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An Overview of Response Surface Methodology Approach to Optimization of Hydrogen and Syngas Production by Catalytic Reforming of Greenhouse Gases (CH$_4$ and CO$_2$)

Bamidele V. Ayodele and Sureena Abdullah

Abstract

Catalytic reforming of Methane (CH$_4$) and carbon dioxide (CO$_2$) is one of the techniques used for the production of hydrogen and syngas. This technique has dual advantages of mitigation of greenhouse gases and production of hydrogen and syngas which are often used as intermediates for the synthesis of valuable chemical products and oxygenates. This study presented an overview of the application of response surface methodology (RSM) in the optimization of hydrogen and syngas production from catalytic reforming of CH$_4$ and CO$_2$. The different catalytic system that has been employed together with the nature of experimental design, input parameters, responses, the optimum conditions and the maximum values of their responses were examined. The future research direction in the application of RSM to optimization of hydrogen and syngas production by catalytic reforming of CH$_4$ and CO$_2$ was recommended.

Keywords: greenhouse gases, response surface methodology, catalytic reforming, hydrogen, syngas

1. Introduction

The frequent environmental pollution often encountered from the consumption of energy derived from fossil fuel has aroused the quest for production of alternative and cleaner source of energy [1, 2]. One of such alternative means of energy production is catalytic methane dry reforming whereby the two principal greenhouse gases, carbon dioxide (CO$_2$) and methane (CH$_4$) are utilized for the production of hydrogen and syngas using active catalysts [3–5]. Compare to other forms of reforming processes which utilized steam and oxygen; the dry

methane reforming has a dual advantage of mitigating greenhouse effect by utilizing the two principal components of greenhouse gases CH_4 and CO_2 as feedstocks. Besides, hydrogen and syngas are produced which can either be used directly as fuel or as a chemical intermediate for the synthesis of value-added chemicals and synthetic fuel [6–8]. Thermodynamically, the dry methane reforming reaction requires temperature >500°C to be feasible [9, 10]. Hence, at a temperature >500°C, coke formation and deposition on the catalyst surface is often induced mainly by methane cracking and Boudouard reactions [11, 12]. The deposited coke usually lead to deactivation of the catalyst thereby reducing the activities and stability [13–15]. To overcome these major challenges, several supported catalysts such as Ni, Co, Pt, Pd, Ru, Rh, Li and so on have been employed to catalyze the production of hydrogen and syngas via dry methane reforming [14, 16, 17]. The findings from these studies revealed that the individual catalysts displayed different degrees of catalytic activities and stabilities during the dry methane reforming reaction. Hence, obtaining a consensus on the optimum conditions that can maximize the hydrogen and the syngas yield has been a bone of contention till date. In view of this, several authors have employed response surface methodology approach to investigate the optimum conditions required for obtaining maximum hydrogen and syngas yield from catalytic methane dry reforming. This study, therefore, presents an overview of the different response surface methodology (RSM) approaches that have been used to optimize hydrogen and syngas production by methane dry reforming using different catalysts.

2. Metal-based dry reforming catalysts

An extensive review by Pakhare and Spivey [14], Budiman et al. [16] and Kathiraser et al. [18] revealed that supported metal catalysts such as Pt, Rh, Ru, Co, and Ni had been widely investigated for hydrogen and syngas production by dry methane reforming. According to Pakhare and Spivey [14] noble metals such as Pt, Rh and Ru displayed high catalytic activities and stabilities towards dry reforming of methane even with minimal metal loading. However, the activities of these noble metals were observed to vary with the nature of support. Supports such as SiO_2, La_2O_3, ZrO_2, TiO_2, CeO_2, Al_2O_3, and MgO have been investigated for these noble metals [14, 19–21]. The significant physicochemical properties that influence the activities of the noble metals-based catalyst are their high metal dispersion and the metal surface area. Nevertheless, noble metals are pricey and not readily available. Hence, their usage might not be economical in the eventuality of a scale-up process.

In view of this, other supported metal catalysts mostly Co, and Ni have been given full attention as catalytic candidates for hydrogen and syngas production by dry methane reforming [16, 18]. Although several studies have shown that Co and Ni catalysts have inferior catalytic activities and stability compared to the noble metals, these metals are inexpensive and readily available. Hence, Co and Ni-based catalysts have been tipped as potential candidates for scale-up of catalytic dry methane reforming. Moreover, the catalytic properties of the Co and Ni catalysts can be improved to be competitive with that of the noble metals by either using suitable supports or promoters [14].

