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Combination of Langmuir-Hinshelwood-Hougen-Watson and microkinetic approaches for simulation of biogas dry reforming over a platinum-rhodium alumina catalyst

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Abstract

Dry reforming of CH₄ on a platinum-rhodium alumina catalyst is selected to numerically investigate biogas reforming process. Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate expressions for dry reforming and reverse water-gas shift reactions are presented. Activation energies are estimated by combining microkinetics with the theory of unity bond index-quadratic exponential potential (UBI-QEP). Pre-exponential factors are initially obtained by using the transition state theory (TST) and optimised, later, by minimising errors between modelling and experimental data. Adsorption of CH₄ on the catalyst surface is found to be the rate determining step in the range of relatively low temperature (600 - 770 °C), while at relatively high temperature (770 - 950 °C) the thermal cracking of adsorbed CH₄ is the rate controlling step. Small effect of reverse water-gas shift reaction results in the ratio of H₂ to CO produced less than unity for all operating conditions. The simulation shows that the dry reforming process proceeds with reaction rate far from equilibrium state. The presented mechanism is capable of predicting the dependence of biogas dry reforming activities (e.g., reactant conversions, product formations, H₂ to CO ratio, and temperature profile inside the catalyst) on operating conditions (e.g., inlet temperature, heat supplied through the catalyst wall, and composition of biogas at inlet).

Keywords: Biogas dry reforming, Langmuir-Hinshelwood-Hougen-Watson approach, Microkinetics, On-board hydrogen production

1. Introduction

Hydrogen (H_2) has been deemed as one of the future energy vectors for transportation. Together with an oxidising agent and fuel cell, it can be used to produce electricity for an electric vehicle with zero emission. ~~In addition to,~~ its importance in the field of automotive catalytic aftertreatment systems is paramount. In a NO_x reduction system of a diesel engine, such as hydrocarbon selective catalytic reduction (HC-SCR), a small amount of hydrogen is used as an ideal co-feeder in order to decrease the minimum temperature needed to drive the NO_x removal process [1–4]. In terms of particulate matter (PM) control, hydrogen promotes the formation of NO_2 which is more active than oxygen to oxidise the PM at low temperatures in the regeneration step [5]. Furthermore, hydrogen utilisation in engines for combustion also enhances auto-ignition of some alternative hydrocarbon fuels [6] and breaks the PM- NO_x trade-off [7–10]. Moreover, the potential of hydrogen on performance of a gasoline direct injection (GDI) engine was carefully investigated. With hydrogen-rich reformat exhaust gas recirculation (REGR), Tsolakis and co-workers found that 1) the indicated engine efficiency was improved; 2) the dilution limit was extended; 3) NO_x emission was dropped; 4) knock was reduced; 5) particulate matter emissions in both mass and number were declined; 6) combustion stability inside the cylinder increased due to high diffusivity and flame speed of hydrogen; and 7) spark timing can be retarded which enhanced the available time for fuel-air mixture [11–13]. Also, hydrogen and carbon monoxide (CO) (also called syngas) are the main source for production/synthesis of liquid hydrocarbons via the Fischer-Tropsch process, methanol/~~alcohol~~ and fine chemicals.

Biogas is an alternative and renewable energy vector. It is easily produced by the biological breakdown of organic matter in which oxygen is absent. Biogas mainly consists of methane (CH_4) and carbon dioxide (CO_2). Normally, the volumetric fraction of CH_4 and CO_2 varies from 50 to 75% and from 50 to 25%, respectively. Biogas used directly in an internal combustion engine is a challenging task because the high content of CO_2 reduces the fuel calorific value. To employ biogas in automotive applications, biogas has to be upgraded to

syngas (~~e.g., hydrogen (H₂) and carbon monoxide (CO)~~) by using fuel reforming processes [14–17]. The reforming of methane including dry reforming, partial oxidation, steam reforming, water-gas shift, and complete combustion is given below:

Dry reforming



Partial oxidation



Steam reforming



Water-gas shift



Complete combustion



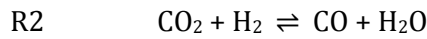
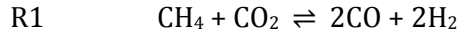
Dry or CO₂ reforming was found to be the major step for the partial oxidation of methane over supported platinum catalysts [18]. First, part of methane is converted to CO₂ and H₂O by the complete combustion process; then, the produced CO₂ and H₂O reacted with the remaining methane to form syngas through dry and steam reforming paths, respectively. The reverse water gas shift (RWGS) was one of chemical reactions taking place during dry reforming of methane over Pt/PrCeZrO [19] and Ni-Co/CeO₂ [20] catalysts. Part of the H₂ produced by the dry reforming was consumed by CO₂ to generate CO and H₂O. So, the ratio of H₂ to CO was always less than unity. Wang et al. [21] suggested that an equimolar amount of H₂ and CO was found at the CH₄ to CO₂ ratio of 2. The authors also proposed that carbon deposited on the Ni catalyst was generated from both CH₄ and CO₂. On the one hand, the adsorbed carbon chemically reacted with surface oxygen to produce adsorbed CO. On the other hand, the carbon was permanently stuck on the catalyst surface and caused the catalyst deactivation. Carbon derived from CO₂ was the main path for the catalyst coking. Highly active surface carbon was

created from the thermal cracking of CH₄. Then, the active carbon was rapidly consumed by CO₂ via the reverse Boudouard reaction. However, O'Connor et al. [22] studied transient CO₂ reforming of CH₄ over Pt/ZrO₂ and Pt/Al₂O₃ catalysts and found that more than 99% of carbon accumulated on both catalysts was derived from the CH₄ molecule. CH₄ decomposition that formed carbon, took place over platinum sites in both catalysts. The difference between the two catalysts was that the Pt/ZrO₂ catalyst was able to dissociate CO₂ in the absence of CH₄ while over the Pt/Al₂O₃ catalyst, the CO₂ dissociation is assisted by hydrogen derived from CH₄. Moreover, in contrast to what has been observed over Ni and Ru catalysts, the direct reaction between CO₂ and adsorbed carbon (the reverse Boudouard reaction) was a small effect and can be excluded. The authors recommended that the CO₂ dissociation was the slowest step for the CO₂ reforming over the platinum supported catalysts. In cases of catalyst stability, non-noble metals (e.g., Fe, Co, and Ni) are easily lost activity with a short time. Rhodium (Rh) is considered as the most suitable catalyst in the methane dry reforming reaction. Low dissociation enthalpies of methane made Rh appropriate in terms of activity and stability [23]. As a support of Pt catalyst, CeO₂ showed highest stability comparing to Al₂O₃, ZrO₂, and Y₂O₃ for the partial oxidation of methane. Due to higher reducibility and oxygen storage/release capacity, CeO₂ was able to continuously remove carbon deposited on active sites [18].

Numerical simulation together with catalytic reaction models formed based on either the Langmuir Hinshelwood Hougen Watson (LHHW) or microkinetic techniques were effectively conducted for the dry reforming of methane to predict effects of operating temperature, contact time, and feed ratio on conversion of methane, yield of syngas, product selectivity, and ratio of hydrogen to carbon monoxide in produced syngas [24–26]. In this work, a reaction mechanism of the biogas dry reforming is presented. Rate expressions and reaction parameters are formed based on combining of the ~~LHHW~~Langmuir–Hinshelwood–Hougen Watson (~~LHHW~~) and microkinetic methods. The comprehensive kinetic models are applied to gain knowledge about the effect of operating conditions on activity and selectivity of biogas dry reforming.

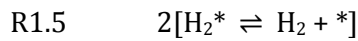
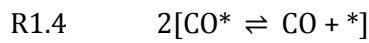
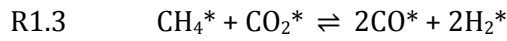
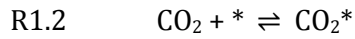
2. Development of the biogas dry reforming mechanism

A heterogeneous reaction mechanism of biogas dry reforming on a Pt/Rh catalyst is formulated based on the LHHW method. Two possible reactions involved in the mechanism are the CH₄ dry reforming and reverse water-gas shift reactions [27], as shown in R1 and R2, respectively.



2.1. CH₄ dry reforming process

To apply the method of LHHW, the catalytic process of CH₄ dry reforming, R1, can be explained in detail as following scheme.



The symbol * is vacant sites.

A molecule with * represents the surface species.

For the CH₄ dry reforming proceeding in a relatively high-temperature range, it is reasonably assumed that the surface reaction, R1.3, is the rate determining step (RDS). Then, the LHHW rate expression can be expressed as:

$$R_{DR} = k_{1.3f} K_{CH_4} K_{CO_2} \left(C_{CH_4} C_{CO_2} - \frac{1}{K_{DR}} C_{CO}^2 C_{H_2}^2 \right) \theta_v^2 \quad (1)$$

The values of C_{CH_4} , C_{CO_2} , C_{CO} , and C_{H_2} are the gas phase concentration at catalyst surface of CH₄, CO₂, CO, and H₂, respectively. The term of $k_{1.3f}$ is the rate constant for the forward direction of R1.3 and it is defined in the Arrhenius form as:

$$k_{1.3f} = \frac{A_{1.3}}{\Gamma} \left(\frac{T}{T_0} \right)^{\beta_{1.3}} \exp \left(-\frac{E_{1.3}}{RT} \right) \quad (2)$$

The terms of A , Γ , T , T_0 , β , E , and R represent for the pre-exponential factor, site density (1.5×10^{15} sites/cm² or 2.49×10^{-9} mol/cm² [28,29]), absolute temperature, reference temperature (300 K), temperature exponent, activation energy, and universal gas constant (8.314 J/mol·K), respectively. The fraction of vacant sites, θ_v , is given by:

$$\theta_v = \frac{1}{1 + K_{CH_4} C_{CH_4} + K_{CO_2} C_{CO_2} + K_{CO} C_{CO} + K_{H_2} C_{H_2}} \quad (3)$$

K_{CH_4} , K_{CO_2} , K_{CO} , and K_{H_2} are the equilibrium constant for the adsorption process of CH₄, CO₂, CO, and H₂, respectively; and K_{DR} is the equilibrium constant for the overall CH₄ dry reforming, R1.

For the dry reforming of CH₄ taking place at relatively low temperature, it is found that the slowest reaction is switched from the surface reaction, R1.3, to the adsorption of CH₄, R1.1. This means that as soon as the adsorbed CH₄ (CH₄^{*}) is formed, it is rapidly consumed by other reactions. Thus, with the assumption that the CH₄^{*} does not appear on the catalyst surface, the rate expression can be obtained as:

$$R_{DR} = k_{1.1f} \frac{1}{C_{CO_2}} \left(C_{CH_4} C_{CO_2} - \frac{1}{K_{DR}} C_{CO}^2 C_{H_2}^2 \right) \theta_v \quad (4)$$

The term of $k_{1.1f}$ is the rate constant for the adsorption of CH₄ and it is evaluated by:

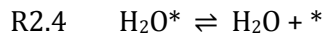
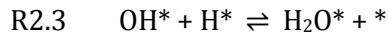
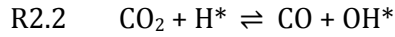
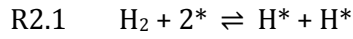
$$k_{1.1f} = \frac{s_{CH_4}}{\Gamma} \sqrt{\frac{RT}{2\pi M}} \left(\frac{T}{T_0} \right)^{\beta_{1.1}} \exp \left(-\frac{E_{1.1}}{RT} \right) \quad (5)$$

The term s_{CH_4} stands for the sticking coefficient of methane adsorbing on the catalyst surface and M is the molecular weight of methane. The site vacancies are calculated by:

$$\theta_v = \frac{1}{1 + K_{CO_2} C_{CO_2} + K_{CO} C_{CO} + K_{H_2} C_{H_2}} \quad (6)$$

2.2. Reverse water-gas shift process

The reverse water-gas shift process, R2, which takes place simultaneously with the CH₄ dry reforming, R1, can be detailed as:



By obtaining the activation of CO₂, R2.2, as the RDS, the LHHW rate expression is formulated as:

$$R_{RWGS} = k_{2.2f} \sqrt{K_{2.1}} \left(C_{\text{CO}_2} C_{\text{H}_2} - \frac{1}{K_{RWGS}} C_{\text{CO}} C_{\text{H}_2\text{O}} \right) \theta_v \quad (7)$$

The rate constant for the forward direction of R2.2, $k_{2.2f}$, is obtained as:

$$k_{2.2f} = \frac{A_{2.2}}{F} \left(\frac{T}{T_0} \right)^{\beta_{2.2}} \exp \left(-\frac{E_{2.2}}{RT} \right) \quad (8)$$

The unoccupied surface sites are estimated by:

$$\theta_v = \frac{1}{\sqrt{C_{\text{H}_2}} + \sqrt{K_{2.1}} C_{\text{H}_2} + K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} \sqrt{C_{\text{H}_2}} + \frac{1}{\sqrt{K_{2.1}} K_{2.3}} K_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}}} \quad (9)$$

As $K_{2.1}$ and $K_{2.3}$ are the equilibrium constant of the reaction R2.1 and R2.3, respectively; and K_{RWGS} is the equilibrium constant of the gas-phase reverse water-gas shift process, R2.

3. Determination of reaction parameters

3.1. Activation energies

Three activation energies for: i) the dry reforming as the surface reaction is the RDS; ii) the dry reforming as the adsorption of CH₄ is the RDS; and iii) the reverse water-gas shift reaction are calculated by applying the microkinetic approach [30] and the theory of unity bond index-quadratic exponential potential (UBI-QEP) [31–33]. [Recently, the UBI-QEP theory was successfully employed with the novel method of density functional theory \(DFT\) to explain at molecular level of catalytic reactions of methane over platinum and rhodium surfaces \[34\].](#)

According to the microkinetic approach, mechanistic details of CH₄ dry reforming, heats of reaction, and activation energies for each step are given in Table 1. The mechanism consists of activated adsorptions of reactants (e.g., reactions DR1-DR3), surface reactions (DR4-DR7), and desorption of products (DR8 and DR9). As already mentioned, at relatively high temperature the surface reaction kinetically controls the overall rate of CH₄ dry reforming process. This assumption is complied with previous publications which indicate that the decompositions of adsorbed CH₄ are the RDS [27,28,35,36]. Thus, the activation energy for this situation is selected from the highest value of the surface reactions (DR4-DR7) in the forward direction. Therefore, the value of 32.12 kcal/mol (from thermal cracking of CH* [36], DR6) is chosen to represent the activation energy of the CH₄ dry reforming process at relatively high temperature. At relatively low temperature, it is found that the RDS is changed from the surface reaction to the dissociative adsorption of CH₄. So, the value of forward-direction activation energy, 19.82 kcal/mol, is picked to represent the activation energy of the dry reforming process at relatively low temperature. Moreover, the activation of the co-reactant, CO₂, with surface hydrogen (H*) to form highly active species OH* was proposed as the crucial step whereas the directly dissociative adsorption of CO₂ to produce adsorbed CO was negligible [27,28,36]. Therefore, the highest value of 26.95 kcal/mol shown in Table 2 is selected as the activation energy for the reverse water-gas shift reaction.

