

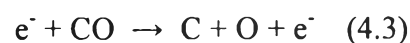
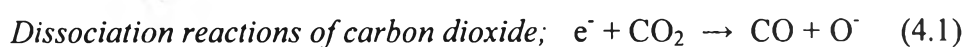


## CHAPTER IV

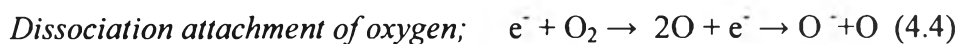
### RESULTS AND DISCUSSION

In a plasma environment, the highly energetic electrons generated by gliding arc discharge collide with the gaseous molecules of hydrocarbons and CO<sub>2</sub>, creating a variety of chemically active radicals. All the possibilities of chemical pathways occurring under the studied conditions are briefly described below to provide a better comprehensive understanding of the plasma reforming reactions of natural gas containing CO<sub>2</sub> under AC non-thermal gliding arc discharge, both without and with partial oxidation. In the absence of oxygen, the radicals of oxygen-active species are produced during the collisions between electrons and CO<sub>2</sub>, as shown in Eqs. 4.1 and 4.2. Moreover, the produced CO can be further dissociated by the collisions with electrons to form coke and oxygen-active species (Eq. 4.3). In the case of added oxygen for partial oxidation, a large amount of oxygen-active species can be produced from the collisions between electrons and oxygen molecules, as described by Eqs. 4.4-4.6. Eqs. 4.7-4.19 show the collisions between electrons and all hydrocarbons presented in the feed to produce hydrogen and various hydrocarbon species for subsequent reactions.

Electron-carbon dioxide collisions:



Electron-oxygen collisions:



Electron-methane collisions:



Electron-ethane collision:

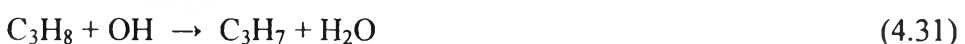
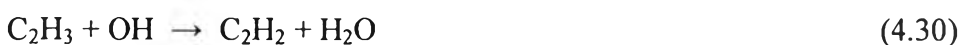
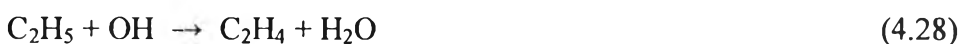


Electron-propane collision:



The oxygen-active species derived from CO<sub>2</sub> and O<sub>2</sub> can further extract hydrogen atoms from the molecules of hydrocarbon gases via the oxidative dehydrogenation reactions (Eqs. 4.20-4.32), consequently producing several chemically active radicals and water.

Oxidative dehydrogenation reactions:



The C<sub>2</sub>H<sub>5</sub>, C<sub>2</sub>H<sub>3</sub>, and C<sub>3</sub>H<sub>7</sub> radicals can further react to form ethylene, acetylene, and propene either by electron collision (Eqs. 4.13-4.15, and 4.18) or by

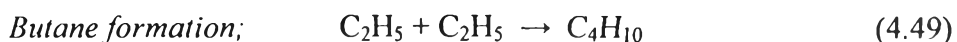
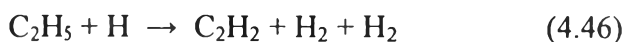
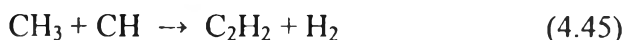
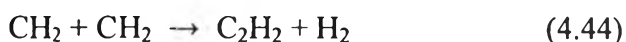
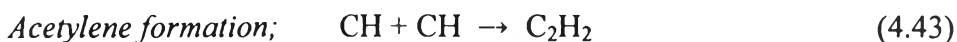
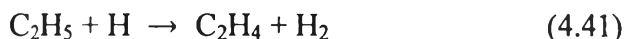
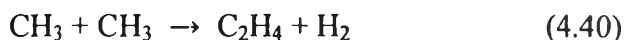
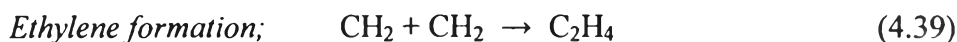
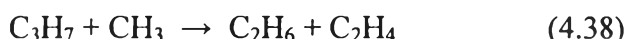
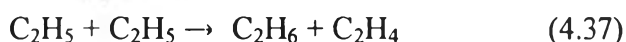
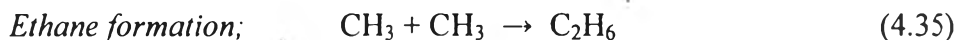
oxidative dehydrogenation reaction (Eqs. 4.22-4.24, 4.28-4.30, and 4.32). The extracted hydrogen atoms immediately form hydrogen gas according to Eq. 4.11. However, no propene was detected in the outlet gas stream. It is therefore believed that the propene species was unstable and may probably undergo further reactions (Eqs. 4.33 and 4.34).

Propene hydrogenation and cracking reactions:



In addition, the radicals of hydrocarbons and hydrogen derived from the earlier reactions react further to combine with one another to form ethane, ethylene, acetylene, propane, and butane, as shown in Eqs. 4.35-4.50. In addition, ethane can be further dehydrogenated to form ethylene, while ethylene can also be dehydrogenated to form acetylene by either electron collision or oxidative dehydrogenation (Eqs. 4.12, 4.13, 4.21, 4.22, 4.27, and 4.28 for ethylene formation; and, Eqs. 4.14, 4.15, 4.23, 4.24, 4.29, and 4.30 for acetylene formation).

Coupling reactions of active species:





Moreover, a significant amount of CO and a very small amount of water were produced under the studied conditions, particularly in feed with high oxygen content. CO may be mainly formed via the partial oxidation reactions of the hydrocarbon reactants. Eqs. 4.51-4.55 show the partial oxidative pathways of methane to form CO and H<sub>2</sub> as the end products. The formation of water is believed to occur via the oxidative hydrocarbon reactions (Eqs. 4.26-4.32). In addition, water can be formed by the reactions between hydrogen or active hydrogen radical and active oxygen radical, as shown in Eqs. 4.56-4.58.

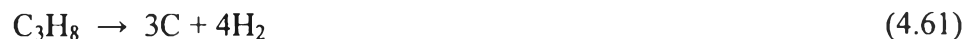
Carbon monoxide formation:



Water formation:



Additionally, hydrocarbon molecules may crack to form carbon and hydrogen via thermal cracking reactions (Eqs 4.59-4.61).



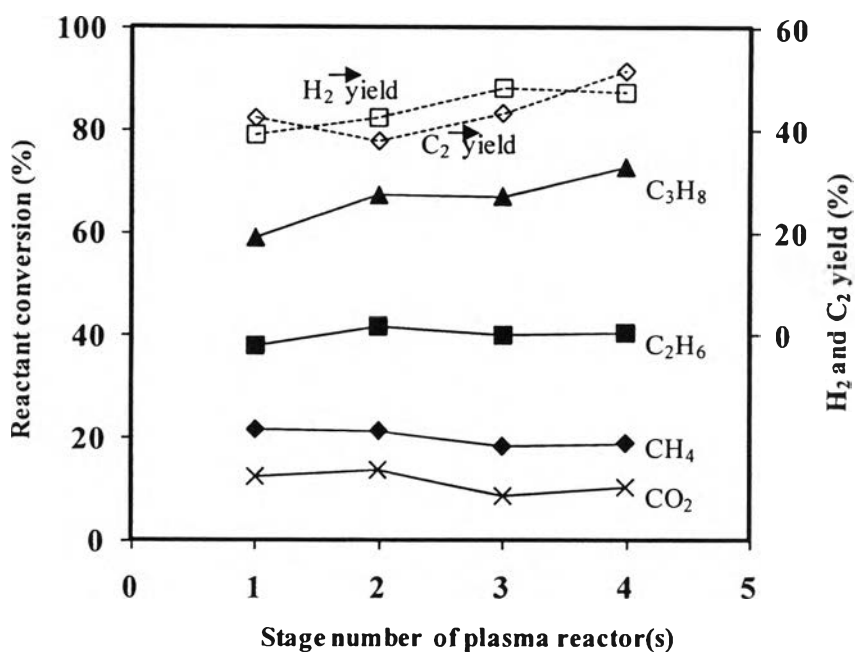
## 4.1 Reforming of Natural Gas without Partial Oxidation

### 4.1.1 Effect of Feed Flow Rate at Constant Residence Time

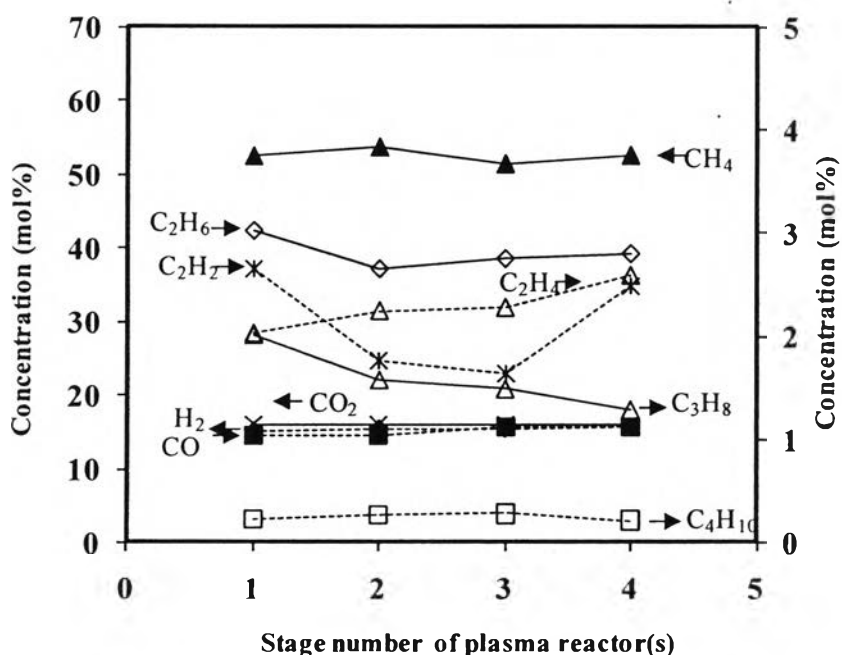
The effect of feed flow rate of reactant gases at a constant residence time was initially investigated to evaluate how it effected the process performance.

#### *4.1.1.1 Effect on reactant conversion and product yield*

The results of the reactant conversions and product yields as a function of stage number of plasma reactors when varying feed flow rate at a fixed residence time of 4.38 s are illustrated in Figure 4.1. The stage number of plasma reactors was varied from 1 to 4 stages. For each stage of plasma reactors, the feed flow rate was controlled at 31.25, 62.50, 93.75, and 125 cm<sup>3</sup>/min, respectively, in order to maintain the same residence time. The results show that only the conversion of C<sub>3</sub>H<sub>8</sub> gradually increased with increasing stage number, whereas the conversion of other reactant components remained almost unchanged. It can be confirmed by the concentrations of outlet gases, presented in Figure 4.2, that the concentration of C<sub>3</sub>H<sub>8</sub> sharply decreased, whereas the CH<sub>4</sub> concentration was nearly unchanged. The explanation is that the conversion of reactant gases depends upon the collision between the highly energetic electrons and reactant gases, which can be controlled by adjusting residence time. However, the plasma operation in this experimental part was performed at a constant residence time, so the probability of collision between reactant gas molecules and highly energetic electrons is quite the same for all stages of plasma reactors, causing the slightly changed conversion of reactant gases. Therefore, when the residence time was fixed, the conversion of reactant gases in simulated natural gas was not much affected by the stage number of plasma reactors. Moreover, the H<sub>2</sub> and C<sub>2</sub> yields only slightly increased with increasing stage number of plasma reactors. It can be suggested that the coupling reactions of the active species and oxidative dehydrogenation reactions may not be significantly affected by the stage number as well.