3. RSM approach to process optimization

Chemical process optimization is an important activity performed on a system or a process to obtain optimum conditions that can give the maximum benefit from such process. This can be achieved statistically by using one-variable-at-a-time for optimizing a response [22]. This method of optimization entails changing the parameters of a variable while keeping the level of the other variables constant [23]. One major drawback of this type of optimization is that the interaction effects of the variables are not usually considered during the optimization process [22]. Hence, the one-variable-at-time technique does not capture the broad effects of the parameters on the responses [24]. Besides, the technique requires a massive number of experimental runs which invariably implies an increase in time of experiment as well as high cost of reagents and materials [22].

The challenges using the one-variable-at-time form of optimization of the chemical process can be overcome using response surface methodology (RSM). RSM is a more robust optimization technique that presents the statistical design of experiment (DoE) which can be employed in achieving process with ultimate performance. RSM as a technique for chemical process optimization is made up of a set of mathematics and statistical tools which work based on empirical model fittings to the obtained experimental data from DoE [25]. The empirical model fittings help in developing a suitable functional relationship between a set of input variables and the targeted response [25]. The different stages involved in the use of RSM for chemical process optimization are depicted in **Figure 1** [22]. These stages include screening of the variables that have been identified for optimization, the choice of the experimental design, the codification of the level of the variables, mathematic-statistic treatment of data, evaluation of fitted model and determination of the optimum conditions.
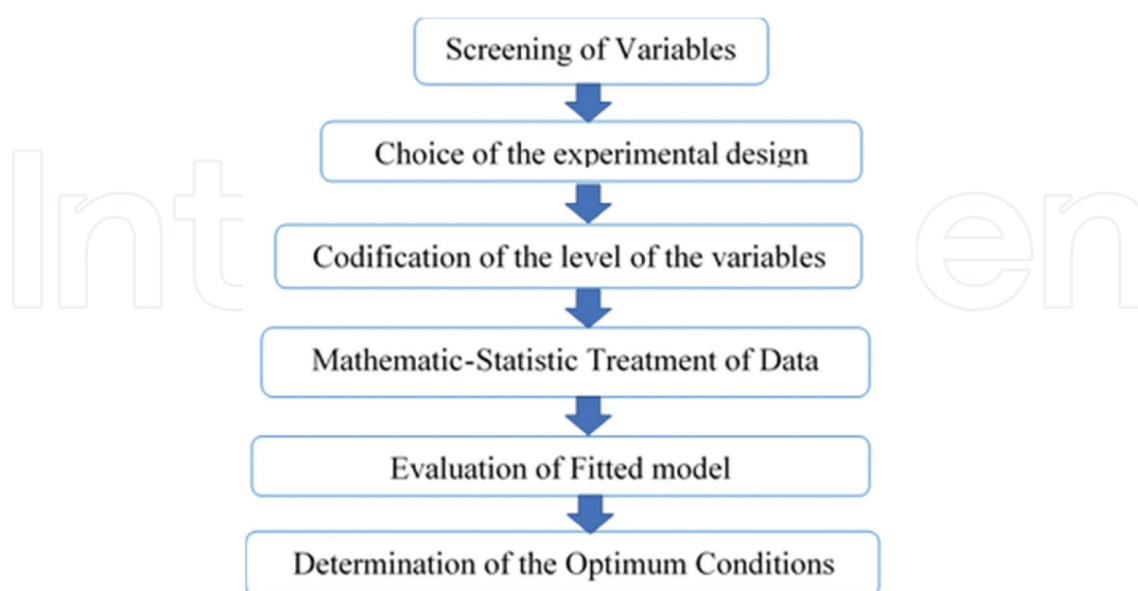

Figure 1. Stages involved in RSM applications [22].

Several parameters are often needed to investigate chemical processes extensively. One of the most significant challenges is to investigate all the effects of these parameters on the process. An attempt to do this might be rigorous, time-consuming and expensive [26]. Hence, it is expedient to determine the parameters that significantly affect the responses from the chemical process. To achieve this, experiment to identify parameters with most significant effects is usually performed at the preliminary stage using factorial designs [26]. Screening of variable before the main DoE has the advantages of preventing the mistake of chosen wrong levels that might negatively influence overall success of the process optimization. Having ascertained the appropriate parameters to be used for the main experiment, the next stage is to choose the right experimental design.

