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

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Abstract. Dry reforming of methane (DRM) which also known as CO_2 reforming of methane is a well-investigated reaction to serve as an alternative technique to attenuate the abundance of greenhouse gases (CO_2 and CH_4). 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 CH_4 and CO_2 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 (CH_4 and CO_2) 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 H_2 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, CO_2 prompted an urgent substitution over the existing reforming technology [4, 5]. Owing to the capability to alleviate the CO_2 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

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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_4/CO_2 feed ratios and partial pressure. Results (**Fig. 1**) indicated both CO_2 and CH_4 conversions increased and less fluctuated with increasing reaction temperature. This can be explained by the carbonaceous deposit removal by CO_2 from the catalyst surface via reverse Boudouard reaction (C + $CO_2 \rightarrow 2CO$) which thermodynamically preferred at high reaction temperature of 700-750ºC [16, 17]. A decline in the activity at 650ºC, was due to the CH_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 (550-1200°C), on the H_2/CO ratio and the carbon deposition. At constant pressure (P=0.1MPa) and CH_4/CO_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 depositions were observed between 546ºC and 703ºC, which can be ascribed to the secondary reactions of CH_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_2 gasification

happened at T ≥ 703 ºC. They also claimed that reducing the reaction pressure or reducing the CH_4/CO_2 mole ratio could possibly have switched the carbon free regime at a lower reaction temperature.
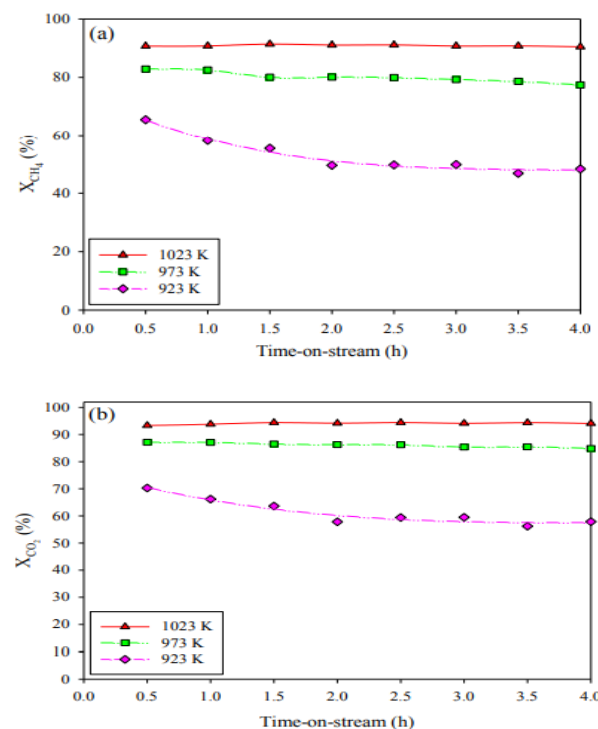

Fig. 1. Effect of reaction temperature on (a) CH_4 and (b) CO_2 conversions over 10%Ni/SBA-15 catalyst. Adapted from [8].

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 [$CH_4 + CO_2 \rightarrow 2CO + 2H_2$ ($\Delta H_{298K} = +247$ kJ mol^{-1})] when using Ni-Co/MSN as catalyst [20]. Poor activity of the catalyst (low CH_4 and CO_2 conversions) can be observed at T < 500ºC (**Fig. 2**), yet approximately CH_4 and CO_2 conversions of 80% were reached at T > 700ºC. Analysis of variance (ANOVA) confirmed that most significant variable that affected the CH_4 conversions was operating temperature. Besides, Zhang et al. (2003) [21] claimed that the composition of the reactant gases (CO_2 and CH_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$_2$O$_3$ catalyst over DRM. Under the feed ratio of CH_4/CO_2 = 1 and T = 750ºC, 62.7% and 82% were the maximum CH_4 and CO_2 conversions achieved, while the maximum H_2 and CO products yield were 59.9% and 62.02%, respectively. At 750 ºC, the CH_4 conversion increased from 12.8% to 62.7% at CH_4: CO_2 of 0.1 to