Table 1

Detailed reaction mechanism of CH₄ dry reforming process.

	Reactions	Δh_R^a (kcal/mol)	E_{for}^b (kcal/mol)	E_{rev}^c (kcal/mol)
DR1	$CH_4 + * \rightleftharpoons CH_4^*$	-19.22	0.00	19.22
DR2	$CH_4^* + * \rightleftharpoons CH_3^* + H^*$	11.92	19.82	7.90
DR3	$CO_2 + H^* \rightleftharpoons CO + OH^*$	26.95	26.95	0.00
DR4	$CH_3^* + * \rightleftharpoons CH_2^* + H^*$	2.80	20.25	17.45

DR5	$\text{CH}_2^* + * \rightleftharpoons \text{CH}^* + \text{H}^*$	-29.80	7.70	37.50
DR6	$\text{CH}^* + * \rightleftharpoons \text{C}^* + \text{H}^*$	19.10	32.12	13.02
DR7	$\text{C}^* + \text{OH}^* \rightleftharpoons \text{CO}^* + \text{H}^*$	-36.41	3.71	40.12
DR8	$\text{H}^* + \text{H}^* \rightleftharpoons \text{H}_2 + 2^*$	20.85	20.85	0.00
DR9	$\text{CO}^* \rightleftharpoons \text{CO} + *$	42.00	42.00	0.00

^a Heat of reaction

^b Activation energy of forward reaction

^c Activation energy of reverse reaction

Table 2

Detailed reaction mechanism of reverse water-gas shift process.

Reactions	Δh_R (kcal/mol)	E_{for} (kcal/mol)	E_{rev} (kcal/mol)
RWGS1 $\text{H}_2 + 2^* \rightleftharpoons \text{H}^* + \text{H}^*$	-20.85	0.00	20.85
RWGS2 $\text{CO}_2 + \text{H}^* \rightleftharpoons \text{CO} + \text{OH}^*$	26.95	26.95	0.00
RWGS3 $\text{OH}^* + \text{H}^* \rightleftharpoons \text{H}_2\text{O}^* + *$	-6.51	12.05	18.56
RWGS4 $\text{H}_2\text{O}^* \rightleftharpoons \text{H}_2\text{O} + *$	10.20	10.20	0.00

3.2. Equilibrium constants

An equilibrium constant of gas molecule i , K_i , adsorbing on a surface catalyst can be computed by using the knowledge about transition state theory (TST) [37].

$$K_i = \exp\left(\frac{\Delta S^{0\ddagger}}{R}\right) \exp\left(-\frac{Q_i}{RT}\right) \quad (10)$$

Heats of adsorption of gas-phase species i , Q_i , used in this work are calculated via the UBI-QEP theory and listed in Table 3.

Table 3

Heat of adsorption on Pt catalyst.

Species	Heat of adsorption, Q (kcal/mol)
---------	------------------------------------

CH ₄	19.22
CH ₃	49.80
CH ₂	95.00
CH	163.30
C	162.60
H	62.50
H ₂	6.69
H ₂ O	10.20
OH	60.00
CO	42.00
CO ₂	4.50

The standard entropy change, $\Delta s^{0\ddagger}$, during an adsorption process of a gas molecule is expressed as:

$$\Delta s^{0\ddagger} = R \left[\ln \left(\frac{\frac{h}{k_B T}}{(2\pi m k_B T)^{1/2}} \left(\frac{A}{N} \right) P^0 \right) - \frac{1}{2} \right] \quad (11)$$

where h , k_B , m , A/N , and P^0 stand for Planck constant, Boltzmann constant, mass per molecule, area occupied per adsorbed molecule, and standard pressure, respectively. Variation in temperatures of equilibrium constants is estimated by application of the van't Hoff equation [38].

4. Simulation

The simulation is set up following experiments presented in our previous publication [14]. The monolithic catalyst size was 20 mm in diameter and 75 mm in length. The reforming catalyst was made from a high-cell density cordierite (900 cells per square inch) which was coated with 2% Pt and 1% Rh (by mass) dispersed on 30% (by mass) ceria-zirconia (3:1 mol ratio) and 70% γ -Al₂O₃. In the simulation part, a single channel is selected from the monolithic

catalyst to study computationally. The channel is reasonably assumed to be an axisymmetric cylinder with radius of 0.2663 mm. Physical and chemical phenomena taking place inside the channel are examined by using the commercial software ANSYS FLUENT 14.

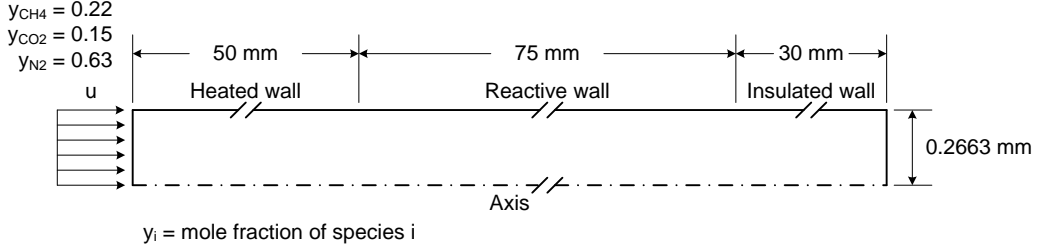


Fig. 1. Computational domain.

The computational domain is separated into three different zones as illustrated in Fig. 1. In the first zone, wall temperature is specified to be equal to the operating temperature; so the temperature of reactants is increased from the ambient to required value. No chemical reaction occurs in the heating up zone. The second zone is where the surface chemical reactions occur causing for depletion of reactants and formation of products. Due to highly endothermic process of CH_4 dry reforming, external energy provided in this zone is necessary. The heat required to be supplied in order to proceed the dry reforming system, \dot{Q}_{in} , is calculated from:

$$\dot{Q}_{in} = \eta_{CH_4} \dot{n}_{CH_4} \Delta h_{R,T}^0 \quad (12)$$

Conversions of CH_4 , η_{CH_4} , are taken from our experiments [14]. Molar flow rate of CH_4 , \dot{n}_{CH_4} , is obtained from:

$$\dot{n}_{CH_4} = \frac{P_{in} \dot{V}_{CH_4}}{RT} \quad (13)$$

The inlet pressure, P_{in} , of 170000 Pa is used for all simulations imitating the value that was used in our previous experiments [14]. The enthalpy change, $\Delta h_{R,T}^0$, during the dry reforming process (R1) is estimated from [38]:

$$\Delta h_{R,T}^0 = \Delta h_{R,298}^0 + \frac{1}{\alpha_{CH_4}} \left[\int_{298}^T \left(\sum_{products} \alpha_i C_p - \sum_{reactants} \alpha_i C_p \right) dT \right] \quad (14)$$

$\Delta h_{R,298}^0$, α_i , and C_p are standard heat of reaction, stoichiometric coefficient of species i (e.g., CH₄, CO₂, CO, and H₂), and heat capacity, respectively. Supplied heat flux in different operating conditions is listed in Table 4. The last zone is presented in order to avoid problems generated from the back pressure at the end of the computational domain. Both supplied heat and chemical reactions are omitted in the last zone. Inlet mole fractions of CH₄ and CO₂ are, respectively, 0.22 and 0.15 to represent the biogas consisting of 60%vol of CH₄ and 40%vol of CO₂. Nitrogen with mole fraction of 0.63 is used as the balance gas. Inlet velocities are 0.8685 and 1.4475 m/s for the gas hourly space velocity (GHSV) of 16500 and 27500 h⁻¹, respectively. Note, to avoid the divide by zero problem (e.g., Eq (9)), the mole fraction of products is specified as a very small value at the initial condition.

Table 4

Supplied heat for dry reforming of CH₄.

Operating temperature (°C)	Heat flux (W/m ²)
GHSV 16500 h ⁻¹	
660	1333
770	1525
870	1697
950	1874
GHSV 27500 h ⁻¹	
625	2325
730	2509
840	2755
910	2907

5. Optimisation

The advantage of LHHW over microkinetic approach is that numbers of chemical reaction are fairly low. So, a sensitivity analysis (SA) is unnecessary to identify important reactions and parameters. In this work, six active parameters (one sticking coefficient, two pre-exponential factors, and three temperature exponents) are needed to be optimised. To avoid the difference in value by many orders of magnitude, the active parameters are scaled to a value which is in the range between -1 and 1. The scaled parameters, X , (called factorial variables) are defined by the following relation [39].

$$X = \frac{\ln\left(\frac{A^2}{A_{min}A_{max}}\right)}{\ln\left(\frac{A_{max}}{A_{min}}\right)} \quad (15)$$

Conversion of CH₄ and productions of H₂ and CO are selected as model responses. A relation of the model responses with several values of factorial variable is systematically constructed and formulated as a second order polynomial. Linear regression analysis is then applied to calculate the values of the factorial variables in order to minimise the error between simulations and experiments [39]. The optimised values including activation energies are summarised in Table 5.

Table 5

Optimised kinetic parameters for the biogas dry reforming and water-gas shift on the platinum-rhodium alumina catalyst.

$A_{1.3}$	(s ⁻¹)	3.5×10^7
$\beta_{1.3}$	(-)	2.0
$E_{1.3}$	(kcal/mol)	32.12
S_{CH_4}	(-)	9.4528×10^{-6}
$\beta_{1.1}$	(-)	1.5483
$E_{1.1}$	(kcal/mol)	19.82
$A_{2.2}$	(s ⁻¹)	0.01

$\beta_{2.2}$	(-)	-1.8
$E_{2.2}$	(kcal/mol)	26.95

6. Results and discussions

6.1. Validation

The validations between model predictions and experimental data are displayed in Figs. 2-6. Note: To follow the results previously published [14], the reactant and product distributions of all conditions are normalised by nitrogen content. The conversions of CH₄ and CO₂, and yield of CO and H₂ are defined as:

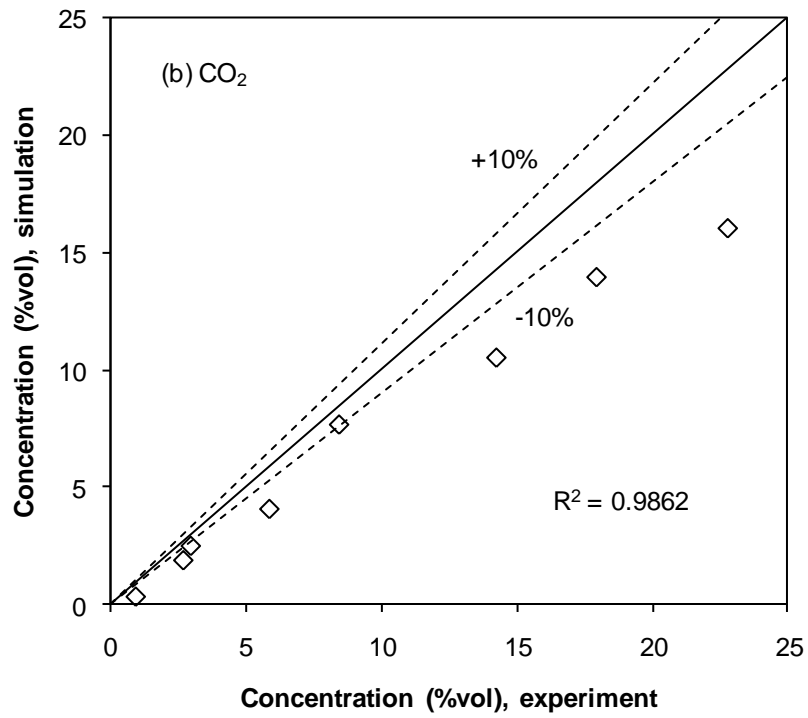
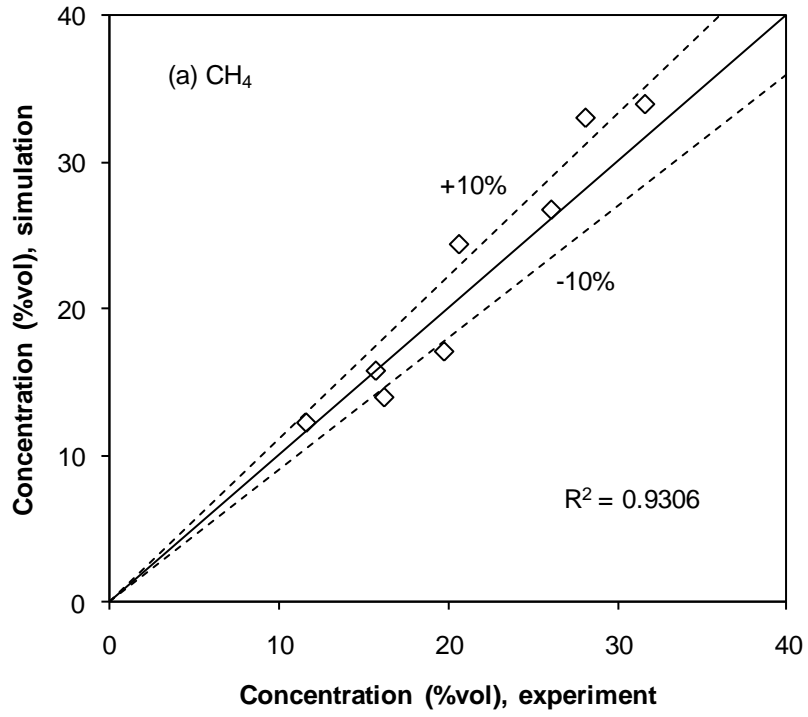
$$CH_4 \text{ conversion (\%)} = \frac{[CH_4]_{inlet} - [CH_4]_{outlet}}{[CH_4]_{inlet}} \times 100 \quad (16)$$

$$CO_2 \text{ conversion (\%)} = \frac{[CO_2]_{inlet} - [CO_2]_{outlet}}{[CO_2]_{inlet}} \times 100 \quad (17)$$

$$CO \text{ yield (\%)} = \frac{[CO]/2}{[CH_4]_{inlet}} \times 100 \quad (18)$$

$$H_2 \text{ yield (\%)} = \frac{[H_2]/2}{[CH_4]_{inlet}} \times 100 \quad (19)$$

With optimised parameters given in Table 5, comparisons of modelling results with measured data are presented in Fig. 2. The linearity between simulation and experiment, R^2 , for all cases is greater than 0.9 and the predicted values are within the margin of $\pm 10\%$ deviation except for CO₂ which simulation predicts lower CO₂ concentration comparing with experiment.



