

Thermodynamic equilibrium study of altering methane partial oxidation for Fischer–Tropsch synfuel production

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ABSTRACT

Thermodynamic equilibrium assessment for methane partial oxidation (MPO) and concomitant parallel side reactions was conducted by employing the Gibbs free energy minimization approach in order to study the tuning of syngas H_2/CO ratio appropriate for downstream Fischer–Tropsch synthesis (FTS). The influences of operating conditions including CH_4/O_2 ratio (5:1–1:2), pressure (1–50 bar) and temperature (200–1000 °C) on MPO performance in terms of reactant equilibrium conversion, product and side product yields and H_2/CO ratio were scrutinized. The results reveal that indirect combustion-reforming pathway was possibly the main contributory factor to the syngas yield during MPO. The lower CH_4/O_2 ratios possessed a positive effect on syngas yield. Carbon formation was favored at low temperatures but it could be suppressed as CH_4/O_2 ratios reduced at elevated temperatures. Although a rising pressure was disadvantageous for MPO performance but the quantity of carbon deposit was hindered since these processes involved gas volume expansion. A temperature at least of 800 °C and CH_4/O_2 ratio of 2:1 or 3:2 are the preferable operating conditions for MPO reaction to achieve the carbon-free region meanwhile maximizing the syngas yield with H_2/CO ratio of 2 that appropriate for FTS process.

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1. Introduction

The rising concerns on the depletion of non-renewable fossil fuels in global energy supply and the severe climate change induced by excessive CH_4 emission from residential and industrial activities have driven a wedge between academia and industry to extensively explore sustainable, renewable and greener energy sources for addressing the aforementioned crises [1–3]. Hence, reducing the substantial reliance on the non-renewable hydrocarbon-based energy by substituting with low-carbon energy sources is an urgent and challenging mission. Syngas (a mixture of CO and H_2) lately emerges as the most prospective energy source among the alternatives owing to its adjustable building blocks for the downstream manufacturing including synfuel via Fischer–Tropsch synthesis (FTS), methanol and its derivatives in petrochemical industries [4–6].

Syngas is conventionally produced from methane steam

reforming (MSR, Eq. (1)) and this is the current implemented technology for commercialization in gas-to-liquid (GTL) plants [7–10]. However, MSR unavoidably emits a significant quantity of anthropogenic CO_2 side product and provides a stoichiometric H_2/CO ratio of 3, which is inappropriate for FTS [11,12]. Although methane dry reforming (MDR, Eq. (2)) is capable to convert CO_2 into syngas, the resulting low H_2/CO ratio (≤ 1) has enormously limited its development in industrial application [13–15]. As a result, employing MSR or MDR technology would increase operating cost due to the installation of ancillary separation and purification stages for tuning the syngas H_2/CO ratio to around 2.



In recent years, methane partial oxidation (MPO, Eq. (3)) has extensively been investigated and appears as a promising candidate to replace other technologies for producing syngas with practical H_2/CO ratio of 2. In fact, catalyst deactivation associated with

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carbon deposits due to CH₄ decomposition is fundamentally inevitable for methane reforming processes [16]. In MPO, regulation of O/C feedstock ratio can strategically inhibit the deposited carbonaceous species and hence, governing the robustness of MPO performance [17,18]. Additionally, MPO is reportedly the most cost-effective approach for syngas production as the energy requirement and capital cost are 10–15% and 25–30% lower than other reforming techniques, respectively [19]. However, MPO is a complex reaction involving direct MPO pathway and indirect combustion-reforming pathway (CH₄ combustion provides CO₂ and H₂O, followed by MSR and MDR) as well as multiple concomitant side reactions including coke and non-coke forming reactions [20], as listed in Table 1. Since the process variables (i.e., feed composition, temperature and pressure) possess significant influence on the MPO reaction pathway [21,22], it is essential to investigate their effects on the MPO performance in order to optimize the operating conditions achieving the direct use of desired syngas ratio in downstream production.

Thermodynamic assessment is always a useful tool for evaluating the impacts of process variables on equilibrium reactant conversions and product distribution. Hence, it conventionally serves as a guide for conducting experimental studies, in particular for the chemical process involving complicated reactions [23–25]. As a result, numerous researches regarding thermodynamic analysis of methane reforming have been studied employing the Gibbs free minimization approach [23,26–28]. Jang et al. [23] performed the thermodynamic equilibrium evaluation for combined steam and dry reforming of methane and subsequently conducted the experiment at simulated conditions for comparison purpose. They revealed that the formation of carbonaceous species was inevitable even though in the presence of excessive oxidizing agents, confirming that the rates of coke forming reactions are non-negligible in the thermodynamic assessment as suggested earlier by Li and the co-workers [29]. The carbon deposits can be hindered at elevated (CO₂ + H₂O)/CH₄ ratios at high temperature but excess CO₂ and H₂O impose an additional operating cost for separation unit. Cao et al. [26] studied the reaction conditions of methane dry reforming using thermodynamic analysis for producing the direct-used syngas ratio for downstream Fischer-Tropsch synthesis. The H₂/CO ratio reportedly could be adjusted by feed composition, temperature and pressure but similarly, the formation of carbon

was unavoidable. Although these thermodynamic studies of methane reforming have been extensively conducted, the presence of concomitant coke deposit is failed to be compromised under the applicable reaction conditions for desirable H₂/CO ratio modification. Based on the literature [30–32], the employment of O₂ as a gasifying agent is comparatively effective for carbon removal via redox process in comparison with CO₂ or H₂O compounds. This suggests that MPO has the possibility of not only optimizing reaction conditions for achieving H₂/CO ratio around 2 but also could realize the carbon-free regions under the similar operating conditions. However, the bibliography of thermodynamic equilibrium assessment on MPO is still little-known with respect to impacts of feedstock ratio, pressure and temperature. Additionally, the previous thermodynamic studies of MPO did not comprehensively deliver systematic and profound understanding to the precondition for the MPO process respecting carbon elimination and syngas H₂/CO ratio production appropriate for FTS application [33–37].

In the present work, thermodynamic assessments of MPO reaction with various operating conditions including feed composition, temperature and pressure were conducted using HSC Chemistry 6. The thermodynamic equilibrium results of main reforming reactions were compared to that of concomitant side reactions in order to comprehensively understand the pathway of MPO reaction. The formation of carbonaceous species from different coke forming reactions were analyzed at various operating conditions in order to identify the carbon-intensive and carbon-free regions. In addition, the simulation of M–O (M = Ru, Rh, Pd, Fe, Co, Ni) systems were investigated to determine the resistibility of metal phases towards oxidation process at various operating conditions during MPO. The relationship of process variables and syngas ratio as well as carbon yield was further explored. Eventually, the optimum reaction conditions for tuning syngas H₂/CO ratio around 2 meanwhile free from carbon deposits were determined.

2. Methodology

The equilibrium composition of reactant and product gases within temperature range of 200–1000 °C were simulated using HSC 6 Chemistry software packaged by GIBBS program operating the Gibbs free energy minimization's principle. Prior to the

Table 1
Summary of propensity of primary and side reactions occur during reaction based on Gibbs free energy change calculations performed by HSC Chemistry 6.

Reactions	Equations	No.	ΔG (kJ mol ⁻¹)	Temperature regions			
				Region 1 (200–400 °C)	Region 2 (400–600 °C)	Region 3 (600–800 °C)	Region 4 (800–1000 °C)
Reforming reactions							
Methane steam reforming (MSR)	$CH_4 + H_2O \rightarrow 3H_2 + CO$	R1	$-0.2446\ T + 150.85$	ND	ND–D	D	D
Methane dry reforming (MDR)	$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	R2	$-0.2797\ T + 179.38$	ND	ND–D	D	D
Methane partial oxidation (MPO)	$CH_4 + 0.5O_2 \rightarrow 2H_2 + CO$	R3	$-0.1921T - 79.924$	ND	ND–D	D	D
Non-coke forming reactions							
CH ₄ combustion	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	R4	$0.0005\ T - 800.78$	D	D	D	D
CO ₂ methanation	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	R5	$0.2096T - 122.32$	D	D–ND	ND	ND
CO methanation	$3H_2 + CO \rightarrow CH_4 + H_2O$	R6	$0.2446\ T - 150.85$	D	D–ND	ND	ND
Water-gas shift (WGS)	$H_2O + CO \rightarrow CO_2 + H_2$	R7	$0.0351\ T - 28.534$	D	D–ND	ND	ND
Revere water-gas shift (RWGS)	$CO_2 + H_2 \rightarrow H_2O + CO$	R8	$-0.0351\ T + 28.534$	ND	ND	ND–D	D
Carbon gasification by CO ₂	$C_{(s)} + CO_2 \rightarrow 2CO$	R9	$-0.177\ T + 124.14$	ND	ND	ND–D	D
Carbon gasification by H ₂ O	$C_{(s)} + H_2O \rightarrow H_2 + CO$	R10	$-0.1419\ T + 95.604$	ND	ND	ND–D	D
Coke forming reactions							
CO dehydrogenation	$H_2 + CO \rightarrow H_2O + C_{(s)}$	R11	$0.1419\ T - 95.604$	D	D–ND	ND	ND
Boudouard reaction	$2CO \rightarrow C_{(s)} + CO_2$	R12	$0.177\ T - 124.14$	D	D	D–ND	ND
CO ₂ hydrogenation	$2H_2 + CO_2 \rightarrow C_{(s)} + 2H_2O$	R13	$0.1069\ T - 67.069$	D	D–ND	ND	ND
CH ₄ decomposition	$CH_4 \rightarrow C_{(s)} + 2H_2$	R14	$-0.1027\ T + 55.246$	ND	ND–D	D	D

D and ND represent dominant and not dominant, respectively while ND–D (or D–ND) represents from not dominant to dominant (or vice versa).

calculation, quantity of reactants employed and the corresponding phases of reactant species at various temperatures were considered as the main input parameters in simulations. Apart from carbon in solid phase due to methane decomposition, the other compounds involved such as O₂, CH₄, CO, H₂, CO₂ and H₂O were considered in gas phase throughout the simulations.