1.0, while the conversion of CO_2 inclined from 50% to roughly 80% in the same CH_4: CO_2 range (CH_4: CO_2=0.1). Since the conversions recorded by both CH_4 and CO_2 were not similar, as opposed to their proposed methane dry reforming reaction (refers to Equation (1)), we posit that the CH_4 may exhibit poorer affinity to the catalyst, most likely due to the presence of stronger basic sites that favoured CO_2 adsorption as indicated by the TPD results.
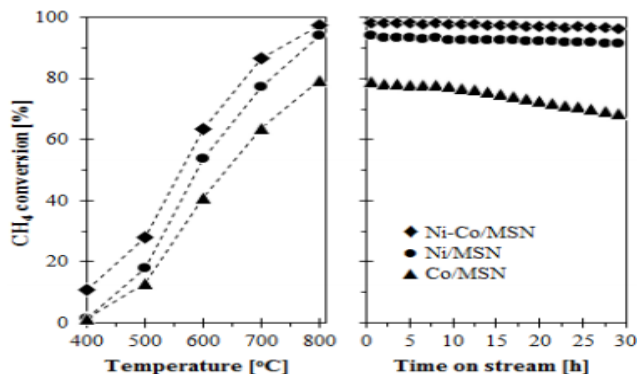

Fig. 2. Catalytic activity and stability of the Co/MSN, Ni/MSN and Ni-Co/MSN. Adapted from [19].

Meanwhile, Khavarian and Mohamed (2013) [23] suggested the CH_4 and CO_2 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 CH_4 at 950ºC, accompanied with insignificant activity loss. As such, the reaction rate of CH_4 and CO_2 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 CH_4 conversion marked a drastic rise from 41.24% at 750ºC to 98.86% at 1000ºC. The CO_2 conversion was slightly surpassed the CH_4 conversion at the temperatures lower than 825ºC but then excelled the CO_2 conversion at higher temperatures. This can be correlated with the CH_4 and CO_2 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 CO_2/CH_4 ratios (0.5–3) as well as reaction pressure (101.3–2533.1 kPa). For all CO_2/CH_4 ratios, CH_4 conversion almost drastically increased with increasing temperature up to 727ºC, meanwhile, for CO_2 conversion, a gradual decline can be observed with temperature start from 300ºC to about 550–600ºC. The decreasing trend for CO_2 conversion can be mainly described by $CO_2+ 2H_2\leftrightarrow C+ 2H_2O$. This exothermic reaction spontaneously occurs at low temperature but diminishes as the equilibrium constant decreases and reduces CO_2 conversion. In addition, side reaction namely carbon dioxide methanation ($CO_2+ 4H_2\leftrightarrow CH_4+$

$2H_2O$) which is exothermic and promoted at a lower temperature (300ºC-650ºC) also devoted to the same declining trend.

Table 1. Influence of reaction temperature on catalytic activity.

Catalyst	WHSV (L.g⁻¹h⁻¹)	CH_4/CO_2	T (ºC)	X (%)		Ref.
				CO_2	CH_4	
Ni/SBA-15	24	1	650	70	64	[8]
			700	87	83	
			750	91	94	
Ni-Co/MSN	15	1	450	-	10	[18]
			550	-	62	
			800	-	97	
Co/Nd₂O₃	30	1	650	74	30	[22]
			700	78	38	
			750	80	63	
Co-Mo-MgO/MWCNTs	140	1	750	17	25	[23]
			850	56	92	
			950	90	98	
15%Ni/Al₂O₃	30	1	600	67	45	[25]
			650	53	30	
			700	83	58	
30%Ni/Al₂O₃			600	45	7	
			650	63	5	
			700	70	67	
Pt/CeO₂/α-Al₂O₃	7.2	1	500	45	33	[21]
			600	65	55	
			700	80	76	
			800	90	90	
Ru/Al₂O₃	18	1	635	81	73	[26]
			735	94	92	
			835	98	97	
LSRuZ	18		635	78	75	
			735	95	93	
			835	98	98	
Ni/Al₂O₃	-	1	200	FBR	21	[27]
			300		40	
Ni/MgO	18	1	700	FBR	57	[28]
			800		73	
			900		92	
Pt/Mg0.85Ni0.15O	15	2	700	FBR	38	[29]
			900		97	
MgCoAl	6	1	400	FBR	19	[30]
			550		65	
Ni/hydrotalcite-	-	1	450	FBR	13	[31]
			600		60	
			800		95	
Ni-Co/La₂O₃-Al₂O₃	6	1	500	FBR	19	[32]
			700		75	
			900		94	
Ni/La₂Zr₂O₇	30	1	600	FBR	69	[33]
			650		79	
			700		89	