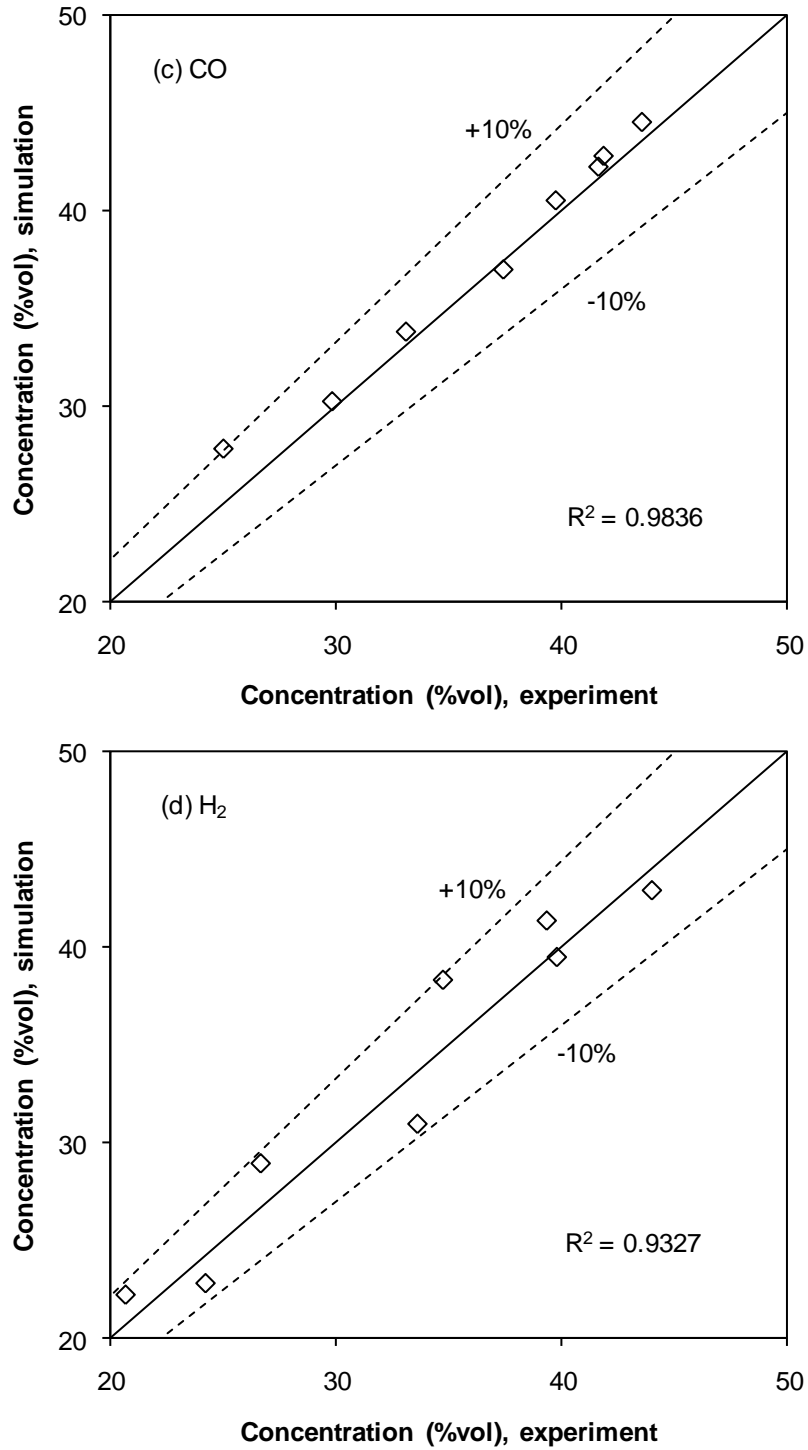


Fig. 2. Parity plots of biogas dry reforming between simulation and experimental data.

Effect of reactor temperature and space velocity on outlet concentration of reactants (e.g., CH₄ and CO₂) and products (e.g., CO and H₂) is illustrated in Fig. 3. Since the dry reforming of CH₄ is the highly endothermic process, the conversion of reactants and creation of products relate

primarily to operating temperature (supplied heat). In contrast, the space velocity has small effect on the reforming process. Results from model show good agreement with measured data.

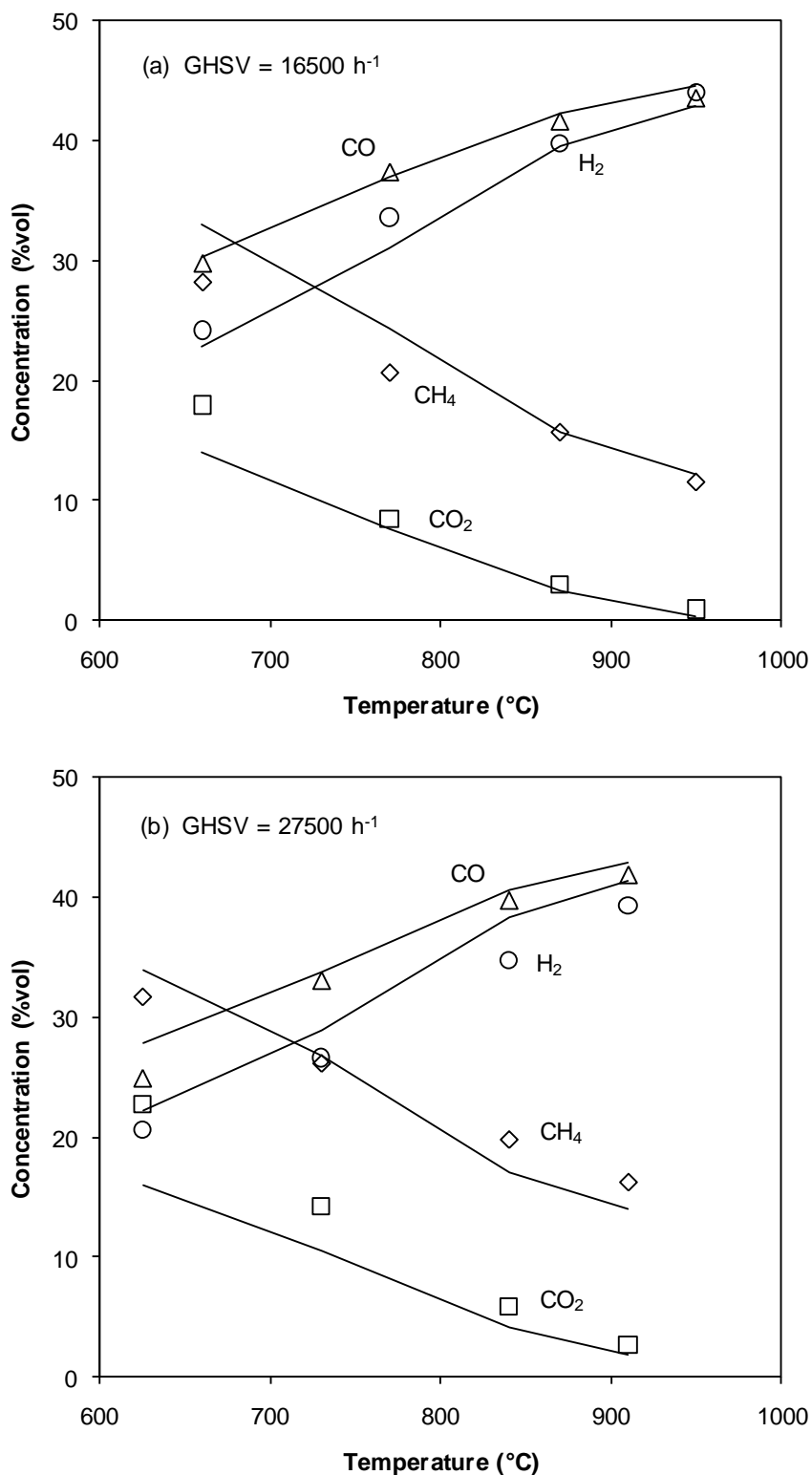


Fig. 3. Outlet concentrations of reactants and products at different operating temperatures and space velocities. (Solid lines: simulation. Symbols: experimental data [14]).

The conversion of reactants into products is illustrated in Fig. 4. The model gives higher conversion than that of experiment for both CH₄ and CO₂. The conversion of CO₂ is larger than that of CH₄. The higher conversion of CO₂ was also found in the literature [27] at CH₄:CO₂ of 1:1. However, when the concentration of CO₂ was increased, for instance CH₄:CO₂ of 1:2 and 1:4, the conversion of CH₄ was larger than CO₂. The conversion at equilibrium state is estimated by using the chemical equilibrium calculation freeware, Gaseq. It indicates the maximum conversion that can be reached at a specific condition (e.g., operating temperature and starting composition of reactants). The figure gives information that at CH₄:CO₂:N₂ of 0.22:0.15:0.63 (actual mole fraction at inlet) or CH₄:CO₂ of 60:40 (percentage after normalised by nitrogen content), the possible conversions of CH₄ and CO₂ are 80 and 100%, respectively, which occur at high temperatures. The conversions obtained from both simulation and experiment approaches the equilibrium values at high temperatures. Nevertheless, at relatively low temperatures, the conversions are much lower than that evaluated from the equilibrium calculation. This suggests that at relatively low temperatures the biogas dry reforming carries out far from the equilibrium state.

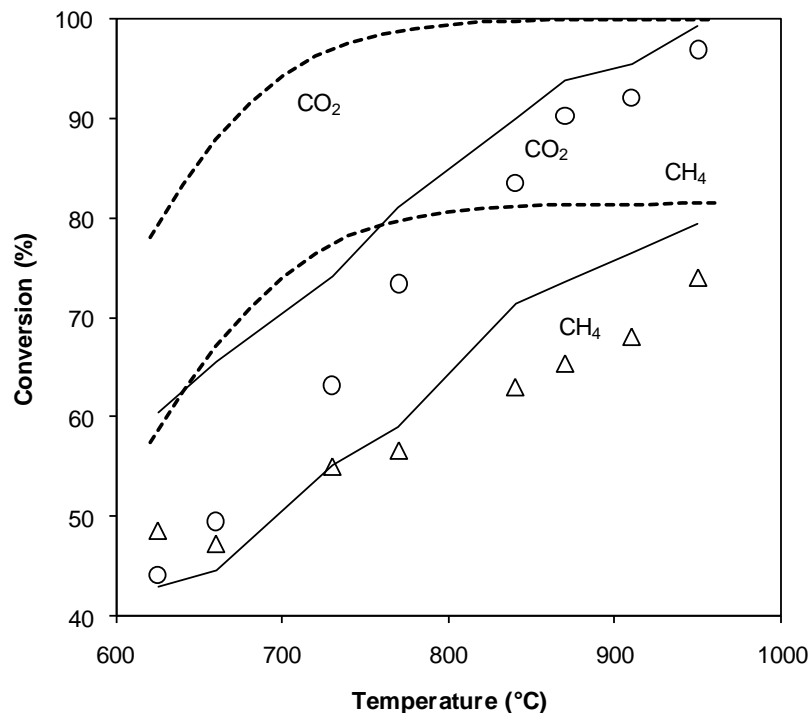


Fig. 4. Conversions of CH₄ and CO₂ at different operating temperatures (Solid lines: simulation. Symbols: experimental data [14]. Dash lines: equilibrium calculation).

Fig. 5 compares yields of CO and H₂ obtained from experiment, modelling, and equilibrium calculation. The yields estimated from the equilibrium calculation represents the maximum yield that can be achieved at a temperature. The figure indicates that the maximum yield is around 37% and can be found in relatively high temperatures. The model shows that the yields of CO and H₂ are close to the values taken from experiments.

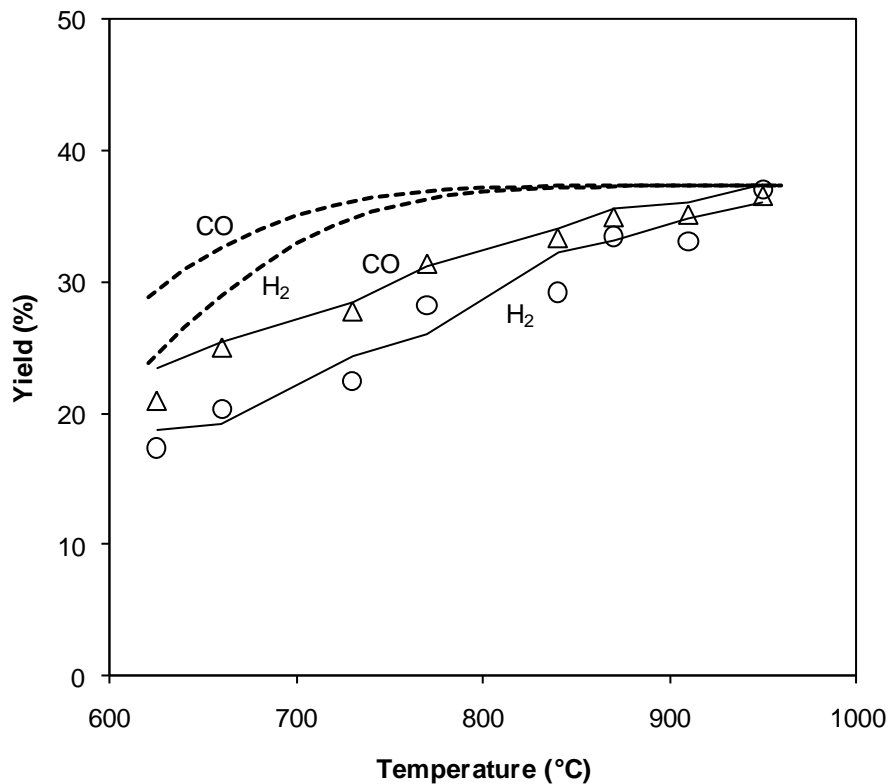


Fig. 5. Yields of CO and H₂ at different operating temperatures (Solid lines: simulation. Symbols: experimental data [14]. Dash lines: equilibrium calculation).

The effect of reverse water gas shift is illustrated in Fig. 6. Two moles of both CO and H₂ are expected to generate from one mole of CH₄ and CO₂ according to the dry reforming pathway, R1. However, the existence of the reverse water gas shift consumes the produced H₂ with CO₂ to create CO which results that the ratio of H₂ to CO is smaller than unity for every operating condition. The H₂ to CO ratio tends to increase as operating temperatures are risen. This

suggests that at relatively high temperatures, dry reforming reaction is more favourable than the reverse water gas shift.

