Effects of operating parameters for dry reforming of methane: A short review

Muhammad Ayoub1,2, Chi Cheng Chong1,2, Asif Zamir3, Yoke Wang Cheng2, Sarah Farrukh1, Salmaa Raza Naqvi3, Herma Dina Setiabudi1, Nadia Riaz2, Naveed Ramzan6

1 Department of Chemical Engineering, University Technologi PETRONAS, 32610 Seri Iskandar, Perak, Malaysia.
2 Center for biofuel and Biochemical Research (CBBR), Institute for Self-sustainable Building, 32610 Seri Iskandar, Perak, Malaysia.
3Department of Chemical Engineering, National University of Science and Technology, Islamabad, Pakistan.
4 Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, 26300 Gambang, Kuantan, Pahang, Malaysia
5Department of Environmental Sciences, COMSATS University Islamabad, Abbottabad Campus, Abbottabad, 22060, Pakistan
6Department of Chemical Engineering, University of Engineering and Technology, G.T. Road, Lahore 54890, Pakistan.

Abstract. Dry reforming of methane (DRM) which also known as CO2 reforming of methane is a well-investigated reaction to serve as an alternative technique to attenuate the abundance of greenhouse gases (CO2 and CH4). The syngas yielded is the main component for the liquid fuels and chemicals production in parallel with the fluctuating price of oil. Major researches were executed to seek for the well-suited catalysts before the commercialization of DRM can be realized. However, severe deactivation due to the carbon formation restricted the usage of promising Ni-based catalysts for DRM. Meanwhile, the deactivation on these catalysts can be associated with the operating conditions of DRM, which subsequently promoted the secondary reactions at different operating conditions. In fact, the parametric study could provide a benchmark for better understanding of the fundamental steps embodied in the CH4 and CO2 activation as well as their conversions. This review explores on the influences of the reaction operating parameters in term of the reaction temperatures, reactant partial pressures, feed ratios, and weight hourly space velocity (WHSV) on catalytic performance and carbon accumulation for the DRM.

1 Introduction

The past few decades have witnessed tremendous progress in the research on greenhouse gases (CH4 and CO2) utilization. This utilization can ensure the continuity of the energy supply for the future generation, which can be applied in internal combustion engines or in the fuel cells to generate electricity while mitigating pollutant emissions [1]. On the other hand, synthesis gas (syngas, a mixture of H2 and CO) is of paramount importance as a building block towards the generation of the praiseworthy chemicals and synthetic fuels by the means of Fischer-Tropsch Synthesis (FTS) [2, 3]. To date, even though methane steam reforming has achieved the commercial grade, the contribution of the primary component of greenhouse gases, CO2 prompted an urgent substitution over the existing reforming technology [4, 5]. Owing to the capability to alleviate the CO2 gas release and transform into useful products, thereupon, dry reforming of methane (DRM) has been instigated as a prestigious replacement for syngas generations [3, 5, 6]. However, challenges related to the carbon accumulation which can be related to the natures of the catalysts and also the operating conditions of DRM have to be addressed before meeting the commercialization level of DRM.

Previously, researchers paid immense focus on the catalysts investigations on catalyst selection. Intriguingly, Ni-based catalysts have been acknowledged their vast prospects over DRM reaction due to its low cost, satisfactory catalytic performance as well as readily available [3, 7]. In fact, the optimal catalytic activity for DRM reaction not only affected by the catalysts adopted, but also the parametric factors such as reaction temperature, reactant partial pressure, feed composition, weight hourly space velocity (WHSV) and reactor type. As far we are concerned, the operating conditions of DRM are indispensable for the kinetic studies as well as efficient reactor design [8].

Therefore, in-depth understanding of the parametric study over DRM is crucial. Thermodynamics studies indicated the DRM process requires a larger amount of energy to operate due to its endothermic nature. Previous review by Usman et al. [9] has been reported on the influence different types of catalysts, active metals, promoters, particle size and reactor selection on catalytic performance and carbon deposition on DRM. Meanwhile, the operating conditions of DRM reaction are also crucial in affecting the catalytic performance for various catalysts. In addition, there are many other review papers [10-14] focused on discussing strategies to remove carbonaceous deactivation of catalysts by relating to the role of catalytic properties...
affected by the types of supports, active metal, promoters used, metal loading effect, catalysts preparation methods as well as thermodynamics study. However, there is almost no literature focus on the comparison of the DRM operating conditions, which are also key factors affecting the reaction performance. Thus, the parametric effects due to variation in reaction temperature, reactant composition, WHSV and the reactor design, which have been reported in the previous literature are summarized in this review to impart better interpretation over the challenges for DRM technology.