Prior to the thermodynamic assessment, identifying chemical phase and equilibrium configurations of a specific system at desirable operating conditions is indispensable. The total Gibbs free energy for a complex system with N number of element 'i' can be derived as shown in Eq. (4).

$$G^t = \sum_{i=1}^N n_i u_i = \sum_{i=1}^N n_i \left(G_i^0 + RT \ln \frac{f_i}{f_i^0} \right) \quad (4)$$

where G^t , N and n_i represent the corresponding total Gibbs free energy, element number and mole quantity of element 'i'. G_i^0 is the standard Gibbs free energy for formation of element 'i' whilst R and T are being the universal gas constant and system temperature, respectively. The f_i is the fugacity of element 'i' in the system whereas f_i^0 is the standard fugacity of element 'i'. Since the reaction system is in gas phase, the f_i can be defined as $y_i \hat{\phi}_i P$ whereas $G_i^0 = \Delta G_{f,i}^0$ and $f_i^0 = p^0$. As a result, the expression can be derived as:

$$G^t = \sum_{i=1}^N n_i \left(G_{f,i}^0 + RT \ln \frac{y_i \hat{\phi}_i P}{p^0} \right) \quad (5)$$

with y_i and $\hat{\phi}_i$ are corresponded to the molar fraction and fugacity coefficient of element 'i' while $G_{f,i}^0$ represents the standard Gibbs free energy for element 'i' formation. P and p^0 are being the system pressure and standard-state pressure (101.325 kPa) in this order. With the employment of Lagrange multiplier, the minimum Gibbs free energy equation can be further expressed as:

$$\sum_{i=1}^{N-1} n_i \left(G_{f,i}^0 + RT \ln \frac{y_i \hat{\phi}_i P}{p^0} + \sum_k \lambda_k a_{ik} \right) = 0 \quad (6)$$

where λ_k and a_{ik} are the Lagrange multiplier and atom quantity of the k th in molecular species. In order to investigate the effect of carbonaceous species formation on MPO activity, carbonaceous species in solid phase was introduced in the simulations. Thus, the total Gibbs free energy for the system can be ultimately expressed by Eq. (7).

$$G^t = \sum_{i=1}^N n_i \left[G_{f,i}^0 + RT \ln \left(\frac{y_i \hat{\phi}_i P}{p^0} \right) + \sum_k \lambda_k a_{ik} \right] + n_c \Delta G_{f,c}^0 = 0 \quad (7)$$

with $\Delta G_{f,c}^0$ being the Gibbs free energy for carbonaceous species formation. Additionally, the Temperature–Partial Pressure (TPP) simulations were performed to study the stability of metal phase for various M–O (M = Ru, Rh, Pd, Fe, Co, Ni) systems as a function of temperature in MPO process.

In this study, the main emphasis was put on understanding of effects of process parameters, namely, temperature (200–1000 °C), pressure (1–50 bar) and CH₄/O₂ feedstock ratio (from 2/1 to 1/2) on the catalytic performance of methane partial in terms of CH₄ conversion (X_{CH_4}), yield of products (Y_i) and H₂/CO ratio as shown in Eqs. (8)–(14).

$$X_{CH_4}(\%) = \frac{M_{CH_4}^{In} - M_{CH_4}^{Out}}{M_{CH_4}^{In}} \times 100\% \quad (8)$$

$$Y_{H_2}(\%) = \frac{M_{H_2}^{Out}}{2M_{CH_4}^{In}} \times 100\% \quad (9)$$

$$Y_{CO}(\%) = \frac{M_{CO}^{Out}}{M_{CH_4}^{In}} \times 100\% \quad (10)$$

$$Y_{H_2O}(\%) = \frac{M_{H_2O}^{Out}}{2M_{CH_4}^{In}} \times 100\% \quad (11)$$

$$Y_{CO_2}(\%) = \frac{M_{CO_2}^{Out}}{M_{CH_4}^{In}} \times 100\% \quad (12)$$

$$Y_C(\%) = \frac{M_C^{Out}}{M_{CH_4}^{In}} \times 100\% \quad (13)$$

$$H_2 / CO = \frac{M_{H_2}^{Out}}{M_{CO}^{Out}} \quad (14)$$

where M^{In} and M^{Out} represent the inlet and outlet mole amount (mol) of component.

3. Model verification

In order to verify the reliability and availability of model employed in this study, the thermodynamic equilibrium of H₂/CO ratio computed by HSC model was compared with the H₂/CO ratio reported by recent experimental studies over 35 catalyst samples at similar reaction conditions [38–46], as depicted in Fig. 1. The comparison studies were conducted at reaction temperature ranging of 700–900 °C and feed composition of CH₄/O₂ in a range

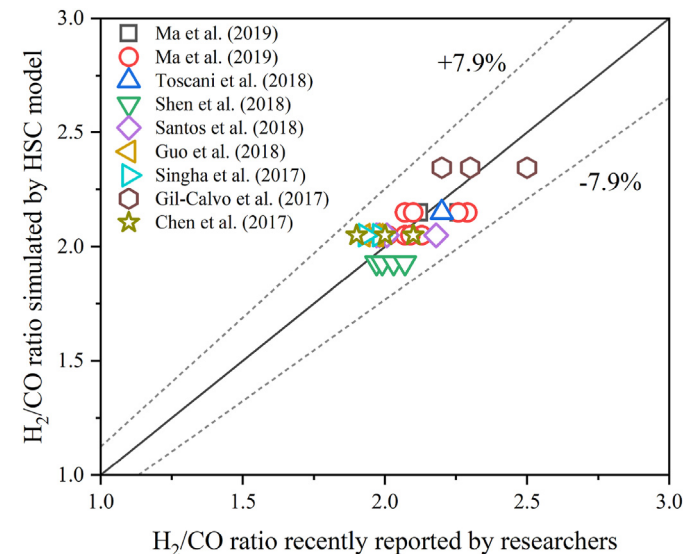


Fig. 1. Comparison between equilibrium H₂/CO molar ratio calculated by the HSC model and experimental H₂/CO molar ratio recently reported by researchers for methane partial oxidation process.

of 1–2 under atmospheric pressure. As seen in Fig. 1, the computed thermodynamic equilibrium H_2/CO ratio was in well accordance with the reported data within an acceptable average difference of 7.9%. This result suggests that the model employed in the present thermodynamic analysis for investigating the feasibility of MPO system is sufficiently reliable.

4. Results and discussions

4.1. Feasibility of reactions

The feasibility of multiple reactions including reforming, non-coke forming and coke forming reactions was determined by Gibbs free energy calculations as function of temperature, as shown in Fig. S1A–S1C, respectively. Thermodynamically, a spontaneous reaction purportedly leads to a negative value in Gibbs free energy change whilst a positive value in Gibbs free energy change is indicative of low tendency for a reaction to occur [47]. Apart from the calculations of Gibbs free energy change, the equilibrium constants (K) for reactions (Fig. S1D–S1F) were also computed in order to determine the extent of their occurrence. Based on literature [47], an alteration in molar ratio of reactants only has substantial influence on product distribution when the K value is close to a unity. Conversely, for the K value that much greater than a unity, reactions could not be shifted to their opposite side by only varying the composition of reactants. Hence, a reaction possesses a negative value in Gibbs free energy change and a larger $\ln K$ value could be indicated as a spontaneous reaction that feasible to occur throughout the process.

In the view of main reforming reactions involved, as seen in Fig. S1A, the Gibbs free energy change values of both methane steam reforming (R1) and methane dry reforming (R2) became negative values at temperature beyond 600 °C (Region 3), indicating their reactivity was highly associated with temperature due to their endothermic nature [48]. Notably, methane partial oxidation (R3) owned a much negative value of Gibbs free energy change amongst the reforming reactions throughout temperature regions from 200 to 1000 °C. Such observation could suggest that methane partial oxidation (R3) is the most spontaneous and dominant reforming process for syngas production, particularly at Regions 1 and 2 where temperature below 600 °C. These speculations could be corroborated by the $\ln K$ values obtained in Fig. S1D. The negative values of $\ln K$ for both methane steam reforming (R1) and methane dry reforming (R2) imply that these reforming reactions are infeasible to occur at a temperature below 600 °C whereas the methane partial oxidation (R3) has the highest tendency to occur owing to its high positive value of $\ln K$ in all Regions 1 to 4. In addition, the methane partial oxidation (R3) exhibited a $\ln K$ value that at least 5-fold higher than that of methane steam reforming (R1) and methane dry reforming (R2), as shown in Fig. S1D.

For non-coke reforming reactions, the CH_4 combustion (R4) exhibited the highest negative value of Gibbs free energy change and largest $\ln K$ value amongst the parallel reactions, indicating the predominance of CH_4 combustion (R4) during MPO process regardless of temperature regions. Hence, this could suggest the direct route and indirect route (i.e., combustion-reforming pathway) in MPO process for syngas production. The detail of the reaction pathway will be further discussed in the following section. Additionally, as temperature increased, the CO_2 methanation (R5), CO methanation (R6) and water-gas shift (R7) appeared to be inviable for occurrence as their Gibbs free energy change turned out to be positive. Conversely, reverse water-gas shift (R8), carbon gasification by CO_2 (R9) and carbon gasification by H_2O (R10) have the sufficient tendency to occur at high-temperature regions (Regions 3 and 4), especially at 600 °C and above. Although these

reactions were favorable at high-temperature regions owing to their negative Gibbs free energy change, these reactions could be influenced by the adjustment in molar feed composition of reactants due to their low $\ln K$ values neared to the vicinity of zero in the studied temperature range.

