



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of O_2/C_2H_4 Molar Ratio

The effect of feed molar ratio was initially studied in order to obtain the most suitable feed gas composition for ethylene epoxidation reaction under the low-temperature cylindrical DBD system. In this study, the effect of O_2/C_2H_4 molar ratio was investigated in the range of 0.2:1 to 1:1, while an applied voltage of 19 kV, an input frequency of 500 Hz, and a residence time of 25.12 s were applied during the reaction. An O_2/C_2H_4 molar ratio lower than 0.2:1 (1:5) could not be studied due to the limitation of the O_2 mass flow controller.

4.1.1 Effect of O_2/C_2H_4 Molar Ratio on Ethylene and Oxygen Conversions, and Ethylene Oxide Yield

The effect of O_2/C_2H_4 molar ratio on the C_2H_4 and O_2 conversions and the C_2H_4O yield is shown in Figure 4.1. The increase in the O_2/C_2H_4 molar ratio slightly affected to the C_2H_4 conversion, but it mainly affected the O_2 conversion and the C_2H_4O yield, especially at the O_2/C_2H_4 molar ratio above 0.25:1 (1:4). The O_2 conversion tended to increase with increasing O_2/C_2H_4 molar ratio up to 0.75:1 (1:1.33) but then decreased with further increasing O_2/C_2H_4 molar ratio, whereas the C_2H_4O yield increased to reach a maximum at an O_2/C_2H_4 molar ratio of 0.25:1 (1:4), but dramatically decreased with further increasing O_2/C_2H_4 molar ratio. It can be observed that at any given O_2/C_2H_4 molar ratio, the O_2 conversion was much higher than the C_2H_4 conversion. This can be explained in that the bond dissociation energy of C_2H_4 (16.7 eV) is much higher than that of O_2 (12.2 eV), consequently causing O_2 molecules to be converted more easily than C_2H_4 molecules. This implies that ethylene epoxidation in the DBD system is favorable under O_2 -lean condition. The optimum O_2/C_2H_4 molar ratio was therefore considered to be 0.25:1 (1:4) because it provided the highest C_2H_4O yield.

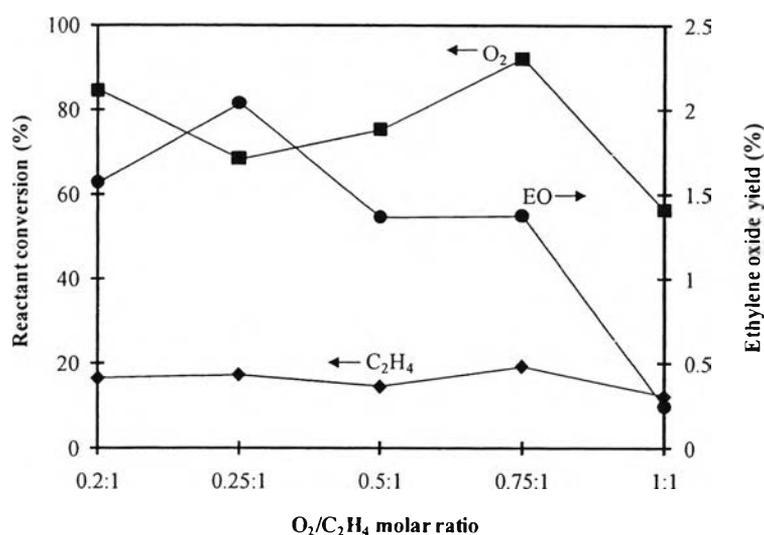


Figure 4.1 Conversions of ethylene and oxygen and yield of ethylene oxide as a function of O₂/C₂H₄ molar ratio by using the cylindrical DBD reactor (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = 50 cm³/min; residence time = 25.12 s; and electrode gap distance = 5 mm).

Figure 4.2 illustrates the comparison of the C₂H₄ and O₂ conversions between the parallel DBD and the cylindrical DBD reactors as a function of O₂/C₂H₄ molar ratio. It can be seen that both C₂H₄ and O₂ conversions for the cylindrical DBD system were somewhat lower than those for the parallel DBD system; however, the C₂H₄ and O₂ conversions are not the only indicators used to verify whether which system provided higher epoxidation performance. The desired product (C₂H₄O) selectivity and yield of each system must be simultaneously considered for the system performance evaluation.

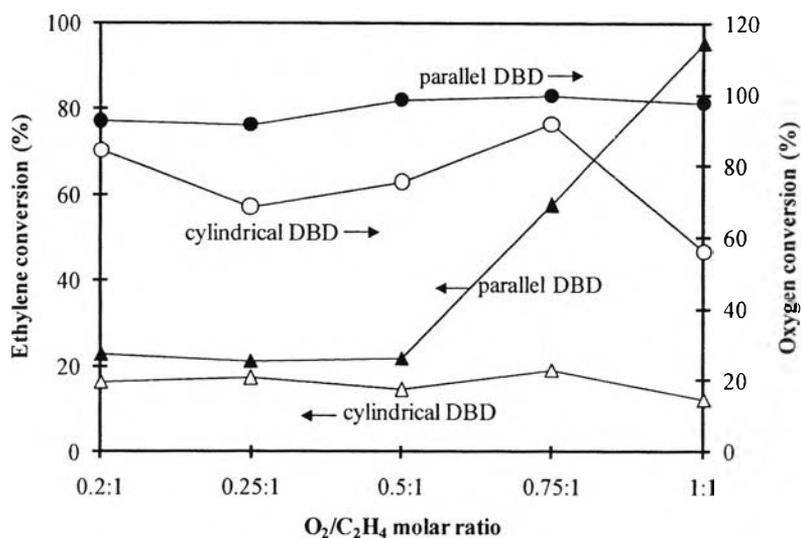


Figure 4.2 Comparison of ethylene and oxygen conversions between the parallel DBD and the cylindrical DBD reactors as a function of O₂/C₂H₄ molar ratio (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = 50 cm³/min; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

The comparison of C₂H₄O selectivity and C₂H₄O yield between the parallel DBD and the cylindrical DBD reactors as a function of O₂/C₂H₄ molar ratio is shown in Figure 4.3. The results show that the C₂H₄O selectivity and C₂H₄O yield of both reactors reached a maximum at an O₂/C₂H₄ molar ratio of 0.25:1, and they rapidly decreased with further increasing O₂/C₂H₄ molar ratio higher than 0.25:1. Interestingly, the cylindrical DBD reactor provided higher C₂H₄O selectivity than the parallel DBD reactor; however, the C₂H₄O yield was quite comparable between both the DBD reactors. The operational parameters need to be further adjusted in order to verify the more suitable DBD reactor for ethylene epoxidation, using the obtained optimum O₂/C₂H₄ molar ratio of 0.25:1.

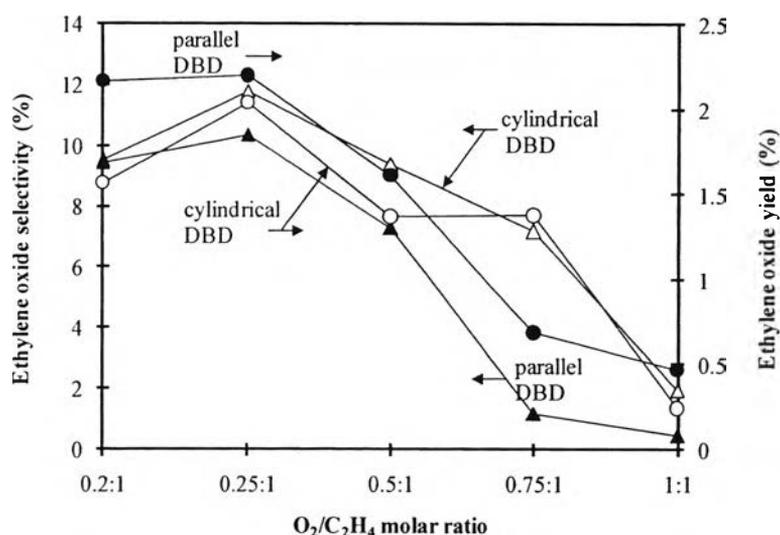


Figure 4.3 Comparison of ethylene oxide selectivity and ethylene oxide yield between the parallel DBD and the cylindrical DBD reactors as a function of O₂/C₂H₄ molar ratio (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = 50 cm³/min; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.1.2 Effect of O₂/C₂H₄ Molar Ratio on By-Product Selectivities

Figure 4.4 illustrates the by-product selectivities at various O₂/C₂H₄ molar ratios. For the cylindrical DBD system operated in the O₂/C₂H₄ molar ratio range of 0.2:1 to 0.75:1, the selectivities for CO, H₂, and C₂H₂ tended to decrease, while the selectivities for CO₂ and CH₄ remain almost unchanged, but the selectivities for C₂H₆, and C₃H₈ decreased with increasing O₂/C₂H₄ molar ratio. Furthermore, the CO, H₂, CH₄, and C₃H₈ selectivities sharply increased with further increasing O₂/C₂H₄ molar ratio up to 1:1, whereas the others remained almost unchanged. Under the studied conditions, the main by-products were CO, H₂, and C₂H₂ with less significant amounts of CO₂ and CH₄. The higher molecular weight hydrocarbons, i.e. C₂H₆ or C₃H₈, were found in a very small fraction. The decrease in the selectivities for these hydrocarbons and H₂ at higher O₂/C₂H₄ molar ratio clearly reveals that the oxidative dehydrogenation and coupling reactions favorably occurred under O₂-lean conditions.

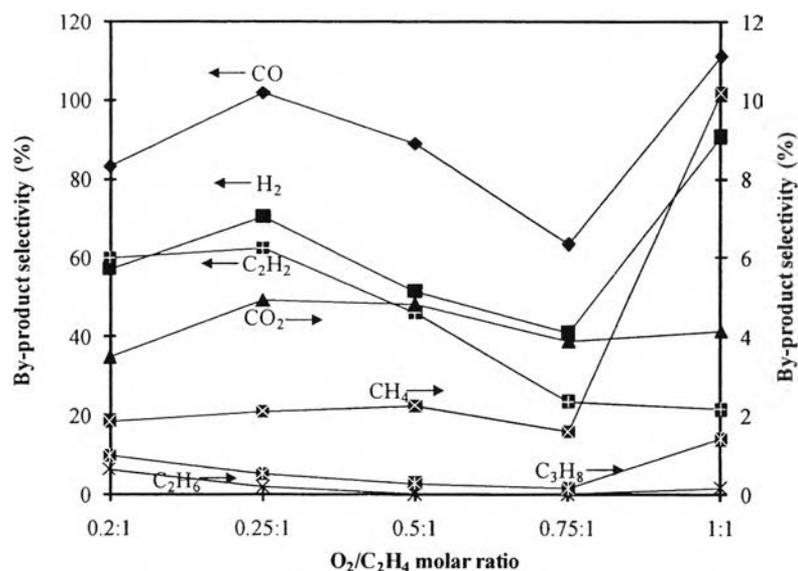


Figure 4.4 By-product selectivities as a function of O₂/C₂H₄ molar ratio by using the cylindrical DBD reactor (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = 50 cm³/min; residence time = 25.12 s; and electrode gap distance = 5 mm).

