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Study of Hydrogen Production from Natural Gas by Autothermal Reforming

Nunticha Konchan[1], Supaporn Therdthianwong[1,*], Apichai Therdthianwong[2] and Navadol Laosiripojana[3]

[1]Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology Thonburi, Bangkok, Thailand

[2]Chemical Engineering Practice School (ChEPS), King Mongkut's University of Technology Thonburi, Bangkok, Thailand

[3]The Joint Graduate School of Energy and Environment (JGSEE), King Mongkut's University of Technology Thonburi,
Bangkok, Thailand

*Author to whom correspondence should be addressed, email: supaporn.the@kmutt.ac.th

Abstract: Hydrogen is the preferred feedstock for use in combining with oxygen in fuel cell. Processes for hydrogen production often use fuel oil as feedstock. In present, price of oil is highly increased so natural gas is given more attention. It consists mainly of methane (i.e. 80-95% CH_4), some higher hydrocarbons and carbon dioxide. In this work a primary study of utilization of natural gas in Thai gulf reservoir as a feedstock for hydrogen production by autothermal process was attempted. Aspen plus 10.2 simulation program was used to simulate the autothermal process and study for the effect of its operating condition. The operating parameters, temperature, water to carbon feed ratio (W:C) and oxygen to carbon feed ratio (O_2:C), were varied to evaluate their effects on changes in product composition. The temperature range of 400-800 °C, water to carbon feed ratio of 0.1-12.0 (mole ratio) and oxygen to carbon feed ratio of 0.01-2.5 (mole ratio), were investigated. The simulation results showed that the maximum H2 yield can be obtained at higher values of water to carbon ratio and lower range of oxygen to carbon ratio. Equilibrium analysis results also showed that autothermal reaction is a suitable process to produce hydrogen from natural gas for fuel cell. For mobile application, autothermal reactor should be operated at the thermal neutral condition by using the optimum conditions of 500 °C, W: C ratio of 4 and O_2: C ratio of 0.9.

Keywords: Natural Gas, Autothermal Reaction, Equilibrium, Hydrogen Production, Aspen Plus.

Introduction

Hydrogen is the one of the important gaseous raw materials for petroleum and petrochemical industries. In the near future, it will be transformed to electrical energy by "Fuel cell" for electrical vehicles and electrical power plants. Automotive fuel cells require hydrogen gas to operate. The most convenient way to obtain the gas would be the use an onboard fuel processor to convert or "reform" commonly [1]. Processes for hydrogen production often use fuel oil as feedstock. In present, cost of oil highly increases so that natural gas is considered to substitute. There are three major thermochemical reforming techniques used to produce hydrogen, i.e., steam reforming, partial oxidation and autothermal reforming [2]. The steam reforming is an endothermic catalytic process of light hydrocarbon with steam by using catalyst [3]. The steam reforming reactions for natural gas (assuming pure methane) are:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad \Delta H^{\circ}_{298} = 206 kJ/mol \quad (1)$$
$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \quad \Delta H^{\circ}_{298} = 165 kJ/mol \quad (2)$$

The partial oxidation is an exothermic process at high temperature.

$$CH_4 + 0.5O_2 \Leftrightarrow CO + 2H_2 \quad \Delta H^{\circ}_{298} = -36 kJ/mol \quad (3)$$
$$CH_4 + O_2 \Leftrightarrow CO_2 + 2H_2 \quad \Delta H^{\circ}_{298} = -319 kJ/mol \quad (4)$$

The autothermal reforming is a combination of steam reforming with partial oxidation reaction by feeding both water and oxygen into the reactor. These systems can be very productive, fast starting and compact, since the exothermic partial oxidation reaction can supply heat to steam reforming reaction directly [4].

$$2CH_4 + H_2O + 0.5O_2 \Leftrightarrow 2CO + 5H_2 \quad (5)$$
$$2CH_4 + 2H_2O + O_2 \Leftrightarrow 2CO_2 + 6H_2 \quad (6)$$

In this investigation, a primary study of utilization of natural gas in Thai gulf reservoir as a feedstock for hydrogen production by autothermal process was attempted. AspenPlus10.2 simulation program was used to simulate the autothermal process and study for the effect of its operating condition to maximize hydrogen yield as well as to minimize carbon-monoxide.