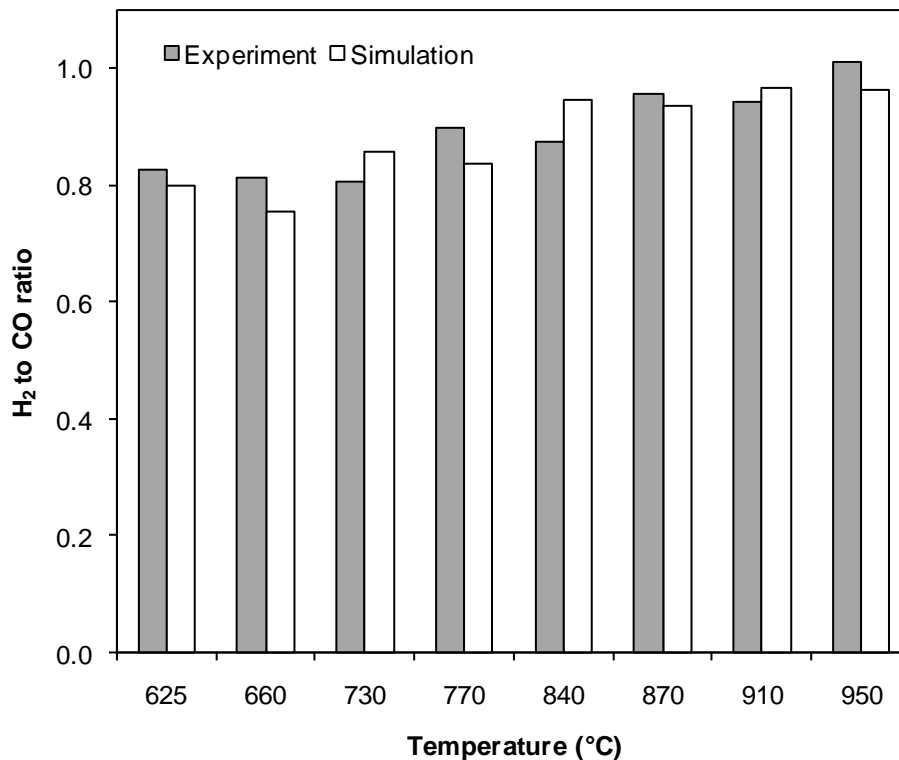


Fig. 6. Comparisons between model predictions and experimental data for the H₂ to CO ratio at various operating temperatures.

6.2. Simulations of biogas dry reforming

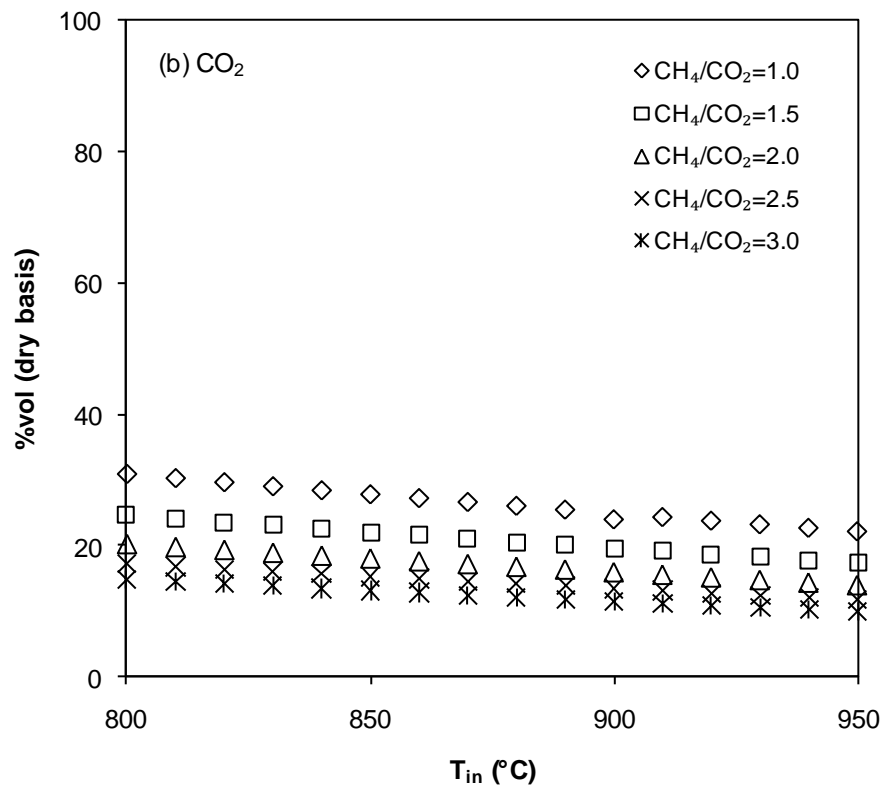
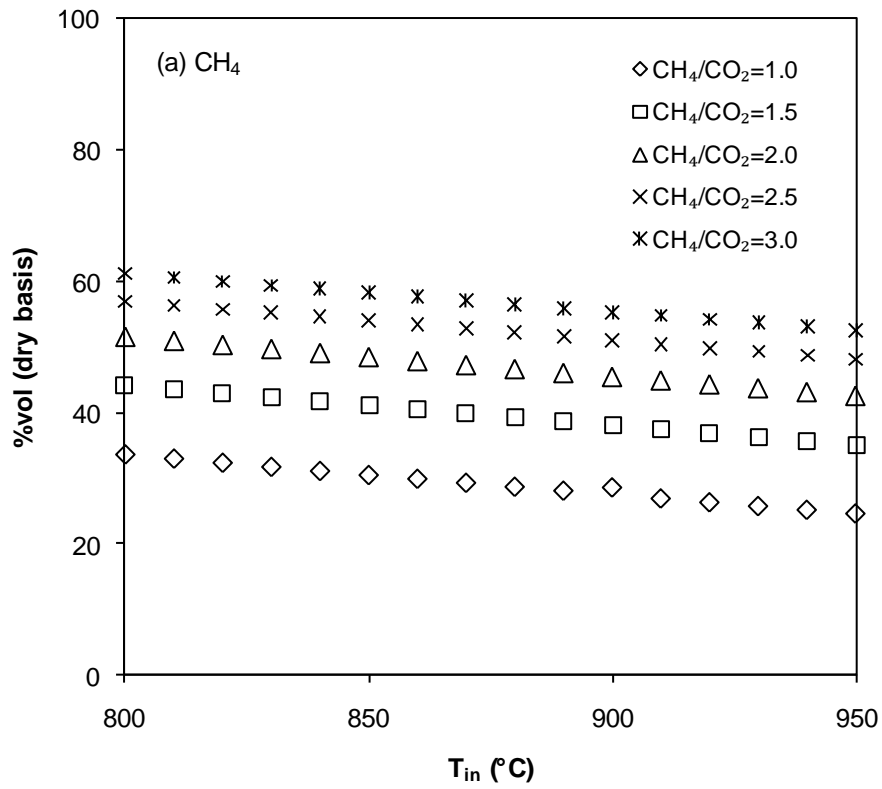
In this section, effects on the biogas dry reforming activities (e.g., gas composition, temperature profile inside catalyst, CH₄ and CO₂ conversions, CO and H₂ yields, and H₂ to CO ratio) of operating conditions (for instant, inlet concentrations of CH₄ and CO₂, inlet temperature, and supplied heat) are predicted without any modification of reaction parameters.

To produce hydrogen from biogas by using the exothermic partial oxidation process, a too high temperature hot spot is avoided. The dry reforming is expected not only to provide more hydrogen production but also to reduce the hot spot temperature resulting from the partial oxidation. With attention to use the endothermic dry reforming to decrease the hot spot temperature during the exothermic partial oxidation which generally proceeds at around 800-

1000 °C, the simulation is performed under high inlet temperatures with and without heat supplied at the catalyst wall.

6.2.1. The effect of inlet temperature on CH₄ dry reforming activity

The effects of inlet temperature and inlet CH₄ to CO₂ ratio on reactant and product concentration at catalyst outlet are shown in Fig. 7. Slow drop of CH₄ and CO₂ (Fig. 7(a) and (b)), as the inlet temperature increases indicates that consumption of reactants increases gradually with the temperature. As the inlet CH₄ to CO₂ ratio increases (with constant CO₂ composition at 15%vol), the improved availability of CH₄ enhanced the dry reforming reaction that consumed additional CO₂ (Fig. 7(b)). In contrast, with limited CO₂ supply, unreacted CH₄ grows quickly resulting in an increase of outlet CH₄ concentration at high CH₄ to CO₂ ratio (Fig. 7(a)). Fig. 7(c) and (d) suggests that CO and H₂ production was improved steadily, with an increase in the inlet temperature. Interestingly, as the inlet CH₄ to CO₂ ratio increases, CO and H₂ show a drop in concentration. Both components concentration should have been increased as more CO₂ was converted (Fig. 7(b)). However, both gases CO and H₂ compositions are calculated through the concentration of each individual component divided by total mixture (not including N₂). As already mentioned, addition of CH₄ results in larger divider and makes lower relative CO and H₂ concentration.



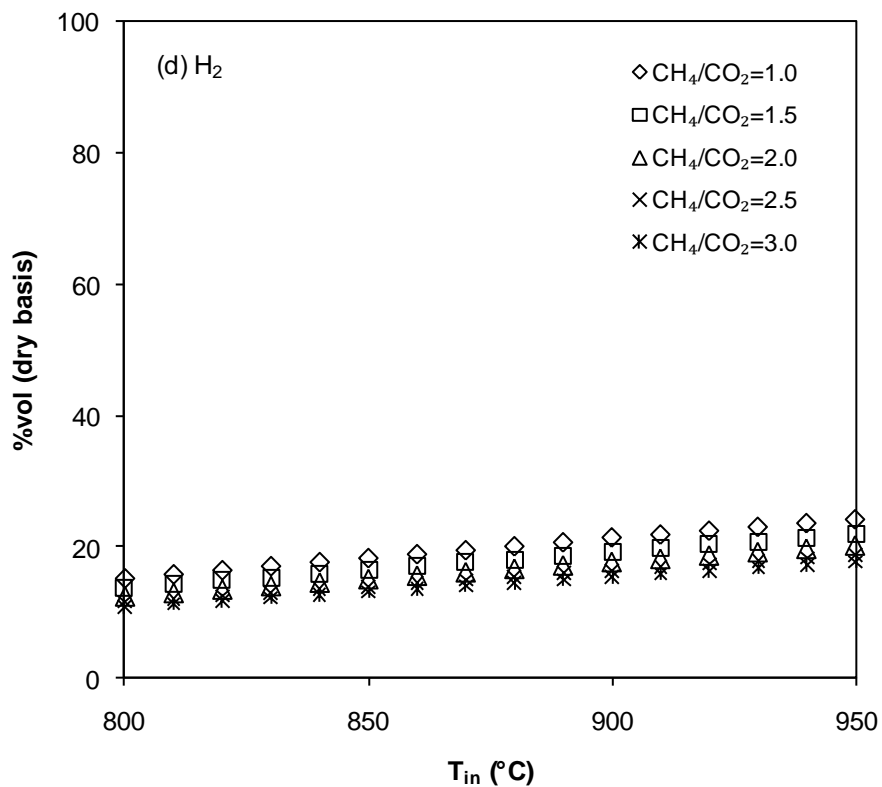
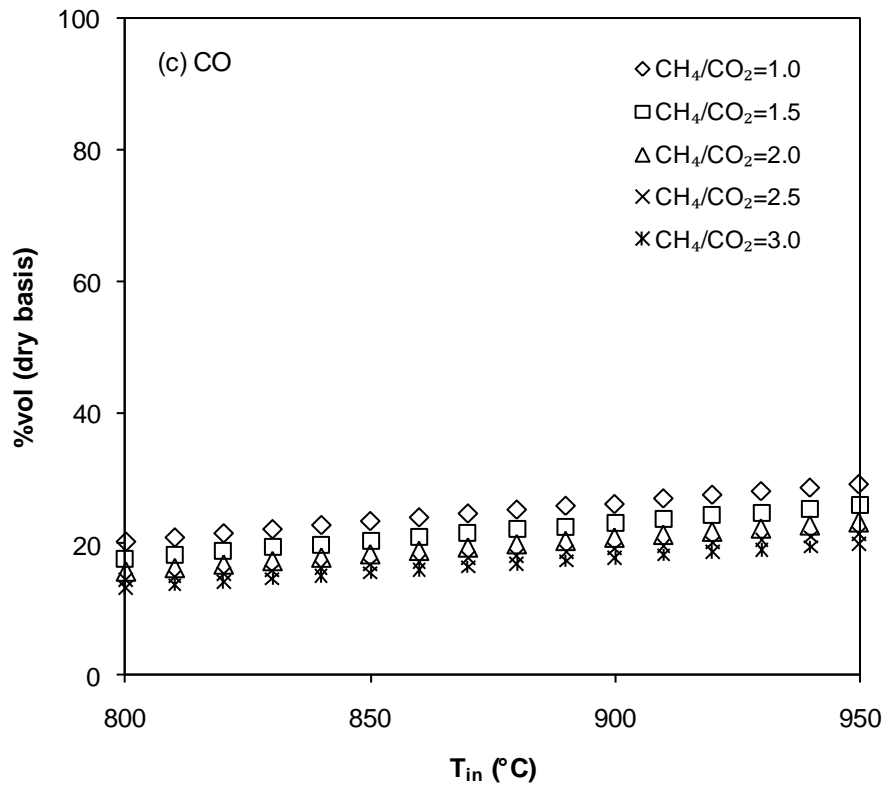
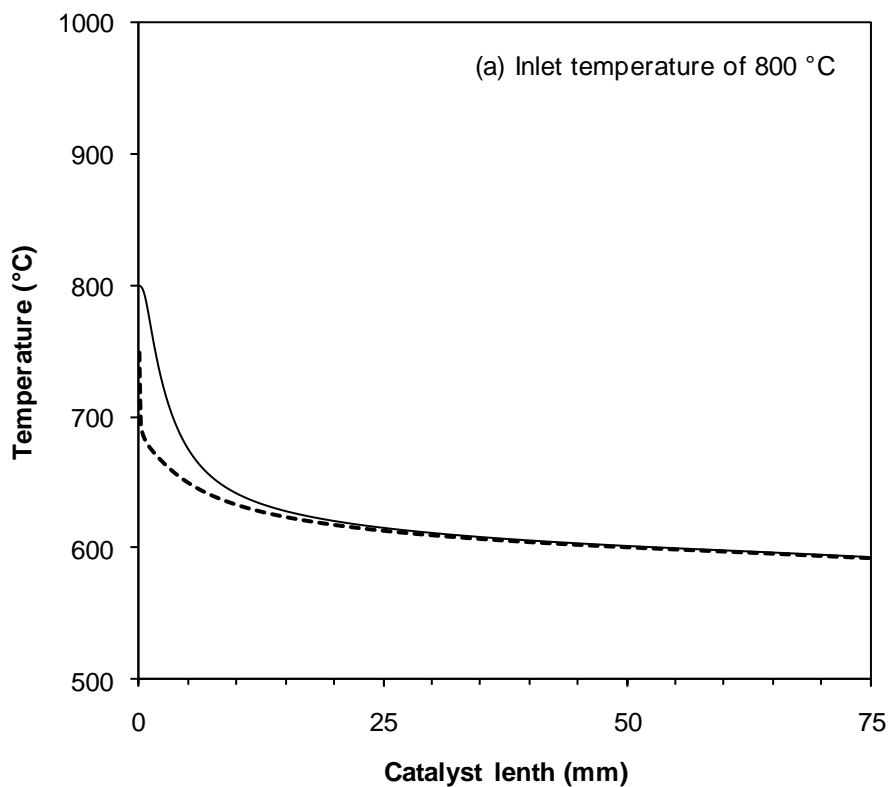
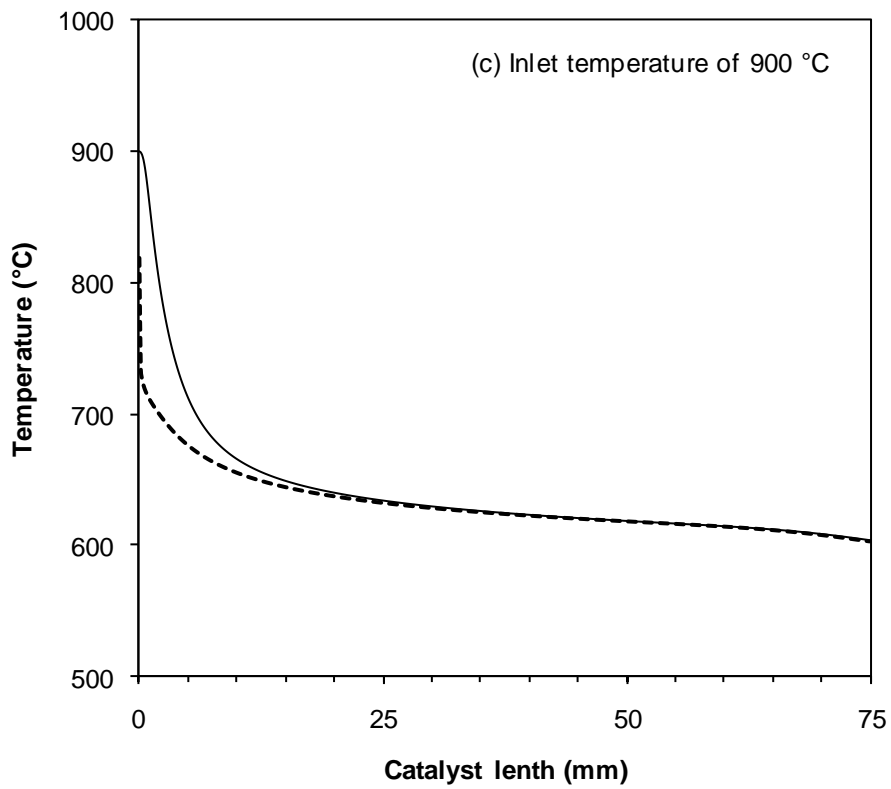
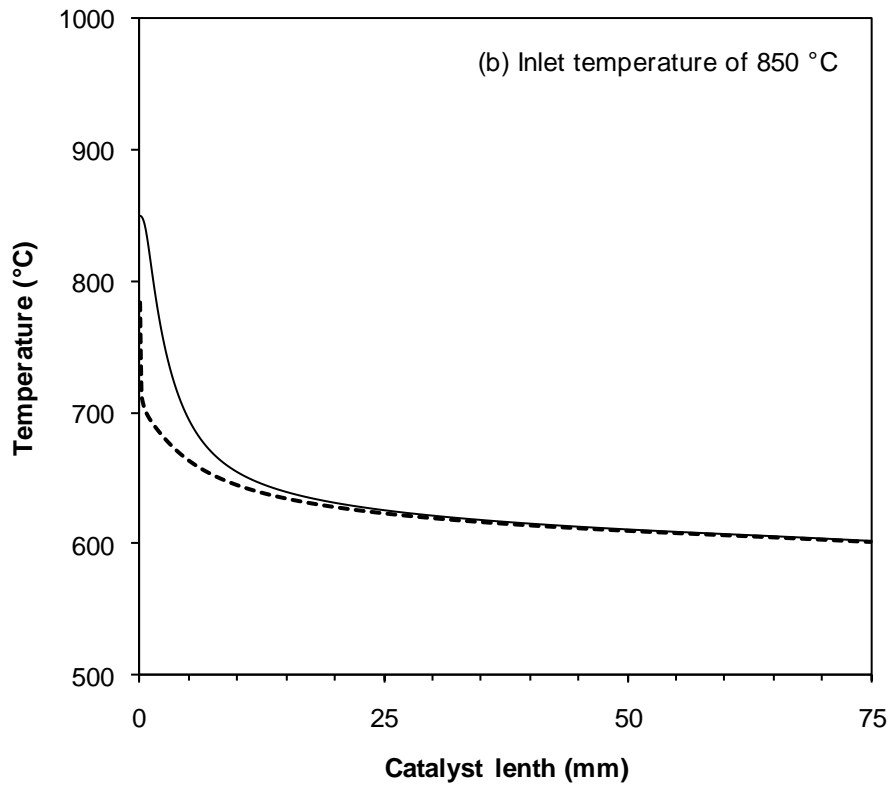