2 Effect of operating parameters

2.1 Reaction Temperature

The promotion of the side decomposition of the reactants induced by the nature of the reactions and the catalysts used led a positive temperature influence on the reactants’ conversions and product yields. DRM is inevitably accompanied with carbon formation and supported catalysts are prone to catalyst deactivation due to the carbon formed and metal sintering effect [7, 15]. Thus, effect of operating temperature of DRM have been studied in numerous previous literatures to provide clear justification on the deactivation happened on DRM. Herein, Table 1 provides a list of the influence of reaction temperature on DRM.

In a study carried out by Omoregbe et al. [8], the catalytic activity of the 10%Ni/SBA-15 over DRM were evaluated under the operating parameters of reaction temperatures (650-750ºC) at ambient pressure with varying CH\textsubscript{4}/CO\textsubscript{2} feed ratios and partial pressure. Results (Fig. 1) indicated both CO\textsubscript{2} and CH\textsubscript{4} conversions increased and less fluctuated with increasing reaction temperature. This can be explained by the carbonaceous deposit removal by CO\textsubscript{2} from the catalyst surface via reverse Boudouard reaction (C + CO\textsubscript{2} → 2CO) which thermodynamically preferred at high reaction temperature of 700-750ºC [16, 17]. A decline in the activity at 650ºC, was due to the CH\textsubscript{4} decomposition reaction that produce carbon deposition resulted from the thermodynamically favoured at 650ºC.

In the meantime, Cao and co-researchers [18] optimized the operating conditions of DRM for carbon deposition elimination by using thermodynamic calculations to investigate the influence of various operating temperatures (550-1200ºC), on the H\textsubscript{2}/CO ratio and the carbon deposition. At constant pressure (P=0.1MPa) and CH\textsubscript{4}/CO\textsubscript{2} ratio (1.0), a reverse trend can be noticed with an increase in temperature ranged from 550-700ºC. The results also inferred that significant and severe carbon depostions were observed between 546ºC and 703ºC, which can be ascribed to the secondary reactions of CH\textsubscript{2} cracking and CO dissociation that are referred as the primary reactions devoting to coke deposition. The former was stimulated at 550ºC≤ T ≤ 1000ºC and P ≤ 0.1MPa, whereas the moderately exothermic latter reaction was enhanced at T ≤ 700ºC and P ≥ 0.1MPa. Meanwhile, the carbon deposits consumer, moderately endothermic CO\textsubscript{2} gasification happened at T ≥ 703 ºC. They also claimed that reducing the reaction pressure or reducing the CH\textsubscript{4}/CO\textsubscript{2} mole ratio could possibly have switched the carbon free regime at a lower reaction temperature.

Same goes to the study carried out by Sidik et al. [19] in which the reaction rate increases with the increased temperature due to the endothermic nature of DRM process [CH\textsubscript{4} +CO\textsubscript{2} → 2CO + 2H\textsubscript{2} (ΔH\textsubscript{298K} = +247 kJ mol\textsuperscript{-1})] when using Ni-Co/MSN as catalyst [20]. Poor activity of the catalyst (low CH\textsubscript{4} and CO\textsubscript{2} conversions) can be observed at T < 500ºC (Fig. 2), yet approximately CH\textsubscript{4} and CO\textsubscript{2} conversions of 80% were reached at T > 700ºC. Analysis of variance (ANOVA) confirmed that most significant variable that affected the CH\textsubscript{4} conversions was operating temperature. Besides, Zhang et al. (2003) [21] claimed that the composition of the reactant gases (CO\textsubscript{2} and CH\textsubscript{4}) decreased whilst the conversions of reactants were increased (38-92%; 28-94%) with the concurrent increased of water production when the temperature was raised (450-800ºC). The incline trend tended to reached plateau and then flattened out at T >700ºC. These results can be attributed to the hot spots formation at a high operating temperature in comparison with the bulk catalysts bed’s average temperature.

Furthermore, Ayodele and co-workers [22] varied the reaction temperatures at the range of 650-750ºC to investigate the feasibility of the 20 wt%Co/80 wt%Nd\textsubscript{2}O\textsubscript{3} catalyst over DRM. Under the feed ratio of CH\textsubscript{4}/CO\textsubscript{2} = 1 and T = 750°C, 62.7% and 82% were the maximum CH\textsubscript{4} and CO\textsubscript{2} conversions achieved, while the maximum H\textsubscript{2} and CO products yield were 59.9% and 62.02%, respectively. At 750 ºC, the CH\textsubscript{4} conversion increased from 12.8% to 62.7% at CH\textsubscript{4}: CO\textsubscript{2} of 0.1 to

![Fig. 1. Effect of reaction temperature on (a) CH\textsubscript{4} and (b) CO\textsubscript{2} conversions over 10%Ni/SBA-15 catalyst. Adapted from [8].](image-url)
investigate the equilibrium conversions, product CO2/CH4 ratios (0.5–3) as well as reaction pressure analysis for DRM was done by Nikoo and Amin [24].