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 (600–700°C range). In general, increasing the reaction temperature in the DRM led to higher H_2 yields and higher conversions of CH_4 and CO_2. Higher CH_4 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 H_2 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 ($CO + H_2O \leftrightarrow CO_2+ H_2$), Boudouard reaction ($2CO \leftrightarrow C + CO_2$) and CO reduction ($CO + H_2$

↔ C + H_2O) that led to coke formation, low product yield and low reactants' conversions [34, 35].

After all, coke accumulations are the main contributor over the catalysts deactivation which leading to severe reactor tubing blockage and physical disintegration of the catalyst framework. This circumstance was evidenced to have close connection on the reaction temperature conducted as DRM reaction was inevitably accompanied by numerous side reactions. Due to the endothermic nature of the reaction, high temperature (>750ºC) is the main accomplishment to attenuate coke deposition.

2.2 CO_2 and CH_4 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 (CO_2 and CH_4) partial pressure on the product yield and carbon deposition over DRM. Appropriate CO_2 and CH_4 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 CO_2 partial pressure (P_{CO_2}) was increased, an increasing trend was observed for CH_4 conversion, whilst CO_2 conversion showed a substantial decline and exhibited an optimum performance at P_{CO_2} = 30-50kPa. The incline trend for CH_4 conversion with increasing of P_{CO2} (20-60kPa) was credited to the escalating intermediate by-product, H_2O formation by RWGS reaction (CO_2 + $H_2 \rightarrow$ CO+ H_2O) which promoted CH_4 steam reforming (CH_4 + $H_2O \rightleftharpoons$ CO + 3 H_2) as well. On the contrary, the considerable decline of CO_2 conversion with rising P_{CO2} (20-60kPa) was owing to the superabundance of CO_2 and inadequate quantity of CH_4 to act as limiting reactant for transforming CO_2-rich feed composition [24, 36]. Furthermore, the drop in CO_2 conversion with rising P_{CO2} also can be linked to the active Ni^0 metallic site oxidation at the catalyst surface to NiO (Ni + $CO_2 \rightarrow$ NiO + CO) in excess CO_2 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 CH_4 cracking ($CH_4 \rightarrow$ C+ $2H_2$) in CH_4-rich feed [32]. Furthermore, CH_4 decomposition was easily facilitated in the CH_4-excess environment further enhance the decomposition rate and promoting carbon deposition [4].
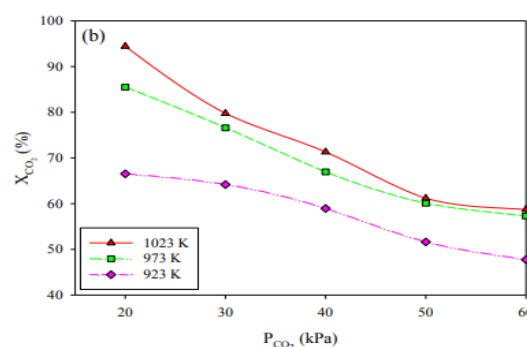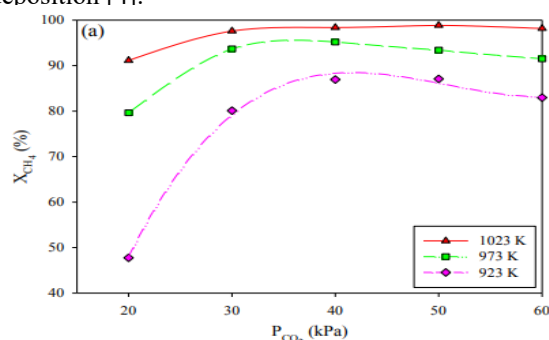