Fig. 7. Model prediction of reactant and product concentrations as a function of inlet temperature at different CH₄ to CO₂ ratios. Inlet conditions: constant CO₂ composition of 15 %vol; GHSV of 27500 h⁻¹; no supplied heat on reactive wall.

Axial and radial velocities and pressure distribution are calculated from the Navier-Stokes equation. Without the assumption about the CH₄ dry reforming taking place under isothermal condition, the temperature profiles inside the channel of catalyst, as shown in Fig. 8, can be obtained by solving the energy equation. The substantial drop of wall and axial temperatures suggests that the endothermic CH₄ dry reforming suddenly starts at the catalyst entrance. Both temperatures approach the same value at around 25 mm of catalyst length for all inlet temperatures. This length indicates the end of chemical activity and is independent on the inlet temperature. Thus, just one third of the catalyst is active and on the catalyst surface beyond this point, there is no existence of dry reforming reaction.





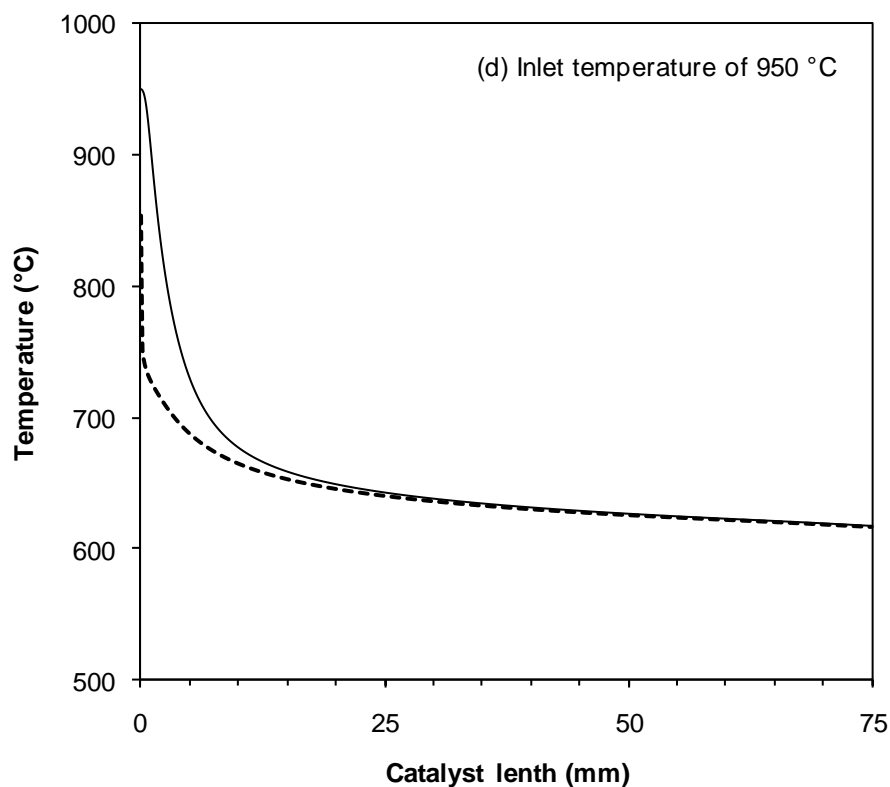


Fig. 8. Temperature profiles inside the catalyst at different inlet temperatures. Inlet conditions: CO₂ composition of 15 %vol; CH₄ to CO₂ ratio of 1; GHSV of 27500 h⁻¹; no supplied heat on reactive wall. (Solid line: axial temperature. Dash lines: wall temperature.)

Comparison of difference in axial and wall temperatures is shown in Fig. 9. Higher inlet temperature gives higher temperature difference which states higher rate of chemical reaction occurring according to Arrhenius law. Interestingly, the highest activity of each inlet temperature (top of the hills) takes place at the same position (0.5 mm).

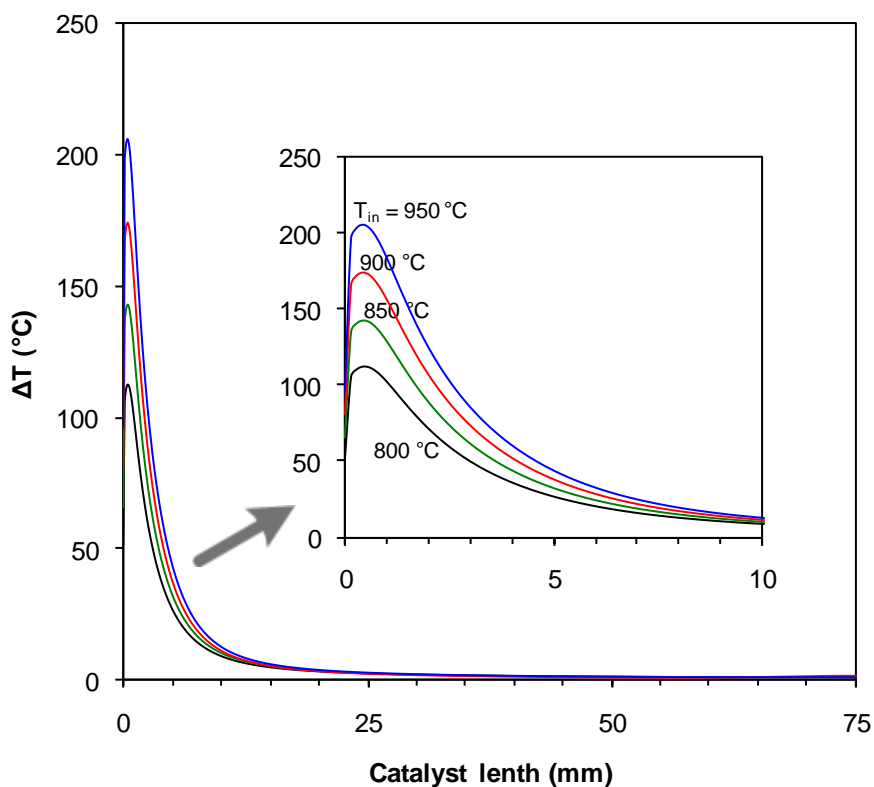


Fig. 9. Difference between axial and wall temperatures at various inlet temperature. Inlet conditions are given in Fig. 8.

The activity of highly endothermic CH_4 dry reforming occurs at high temperatures, potentially near the catalyst durability limits. As expected, conversions of CH_4 and CO_2 vary proportionally with the temperature. Since no heat is supplied to the catalyst wall, conversions of CH_4 and CO_2 were limited to around 40-50%. Decrease of CH_4 conversion, Fig. 10(a), as CH_4 to CO_2 ratio raised is noticed due to remaining of excess CH_4 , as already stated. Conversions of CO_2 , Fig. 10(b), are almost independent of CH_4 to CO_2 ratio due to its constant composition (15 %vol) at inlet. Their conversions are higher than that of CH_4 because it is consumed via both dry reforming with CH_4 and reverse water-gas shift with H_2 .

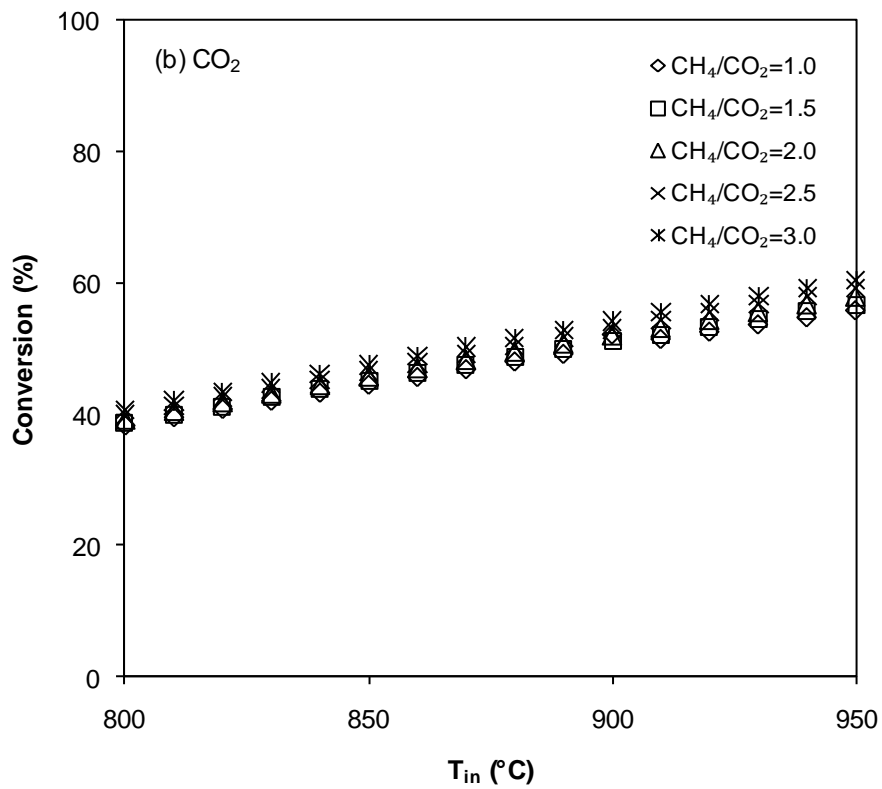
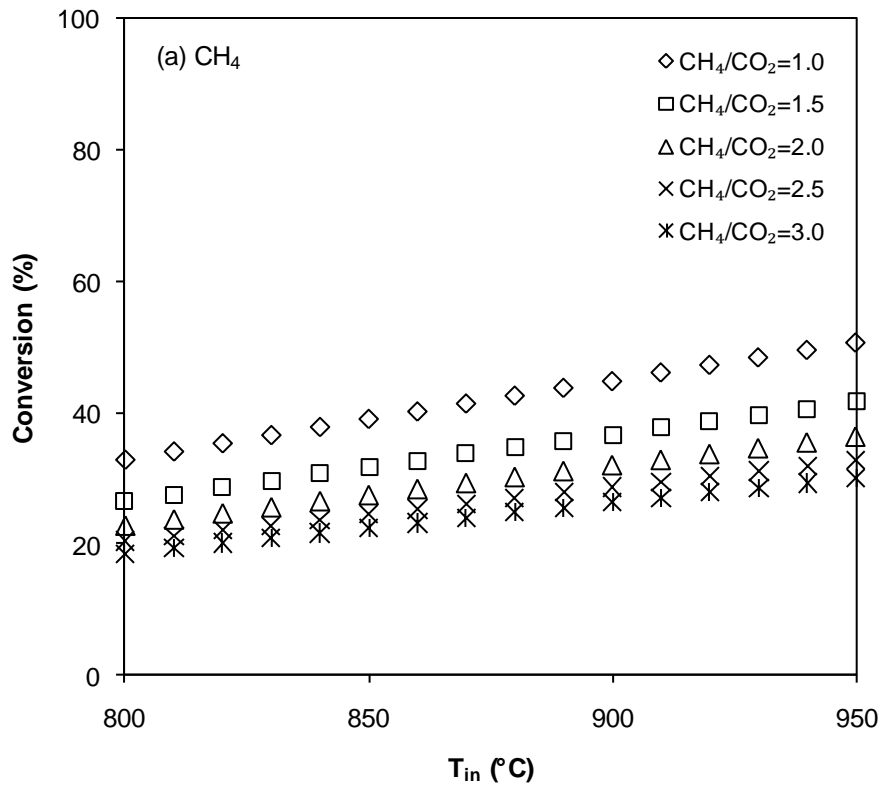
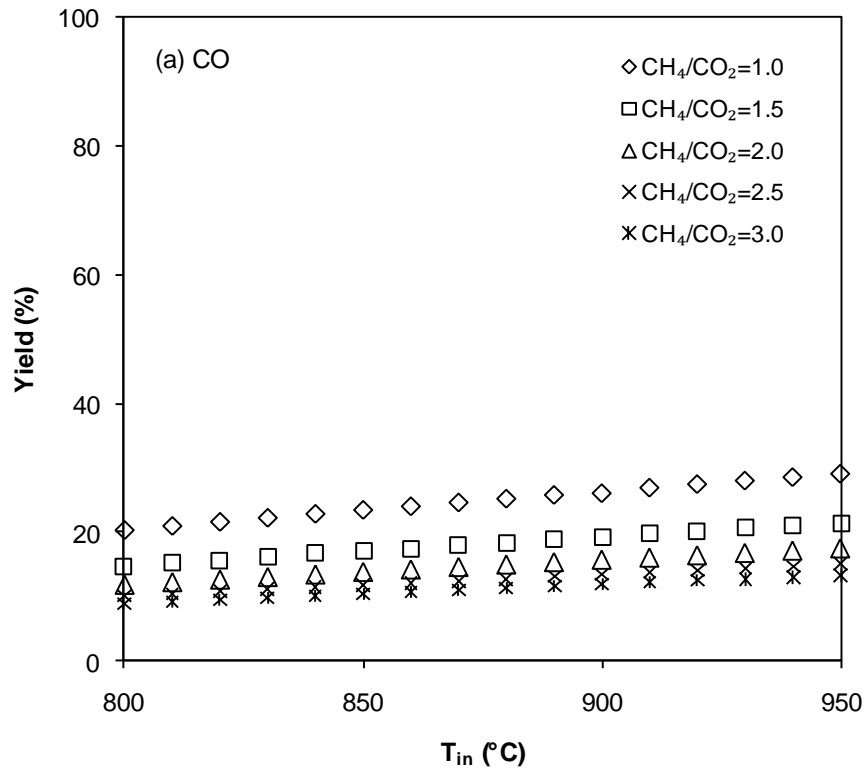