Simulation

Thermodynamics approach

The thermodynamic equilibrium in a reforming reactor can be calculated by two different methods, the use of equilibrium constant with specified possible multiple reaction and the minimizing Gibbs free energy methods [5]. In fuel-reforming reactor analysis the method of minimizing the Gibbs free energy is normally preferred. In this work, for given operating condition (reactant composition and inlet condition, reaction temperature and pressure), the equilibrium compositions of product gas containing H_2, CO, CO_2, CH_4 and H_2O have been calculated. This calculation can be made with any commercially available software. In this investigation, Aspen Plus® was used. In the simulation, 1 kmol/hr of natural gas, oxygen to carbon feed ratio and water to carbon feed ratio were directly fed into the reactor. The composition of natural gas from Thai Gulf reservoir is shown in Table 1. The objective of this work was to study the effect of operating parameters, temperature, water to carbon feed ratio (W:C) and oxygen to carbon feed ratio (O_2:C) on product gas compositions. These parameters are defined as follows:

$$\text{Water to carbon feed ratio (W:C)} = \frac{\textit{molar flow rate of water}}{\textit{carbon molar flow rate in natural gas}} \tag{7}$$

$$\text{Oxygen to carbon feed ratio } (O_2\text{:C}) = \frac{\textit{molar flow rate of oxygen}}{\textit{carbon molar flow rate in natural gas}} \tag{8}$$

Table 1 Composition of natural gas from Thai Gulf reservoir

Component	Mol%
CH_4	67.39
C_2H_6	9.33
C_3H_8	5.15
i-C_4H_{10}	1.16
n-C_4H_{10}	1.06
i-C_5H_{12}	0.34
n-C_5H_{12}	0.19
C_6H_{14}	0.18
CO_2	14.26
N_2	0.94
H_2S	>10-20 ppm
H_2O	-

Sensitivity analysis [6,7]

Sensitivity blocks of AspenPlus 10.2 was used to analyze the effect of operating variables of the process that generates a matrix of manipulated variables versus sampled variables. If there is more than one manipulated variable, the sensitivity analysis is performed for each combination of manipulated variables.

In sensitivity analysis tools, the studying parameters were varied as followed: the reaction temperature increased from 400 to 800 °C with a step change of 100°C, oxygen to carbon feed ratio was in the range of 0.01-2.5 with a step change of 0.1 and water to carbon feed ratio increased from 0.1 to 12.0 with a step change of 0.5 while keeping the reaction pressure at 1 bar. The conversion of natural gas is defined as follows:

$$\text{Conversion } CH_4 = \frac{(CH_4)_{in} - (CH_4)_{out}}{(CH_4)_{in}} \tag{9}$$

Gas products, H_2, CO, CO_2, CH_4 and H_2O, can be considered in terms of product yields defined as mole of component *x* per mole of carbon component in feed as follows:

$$X\ yield = \frac{\textit{mole flowrate of component x in product}}{\textit{mole flowrate of carbon in feed}} \tag{10}$$

Simulation Results and Discussion

Methane conversion in autothermal reactor

Fig.1-5 show three-dimensional plots of methane conversion as a function of water to carbon feed ratio and oxygen to carbon feed ratio at five different temperatures of 400, 500, 600, 700, and 800 °°C, respectively.

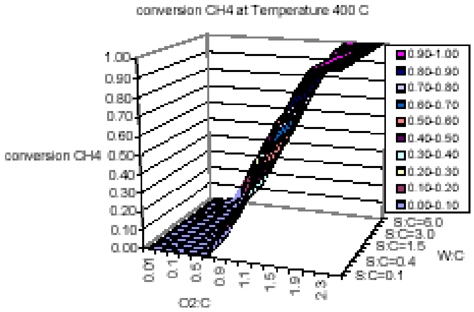


Fig. 1 Effect of oxygen to carbon ratio and water to carbon ratio on methane conversion at temperature 400 °C.