Experimental design can be selected based on the intention of using a simple model which can be employed as a linear function depicted in Eq. (1)

$$y = \beta_o \sum\nolimits_{i=1}^{k} \beta_i x_i + \varepsilon \tag{1}$$

where k, β_o, β_i, x_i and ε depicts number of variables, the constant term, coefficients of the liner parameters, the input variables and the residual associated with the experiments, respectively. The response obtained from the linear model cannot be used to determine curvature. Hence the need for a second-order model represented in Eq. (2).

$$y = \beta_o + \sum\nolimits_{i=1}^{k} \beta_i x_i + \sum\nolimits_{1 \leq i \leq j}^{k} \beta_{ij} x_j + \varepsilon \tag{2}$$

where the coefficient of the interaction parameter is denoted as β_{ij}. The critical point which could either be maximum, minimum or saddle can be determined by including quadratic terms to the polynomial terms in Eq. (2) as shown in Eq. (3).

$$y = \beta_o + \sum\nolimits_{i=1}^{k} \beta_i x_i + \sum\nolimits_{1z \leq x_j \; i \leq j}^{k} \beta_{ij} + \sum\nolimits_{1=i}^{k} \beta_{ii} x_i^2 + \varepsilon \tag{3}$$

where the coefficient of the quadratic parameter is denoted as β_{ii}.

Eq. (3) can be identified as a form two-modeling, symmetrical response surface designs which could be three-level factorial design, Box-Behnken design (BBD), central composite design (CCD), and Doehlert design. The main difference between these two modeling, symmetrical response surface designs is the selection of their experimental points, number of levels for variables, and the number of runs and block [22].

After choosing the appropriate experimental design, the next stage is the codification of the level of the variables which entail the transformation of the process real values to a coordinate within dimensionless value scale proportional to the localization in the experimental space [22]. One significant advantage of codification is that it allows the variables of different orders of magnitude to be determined without substantial influence on the lesser values.

The data obtained for each of the experimental point based on the selected experimental design can be subjected to mathematical-statistical treatment. The mathematical-statistical

treatment entails the fitting of an appropriate mathematical equation that can best describe the behavior of the responses. The method of least squares which is a statistical approach can also be employed to fit a mathematical model to a given set of experimental data [27]. The mathematic model obtained from the treatment of the data can subsequently be evaluated to determine if it appropriately explains the experimental sphere investigated. This can be achieved by employing the analysis of variance (ANOVA). The use of ANOVA enables the comparison between the variations that arise from the treatment of the experimental data and the variation as a result of the random errors that accompanied the measurement of the obtained responses [28]. Moreover, the ANOVA helps to determine the significance and the mathematical model adequacy [28]. Besides ANOVA, other tools such as normality test, regression analysis and lack of fit test can be employed to examine the model adequacy of the RSM optimization. The normality of the experimental data can be performed using the normal plot of the internally studentized residuals. The data points in a normal plot is linear when the studentized residuals are normally distributed. Otherwise, when the data points in a normal plot is non-linear, it implies that the studentized residuals are not normally distributed. Hence, there is a need for the correction of the responses. Regression analysis is often performed on the fittings of the model denoted by the equation to the experimental data. The regression analysis of the model helps to determine to what extent the fitted model accounted for the variations in the experimental data. In order to further test the adequacy of the specified model, the lack of fits test can be employed. A significant lack of fit implies that the specific model is not suitable to explain the experimental data. Hence, a different form of model would adequately fit the data if investigated. The last stage of the application of the RSM is the determination of the optimum conditions that can maximize the response values. Numerical optimization using the RSM techniques can be employed to obtain the desired value for each of the input variables as a function of the target response. This is dependent on the input optimization strategies such as the range, maximum, minimum or target set to obtain the maximum achievable desired responses of the chemical process [29].

4. Optimization of hydrogen and syngas production using RSM

The details of the optimization studies on the catalytic reforming of CH_4 and CO_2 to hydrogen and syngas is depicted in **Table 1**. It can be seen that there is a dearth of literature on the optimization of hydrogen and syngas by the catalytic reforming of CH_4 and CO_2 despite the volume of literature available on their catalytic activities, stabilities and kinetic studies as reported by Budiman et al. [16], Pakhare and Spivey [14], and Kathiraser et al. [18]. The studies show that supported Ni-based catalysts such as Ni/γ-Al_2O_3, and Ni/SiO_2 has been employed for investigating the optimum conditions of hydrogen and syngas production from reforming of CH_4 and CO_2 using CCD. CCD as an RSM technique entails the use of a full factorial or fractional factorial design, a star design which consist of experimental points at a distance α from its center and the central point [30, 34]. For the Ni/γ-Al_2O_3 catalyst, the effect of factors such as discharge power, total flow rate CO_2/CH_4 molar ratio and Ni-loading on responses such as CO_2 conversion, CH_4 conversion, and CO yield, H_2 yield and the fuel production efficiency were investigated [30]. The ANOVA results show that all the factors investigated