The H₂ production in terms of H₂ selectivity and H₂ yield in the parallel DBD and the cylindrical DBD reactors is illustrated in Figure 4.5. The results show that the H₂ production in both reactors tended to decrease with increasing O₂/C₂H₄ molar ratio; however, the parallel DBD reactor generated higher amounts of H₂ than the cylindrical DBD reactor. This implies that the parallel DBD reactor is more favorable for the dehydrogenation reaction in the plasma zone. Therefore, it may suggest that the cylindrical DBD reactor was suitable for the C₂H₄O production, although it gave higher amounts of CO and C₂H₂, but at the same time, lower fraction of CO₂, H₂, and light hydrocarbons, i.e. CH₄, C₂H₆, and C₃H₈, than the parallel DBD reactor, as shown in Figure 4.6. Moreover, the cylindrical DBD reactor provided the highest C₂H₄O selectivity, as aforementioned.

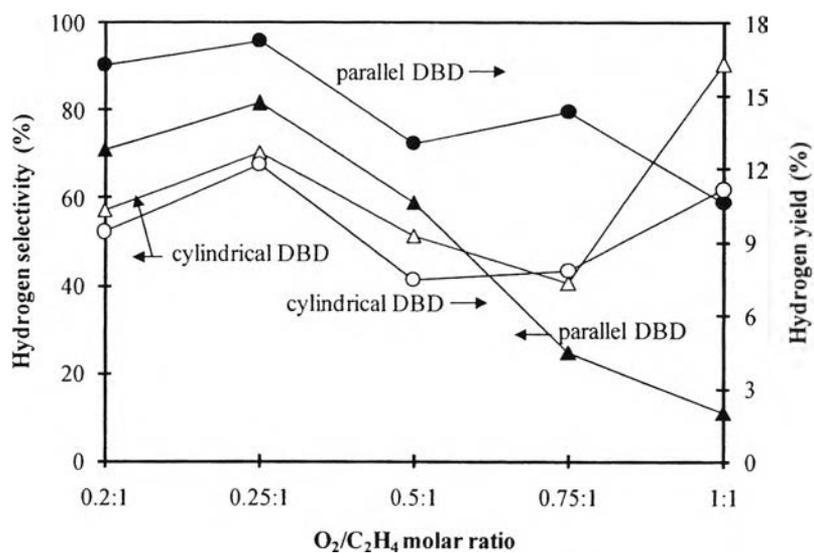


Figure 4.5 Comparison of hydrogen selectivity and hydrogen yield between the parallel DBD and the cylindrical DBD reactors as a function of O₂/C₂H₄ molar ratio (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = 50 cm³/min; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

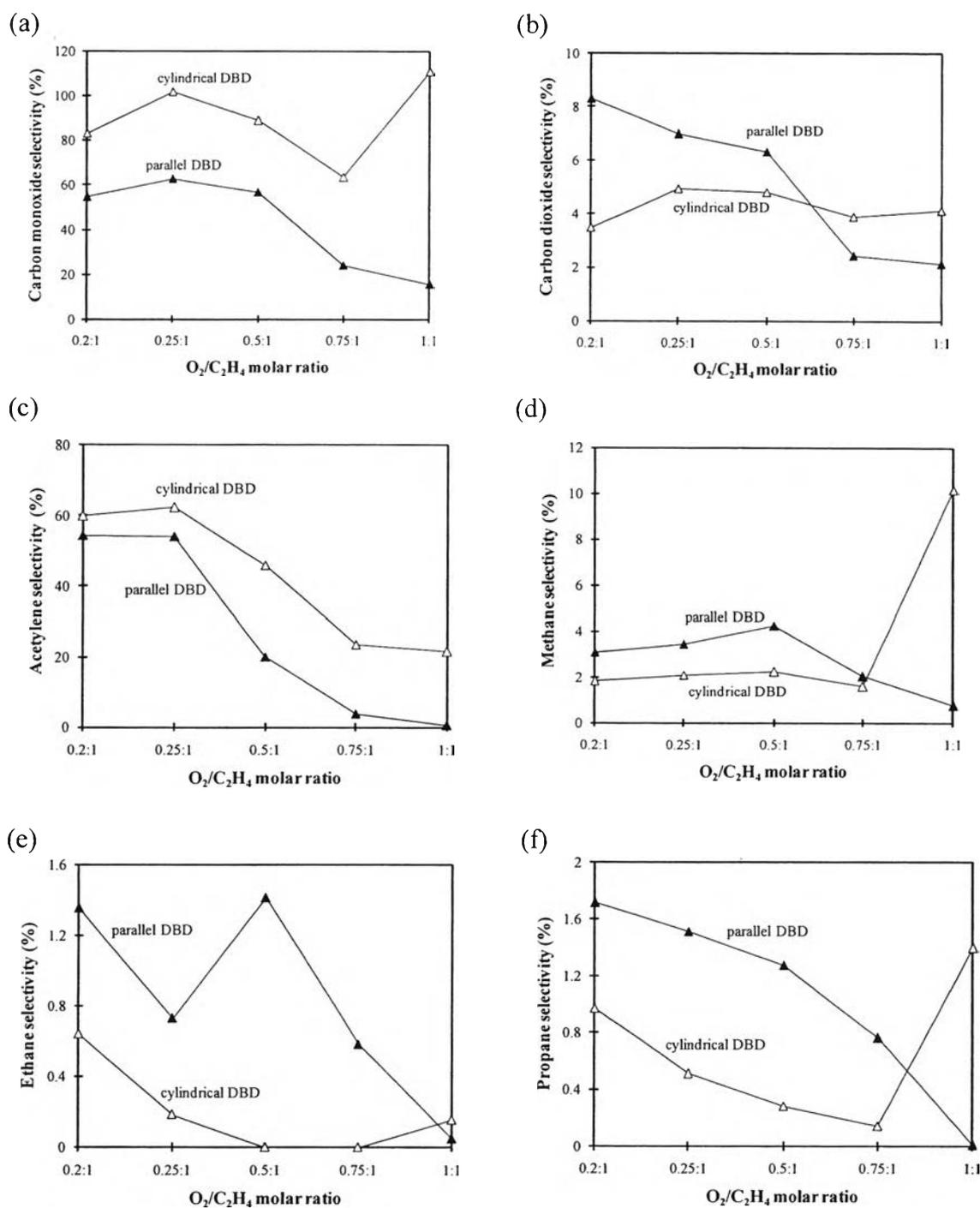


Figure 4.6 Comparison of by-product selectivities between the parallel DBD and the cylindrical DBD reactors as a function of O_2/C_2H_4 molar ratio: (a) carbon monoxide, (b) carbon dioxide, (c) acetylene, (d) methane, (e) ethane, and (f) propane (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.1.3 Effect of O_2/C_2H_4 Molar Ratios on Specific Power Consumptions

Figure 4.7 shows the power consumptions used to convert C_2H_4 molecule and to produce C_2H_4O molecule at different O_2/C_2H_4 molar ratios. The power consumption per molecule of C_2H_4 converted gradually increased with increasing O_2/C_2H_4 molar ratio up to 1:1. However, there was a more significant increase in the power consumption per molecule of C_2H_4O produced with increasing O_2/C_2H_4 molar ratio, especially at the molar ratio higher than 0.75:1. It can also be noticed that since the power consumption per molecule of C_2H_4O produced was approximately two orders of magnitude higher than that per molecule of C_2H_4 converted, the former must be taken into much more consideration. Hence, an O_2/C_2H_4 molar ratio of 0.25:1 was therefore selected for further experiments because it provided the highest selectivity and yield for C_2H_4O and the comparatively low power consumption per molecule of C_2H_4O produced.

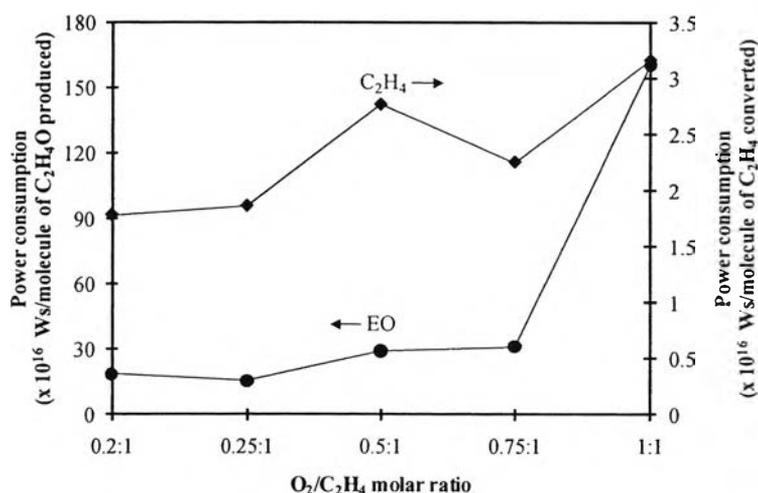


Figure 4.7 Comparison of specific power consumptions for different O_2/C_2H_4 molar ratios by using the cylindrical DBD reactor (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

Figure 4.8 shows the comparison of the specific power consumptions between the parallel DBD and the cylindrical DBD reactors at different O_2/C_2H_4 molar ratios. Although the power consumption per molecule of C_2H_4 converted for the cylindrical DBD reactor was higher than that for the parallel DBD reactor, the power consumption per molecule of C_2H_4O produced for both the DBD reactors was quite comparable in low O_2/C_2H_4 molar ratio range, especially the O_2/C_2H_4 molar ratio of 0.25:1 exhibiting the lowest power consumption per molecule of C_2H_4O produced for the cylindrical DBD reactor. Therefore, the O_2/C_2H_4 molar ratio of 0.25:1 was selected for further experiments.

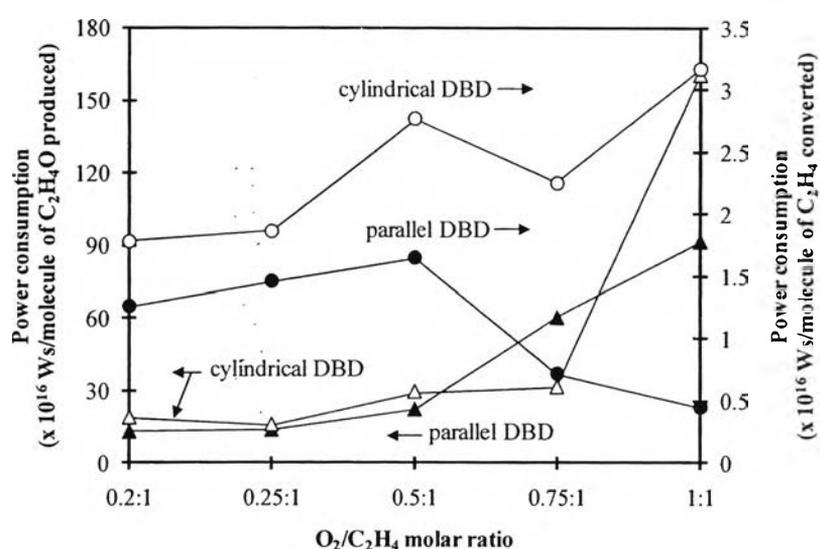


Figure 4.8 Comparison of specific power consumptions between the parallel DBD and the cylindrical DBD reactors as a function of O_2/C_2H_4 molar ratio (applied voltage = 19 kV; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.2 Effect of Applied Voltage

Under the studied conditions, the break-down voltage or the lowest voltage (onset voltage) to generate plasma was found to be about 13 kV for the cylindrical DBD system, and the system could not be operated at the applied voltage higher than

19 kV since the generated plasma was found to become single discharge stream with very high strength, and it could destroy the dielectric glass plate. Therefore, the reaction experiments were investigated in the applied voltage range of 13 to 19 kV. For a comparison, the parallel DBD reactor was also operated under different applied voltages in the range of 15 to 21 kV, with the same reasons used for selecting the applied voltage range.