Fig. 3. Effect of CO_2 partial pressure on (a) CH_4, and (b) CO_2 conversions over 10%Ni/SBA-15 catalyst at temperature range of 650-750 ºC. Adapted from [8].

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 ($2CO \rightleftharpoons$ C + CO_2) 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/Nd_2O_3 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 CH_4 and CO_2 conversions, main products distribution and H_2/CO ratio at 900 ºC, CO_2/CH_4 ratio of 1. CO_2 and CH_4 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, CH_4 decomposition ($CH_4 \rightarrow$ C + $2H_2$) and CO disproportionation ($2CO \rightarrow$ CO_2 + C) facilitate in lowering CH_4 and CO_2 conversions, as well as obstructing CO and H_2 formation at the higher pressures. Another research done by Ayodele et al. (2015) [38] investigated on the influences of reactants' (CH_4 and CO_2) 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 CH_4 and CO_2 were acquired to be 78 and 80% at CH_4 and CO_2 partial pressure of 45 and 25 kPa, respectively. Syngas ratio of 1.0 was yielded at CH_4 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

CO_2. In the region of low partial pressure of CO_2, due to the prevalence of excess CH_4 and lack of CO_2, most likely, CH_4 underwent catalytic decomposition into C and H_2. Consequently, the reverse Boudouard reaction is favored leading to high conversion of CO_2.

In a nutshell, neither CO_2 nor CH_4 surplus environment can escaped from the co-occurrence of the secondary reactions that arose depends on the supply of the reactant gases. Thereupon, the optimal partial pressures for reactant gases varied with distinct catalysts adopted as well as other operating conditions.

Table 2. Influence of CO_2 and CH_4 partial pressure on catalytic activity.

Catalyst	T (ºC)	CO_2 /CH_4	W (L.g^{-1}h^{-1})	P (kPa)		X (%)		Ref.
				CO_2	CH_4	CO_2	CH_4	
Ni/ SBA-15	750	1	24	20	20	95	90	[8]
				40	20	73	97	
				60	20	64	96	
				20	20	92	90	
				20	40	84	56	
				20	60	78	40	
Co/ CeO$_2$	750	1	30	10	50	93	62	[38]
				30	50	87	75	
				50	50	70	73	
				50	10	37	35	
				50	30	64	48	
				50	45	84	62	

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

2.3. CH₄/CO₂ ratio

According to the stoichiometric equation of DRM (CO_2 + $CH_4 \rightarrow 2CO + 2H_2$), the $CO_2/CH_4 = 1$ case represents the stoichiometric oxidant supply of reactants. Since the role of CO_2 in DRM is similar to the oxidant in combustion, CO_2/CH_4 with values less or greater than 1 represent the oxidant-lean and oxidant-rich cases, respectively. Thus, investigations on the CH_4/CO_2 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 CH_4/CO_2 mole ratio was the key factor to adjust H_2/CO mole ratio, rather than adjusting the reaction pressure. Moreover, carbon formation decreased as CH_4/CO_2 mole ratio decreased, which indicates that reaction CH_4 decomposition ($CH_4 \rightarrow C + 2H_2$) was promoted to eliminate carbon formation with larger CH_4/CO_2 mole ratio for the whole temperature range. The statement was only valid for the operating temperature > 900ºC, meanwhile changing pressure could be used as an alternative option at operating temperature < 900ºC for adjustment of H_2/CO mole ratio as compared to varying CH_4/CO_2 mole ratio. According to the stoichiometric equation of CRM ($CO_2 + CH_4 \rightarrow 2CO + 2H_2$), the $CO_2/CH_4 = 1$ case represents the stoichiometric oxidant supply of reactants. Since the role of CO_2 in DRM is similar to the oxidant in combustion, CO_2/CH_4 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 CO_2 supply was excessive, CH_4 conversion can be further improved as compared to the lower CO_2 conversion results for the oxidant-rich case.