Fig. 10. Prediction of CH₄ and CO₂ conversions as a function of inlet temperature at different CH₄ to CO₂ ratios. Inlet conditions are given in Fig. 7.

Yields of CO and H₂ as a function of inlet temperature and inlet CH₄ to CO₂ ratio are presented in Fig. 11. The product yields rise slowly with inlet temperature. The drops in product yield with increases of CH₄ to CO₂ ratio are resulted from the declines of CH₄ conversion, Fig. 10 (a).



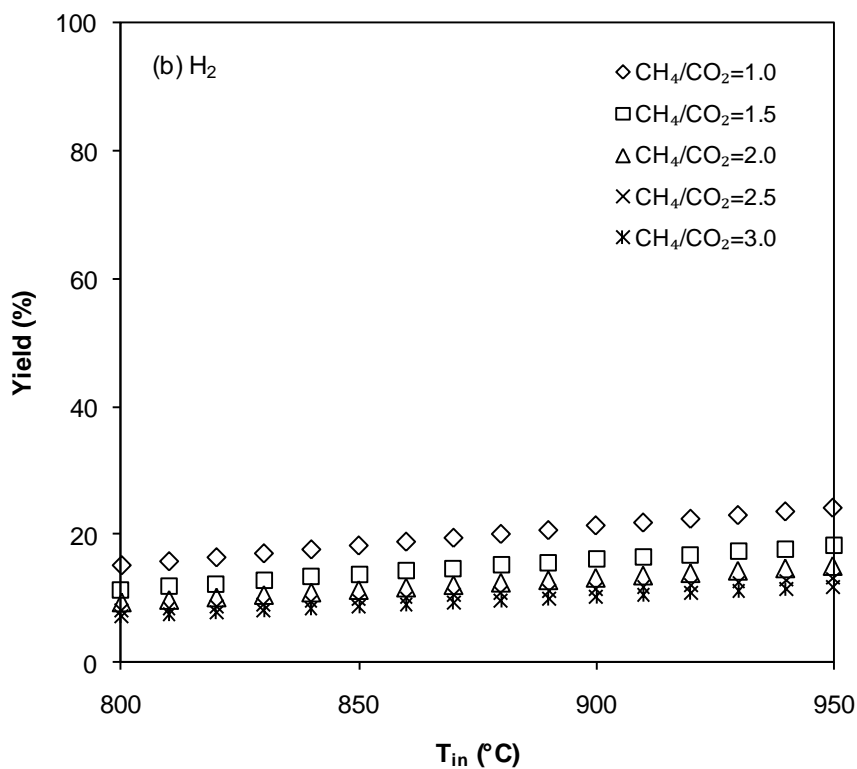


Fig. 11. Prediction of CO and H₂ yields as a function of inlet temperature at different CH₄ to CO₂ ratios. Inlet conditions are given in Fig. 7.

Dependence of H₂ to CO ratio on inlet temperature and CH₄ to CO₂ ratio is displayed in Fig. 12. All H₂ to CO ratios are less than 1.0 and in the range between 0.76 and 0.88. These results indicate the presence of the reverse water-gas shift reaction. Rising of H₂ to CO ratio with inlet temperature indicates that the reverse water-gas shift is less favourable at high temperatures since it is relatively small endothermic comparing with the CH₄ dry reforming.

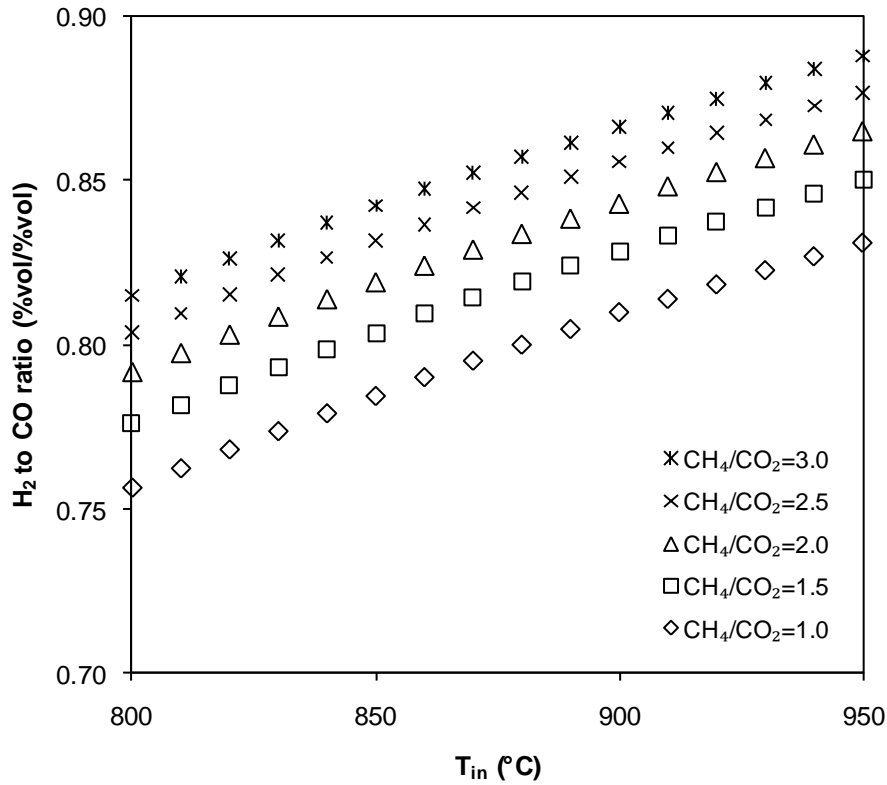
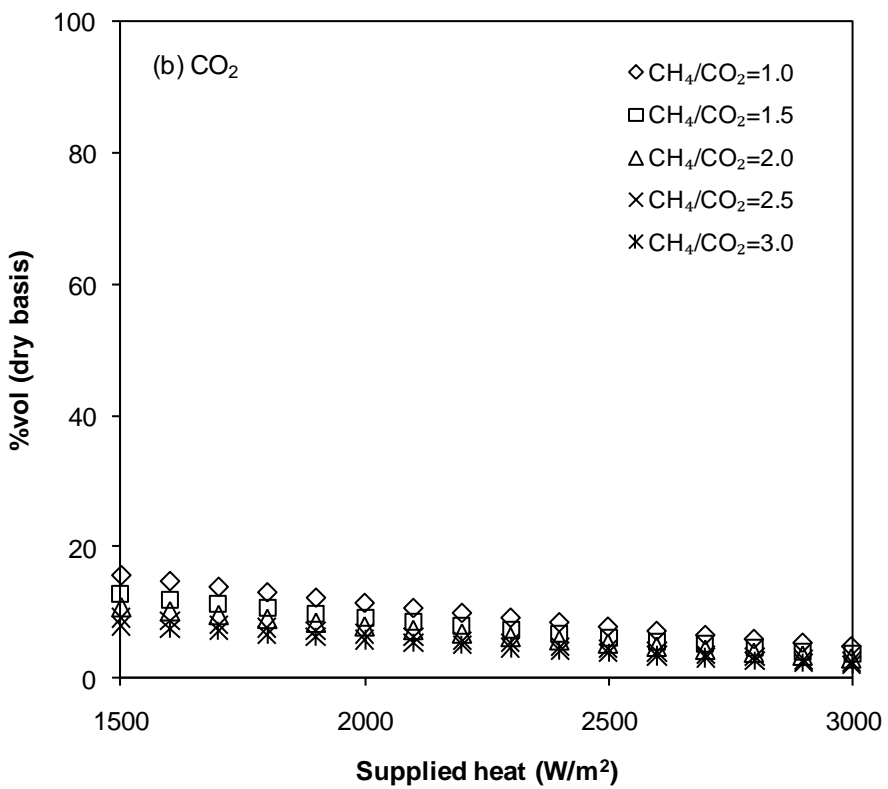
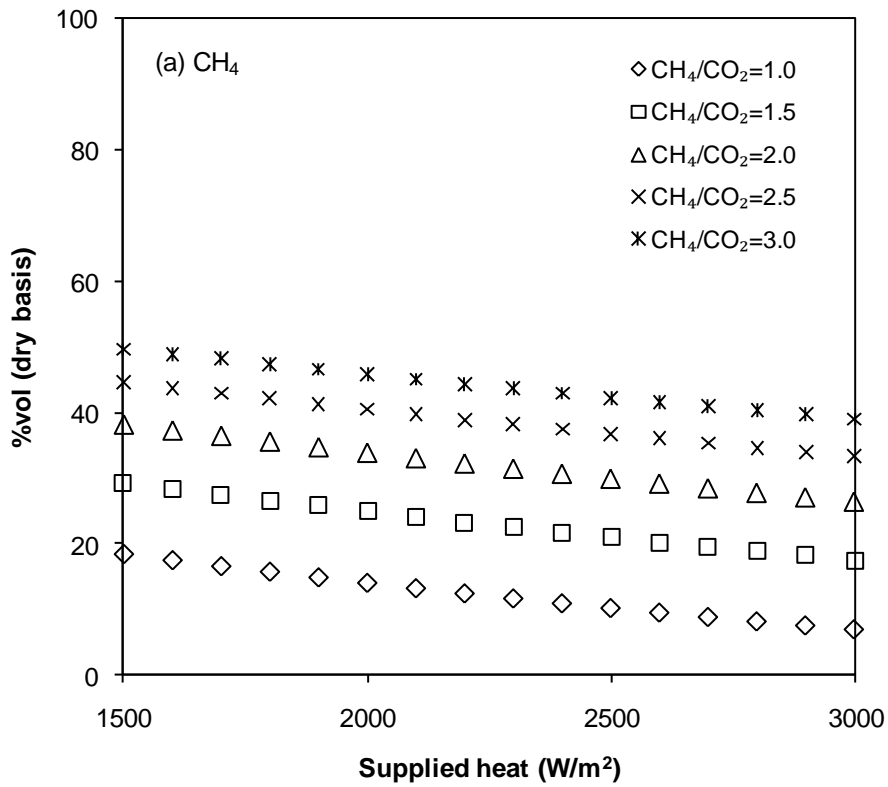


Fig. 12. Prediction of H₂ to CO ratios as a function of inlet temperature at different CH₄ to CO₂ ratios. Inlet conditions are given in Fig. 7.

6.2.2. The effect of supplied heat on CH₄ dry reforming activity

In a biogas reforming system without O₂ addition, there are no exothermic reactions (e.g., partial oxidation and complete combustion) taking place. Thus, external energy is necessary (preferably heat that has been wasted such as engine exhaust gas) to drive the dry reforming process. Effects of supplied heat at several CH₄ to CO₂ ratios on gas composition, temperature profile, reactant conversions, product yields, and produced H₂ to CO ratio are given in Figs. 13-17. As presented in Fig. 13, when the supplied heat is increased, enhancement of reaction rates leads to improvement in reactant consumption, Fig. 13(a) and (b), and product generation, Fig. 13(c) and (d). The biogas dry reforming activity is limited by the constant quantity of CO₂, as already mentioned; addition of excess CH₄ (higher CH₄ to CO₂ ratios) results in lower concentrations of CO and H₂.