Reaction temperatures were set at 200–1200ºC to study the temperature. Meanwhile, Khavarian and Mohamed (2013) [23] suggested the CH4 and CO2 conversions over the synthesized MWCNTs were greatly influenced by the reaction temperatures within the range of 750-1000ºC which also related to the endothermic nature of DRM. The catalyst exhibited high activity and stability with 82.68% conversion of CH4 at 950ºC, accompanied with insignificant activity loss. As such, the reaction rate of CH4 and CO2 over carbon nanotubes was affected significantly by the reaction temperature. Within the range of the reaction temperature studied, almost no coke formation over the catalyst surface and the syngas ratio was close to unity. The CH4 conversion was slightly surpassed the CO2 conversion at the temperatures lower than 825ºC but then excelled the CO2 conversion at higher temperatures. This can be correlated with the CH4 and CO2 adsorption and reaction rate competition over the MWCNTs with the temperature.

Furthermore, a thermodynamic equilibrium analysis for DRM was done by Nikoo and Amin [24]. Reaction temperatures were set at 200-1200ºC to investigate the equilibrium conversions, product compositions and solid carbon formation at different CO2/CH4 ratios (0.5–3) as well as reaction pressure (101.3–2533.1 kPa). For all CO2/CH4 ratios, CH4 conversion almost drastically increased with increasing temperature up to 727ºC, meanwhile, for CO2 conversion, a gradual decline can be observed with temperature start from 300ºC to about 550–600ºC. The decreasing trend for CO2 conversion can be mainly described by CO2+ 2H2↔C+ 2H2O. This exothermic reaction spontaneously occurs at low temperature but diminishes as the equilibrium constant decreases and reduces CO2 conversion. In addition, side reaction namely carbon dioxide methanation (CO2+ 4H2↔CH4+ 2H2O) which is exothermic and promoted at a lower temperature (300ºC–650ºC) also devoted to the same declining trend.

| Catalyst       | WHSV (L·g⁻¹·h⁻¹) | CH4/CO2 | T (ºC) | X (%) | Ref. |
|----------------|-------------------|---------|--------|------|-----|
| Ni/SBA-15      | 24                | 1       | 650    | 70   | 64  | [8] |
| Ni-Co/MSN      | 15                | 1       | 450    | -    | 10  | [18]|
| Co/Ni/Na2O3    | 30                | 1       | 650    | 74   | 30  | [22]|
| Co-Mo-MgO/MWCNTs | 140            | 1       | 750    | 17   | 25  | [23]|
| 15%Ni/Al2O3    | 30                | 1       | 600    | 67   | 45  | [25]|
| 30%Ni/Al2O3    | 7.2               | 1       | 500    | 45   | 33  | [21]|
| Pt/Co3O4/α-Al2O3 |                | 1       | 635    | 81   | 73  | [26]|
| Ru/Al2O3       | 18                | 1       | 735    | 94   | 92  |       |
| La2Zr2O7       | 18                | 1       | 835    | 98   | 97  |       |
| Ni-Al2O3       | 18                | -       | 200    | FBR  | 21  | [27]|
| Ni-MgO         | 15                | 2       | 500    | FBR  | 38  | [29]|
| MgCoAl         | 6                 | 1       | 400    | FBR  | 19  | [30]|
| NiHydroCelite  | -                 | 1       | 450    | FBR  | 13  | [31]|
| Ni-Co/La(O1-x)Al2O3 | 6             | 1       | 500    | FBR  | 19  | [32]|
| Ni-La2Zr2O7    | 30                | 1       | 600    | FBR  | 69  | [33]|

T= temperature, X= conversion.

Additionally, Schwengber at al. [25] performed DRM catalytic reaction tests by using 15% Ni/Al2O3 and 30% Ni/Al2O3 catalysts under the reaction temperature (600–700ºC range). In general, increasing the reaction temperature in the DRM led to higher H2 yields and higher conversions of CH4 and CO2. Higher CH4 conversion (average of 59%) was found to be at the 650ºC by 30% Ni/Al2O3 catalyst, while other conversions fall in the range of 30 to 40%. The H2 yield was obtained at 700ºC for both 15% Ni/Al2O3 and 30% Ni/Al2O3 catalysts, but the formation rate dropped at the 4th hour time-on-stream. These results showed that not only complete DRM occurred, but also other undesired reactions. The results proposed the co-existence of secondary reactions, which included reverse water-gas shift reaction (CO + H2O ↔ CO2+ H2), Boudouard reaction (2CO ↔ C + CO2) and CO reduction (CO + H2 →
Furthermore, the drop in CO₂ conversion with rising over 10%Ni/SBA-15 catalyst at feed partial pressure of occurred via CH₄ cracking (CH₄ increased carbon formation rate along with the reactants conversions, which was due to the RWGS reaction (CO₂ + H₂ → C + 2H₂) in CH₄-rich feed [32]. Furthermore, CH₄ decomposition was easily facilitated in the CH₄-excess environment further enhance the decomposition rate and promoting carbon deposition [4].