As depicted in Fig. S1C, the formation of carbonaceous deposit was inevitable throughout the MPO process as function of temperature. At low-temperature regions (Regions 1 and 2), the large negative values of Gibbs free energy change and high positive values of $\ln K$ for CO dehydrogenation (R11), Boudouard reaction (R12) and CO_2 dehydrogenation (R13) indicate that these reactions were the main contributory factors for the formation of carbonaceous species. On the contrary, CH_4 decomposition (R14) was the only reaction accounts for the carbon formed at high-temperature regions (Regions 3 and 4) as seen in Fig. S1C and S1E. Notably, the $\ln K$ values for these coke forming reactions (R11 to R14) were close to vicinity of zero at temperature greater than 600 °C, implying the carbonaceous species composition could be prominently altered via the manipulation of molar feed composition of reactants.

4.2. Thermodynamic equilibrium analysis

Thermodynamic simulations were conducted by the HSC Chemistry 6 program to compute the MPO reaction performance at various temperatures and atmospheric pressure with stoichiometric feedstock ratio ($M_{CH_4}^{in}/M_{O_2}^{in} = 2$). In order to ease the understanding of the correlation between simulated data and the involved reactions, the calculation of Gibbs free energy change for each involved reaction was performed. With the employment of Gibbs free energy calculations, the propensities of plausible reactions and their favorable temperature regions were determined, as provided in Table 1. Additionally, the carbon in solid phase is taken into consideration in simulations as it is a non-negligible side product originated from coke-forming reactions. As summarized in Table 1, MPO process owns a complex reaction network involving multiple main reforming reactions (viz., MPO, MSR and MDR), non-coke reforming reactions (i.e., CH_4 combustion, water-gas shift, reverse water-gas shift, carbon gasification by CO_2 or H_2O) and coke reforming reactions (i.e., CO hydrogenation, Boudouard reaction, CO_2 hydrogenation and CH_4 decomposition) at temperature ranging of 200–1000 °C.

Based on reported literature [49–52], the activation of CH_4 is the very first crucial step in CH_4 reforming reactions before reacting with oxidants (i.e., CO_2 , H_2O or O_2) to yield syngas. However, high temperature is a prerequisite for efficiently activating CH_4 reactant [50]. As shown in Fig. 2A, the equilibrium amount of both H_2 and CO exponentially increased as CH_4 amount significantly declined at temperature beyond 500 °C, implying the dominance of multiple methane reforming reactions (Table 1). In addition, the absence of O_2 amount and diminishing H_2O and CO_2 amount at elevated temperature could suggest the existing indirect combustion-reforming pathway, of which CH_4 combustion (also known as CH_4 total oxidation) followed by MSR and MDR [20,32]. Notably, the CH_4 combustion constantly possesses a significant influence throughout all temperature regions (Table 1), which may possibly be the main factor leading to the O_2 conversion of 100% in Fig. 2B.

Apart from the direct MPO route, the existing CH_4 combustion may suggest the indirect combustion-reforming route (Fig. 3) as an essential pathway for the MPO process to produce H_2 and CO [53–55]. In the study of temperature programmed MPO over bifunctional Ni^0/La_2O_3 catalyst, Nguyen et al. [53] proposed a two-step combustion-reforming route, in which the active oxygen vacancy site of La_2O_3 induced the CH_4 combustion producing CO_2 and

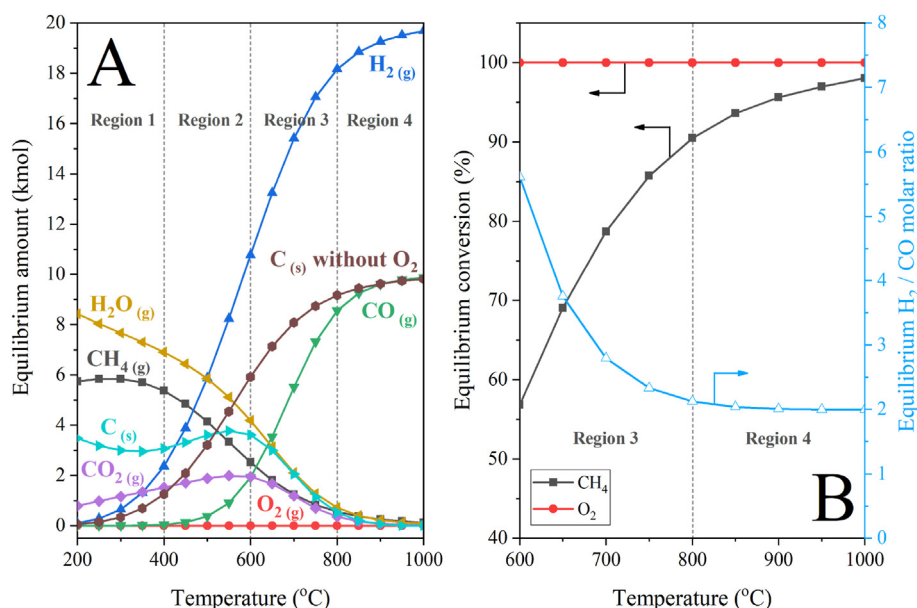


Fig. 2. (A) Equilibrium composition and (B) Equilibrium reactant conversions and H_2/CO molar ratio for methane partial oxidation at various temperatures and atmospheric pressure calculated by HSC Chemistry 6.

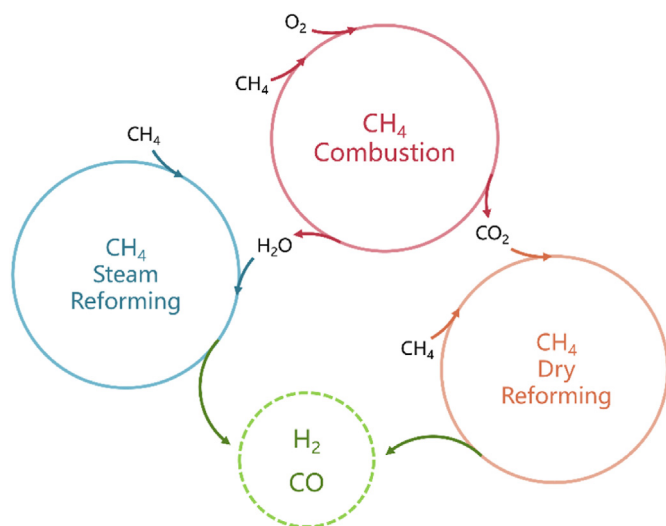


Fig. 3. Pictorial illustration of syngas production via combustion-reforming process.

H_2O whilst metallic Ni phase catalyzed the subsequent CO_2 (or H_2O) with excessive CH_4 to yield syngas. Similar findings were also reported by Nandi and his co-workers in their investigation of TiO_2 supported Au–Pd catalyst for MPO activity [54]. They found that both direct and indirect mechanisms occurred concurrently but the former route was favorable over Au–Pd system since the quantity detected for intermediate CO_2 and H_2O was insignificant during short contact time reaction in packed bed reactor. Wang et al. [55] inspected the effect of axial temperature along catalyst bed on MPO reaction pathway and corroborated the existence of combustion-reforming route. Particularly, CH_4 combustion and direct MPO processes occurred initially in the hot zones before reaching the catalyst bed and subsequently, the dominant reactions shifted from CH_4 combustion to MSR and MDR processes when in the catalyst bed. From the literature, the combustion-reforming route is inevitable in MPO reaction and thus, evaluating the impacts of process

variables on MPO reaction pathway is crucial in order to optimize the syngas H_2/CO ratio via appropriate reaction conditions.

Generally, CH_4 decomposition and Boudouard reaction are the main factors accounting for the heterogeneous catalyst deactivation induced by the deposition of carbonaceous species during reforming processes [16]. As shown in Fig. 2A, in the absence of O_2 , the equilibrium amount of carbon formed substantially increased with growing temperature, implying a high probability of severe deactivation during high-temperature reaction. On the contrary, in the existence of O_2 , carbonaceous species can be enormously reduced at higher temperature regions (Regions 3 and 4) due to carbon gasification by the intermediate oxidizing agent (viz., H_2O and CO_2) originated from CH_4 total oxidation. Additionally, an exponentially increased CH_4 conversion and ratio of H_2/CO above 2 were observed in Fig. 2B at temperature in a range of 600–800 °C (Region 3). This suggests the predominance of MPO, MSR and MDR contributing to H_2 -rich syngas production. However, these trends have changed at temperatures above 800 °C. At the temperature above 800 °C, the value of H_2/CO ratio gradually reduced and eventually plateaued at 2, implying the significance of reverse water gas shift (RWGS) reaction at high temperature [53]. The participation of multiple reactions as the function of temperature under various operating conditions will be discussed in the following sections.

