ORIGINAL ARTICLE

Response surface methodology for optimization of dry oxidative reforming for hydrogen enrichment of biogas

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Abstract

The exploration of domestically available clean and renewable fuel is essential for the attainment of sustainable development goals. The hydrogen (H_2)-enriched biogas being renewable and clean can be a highly favorable fuel. In this study, the response surface optimization of dry oxidative reforming using a three-level, three-factor experimental design for hydrogen enrichment of biogas over the nickel-cobalt bimetallic catalyst was investigated. The Box-Behnken design of experimentation was employed to assess the interaction and discrete effect of reforming temperature and ratios of CH_4/CO_2 and O_2/CH_4. The effects of CH_4/CO_2 ratio (1–2) and O_2/CH_4 ratio (0.3–0.5) on catalytic activity were assessed in the temperature range of 700–800 °C. The conversion of both reactants (CH_4 and CO_2), yield of products (H_2 and CO), and ratio of products (H_2/CO ratio) were selected as responses for statistical study. The analysis of variance demonstrated that reforming temperature and O_2/CH_4 ratio have a statistically considerable impact on the H_2 enrichment of biogas by the virtue of higher endothermic nature of the reaction. Experimentally, the maximum H_2 enrichment of 44.04% was obtained at 800 °C with 1.5 and 0.5 CH_4/CO_2 and O_2/CH_4 ratio, respectively. However, from the statistical model, the optimum H_2 enrichment of 36.9% was obtained at 725.68 °C with CH_4/CO_2 and O_2/CH_4 ratios of 1.32 and 0.42, respectively. The close agreement between predicted and experimental data shows that the combination of response surface methodology and dry oxidative reforming could be an efficient approach for optimizing the H_2 enrichment of biogas and the generation of environment friendly fuel.

Keywords Biogas · Dry oxidative reforming · Optimization · RSM · Hydrogen

1 Introduction

The non-renewable nature of fossil fuels coupled with harmful gaseous emissions has created adverse impacts on the economies and environment [1]. The locally available sustainable and renewable energy sources could be very helpful in overcoming this issue. Biogas, being a renewable and cleaner source of energy, could be highly beneficial for mitigating the issues related to alternative fuels [2]. It is essentially a blend of methane (CH_4) and carbon dioxide (CO_2) containing trails of various gases like NH_3 (ammonia) and H_2S (hydrogen sulfide) and could be produced through a variety of locally available feedstock such a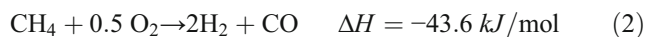s municipal solid waste (MSW), cow dung, and pig manure [3]. Its energy content mainly depends on CH_4 content, which makes it an interesting candidate for utilization in internal combustion engines. However, the presence of inert CO_2 acts as a coolant in the combustion chamber that reduces the efficiency of the engine [4]. Therefore, hydrogen (H_2) as an alternative renewable, sustainable, and cleaner fuel has gained significant attention in recent times. However, the utilization of pure H_2 in the internal combustion engines is retarded by the storage issue. In respect of this issue, hydrogen-enriched natural gas and biogas both could be used in the existing technologies [5]. The renewable nature and domestic availability of biogas support its utilization in transportation applications.

Hydrogen-enriched biogas can be efficiently produced through dry reforming reaction as it involves both methane (CH_4) and carbon dioxide (CO_2) [6–8]. However, issues related to economics and catalyst deactivation hinder its industrial applicability. To counter these hurdles, the combination of dry (Eq. 1) and partial oxidative reforming (Eq. 2) (dry oxidative reforming) could be very interesting as it will use

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the advantages of partial oxidative reforming to overcome the limitations of catalyst deactivation and higher temperature requirements [9–11]. Various researchers have shown the impact of oxygen (O_2) addition to dry reforming of methane or biogas reforming. The addition of O_2 results in the enhanced conversion of CH_4 coupled with a higher yield of H_2 [12]. Rosha et al. explored the dry oxidative reforming using pure nickel as a catalyst in the temperature range of 800–900 °C. They showed that CH_4 conversion and H_2 yield increased with increasing temperature and oxygen content; however, CO_2 conversion decreased with O_2 addition [13]. In their other study, Rosha et al. used Ni nanoparticles for combined reforming of synthetic biogas. It was demonstrated that the addition of oxygen ($O_2/CH_4 = 0.17$) at high temperature ($\geq$ 850 °C) resulted in 81% CH_4 conversion and 36% H_2 selectivity without coke deposition [14]. Moreover, Rosha et al. showed the effects of O_2/CH_4 ratio on CH_4 conversion and H_2/CO ratio at a temperature of 650 °C using nickel catalyst supported on the complex of zinc and ceria (CeO_2). They obtained 39.3% CH_4 conversion and H_2/CO ratio of 1.4 at O_2/CH_4 ratio of 0.57 [11].