Under the same CH_4 supply but less than the stoichiometric amount CO_2 supply, less CO can be produced with excessive CO_2 supply, since CO is one of the product elements [24].

Meanwhile, the CH_4 conversion increased gradually with the increase of CO_2: CH_4 ratio from 1 to 5 as suggested by Sidik et al. (2016) [19] (**Fig. 4**). This observation implied that the CO_2 has a positive impact on the CH_4 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 surpass CO_2 could enhance the amount of CH_4 being converted to CO and H_2. Besides, the stoichiometric effects of feed ratio on DRM to produce H_2 and CO also examined by Osazuwa and Cheng (2017) [40] using three different stoichiometric feed ratios ($CO_2/CH_4 = 0.5, 1, 2$) at temperature of 750ºC. At CO_2/CH_4 ratio of 0.5 where CO2 was the limiting reagent, 66 % CH_4 conversion was achieved. When DRM was carried out at equimolar feed ratio ($CO_2/CH_4 = 1$), the highest CH_4 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 H_2 production from 45% to 60%. Moreover, the reverse gas shift ($CO_2 + H_2 \rightarrow CO + H_2O$) uses up the H_2 produced, thus leading to a drop in H_2 yield.
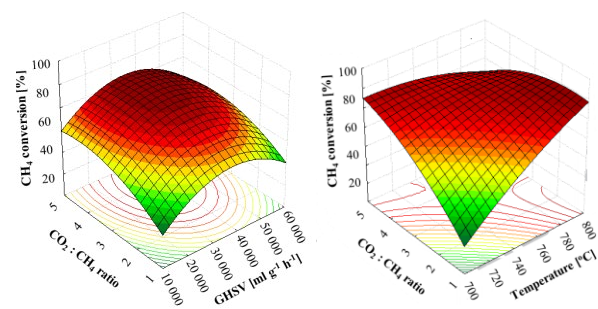

Fig. 4. Response surface plot of the combined (a) CO_2:CH_4 ratio and GHSV, (b) CO_2:CH_4 ratio and reaction temperature. Adapted from [19].

In addition, the effect of varying the feed molar ratios of CO_2: CH_4 on the conversions and product selectivity was investigated over the catalyst Pt (8%)/CeO_2(20%)/α-Al_2O_3 in a range of feed molar ratios (CO_2: CH_4) from 1.0: 3.0 to 3.0: 1.0 at 650ºC were reported by Zhang et al. (2003) [21]. The CH_4 conversion was found to increase with the increment of CO_2: CH_4 ratio, while the CO_2 conversion decreased. The secondary reaction between CO_2 and H_2 took place when CO_2 was in excess to produce the by-products, thus resulted in the decrease in H_2:CO ratio in the product. This demonstrated that the reforming reaction was inactive while accompanied with the reverse water–gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$). Gaur et al. (2012) [26] studied the effect of the CH_4/CO_2 feed ratio (0.5, 1, 2) on $La_{1.97}Sr_{0.03}Ru_{0.05}Zr_{1.95}O_7$ (LSRuZ) and 0.5% Ru/Al_2O_3 catalyst [26]. The superior performance of 0.5% Ru/Al_2O_3 over LSRuZ suggested kinetically faster happening of RWGS reaction than on LSRuZ.

Meanwhile, the CH_4 conversions for 0.5% Ru/Al_2O_3 and LSRuZ were 62% and 58%, respectively at CH_4/CO_2 = 2:1. This can be elucidated that higher CH_4 decomposition over 0.5% Ru/Al_2O_3 than LSRuZ at this feed ratio.