2.2 CO₂ and CH₄ partial pressure
Owing to the vital role of reactants partial pressures on DRM on providing the quantities of reactants, a number of the reported papers are dedicated to elucidate the relationship between the reactants (CO₂ and CH₄) partial pressure on the product yield and carbon deposition over DRM. Appropriate CO₂ and CH₄ partial pressures can minimize the happening of secondary reactions that were known to be main culprits for coke formation and catalyst deactivation. Table 2 summarizes the comparison study on the effect of reactants partial pressure on the catalytic performance over DRM.

Omoregbe et al. [8] reported on the DRM activity over 10%Ni/SBA-15 catalyst at feed partial pressure of (20-60kPa) (Fig. 3). When CO₂ partial pressure (P CO₂) was increased, an increasing trend was observed for CH₄ conversion, whilst CO₂ conversion showed a substantial decline and exhibited an optimum performance at P CO₂ = 30-50kPa. The incline trend for CH₄ conversion with increasing of P CO₂ (20-60kPa) was credited to the escalating intermediate by-product, H₂O formation by RWGS reaction (CO₂ + H₂ → CO + H₂O) which promoted CH₄ steam reforming (CH₄ + H₂O → CO + 3 H₂) as well. On the contrary, the considerable decline of CO₂ conversion with rising P CO₂ (20-60kPa) was owing to the superabundance of CO₂ and inadequate quantity of CH₄ to act as limiting reactant for transforming CH₄-rich feed composition [24, 36]. Furthermore, the drop in CO₂ conversion with rising P CO₂ also can be linked to the active NiO metallic site oxidation at the catalyst surface to NiO (Ni + CO₂ → NiO + CO) in excess CO₂ circumstance. However, the rising in the P CH₄ (20-60kPa) remarkably decreased both the reactants conversions, which was due to the increased carbon formation rate along with the occurrence via CH₄ cracking (CH₄→ C + 2H₂) in CH₄-rich feed [32]. Furthermore, CH₄ decomposition was easily facilitated in the CH₄-excess environment further enhance the decomposition rate and promoting carbon deposition [4].

Likewise, Cao et al. [18] found that the reactants partial pressure reaction also affected the carbon formation rate during DRM. Results indicated that carbon deposition decreased when the partial pressures varied from 0.05 to 5MPa at 1200ºC. This finding was due to the CO dissociation (2CO ↔ C + CO₂) to form carbon was inhibited as the partial pressure increased, thus the carbon formation tendency shifted to higher temperature region [18, 37]. Therefore, it would be preferable to yield syngas suitable for the long-chain hydrocarbons synthesis at high pressure, as post syngas compression by using high CO content is not a technically liable mission. Another previous literature reported by Ayodele and co-researchers (2017) [22] also found that reactants consumption rates increased proportionally with the increase in pressure (5-50 kPa) when Co/Nd₂O₃ was employed as catalyst according to the proposed Langmuir-Hinshelwood kinetic mechanism.

Furthermore, Nikoo and Amin (2011) [24] investigated on the effect of system pressure on CH₄ and CO₂ conversions, main products distribution and H₂/CO ratio at 900 ºC, CO₂/CH₄ ratio of 1. CO₂ and CH₄ conversions were always excelled at lower pressures than those at higher pressures during reaction temperature at 900ºC. This proposes that at such a high temperature, greater pressures can impede the effect of temperature on increased reactant conversion. These decreased trends can be expressed by the endothermic trait of CRM. Besides, CH₄ decomposition (CH₄→ C + 2H₂) and CO disproportionation (2CO ↔ CO₂ + C) facilitate in lowering CH₄ and CO₂ conversions, as well as obstructing CO and H₂ formation at the higher pressures. Another research done by Ayodele et al. (2015) [38] investigated on the influences of reactants’ (CH₄ and CO₂) partial pressures on the catalytic performance of the ceria-supported cobalt catalyst. The experiment was conducted by maintaining the partial pressure of one reactant constant at 50 kPa and varied the other reactant pressure between 5-50 kPa and vice versa at reaction temperatures of 650-750ºC. The highest conversion of CH₄ and CO₂ were acquired to be 78 and 80 % at CH₄ and CO₂ partial pressure of 45 and 25 kPa, respectively. Syngas ratio of 1.0 was yielded at CH₄ partial pressure of 40 kPa. They also expressed that catalysts with basic support (electron-rich surface) such as ceria could improve the acidic gas adsorption such as

![Fig. 3. Effect of CO₂ partial pressure on (a) CH₄, and (b) CO₂ conversions over 10%Ni/SBA-15 catalyst at temperature range of 650-750 ºC. Adapted from [8].](image-url)
CO₂. In the region of low partial pressure of CO₂, due to the prevalence of excess CH₄ and lack of CO₂, most likely, CH₄ underwent catalytic decomposition into C and H₂. Consequently, the reverse Boudouard reaction is favored leading to high conversion of CO₂.