4.2.1 Effect of Applied Voltage on Ethylene and Oxygen Conversions, and Ethylene Oxide Yield

The effect of applied voltage on the C_2H_4 and O_2 conversions and the C_2H_4O yield is illustrated in Figure 4.9. The C_2H_4 conversion remained almost unchanged over the entire applied voltage range, but the O_2 conversion initially increased with increasing applied voltage to 14 kV, remained almost unchanged when the applied voltage was further increased up to 18 kV, and after that decreased with further increasing applied voltage to 19 kV. Meanwhile, the C_2H_4O yield tended to considerably increase with increasing applied voltage until reaching a maximum at 15 kV, and the C_2H_4O yield tended to decrease with further increasing applied voltage higher than 15 kV. The explanation of more rapid increment in the C_2H_4O yield is that a higher voltage results in a higher current (stronger field strength), as shown in Figure 4.10, leading to more available electrons to increase an opportunity for collision with oxygen. However, at applied voltage higher than 15 kV, the higher generated current and the corresponding higher number of active oxygen species may undesirably lead to higher probability of further oxidation to form carbon monoxide, as shown later. This could possibly result in less C_2H_4O yield at too high applied voltage. The applied voltage of 15 kV might be sufficient for the desired product formation by using the cylindrical DBD reactor. Therefore, the applied voltage of 15 kV could be considered as the optimum point for the cylindrical DBD system since the highest C_2H_4O yield was achieved.

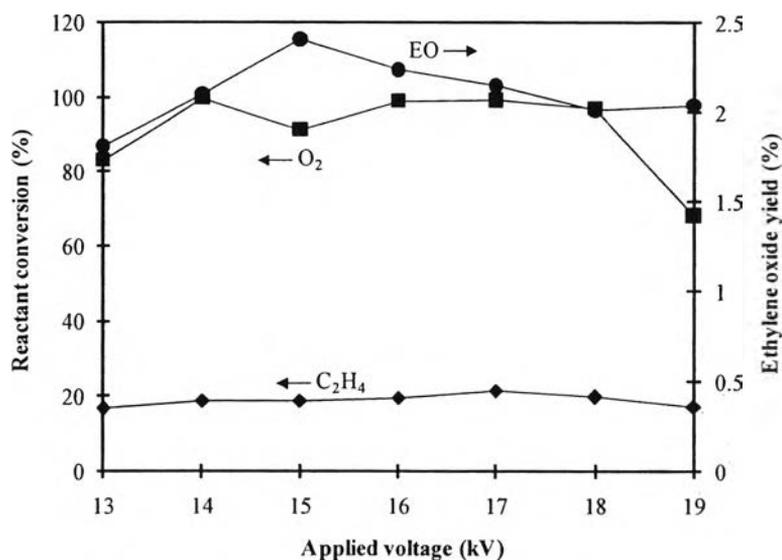


Figure 4.9 Conversions of ethylene and oxygen and yield of ethylene oxide as a function of applied voltage by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

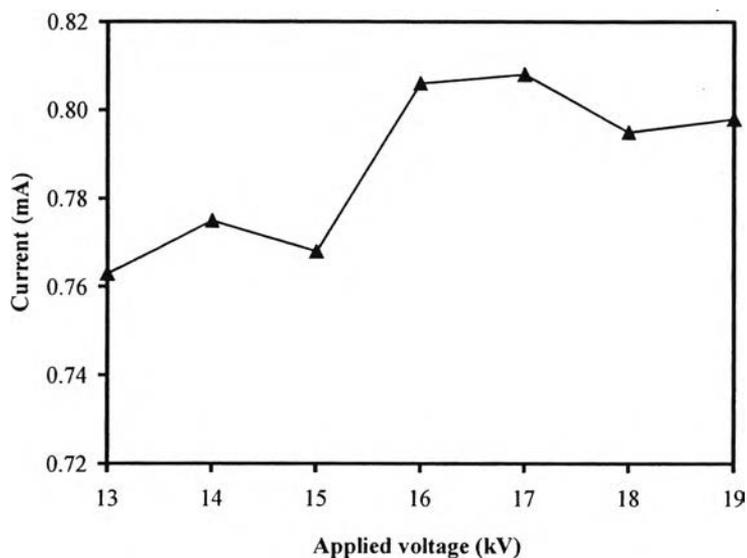


Figure 4.10 Effect of applied voltage on generated current by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

The C_2H_4 and O_2 conversions for both the cylindrical and the parallel DBD reactors are comparatively shown in Figure 4.11. The results show that the cylindrical DBD reactor provided higher O_2 conversion than the parallel DBD reactor, while the C_2H_4 conversion for both the DBD reactors was not significantly different.

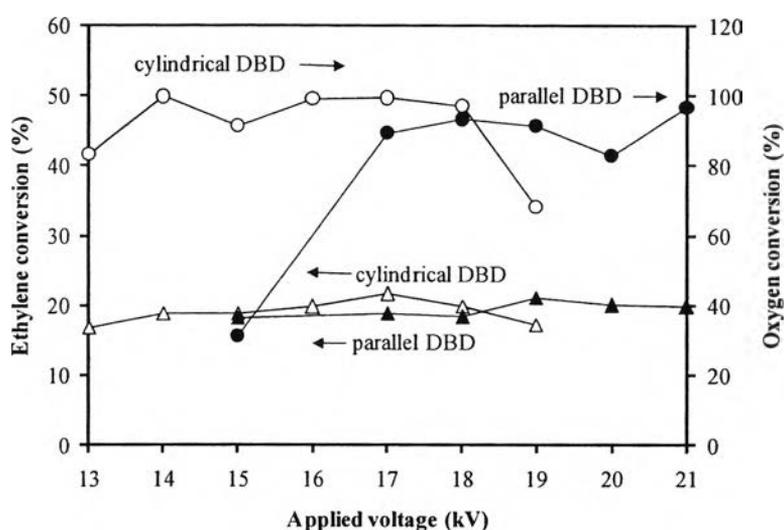


Figure 4.11 Comparison of ethylene and oxygen conversions between the parallel DBD and the cylindrical DBD reactors as a function of applied voltage (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

The C_2H_4O selectivity and the C_2H_4O yield for both the DBD reactors are also comparatively shown in Figure 4.12. The C_2H_4O yield of both the DBD reactors was almost the same in the high applied voltage range, but in the low applied voltage range, the cylindrical DBD reactor tended to provide higher C_2H_4O yield than the parallel DBD reactor, which was in the same manner as the C_2H_4O selectivity. It could be seen that the C_2H_4O yield for both the DBD reactors gradually increased until reaching a maximum and then decreased. The C_2H_4O yield for the cylindrical DBD reactor reached a maximum at 15 kV, while the maximum C_2H_4O yield for the parallel DBD reactor was observed at 19 kV. Clearly, the maximum

C_2H_4O yield for the cylindrical DBD reactor at 15 kV was higher than that for the parallel DBD reactor at 19 kV. It can be possibly believed that the geometry of the cylindrical DBD reactor with lower electrode edge length-to-reaction volume ratio might generate more uniform microdischarges over the whole concentric electrode surfaces than the parallel DBD reactor in low applied voltage range. Hence, the O_2 conversion in the case of the cylindrical DBD reactor was higher in such a range (Figure 4.11), leading to the higher C_2H_4O selectivity and C_2H_4O yield, as illustrated in Figure 4.12. Therefore, the cylindrical DBD reactor operated at an applied voltage of 15 kV was employed for further experiments.

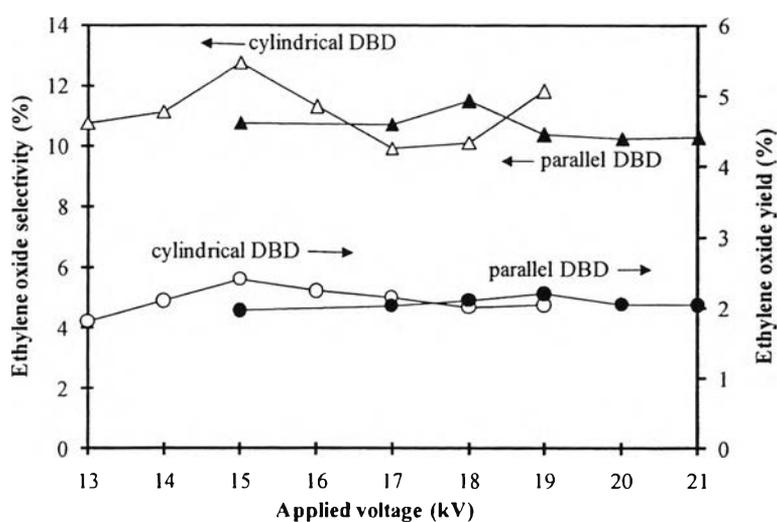


Figure 4.12 Comparison of ethylene oxide selectivity and ethylene oxide yield between the parallel DBD and the cylindrical DBD reactors as a function of applied voltage (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.2.2 Effect of Applied Voltage on By-Product Selectivities

The effect of applied voltage on the by-product selectivities is shown in Figure 4.13. The CO_2 selectivity tended to decrease with increasing applied voltage, but the CO selectivity tended to adversely increase. Interestingly, the selectivities for the others became insignificantly changed for the cylindrical DBD

reactor. It was observed that the selectivities for CO and CO₂ were in the opposite trend. When increasing applied voltage, the selectivity for CO was gradually increased possibly because the partial oxidation is more preferable to occur than the complete oxidation, so CO was not further oxidized to form CO₂, resulting in lowering the CO₂ selectivity at high applied voltage.

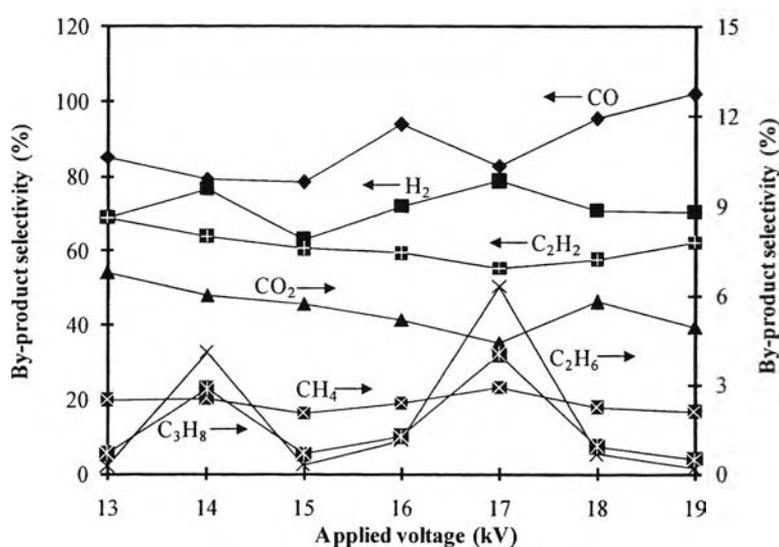


Figure 4.13 By-product selectivities as a function of applied voltage by using the cylindrical DBD reactor (molar ratio of O₂/C₂H₄ = 0.25:1; input frequency = 500 Hz; feed flow rate = 50 cm³/min; residence time = 25.12 s; and electrode gap distance = 5 mm).

