



# Thermodynamic equilibrium composition analysis of methanol autothermal reforming for proton exchanger membrane fuel cell based on FLUENT Software

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## ABSTRACT

Methanol autothermal reforming was thermodynamically analyzed using FLUENT software. The calculation methodology using this software is simple and convenient, and its validity was confirmed by comparing the obtained data with previous studies. As a function of the effects of temperature, pressure, molar steam-to-carbon ratio (S/C), and molar oxygen-to-carbon ratio (O/C) on the objective products, favorable operational parameters were evaluated, under which H<sub>2</sub> yield maximizes, the CO molar fraction minimizes and carbon deposition can be eliminated. The equilibrium constants of the possible reactions involved in oxidative methanol steam reforming, coupled with the reaction mechanism for the entire investigated temperature range, were elucidated and discussed. On the basis of the concluded possible mechanisms, three areas are inferred. In each individual area, H<sub>2</sub> or CO yield reached a maximum, or solid C was efficiently suppressed. Therein, a favorable operational range is proposed to assure the most optimized product yield.

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## 1. Introduction

Increasing environmental awareness and the associated development of fuel cell technologies has directed greater attention to fuel processing technologies for hydrogen generation. Presently, hydrogen refueling stations are rare, and do not have the ubiquitous infrastructure available to gasoline, diesel-fuel, and natural gas fueling technologies. Furthermore, the complex compositions of these petroleum products, specifically their sulfur content, hinder their application as feedstocks for generating hydrogen, especially in countries like China. Natural gas has a higher hydrogen-to-carbon ratio (H/C), which is more favorable for producing hydrogen; however it is only used in on-site hydrogen generation due to its inconvenient storage and transportation.

Significant effort has been devoted to the development of liquid fuels for on-board hydrogen generation, especially liquids composed of hydroxyl-containing hydrocarbons. Methanol in particular is regarded as the most feasible fuel for on-board hydrogen generation, primarily due to its higher H/C and low reforming temperature.

Three technologies have historically been used to optimally generate hydrogen from methanol, namely, partial oxidation (POX), steam reforming (SR), and oxidative steam reforming (OSR) or autothermal reforming (ATR). POX is an exothermic process that

requires a high reaction temperature, and unfortunately produces products with low hydrogen concentrations. SR is an endothermic process, and requires additional heaters or burners to provide driving energy for the reaction. Exothermic processes have an intrinsically faster transient response compared to endothermic processes. It is important to note that ATR combines the partial oxidation and steam reforming processes, wherein, by properly adjusting the reactive conditions, the reaction system can be run autothermally. The reaction temperature and the quality of the fuel cell feed in the ATR lie between POX and SR. Further, a higher thermal efficiency is possible with an optimally developed ATR process.

For such a complex reaction system, thermodynamic equilibrium calculations can be performed via two common approaches [1]. One approach is based on chemical equilibrium constants, and is called the chemical stoichiometric method, while the other is derived from the minimization of the Gibbs free energy. The former is inapplicable to liquid or solid species in the reaction system. For a heterogeneous system, the approach using the minimization of the Gibbs free energy is commonly used for thermodynamic analysis. Commercial software, based on the Gibbs free energy function, has been widely used for thermodynamic calculations, such as AspenPlus™ [2] and HSC-Chemistry (Outokumpu, Finland) [3]. Equilibrium calculations can also be performed through programming.

Chan [4] thermodynamically analyzed ATR based on the Fortran code developed by NASA under the assumption that the inlet temperature of the reactants was 298.15 K and the fuels were

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completely converted. Generally, this scenario is not true in most practical cases, therefore we used optimized practical operational parameters dependant on a similar method described in [5]; however the solutions and the data post-processing are complicated. Win et al. [6] investigated a complex numerical algorithm for methanol steam reforming. The probability of carbon formation in practical scenarios was determined by the direct inclusion of carbon in the objective function of the minimization scheme, such that an intricate solution for the minimization of the Gibbs free energy function was unavoidable. The stoichiometric method was also used to perform thermodynamic analysis [7]; however, the assumption of no formed liquid or solid species limits its application.

In this work, a method has been developed to perform the thermodynamic analysis of methanol OSR for PEMFC. Independent parameters that effect ATR reactor performance, that is, the inlet feed temperature, pressure, S/C, and O/C were investigated. As a function of the equilibrium constants of the possible reactions in the reactive system, the formation mechanisms of the object products were established. On the basis of the thermodynamic analysis and formation mechanism, the optimal operational parameters that maximized H<sub>2</sub> yield, minimized the CO molar fraction, and eliminated carbon deposition were confirmed. In addition, the proposed analysis method was validated by comparing the obtained results with those reported in the literature.

## 2. Theorem and simulation methodology

### 2.1. Theorem

In contrast to the chemical stoichiometric method, the minimization of Gibbs free energy method is applicable to systems with condensed phase species. H<sub>2</sub> generation systems using a fossil fuel feed can produce coke under certain thermodynamic conditions. To avoid the negative impact of coke formation, these thermodynamic conditions can be identified using the minimization of Gibbs free energy method. A closed system at equilibrium satisfies the minimized Gibbs free energy for a specified temperature and pressure, while is also simultaneously constrained by the conservation of atoms. In this vein, many equations have been established and solved using species composition and thermodynamic data. A significant amount of code is available that can solve these equations, most notably the NASA and STANJAN equilibrium codes. NASA program has been used in the analysis of generating hydrogen process fed by fossil fuels [4,8]. In addition, STANJAN has been adopted in some commercial thermodynamic software, such as CHEMKIN. The Gibbs free energy minimization method and the STANJAN code were applied to preprocess the non-premixed combustion model in the FLUENT software. A conserved scalar quantity, known as the mixture fraction  $f$ , was introduced to perform thermodynamic equilibrium analysis in the solving process. The mixture fraction can be written in terms of the atomic mass fraction as