4.3. Influence of CH_4/O_2 ratio

Fig. 4A–F demonstrates the influence of CH_4/O_2 ratio on the CH_4 conversion, H_2O yield, CO_2 yield, H_2 yield, CO yield and carbon yield for MPO process as function of temperature at atmospheric pressure. As seen in Fig. 4A, regardless of the CH_4/O_2 ratio, the rising temperature possessed a positive effect on the CH_4 conversion mainly due to the endothermic nature of CH_4 combustion, MSR, MDR and MPO [52]. The higher CH_4/O_2 ratios exhibited lower CH_4 conversions at all temperature regions, however, this disparity was gradually reduced with rising temperature. At temperature of 800 °C, CH_4 conversion about 95% and above could be achieved. These observations indicate that deficiency of oxidizing agents (i.e., O_2 , H_2O and CO_2) resulted in a lower value in CH_4 conversion since

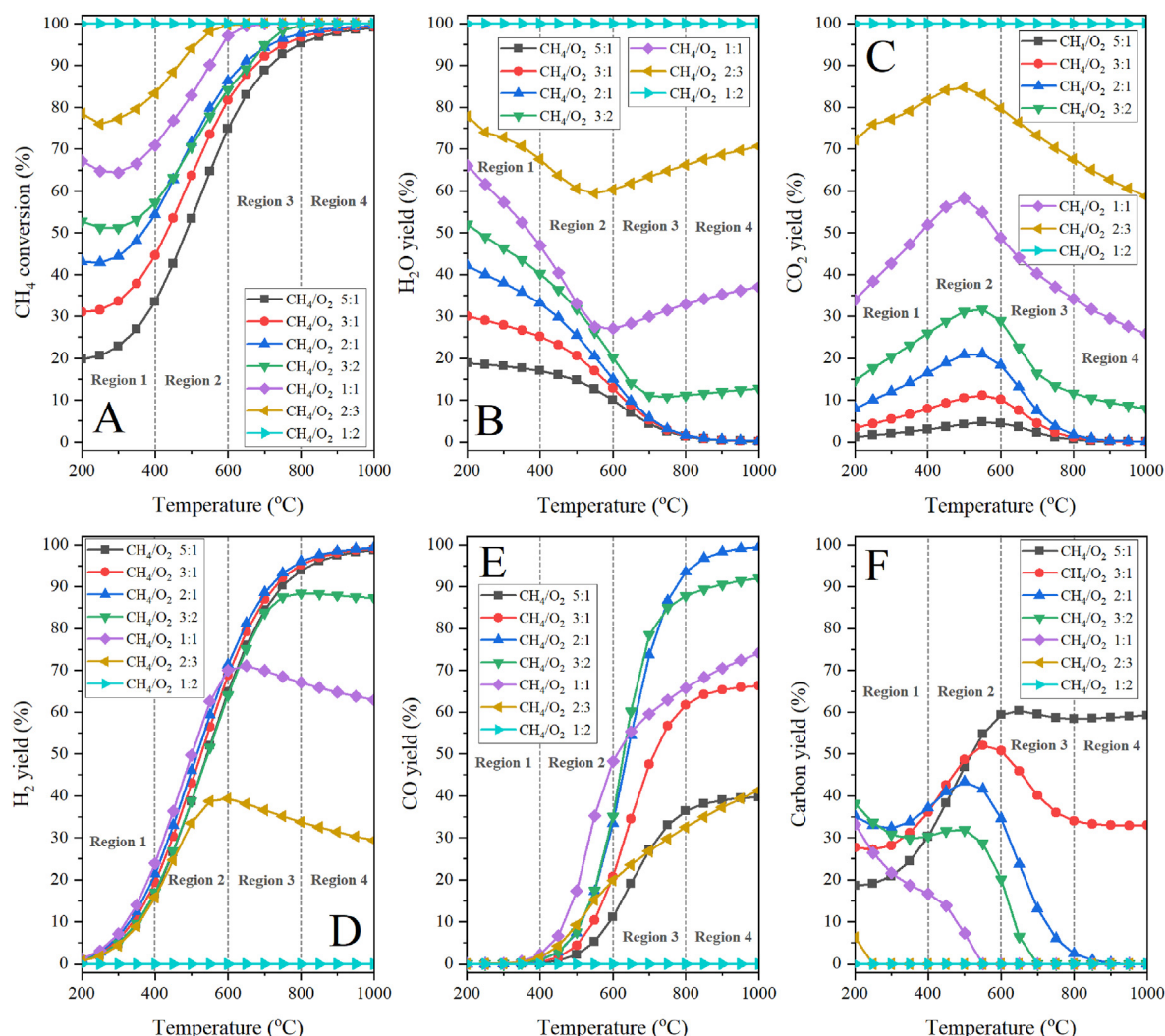


Fig. 4. Influence of CH_4/O_2 ratio on equilibrium (A) CH_4 conversion, (B) H_2O yield, (C) CO yield, (D) H_2O yield, (E) CO_2 yield and (F) Carbon yield for MPO at various temperatures and atmospheric pressure.

the oxidizing agents play as a limiting reactant at higher CH_4/O_2 ratios. Notably, a decrease in CH_4 conversion was found in Region 1 at the CH_4/O_2 ratios ranging of 5:1 to 2:3, which could be a result of partial CO_2 (or CO) methanation [56–58]. As the CH_4/O_2 ratios reduced, the gradient of the CH_4 conversion shifted from Region 3 to Region 2 (Fig. 4A) and the 100% CH_4 conversion could be readily achieved at lower temperature, signifying the enhanced rate of CH_4 combustion at O_2 -rich atmosphere. This deduction could be ascertained by the high H_2O and CO_2 yields obtained at low-temperature regions (200–600 °C) with reducing CH_4/O_2 ratios, as depicted in Fig. 4B and C.

Fig. 4B shows two trends of H_2O yield for all the CH_4/O_2 ratios as a function of temperature. Initially, a rise in temperature from Region 1 to Region 3 led to a drop in H_2O yield reasonably due to the favoritism of H_2O consumption by WGS at low temperature (Table 1). Consequently, the increased quantity of CO_2 due to WGS resulting in a growth in CO_2 yield as demonstrated in Fig. 4C. This could explain the opposite behavior of CO_2 yield compared to that of H_2O yield at temperature below 600 °C. At temperature beyond 600 °C, the H_2O yield only continuously decreased for higher CH_4/O_2 ratios (2:1, 3:1 and 5:1) whilst for CH_4/O_2 ratios below 2:1, an increasing quantity of H_2O yield was observed (Fig. 4B). This was

due to the arising significance of endothermic RWGS at high-temperature zone (Regions 3 and 4 in Fig. 4B). At higher CH_4/O_2 ratios (2:1, 3:1 and 5:1), the rate of RWGS producing H_2O was slower than that of MSR consuming H_2O and thus, reduction in H_2O yield. Conversely, as CH_4 was insufficient at lower CH_4/O_2 ratios, RWGS rate turned out to be superior to MSR rate and therefore, an increase in H_2O yield.

Alternatively, as shown in Fig. 4C, the lower CH_4/O_2 ratios exhibited greater CO_2 yield owing to the predominance of CH_4 combustion at low temperature under O_2 -rich environment. A noticeable drop in CO_2 yield was observed at temperature beyond 600 °C, indicating the dominance of MDR consuming CO_2 . Likewise, due to the propensity of RWGS, the CO_2 yield was drastically declined for all CH_4/O_2 ratios. These results evidently show that CH_4 combustion provides the required oxidizing agents (*viz.*, H_2O and CO_2) for the following MSR and MDR, known as combustion-reforming pathway, to yield H_2 and CO gaseous product. However, enhancing the rate of CH_4 combustion by lowering the CH_4/O_2 ratios unpredictably poses a detrimental effect on the syngas production instead of a beneficial influence.

Fig. 4D shows the H_2 yield as a function of temperature at different CH_4/O_2 ratios. Interestingly, there are two tendencies were

noticed in H_2 yield profile. As the CH_4/O_2 ratios reduced from 5:1 to 2:1, the H_2 yield was gradually increased with growing temperatures. This suggests that O_2 amount for higher CH_4/O_2 ratios (5:1, 3:1 and 2:1) was sufficient to provide intermediate oxidizing agents for the H_2 production via WGS, MSR and MDR. Interestingly, at CH_4/O_2 ratios greater than 2:1, the H_2 yield was approximately achieving its highest value and always relatively larger than CO yield, suggesting the predominant CH_4 decomposition generates excessive H_2 and carbon deposit, as evidenced by the carbon yield obtained in Fig. 4F. Similarly, the H_2 yield for the lower CH_4/O_2 ratios (3:2, 1:1 and 2:3) grew with a rise in temperature up to 600–800 °C but a decline in H_2 yield was subsequently determined at higher temperatures. Notably, the temperature for turning point of the reduction in H_2 yield was consistent with that of H_2O yield where began to increase, further corroborating the significance of RWGS for lower CH_4/O_2 ratios at higher temperatures. In addition, the reduction trend of H_2 yield for lower CH_4/O_2 ratios was observably shifted to lower temperatures, denoting the decreasing rates of methane reforming processes (i.e., MPO, MSR and MDR) due to deficiency of CH_4 amount and indicative of the enhancement in RWGS rate.

Fig. 4E depicts the CO yield with respect to CH_4/O_2 ratios as a function of temperature. As a result of endothermic methane reforming reactions at high-temperature zones, the CO yield substantially rose with growing temperature, regardless of the CH_4/O_2 ratios. Similar to H_2 yield (Fig. 4D), the CO yield (Fig. 4E) also possessed two trends under different CH_4/O_2 ratios. Initially, as CH_4/O_2 ratios reduced from 5:1 to 2:1, an increase in CO yield was discerned rationally owing to the enhanced reaction rates of reforming reactions at O_2 -sufficient atmosphere. On the contrary, the CO yield obtained for CH_4/O_2 ratios below 2:1 has sharply reduced with decreasing CH_4/O_2 ratios as the CH_4 became the limiting reactant. Notably, the CH_4 conversion, H_2O and CO_2 yields could consistently achieve 100% across temperature regions under CH_4/O_2 ratio of 1:2. However, at CH_4/O_2 ratio of 1:2, there were no H_2 and CO gaseous product (Fig. 4D and E) were detected. These observations could imply that the prevalent CH_4 combustion has completely consumed the limited CH_4 reactant in O_2 -rich environment.

Fig. 4F demonstrates the carbon yield with respect to different CH_4/O_2 ratio as a function of temperature. An increase in temperature led to two behavior of carbon yield profile. The lower CH_4/O_2 ratios (3:2, 1:1, 2:3 and 1:2) showed higher carbon yield at Region 1 probably because of the dominance of Boudouard reaction under O_2 -rich atmosphere. However, a drastic reduction trend was subsequently discerned with the growing temperature, indicating the suppression on Boudouard reaction due to its exothermic nature. For the CH_4/O_2 ratios above 3:2, the carbon yield was significantly increased at Region 2 where the reforming reactions (i.e., MSR, MDR, and MPO) began to dominantly occur and concurrently resulted in the formation of carbonaceous species due to the CH_4 dissociation [50,52]. The carbon yield would expectedly increase as temperature rises due to the endothermicity of CH_4 decomposition (Table 1) but in contrast, it demonstrated an unpredictable drop after achieved its maximum value within Region 2 and with decreasing CH_4/O_2 ratios, it could successfully eliminate the carbon deposit (Fig. 4F). In addition, a red shift of the carbon elimination temperature towards lower temperature regions was observed for the CH_4/O_2 ratios below 3:1. This behavior was possibly attributable to the enhanced carbon gasification by oxidizing agents (i.e., H_2O and CO_2) that superior to coke-reforming reactions, which was in accordance with the findings of Jang et al. [23]. Nevertheless, elimination of carbonaceous species could not be achieved for the higher CH_4/O_2 ratios (3:1 and 5:1) possibly because of the higher rate of CH_4 decomposition in CH_4 -enriched surrounding.