Figures 4.14 and 4.15 comparatively illustrate the by-product selectivities of the parallel DBD and the cylindrical DBD reactors as a function of the applied voltage. The H₂ production of the cylindrical DBD reactor was relatively similar to that for the parallel DBD reactor, where the insignificant difference was also observed for the C₂H₂ selectivity. The selectivities for CO₂ and CH₄ of the cylindrical DBD reactor were found to be higher than these of the parallel DBD system, whereas the opposite trends were found for the selectivities for CO, C₂H₆, and C₃H₈. This might be because the partial oxidation in the cylindrical DBD reactor was more favorable to take place than the complete oxidation, which favorably occurred in the parallel DBD reactor. Moreover, the cylindrical DBD reactor seemed

to provide higher tendency for the coupling reaction to form higher hydrocarbons, i.e. C_2H_6 and C_3H_8 , whereas the parallel DBD reactor gave higher cracking possibility to form lower hydrocarbon, i.e. CH_4 . However, tendency for the dehydrogenation reaction to form H_2 and C_2H_2 for both the DBD reactors was not significantly different.

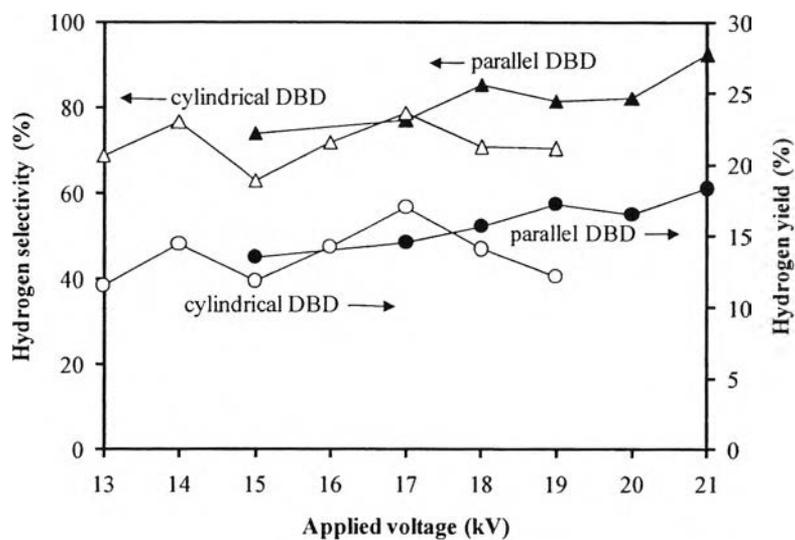


Figure 4.14 Comparison of hydrogen selectivity and hydrogen yield between the parallel DBD and the cylindrical DBD reactors as a function of applied voltage (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = 50 cm^3/min ; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

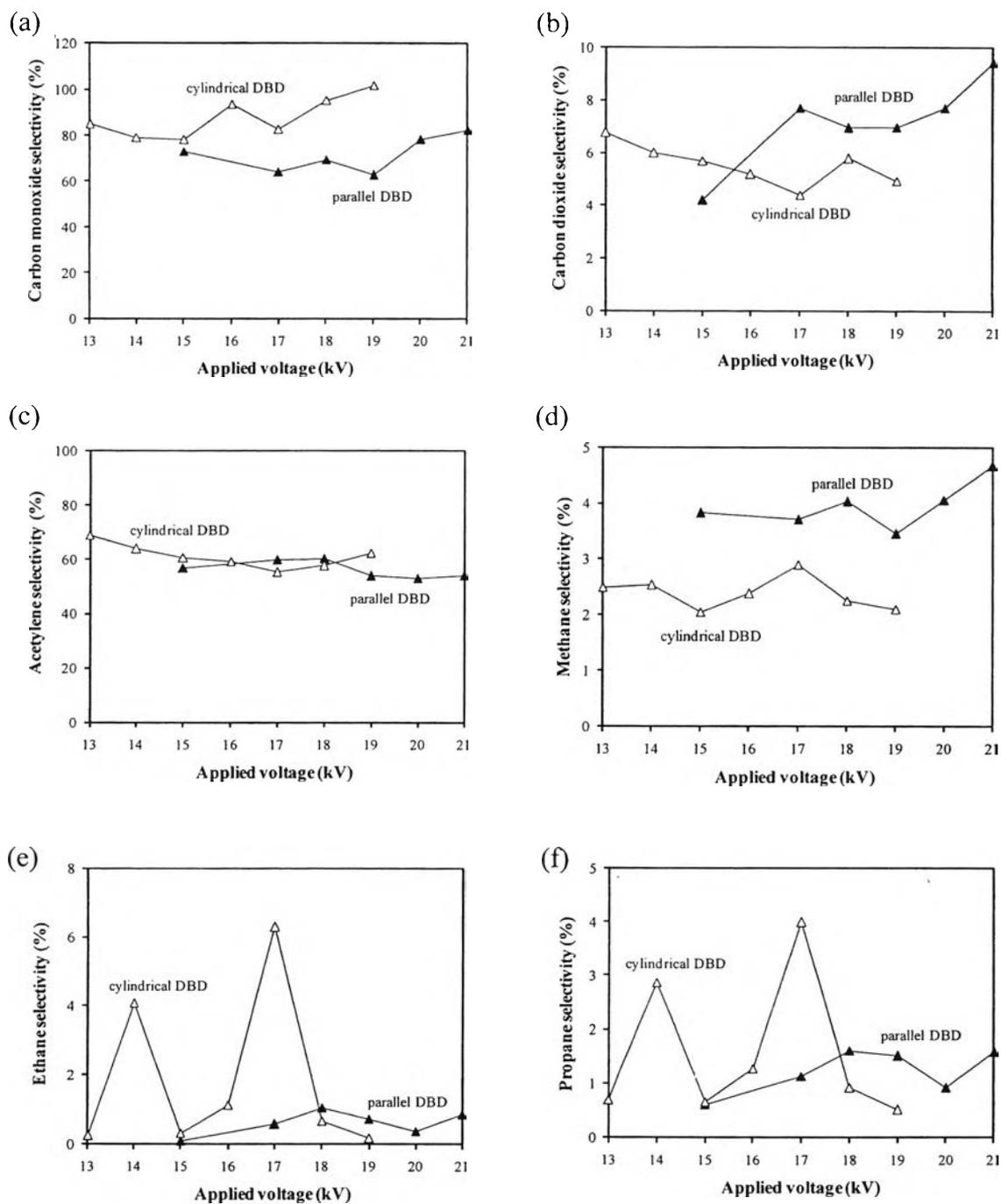


Figure 4.15 Comparison of by-product selectivity between the parallel DBD and the cylindrical DBD reactors as a function of applied voltage: (a) carbon monoxide, (b) carbon dioxide, (c) acetylene, (d) methane, (e) ethane, and (f) propane (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.2.3 Effect of Applied Voltages on Specific Power Consumptions

Figure 4.16 shows the effect of applied voltage on the power consumptions. With increasing applied voltage, the power consumption per molecule of converted C_2H_4 remained almost unchanged, whereas the power consumption per molecule of produced C_2H_4O dramatically decreased until reaching a minimum at an applied voltage of 15 kV and then increased with further increasing applied voltage. From the results, the applied voltage of 15 kV was selected to be the optimum value for the cylindrical DBD reactor because this applied voltage provided comparatively high conversions of C_2H_4 and O_2 , and the highest selectivity and yield for C_2H_4O , as well as the lowest power consumption per C_2H_4O molecule produced.

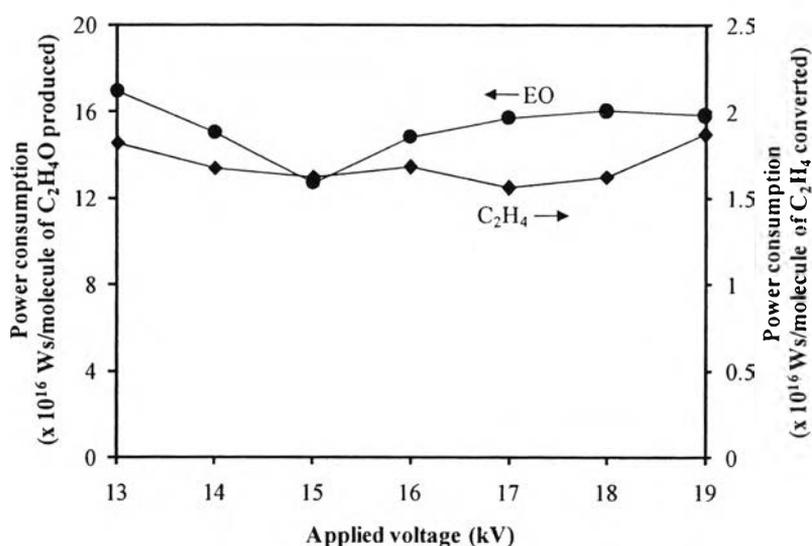


Figure 4.16 Comparison of specific power consumptions for different applied voltages by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

Figure 4.17 illustrates the comparison of power consumptions per C_2H_4 molecule converted and power consumptions per C_2H_4O molecule produced between the parallel DBD and the cylindrical DBD reactors. From the results, the power consumption per C_2H_4 molecule converted of both the DBD reactors was not largely different, while the power consumption per C_2H_4O molecule produced of

both the DBD reactors had a minimum point. The minimum power consumption per C_2H_4O molecule produced of the cylindrical DBD reactor occurred at 15 kV, as above mentioned, but that of the parallel DBD reactor occurred at 19 kV. However, such the power consumption at the minimum point of the cylindrical DBD reactor was lower than that of the parallel DBD reactor. This is another advantage of the cylindrical DBD reactor as compared to the parallel DBD reactor if the optimum operating conditions were obtained.

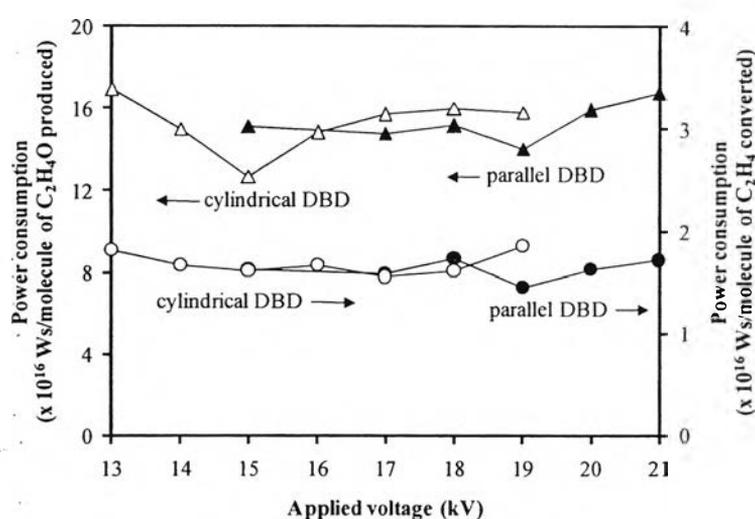


Figure 4.17 Comparison of specific power consumptions between the parallel DBD and the cylindrical DBD reactors as a function of applied voltage (molar ratio of $O_2/C_2H_4 = 0.25:1$; input frequency = 500 Hz; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.3 Effect of Input Frequency

Input frequency is one of the most important parameters in plasma reactor operation, significantly affecting the field strength in the plasma zone. The studied cylindrical DBD system was operated in the frequency range of 400-800 Hz. At a frequency lower than 400 Hz, the plasma distribution with high strength tended to become single stream plasma discharge on the electrode surface, and it tended to

destroy the dielectric glass plate, whereas the plasma could not exist at a frequency higher than 800 Hz.