$$f = \frac{Z_i - Z_{i,OX}}{Z_{i,fuel} - Z_{i,OX}} \quad (1)$$

where  $Z_i$  is the elemental mass fraction for some element  $i$ . The subscript "OX" denotes the value at the oxidizer stream, and the subscript "fuel" denotes the value at the fuel stream. Due to unique relations between all of the thermochemical scalars (species mole fraction  $y_i$ , density, and temperature) and the mixture fraction,  $f$ , the species mole fraction can be solved based on the minimization of Gibbs free energy using the STANJAN code [9]. The species mole fractions were then converted into a dry basis and displayed

in figures by the expression:

$$y_{i,dry} = \frac{y_i}{1 - y_{H_2O}} \quad (2)$$

In addition, the mixture fraction,  $f$ , was transferred into the horizontal coordinate of the O/C in terms of the expression:

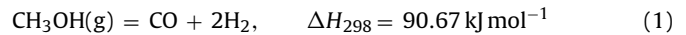
$$\frac{O}{C} = 0.21 \frac{M_{CH_3OH}}{M_{Air}} \left( \frac{1}{f} - 1 \right) \left( \frac{1+S}{C} \frac{M_{O_2}}{M_{CH_3OH}} \right), \quad (3)$$

where  $M_{CH_3OH}$ ,  $M_{Air}$ , and  $M_{O_2}$  are the CH<sub>3</sub>OH, air, and O<sub>2</sub> molecular weights, respectively.

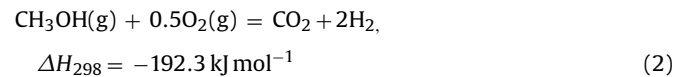
### 2.2. Thermodynamically feasible reactions and products

On the basis of thermodynamic analysis and experimental observation [10–17], the following reactions are primarily involved by neglecting the intermediates and products from side reactions; however, the contribution to the product distribution by each reaction differs depending on the specified operational conditions. Among them, the primary reactions contributing to the conversion of methanol include:

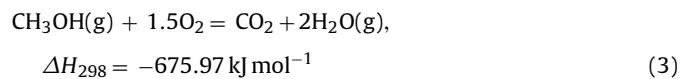
Methanol decomposition:



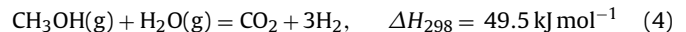
Methanol partial oxidation (POX):



Methanol combustion:



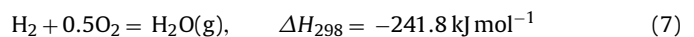
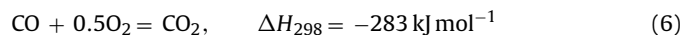
Methanol steam reforming (SR):



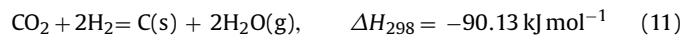
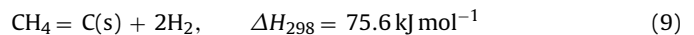
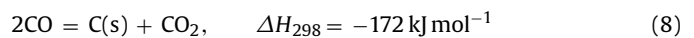
The water-gas shift reaction (WGS) is favorable for generating further H<sub>2</sub> at the expense of CO, and occurs as



When O<sub>2</sub> is in excess, the CO will be transformed into CO<sub>2</sub>, and a partial depletion of H<sub>2</sub> will take place via the preferential oxidation reaction:



Solid C formation can also occur via the following reactions [10]:



If the molar S/C is kept lower, methanation reactions can also occur:



In addition, it is thermodynamically possible to form ammonia and hydrogen cyanide in the presence of N<sub>2</sub>; however their respective effluent fractional concentrations are exceedingly small (in the range of ppm or ppb) under the simulation conditions

[11], and are therefore neglected. As per the analysis above,  $H_2$ ,  $CO$ ,  $CO_2$ ,  $N_2$ ,  $H_2O$ ,  $O_2$ ,  $CH_3OH$ ,  $CH_4$ , and solid graphite carbon  $C(s)$  are all the plausible products resulting from the OSR of methanol. The impact of various operational parameters on these equilibrium compositions and the adiabatic temperature were performed using this methodology. In addition, the validation of the methodology was also confirmed on the basis of the referred results.

### 3. Results and discussion

#### 3.1. Validation of the methodology

To confirm the reliability of the methodology, the FORTRAN code developed at the NASA Lewis Research Center was also used to iteratively compute the chemical equilibrium products. The FORTRAN program is also based on the minimization of Gibbs free energy, but uses a different thermodynamic database than the FLUENT software. The FORTRAN code was compiled using the NASA data format; however, The CHEMKIN polynomial format was used in the FLUENT software. Thermodynamic equilibrium calculations were performed using the two methods, respectively. Equilibrium compositions and temperatures are shown in Figs. 1–5, wherein A denotes the results of the discussed method, and B, the results from the literature. Partial results based on the FORTRAN code were published in [5]. From Fig. 1, it can be observed