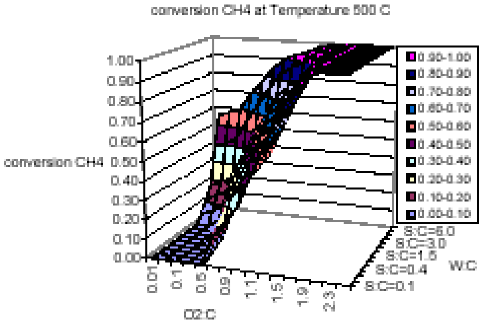


Fig. 2 Effect of oxygen to carbon ratio and water to carbon ratio on methane conversion at temperature 500 °C.

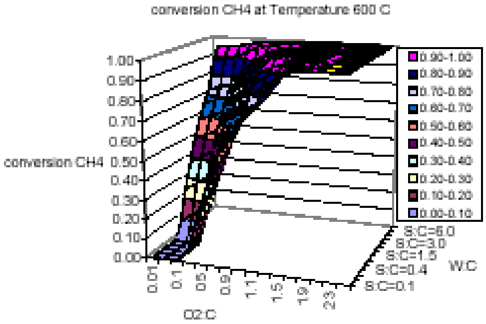


Fig. 3 Effect of oxygen to carbon ratio and water to carbon ratio on methane conversion at temperature 600 °C.

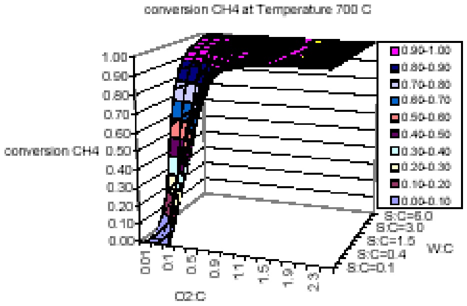


Fig. 4 Effect of oxygen to carbon ratio and water to carbon ratio on methane conversion at temperature 700 °C.

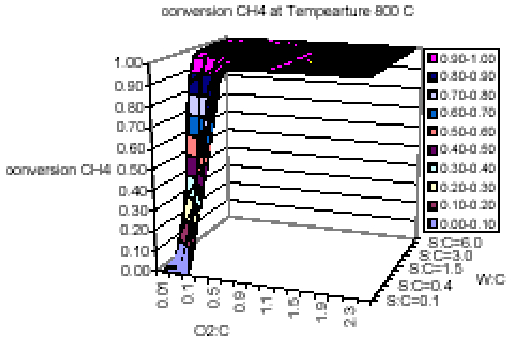


Fig. 5 Effect of oxygen to carbon ratio and water to carbon ratio on methane conversion at temperature 800 °°C.

For all analyzed temperatures, CH_4 conversion increases when O_2:C and W:C increase. It must be noted that in low temperature range, higher O_2:C ratios are required for complete CH_4 conversion. On the contrary, at the reaction temperature of 800 °°C the CH_4 conversion is always greater than 0.9 as O_2:C is higher than 0.6. The high CH_4 conversion region is large when the temperature rises especially at temperature higher than 600 °°C. By comparing between these two operating parameters, O_2:C ratio has more influence on CH_4 conversion than W:C ratio except in low reaction temperature range (< 600 °°C). At higher temperature (800 °°C), CH4 is converted almost 100% not depending on W:C ratio when O_2: C ratio is higher than 0.5.

Effect of operating parameters on gas product compositions

Equilibrium compositions of autothermal reformed gas obtained from the simulation have been shown that only light products at equilibrium, H_2, CO, CO_2, CH_4 and H_2O, were produced whereas higher molecular weight hydrocarbons, i.e. C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12} and C_6H_{14} were completely converted to lower molecular weight gases. The effect of operating parameters (temperature, W:C ratio and O_2:C feed ratio) on equilibrium gas products can be considered from equation (10).