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad\quad \Delta H = 247 \, kJ/mol \quad\quad (1)$$

$$CH_4 + 0.5 \, O_2 \rightarrow 2H_2 + CO \quad\quad \Delta H = -43.6 \, kJ/mol \quad\quad (2)$$

The nickel and cobalt-based catalyst have been extensively utilized in the reforming application due to their low cost and high activity. However, they suffer from the issue related to coke deposition and re-oxidation [15, 16]. The utilization of bimetallic catalysts using nickel and cobalt could be an effective method for overcoming these hurdles through the synergic effects of both the metals [17, 18]. It has been reported that bimetallic nickel-cobalt catalysts provide higher activity and stability when compared to single metal catalyst [19–22]. The catalytic activity can also be enhanced through optimizing process parameters by using various optimization or design of experiment (DoE) tools. DoE methods are more favored and accurate when compared to the single-factor method due to their higher efficiency and simultaneous study of various factors [23].

Response surface methodology (RSM) is one of these tools that have been reported for optimization in dry reforming applications [24–26]. RSM analyzes the interaction effect of various factors on the desired responses and predicts the suitable optimum conditions [27]. The Box-Behnken design requires a lesser number of experimental runs when compared to a normal factorial technique for generating a higher-order response surface [28]. This design method is considered when operating factors are greater than two and the optimum value is expected to lie within the selected range of parameters [29]. The literature review on this aspect indicates that optimization through RSM for H_2 enrichment over nickel-cobalt bimetallic catalyst has not been reported. The prospective study is

focused on finding the optimized conditions for the dry oxidative reforming of biogas using DoE. The three main reaction-related variables, reforming temperature, carbon dioxide to methane (CH_4/CO_2) ratio, and oxygen to methane (O_2/CH_4) ratio, were studied over a previously synthesized nickel-cobalt bimetallic catalyst for optimizing the hydrogen enrichment of biogas.

2 Materials and method

2.1 Materials

The nickel-cobalt bimetallic catalyst was synthesized through the wet-impregnation method. The synthesis procedure and characterization have been presented previously by us [19]. The ultrapure reactant gases methane (CH_4; 99.999%), carbon dioxide (CO_2; 99.999%), and oxygen (O_2; 99.999%) were acquired locally.

2.2 Experimental setup

The dry oxidative reforming of synthetic biogas using bimetallic catalyst was performed using a tube-type fixed-bed down-flow reactor under atmospheric pressure conditions. The details of the reforming reactor and reaction setup have been provided previously by us [19]. The reactions were performed under the temperature range of 700 to 800 °C at 1 bar with varying CH_4/CO_2 and O_2/CH_4 ratios. The catalyst (0.15 g) was kept between the two layers of quartz wool, and the required temperature was attained using inert N_2 gas with a heating rate of 10 °C/min. The product gases were then taken to the continuous biogas flow analyzer for analyzing the composition of product gases. The analyzer is capable of measuring the various gases (ranges) such as H_2 (0–100%), CO (0–100%), CH_4 (0–100%), and CO_2 (0–50%). The catalytic performance was evaluated by recording the data after 2 h of reaction time at fixed parameters. To ensure the consistency and reproducibility of the data, all the readings were recorded three times and their average values were considered for analysis. The catalytic performance parameters were evaluated using the following equations (Eqs. 3, 4, 5, and 6):

$$\text{Reactant conversion} \ (R, \%) = \frac{(R_{in} - R_{out})}{R_{in}} \times 100 \quad\quad (3)$$

$$H_2 \text{ yield} \ (\%) = \frac{H_{2(out)}}{2 \times CH_{4(in)}} \times 100 \quad\quad (4)$$

$$CO \text{ yield} \ (\%) = \frac{CO_{(out)}}{CH_{4(in)} + CO_{2(in)}} \times 100 \quad\quad (5)$$

$$\frac{H_2}{CO} \text{ ratio} = \frac{H_{2(out)}}{CO_{(out)}} \quad\quad (6)$$

Table 1 Experimental parameter matrix

Factor	Independent variable	Units	Minimum	Maximum	Coded low	Coded high
A	Temperature	°C	700.0	800.0	$-1 \leftrightarrow 700.0$	$+1 \leftrightarrow 800.0$
B	CH_4/CO_2 ratio		1.0	2.0	$-1 \leftrightarrow 1.0$	$+1 \leftrightarrow 2.0$
C	O_2/CH_4 ratio		0.3	0.5	$-1 \leftrightarrow 0.3$	$+1 \leftrightarrow 0.5$

where R represents reactants; R_{in}, inlet reactant flow rate; R_{out}, outlet reactant flow rate; $CH_{4\ (in)}$, inlet flow rate of methane; $H_{2\ (out)}$, outlet flow rate of hydrogen; and $CO_{(out)}$, outlet flow rate of carbon monoxide.