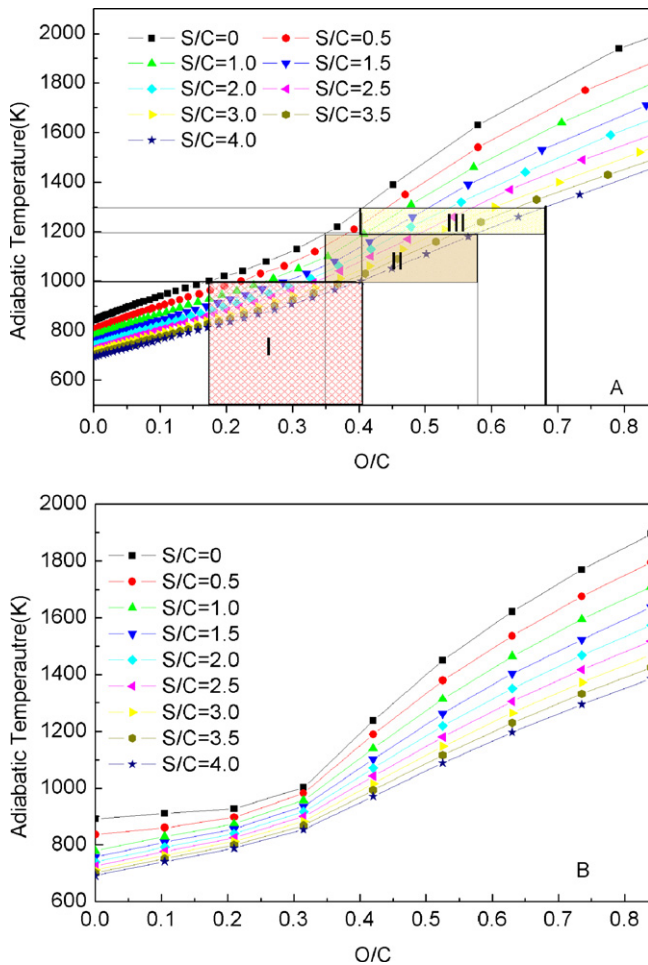


Fig. 1. Effect of the O/C and S/C on the adiabatic temperature (inlet temperature of the reactants was 573.15 K at a pressure of 0.1 MPa).

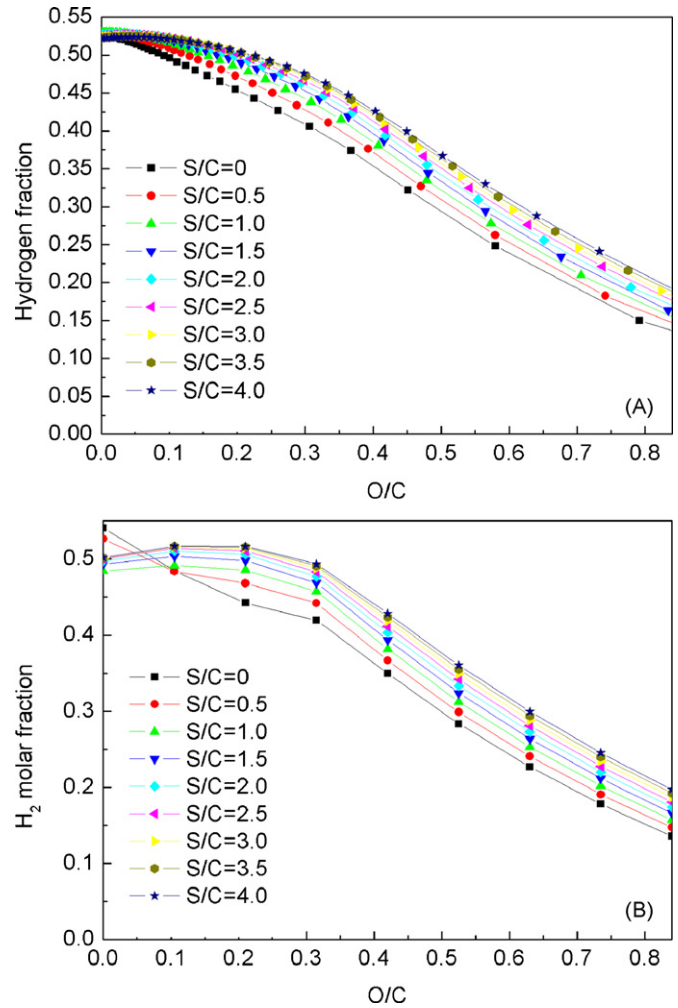


Fig. 2.  $H_2$  mole fraction as a function of the O/C and S/C (inlet temperature of the reactants was 573.15 K at a pressure of 0.1 MPa).

that similar data trending validates the feasibility of the proposed methodology. In addition, the thermodynamic analysis of the methane reforming process provides the evidence for its applicability [12]. A distinct divergence occurred for coke formation prediction, which is due to the discrepancies between the thermodynamic parameters supplied for solid C from the two different databases.

#### 3.2. Influence of inlet temperature on the equilibrium compositions and adiabatic temperature

The profiles of the equilibrium compositions and temperature were plotted as a function of the O/C and inlet temperature in Fig. 6. These profiles suggest that a higher inlet temperature favors  $H_2$  generation and C removal; however, higher inlet temperature also affords more favorable conditions for CO formation. In the vein of thermodynamic analysis, the equilibrium state generally depends on the equilibrium temperature of the autothermal system. Therefore, diverse inlet temperatures will shift the equilibrium state due to their indirect effects on the equilibrium temperature, as can be observed in Fig. 6. At 1000 K,  $H_2$  yield maximizes, and the corresponding O/C is between 0.21 and 0.37 for the investigated inlet temperature. Similarly, the maximum CO molar fraction and  $C(s)$  removal respectively match an equilibrium temperature of about 1300 K and 1200 K when the S/C is 1.5. Operational pressure and the

O/C can also influence the equilibrium compositions, and are the reasons that the equilibrium state is a function of the temperature, pressure, O/C, and S/C.