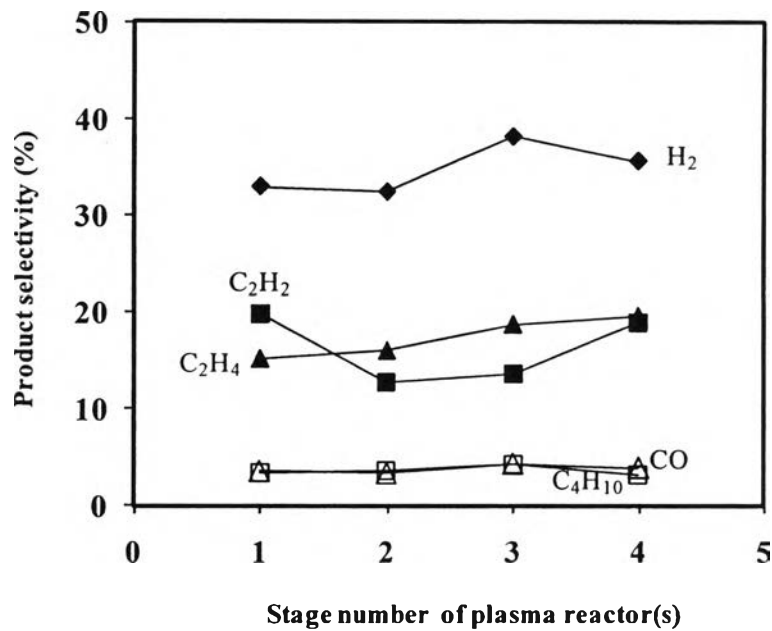
**Figure 4.1** Effect of stage number of plasma reactors on reactant conversions and product yields for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).



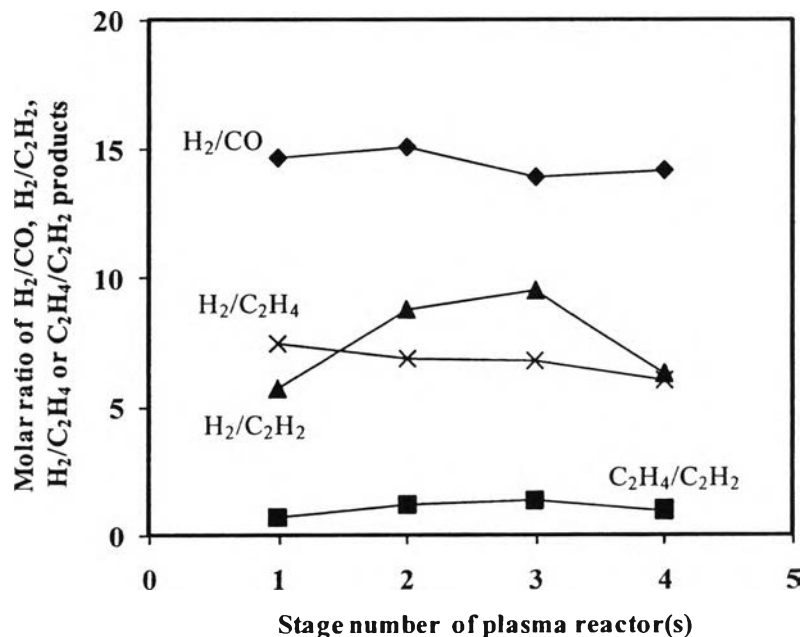
**Figure 4.2** Effect of stage number of plasma reactors on concentrations of outlet gases for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

#### *4.1.1.2 Effect on product selectivity*

The effect of stage number of plasma reactors on the selectivities for  $H_2$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_4H_{10}$ , and CO is depicted in Figure 4.3. The selectivities for  $H_2$  and  $C_2H_4$  tended to slightly increase with increasing stage number from 1 to 3 stages, and the selectivities for CO and  $C_4H_{10}$  were almost unchanged with the stage number of plasma reactors. The results are relevant to the molar ratios of  $H_2/C_2H_2$  and  $C_2H_4/C_2H_2$ , as shown in Figure 4.4, while the molar ratio of  $H_2/C_2H_4$  gradually decreased. This implies that the increase in  $C_2H_4$  production exceeds the increase in  $H_2$  production, resulting in the gradual decrease in  $H_2/C_2H_4$  ratio. It should be therefore noted that the hydrogenation of  $C_2H_2$  more favorably occurs than the coupling reaction of hydrocarbon active species with increasing stage number of plasma reactors from 1 to 3 stages, leading to the consumption of  $H_2$  for some extent to produce  $C_2H_4$ . At 3 stages of the plasma reactors, the maximum selectivity for  $H_2$  was obtained at approximately 38.23 %. From this point of view, it could be concluded that the increase in stage number of plasma reactors from 1 to 3 stages assists in improving the desired product selectivity, anyhow it did not provide the synergistic effect on the reactant conversion.



**Figure 4.3** Effect of stage number of plasma reactors on product selectivities for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

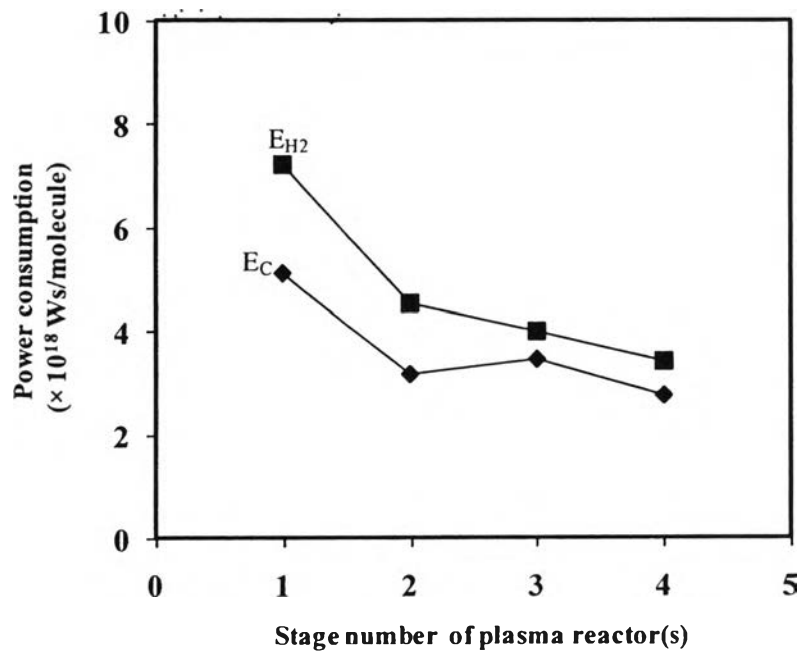


**Figure 4.4** Effect of stage number of plasma reactors on product molar ratios for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).



#### 4.1.1.3 Effect on power consumption

The effect of stage number of plasma reactors on power consumptions per reactant molecule converted and per hydrogen molecule produced is shown in Figure 4.5. The power consumption per hydrogen molecule produced sharply declined from 1 to 2 stages of plasma reactors and then gradually decreased with increasing stage number from 2 to 4 stages, while the power consumption per reactant molecule converted also decreased in the same trend as the power consumption per hydrogen molecule produced when the stage number was increased from 1 to 2 stages but became almost unchanged with further increasing stage number to 4 stages. The minimum power consumptions were about  $2.75 \times 10^{-18}$  Ws (17.18 eV) per molecule of converted reactant and  $3.41 \times 10^{-18}$  Ws (21.28 eV) per molecule of produced hydrogen at the stage number of 4 stages.



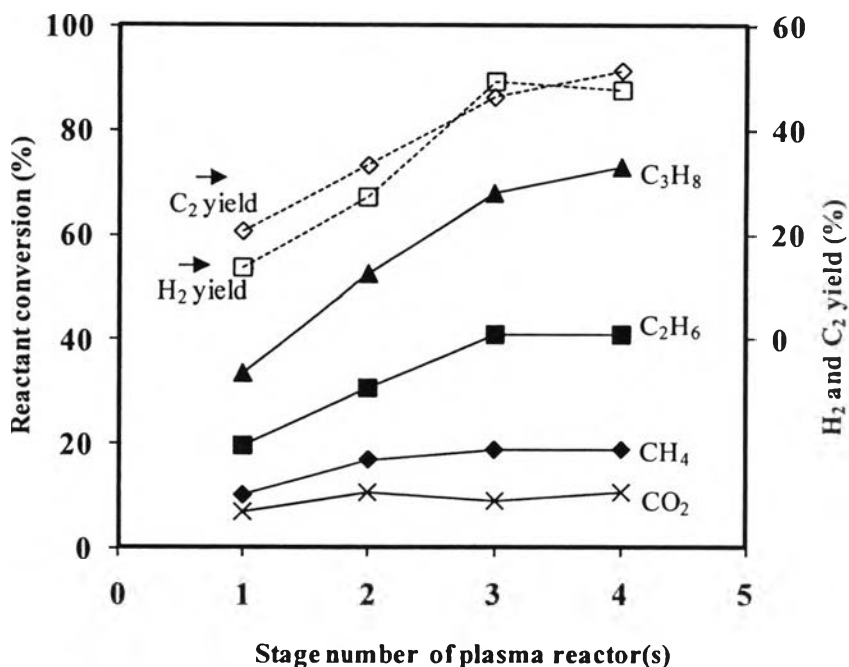
**Figure 4.5** Effect of stage number of plasma reactors on power consumptions for reforming of natural gas without partial oxidation in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

#### 4.1.2 Effect of Residence Time at Constant Feed Flow Rate

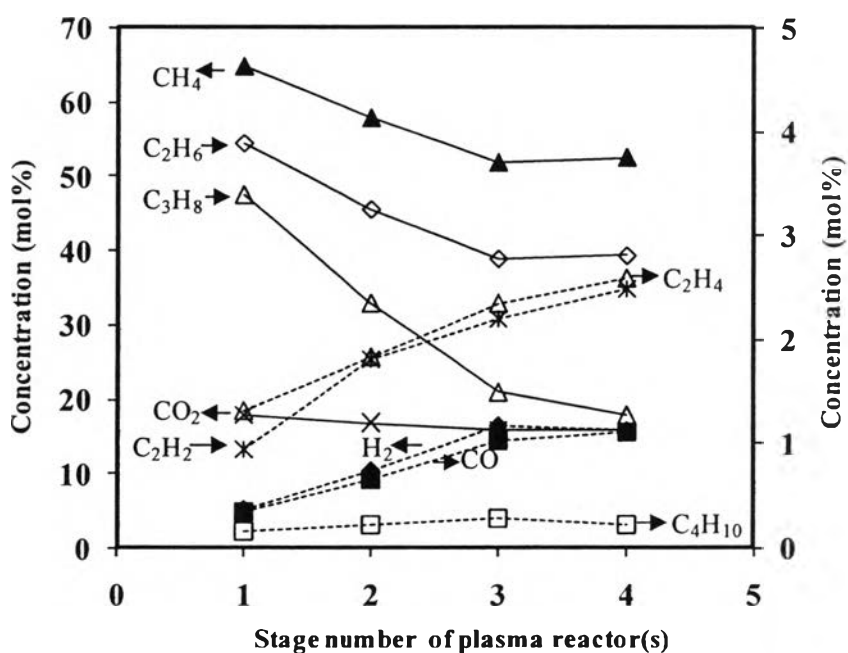
Since the effect of feed flow rate at a constant residence time was found to insignificantly affect the process performance, the effect of residence time at a constant feed flow rate was next comparatively investigated.

##### *4.1.2.1 Effect on reactant conversion and product yield*

The results of the reactant conversions and product yields as a function of stage number of plasma reactors when varying residence time at a fixed feed flow rate of 125 cm<sup>3</sup>/min are illustrated in Figure 4.6. For each stage of plasma reactors, the residence time was controlled at 1.09, 2.19, 3.29, and 4.38 s, respectively, in order to maintain the same feed flow rate. The conversions of all hydrocarbons, except CO<sub>2</sub>, considerably increased due to the longer residence time or contact time in the plasma reaction zone with increasing number of stage from 1 to 3 stages. Beyond the 3 stages, only propane conversion increased, but other reactant conversions remained almost unchanged. Comparatively, the propane conversion increased rapidly with increasing stage number of plasma reactors, whereas the methane conversion tended to slightly increase. The conversions of all reactant gases were in the following order: propane > ethane > methane > CO<sub>2</sub>, resulting from their bond dissociation energies, which are 4.33, 4.35, 4.55, and 5.52 eV, respectively. The higher bond dissociation energy leads to more difficulty to be dissociated for further reacting to form other species (Dean, 1999). It can be supposed that the unchanged CO<sub>2</sub> conversion might be due to its relatively much higher bond dissociation energy. For the H<sub>2</sub> and C<sub>2</sub> yields, the increase in residence time due to the increase in the stage number of plasma reactors enhances the conversion of all reactants, as aforementioned, and consequently leads to increasing production yields. The outlet concentrations of all reactant gases shown in Figure 4.7 significantly decreased with increasing stage number of reactors from 1 to 3 stages except that the concentration of CO<sub>2</sub> remained unchanged due to the almost constant CO<sub>2</sub> conversion.