Fig. 6 shows the autothermal equilibrium percent yield of hydrogen (H_2 yield) at operating temperature of 600 °°C. The maximum H_2 yield is observed at lower value of O_2:C ratio and higher value of W:C ratio. At this condition, the reforming reaction is dominant. At higher W:C ratio, the H2 yield is decreased as O_2:C ratio increases since the H_2 gas product is further reacted with excess O_2 to form water (see Fig.7) according to the combustion reaction as follows:

$$H_2 + 0.5O_2 \Leftrightarrow H_2O \qquad (exothermic) \qquad\qquad (11)$$

However, at lower W:C ratio, the O_2:C ratio has the optimum value in which the maximum H_2 yield is obtained. Starting from the lower O_2:C ratio, partial oxidation reaction of hydrocarbon is enhanced as O_2:C ratio increases resulting in the increase of H_2 yield. Further increase of O_2:C ratio promotes total oxidation of H_2 and diminishes H_2 yield as in the above equation. Among the hydrocarbon in natural gas, methane is the only hydrocarbon component that exists in the equilibrium as illustrated in Fig. 8. The methane yield (CH_4 yield) decreases when both W: C ratio and O_2: C ratio increase. It can be seen that the CH_4 yield falls abruptly at W: C ratio and O_2: C ratio higher than 0.5 and 0.3, respectively.

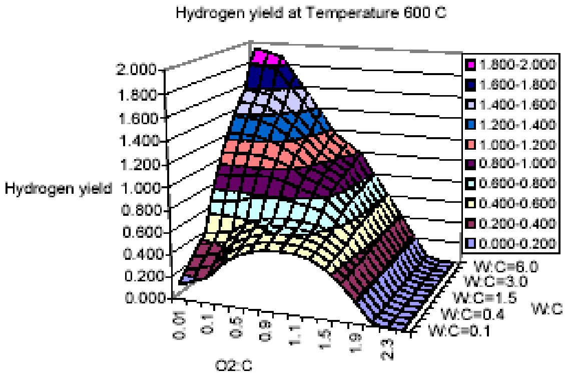


Fig. 6 Effect of oxygen to carbon ratio and water to carbon ratio on hydrogen yield at temperature 600 °C.

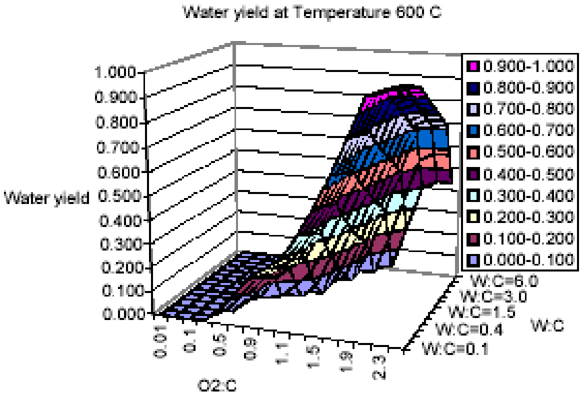


Fig. 7 Effect of oxygen to carbon ratio and water to carbon ratio on water yield at temperature 600 °°C.

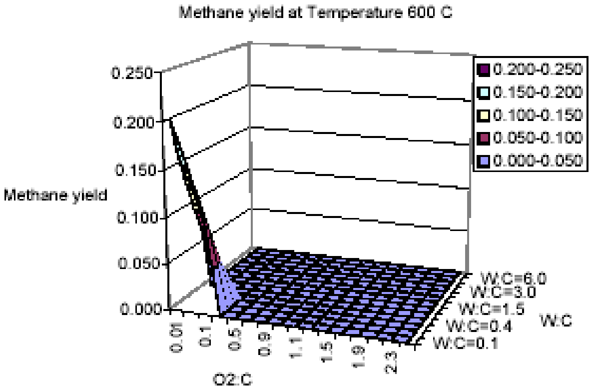


Fig. 8 Effect of oxygen to carbon ratio and water to carbon ratio on methane yield at temperature 600 °°C.

In addition to CH_4 and H_2, the oxygenated components, CO and CO_2, are also the main components in reforming gas as displayed in Fig. 9 and 10, respectively. The carbon-dioxide production evolves inversely to the carbon-monoxide one. As O_2:C ratio increases, the CO_2 yield increases with the corresponding decrease of CO yield. This is because of the oxidation reaction of CO as follows:

$$CO + 0.5O_2 \Leftrightarrow CO_2 \qquad (12)$$

Fig.10 also indicates that CO yield is reduced as the W:C ratio increases. This can be explained by the water-gas shift reaction.