### 3.3. Influence of operational pressure on the equilibrium compositions

When there are gases in the reaction as reactants or products, a change in the pressure can shift the reaction direction due to non-conservation of chemical stoichiometric coefficients. For  $H_2$  generation, many gaseous reactions are involved in the system, and therefore, it is necessary to optimize the operation pressure. The impact of different operation pressures on the main parameters was simulated, as depicted in Fig. 7. The simulation results indicate that equilibrium compositions were primarily constant when the O/C was more than 0.32 at different operational pressures. When the O/C was less than 0.32, the  $H_2$  molar fraction decreased slightly with increasing pressure, and trended conversely for CO. Meanwhile, higher pressures were favorable for C(s) removal. In consideration of safety and economy, the system should be operated at atmospheric pressure.

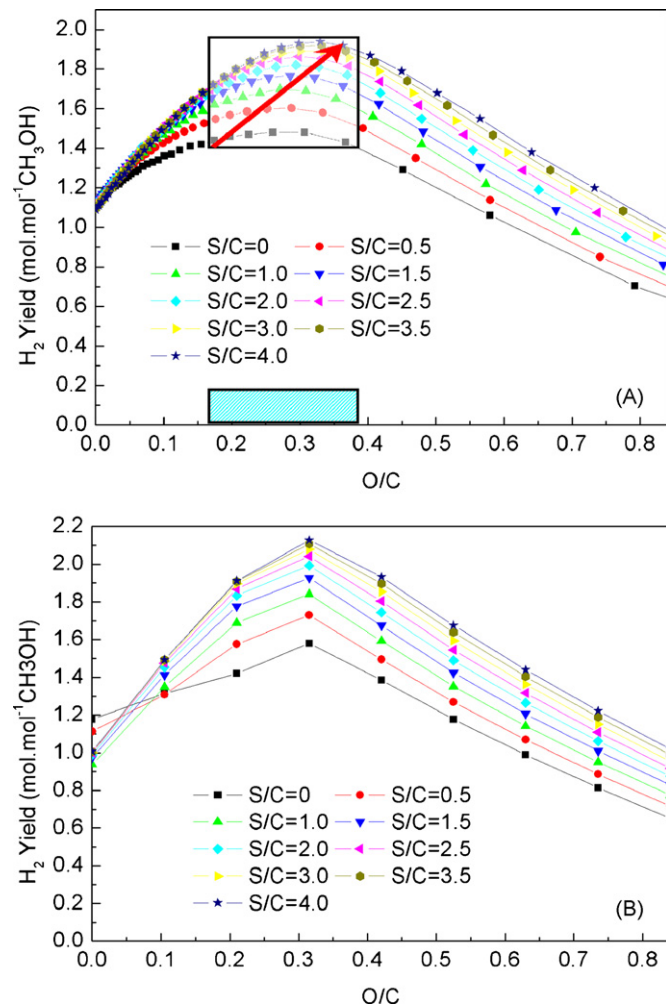


Fig. 3. Effect of different O/C and S/C on generated hydrogen yield (preheated temperature of reactants was 573.15 K at a pressure of 0.1 MPa).

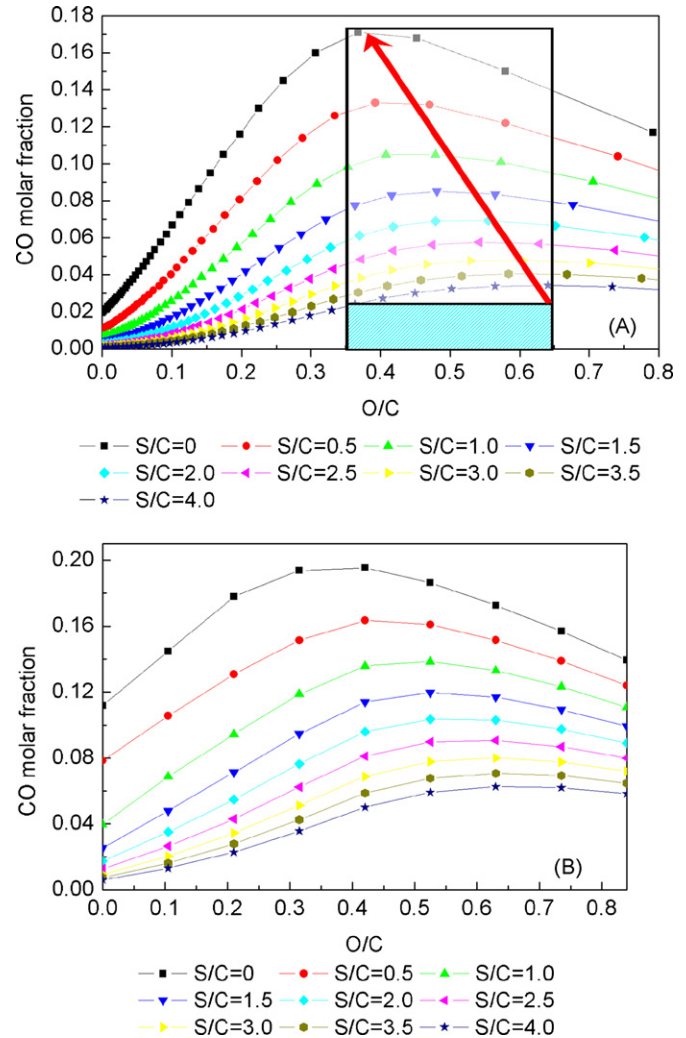


Fig. 4. Influence of the O/C and S/C on the mole fractions of CO in the reformer (inlet temperature of the reactants was 573.15 K at a pressure of 0.1 MPa).