In a nutshell, neither CO₂ nor CH₄ surplus environment can escaped from the co-occurrence of the secondary reactions that arose depends on the supply of the reactant gases. Therefore, the optimal partial pressures for reactant gases varied with distinct catalysts adopted as well as other operating conditions.

Table 2. Influence of CO₂ and CH₄ partial pressure on catalytic activity.

| Catalyst | T (°C) | CO₂/CH₄ | W (L·g⁻¹·h⁻¹) | P (kPa) | X (%) | Ref. |
|----------|--------|---------|----------------|---------|-------|------|
| Ni/SBA-15 | 750 | 1 | 24 | 20 | 20 | 95 | 90 | [8] |
| Ni/SBA-15 | 750 | 1 | 30 | 10 | 50 | 93 | 62 | [38] |

2.3. CH₄/CO₂ ratio

According to the stoichiometric equation of DRM (CO₂ + CH₄ → 2CO + 2H₂), the CO₂/CH₄ = 1 case represents the stoichiometric oxidant supply of reactants. Since the role of CO₂ in DRM is similar to the oxidant in combustion, CO₂/CH₄ with values less or greater than 1 represent the oxidant-lean and oxidant-rich cases, respectively. Thus, investigations on the CH₄/CO₂ ratio using different catalysts for DRM have been reported and compared as well in Table 3. Intriguingly, the results obtained by Cao et al. (2017) [18] evidenced that the CH₄/CO₂ mole ratio was the key factor to adjust H₂/CO mole ratio, rather than adjusting the reaction pressure. Moreover, carbon formation decreased as CH₄/CO₂ mole ratio decreased, which indicates that reaction CH₄ decomposition (CH₄ → C + 2H₂) was promoted to eliminate carbon formation with larger CH₄/CO₂ mole ratio for the whole temperature range. The statement was only valid for the operating temperature > 900°C, meanwhile changing pressure could be used as an alternative option at operating temperature < 900°C for adjustment of H₂/CO mole ratio as compared to varying CH₄/CO₂ mole ratio. According to the stoichiometric equation of CRM (CO₂ + CH₄ → 2CO + 2H₂), the CO₂/CH₄ = 1 case represents the stoichiometric oxidant supply of reactants. Since the role of CO₂ in DRM is similar to the oxidant in combustion, CO₂/CH₄ with values less or greater than 1 represent the oxidant-lean and oxidant-rich cases, respectively. Chein et al. (2017) [39] implied that at the oxidant-rich condition in which the CO₂ supply was excessive, CH₄ conversion can be further improved as compared to the lower CO₂ conversion results for the oxidant-rich case.

Under the same CH₄ supply but less than the stoichiometric amount CO₂ supply, less CO can be produced with excessive CO₂ supply, since CO is one of the product elements [24].

Meanwhile, the CH₄ conversion increased gradually with the increase of CO₂/CH₄ ratio from 1 to 5 as suggested by Sidik et al. (2016) [19] (Fig. 4). This observation implied that the CO₂ has a positive impact on the CH₄ conversion as it can act as an active oxidant [38]. This result could also be interpreted through the disproportionation reaction by the Le Chatelier’s principal which explained that the surplus CO₂ could enhance the amount of CH₄ being converted to CO and H₂. Besides, the stoichiometric effects of feed ratio on DRM to produce H₂ and CO also examined by Osazuwa and Cheng (2017) [40] using three different stoichiometric feed ratios (CO₂/CH₄ = 0.5, 1, 2) at temperature of 750°C. At CO₂/CH₄ ratio of 0.5 where CO₂ was the limiting reagent, 66 % CH₄ conversion was achieved. When DRM was carried out at equimolar feed ratio (CO₂/CH₄ = 1), the highest CH₄ conversion was marked at 84% due to the exact matching with the stoichiometry ratio. Moreover, an increase in feed ratio from 0.5 to 1.0 witnessed a noticeable rise in the H₂ production from 45% to 60%. Moreover, the reverse gas shift (CO₂ + H₂ → CO + H₂O) uses up the H₂ produced, thus leading to a drop in H₂ yield.