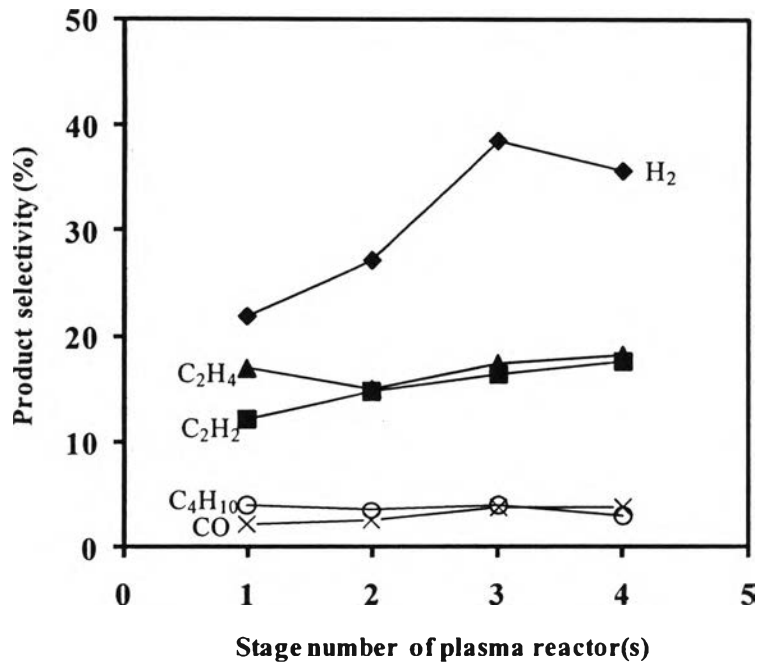
**Figure 4.6** Effect of stage number of plasma reactors on reactant conversions and product yields for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).



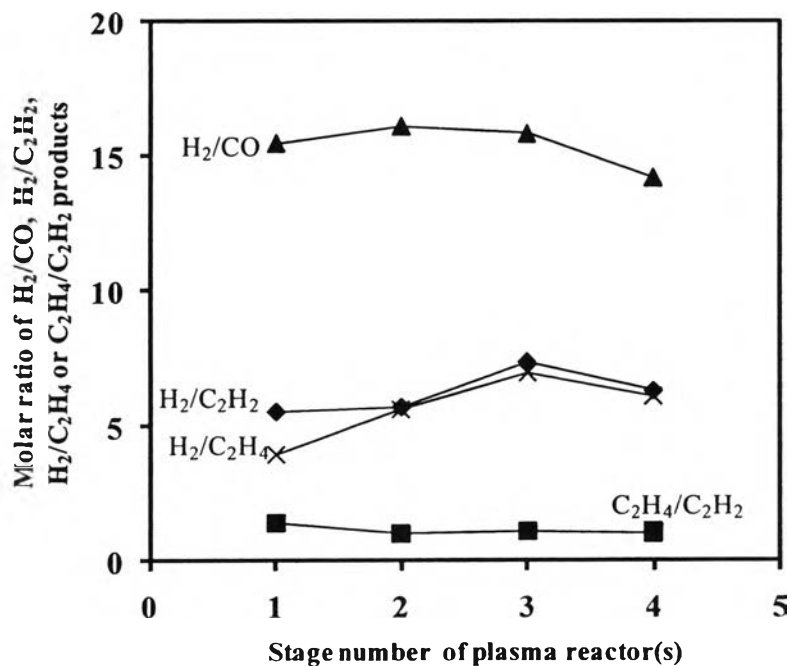
**Figure 4.7** Effect of stage number of plasma reactors on concentrations of outlet gases for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).

#### 4.1.2.2 Effect on product selectivity

Figure 4.8 illustrates the effect of stage number of plasma reactors on the product selectivities. The experimental results reveal that the selectivities for  $H_2$  and  $C_2H_2$  tended to increase with increasing stage number of plasma reactors, whereas those for  $C_2H_4$ ,  $C_4H_{10}$ , and CO remained almost unchanged. This implies that the oxidative dehydrogenation is preferable at high residence time. As confirmed by the product molar ratios in Figure 4.9, the  $H_2/C_2H_4$  ratio increased with increasing stage number of plasma reactors from 1 to 3 stages, and also the molar ratio of  $C_2H_4/C_2H_2$  slightly decreased, suggesting that the dehydrogenation of  $C_2H_4$  is likely to occur when the stage number of plasma reactors is increased. Moreover, the coupling reaction of hydrogen radicals could occur and resulted in the great increase in the selectivity for  $H_2$  at 3 stages of plasma reactors. In contrast, the selectivities for  $C_2H_4$ ,  $C_4H_{10}$ , and CO remained almost unchanged. From these experimental results, it can be concluded that the rate of dehydrogenation increases with increasing stage number of plasma reactors when the multistage system is operated at constant feed flow rate.



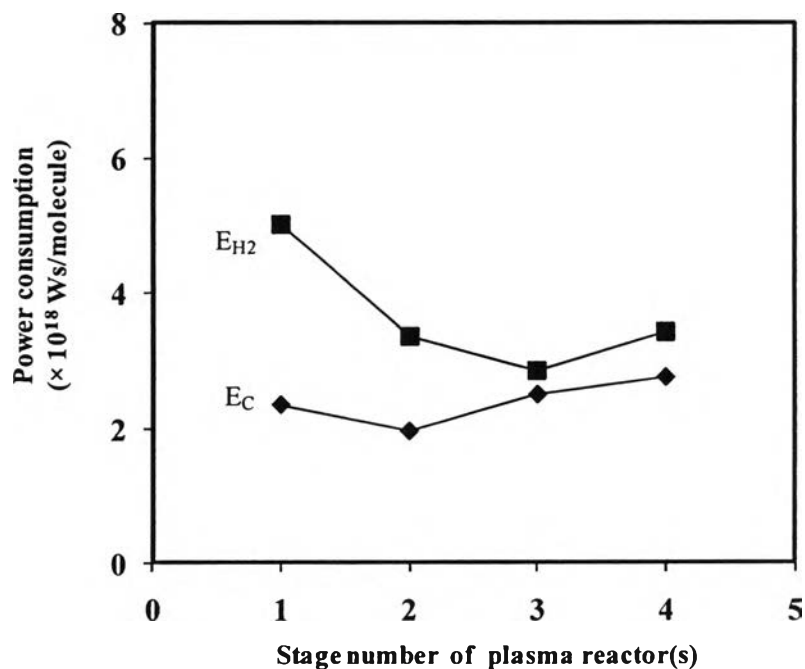
**Figure 4.8** Effect of stage number of plasma reactors on product selectivities for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).



**Figure 4.9** Effect of stage number of plasma reactors on product molar ratios for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).

#### 4.1.2.3 Effect on power consumption

The effect of stage number of plasma reactors on power consumptions per reactant molecule converted and per hydrogen produced is depicted in Figure 4.10. The power consumption per hydrogen molecule produced substantially decreased when the stage number of plasma reactors was increased from 1 to 3 stages, but the power consumption per reactant molecule converted was insignificantly changed. At the 3 stages, the minimum power consumption about  $2.85 \times 10^{-18}$  Ws (17.77 eV) per molecule of produced hydrogen was achieved.



**Figure 4.10** Effect of stage number of plasma reactors on power consumptions for reforming of natural gas without partial oxidation in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate,  $125 \text{ cm}^3/\text{min}$ ).

## 4.2 Reforming of Natural Gas with Partial Oxidation

For the combined plasma reforming and partial oxidation of the simulated natural gas, the effect of feed flow rate and residence time were systematically investigated to determine whether or not the addition of oxygen to the natural gas

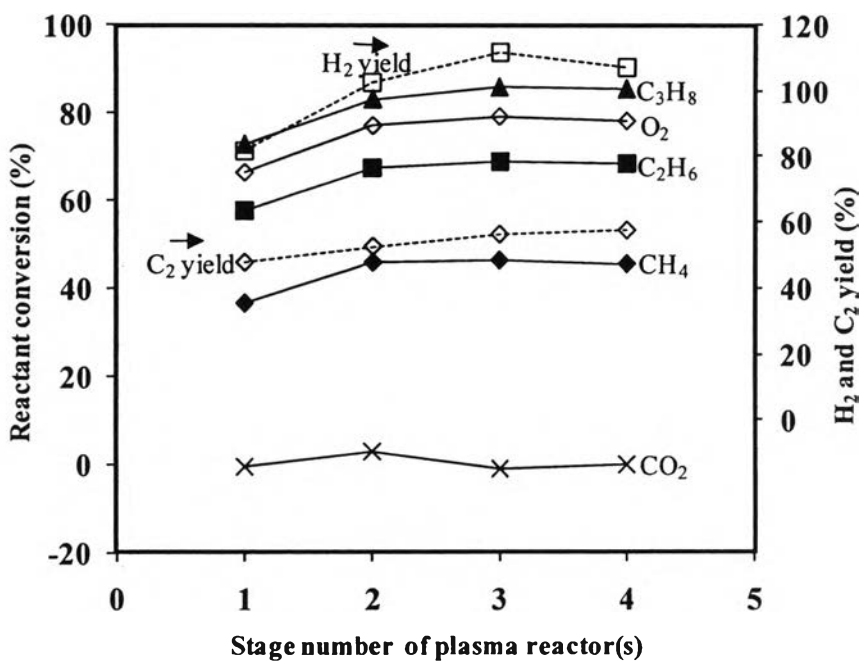
feed improved the system performance by using two different oxygen sources: pure oxygen and air.

#### 4.2.1 Reforming of Natural Gas with Partial Oxidation by Using Pure Oxygen

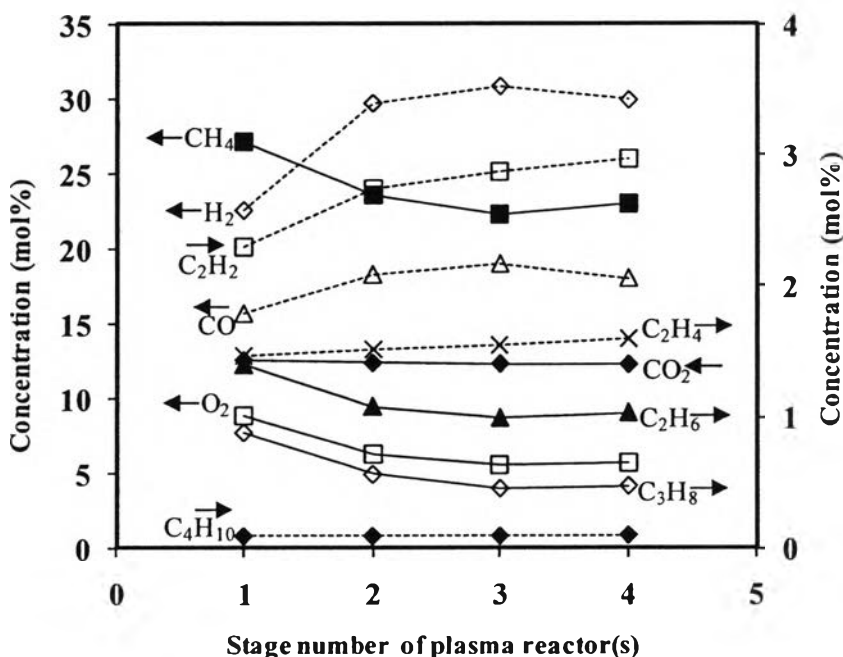
##### 4.2.1.1 *Effect of Feed Flow Rate at Constant Residence Time*

###### 4.2.1.1.1 Effect on reactant conversion and product yield

The combined reforming and partial oxidation of natural gas by using pure oxygen as an oxygen source at a constant residence time under multistage gliding arc discharge was operated at the hydrocarbons-to-oxygen molar ratio of 2/1, which was the optimum ratio in the previous work (Rueangjitt *et al.*, 2008). Figure 4.11 shows that all reactant conversions only slightly increased with increasing stage number from 1 to 2 stages. Beyond 2 stages, those remained almost unchanged. The H<sub>2</sub> and C<sub>2</sub> yields gradually increased with the stage number of plasma reactors. The value of H<sub>2</sub> yield was somewhat greater than 100 due to the complexity of the reaction, of which both forward and backward reactions simultaneously occurred in the plasma reactors. The concentrations of the outlet gases are shown in Figure 4.12. The outlet concentrations of all reactants decreased with increasing stage number of plasma reactors, except that the outlet concentration of CO<sub>2</sub> remained unchanged, which might result from the high bond energy dissociation, as mentioned previously.



