H_4 feed molar ratio of 0.17:1, after that it adversely tended to decrease with further increasing N_2O/C_2H_4 feed molar ratio since at high N_2O/C_2H_4 feed molar ratio led to the combustion reaction to occur more favorably than partial oxidation.
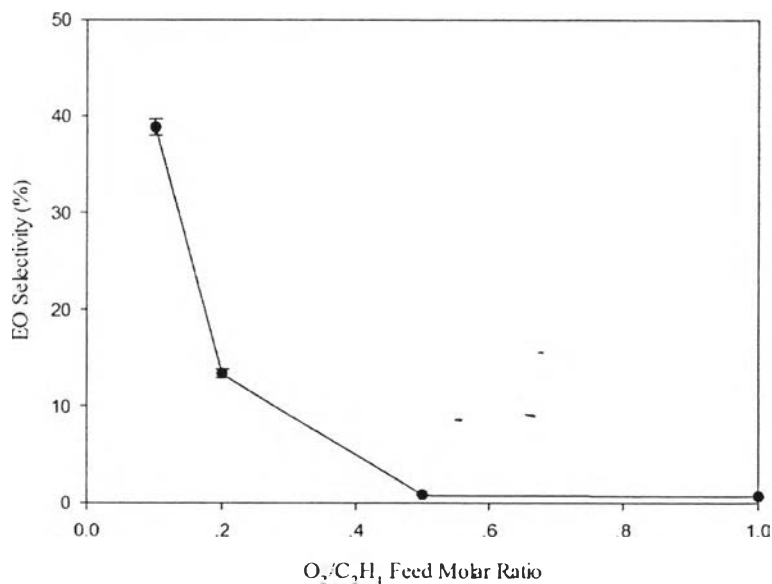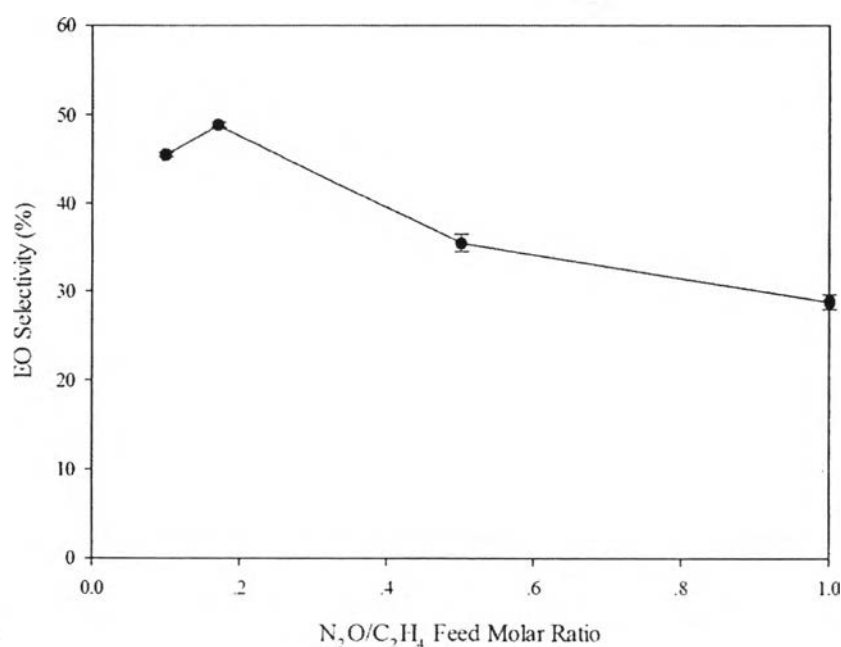

Figure 4.18 EO selectivity in DBD system with 0.1 wt% Ag catalyst coated on upper plate as a function of an N_2O/C_2H_4 feed molar ratio (voltage = 19 kV, frequency = 500 Hz, an C_2H_4 feed position fraction = 0.5, and total feed flow rate = 50 cm^3/min).

4.3 Oxygen Sources Activity Comparison

The comparisons of the ethylene epoxidation performance were summarized in figure 4.19 and table 4.2. The result shows that under their own optimum conditions, under sole plasma system, nitrous oxide exhibited better ethylene oxide selectivity and ethylene oxide yield than oxygen (Dulyalaksananon,