RSM approach	Catalyst	Factors	Low-level	High-level	Responses	Optimum conditions		References
						Factors	Responses	
CCD	Ni/γ-Al$_2$O$_3$	Discharge power	30	50	CO$_2$ conversion	Discharge power = 60 W	CO$_2$ conversion = 31.7%	[30]
		Total flow rate	50	100	CH$_4$ conversion	Total flow rate = 56.1 mL/min	CH$_4$ conversion = 48.1%	
		CO$_2$/CH$_4$ molar ratio	0.75	1.25	CO yield (%)	CO$_2$/CH$_4$ molar ratio = 1.03	CO yield (%) = 21.7%	
		Ni loading	7.5	12.5	H$_2$ yield (%)	Ni loading = 9.5%	H$_2$ yield (%) = 17.9%	
					Fuel production efficiency (%)		Fuel production efficiency (%) 7.9%	
CCD	Li/MgO	Reaction temperature	650	800	% CH$_4$ conversion	Temperature = 725°C	% CH$_4$ conversion = 41.4	[31]
		GHSV (F/W)	5140	12,000	% C$_2$ selectivity	GHSV (F/W) = 8570 cm^3 g^{-1} h^{-1}	% C$_2$ selectivity = 77.2	
		Li loaded	0.05	0.15	% C$_2$ yield	Li loaded = 0.1	% C$_2$ yield = 32	
CCD	15wt%Rh/MgO	Reaction temperature	650	850	% CH$_4$ conversion	Temperature = 918°C	% CH$_4$ conversion = 93.91720	[32]
		O$_2$/CH$_4$ ratio	0.1	0.2	% H$_2$ selectivity	O$_2$/CH$_4$ ratio = 0.15	% H$_2$ selectivity = 34.55	
		Catalyst weight	100	300	H$_2$/CO product ratio	Catalyst weight = 200	H$_2$/CO product ratio = 1.42	
CCD	Ni–Co/MSN	Temperature	700	800	% CH$_4$ conversion	Temperature = 783°C	% CH$_4$ conversion = 97	[33]
		CO$_2$/CH$_4$ ratio	1	5		CO$_2$/CH$_4$ ratio = 3		
		GHSV	10,000	60,000		GHSV = 38,726 mL g^{-1} h^{-1}.		
CCD	Ni/SiO$_2$	Reaction temperature	600	800	CH$_4$ conversion	Reaction temperature = 800°C	CH$_4$ conversion = 79.6	[34]
		CH$_4$/CO$_2$ molar ratio	0.25	4	CO$_2$ conversion	CH$_4$/CO$_2$ molar ratio = 2.125	CO$_2$ conversion = 84.2	
					The H$_2$/CO ratio		H$_2$/CO ratio = 0.4	
					Carbon content		Carbon content = 51.1	

RSM approach	Catalyst	Factors	Low-level	High-level	Responses	Optimum conditions		References
						Factors	Responses	
BBD	Fe/Mg/Al$_2$O$_3$	Reaction temperature	550	750	CH$_4$ conversion	Reaction temperature = 650°C	CH$_4$ conversion = 100%	[35]
		Mg loading	0	10	% H$_2$ yield	Mg loading = 5	% H$_2$ yield = 83.7%	
		Synthesis method	Co-impregnation	Sequential impregnation	CO/CO$_2$ molar ratio	Synthesis method = Sequential impregnation	CO/CO$_2$ molar ratio = 16.5%	
CCD	Ni-Co/MgO-ZrO$_2$	CO$_2$/CH$_4$ ratio	1	5	CH$_4$ conversion	CO$_2$/CH$_4$ ratio = 3	CH$_4$ conversion = 88 mol%	[30]
		GHSV	8400	200,000	H$_2$ yield (%)	GHSV = 145,190 mL g^{-1} h^{-1}	H$_2$ yield (%) = 86 mol%	
		Oxygen concentration in the feed	3	8		Oxygen concentration in the feed = 7 mol%		
		Reaction temperature	700	800		Reaction temperature = 749°C		
CCD	ZnO	Weight of catalyst	5	8		Weight of catalyst = 8 g	CH$_4$ conversion = 11.88%	[36]
		Total pressure	30	90		Total pressure = 30 Psi	CO$_2$ conversion = 15.69%	
		CO$_2$:CH$_4$:He (% CO$_2$)	10	80		CO$_2$:CH$_4$:He (% CO2) = 10%		
		UV light power	80	250		UV light power = 250 W		
BBD	Co/Sm$_2$O$_3$	CH$_4$ partial pressure	10	50	H$_2$ yield (%)	CH$_4$ partial pressure = 47.9 kPa	H$_2$ yield (%) = 79.4	[37]
		CO$_2$ partial pressure	10	50	CO yield (%)	CO$_2$ partial pressure = 48.9 kPa	CO yield (%) = 79.0	
		Reaction temperature	650	750		Reaction temperature = 735°C		