In addition, the effect of varying the feed molar ratios of CO₂: CH₄ on the conversions and product selectivity was investigated over the catalyst Pt (8%)/CeO₂(20%)/α-Al₂O₃ in a range of feed molar ratios (CO₂: CH₄) from 1.0: 3.0 to 3.0: 1.0 at 650°C were reported by Zhang et al. (2003) [21]. The CH₄ conversion was found to increase with the increment of CO₂: CH₄ ratio, while the CO₂ conversion decreased. The secondary reaction between CO₂ and H₂ took place when CO₂ was in excess to produce the by-products, thus resulted in the decrease in H₂:CO ratio in the product. This demonstrated that the reforming reaction was inactive while accompanied with the reverse water–gas shift reaction (CO₂ + H₂ → CO + H₂O). Gaur et al. (2012) [26] studied the effect of the CH₄/CO₂ feed ratio (0.5, 1, 2) on La₁₋₀·₇Sr₀·₃O₃(0.5Ru₀·₅Zr₁·₅O₇ (LSRuZ) and 0.5% Ru/Al₂O₃ catalyst [26]. The superior performance of 0.5% Ru/Al₂O₃ over LSRuZ suggested kinetically faster happening of RWGS reaction than on LSRuZ.

![Fig. 4. Response surface plot of the combined (a) CO₂:CH₄ ratio and GHSV, (b) CO₂:CH₄ ratio and reaction temperature. Adapted from [19].](https://doi.org/10.1051/e3sconf/202128704015)
Meanwhile, the CH₄ conversions for 0.5% Ru/Al₂O₃ and LSRuZ were 62% and 58%, respectively at CH₄/CO₂ = 2:1. This can be elucidated that higher CH₄ decomposition over 0.5% Ru/Al₂O₃ than LSRuZ at this feed ratio.

The effects of feed ratios (CH₄:CO₂) ranged 0.1-1.0 also investigated by Ayodele et al. (2016) [22]. Maximum CH₄ and CO₂ conversions of 62.7% and 82%, respectively, were obtained at feed ratio of 1.0 (highest ratio employed) and reaction temperature of 750°C (Fig. 5). Moreover, the production of syngas was observed to increase with feed ratio, reaching the maximum product yield of 59.9% and 62.02% for H₂ and CO. Additionally, the effects of CO₂/CH₄ ratio (0.5-3) on equilibrium conversions, product compositions and solid carbon was studied by Nikko and Amin (2011) [24]. Meanwhile, CH₄ conversion increases with CO₂/CH₄ ratio implying the CO₂ gas as a soft oxidant has a positive effect on CH₄ conversion. When CO₂/CH₄ ratios <1, the amount of H₂ produced enhances within the whole investigated temperature, as CO₂ is the limiting reactant and the RWGS reaction cannot simultaneously improve along with partial oxidation of methane (CH₄+½O₂→CO+2H₂). Meanwhile, the number of H₂ moles produced decreases with increasing CO₂/CH₄ ratio from 0.5 to 1 at a specified temperature. The declining trend of H₂ either for specified CO₂/CH₄ ratios (>1) versus different CO₂/CH₄ ratios (>1) are presumably ascribed to RWGS reaction in which H₂ produced reacts with CO₂ to form water and CO. Generally, H₂ production becomes lower with increasing CO₂/CH₄ ratio due to CH₄ being a more intensive limiting reactant restricted the source of hydrogen atoms.

Fakheeh et al. [41] also found that an increase in CH₄/CO₂ ratio (0.25-2.33) over Ni/SiO₂ increased the CO₂ conversion, but decreased the CH₄ conversion. The higher CH₄ conversion than thermodynamic equilibrium suggested the happening of side reaction, CH₄ decomposition. When CH₄/CO₂ ratio was >1, CH₄ conversion increased and was quite similar with the thermodynamic equilibrium. Similar trends also reported by Serrano-Lotina et al. [31], Xu et al. [32], Meshkani et al. [42], and Meshkani and Rezaei [43]. Indeed, high CH₄ composition in the reactants facilitates CH₄ cracking and coke deposition, resulting in catalyst instability. When the feedstock of CH₄ = CO₂, the coke removal rate by CO₂ is less than that of coke formation by CH₄ cracking.

In summary, a superabundance of CO₂ led to lower CO₂ conversion but higher CH₄ conversions. At this circumstance, higher quantity of H₂ was taken by RWGS reaction, so decreased H₂ selectivity. Thus, CH₄/CO₂ > 1, CH₄ conversion decreased but H₂ selectivity higher. From the previous studies, it can be concluded that CH₄/CO₂ ratios between 1 and 1.43 seem to be the most optimal feedstock ratio to attain the best catalytic performance with low coke deposition and metal sintering.