2013). As same as catalytic system, a use of nitrous oxide as oxygen source also provided higher ethylene epoxidation performance in term of ethylene conversion, ethylene oxide selectivity, and ethylene oxide yield than that a used of molecular oxygen. The possible reasons could be explained by the fact that epoxidation reaction of ethylene to ethylene oxide requires one oxygen atomof oxygen but O_2 provide 2 atoms of oxygen which can transfer only one of them to be oxidized, reserving the second atom for next catalytic cycle with another molecule. Moreover, high amount of oxygen atom on surface, the reaction tended to favorably occur the combustion reaction instead, leading to the reduction in ethylene opoxidation performance (Gennady et al., 2009).
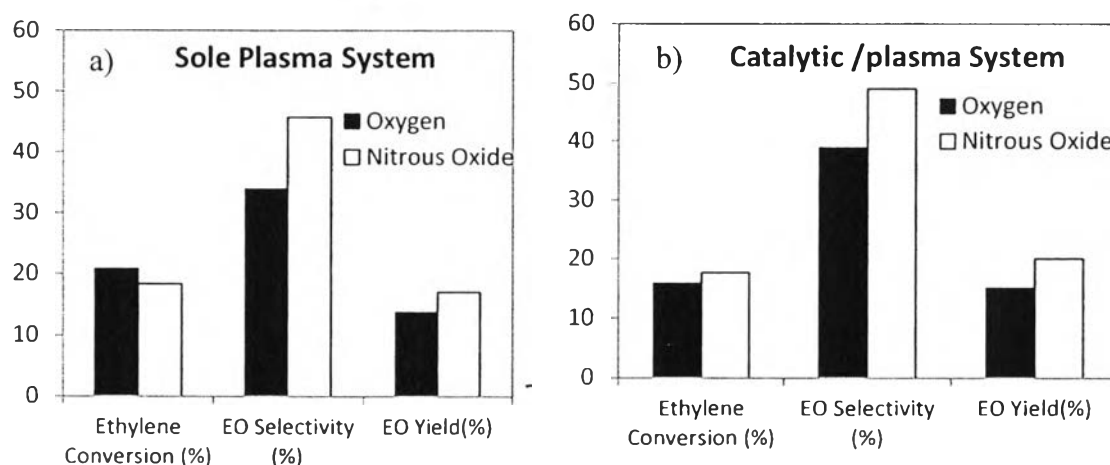

Figure 4.19 Comparison of oxygen sources in term of ethylene conversion ethylene oxide selectivity and yield: (a) sole plasma system (in DBD reactor by using oxygen: frequency = 500 Hz, voltage = 23 kV, feed flow rate = 50 cm^3/min, and a O_2:C_2H_4 ratio 0.2:1; in DBD reactor by using nitrous oxide: frequency = 500 Hz, voltage = 19 kV, feed flow rate = 50 cm^3/min, and a N_2O:C_2H_4 ratio 0.17:1)

(b) catalytic/plasma system (in DBD reactor and 0.1 wt% Ag coated on upper plate by using oxygen : frequency = 500 Hz, voltage = 19 kV, feed flow rate = 50 cm^3/min, and a O_2:C_2H_4 ratio 0.1:1; in DBD reactor by using nitrous oxide: frequency = 500 Hz, voltage = 19 kV, feed flow rate = 50 cm^3/min, and a N_2O:C_2H_4 ratio 0.17:1).

Table 4.2 Comparisons the ethylene epoxidation performance of different oxygen sources in the sole plasma systems and catalytic plasma systems

System	Conversion (%)		EO Selectivity (%)		EO Yield (%)	Power Consumption ($\times 10^{16}$ Ws/Molecule)	
	C_2H_4	O_2	*	**		C_2H_4 Converted	EO Produced
Corona discharge with 12.5 wt% Ag/(α-Al$_2$O$_3$)	27.18	57.62	12.9	16.54	4.5	1.7	12.6
Corona discharge with 0.2 wt%Au-12.5 wt% Ag/(α-Al$_2$O$_3$) (Chvadej*et al.*, 2008)	46.04	65.23	9.39	14.55	6.7	0.62	6.5
Parallel DBD (Sreethawong*et al.*, 2008)	90.95	93.67	6.18	9.7	8.8	0.37	6.07
Cylindrical DBD (Sreethawong *et al.*, 2010)	18.86	91.38	13.5	5.71	1.0	0.75	5.9
Parallel DBD with 20 wt% Ag/SiO$_2$ (Suttikul *et al.*,2011)	7	64.36	30.6	16.81	1.2	4.6	15.26
Cylindrical DBD (Suttikul et al.,2012)	3.68	74.57	203.16	33.85	1.3	3.49	5.21
Corona Discharge (Suttikul*et al.*,2013)	2.25	44.33	78.12	8.42	0.18	4.74	6.07
DBD Jet (Suttikul *et al.*,2013)	49.95	91.23	55.19	85.24	42.57	3.33	6.03
Parallel DBD : sole plama : 10 wt%Ag (Paosombat*et al.*,2012)	19 / 1.6	90 / 85	32 / 72	14.03 / 29.63	2.7 / 0.5	2.1 / 22.9	8 / 16.56

System	Conversion (%)		EO Selectivity (%)		EO Yield (%)	Power Consumption ($\times 10^{16}$ Ws/Molecule)	
	C_2H_4	O_2	*	**		C_2H_4 Converted	EO Produced
Parallel DBD two roughness glass plates : Sole Plasma (Dulyalaksananon, 2013)	14.03	98.36	68.15	24.22	3.4	1.88	2.76
Present Work with 0.1wt% Ag							
N_2O	17.68	13.36	113.3	48.87	8.6	0.42	1
O_2	7.48	97.92	136.2	42.34	3.16	1.86	1.37
Present Work Sole Plasma							
N_2O	18.37	4.15	92.65	45.75	8.4	1.09	1.17
O_2	15.86	99.63	95.14	38.82	6.2	0.43	1.28

* Ethylene oxide selectivity base on ethylene converted.

** Ethylene oxide selectivity base on total product produced