2.3 Design of experiment

The process parameter optimization for hydrogen enrichment of biogas was performed through the Box-Behnken factorial design method of response surface methodology (RSM) using Design-Expert (Version 12.0.12.0) software. A 17-run, three-factors, three-level, randomized design of Box-Behnken (BBD) was employed for interpreting the effects of distinct input variables on output. Three distinct variables, namely, (A) temperature of reforming, (B) the ratio of CH_4/CO_2, and (C) the ratio of O_2/CH_4, were investigated at three levels (-1, 0, and 1) for optimization study. The design matrix has been shown in Table 1. The conversion of both reactants (CH_4 and CO_2), yield of products (H_2 and CO), and ratio of products (H_2/CO) were selected as the response for evaluating the catalytic activity in dry oxidative reforming. For the statistical model, the p values less than 0.0500 indicate parameters have

a significant impact on the model; values greater than 0.1000 indicate the parameters are not significant.

After the experimentation, a polynomial equation of second order (Eq. 7) was used to evaluate the relationship between independent variables and responses. An analysis of variance (ANOVA) method at 95% confidence level was used to evaluate the data fitting.

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC$$
$$+ \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 \qquad (7)$$

where Y represents response predicted; β_0 represents offset constant; β_1, β_2, and β_3 represent the linear effect; β_{12}, β_{13}, and β_{23} represent the intersection effects; and β_{11}, β_{22}, and β_{33} represent squared coefficients.

3 Results and discussion

The impact of input parameters was evaluated for the hydrogen enrichment of biogas through dry oxidative reforming over bimetallic Ni-Co catalyst. The bimetallic catalysts have

Table 2 Experimental design and responses for RSM

	Factor 1	Factor 2	Factor 3	Response 1	Response 2	Response 3	Response 4	Response 5
Run	A:Temperature	B:CH_4/CO_2 ratio	C:O_2/CH_4 ratio	CH_4 conversion (%)	CO_2 conversion (%)	H_2 yield (%)	CO yield (%)	H_2/CO ratio
1	750	1	0.5	71.4	52.2	41.27	45.38	0.91
2	750	1	0.3	67.7	56.53	36.73	37.62	0.98
3	750	1.5	0.4	76.5	44.33	38.32	41.68	0.92
4	700	1	0.4	63.1	26.54	32.92	34.93	0.94
5	700	1.5	0.5	67.2	25.37	37.25	34.93	1.06
6	800	1	0.4	71.4	36.87	38.77	35.21	1.10
7	700	1.5	0.3	64.8	45.4	33.77	33.86	0.99
8	750	1.5	0.4	76.5	44.33	38.32	41.68	0.92
9	750	1.5	0.4	76.5	44.33	38.32	41.68	0.92
10	700	2	0.4	66.9	20.83	33.98	33.28	1.02
11	800	1.5	0.5	76.4	54.1	44.04	44.35	0.99
12	750	1.5	0.4	76.5	44.33	38.32	41.68	0.92
13	750	1.5	0.4	76.5	44.33	38.32	41.68	0.92
14	800	2	0.4	76.1	41.08	37.79	39.48	0.96
15	800	1.5	0.3	74.5	53.75	39.17	34.46	1.13
16	750	2	0.3	74.7	57.2	37.56	41.15	0.91
17	750	2	0.5	77.2	44.16	42.4	45.41	0.93

Fig. 1 3D plot of H$_2$ yield representing the interaction effects of **a** temperature and CH$_4$/CO$_2$ ratio, **b** temperature and O$_2$/CH$_4$ ratio, and **c** CH$_4$/CO$_2$ ratio and O$_2$/CH$_4$ ratio

(a)

(b)