**Figure 4.11** Effect of stage number of plasma reactors on reactant conversions and product yields for reforming of natural gas with pure O<sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

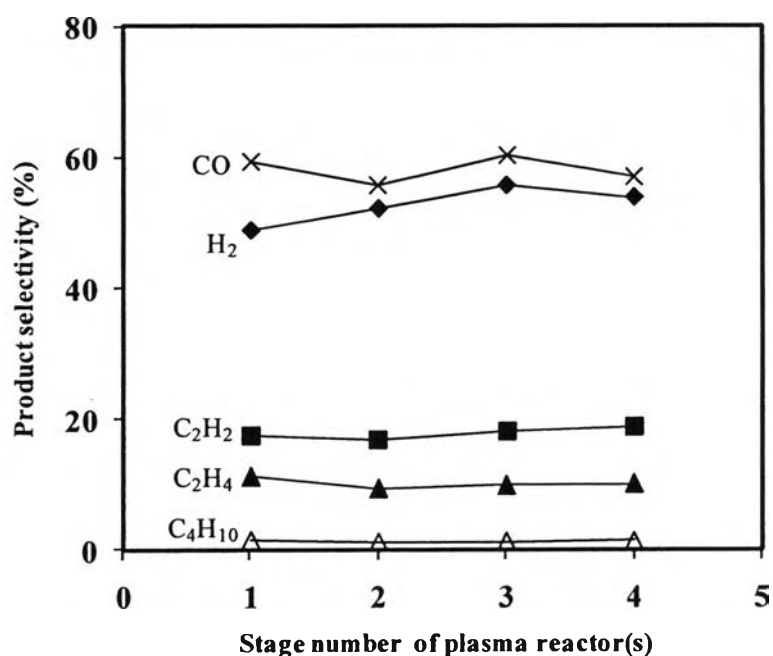


**Figure 4.12** Effect of stage number of plasma reactors on concentrations of outlet gases for reforming of natural gas with pure O<sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

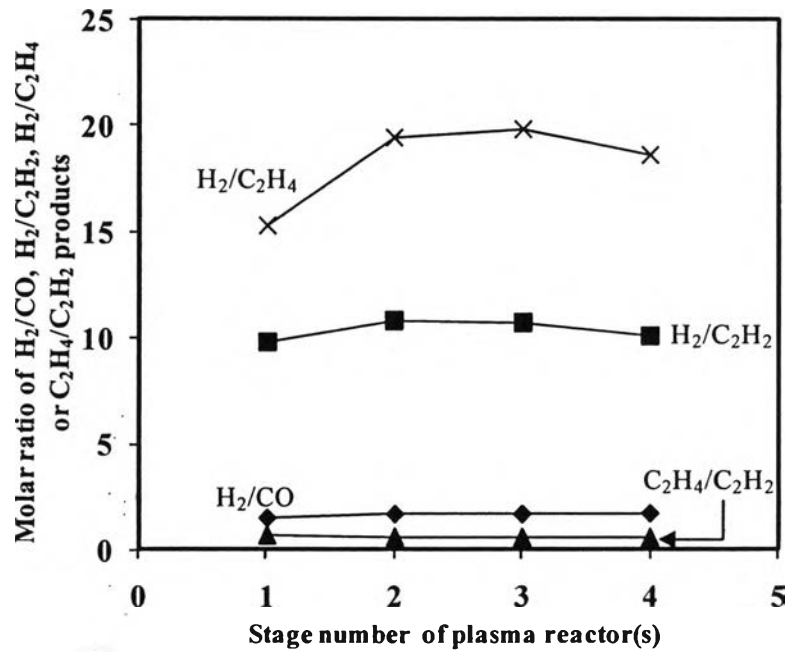


#### 4.2.1.1.2 Effect on product selectivity

Figure 4.13 shows that most product selectivities did not significantly change when the stage number of plasma reactors was increased except that the selectivity for H<sub>2</sub> tended to slightly increase. The molar ratio of H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> increased as the number of plasma reactors increased from 1 to 2 stages and then remained almost unchanged with further increasing stage number, whereas other product molar ratios were almost constant, as shown in Figure 4.14. This can be explained in that both the dehydrogenation reactions and the coupling reaction of hydrogen radicals to produce H<sub>2</sub> have high possibility to occur owing to the high opportunity to collide with the active species at the early stages of plasma reactors at the residence time of 4.38 s.



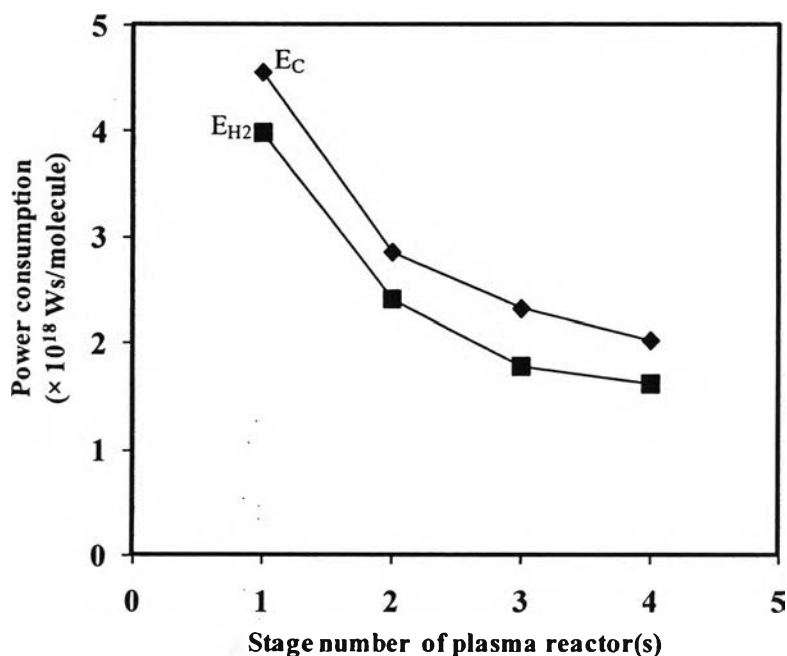
**Figure 4.13** Effect of stage number of plasma reactors on product selectivities for reforming of natural gas with pure O<sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).



**Figure 4.14** Effect of stage number of plasma reactors on product molar ratios for reforming of natural gas with pure O<sub>2</sub> addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

#### 4.2.1.2.3 Effect on power consumption

As shown in Figure 4.15, the decrease in the power consumptions per both reactant molecule converted and hydrogen produced with increasing stage number of plasma reactors was observed, as previously obtained. The optimum power consumptions were  $2.02 \times 10^{-18}$  Ws (12.58 eV) per molecule of hydrocarbon converted and  $1.61 \times 10^{-18}$  Ws (10.09 eV) per molecule of hydrogen produced at the 4 stages of plasma reactors.



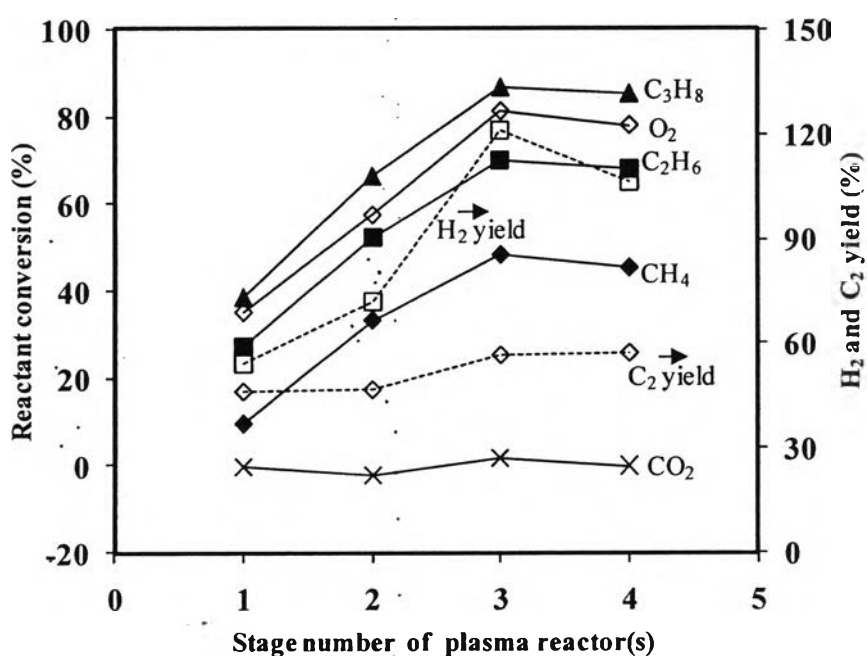
**Figure 4.15** Effect of stage number of plasma reactors on power consumptions for reforming of natural gas with pure  $O_2$  addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

#### 4.2.1.2 Effect of Residence Time at Constant Feed Flow Rate

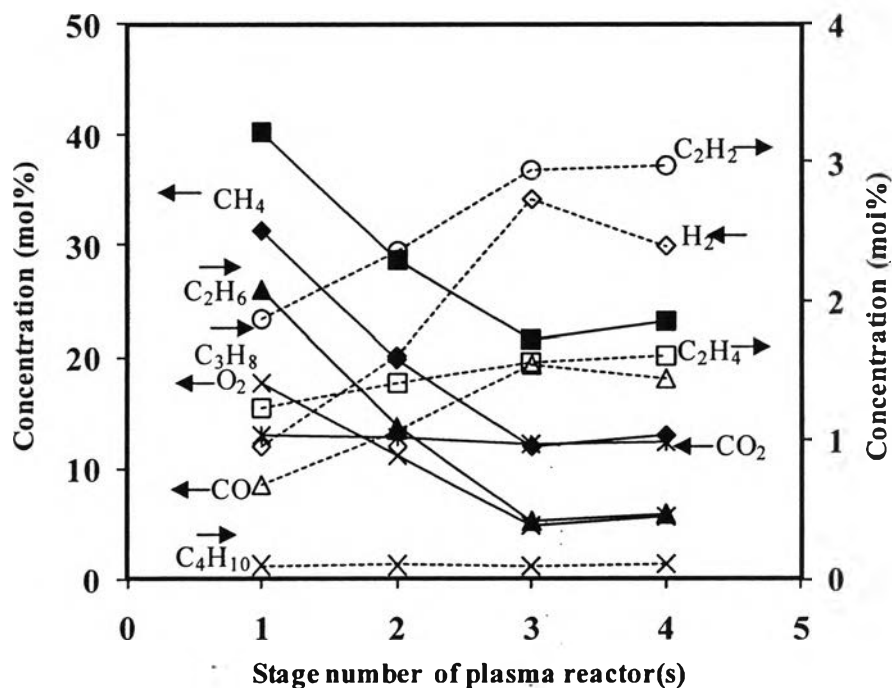
##### 4.2.1.2.1 Effect on reactant conversion and product yield

As shown in Figure 4.16, the conversion of all reactants, except  $CO_2$ , considerably increased when the stage number of plasma reactors was increased from 1 to 3 stages, and remained almost unchanged with further increasing stage number to 4 stages, probably due to the small amounts of oxygen active species left, which can be clearly confirmed from the outlet gas concentration, as shown in Figure 4.17. For the  $CO_2$  conversion, the minus value of the  $CO_2$  conversion at the HCs/ $O_2$  molar ratio of 2/1 was observed. It can be explained that the formation rate of  $CO_2$  by the hydrocarbon oxidation is higher than the  $CO_2$  consumption rate by the reforming reactions (Rueangjitt *et al.*, 2008). The  $H_2$  yield also significantly increased with increasing stage number of plasma reactors to reach the maximum at 3 stages, and after that it greatly decreased. In the meantime, the  $C_2$  yield slightly increased with increasing stage number. Moreover,

the  $H_2$  yield was found to be much higher than the  $C_2$  yield. At the 3 stages of plasma reactors, the most significant difference between  $H_2$  and  $C_2$  yields was noticed. This implies that at higher stage number of plasma reactors up to 3 stages, the production of  $H_2$  via the dehydrogenation reactions occurs more favorably than the production of  $C_2$  via the coupling reactions. However, at much higher stage number of 4 stages, the less  $H_2$  production due to less reactant conversion, as well as its higher consumption for hydrogenation reactions, might occur instead.