4.4. Influence of pressure

Fig. 5A–F demonstrates the pressure effect on the MPO performance in terms of CH_4 conversion, H_2 yield, CO yield, H_2O yield, CO_2 yield and carbon yield at stoichiometric CH_4/O_2 ratio of 2. Similarly, growing temperature has a beneficial effect on the syngas formation owing to the endothermic nature of reforming reactions [50], regardless of pressure effect. However, as seen in Fig. 5A–F, a rise in pressure from 1 to 50 bar would adversely cause a substantial drop in CH_4 conversion and gaseous product yields, specifically at temperature above 450 °C. At temperature below 450 °C, a reduction in CH_4 conversion could be assigned to the CO (or CO_2) methanation favoring at high-pressure environment [59,60]. In the thermodynamic studies of methanation reaction under different operating conditions, Su and his co-workers [61] reported that an increase in pressure from 1 to 30 atm reportedly resulted in high CO conversion and high CH_4 selectivity at low reaction temperature (<400 °C) as methanation is a volume reducing process.

According to Le Chatelier's principle, an increase in pressure disfavor the reaction involving gas volume expansion due to an increase in total product mole number, particularly in endothermic reforming processes [4]. The suppression on reforming processes, namely, MSR and MDR due to high-pressure effect could be validated by Fig. 5B and C. In the Regions 3 and 4, a larger amount of H_2O and CO_2 yields were observed with increasing pressure, indicating the slower consumption rate of H_2O and CO_2 for reforming processes. In addition, an apparent shift of the negative slope for both H_2O and CO_2 yields to higher temperature region suggests that endothermic reforming processes could counteract the negative effect of pressure by compensating higher energy provided at high-temperature surrounding [32]. This speculation also explains the noticed shift of ignition temperature of H_2 and CO yields from low- to high-temperature zone at elevated pressure, as demonstrated in Fig. 5D and E. Interestingly, the pressure effect is negligible in Region 1 for both H_2 yield and CO yield where temperature below 400 °C reasonably due to the inactivation of reforming reactions. The similar trend of pressure effect on H_2 and CO yields was also suggested by the findings of Zhu et al. [62] and Özkara-Aydınoglu [63] in their thermodynamic equilibrium studies of methane reforming.

As seen in Fig. 5F, the formation of carbon began to rise at Region 2 and reached its maximum yield value at 550 °C under 1 bar (approximate to atmospheric pressure) due to the activation of reforming and coke forming reactions (Table 1) considerably generating the carbonaceous deposits. However, as the pressure grew from 1 to 50 bar, a reduction in carbon yield and a shift of the maximum carbon yield towards higher temperature region were observed. Such behavior could be a result of endothermic reforming reactions counteracting the suppression effect caused by high-pressure atmosphere at high-temperature regions [32]. Since the rising pressure possess negative effect on reforming processes resulting in excessive H_2O (Fig. 5D) and CO_2 gases (Fig. 5E) at surrounding, the subsequent H_2O and CO_2 could prominently contribute to carbon gasification by H_2O and CO_2 (Table 1), particularly at high-temperature regions and thus, inhibiting the carbon yield at elevated pressure. Hence, from the views of eliminating the carbon formed and maximizing the syngas yield, the pressure of 1 bar (approximate to atmospheric pressure) could be determined as the appropriate pressure for MPO system.

4.5. Formation of carbonaceous species at various operating conditions

Deposition of carbonaceous species on active sites of catalyst is

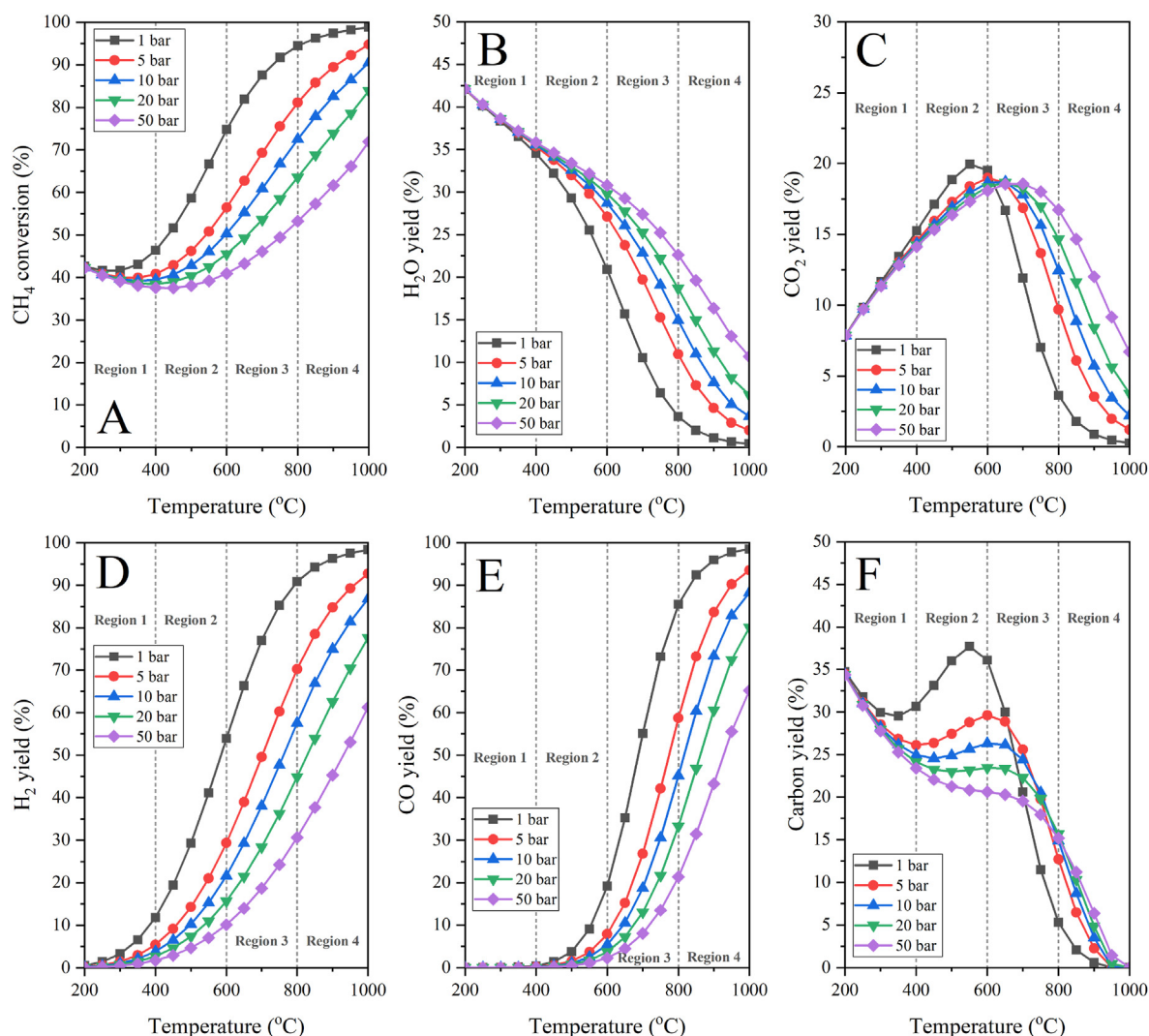


Fig. 5. Influence of pressure on equilibrium (A) CH₄ conversion, (B) H₂ yield, (C) CO yield and (D) H₂O yield, (E) CO₂ yield and (F) Carbon yield for MPO at various temperatures with stoichiometric CH₄/O₂ ratio of 2.

always the severe drawback inducing the catalytic deactivation for reforming processes and thus, restraining the reforming technologies from the industrial application and commercialization [16,52]. From the above reasons, studying the effect of the operating conditions on the source of carbon formation is essential. Hence, thermodynamic assessment of C-containing products from coke-forming reactions (Table 1) including CO hydrogenation, Boudouard reaction, CO₂ hydrogenation and CH₄ decomposition were performed in this work at various operating conditions with stoichiometric CH₄/O₂ ratio of 2 under atmospheric pressure.