### Table 3. Influence of CH₄/CO₂ ratio on catalytic activity.

| Catalyst | T (°C) | CH₄/CO₂ ratio | W (L.g⁻¹.h⁻¹) | X (%) | CO₂ | CH₄ |
|----------|--------|---------------|---------------|-------|-----|-----|
| Ni-Co/MSN | 750    | 1.0           | 15            | -     | 87  |     |
|          |        | 3.0           | -             | -     | 85  |     |
|          |        | 5.0           | 30            | 90    | 65  |     |
| SmCoO₃   | 750    | 0.5           | 7.2           | 93    | 53  |     |
|          |        | 1.0           | 53            | 65    | 55  |     |
|          |        | 2.0           | 93            | 55    | 55  |     |
|          |        | 3.0           | 58            | 48    | 90  |     |
| Pr/CoO₃/α-Al₂O₃ | 750 | 0.5           | 80            | 63    | 30  |     |
|          |        | 1.0           | 75            | 40    | 40  |     |
|          |        | 2.0           | 75            | 48    | 48  |     |
| Co/ Nd₂O₃ | 750    | 0.4           | 75            | 75    | 55  |     |
|          |        | 0.6           | 75            | 48    | 48  |     |
|          |        | 0.8           | 75            | 48    | 48  |     |
|          |        | 1.0           | 78            | 62    |     |     |
| Ru/ Al₂O₃ | 785    | 0.5           | 80            | 96    | 99  |     |
|          |        | 1.0           | 75            | 95    | 95  |     |
|          |        | 2.0           | 64            | 62    |     |     |
| LSRuZ    | 785    | 0.5           | 96            | 60    | 98  |     |
|          |        | 1.0           | 95            | 95    | 95  |     |
|          |        | 2.0           | 95            | 95    | 95  |     |
| Ni/SiO₂  | 575    | 0.25          | -             | -     | 31  |     |
|          |        | 0.67          | -             | -     | 45  |     |
|          |        | 1.00          | 49            |       |     |     |
|          |        | 1.50          | 55            |       |     |     |
|          |        | 2.33          | 65            |       |     |     |
| Ni/Hydro-talcite | 700 | 0.67          | 21            | FBR   | 60  |     |
|          |        | 0.83          | 73            |       |     |     |
|          |        | 1.00          | 81            |       |     |     |
|          |        | 1.43          | 82            |       |     |     |
|          |        | 2.50          | 86            |       |     |     |
| Ni-Co/ La₂O₃-Al₂O₃ | 800 | 0.33          | 6             | FBR   | 59  |     |
|          |        | 0.67          | 73            |       |     |     |
|          |        | 1.00          | 96            |       |     |     |
|          |        | 1.50          | 100           |       |     |     |
|          |        | 3.00          | 100           |       |     |     |
| Ni/MgO   | 700    | 0.50          | 18            | FBR   | 60  |     |
|          |        | 0.67          | 66            |       |     |     |
|          |        | 1.00          | 77            |       |     |     |
|          |        | 2.00          | 82            |       |     |     |
| Ni/MgO   | 700    | 0.33          | 10            | FBR   | 62  |     |
|          |        | 0.50          | 66            |       |     |     |
|          |        | 1.00          | 77            |       |     |     |
|          |        | 2.00          | 82            |       |     |     |

[Image 67x84 to 276x207]

Fig. 5. Conversion of (a) CH₄ and (b) CO₂ from methane dry reforming over 20 wt%Co/80 wt%Nd₂O₃ catalyst. Adapted from [22].
2.4 WHSV

Weight hourly space velocity (WHSV) is related to the residence time for the interaction between catalyst particles and the reactants on the catalyst bed. Optimal WHSV can facilitate the reactants’ conversions by providing satisfactory catalyst-reactant interaction. Published journals on the effects of weight hourly gas velocity (WHSV) on DRM using distinct catalysts were tabulated in Table 4. Parametric study on the DRM performance over the reactant volumetric flow rate effect in terms of catalyst weight versus reactant flow rate (W/F₀) were executed by Chein et al. [39]. In this study, WHSV can facilitated the reactants’ conversions by increasing the crys tallites sizes during the sintering and increasing the crystallites sizes during the catalytic reaction tests at different space velocities (WHSV of 15 and 45 L·h⁻¹·gcat⁻¹) by using 15%Ni/Al₂O₃ catalysts and the reactants on the catalyst bed. Optimal WHSV can facilitate the reactants' conversions by prolonging the residence time between the reactants and the catalyst, thus lowering its catalytic activity. Shorter contact time for the interaction between reactants and the catalyst, thus lower CH₄ and CO₂ conversions were resulted. This enhancement was due to the increased residential contact time of the reactants with the catalyst. In addition, the high reaction rate resulted from higher W/F₀, resulted in lower carbon yield as well. Meanwhile, CH₂ and CO₂ conversions became independent of W/F₀ when operating temperatures are > 1000°C and 800°C, respectively.