4.3.1 Effect of Input Frequency on Ethylene and Oxygen Conversions and Ethylene Oxide Yield

The effect of input frequency on the C_2H_4 and O_2 conversions and yield of C_2H_4O is illustrated in Figure 4.18. When increasing input frequency in the range of 500-800 Hz, the O_2 conversion and the C_2H_4O yield dramatically decreased. The explanation is that a higher frequency results in a lower current that corresponds to the reduction of the number of electrons generated (weaker field strength), as shown in Figure 4.19. It therefore caused the decrease in amount of active species for further reactions, resulting in the decrease in the O_2 conversion and subsequently leading to the lower yield of C_2H_4O ; however, the C_2H_4 conversion only slightly decrease in this frequency range. Moreover, the current tended to decrease with decreasing frequency from 500 to 400 Hz since the uniform discharge distribution over the electrode surface did not occur, leading to the reduction of conversion and yield in this frequency range. Hence, the C_2H_4O yield was found to increase with increasing input frequency until reaching an input frequency of 500 Hz probably due to the dramatic increase in O_2 conversion.

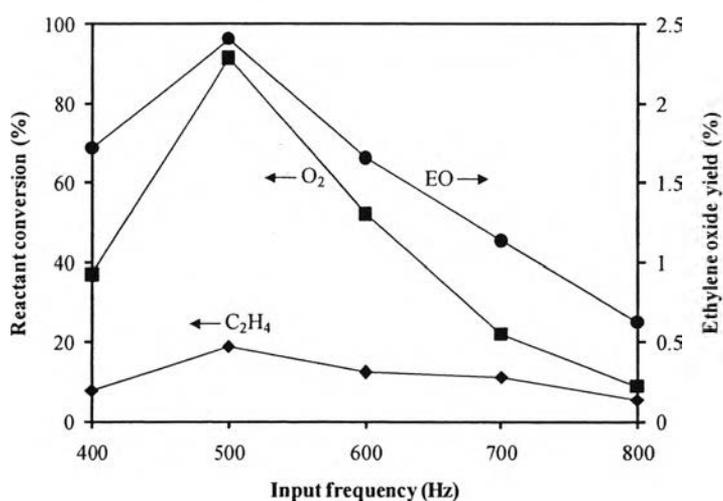


Figure 4.18 Conversions of ethylene and oxygen and yield of ethylene oxide as a function of input frequency by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 15 kV; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

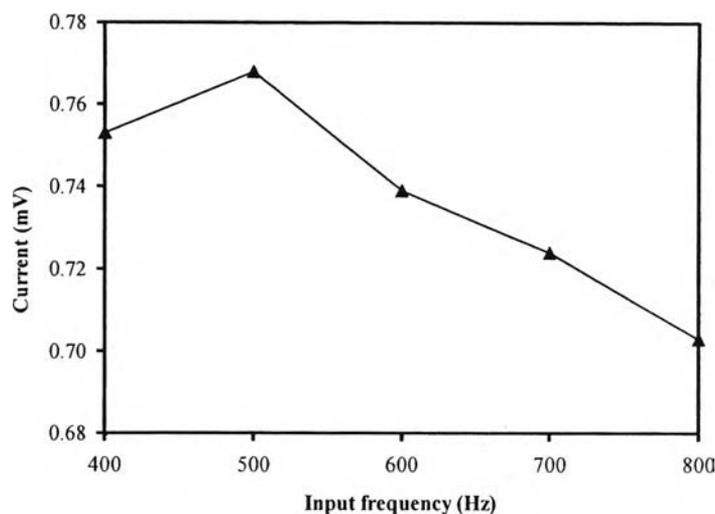


Figure 4.19 Effect of input frequency on generated current by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 15 kV; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

The effect of input frequency on the C_2H_4 and O_2 conversions between the parallel DBD and the cylindrical DBD reactors is comparatively shown in Figure 4.20. The results show that the highest C_2H_4 conversion of both systems was found at an input frequency of 500 Hz, and the O_2 conversion tended to linearly decrease when increasing input frequency, as aforementioned. The C_2H_4O selectivity and C_2H_4O yield between the two DBD systems are comparatively shown in Figure 4.21. The C_2H_4O selectivity of the cylindrical DBD reactor tended to be higher than that of the parallel DBD reactor in low input frequency range because the cylindrical DBD reactor probably has the electrode geometry, by which the microdischarges can occur in more uniform manner in all directions, leading to the highest C_2H_4O yield at an input frequency of 500 Hz. Therefore, the input frequency of 500 Hz was suitable for both types of DBD reactor.

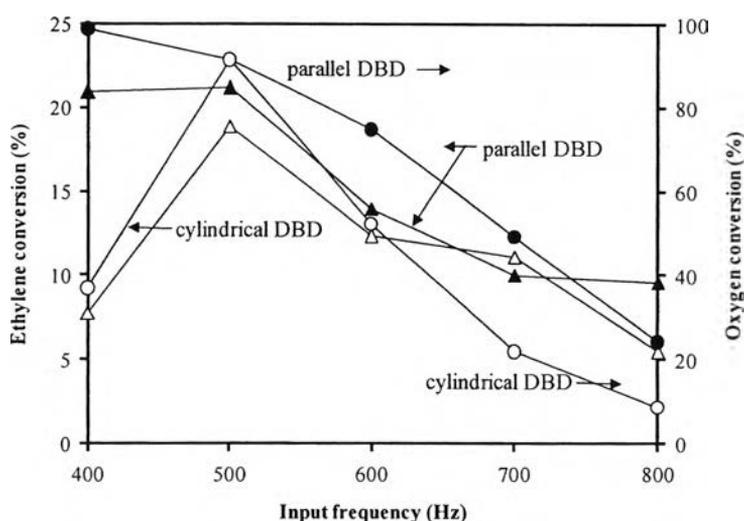


Figure 4.20 Comparison of ethylene and oxygen conversions between the parallel DBD and the cylindrical DBD reactors as a function of input frequency (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), 15 kV (cylindrical DBD); feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

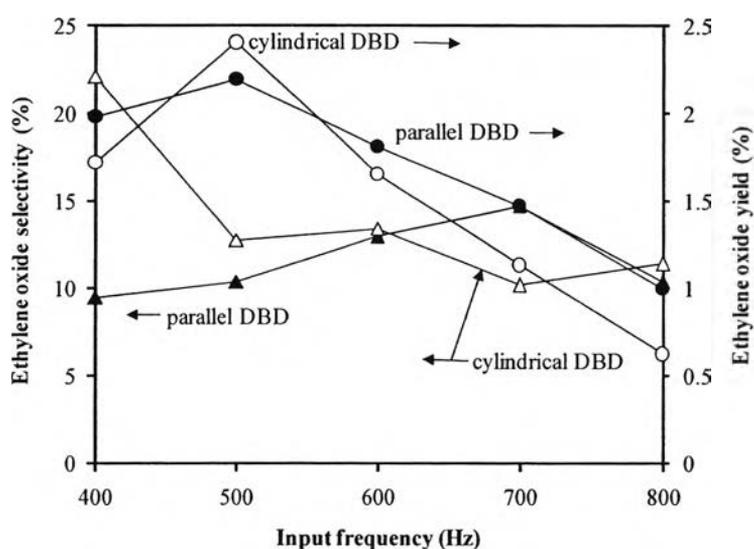


Figure 4.21 Comparison of ethylene oxide selectivity and ethylene oxide yield between the parallel DBD and the cylindrical DBD reactors as a function of input frequency (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), 15 kV (cylindrical DBD); feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.3.2 Effect of Input Frequency on By-Product Selectivities

The effect of input frequency on the by-product selectivities of the cylindrical DBD reactor is shown in Figure 4.22. In the input frequency range of 400-500 Hz, the selectivities for all by-products, except CO_2 , tended to decrease possibly due to the decrease in the generated current, leading to the decrease in the amount of active O_2 species; however, the generated active species had a high tendency to induce the complete oxidation, as observed by the increase in the CO_2 selectivity. For the input frequency higher than 500 Hz, the selectivities for all by-products decreased along with the decrease in the current, which could be directly related to lower amount of active O_2 species for the reaction. However, the input frequency of 500 Hz can be considered as a potentially optimum value, exhibiting the highest $\text{C}_2\text{H}_4\text{O}$ yield with a reasonably high $\text{C}_2\text{H}_4\text{O}$ selectivity and a relatively low CO selectivity.

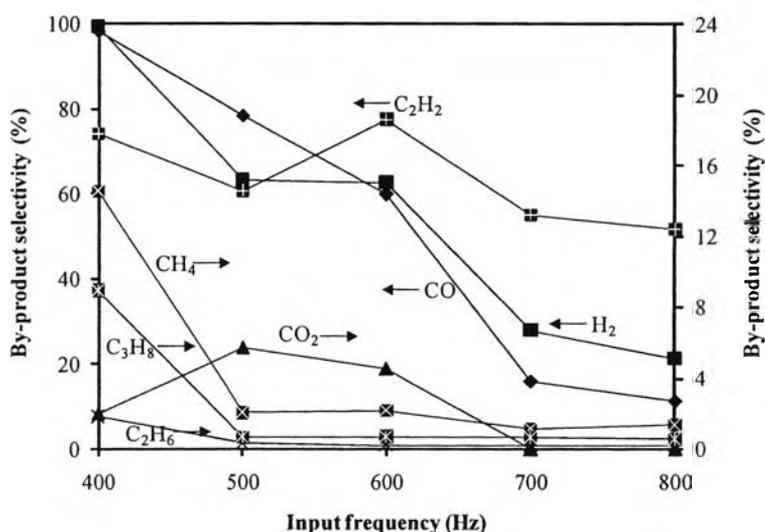


Figure 4.22 By-product selectivities as a function of input frequency by using the cylindrical DBD reactor (molar ratio of $\text{O}_2/\text{C}_2\text{H}_4 = 0.25:1$; applied voltage = 15 kV; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

The by-product selectivities by using the cylindrical DBD and the parallel DBD reactors are comparatively shown in Figures 4.23 and 4.24. It was found that the selectivities for H_2 , CH_4 , C_2H_6 , C_3H_8 , CO_2 , and CO tended to decrease,

except the selectivity for C_2H_2 , for both the parallel DBD and the cylindrical DBD reactors. The explanation is that C_2H_2 was widely reported as a major gaseous hydrocarbon found in DBD system because of the recombination of radicals or the inelastic collision of CH_4 molecules with radicals (Zheng *et al.*, 2008).