As depicted in Fig. 6A–D, the formation of carbonaceous species was concomitant with the changes of CO, CO₂ and CH₄ species, implying that the carbon yield is highly associated with CO yield, CO₂ yield and CH₄ conversion, as proven in previous sections. Theoretically, the syngas yield could reach 100% at O₂-rich atmosphere due to the excessive intermediate oxidizing agents (*viz.*, H₂O and CO₂) enhancing the rate of MSR and MDR reactions. However, the value of syngas yield obtained at lower CH₄/O₂ ratios was greater than that of higher CH₄/O₂ ratios as function of temperature. Apart from the profound effect of RWGS, this could also be a result of the consumption of H₂, CO, CO₂ and CH₄ by coke-forming reactions (Table 1). The changes of C-containing products from the

coke-forming reactions in the absence of O₂ were investigated in order to ascertain the dependency of carbon formation on temperature. As temperature grows, a reduction in quantity of carbon originated from CO hydrogenation (Fig. 6A), Boudouard reaction (Fig. 6B) and CO₂ hydrogenation (Fig. 6C) was clearly observed. Although CO hydrogenation, Boudouard reaction and CO₂ hydrogenation were favored at low-temperature regions, a substantial carbon quantity was still observed at high-temperature regions, as shown in Fig. 6A–C. These behaviors were indubitably supported by the estimation of Gibbs free energy change (figS1Fig. S1C) and their corresponding equilibrium constants (figS1Fig. S1F) as discussed in the previous section. Such postulation was also proposed by other similar reported experimental studies [64–67]. In the study of low-temperature methane steam reforming, Nieva et al. found that the rapid deactivation of their catalyst was mainly accounted by the deposition of carbonaceous deposit induced by Boudouard reaction [64]. In addition, Bartholomew et al. suggested that filamentous carbon was unavoidably generated in both steam reforming and hydrogenation processes inducing the catalyst deactivation even at low temperature [65,66]. In the view of mechanism of CO hydrogenation, Jalil and the co-workers confirmed the formation of carbonaceous deposit from

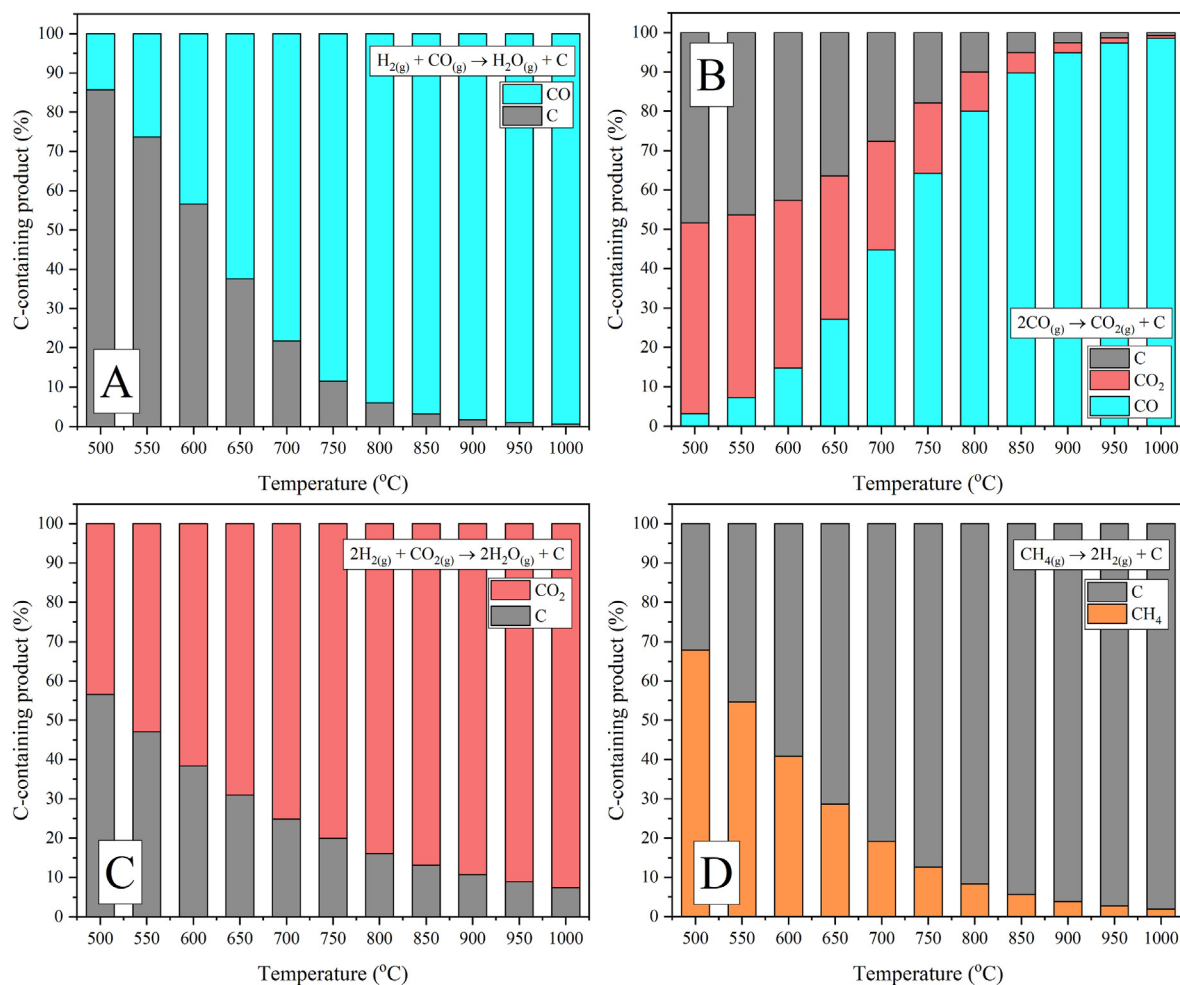


Fig. 6. C-containing products obtained from (A) CO hydrogenation, (B) Boudouard reaction, (C) CO₂ hydrogenation and (D) CH₄ decomposition as a function of temperature at stoichiometric feed composition.

Boudouard reaction via mechanistic study using *in situ* FTIR measurement [67], which was in line with the thermodynamic results obtained in this section.

Conversely, CH₄ decomposition was the only dominant carbon-forming reaction favored at high-temperature regions (Fig. 6D) leading to a large amount of carbon formed. From the Gibbs free energy change (figS1Fig. S1C) and equilibrium constants (figS1Fig. S1F), the CH₄ decomposition was deduced to be viable and irreversible at temperature beyond 500 °C as it possesses a negative Gibbs free energy change and transits into positive $\ln K$ value. According to literature [14,66], the carbon formed at temperature above 600 °C could be categorized as pyrolytic carbon, normally originated from CH₄ decomposition encapsulating the catalyst surface and thus, catalyst deactivation at high-temperature region. Thermodynamically, at temperature above 600 °C, CH₄ reportedly deprotonated to form CH_x^{*}, adsorbed C^{*} (C_x) or polymeric C_β^{*} and H^{*} (known as CH₄ decomposition) [68]. In general, the C_x atomically diffuses into the lattice of hosting metal on catalyst surface forming surface carbon or whisker carbon (C_β^{*}) via nucleation. Subsequently, graphene islands are formed and the further nucleation process would lead to the development of graphite that eventually deactivates catalytic reactivity [48,69]. Such speculation was also verified by the findings of Xu and Saeys in their first principles density functional theory (DFT) studies about the mechanism of carbon deposition on Ni-based catalysts

[69]. Overall, these observations advocate that the formation of carbon was unavoidable during the reaction regardless of low- or high-temperature region.

Despite the effect of temperature, the thermodynamic simulations of pressure impact on the coke-forming processes were also conducted at a range of 1–50 bar. A rising pressure resulted in an increase in total amount of carbonaceous species for CO hydrogenation, Boudouard reaction and CO₂ hydrogenation (Fig. 7A–C) whilst CH₄ decomposition exhibited an opposite behavior (Fig. 7D). These results were in accordance with other reported thermodynamic studies [23,26]. As aforementioned formerly, reactions involving gas volume expansion was favored at low-pressure atmosphere according to the Le Chatelier's principle. Thus, this could explain the reverse behavior observed in CH₄ decomposition in comparison with gas-reducing reactions (i.e., CO hydrogenation, Boudouard reaction and CO₂ hydrogenation) at elevated pressure. From the above results, the carbon produced from CO hydrogenation, Boudouard reaction and CO₂ hydrogenation was favorable at low-temperature and high-pressure atmosphere while the coke originated from CH₄ decomposition was favorable at high-temperature and low-pressure environment.

In fact, the distribution of carbon formed and relevant C-containing product are greatly reliant on the type of oxidants (i.e., CO₂ and H₂O) involved during MPO process. Hence, simulations of H₂O and CO₂ to CH₄ reforming were conducted in order to investigate