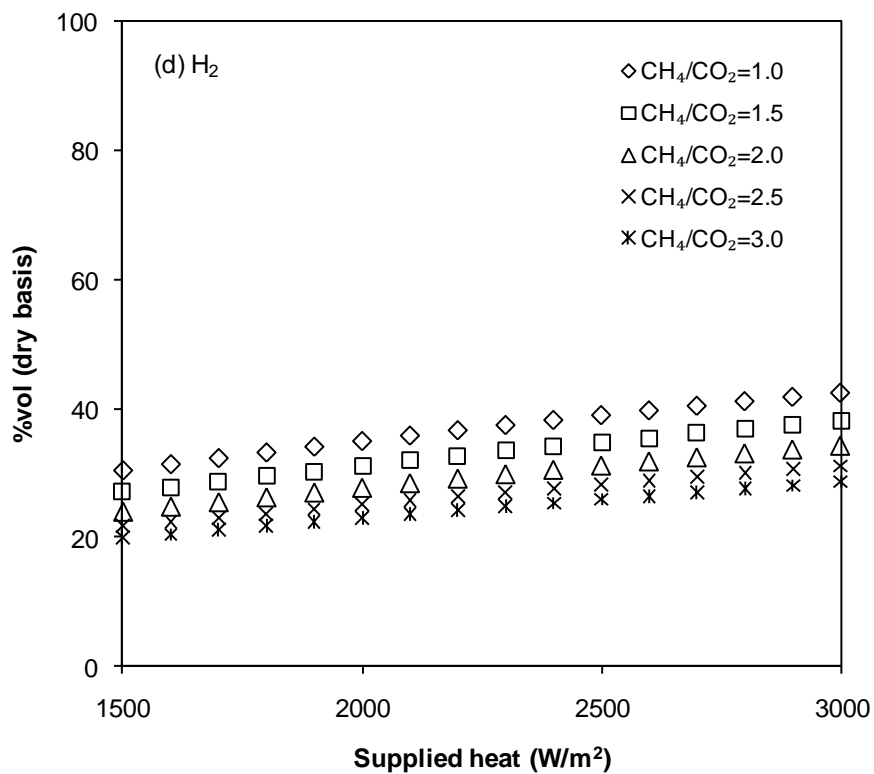
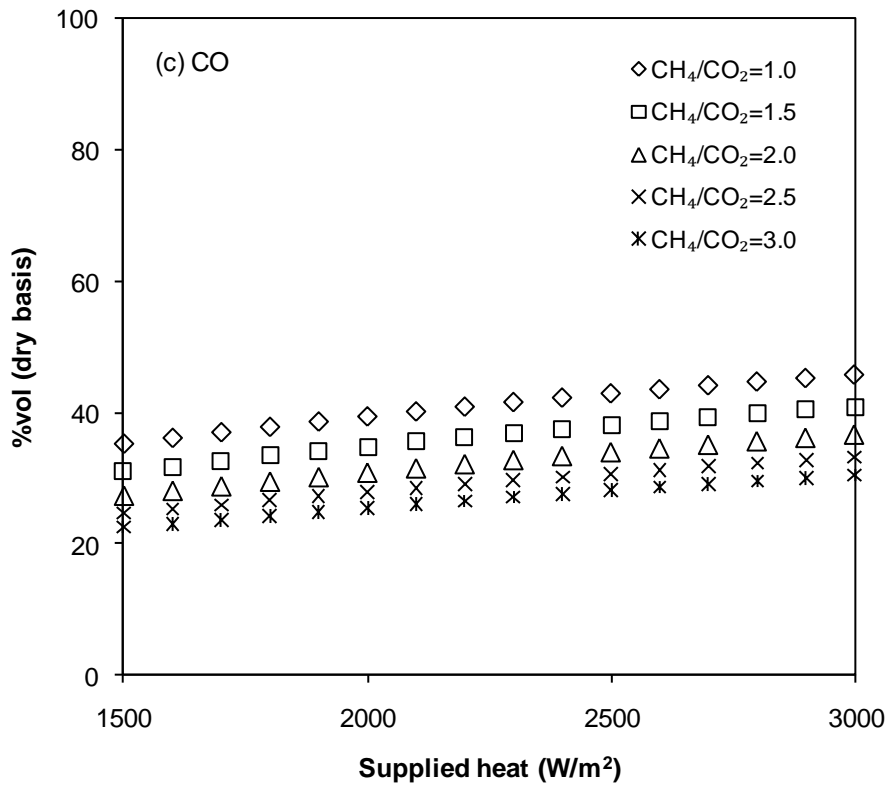
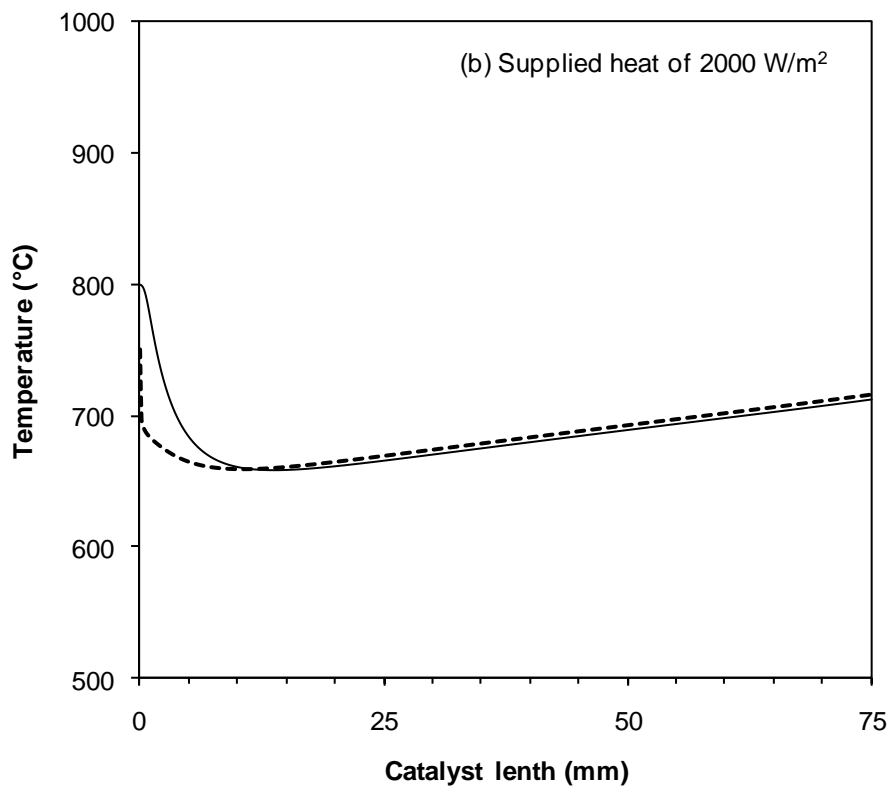
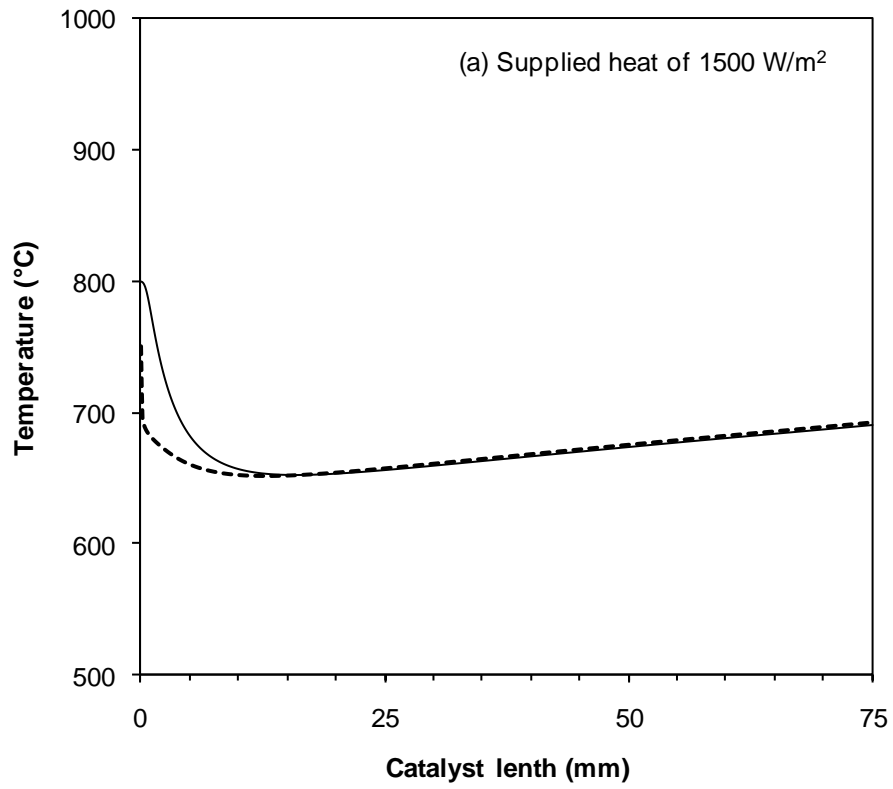


Fig. 13. Model prediction of reactant and product concentrations as a function of supplied heat on reactive wall at different CH₄ to CO₂ ratios. Inlet conditions: constant CO₂ composition of 15 %vol; GHSV of 27500 h⁻¹; inlet temperature of 800 °C.

Effect of supplied heat on temperature profile inside the catalyst is illustrated in Fig. 14. The biogas dry reforming starts immediately at the beginning of catalyst which is characterised by the sharp drop of wall temperature. The nature of endothermic process in this region is noticeable via the lower value of wall temperature comparing with the temperature along the centreline of channel. Interestingly, the value and position of minimum temperatures are nearly independent of supplied heats implying that the chemical reaction of dry reforming is faster than the rate of heat supplied to the system. The end of reforming process is indicated at the point in which wall and axial temperatures are equivalent. Comparison with simulations in the previous section which no external heat provides to the system, the chemical activity is terminated at 25 mm of catalyst length with 615 °C of catalyst temperature in the case of no supplied heat, Fig. 8(a); while, with supplied heat, the dry reforming process finishes at 10 mm and 660 °C. Although the amount of supplied heat does not effect on the terminated characteristics (e.g., position and temperature), the biogas dry reforming activities are dependent on the supplied heat. After the terminated point, supplied heat results in increment of both wall and axial temperatures. Nevertheless, the wall temperature is slightly higher than axial temperature since heat is directly delivered at the catalyst wall.



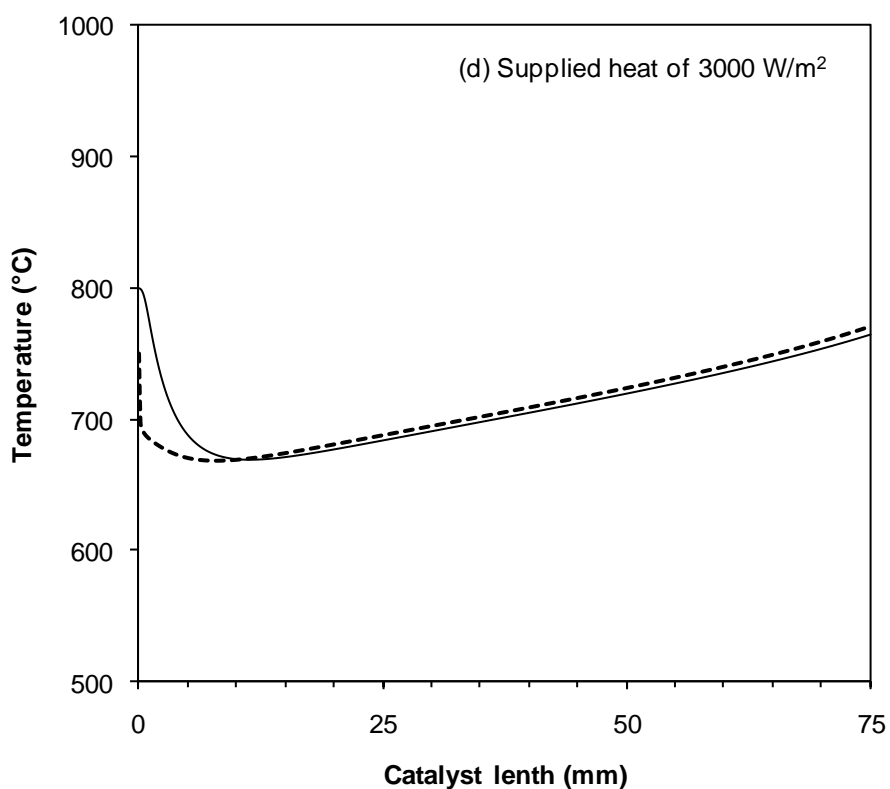
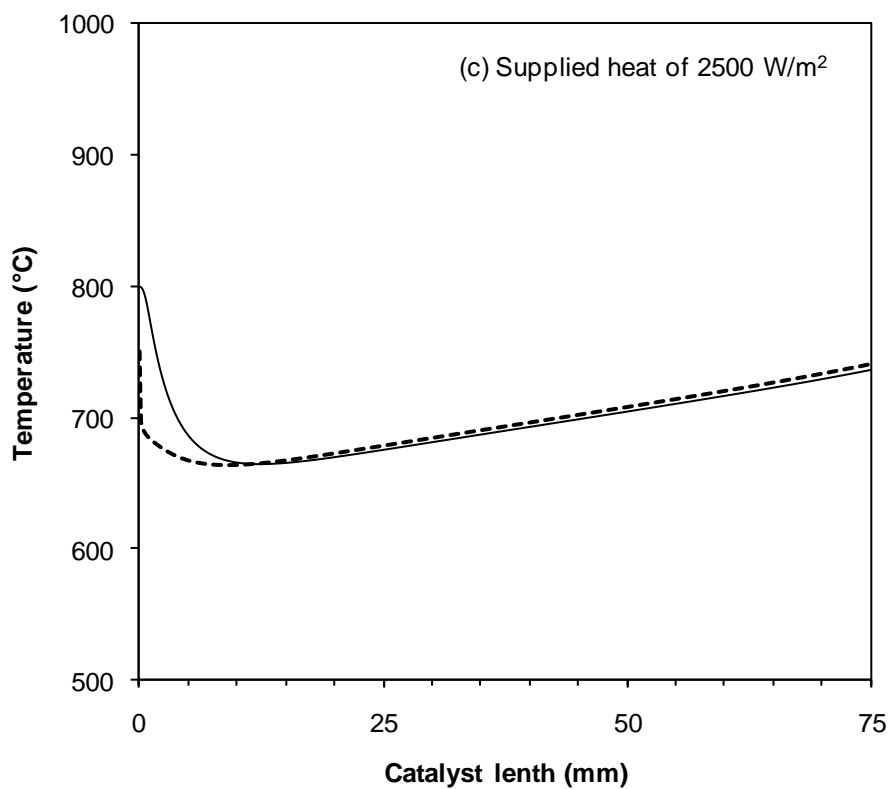
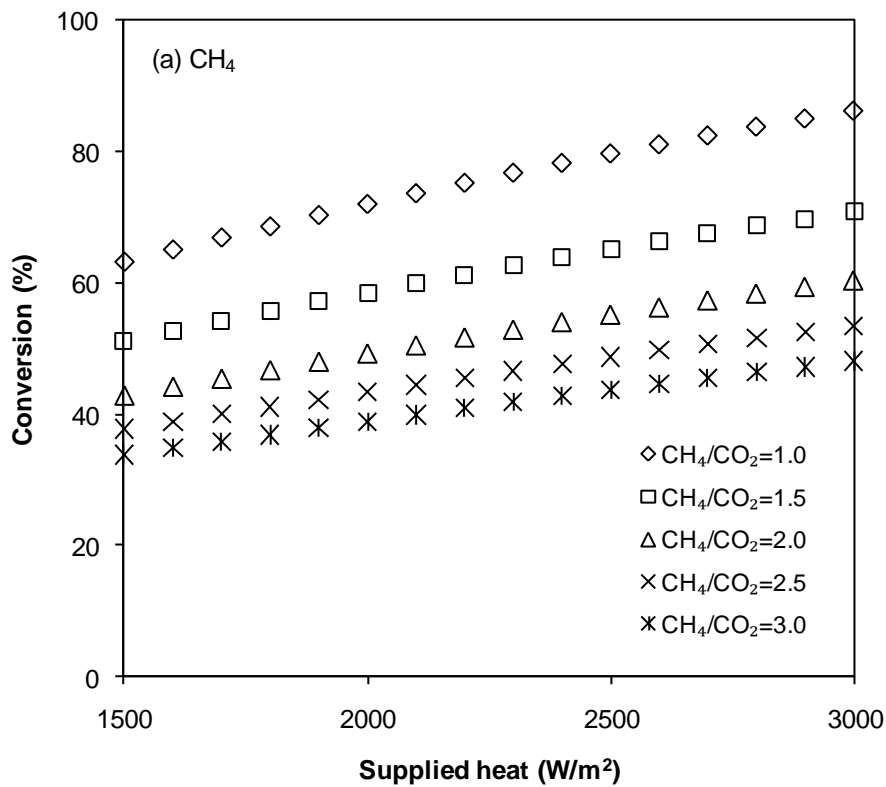


Fig. 14. Temperature profiles inside the catalyst at different supplied heats. Inlet conditions: CO₂ composition of 15 %vol; CH₄ to CO₂ ratio of 1; GHSV of 27500 h⁻¹; inlet temperature of 800 °C. (Solid line: axial temperature. Dash lines: wall temperature.)