### 3.4. The optimal operation parameter for OSR of methanol

When generating  $H_2$  for PEM fuel cell applications, the primary goal is to produce the largest amount of  $H_2$  with a minimal amount of CO effluent with a molar fraction in the ppm range. To avoid catalyst deactivation from C deposition, coke formation needs to be suppressed. Therefore, the product distributions are presented under specified thermodynamic processing conditions, and are aimed to maximize  $H_2$  yield, while minimizing CO and coke production.

By optimizing the S/C and O/C, it is possible to shift the reaction route and change the ratios of the possible occurring reactions. As a result, the equilibrium composition and temperature will approach the expectation about the maximum  $H_2$  yield, minimum CO and coke formation. Therefore, the impact of different S/C and O/C on the adiabatic temperature and reformat were simulated. From Figs. 1–5, it can be seen that the adiabatic temperature and equilibrium compositions have a stronger dependence on the O/C. In addition, the S/C is also a key parameter related to the optimal product compositions.

A higher methanol conversion rate reduces the cost, and enhances the power per volume or per weight of the system. In addition, any residual methanol can have a harmful effect on the proton exchange membrane. Accordingly, a complete methanol

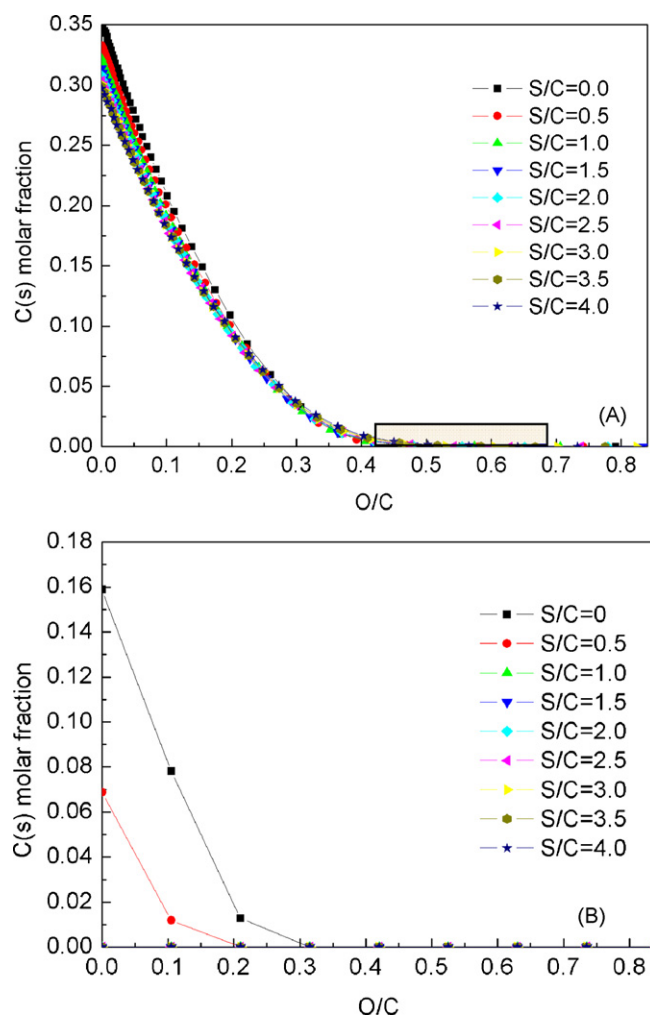


Fig. 5. Effect of the O/C and S/C on the mole fractions of C(s) in the reformer (inlet temperature of the reactants was 573.15 K at a pressure of 0.1 MPa).

conversion is considered necessary. Fortunately, the aforementioned thermodynamic analysis demonstrated that methanol was converted completely under the given parameters, as was also proved in [13]. They additionally observed a 100% methanol conversion rate at temperatures greater than 623 K.

The  $H_2$  free-water molar fraction as a function of the S/C and O/C is depicted in Fig. 2. From Fig. 2, it can be observed that a higher S/C favors  $H_2$  production, and that the  $H_2$  effluent fraction concentration decreases with increasing O/C. To exclude the impact induced by the dilution of  $N_2$ , a more favorable criterion should be used, namely, the moles of generated  $H_2$  per mole of methanol, which is also known as the  $H_2$  yield. Accordingly, the  $H_2$  yield was studied under different operating conditions, as depicted in Fig. 3. When the O/C was around 0.32, a maximum value for the  $H_2$  yield was observed.

To evaluate which intrinsic factors caused equilibrium composition changes as a function of the S/C and O/C, the equilibrium constants of all feasible reactions were plotted as a function of temperature in Fig. 8. It is well known that, when the equilibrium constant,  $K_p$ , is much larger than 1, the reaction cannot be shifted by adjusting the reactant stoichiometric ratio. For a multi-reaction system, only the contribution of each reaction to the product will be altered; however when  $K_p$  approaches 1, the impact of reactant stoichiometric ratio on the reaction widely diverges. The addition of reactants will shift the equilibrium to product accumulation. A

maximized objective product depends on the reactions for a multi-reaction system, whose  $K_p$ s are higher. For these reactions, the equilibrium composition is a strong function of the temperature. For a reaction with a  $K_p$  closer to 1, the addition of reactants can only alter the relative magnitude of the maximum. From Fig. 1, it can be observed that the adiabatic temperature is closely associated with the O/C, and only a slight variation was associated with the S/C. As such, the maximum or minimum of the target product will primarily be influenced by the O/C.