**Figure 4.16** Effect of stage number of plasma reactors on reactant conversions and product yields for reforming of natural gas with pure  $O_2$  addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate,  $125 \text{ cm}^3/\text{min}$ ).

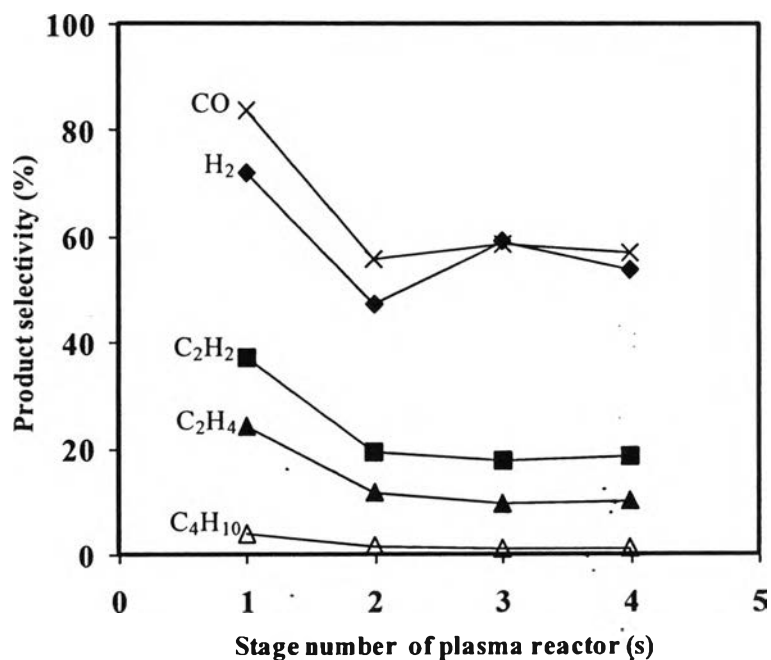


**Figure 4.17** Effect of stage number of plasma reactors on concentrations of outlet gases for reforming of natural gas with pure O<sub>2</sub> addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).

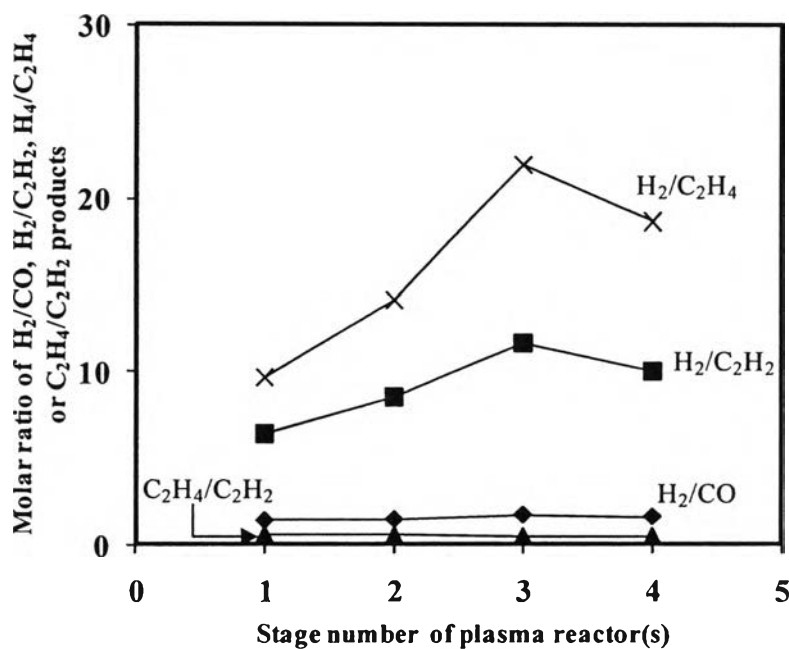
#### 4.2.1.2.2 Effect on product selectivity

All of product selectivities gradually decreased with increasing stage number of plasma reactors, as illustrated in Figure 4.18. The decreased selectivity for CO is due to the fact that with increasing stage number of plasma reactors, the residence time is enhanced. Therefore, CO has more opportunity to oxidize to CO<sub>2</sub> when increasing stage number of plasma reactors and accordingly the residence time. However, the outlet concentration of CO<sub>2</sub>, as shown in Figure 4.17, was almost unchanged probably because of the equivalent rates of formation and consumption of CO<sub>2</sub>. Moreover, the declines of other product selectivities when increasing stage number from 1 to 2 stages were affected from the extraction of oxygen-active species in the system. As presented in Figure 4.19, the molar ratio of H<sub>2</sub>/C<sub>2</sub> products dramatically increased with increasing stage number from 1 to 3 stages and then decreased when the stage number of plasma reactors was further

increased, whereas the  $H_2/CO$  molar ratio did not much change. These also imply that the dehydrogenation and coupling reaction were favorable to take place at high residence time, but not higher than 3.29 s at 3 stages.



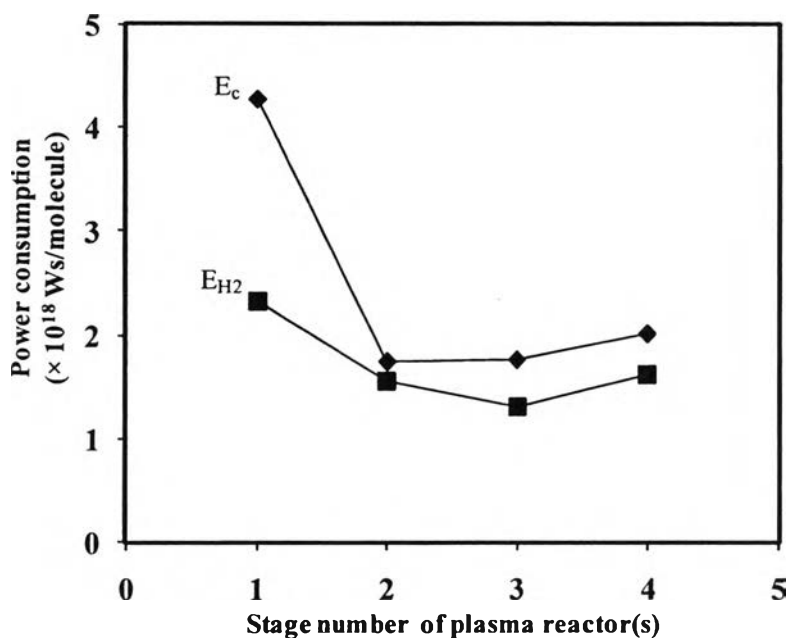
**Figure 4.18** Effect of stage number of plasma reactors on product selectivities for reforming of natural gas with pure  $O_2$  addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate,  $125 \text{ cm}^3/\text{min}$ ).



**Figure 4.19** Effect of stage number of plasma reactors on product molar ratios for reforming of natural gas with pure O<sub>2</sub> addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).

#### 4.2.1.2.3 Effect on power consumption

The power consumption per hydrocarbon converted rapidly declined with increasing stage number of reactors from 1 to 2 stages, and after that it remained almost constant, as depicted in Figure 4.20. Moreover, the power consumption per molecule of hydrogen produced dropped until the 3 stages, and then it slightly increased at the 4 stages. The optimum power consumptions were observed about  $1.75 \times 10^{-18}$  Ws (10.93 eV) per molecule of hydrocarbon converted at 2 stage numbers of plasma reactors and  $1.31 \times 10^{-18}$  Ws (8.15 eV) per molecule of hydrogen produced at 3 stages of plasma reactors.



**Figure 4.20** Effect of stage number of plasma reactors on power consumptions for reforming of natural gas with pure  $O_2$  addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate,  $125 \text{ cm}^3/\text{min}$ ).

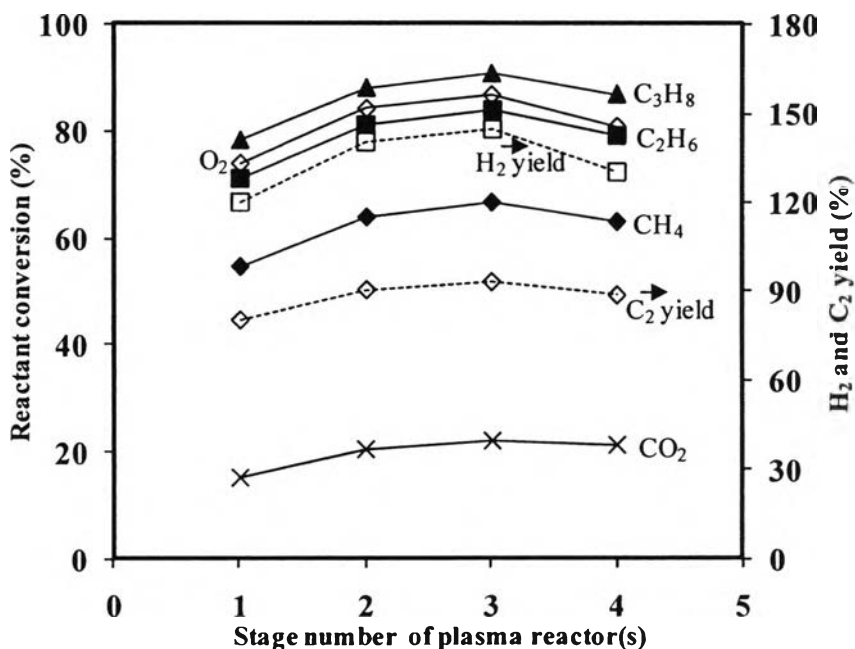
#### 4.2.2 Reforming of Natural Gas with Partial Oxidation by Using Air

##### 4.2.2.1 Effect of Feed Flow Rate at Constant Residence Time

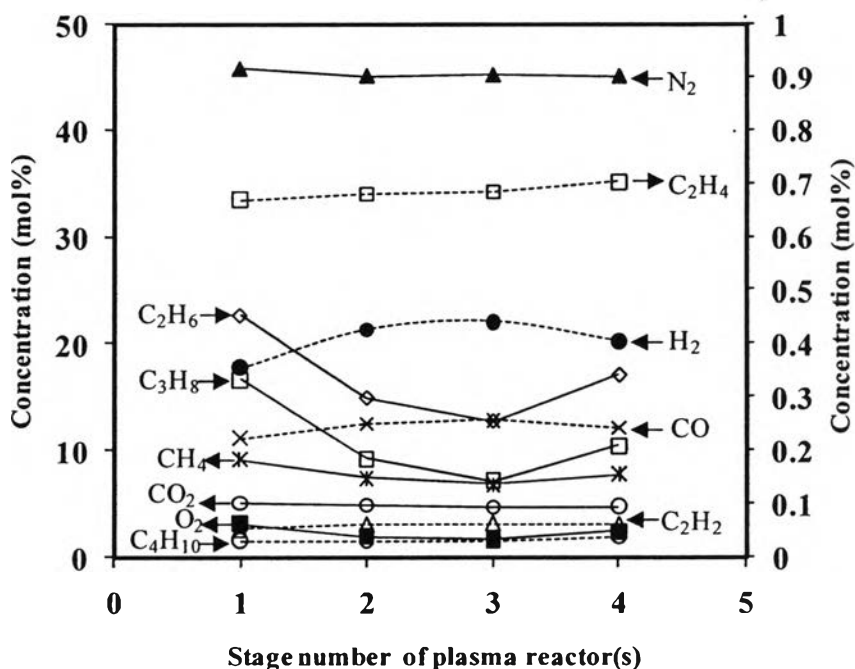
###### 4.2.2.1.1 Effect on reactant conversion and product yield

The conversions of all reactants slightly increased with increasing stage number from 1 to 3 stages, like the yields of  $H_2$  and  $C_2$ , as presented in Figure 4.21. These suggest that the increase in all reactant conversions at 2-3 stages of plasma reactors may be because some highly energetic products and active species, which were generated in the plasma zone of the first stage, easily induced further reactions in the successive stages, resulting in the higher conversions. However, at the 4 stages, the conversions adversely decreased. This may be proposed that the backward reactions of some products may take place. In contrast, the  $CO_2$  conversion slightly increased when the stage number of plasma reactors was increased. The concentrations of outlet gases shown in Figure 4.22 also well agree with the values of conversions.