The effects of feed ratios (CH_4: CO_2) ranged 0.1-1.0 also investigated by Ayodele et al. (2016) [22]. Maximum CH_4 and CO_2 conversions of 62.7% and 82%, respectively, were obtained at feed ratio of 1.0 (highest ratio employed) and reaction temperature of 750ºC (**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 H_2 and CO. Additionally, the effects of CO_2/CH_4 ratio (0.5–3) on equilibrium conversions, product compositions and solid carbon was studied by Nikko and Amin (2011) [24]. Meanwhile, CH_4 conversion increases with CO_2/CH_4 ratio implying the CO_2 gas as a soft oxidant has a positive effect on CH_4 conversion. When CO_2/CH_4 ratios <1, the amount of H_2 produced enhances within the whole investigated temperature, as CO_2 is the limiting reactant and the RWGS reaction cannot simultaneously improve along with partial oxidation of methane ($CH_4 + \frac{1}{2} O_2 \leftrightarrow CO + 2H_2$). Meanwhile, the number of H_2 moles produced decreases with increasing CO_2/CH_4 ratio from 0.5 to 1 at a specified temperature. The declining trend of H_2 either for specified CO_2/CH_4 ratios (>1) versus different temperatures or for specified temperature (> 973 K) versus different CO_2/CH_4 ratios (>1) are presumably ascribed to RWGS reaction in which H_2 produced reacts with CO_2 to form water and CO. Generally, H_2 production becomes lower with increasing CO_2/CH_4 ratio due to CH_4 being a more intensive limiting reactant restricted the source of hydrogen atoms.

Fakeeh et al. [41] also found that an increase in CH_4/CO_2 ratio (0.25-2.33) over Ni/SiO_2 increased the CO_2 conversion, but decreased the CH_4 conversion. The higher CH_4 conversion than thermodynamic equilibrium suggested the happening of side reaction, CH_4 decomposition. When CH_4/CO_2 ratio was > 1, CH_4 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 CH_4 composition in the reactants facilitates CH_4 cracking and coke deposition, resulting in catalyst instability. When the feedstock of CH_4 = CO_2, the coke removal rate by CO_2 is less than that of coke formation by CH_4 cracking.
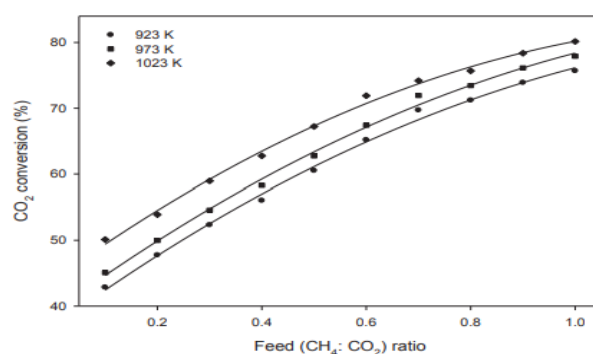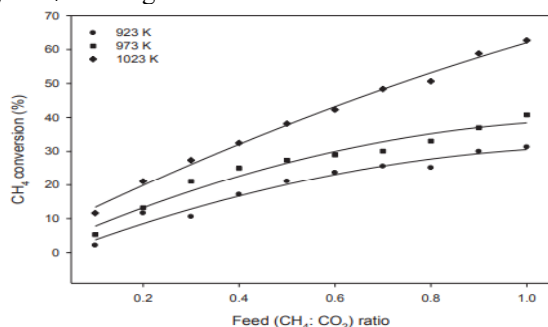

Fig. 5. Conversion of (a) CH_4 and (b) CO_2 from methane dry reforming over 20 wt%Co/80 wt%Nd_2O_3 catalyst. Adapted from [22].

In summary, a superabundance of CO_2 led to lower CO_2 conversion but higher CH_4 conversions. At this circumstance, higher quantity of H_2 was taken by RWGS reaction, so decreased H_2 selectivity. Thus, when CH_4/CO_2 > 1, CH_4 conversion decreased but H_2 selectivity higher. From the previous studies, it can be concluded that CH_4/CO_2 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 CH_4/CO_2 ratio on catalytic activity.