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (endothermic) \qquad (13)$$

As the amount of H_2O increases, the equilibrium is shifted to the right hand side of eq.(13). Hence, the H_2 production is promoted as confirmed in Fig.8.

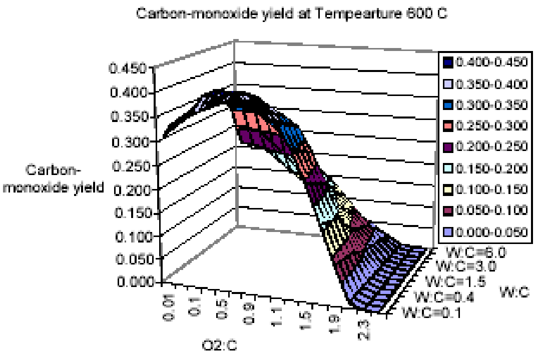


Fig. 9 Effect of oxygen to carbon ratio and water to carbon ratio on carbon-monoxide yield at temperature 600 °C.

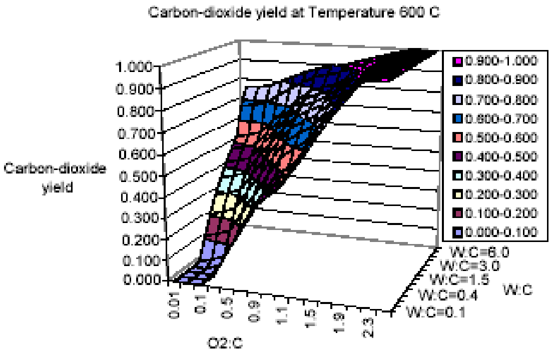


Fig. 10 Effect of oxygen to carbon ratio and water to carbon ratio on carbon-dioxide yield at temperature 600 °C.

Unlike steam reforming reaction, autothermal reaction does not require external heat supply since both water and oxygen are fed with fuel to the reactor. All of the heat for steam reforming reaction is provided by partial oxidation (POX) of fuel. So no complex heat management engineering is required which makes autothermal process very attractive for mobile application.

In the simulation method, the reactor in the model was run with isothermal mode in order to study the effect of reaction temperature. To find the conditions of thermal neutral point, heat duty of the reactor for each case must be plotted, as shown the example of 600 ºC case in Fig.11.

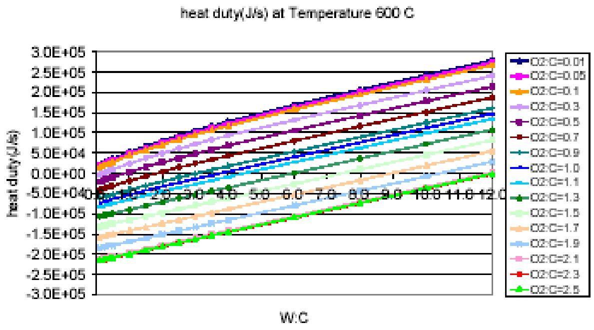
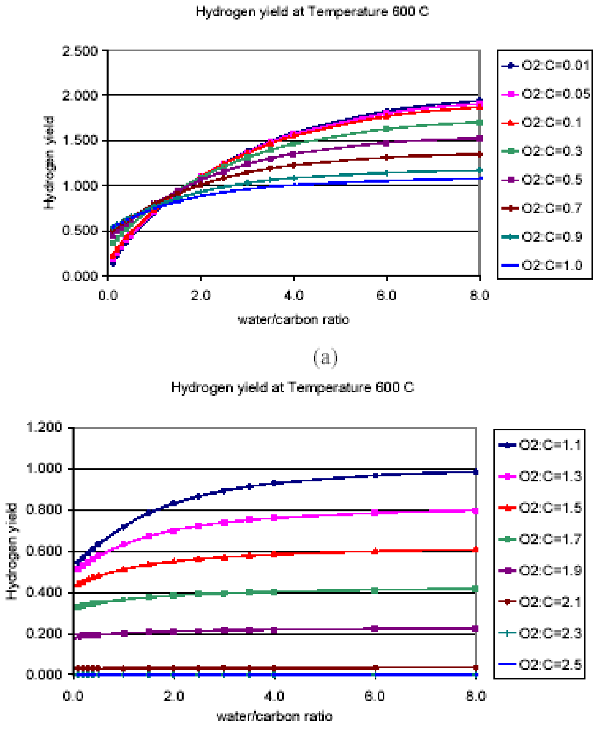


Fig. 11 Effect of oxygen to carbon ratio and water to carbon ratio on heat duty at temperature 600 °°C.