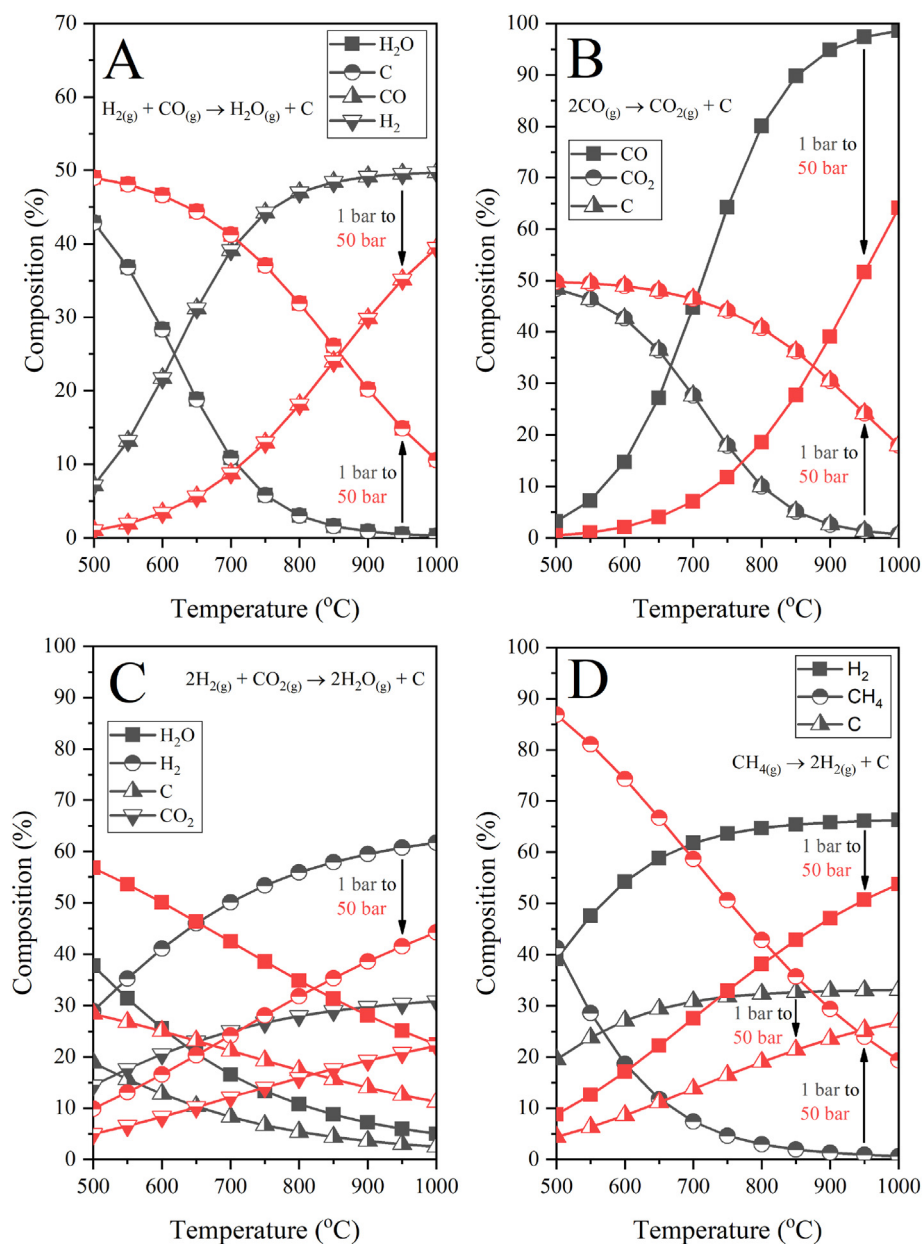


Fig. 7. Thermodynamic equilibrium composition of (A) CO hydrogenation, (B) Boudouard reaction, (C) CO₂ hydrogenation and (D) CH₄ decomposition as a function of temperature at pressure ranging of 1–50 bar with stoichiometric feed composition.

the impact of type of oxidant on the C-containing product distribution as shown in figS2 Figs. S2A and S2B. Interestingly, the main C-containing product was CH₄ in the presence of H₂O (figS2Fig. S2A) whilst the carbon was the main residue in the existence of CO₂ (figS2Fig. S2B). This implies that the H₂O could efficiently inhibit the carbon formation compared to CO₂. A similar assumption was also proposed by Olah et al. in their experimental single step bi-reforming research and they assigned this credit to the presence of excessive steam readily triggering the carbon gasification process [4]. Unlike H₂O, the CO₂ facilitates the carbon formation via significantly reacting with CH₄, as proven by the C-containing product distribution in Fig. S2B. Based on figS2Figs. S2A and S2B, the presence of oxidizing agents (i.e., H₂O and CO₂) could suppress the formation of carbonaceous species to certain extent but it is impractical to completely diminish the carbonaceous deposit at low-temperature regions. However, the amount of carbon

formed could be appreciably inhibited at high-temperature regions, reflecting the major factors for suppressing the coke formation are the temperature and type of oxidizing agents employed for the gasification process. Hence, formation of carbonaceous deposit at low-temperature regions largely associated with these above-mentioned factors while the carbon formed at high-temperature regions merely depends on the type of oxidizing agents. Since the H₂O and CO₂ are primarily originated from CH₄ combustion in MPO, these factors should be considered to ascertain the applicable catalytic reaction condition for MPO process.

4.6. M–O (M = Ru, Rh, Pd, Fe, Co, Ni) systems

Apart from the formation of carbonaceous species, another factor leads to a loss in catalytic performance is the tendency of reoxidation for transition metal catalysts in the presence of

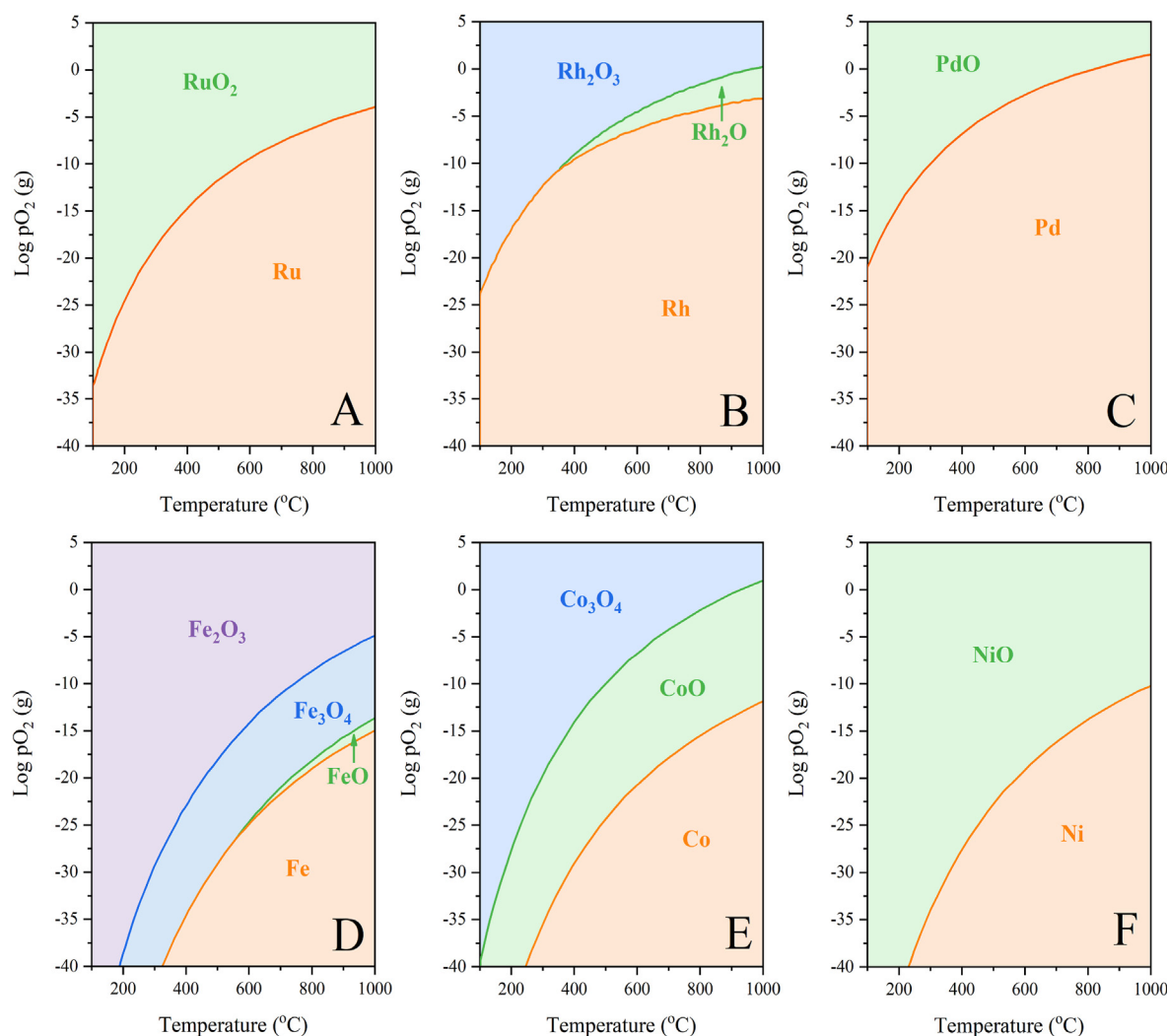


Fig. 8. The TPP profile of (A) Ru–O, (B) Rh–O, (C) Pd–O, (D) Fe–O, (E) Co–O and (F) Ni–O system at temperature ranging of 100–1000 °C.

excessive oxidizing agents during reforming processes [70–72]. Thus, in order to correlate the phase transformation of metallic form to metal oxide with the O_2 concentration in a system, TPP stability simulations of conventional transition metals including Ru, Rh, Pd, Fe, Co and Ni were conducted as demonstrated in Fig. 8A–F. Interestingly, regardless of the type of metal, a growth in temperature could largely retain the metallic phase for all transition metals at their respective O_2 concentration. As seen in Fig. 8A–C, the metallic form of noble metal elements (Ru, Rh and Pd) could be achieved at low temperature (150 °C) whilst a minimum temperature needed for retaining the metallic phase of non-noble elements (Fe, Co and Ni) was 230 °C (Fig. 8D–F). This suggests that noble metal elements are relatively more reducible compared to non-noble metal elements, and thereby, suppression on catalyst reoxidation [73]. Additionally, noble metal elements could still retain in the metallic form at an environment containing 2- to 3-fold higher of O_2 concentration in comparison with the non-noble metal elements. This behavior implies that noble metal elements possess a greater resistance towards reoxidation of metallic form to metal oxides at O_2 -excessive atmosphere.

The noble metal elements indeed possess low-temperature reducibility and high resistance towards reoxidation process, however, reoxidation is still unpreventable at extreme O_2 -excessive environment, as shown in TPP stability diagrams. Thus, the

simulations of transition metal behavior during the MPO process under various temperatures and feed compositions were investigated and the corresponding data are summarized in Table 2. The CH_4/O_2 ratios ranging of 2:1 to 1:2 was selected for catalyst reoxidation evaluation as the concentration of O_2 was gradually enriched in surrounding. As seen in Table 2, Fe was the most active metal towards reoxidation process to form Fe oxides amongst the transition metals. Although rising temperature could retain the metallic phase of Fe, the formation of metal oxides were still unavoidable at the temperature above 700 °C and CH_4/O_2 ratio below 3:2. Surprisingly, excepting the Fe, all transition metal elements possess an excellent resistance towards metal reoxidation process despite of at low temperature of 500 °C or feed composition with high O_2 content up to CH_4/O_2 ratio of 2:3. However, at CH_4/O_2 ratio of 1:2, no pure metallic form was observed for all transition metal cases even at high temperature up to 1000 °C, implying the irreversible reoxidation of active metal at H_2 -deficient atmosphere [32]. These results suggest that CH_4/O_2 ratios above 1:2 are advantageous for MPO reaction as it can eliminate the reoxidation process for all transition metals (except Fe) regardless of temperature. However, increasing CH_4/O_2 ratio could impose the carbon formation leading to catalyst deactivation and thus, selecting the appropriate operating conditions for MPO is indispensable and this will be further discussed in section 3.6.