The  $K_p$ s associated to reactions involving  $H_2$  are displayed as a function of temperature in Fig. 8. It can be observed that reactions (1), (2), (4), (6) and (7) proceed more easily in the investigated temperature range. Reactions (10)–(13) are influenced by equilibrium limitations in the temperature range of 700–1000 K. Reaction (5) is especially limited within the entire investigated temperature range. At temperatures above 1200 K, reactions (8) and (10)–(13) can be avoided, while their reverse reactions are more prone to occur. Although reaction (9) is thermodynamically favorable, the methane formation reactions are removed, and therefore, reaction (9) will be excluded when temperatures exceed 1200 K.

Reaction (3) occurs much more easily compared to other reactions. The  $K_p$  profile for reaction (3) is not depicted in Fig. 8, and therefore, reaction (3) is superior for methanol conversion. Therein, only excess methanol will be decomposed and steam reformed to yield  $H_2$  [14]. Such reaction steps were proposed for the OSR of methanol by Lyubovsky and Roychoudhury [15]. Thus, a  $H_2$  fraction maximum exists when the value of the O/C is equal to 0, as exhibited in Fig. 2; however, the  $H_2$  yield still increases with increasing temperature, as depicted in Fig. 3. This is the reason that higher temperatures suppress and eliminate methanation, in reactions (13) and (12), and C formation, in reactions (11) and (10). The initial reduction of  $H_2$  content with the O/C increase is due to the dilution of  $N_2$ ; however further addition of air will reduce the  $H_2$  yield due to redundant methanol combustion. In fact, after methanation and C formation were efficiently suppressed beyond the temperature of 900 K,  $H_2$  production is primarily ascribed to methanol decomposition in reaction (1), and to methanol steam reforming in reaction (4). In comparison to the complete methanol oxidation in reaction (3),  $H_2$  depletion resulted from reaction (7) can be ignored. Ideally, the OSR process can be thermally neutral for an appropriate O/C and S/C, and the energy needed for steam reforming and methanol decomposition is supplied by the complete methanol combustion. According to Fig. 3, the favorable O/C should be between 0.17 and 0.38 for a S/C of 0–4, under which the equilibrium temperature should be about 1000 K, as is defined by area I in Fig. 1.

C formation is possible from reactions (8) to (11). Although the influence of C formation on  $H_2$  yield can be ignored when the temperature exceeds 900 K, these reactions are easily impacted by operational parameters, as indicated by Fig. 8, due to their relatively lower equilibrium constants. When the temperature is lower than 1000 K, a disproportionation reaction is predominant. Only when the temperature exceeds 1200 K, are their reverse reactions thermodynamically feasible, such that C formation can be completely removed. The corresponding O/C is between 0.4 and 0.58 for an S/C value of 0–4, as is referred to by area II in Fig. 1. In addition, the S/C also changes the equilibrium state in the investigated temperature range of 700–1200 K. A higher S/C will suppress the occurrence of reactions (10) and (11). Therefore, the boundary of area II is not defined only as a function of temperature, but is merely a generalization.

Fig. 8 also depicts the equilibrium constants as a function of temperature for each reaction involving CO. This is to determine the thermodynamic role of each reaction in CO formation and transformation. Reaction (1) is thermodynamically favorable throughout the entire investigated temperature range. Reaction (3) is ther-