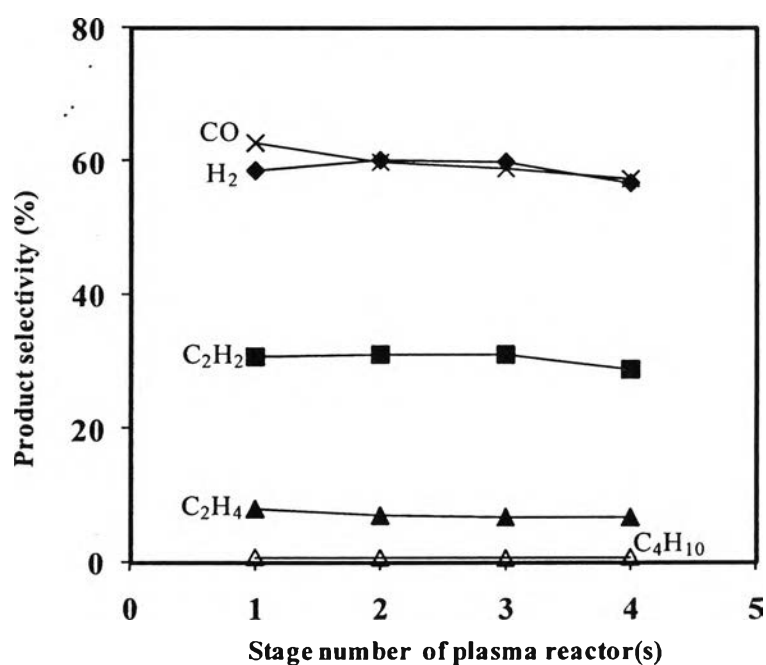
**Figure 4.21** Effect of stage number of plasma reactors on reactant conversions and product yields for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).



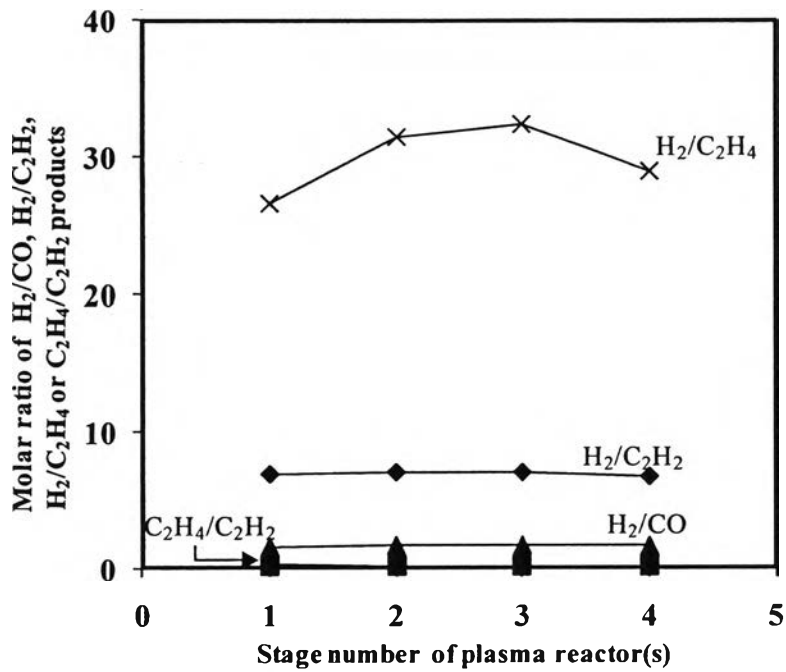
**Figure 4.22** Effect of stage number of plasma reactors on concentrations of outlet gases for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

#### 4.2.2.1.2 Effect on product selectivity

The selectivities for  $C_2H_2$ ,  $C_2H_4$ , and  $C_4H_{10}$  were nearly unchanged while the selectivity for CO slightly declined, with increasing stage number of plasma reactors, as shown in Figure 4.23. It can be explained that increasing the stage number of plasma reactors resulted in less opportunity of CO formation, causing from the less availability of O active species. For the molar ratio of  $H_2/C_2H_4$  shown in Figure 4.24, it increased with the stage number of plasma reactors from 1 to 3 stages; however, after that it tended to decrease. This suggests that the oxidative dehydrogenation of  $C_2H_4$  is likely to occur, leading to the increase in the  $H_2$  selectivity with increasing stage number of plasma reactors from 1 to 3 stages, as shown in Figure 4.23.



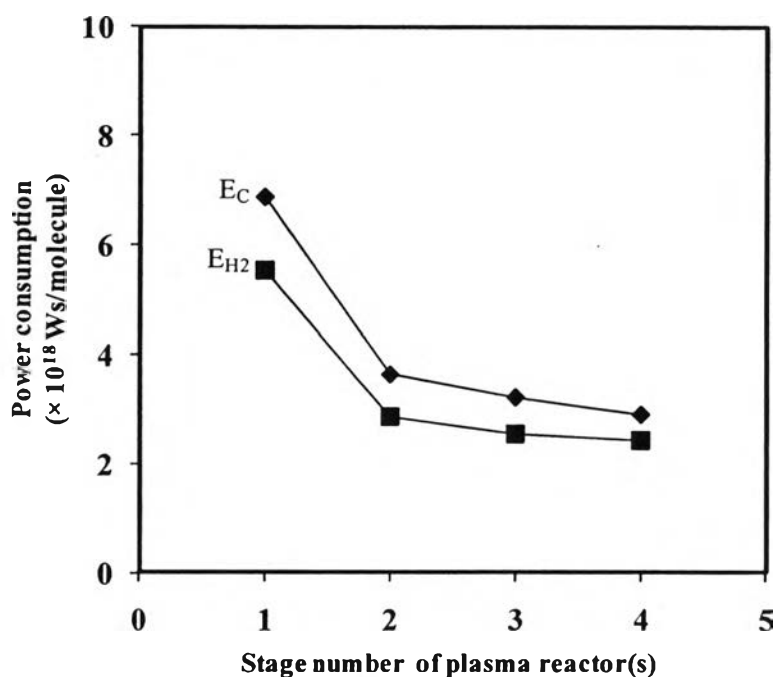
**Figure 4.23** Effect of stage number of plasma reactors on product selectivities for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).



**Figure 4.24** Effect of stage number of plasma reactors on product molar ratios for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

#### 4.2.2.1.3 Effect on power consumption

Figure 4.25 shows the same tendency of the power consumptions per hydrocarbon molecule converted and per hydrogen molecule produced, as previously observed. It was found that they tended to rapidly decline from 1 to 2 stages, but after that they became almost unchanged.

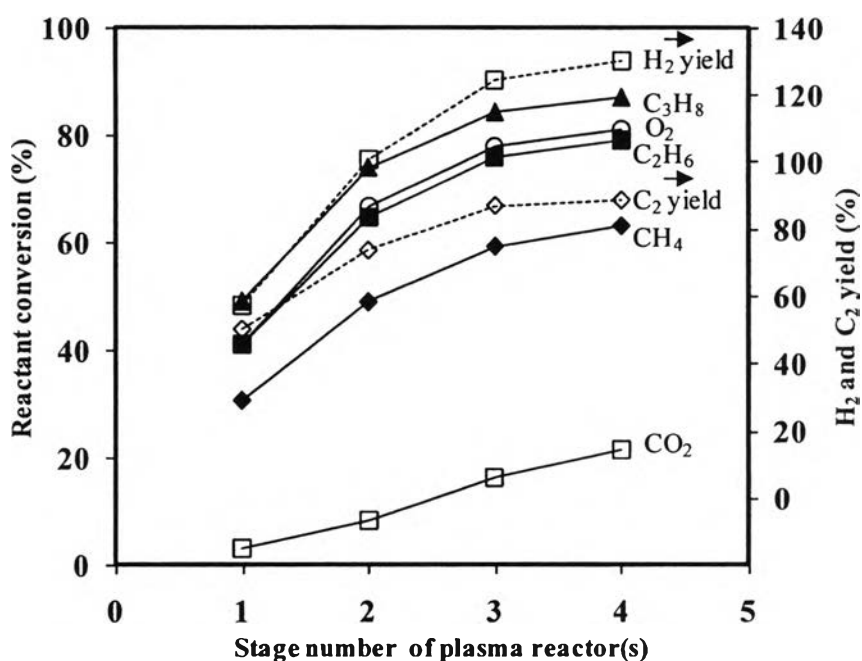


**Figure 4.25** Effect of stage number of plasma reactors on power consumptions for reforming of natural gas with air addition in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

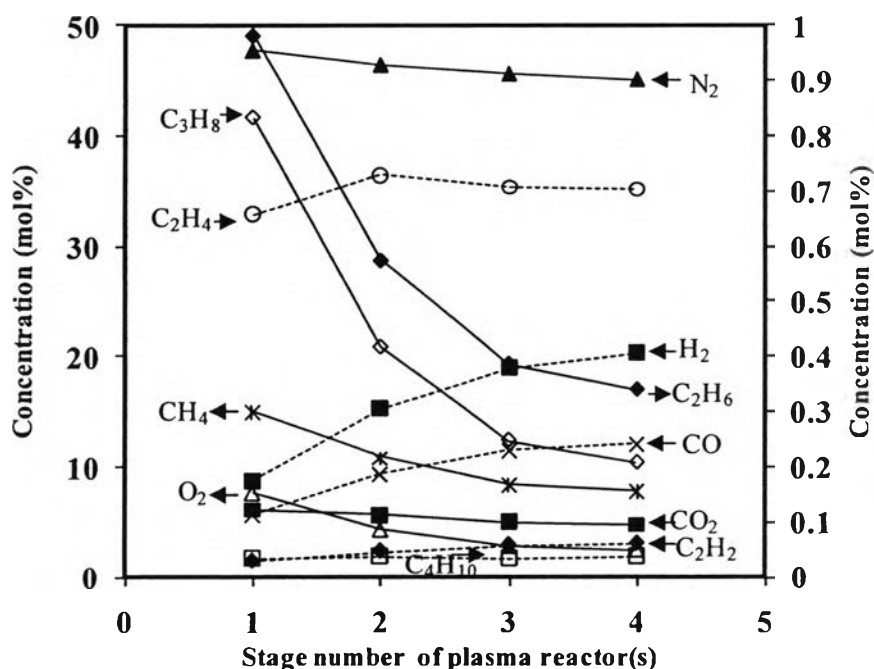
#### 4.2.2.2 Effect of Residence Time at Constant Feed Flow Rate

##### 4.2.2.2.1 Effect on reactant conversion and product yield

As depicted in Figure 4.26, both reactant conversions and product yields markedly increased as the stage number of plasma reactors was increased. It can be concluded that the higher stage number of plasma reactors or longer residence time allows more chance for highly energetic electrons to collide with reactants for subsequent reactions, leading to higher reactant conversions and product yields. It can be noticed that the  $H_2$  yield became much higher than the  $C_2$  yield at a higher stage number of plasma reactors, indicating that the dehydrogenations and oxidative dehydrogenations to produce hydrogen are more favorable to occur than the coupling reactions at a longer residence time. Moreover, the concentrations of outlet gases are depicted in Figure 4.27. It can be described that the outlet concentrations of  $C_2H_6$  and  $C_3H_8$  tremendously dropped when the stage number of plasma reactors increased, corresponding to their conversions.