RSM approach	Catalyst	Factors	Low-level	High-level	Responses	Optimum conditions		References
						Factors	Responses	
BBD	Co/CeO_2	CH_4 partial pressure	10	50	CH_4 conversion (%)	CH_4 partial pressure = 46.85		
		Reaction temperature	650	750	CO_2 conversion (%)	Reaction temperature = 727°C	CH_4 conversion (%) = 74.85	[38]
		CO_2/CH_4 ratio	0.4	1	Syngas ratio	CO_2/CH_4 ratio = 0.6	CO_2 conversion (%) = 76.49	
							Syngas ratio = 0.97	

Table 1. Summary of literature on optimization of hydrogen and syngas production from catalytic reforming of CH_4 and CO_2 using RSM.

have significant effects on the responses since their p-values were <0.05. Optimum conditions of 60 W, 56.1 mL/min, 1.03, and 9.5% were obtained for the power discharged, total flow rate, CO_2/CH_4 molar ratio, and Ni-loading, respectively. These optimum conditions resulted in maximum values of 31.7%, 48.1%, 21.7%, 17.9%, and 7.9% of CO_2 conversion, CH_4 conversion, CO yield, H_2 yield, and fuel production efficiency, respectively. Similarly, for the Ni/SiO_2 catalyst, the effect of input variables such as reaction temperature and CH_4/CO_2 molar ratio on the CH_4 conversion, CO_2 conversion, H_2/CO ratio and carbon content were investigated using CCD [34]. Based on the ANOVA results, the factors investigated were observed to have a significant effect on the CH_4 conversion, CO_2 conversion, H_2/CO ratio and carbon content (p < 0.05). The optimum process conditions of 800°C and 2.125 were obtained for reaction temperature and CH_4/CO_2 molar ratio, respectively yielding maximum values of 79.6%, 84.2%, 0.4 and 51.1% for CH_4 conversion, CO_2 conversion, H_2/CO ratio and carbon content, respectively.

In addition to supported Ni catalysts, other Ni-containing bimetallic catalysts such as Ni–Co/MSN, and $Ni-Co/MgO-ZrO_2$ catalyst have been employed to study the effect of different process variables on their respective responses using CCD [30, 33]. The variables investigated include reaction temperature, CO_2/CH_4 ratio, GHSV, and O_2 concentration in the feed while the responses include CH_4 conversion and H_2 yield. The ANOVA results of the fittings of the experimental data obtained using both the Ni-Co/MSN, and $Ni-Co/MgO-ZrO_2$ catalysts showed that the input variables had significant influence on the responses. The reforming of CH_4 and CO_2 over the Ni-Co/MSN gave optimum conditions of 783°C, 3, and 38,726 mL g^{-1} h^{-1} for the reaction temperature, CO_2/CH_4 ratio, GHSV, respectively yielding maximum value 97% for the CH_4 conversion. Similarly, the reforming of CH_4 and CO_2 over the $Ni-Co/MgO-ZrO_2$ catalyst gave optimum conditions of 749°C, 3, 145,190 mL g^{-1} h^{-1}, and 7 mol% for the reaction temperature, CO_2/CH_4 ratio, GHSV O_2 concentration in the feed, respectively. Consequently, maximum values of 88% and 86% for CH_4 conversion and H_2 yield, respectively were obtained at the optimum conditions.