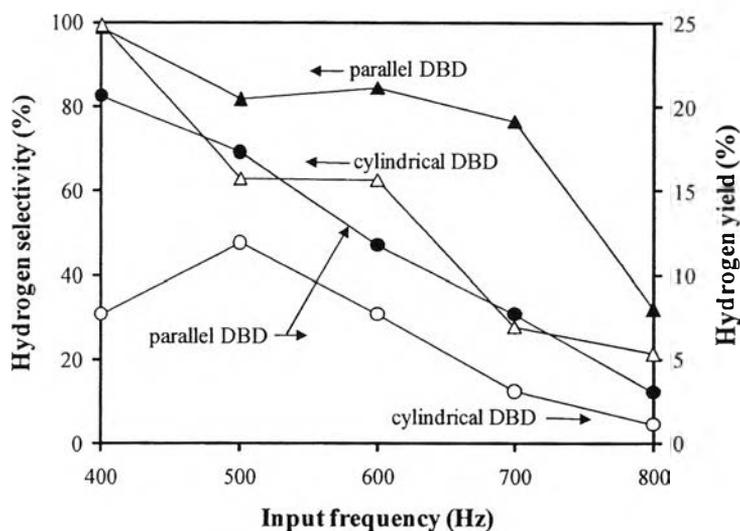


Figure 4.23 Comparison of hydrogen selectivity and hydrogen yield between the parallel DBD and the cylindrical DBD reactors as a function of input frequency (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), 15 kV (cylindrical DBD); feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

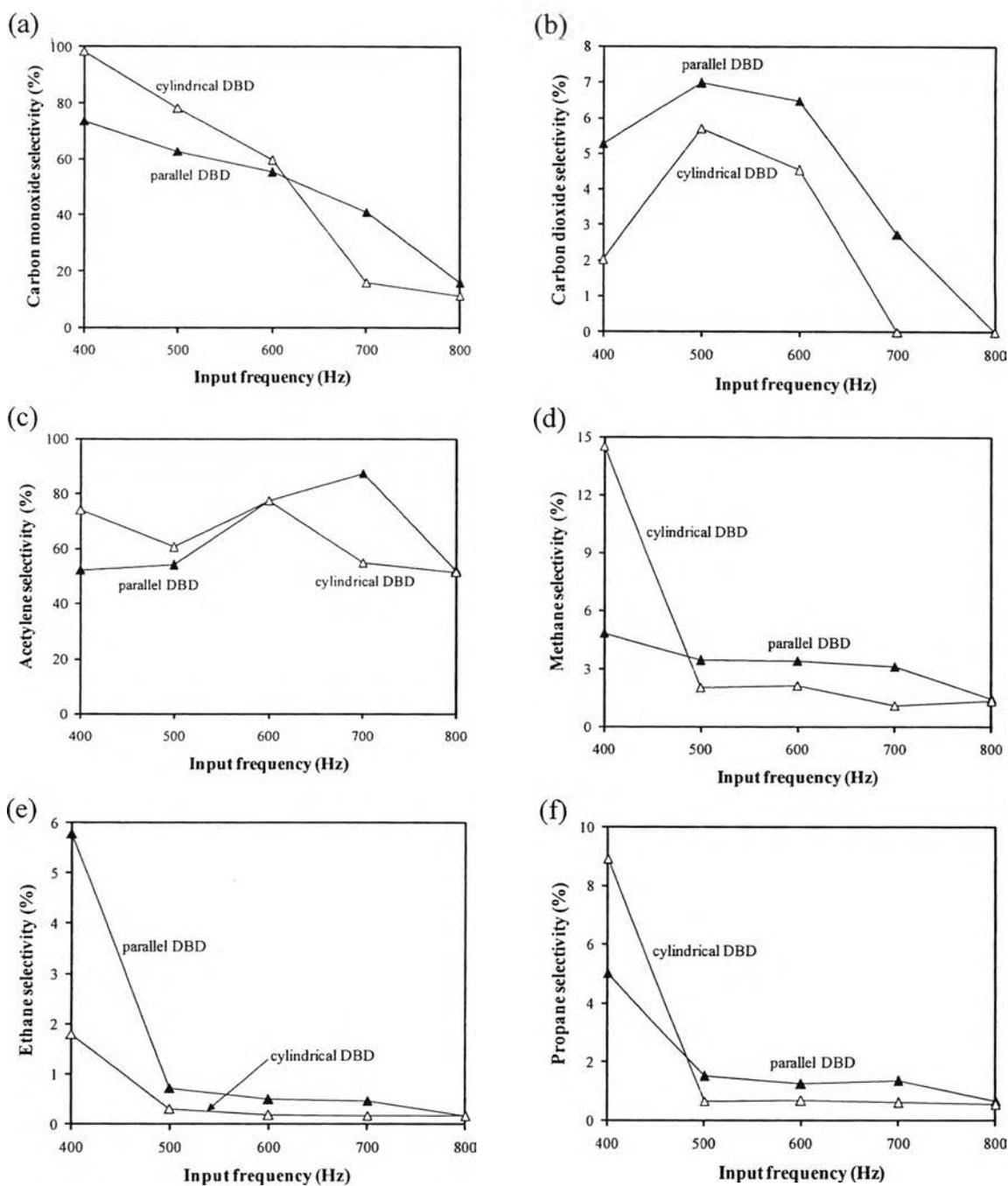


Figure 4.24 Comparison of by-product selectivities between the parallel DBD and the cylindrical DBD reactors as a function of input frequency: (a) carbon monoxide, (b) carbon dioxide, (c) acetylene, (d) methane, (e) ethane, and (f) propane (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), 15 kV (cylindrical DBD); feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.3.3 Effect of Input Frequency on Specific Power Consumptions

The effect of input frequency on the power consumptions to break down each C_2H_4 molecule and to create each C_2H_4O molecule is shown in Figure 4.25. The results show that both the power consumptions per C_2H_4 molecule converted and per C_2H_4O molecule produced first tended to decrease with increasing input frequency from 400 to 500 Hz and then increased with further increasing input frequency higher than 500 Hz. At the input frequency lower than 500 Hz, the coke formation was experimentally observed on the electrode surface, leading to decreasing the power efficiency. Based upon relatively high ethylene oxide yield and the lowest power consumption per molecule of ethylene oxide produced, the optimum input frequency of 500 Hz was selected for further experiments.

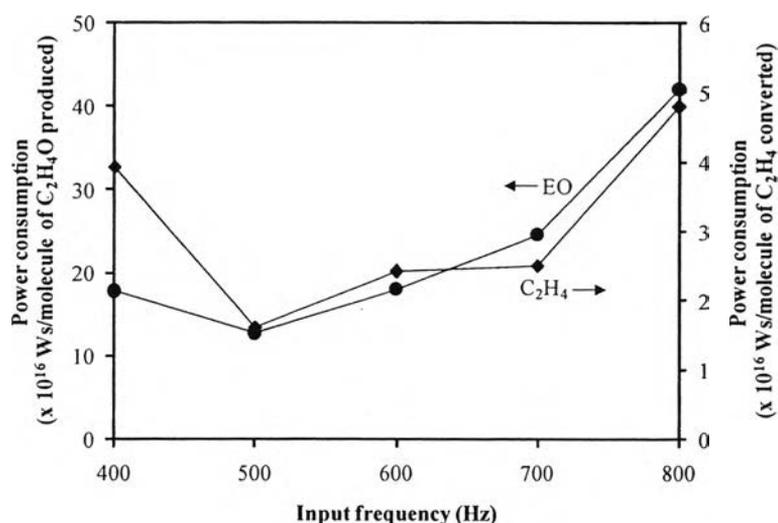


Figure 4.25 Comparison of specific power consumptions as a function of input frequency by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 15 kV; feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 25.12 s; and electrode gap distance = 5 mm).

Figure 4.26 illustrates the comparison of power consumption per C_2H_4 molecule converted and power consumption per C_2H_4O molecule produced between the parallel DBD and the cylindrical DBD reactors. It can be seen that both the power consumptions exhibited the tendency as previously explained; however, the

cylindrical DBD reactor consumed slightly higher power per C_2H_4 molecule converted than the parallel DBD reactor over the entire range of the investigated input frequency. Even though the power consumption per C_2H_4O molecule produced for the cylindrical DBD reactor was much higher than that for the parallel DBD reactor at the applied voltage range higher than 700 Hz, it was almost comparable for both the DBD reactors at low applied voltage range, indeed even lower for the cylindrical DBD reactor at 500 Hz. Interestingly, at the input frequency of 500 Hz, the power consumptions of both the DBD reactors are the lowest. Therefore, input frequency of 500 Hz was used for further experiments for both the DBD reactors.

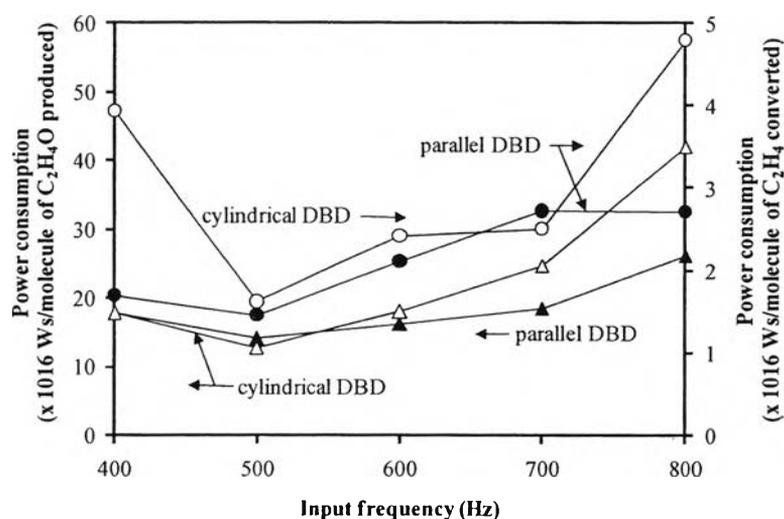


Figure 4.26 Comparison of specific power consumptions between the parallel DBD and the cylindrical DBD reactors as a function of input frequency (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), 15 kV (cylindrical DBD); feed flow rate = $50 \text{ cm}^3/\text{min}$; residence time = 17.10 s (parallel DBD), 25.12 s (cylindrical DBD); and electrode gap distance = 5 mm).

4.4 Effect of Residence Time

The residence time has a significant effect on the reactions of gas molecules within the plasma zone, affecting the performance of the plasma system. The experiments were performed by varying residence time from 25.12 to 16.74, 12.56,

10.05, and 8.37 s, corresponding to the feed flow rate of 50, 75, 100, 125, and 150 cm³/min, respectively. At a feed flow rate lower than 50 cm³/min, the O₂ flow rate cannot be adjusted due to the limitation of a mass flow controller. The studied plasma system conditions of an O₂/C₂H₄ molar ratio of 0.25:1, an applied voltage of 15 kV, and an input frequency of 500 Hz were applied during the reaction.

4.4.1 Effect of Residence Time on Ethylene and Oxygen Conversions and Ethylene Oxide Yield

Figure 4.27 illustrates the influence of the residence time on the C₂H₄ and O₂ conversions and the C₂H₄O yield. The O₂ conversion and C₂H₄O yield tended to gradually increase with increasing residence time, while the C₂H₄ conversion remained almost unchanged. An increase in the feed flow rate generally reduces the gas residence time in the reaction zone, resulting in having a shorter contact time of ethylene and oxygen molecules to collide with electrons. Moreover, it was experimentally observed that a decrease in the residence time requires higher current to generate the microdischarges for the plasma operation, as shown in Figure 4.28. As a result, an increase in the residence time (a reduction in the feed flow rate) enhanced the O₂ conversion, reasonably leading to an increase in the C₂H₄O yield.