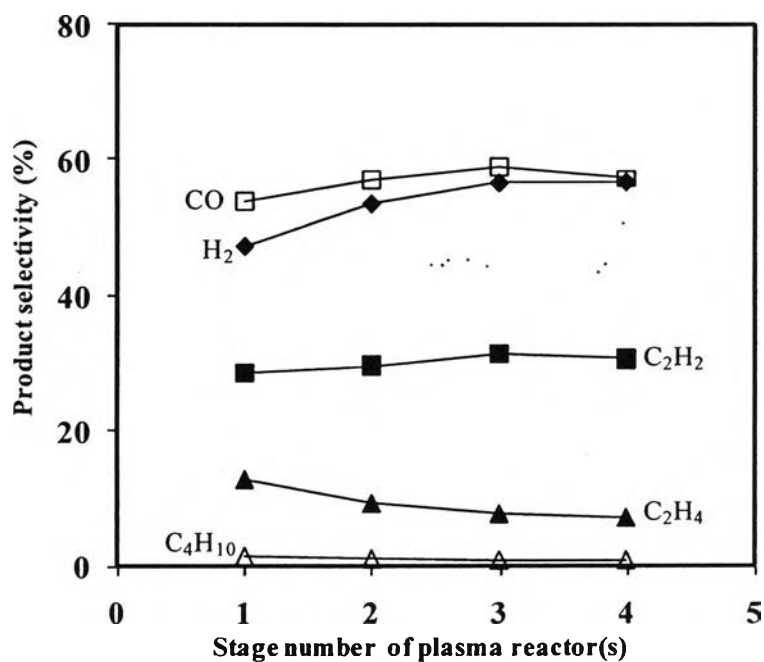
**Figure 4.26** Effect of stage number of plasma reactors on reactant conversions and product yields for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).



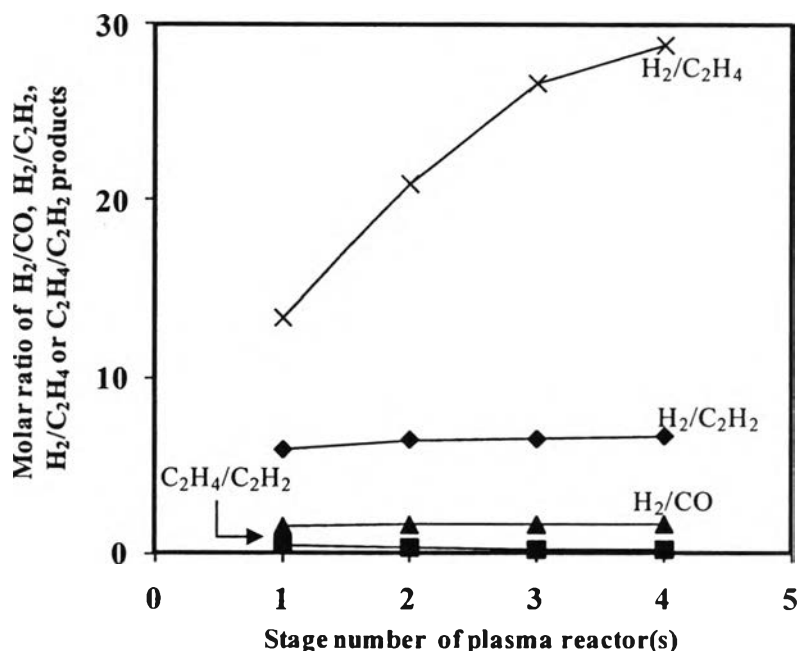
**Figure 4.27** Effect of stage number of plasma reactors on concentrations of outlet gases for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).

#### 4.2.2.2.2 Effect on product selectivity

The selectivities for CO, H<sub>2</sub>, and C<sub>2</sub>H<sub>2</sub> slightly increased with increasing stage number of plasma reactors, whereas the selectivity for C<sub>2</sub>H<sub>4</sub> tended to decrease, and the selectivity for C<sub>4</sub>H<sub>10</sub> remained unchanged, as shown in Figure 4.28. Figure 4.29 shows the rapid increase in the molar ratio of H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub>, while the molar ratios of the others nearly unchanged. These results can be explained in that with increasing stage number of plasma reactors, the oxidative dehydrogenation reactions more favorably occur, as previously stated.



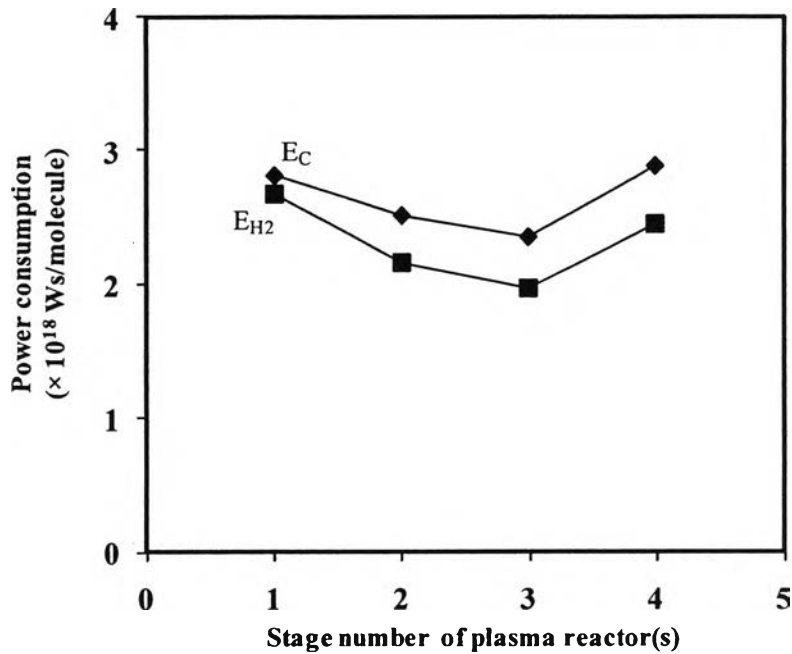
**Figure 4.28** Effect of stage number of plasma reactors on product selectivities for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).



**Figure 4.29** Effect of stage number of plasma reactors on product molar ratios for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).

#### 4.2.2.2.3 Effect on power consumption

The power consumptions are presented in Figure 4.30. The decreases in the power consumptions both per hydrogen molecule produced and per hydrocarbon molecule converted were obtained with increasing stage number of plasma reactors from 1 to 3 stages, but beyond 3 stages, they conversely increased. The optimum power consumptions were  $1.96 \times 10^{-18}$  Ws (12.26 eV) per molecule of hydrogen produced and  $2.36 \times 10^{-18}$  Ws (14.73 eV) per molecule of hydrocarbon converted at the 3 stages of plasma reactors. At the 4 stages, the higher power consumptions were observed due to less reactant conversion and too much input power, despite higher H<sub>2</sub> production as compared with the 3 stages of plasma reactors.



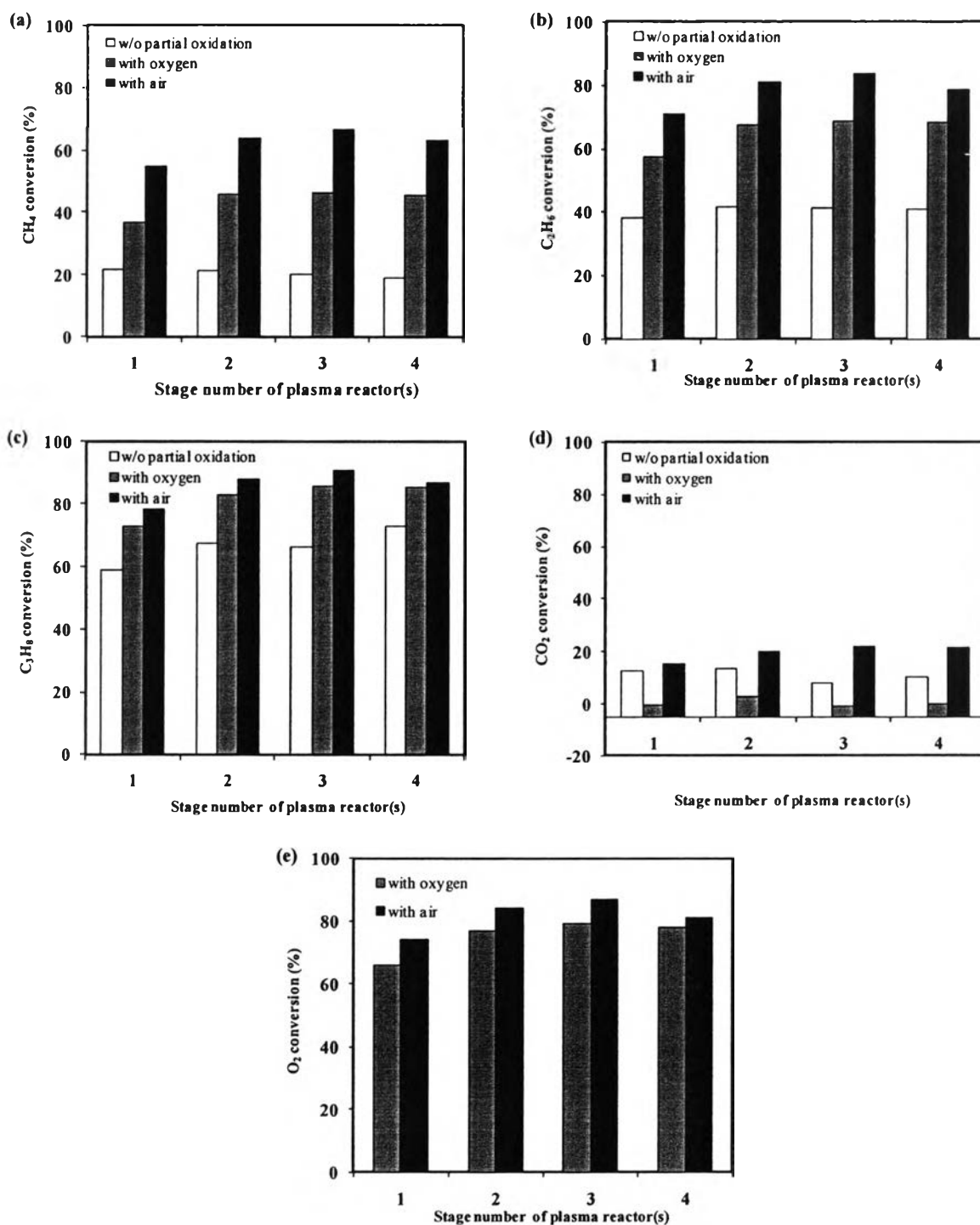
**Figure 4.30** Effect of stage number of plasma reactors on power consumptions for reforming of natural gas with air addition in the case of varying residence time (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and feed flow rate, 125 cm<sup>3</sup>/min).

### 4.3 Comparison of Reforming of Natural Gas without and with Partial Oxidation Using either Oxygen or Air

Two series of systems with a constant residence time and a constant feed flow rate were so far investigated. Even though the system operated at a constant feed flow rate provided more distinguishable, but expectable, results than that operated at a constant residence time when changing the stage number of plasma reactors, the system operated at a constant residence time under different conditions without and with oxygen addition was more interesting for comparison. Therefore, to obtain more understanding, the comparative results of the CO<sub>2</sub>-containing natural gas reforming without and with addition of either pure oxygen or air at a constant residence time using the multistage plasma system are shown in Figures 4.31-4.34, under operating conditions of a fixed residence time of 4.38 s, an applied voltage of 17.5 kV, a frequency of 300 Hz, an electrode gap distance of 6 mm, and a HCs/O<sub>2</sub> molar ratio of 2/1 in the case of addition of pure oxygen or air as an oxygen source.