Catalyst	T (ºC)	CH_4/CO_2 ratio	W (L.g⁻¹h⁻¹)	X (%)		Ref.
				CO_2	CH_4	
Ni-Co/ MSN	750	1.0	15	-	87	[19]
		3.0		-	85	
		5.0		-	83	
$SmCoO_3$	750	0.5	30	90	65	[40]
		1.0		85	85	
		2.0		53	55	
$Pt/CeO_2/$ α-Al_2O_3	750	0.5	7.2	93	53	[21]
		1.0		75	65	
		2.0		58	85	
		3.0		48	90	
Co/ Nd_2O_3	750	0.4	30	63	30	[22]
		0.6		72	40	
		0.8		75	48	
		1.0		78	62	
Ru/ Al_2O_3	785	0.5	18	96	99	[26]
		1.0		95	96	
		2.0		64	62	
LSRuZ	785	0.5		60	98	
		1.0		95	95	
		2.0		95	57	
Ni/SiO_2	575	0.25	-	-	31	[41]
		0.67			45	
		1.00			49	
		1.50			57	
		2.33			65	
Ni/ Hydro-talcite	700	0.67	21	FBR	60	[31]
		0.83			73	
		1.00			81	
		1.43			82	
		2.50			86	
Ni-Co/ La_2O_3-Al_2O_3	800	0.33	6	FBR	59	[32]
		0.67			75	
		1.00			96	
		1.50			100	
		3.00			100	
Ni/MgO	700	0.50	18	FBR	60	[42]
		0.67			66	
		1.00			77	
		2.00			82	
Ni/MgO	700	0.33	10	FBR	62	[43]

		0.50			69	
		1.00			84	
		2.00			90	

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

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 facilitated 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/F_0) were executed by Chein et al. [39]. In this study, W is fixed while F_0 was varied throughout the investigation. With the increased W/F_0 by decreasing the reactant flow rate, the higher reaction rate was achieved which led to higher reactants conversions. 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/F_0, resulted in higher carbon yield as well. Meanwhile, CH_4 and CO_2 conversions became independent of W/F_0 when operating temperatures are > 1000ºC and 800ºC, respectively.

Similar finding was also reported by Sidik et al. [19] , that CH_4 conversion also increased with the increased in the WHSV until reached the optimal point, the further increment in the WHSV value decreased the CH_4 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}·g$_{cat}^{-1}$) by using 15%Ni/Al_2O_3 and 30%Ni/Al_2O_3 catalyst. From the results acquired, CH_4 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 beg 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/La_2O_3-Al_2O_3 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 CH_4 and CO_2 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/$La_2Zr_2O_7$ 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 CO_2. Furthermore, it was also noted that CH_4 conversion decreased by a greater extent than CO_2, owing to the difficulty in overcoming the relatively stable C-H bonds present in CH_4 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.

Table 4. Influence of weight hourly space velocity (WHSV) on catalytic activity.

Catalyst	W (L.g^{-1} h^{-1})	CH_4/CO_2	T (ºC)	X (%)		Ref.
				CO_2	CH_4	
Ni-Co/MSN	20	1	750	-	82	[19]
	40			-	76	
	60			-	44	
15% Ni/Al_2O_3	15	1	650	43	85	[25]
	30			55	28	
	45			52	42	
30% Ni/Al_2O_3	15			55	62	
	30			68	5	
	45			45	28	
Ni-Co/ La_2O_3-Al_2O_3	3	1	800	96	85	[32]
	6			95	88	
	9			90	86	
	12			93	85	
	18			90	80	
Ni/ $La_2Zr_2O_7$	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 (CO_2 and CH_4) to generate syngas (H_2+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 (>750ºC) 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 CH_4/CO_2 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 $L \cdot h^{-1} \cdot g_{cat}^{-1}$ has been suggested to be able in enhancing 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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