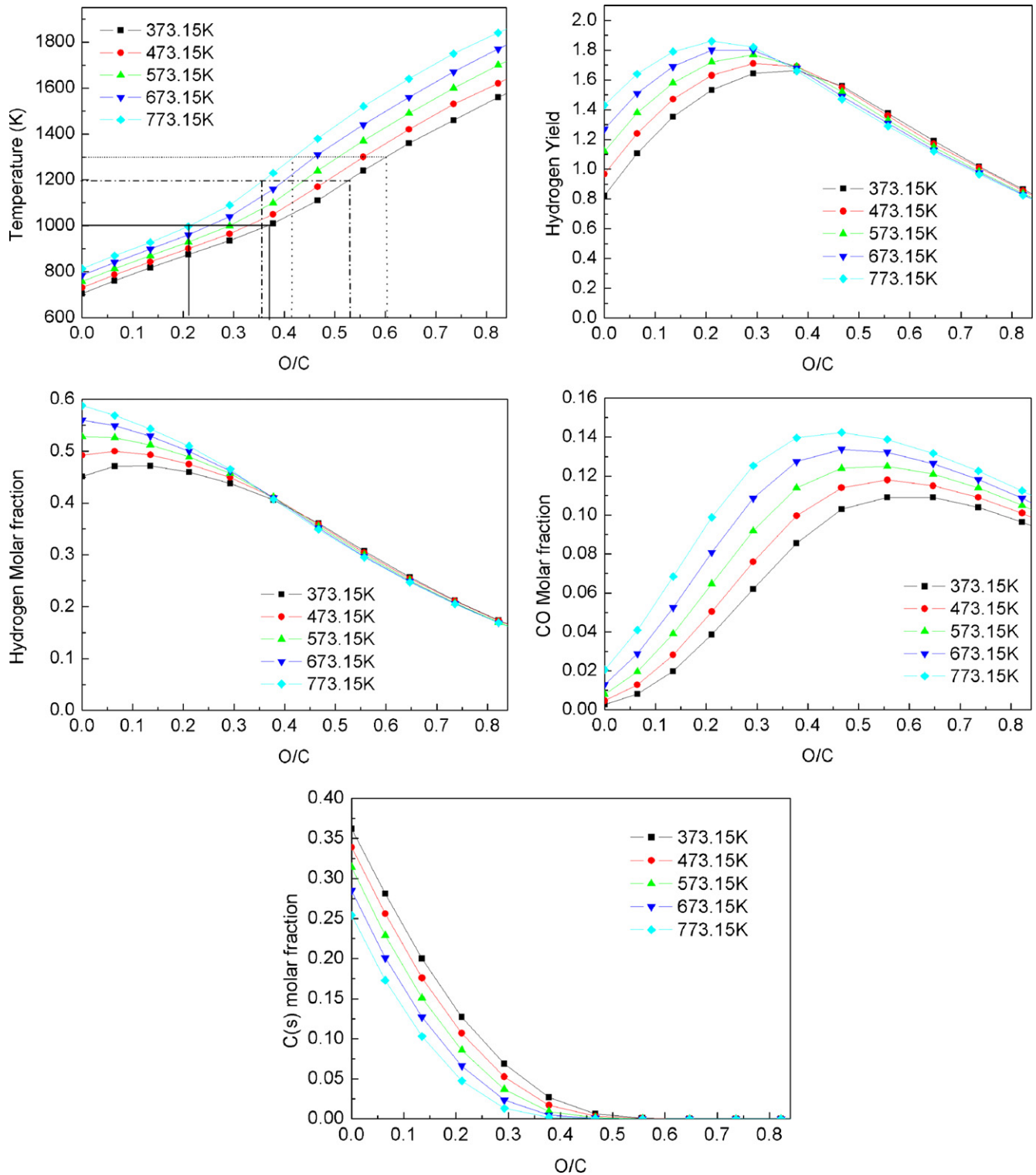
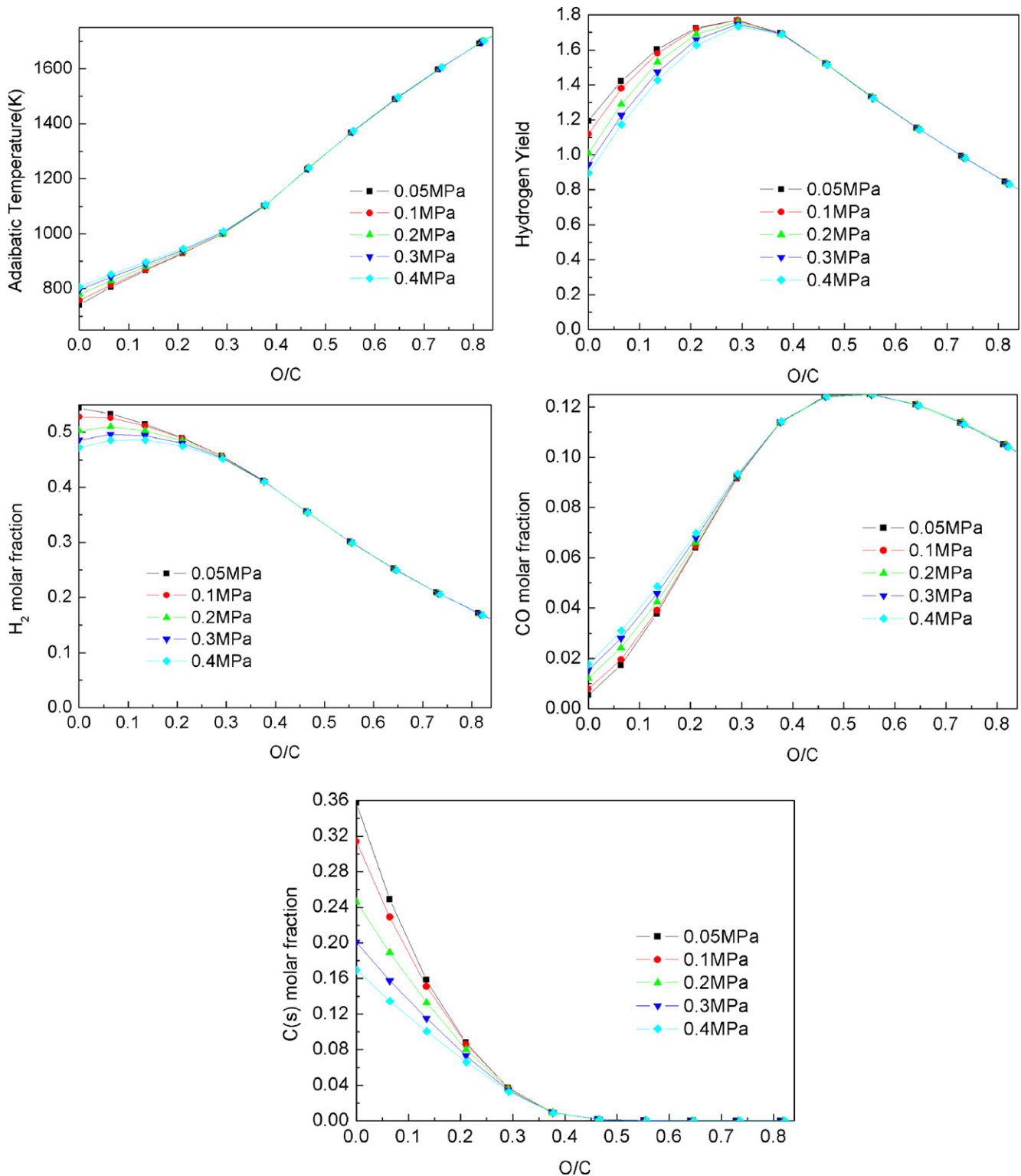