From Fig. 11, as water to carbon feed ratio is increased, heat duty of the reactor has more positive number indicating that more steam reforming (SR) is occurred (see Fig.11). On the other hand, the heat duty approaches the negative values as oxygen to carbon feed ratio increases since the partial oxidation reaction is an exothermic reaction.

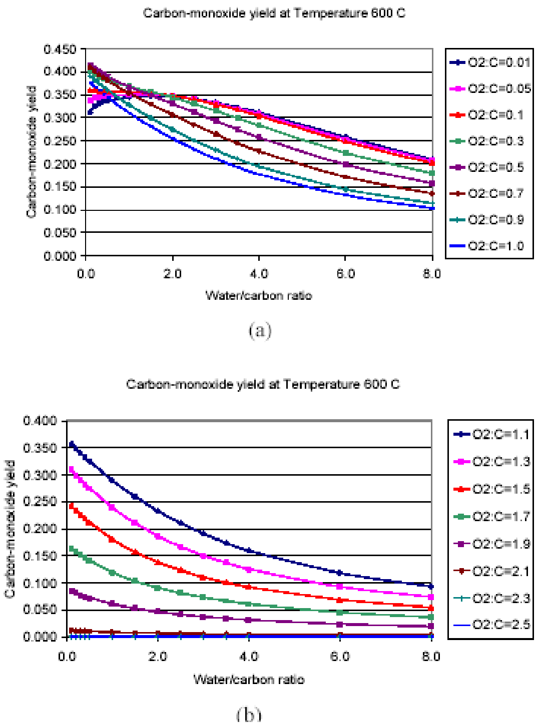
The balance of heat consuming by steam reforming reaction and heat generating by partial oxidation reaction occurs at the thermal neutral point which is located at the intersection between heat duty curve and the abscissa. Therefore for each O_2:C feed ratio condition, the W:C feed ratio at the neutral point can be specified from Fig. 11. The corresponding H_2 and CO yield at the neutral point can be determined from Fig.12 and Fig.13, respectively. This method was used in the same manner at all temperature values studied. The results are concluded in Table 2.



(a)

(b)

Fig. 12 Effect of oxygen to carbon ratio (a) O_2:C =0.01-1.0 and (b) O_2:C=1.1-2.5 and water to carbon ratio on hydrogen yield at temperature 600 °C.



(a)

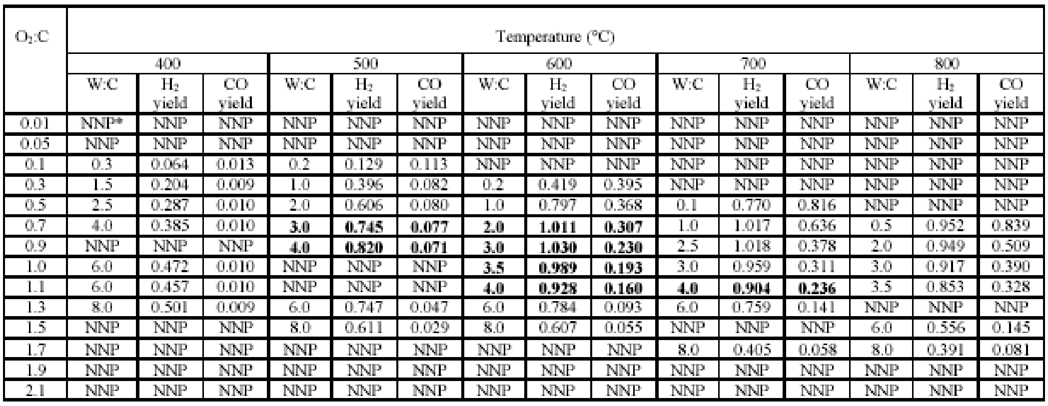
(b)

Fig. 13 Effect of oxygen to carbon ratio (a) O_2:C = 0.01-1.0 and (b) O_2:C = 1.1-2.5 and water to carbon ratio on carbon- monoxide yield at temperature 600 °C.