Conversions of CH₄ and CO₂ are given in Fig. 15. Role of CO₂ as an important factor to limit the CH₄ dry reforming process is confirmed, as shown in Fig. 15(b), which its conversion is not affected by CH₄ to CO₂ ratios. In general, the CH₄ to CO₂ ratio of natural biogas is between 1 and 3. Therefore, the maximum activity of biogas dry reforming is controlled by the fraction of CO₂. Interestingly, the conversion of CH₄ via dry reforming process has never reached to 100%. This suggests that other reforming methods (e.g., partial oxidation and steam reforming) are required to transform CH₄ completely.



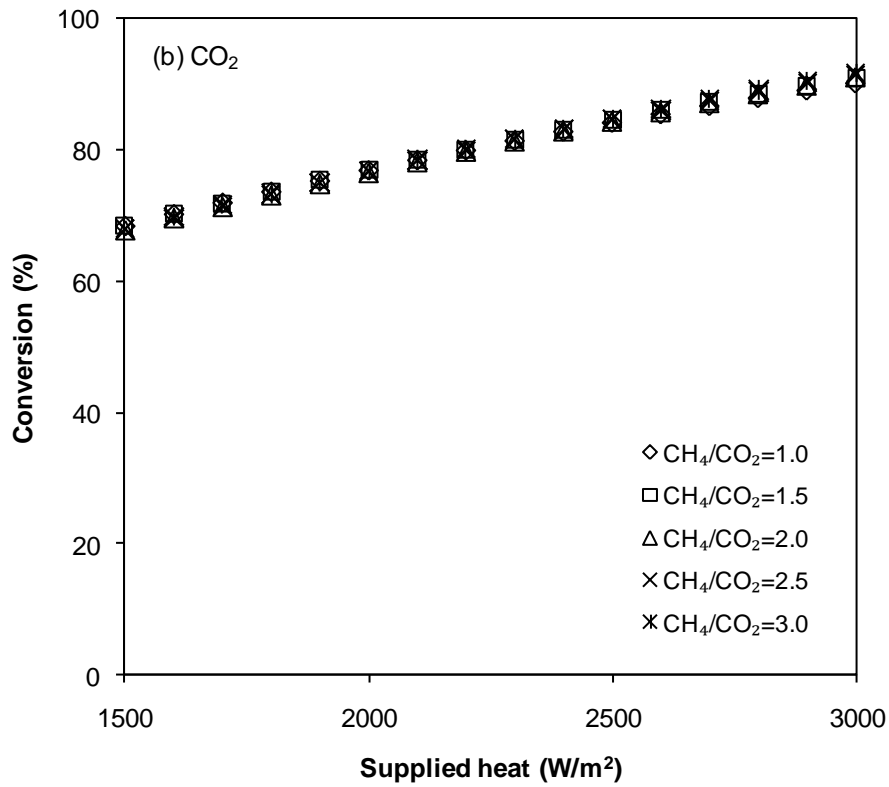


Fig. 15. Prediction of CH₄ and CO₂ conversions as a function of supplied heat on reactive wall at different CH₄ to CO₂ ratios. Inlet conditions are given in Fig. 13.

The effect of supplied heat and CH₄ to CO₂ ratio on product yields is provided in Fig. 16. The increment of un-converse CH₄ as the ratio of CH₄ to CO₂ is raised causes the drop of product yields because the yields are estimated through the amount of inlet CH₄. The side reaction, the reverse water-gas shift, makes the yield of H₂ always lower than that of CO.

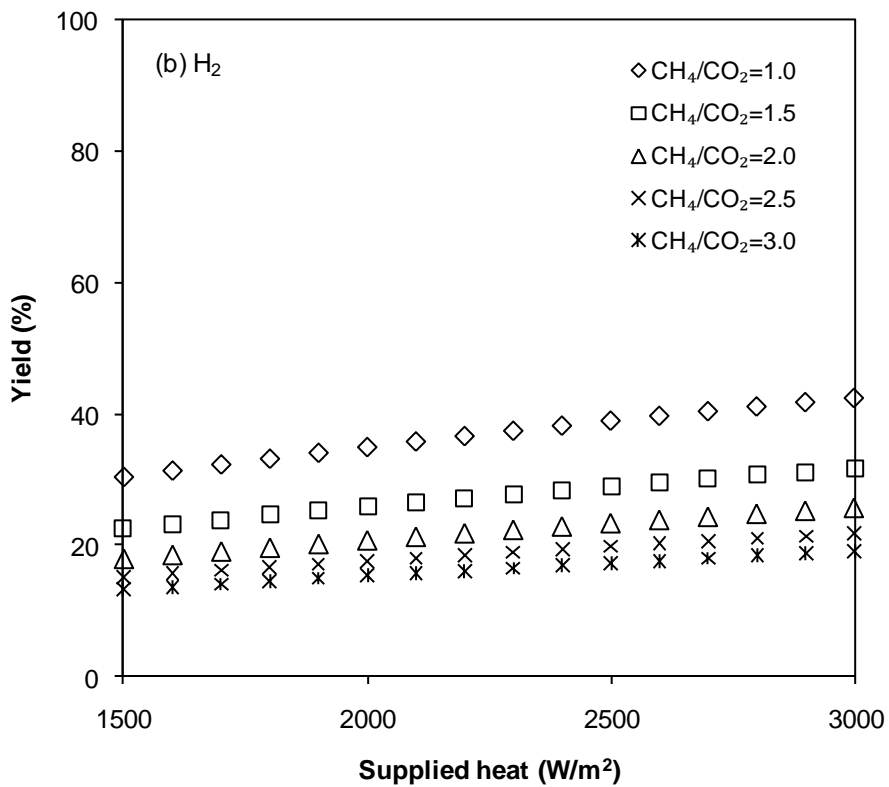
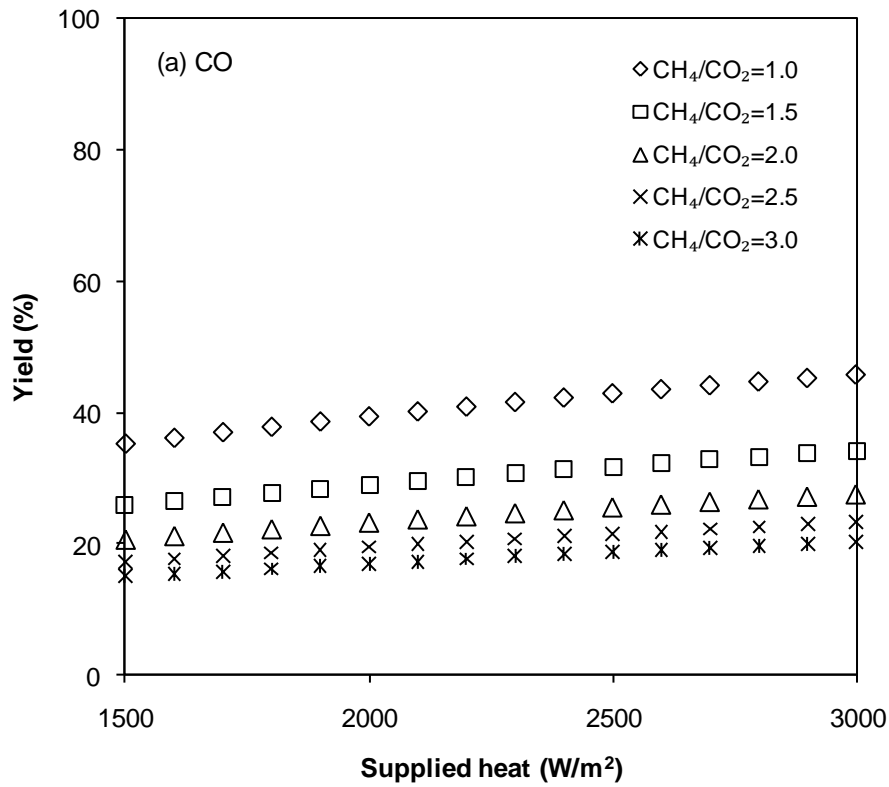


Fig. 16. Yield of CO and H₂ as a function of supplied heat on reactive wall at different CH₄ to CO₂ ratios. Inlet conditions are given in Fig. 13.

The relation of H₂ to CO ratio to supplied heat and inlet CH₄ to CO₂ ratio is explained in Fig. 17. The H₂ to CO ratio depends strongly on supplied heat. Increase of supplied heat promotes the H₂ to CO ratio by decelerating the activity of reverse water-gas shift, as already mentioned in the last section. With supplied heats, the H₂ to CO ratios are between 0.875 and 0.925 while without supplied heat, the ratios are in the range of 0.77 and 0.87. These can be explained by using temperature profiles as shown in Fig. 8 and 14. There are found that with supplied heat, the temperature has never been lower than 660 °C while the temperature is always lower than 640 °C for the reforming without supplied heat. In high operating temperature, the CH₄ dry reforming is promoted and the water gas-shift reaction is suppressed simultaneously; so, higher H₂ to CO ratios are obtained.

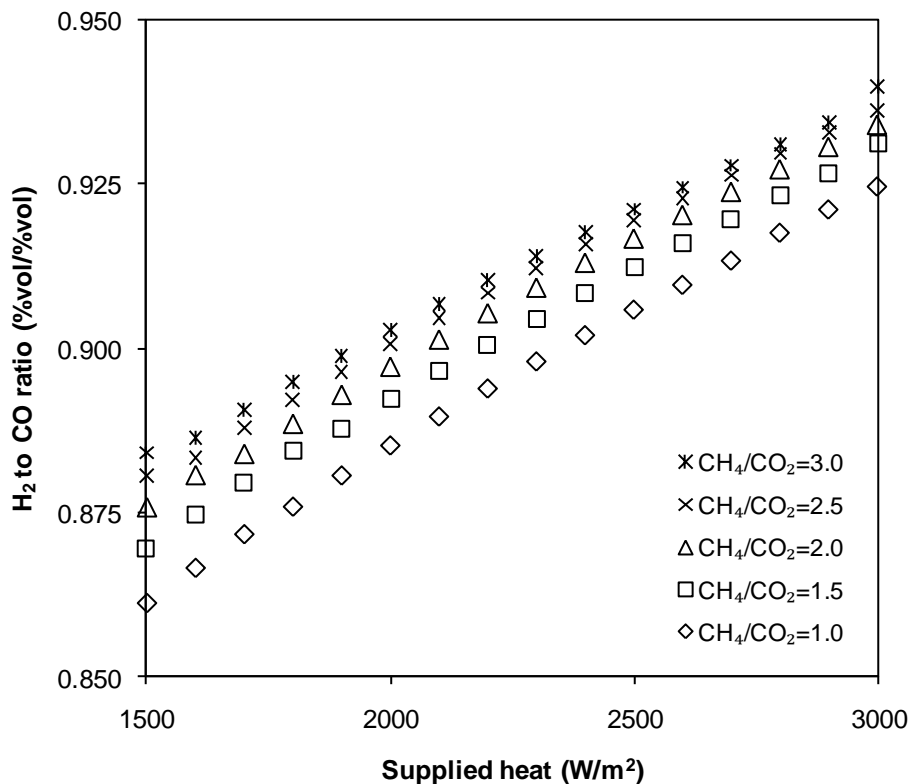


Fig. 17. Prediction of H₂ to CO ratios as a function of supplied heat on reactive wall at different CH₄ to CO₂ ratios. Inlet conditions are given in Fig. 13.

The activity of biogas dry reforming including reactant conversions, product yields, and temperature profiles as a function of inlet temperature, supplied heat, and CH₄ to CO₂ ratio has been presented in previous sections. For a specific value of CH₄ to CO₂ ratio, the model can be utilised to design a biogas reforming system with suitable inlet temperature and supplied heat to provide desired product yields and catalyst temperature that the catalytic materials can be tolerated. The model also shows that there are always existences of unconverted CO₂ due to thermodynamic limitation and CH₄ which is limited by the less amount of CO₂. Thus, to deal with the remaining CH₄, other reforming processes are adopted together with the dry reforming. To construct a fuel reforming system for using in an automotive aftertreatment, external supplied heat is first provided from exhaust gas. Moreover, the main supplied heat is produced from both partial oxidation and complete combustion by adding a controlled value of O₂ into the system. At this circumstance, the endothermic dry reforming is one of parameters used to prevent too high operating temperature. Finally, the model of dry reforming is expected to be applied with other fuel reforming models (e.g., partial oxidation, complete combustion, steam reforming, and water-gas shift), which will be created later to design an effective biogas reforming system for on-board a vehicle processes.

7. Conclusion

Simulation for catalytic biogas dry reforming over a single channel of a monolithic platinum-rhodium alumina catalyst is presented in this work. Based on combination of LHHW and microkinetic modelling approaches, a compact mechanism consisting of CH₄ dry reforming and reverse water-gas shift reactions is formulated. The LHHW method is applied to form rate expressions while microkinetics is utilised to estimate activation energies. As always accompanied with the LHHW rate expression, equilibrium constants for adsorption and desorption processes of various gases are calculated by using the transition state theory. It is found that the Langmuir-Hinshelwood surface reaction is the rate determining step when the reforming process proceeds in relatively high operating temperature range; whereas in

relatively low temperature range, the dissociative adsorption of CH₄ is the rate controlling step. The proposed mechanism is optimised and validated against experimental data at different operating conditions (e.g., temperatures and space velocities). The proposed model is able to predict the effect of inlet temperature, supplied heat, and inlet CH₄ to CO₂ ratio on conversion of CH₄ and CO₂, production of CO and H₂, produced H₂ to CO ratio, and temperature profile inside the catalyst with reasonable precision.

Acknowledgments

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