Fig. 6. The equilibrium composition and adiabatic temperature profiles with respect to the O/C and inlet temperature at atmospheric pressure when the S/C is 1.5.

modynamically the easiest occurring reaction for all reactions including  $O_2$ , and as a result, the contribution to the CO reduction can be neglected for reaction (6). Reactions (8), (10) and (12) are favorable at low temperatures, while their reverse reactions are favorable at high temperatures. Since the  $K_p$  is always close to 1 within the specified temperature range for reaction (5), the reaction is at equilibrium state. The addition of reactant can promote the positive reaction or restrain the negative reaction. To

reduce the CO content as much as possible, a higher S/C should be selected. On the basis of the above analysis, CO formation will be enhanced at high temperature; however high temperatures result from more methanol combustion, which leads to a reduction in methanol decomposition. Thus, there exists a CO maximum with increasing temperature, as depicted in Fig. 4. At the same time, the CO maxima will move to a higher O/C, accompanied by an increase in the S/C. A CO maximum exists at an O/C of 0.4–0.7, when the S/C is



**Fig. 7.** The equilibrium composition and adiabatic temperature profiles with respect to the O/C and operational pressure when the S/C is 1.5 and the inlet temperature is 573.15 K.

between 0 and 4, and is labeled as area III in Fig. 1. The corresponding temperature is 1300 K, wherein the CO concentration reaches a maximum due to the competition between preferential methanol complete oxidation, decomposition, and the steam reforming of excess methanol.

An increase in the S/C shifts the directions of reactions (5) and (10)–(13), as they are equilibrium limited. Therefore, a H<sub>2</sub>

increase and CO reduction is partially a result of these reactions being promoted or suppressed. Since the occurrence of a H<sub>2</sub> and CO maximum is primarily dependant on the temperature, the S/C can only be of comparable magnitude. In the case of C formation, this behavior is different. C removal is simultaneously dominated by temperature and thermodynamic equilibrium. When temperature exceeds a certain value or if the S/C is sufficiently high, C

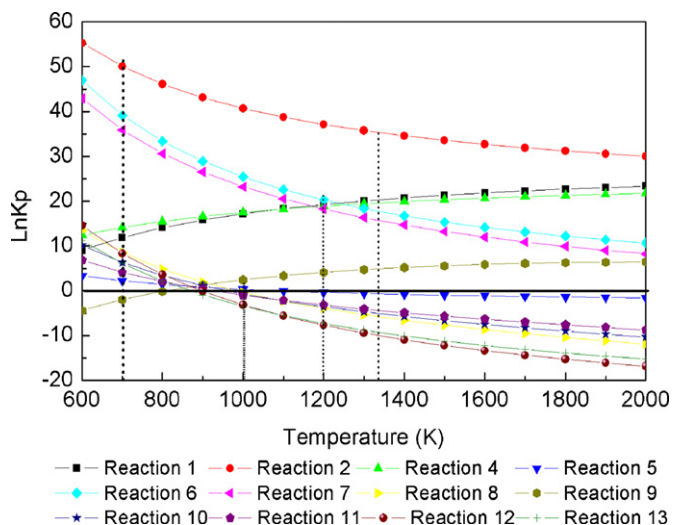


Fig. 8. The equilibrium constants for reactions participating in the methanol OSR as a function of temperature.

elimination will be thermodynamically possible. This behavior is also confirmed in references [4,8].

#### 4. Conclusions

A calculation method based on FLUENT software has been developed and successfully used to thermodynamically analyze methanol autothermal reforming for PEMFC. The effects of temperature, pressure, S/C, and O/C on the OSR of methanol were identical to previous published results. Slight variations in the data are due to differences in the thermodynamic database used in the two methods. The equilibrium constants and the possible reactions involved in OSR of methanol were calculated to elucidate the reaction mechanisms in the entire investigated temperature range. It can be concluded that four major reactions, including methanol combustion, methanol decomposition, steam reforming, and water-gas shift reaction, are involved in OSR of methanol. Methanol combustion was observed to be dominant, while only excess methanol decomposed and steam reformed. Reversible water-gas shift reactions also occur in the investigated temperature range. Further, other reversible reactions involving  $H_2$  and CO have a slight effect

on the  $H_2$  yield and CO content, and therefore, the  $H_2$  yield and CO maximum depend primarily on temperature. In addition, solid C formation is derived from some reactions that are reversible in the investigated temperature range. Hence, the elimination of solid C is simultaneously dominated by temperature and thermodynamic equilibrium. On the basis of these possible mechanisms, three areas were plotted. Under area I, the temperature is maintained at 1000 K, and the relevant O/C is between 0.17 and 0.38 for a S/C of 1–4, to produce a maximum  $H_2$  yield. Under area II, the boundary for solid C formation is defined. When the temperature exceeds 1200 K, solid C can be removed. For area II, the relevant O/C is between 0.4 and 0.58 for a S/C of 1–4; however, this boundary still reverts to a low O/C for a higher S/C due to equilibrium limitations. Under area III, the CO content will reach a maximum, and therefore, the operational temperature should be lower than 1300 K to reduce the CO molar fraction in the product gas. These data provide guidance for practical system development and application.

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