Table 2

Dependence of metal oxide formation on various operating conditions for MPO at atmospheric pressure calculated using the HSC chemistry code.

Temperature (°C)	CH ₄ :O ₂ ratio	Transition metal phase (mol%)																	
		Ru ⁰	RuO ₂	RuO ₄	Rh ⁰	RhO	Rh ₂ O	Rh ₂ O ₃	Pd ⁰	PdO	Fe ⁰	FeO	Fe ₃ O ₄	Fe ₂ O ₃	Co ⁰	CoO	Co ₃ O ₄	Ni ⁰	NiO
500	2:1	100	0	0	100	0	0	0	100	0	27.6	32.4	38.8	1.2	100	0	0	100	0
	3:2	100	0	0	100	0	0	0	100	0	27.2	24.2	40.3	1.3	100	0	0	100	0
	1:1	100	0	0	100	0	0	0	100	0	2.6	39.5	56	1.9	100	0	0	100	0
	2:3	100	0	0	100	0	0	0	100	0	0	35.6	62	2.3	100	0	0	100	0
600	1:2	0	100	0	0	0.6	0.1	99.2	0.1	99.9	0	7.1	78.1	14.8	0	7	93	0	100
	2:1	100	0	0	100	0	0	0	100	0	92.1	5.1	2.7	0.1	100	0	0	100	0
	3:2	100	0	0	100	0	0	0	100	0	90.8	5.9	3.2	0.1	100	0	0	100	0
	1:1	100	0	0	100	0	0	0	100	0	4.8	59.3	34.8	1	100	0	0	100	0
700	2:3	100	0	0	100	0	0	0	100	0	0	50.7	47.6	1.7	100	0	0	100	0
	1:2	0	100	0	0	1.9	1.8	96.3	6	94	0	8.9	75.8	15.3	0	18.9	81.1	0	100
	2:1	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
	3:2	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
800	1:1	100	0	0	100	0	0	0	100	0	0	74.8	24.5	0.7	100	0	0	100	0
	2:3	100	0	0	100	0	0	0	100	0	0	58.2	40.3	1.5	100	0	0	100	0
	1:2	0	100	0	0	4	11.1	84.9	100	0	0	10.2	73.9	15.9	0	39.1	60.9	0	100
	2:1	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
900	3:2	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
	1:1	100	0	0	100	0	0	0	100	0	0	79.6	19.7	0.6	100	0	0	100	0
	2:3	100	0	0	100	0	0	0	100	0	0	63.2	35.3	1.5	100	0	0	100	0
	1:2	0	100	0	0	6.5	39.2	54.3	100	0	0	11.4	72.1	16.6	0	63.9	36.1	0	100
1000	2:1	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
	3:2	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
	1:1	100	0	0	100	0	0	0	100	0	0	82.9	16.5	0.6	100	0	0	100	0
	2:3	100	0	0	100	0	0	0	100	0	0	67.2	31.4	1.4	100	0	0	100	0
	1:2	0	100	0	0	7.3	75.3	17.4	100	0	0	12.3	70.4	17.3	0	84.5	15.5	0	100
	2:1	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
	3:2	100	0	0	100	0	0	0	100	0	100	0	0	0	100	0	0	100	0
	1:1	100	0	0	100	0	0	0	100	0	0	85.4	14	0.6	100	0	0	100	0
	2:3	100	0	0	100	0	0	0	100	0	0	70.4	28.2	1.4	100	0	0	100	0
	1:2	0	100	0	0	6.2	90.5	3.3	100	0	0	13.1	68.9	18	0	95	5	0	100

4.7. Choices of catalytic condition for MPO reaction

In general, the abovementioned process variables including reaction temperature, system pressure and feedstock composition indubitably have considerable impacts on the generation of H₂/CO ratio. Since the productivity of Fischer–Tropsch process is highly reliant on the composition of H₂/CO ratio, determining the operating conditions of catalytic MPO reaction for directly altering the syngas H₂/CO ratios is important. Apart from that, another crucial factor that need to be considered is the inhibition on the formation of carbonaceous species in order to ensure the stability of reaction

process. Although excessive oxidizing agents excellently suppress the formation of carbonaceous species, it could lead to an undesirable fluctuation in product yields. From the above reasons, the selection of reaction conditions for the MPO system should not only be considering the desirable syngas H₂/CO ratios but also be ensuring the catalytic stability throughout the process.

In order to determine the availability of syngas ratio under various operating conditions, thermodynamic assessments for equilibrium ratio of H₂ to CO and carbon yield are compared, as depicted in the corresponding Fig. 9A and B. The system pressure of 1 bar (approximate to atmospheric pressure) was employed for thermodynamic assessments since it is the most favorable pressure condition for MPO process as evidenced in the previous sections. As shown in Fig. 9A, regardless of CH₄/O₂ ratios, the H₂/CO ratio decreased with the rising temperature from 600 to 1000 °C. Notably, the temperature effect was insignificant to the H₂/CO ratio at temperature beyond 800 °C. As CH₄/O₂ ratio decreased from 5:1 to 3:2, the H₂/CO ratio around of 2 could be achieved eventually. However, two different trends were observed at CH₄/O₂ ratios below 3:2 for different temperature. For temperature at 800 °C and below, an increase trend in H₂/CO ratio was noticed whilst a further drop in H₂/CO ratio was found for temperature above 800 °C as CH₄/O₂ ratio continuously declined to 1:1 and 2:3. These observations corroborate the significance of transformation from WGS to RWGS at higher temperatures under O₂-excessive atmosphere.

Fig. 9B displays the carbon yield as a function of CH₄/O₂ ratio at various temperatures. At a fixed CH₄/O₂ ratio, the value of carbon yield for higher temperature was relatively lesser than that of lower temperature. Based on the Gibbs free energy change (figS1Fig. S1B) and equilibrium constant (figS1Fig. S1E) diagrams for non-coke forming, carbon gasification by CO₂ (R9) and H₂O (R10) have the sufficient tendency to occur, particularly at high-temperature

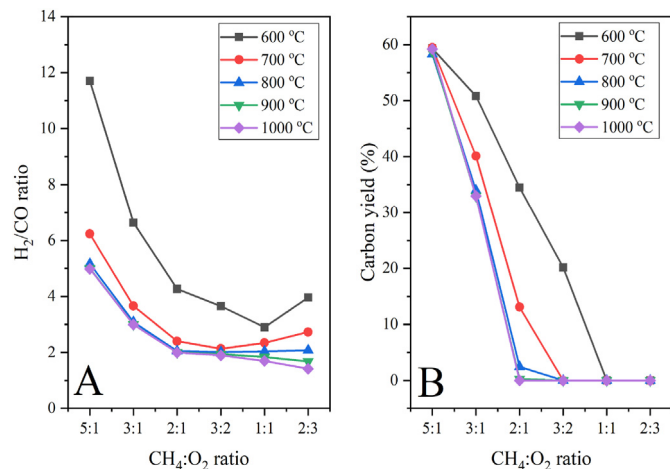


Fig. 9. Thermodynamic equilibrium (A) Carbon yield and (B) H₂/CO ratio as a function of CH₄/O₂ ratios at atmospheric pressure.

regions. This evolution could illustrate the lower carbon yield obtained at higher temperatures in Fig. 9B even at a fixed CH_4/O_2 ratio. Similar to the results of H_2/CO ratio, the carbon yield appeared independent of temperature above 800 °C. As CH_4/O_2 ratio increased, the carbon yield was substantially reduced for all temperatures ranging of 600–1000 °C. Notably, as seen in Figs. 9B and 0% of carbon yield could be achieved with the minimum prerequisite of temperature above 800 °C and CH_4/O_2 ratio of 2:1. In the gas-to-liquid (GTL) technology, a practical H_2/CO ratio around of 2 is always favorable for Fischer-Tropsch synthesis (FTS) in synfuel production [4]. Hence, from economic and industrial perspectives, the temperature at least of 800 °C and CH_4/O_2 ratio of 2:1 or 3:2 are the preferable operating conditions for catalytic MPO process producing syngas ratio of 2 appropriate for downstream FTS process.

5. Conclusion

Thermodynamic assessments regarding the effects of operating conditions (i.e., temperature, CH_4/O_2 ratio and pressure) on methane partial oxidation reaction, formation of carbonaceous species and M – O system (M = Ru, Rh, Pd, Fe, Co, Ni) were conducted by employing the HSC Chemistry 6. The results revealed that intermediate H_2O and CO_2 produced from CH_4 combustion had significant effects on the syngas yield, corroborating the importance of indirect combustion-reforming pathway. The CH_4/O_2 ratios reduced from 5:1 to 2:1 had positive effect on syngas yield, however, negative impact on syngas yield was discerned for CH_4/O_2 ratios below 2:1. In addition, the formation of carbon deposit was inevitable but it could be progressively suppressed as CH_4/O_2 ratios increased at elevated temperature. Increasing pressure adversely affect the syngas yield and lead to a suppression on carbon formation as these processes involve gas volume expansion. The CH_4/O_2 ratios above 1:2 are advantageous for M – O system during MPO reaction as it can eliminate the reoxidation process for all transition metals (except Fe) regardless of temperature. The thermodynamic assessments revealed that the 0% carbon deposit and the practical syngas ratio could be achieved at O_2 -moderate atmosphere. Hence, it has been concluded that the temperature at least of 800 °C and CH_4/O_2 ratio of 2:1 or 3:2 are the preferable operating conditions for MPO reaction generating syngas with H_2/CO ratio of 2 that appropriate for FTS process.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

T.J. Siang: Data curation, Formal analysis, Investigation, Methodology, Software, Visualization, Writing - original draft. **A.A. Jalil:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing - review & editing. **A.A. Abdulrasheed:** Formal analysis, Methodology, Validation, Visualization, Writing - review & editing. **H.U. Hambali:** Validation, Visualization, Writing - review & editing. **Walid Nabgan:** Validation, Visualization, Writing - review & editing.

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Appendix A. Supplementary data

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