For the fuel cell application, hydrogen is the most preferable product among all reformed gas. Since the anode of the proton exchange membrane fuel cell (PEMFC) can not tolerate carbon-monoxide which is a component in the reformed gas. Therefore, another objective is to determine an optimum operating regime (optimal W:C and O_2:C ratio) that can maximize the hydrogen yield with the lowest possible carbon-monoxide production under the desirable equilibrium temperature.

Table 2 illustrates that for all W:C ratio under the neutral condition, there exists a range for maximum H_2 yield between

Table 2 Thermal neutral points of autothermal reactor



O_2:C	Temperature (°C)														
	400			500			600			700			800		
	W:C	H_2 yield	CO yield	W:C	H_2 yield	CO yield	W:C	H_2 yield	CO yield	W:C	H_2 yield	CO yield	W:C	H_2 yield	CO yield
0.01	NNP*	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP
0.05	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP
0.1	0.3	0.064	0.013	0.2	0.129	0.113	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP
0.3	1.5	0.204	0.009	1.0	0.396	0.082	0.2	0.419	0.395	NNP	NNP	NNP	NNP	NNP	NNP
0.5	2.5	0.287	0.010	2.0	0.606	0.080	1.0	0.797	0.368	0.1	0.770	0.816	NNP	NNP	NNP
0.7	4.0	0.385	0.010	**3.0**	**0.745**	**0.077**	**2.0**	**1.011**	**0.307**	1.0	1.017	0.636	0.5	0.952	0.839
0.9	NNP	NNP	NNP	**4.0**	**0.820**	**0.071**	**3.0**	**1.030**	**0.230**	2.5	1.018	0.378	2.0	0.949	0.509
1.0	6.0	0.472	0.010	NNP	NNP	NNP	**3.5**	**0.989**	**0.193**	3.0	0.959	0.311	3.0	0.917	0.390
1.1	6.0	0.457	0.010	NNP	NNP	NNP	**4.0**	**0.928**	**0.160**	**4.0**	**0.904**	**0.236**	3.5	0.853	0.328
1.3	8.0	0.501	0.009	6.0	0.747	0.047	6.0	0.784	0.093	6.0	0.759	0.141	NNP	NNP	NNP
1.5	NNP	NNP	NNP	8.0	0.611	0.029	8.0	0.607	0.055	NNP	NNP	NNP	6.0	0.556	0.145
1.7	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	8.0	0.405	0.058	8.0	0.391	0.081
1.9	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP
2.1	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP	NNP

*NNP = no neutral point

Acknowledgements

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References

[1] http://www.crc.dicp.ac.cn/eth.pdf

[2] Chan, S.H. and Wang, H.M., (2000), Effect of natural gas composition on autothermal fuel forming products, *Fuel Processing Technology,* **64***,* pp. 221-239.

[3] Heinzel, A. and Vogel, B., (2002), Reforming of natural gas- hydrogen generation for small scale stationary fuel cell system, *Power Sources*, **105**, pp. 202-207. 4] Bijan F.Hagh, Optimization of autothermal reactor for maximum hydrogen production, *Hydrogen Energy*, *In press*.

[5] Seo, Y.-S. and Shirley, A., (2002), Evaluation of thermodynamically favourable operating conditions for production of hydrogen in three different reforming technologies, *Power Sources*, **108,** pp. 213-225.

[6] Aspen plus help, Aspen plus version 10.2.1, Aspen Technology, Inc., Cambridge, MA, USA, (2000).

[7] Khoshnoodi, M. and Lim, Y.S., (1997), Simulation of partial oxidation of natural gas to synthesis gas using ASPEN PLUS, *Fuel Processing Technology,* **50**, pp. 275-289.