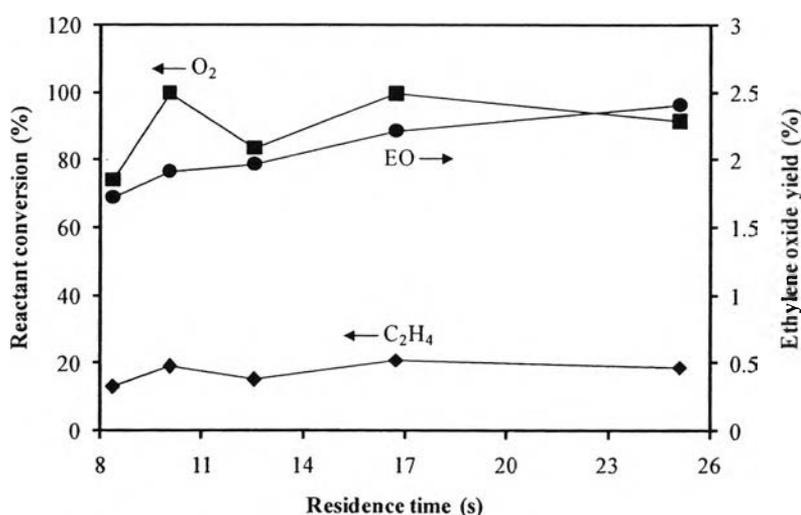


Figure 4.27 Conversions of ethylene and oxygen and yield of ethylene oxide as a function of residence time by using the cylindrical DBD reactor (molar ratio of O₂/C₂H₄ = 0.25:1; applied voltage = 15 kV; input frequency = 500 Hz; and electrode gap distance = 5 mm).

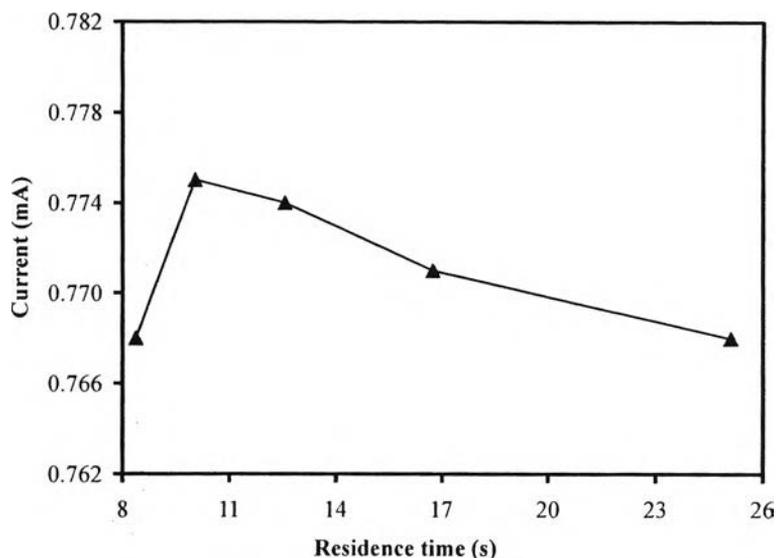


Figure 4.28 Effect of residence time on generated current by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 15 kV; input frequency = 500 Hz; and electrode gap distance = 5 mm).

The C_2H_4 and O_2 conversions between the parallel DBD and the cylindrical DBD reactors as a function of residence time are comparatively shown in Figure 4.29. The results show that the cylindrical DBD reactor gave higher C_2H_4 conversion than the parallel DBD reactor. From the results, the C_2H_4 conversion of the parallel DBD reactor slightly decreased with decreasing residence time from 17.10 to 11.40 s (or increasing feed flow rate from 50 to 75 cm^3/min) and then remained almost unchanged between 11.40 and 5.70 s, while that of the cylindrical DBD reactor remained almost unchanged over the low entire range of the investigated residence time. On the other hand, the O_2 conversion of the parallel DBD reactor dramatically decreased, while that of the cylindrical DBD reactor slightly decreased (still remained nearly ~100% in the residence time between 25.12 and 16.74 s) with decreasing residence time. This is possibly because the investigated cylindrical DBD reactor had slightly larger reaction volume than the parallel DBD reactor, therefore slightly affecting the residence time of the reactants in the plasma zone.

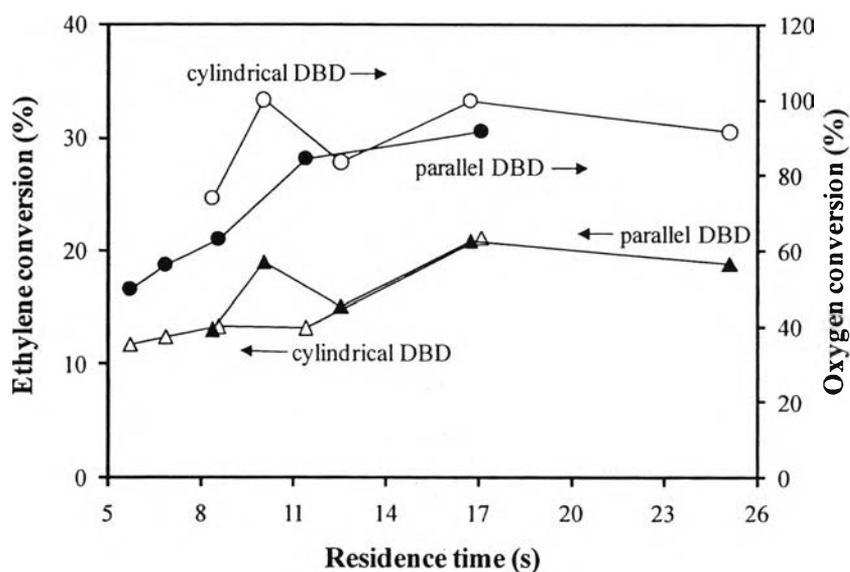


Figure 4.29 Comparison of ethylene and oxygen conversions between the parallel DBD and the cylindrical DBD reactors as a function of residence time (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), = 15 kV (cylindrical DBD); input frequency = 500 Hz; and electrode gap distance = 5 mm).

Figure 4.30 illustrates the comparison of the C_2H_4O selectivity and C_2H_4O yield between the parallel DBD and the cylindrical DBD reactors. It can be seen that the C_2H_4O yield tended to decrease with decreasing residence time. This is because, at the lower residence time (higher feed flow rate), the concentrations of the reactive oxygen species in the plasma region decreases since a fraction of these generated species quickly passes and leaves the plasma zone. When increasing residence time higher than 15 s, the C_2H_4O yield of the cylindrical DBD reactor tended to be higher than that of the parallel DBD reactor, but the opposite trend was observed for the residence time lower than 15 s. Moreover, the higher C_2H_4O selectivity of the cylindrical DBD reactor was obtained at the higher residence time. Therefore, the residence time has a critical effect on the plasma efficiency that it should be used as high as possible (Morent *et al.*, 2008). The maximum C_2H_4O yield of 2.41% was obtained using the cylindrical DBD reactor at the residence time of 25.12 s (feed flow rate = $50 \text{ cm}^3/\text{min}$).

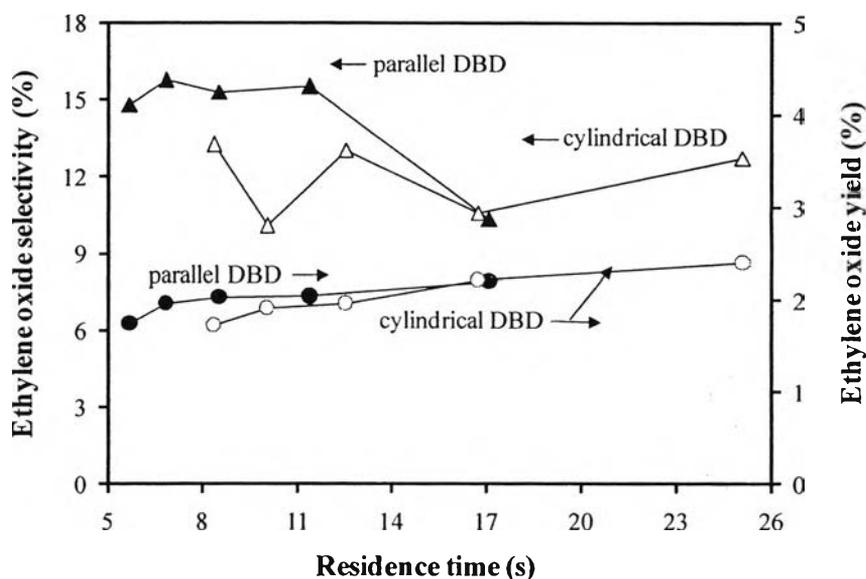


Figure 4.30 Comparison of ethylene oxide selectivity and ethylene oxide yield between the parallel DBD and the cylindrical DBD reactors as a function of residence time (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), = 15 kV (cylindrical DBD); input frequency = 500 Hz; and electrode gap distance = 5 mm).

4.4.2 Effect of Feed Flow Rate on By-Product selectivities

The residence time dependence of by-product selectivities using the cylindrical DBD reactor is depicted in Figure 4.31. The results show that the selectivities for CO , CO_2 , and CH_4 tended to increase, but the selectivity for C_2H_2 tended to decrease, whereas the selectivities for other by-products remained almost unchanged with increasing residence time (decreasing feed flow rate). These imply that the partial and complete oxidations are favorable to occur at high residence time (low feed flow rate), while the dehydrogenation reaction is likely to take place at low residence time (high feed flow rate). Interestingly, the H_2 selectivity did not increase as the C_2H_2 selectivity according to the dehydrogenation reaction, but remained almost unchanged. It can be believed that H_2 was consumed to form higher hydrocarbons at low residence time (high feed flow rate).

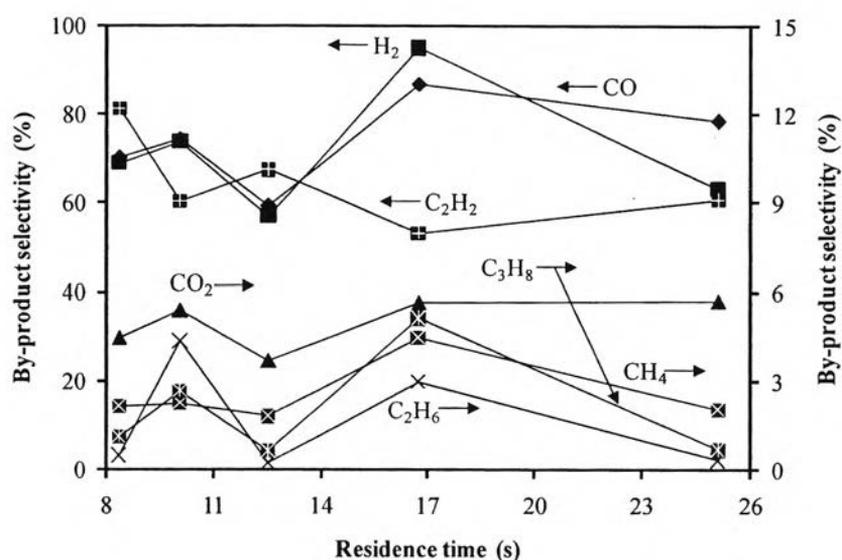


Figure 4.31 By-product selectivities as a function of residence time by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 15 kV; input frequency = 500 Hz; and electrode gap distance = 5 mm).

Figure 4.32 shows the comparison of the H_2 selectivity and H_2 yield between the parallel DBD and the cylindrical DBD reactors. The results show that the H_2 selectivity of both DBD reactors is quite high around $\sim 70\%$; however, the cylindrical DBD reactor tended to provide higher H_2 selectivity and H_2 yield than the parallel DBD reactor. Since H_2 was obtained as a main by-product, H_2 is greatly considered very valuable to be produced by the studied epoxidation reaction using the investigated cylindrical DBD reactor. Therefore, H_2 has high potential to be a desired product along with the C_2H_4O production.