The optimization of hydrogen and syngas production from catalytic reforming of CH_4 and CO_2 over Sm_2O_3 and CeO_2 supported Co catalysts have been investigated using BBD [37, 38]. The BBD is more efficient and less costly compared to the three-factor design. This is because the BBD allows an effective estimate of the first and second-order coefficients of the mathematical model [22]. The effects of process factors such as reaction temperature, CH_4 partial pressure, CO_2 partial pressure, and CO_2/CH_4 ratio on H_2 yield, CO yield, CH_4 conversion, and CO_2 conversion were investigated using both Co/Sm_2O_3 and Co/CeO_2 catalysts. The p-value (<0.05) obtained from the ANOVA results of the study revealed that all the factors investigated significantly influence the responses. The reforming of CH_4 and CO_2 over the Co/Sm_2O_3 catalyst led to optimum conditions of 727°C, 47.9 kPa, 48.9 kPa for the reaction temperature, CH_4 partial pressure, and CO_2 partial pressure, respectively leading to the maximum values of 79.4% and 79% for H_2 yield, and CO yield respectively. Likewise, the reforming of CH_4 and CO_2 over the Co/CeO_2 catalyst resulted in optimum conditions of 727°C for the reaction temperature, 46.85 kPa for the CH_4 partial pressure, and 0.6 for the CO_2/CH_4 ratio. These optimum conditions resulted in maximum values of 74.85% for CH_4 conversion, 76.49% for CO_2 conversion and 0.97 for the syngas ratio. Besides Ni and Co-based catalysts, other catalysts such as Li/MgO, 15wt%Rh/MgO, $Fe/Mg/Al_2O_3$, and ZnO catalysts have been investigated

for optimization of hydrogen and syngas production from reforming of CH_4 and CO_2 [31, 32, 35, 36]. The ANOVA results obtained from these studies indicate that the all the factors investigated had significant effects on their responses.

5. Implications for further research

The overview of RSM approach to the optimization of hydrogen and syngas from reforming of CH_4 and CO_2 over different catalysts performed in this study has revealed that every reforming catalyst displayed a unique set of optimum conditions. This trend might be due to the temperature dependent nature of the reforming reaction and the unique physicochemical properties of each of the catalysts investigated. As a result, there is no consensus on unified optimum conditions for hydrogen and syngas production by catalytic reforming of CH_4 and CO_2. Moreover, the study also shows that only CCD and BBD has been employed for the optimization of the hydrogen and syngas production over the catalysts investigated. Hence, other forms of experimental design such as Doehlert design and Taguchi can further be explored for the optimization study and then compare with existing one in literature. Furthermore, none of the work reported in this study perform an initial screening of the variable. A school of thought has argued that screening of variable is only essential when using Plackett-Burman design. However, it is worthwhile investigating the effect of initial screening of the different variables that can potentially influence hydrogen and syngas production from reforming of CH_4 and CO_2. Moreover, to ensure reliability and accuracy, high fractional factorial design can be employed during the pre-screening stage. An efficient pre-screening of all possible factors that influence the production of hydrogen and syngas by dry methane reforming will enable the most significant factors to be obtained for subsequent optimization. A consensus can be arrived at using these significant factors for further optimization of the hydrogen and syngas production with different catalytic system.

Although, response surface design is usually carried out using continuous factors (factors whose values are fixed to investigate their relationship to a response), it will be worthy of investigation is research efforts can be geared towards response surface design using categorical factors since such factors have discrete settings with no specific order. This could help eliminating the discrepancy in the variations in the optimum conditions obtained using different catalytic system in the optimization reforming reactions.

6. Conclusion

There is a growing interest in the application of RSM for the optimization of chemical processes due to its numerous advantages over the traditional one-variable-a-time optimization techniques. Such advantages include the tendency to obtain a large aggregate of information from a small set of experimental runs and propensity to determine the effect of interaction between the variables on the process responses. In this overview, RSM as an optimization technique has been applied for optimization of catalytic reforming of CH_4 and CO_2 over few

catalytic systems mainly supported Ni and Co catalysts as well as their bi-metallic components. This study also affirms that the choice of the experimental design employed for the optimization process was limited to CCD and BBD. Despite that all the literature considered in this study reported the significant interactive effect of the input variables on their respective responses, there was, however, no consensus of the optimum conditions of all the catalysts investigated. Each of the catalysts was observed to yield a unique set of optimum conditions primarily due to the differences in their physicochemical properties. This study has revealed that there is dearth literature in the application of RSM to optimization of hydrogen and syngas production from the catalytic reforming of CH_4 and CO_2. Hence, it is therefore recommended that research efforts should be concentrated on investigating other RSM techniques besides BBD and CCD as well as considering using more catalytic system for the future optimization study.

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