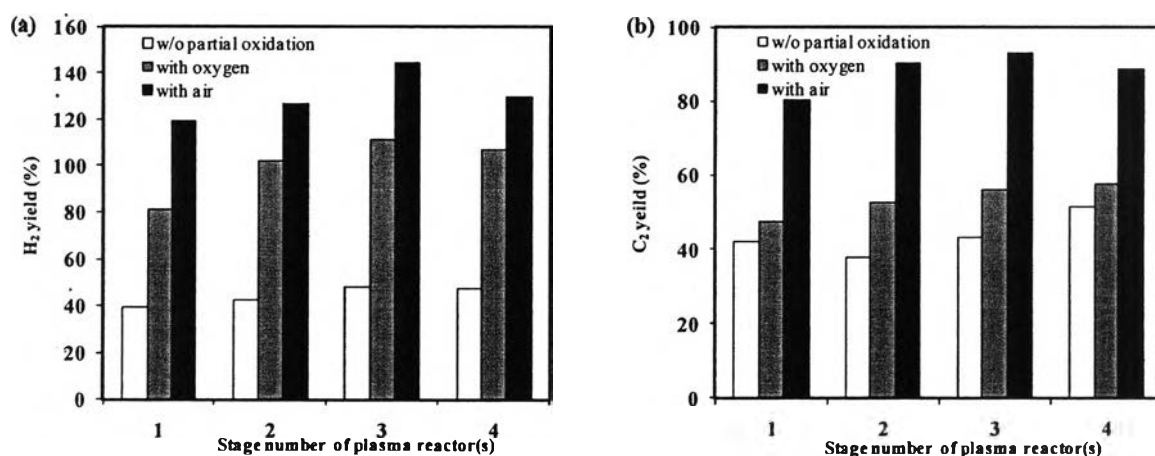


Figure 4.31 illustrates that the conversions of all reactants, except  $\text{CO}_2$ , increased substantially when oxygen was added into the natural gas feed because oxygen is believed to assist in improving the performance of the reaction, especially via the oxidative dehydrogenation to produce hydrogen. In comparison between the two oxygen sources, air provided a better process performance in terms of reactant conversions than pure oxygen. The results reveal that the addition of air in the feed potentially contributes the positive effect to the activation of reactant gases for the reforming of  $\text{CO}_2$ -containing natural gas. For the  $\text{CO}_2$  conversion in the case of adding pure oxygen, the comparatively low values at all stages of plasma reactors are plausibly because the formation rate of  $\text{CO}_2$  due to the complete hydrocarbon oxidations is higher than the consumption rate due to the plasma-induced dissociation reactions, as mentioned previously. It can be observed that the highest reactant conversions were attained at 3 stages of plasma reactors when using air as an oxygen source.



**Figure 4.31** Comparison of conversions of (a) CH<sub>4</sub>, (b) C<sub>2</sub>H<sub>6</sub>, (c) C<sub>3</sub>H<sub>8</sub>, (d) CO<sub>2</sub>, and (e) O<sub>2</sub> for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

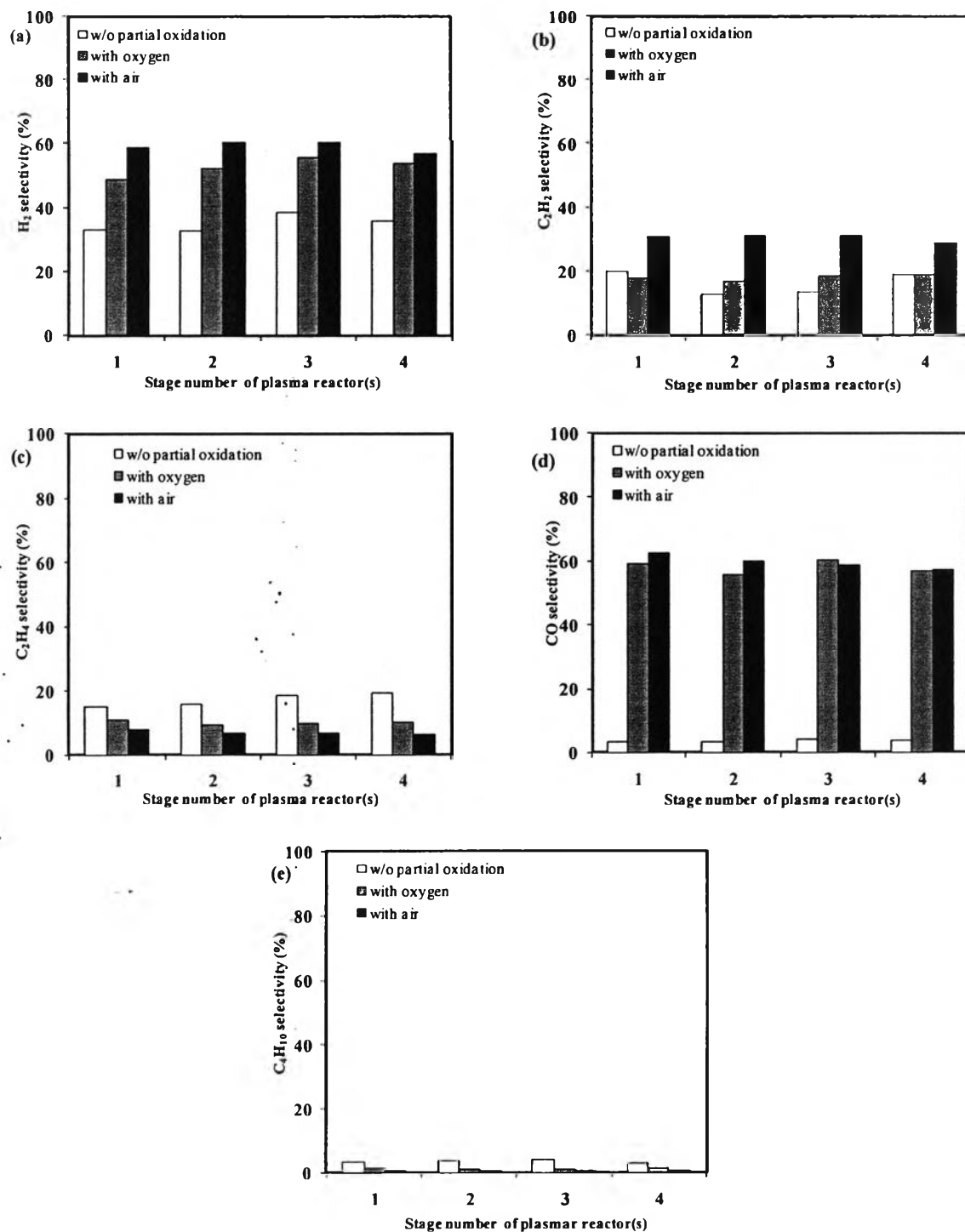
Regarding the results of  $H_2$  and  $C_2$  yields as presented in Figure 4.32, the system with oxygen addition provided higher product yields than the system without oxygen addition because the oxygen molecules can be easily activated by the plasma and provide the oxygen active species for extracting the H atom from the hydrocarbons, as aforementioned. Interestingly, for the case of adding oxygen, the results show that the use of air as an oxygen source also provided significantly higher product yields than that of pure oxygen. These could be explained in that nitrogen in air could possibly act as the third body in the reaction to receive the excessive energy of the products and make them stable. Therefore, it might bear the responsibility in promoting the plasma-chemical reactions. Moreover, the 3 stages of plasma reactors were clearly observed to provide the highest yields, an additional advantage to the highest reaction conversions as above mentioned.



**Figure 4.32** Comparison of yields of (a)  $H_2$  and (b)  $C_2$  for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38).

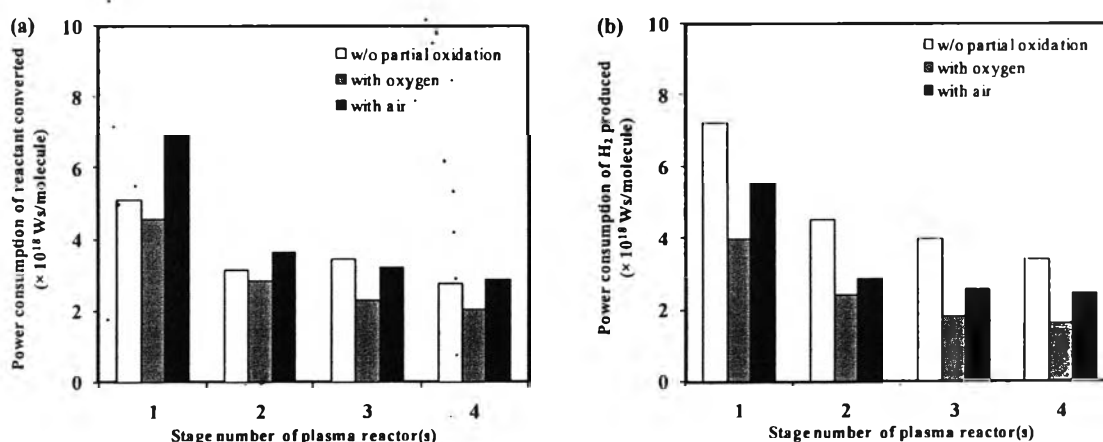
The product selectivities are comparatively shown in Figure 4.33. Most product selectivities, except  $C_2H_4$  and  $C_4H_{10}$ , significantly increased, especially for the CO selectivity, when adding both oxygen sources to the system. However, the addition of oxygen into the system did not provide the positive effect on the  $C_2H_4$  and  $C_4H_{10}$  selectivities because the presence of the oxygen active species led to more probability of the oxidative dehydrogenations of both reactants and intermediates to

form  $\text{H}_2$  and  $\text{C}_2\text{H}_2$  products instead of more saturated  $\text{C}_2\text{H}_4$  and  $\text{C}_4\text{H}_{10}$  products. Particularly, this might be the main reason in achieving more  $\text{H}_2$  formation under  $\text{O}_2$ -containing system. Moreover, when comparing the ability to induce the  $\text{H}_2$  formation between pure oxygen and air, it was clearly observed that using air as an oxygen source provided the superior performance.



**Figure 4.33** Comparison of selectivities for (a)  $H_2$ , (b)  $C_2H_2$ , (c)  $C_2H_4$ , (d) CO, and (e)  $C_4H_{10}$  for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

The power consumptions of the investigated systems are comparatively shown in Figure 4.34. The power consumption for converting reactant for the system with oxygen addition tended to become lower than that without oxygen addition at the stage numbers more than 3 stages. However, the power consumption for producing hydrogen for the system with oxygen addition was obviously lower than that without oxygen addition at all stage numbers of plasma reactors. When considering the power consumptions at higher stage numbers in the case of adding pure oxygen and air, even though using pure oxygen as an oxygen source consumed slightly lower power for the plasma system operation, the difference in both the power consumptions between the cases of two oxygen sources seemed to be plausibly insignificant and negligible due to their extremely small values.



**Figure 4.34** Comparison of power consumptions for combined reforming and partial oxidation of natural gas in the case of varying feed flow rate: (a) power consumption per reactant molecule converted, (b) power consumption per hydrogen molecule produced) (applied voltage, 17.5 kV; frequency, 300 Hz; electrode gap distance, 6 mm; and residence time, 4.38 s).

From these comparative results, it can be concluded that the addition of oxygen into the feed provided the positive effects on the reforming of  $CO_2$ -containing natural gas with not only enhancing the reactant conversions, the desired product yield and selectivity, but also consuming comparatively lower energy

consumption for producing hydrogen, as compared with the system without oxygen addition. In addition, the utilization of air as an oxygen source assisted in improving the reforming of CO<sub>2</sub>-containing natural gas more effectively than pure oxygen because it provided the better reactant conversions and better desired product yield and selectivity. Finally, from careful consideration of the overall results, it can also be reasonably concluded that the 3 stages of plasma reactors were satisfactorily sufficient to achieve excellent process performance. The operation with a higher stage number was not required due to the insignificant enhancement of the performance.