Similar finding was also reported by Sidik et al. [19], that CH₄ conversion also increased with the increased in the WHSV until reached the optimal point, the further increment in the WHSV value decreased the CH₄ conversion. This was also related to the effect of residence time brought by WHSV, that resulted in the shorter contact time for the interaction between reactants and the catalyst, thus lowering its catalytic activity. Moreover, similar observation was reported by Schwengber et al. (2016) [25] that demonstrated the catalytic reaction tests at different space velocities (WHSV of 15 and 45 L·h⁻¹·gcat⁻¹) by using 15% Ni/Al₂O₃ and 30%Ni/Al₂O₃ catalyst. From the results acquired, CH₄ conversion was also found to be decreased when WHSV increased. Apart from relating with the residence time, the finding can be understood in another way round that larger quantity of catalyst or longer bed length (lower WHSV) in the reaction bed favoured the reactants conversion and product formation [44].

In another studies by Xu et al. [32] and Meshkani et al. [42] whom adopted Ni-Co/La₂O₃-Al₂O₃ and Ni/MgO catalysts also witnessed the decline trends of the conversions with increasing GHSV. They proposed that high GHSV is beneficial in reducing metallic sintering and increasing the crystallites sizes during the reaction. They further declared that even though high GHSV offers higher contact frequency between the reactants and the catalyst but a shorter residence time, thus lower CH₄ and CO₂ conversions were resulted. This phenomena were also in agreement with the findings obtained by Meshkani and Rezaei. [43], which also reported the negative effect on conversions upon increasing GHSV.

The effect of gas hour space velocity (GHSV) on the catalytic performance of Ni/La₂Zr₂O₇ and Ni/hydrotalcite-like precursor catalysts were also studied by le Saché et al. [33] and Serrano-Lotina et al. [36]. Similar findings also observed when a greater extent of activity drop was witnessed after doubling the GHSV; however, the overall conversions achieved were still comparably good especially for CO₂. Furthermore, it was also noted that CH₄ conversion decreased by a greater extent than CO₂, owing to the difficulty in overcoming the relatively stable C-H bonds present in CH₄ for its activation.

In summary, large WHSV was not favoured for the conversions of reactants and product yield, which can be claimed on the shorter residence time between both catalyst and reactants. Lower WHSV was somehow preferable in enhancing DRM activity which enable a longer contact time for catalyst to activate the reactants’ behaviours. At these conditions, mass transfer dominates and kinetic control is the decisive factor when the reactants conversions achieved up to the thermodynamics equilibrium points.

| Catalyst | W (L·g⁻¹·h⁻¹) | CH₄/CO₂ | T (°C) | X (%) | Ref. |
|----------|---------------|---------|--------|-------|-----|
| NiCo/MSN | 20            | 1       | 750    | -     | 82  | [19] |
|          | 40            | 1       |        | -     | 76  |     |
|          | 60            | 1       | 650    | 43    | 85  | [25] |
| 15% NiAl₂O₃ | 15           | 1       | 55     | 28    |     |
|          | 30            | 1       | 55     | 62    |     |
| 30% NiAl₂O₃ | 15           | 1       | 68     | 5     |     |
|          | 45            | 1       | 45     | 28    |     |
| NiCo/La₂O₃ | 3             | 1       | 800    | 96    | 85  | [32] |
|          | 6             | 1       |        | 95    | 88  |
|          | 9             |         |        | 90    | 86  |
|          | 12            |         |        | 93    | 85  |
|          | 18            |         |        | 90    | 80  |
| NiCo/La₂Zr₂O₇ | 15           | 1       | 700    | 91    | 87  | [33] |
|          | 30            |         |        | 90    | 86  |
|          | 60            |         |        | 75    | 55  |

T= temperature, W= WHSV, X= conversion.

3 Conclusion

The great potential of dry reforming of methane (DRM) to be served as energy transformation and storage system that provide alternatives energies is undeniably the most crucial technology for the sake of future chemical industry and environment. The greatest strength of this reaction is the consumption of the two main components of greenhouse gases (CO₂ and CH₄) to generate syngas (H₂+CO). Meanwhile, this reaction was prone to catalyst deactivation due to the thermodynamic nature of the reaction impelled coke formation with the happening of several side reactions. Researches on seeking the excellent and efficient catalysts had achieved the desired accomplishment with the Ni-based catalysts are the most promising in term of its application and economic value. Although the nature and morphology of the supports, active metals used or even the promoters adopted affected the operation of DRM, still the operating conditions during DRM are the other issues that result in
the carbon deposition. High temperature (>750°C) is favourable for the endothermic DRM reaction, where this temperature will result in minimal of coke deposition. The optimal partial pressures for reactant gases could not be determined specifically as they may vary with different types of catalysts used. It can be concluded that CH4/CO2 ratios between 1 and 1.43 seem to be the most optimal feedstock ratio to attain the best catalytic performance with low coke deposition and metal sintering. WHSV between 15-30 L·h⁻¹·g⁻¹ has been suggested to be able to enhance DRM activity by enabling an appropriate contact time for catalyst to activate the reactants’ behaviours. In short, this review summarized the various operating conditions studied in the previous literature to provide a clear benchmark for the future DRM studies for the sake to realize the commercialization of this technology in the foreseeable future.

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