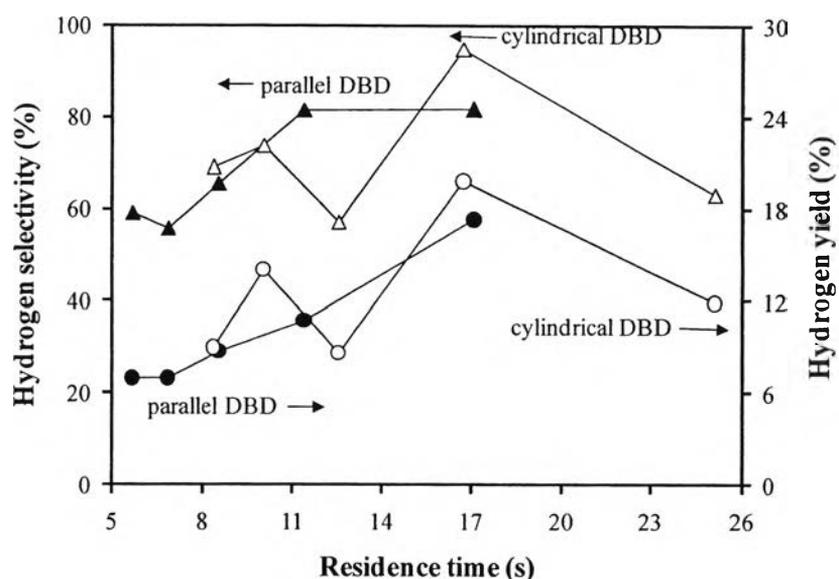


Figure 4.32 Comparison of hydrogen selectivity and hydrogen yield between the parallel DBD and the cylindrical DBD reactors as a function of residence time (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), = 15 kV (cylindrical DBD); input frequency = 500 Hz; and electrode gap distance = 5 mm).

The comparison of the by-products between the parallel DBD and the cylindrical DBD reactors as a function of residence time is shown in Figure 4.33. The CO , CO_2 , and CH_4 selectivities for both the DBD reactors tended to increase with increasing residence time (decreasing feed flow rate). The C_2H_2 selectivity slightly decreased; meanwhile, the selectivities for C_2H_6 and C_3H_8 remain almost unchanged for both the DBD reactors in the studied residence time range. From the results, the cylindrical DBD reactor tended to generate lower amount of CO_2 than the parallel DBD reactor, especially under the operation with high residence time above 10 s.

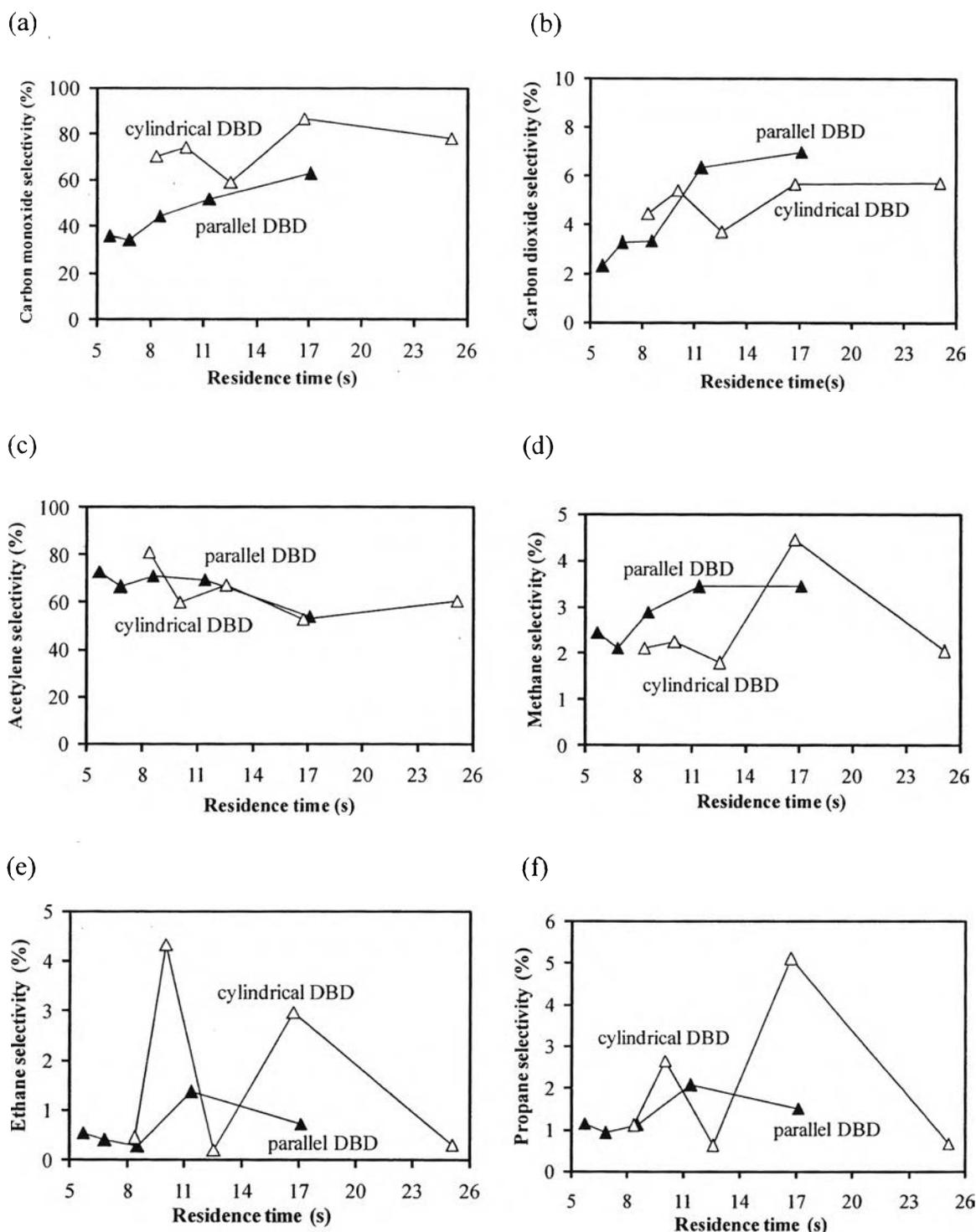


Figure 4.33 Comparison of by-product selectivities between the parallel DBD and the cylindrical DBD reactors as a function of residence time: (a) carbon monoxide, (b) carbon dioxide, (c) acetylene, (d) methane, (e) ethane, and (f) propane (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), = 15 kV (cylindrical DBD); input frequency = 500 Hz; and electrode gap distance = 5 mm).

4.4.3 Effect of Feed Flow Rate on Specific Power Consumptions

Figure 4.34 shows the effect of residence time on the power consumptions for the cylindrical DBD reactor. The power consumption per molecule of converted C_2H_4 slightly decreased, while the power consumption per molecule of produced C_2H_4O tended to dramatically decrease when decreasing residence time. The higher residence time (lower feed flow rate) consumed comparatively high power to produce C_2H_4O molecule; however, higher reactant conversions and C_2H_4O selectivity and yield were obtained at higher residence time (Figure 4.27). Therefore, the residence time of 25.12 s (feed flow rate of $50 \text{ cm}^3/\text{min}$) was considered as an optimum value. Interestingly, the comparative results shown in Figure 4.35 reveal that the cylindrical DBD reactor consumed lower powers both to convert C_2H_4 molecule and to produce C_2H_4O molecule than the parallel DBD reactor.

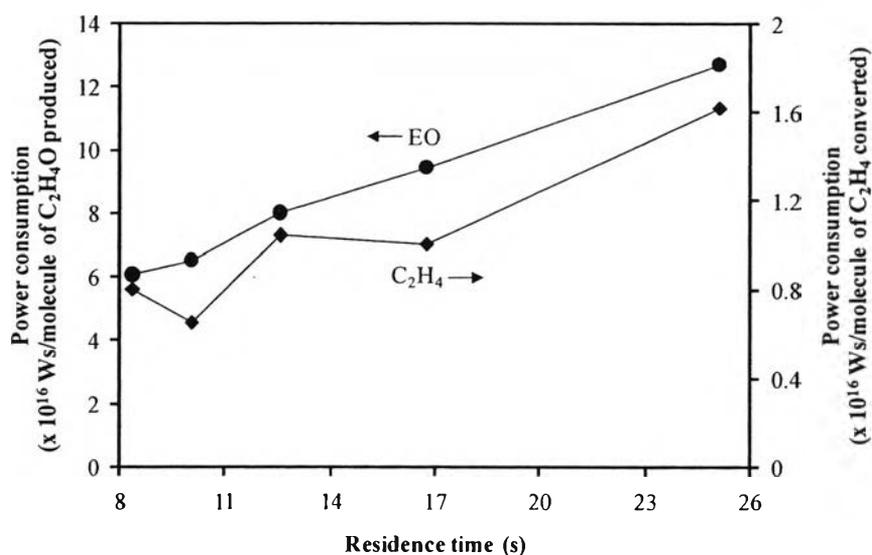


Figure 4.34 Comparison of specific power consumptions as a function of residence time by using the cylindrical DBD reactor (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 15 kV; input frequency = 500 Hz; and electrode gap distance = 5 mm).

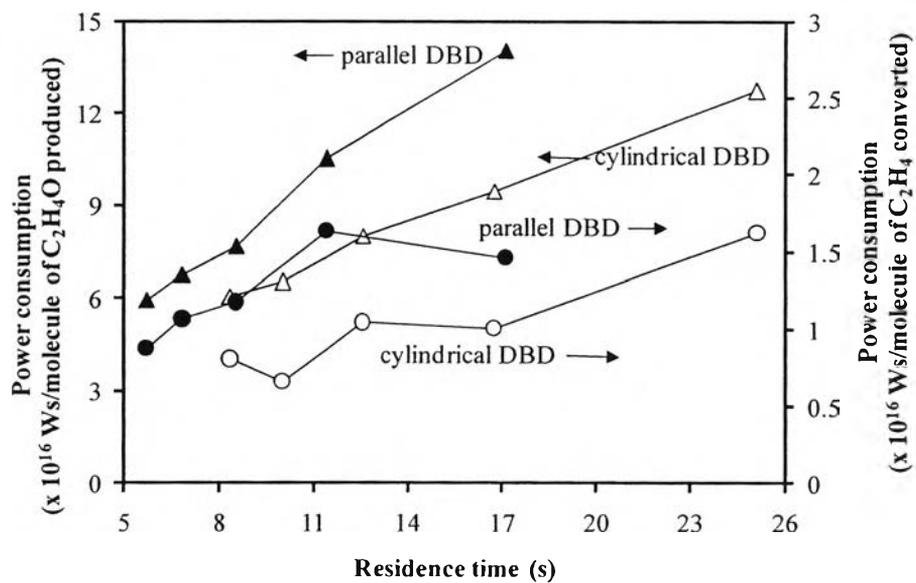


Figure 4.35 Comparison of specific power consumptions between the parallel DBD and the cylindrical DBD reactors as a function of residence time (molar ratio of $O_2/C_2H_4 = 0.25:1$; applied voltage = 19 kV (parallel DBD), = 15 kV (cylindrical DBD); input frequency = 500 Hz; and electrode gap distance = 5 mm).