(c)
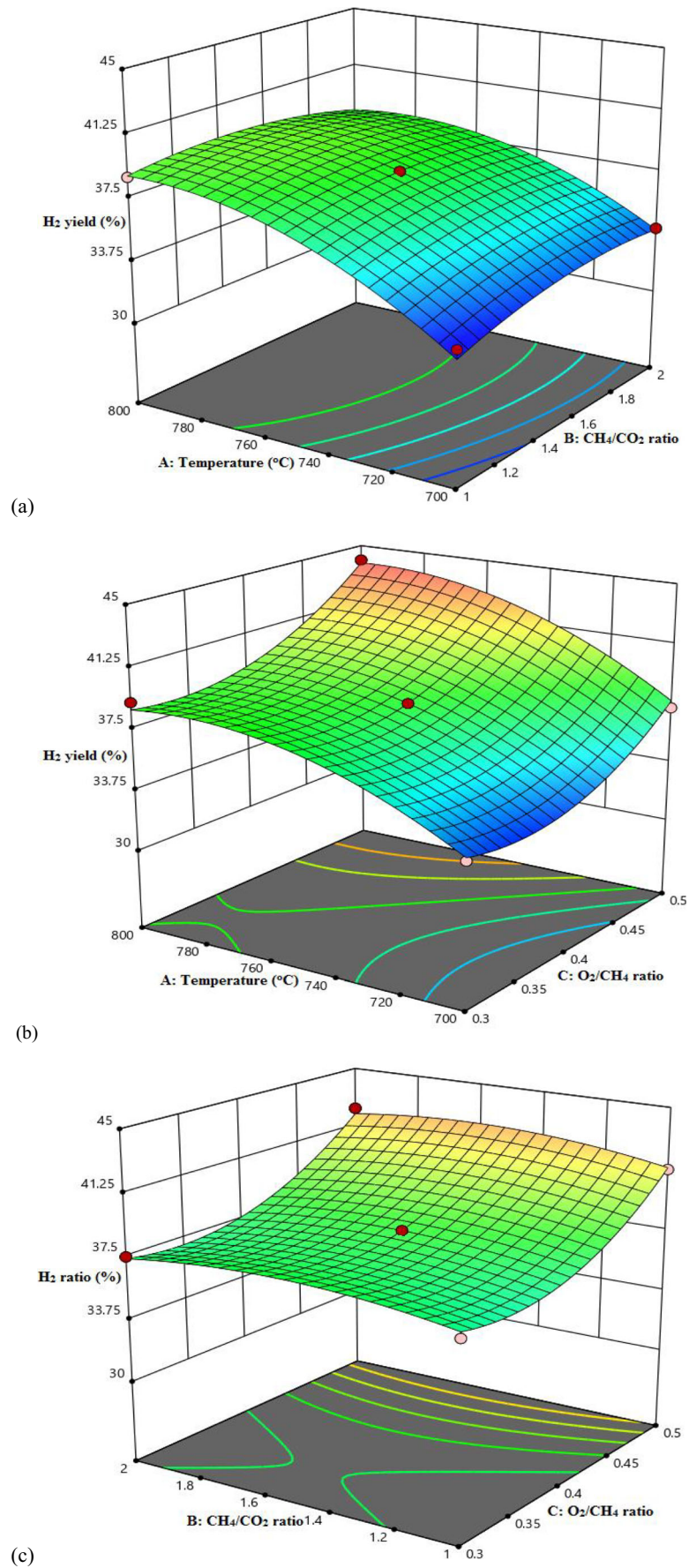
been reported to possess higher activity and stability when compared to mono-metallic catalyst due to the synergetic effect of constituent metals, higher reducibility, and strong metal-support interaction [19, 30]. The three major input parameters such as inlet temperature, CH_4/CO_2, and O_2/CH_4 ratios were selected for the optimization study. The inlet temperature (750–850 °C) was chosen due to the endothermic nature of the reforming reaction; the minimum temperature of 750 °C was selected to counter the side reactions. The CH_4/CO_2 ratio (1, 1.5, and 2) was adjusted to study the impact of different compositions of the biogas, and O_2/CH_4 ratio (0.3, 0.4, and 0.5) is essential for analyzing the extent of oxidative reforming and increase in hydrogen enrichment when compared to dry reforming only. A total of 17 experiments were performed for establishing the relation between independent input parameters and output responses. The five responses: CH_4 and CO_2 conversion, H_2 and CO yield, and H_2/CO ratio were selected for optimization study. The inlet experimental design and corresponding responses are presented in Table 2.

3.1 Effect of inlet parameters on dry oxidative reforming

The outcomes of experimentation show that H_2 enrichment increase with increasing all the input parameters in the dry oxidative reforming. The three-dimensional (3D) plot depicting the effects of inlet independent parameters (temperature and CH_4/CO_2 ratio; temperature and O_2/CH_4 ratio; CH_4/CO_2 and O_2/CH_4 ratio) on the yield of hydrogen are presented in Fig. 1. The synergetic interaction among parameters resulted in a significant change in response. Figure 1 a demonstrates the combined impact of temperature and CH_4/CO_2 ratio on H_2 enrichment. The H_2 yield was reported to increase with increasing both temperature and reactant (CH_4/CO_2) ratio and attained a maximum value of 44.04%. The increase in temperature is favorable for enhancing the rate of reforming reaction owning to its high endothermic nature. The maximum H_2 yield was obtained at 850 °C with 1.5 and 0.5 CH_4/CO_2 and O_2/CH_4 ratio, respectively. The increase in both inlet parameters also results in enhanced conversion of reactant and product yield; however, the temperature has a more pronounced effect when compared to reactant ratio as reforming reactions are more favorable at higher temperature regions. Mageed et al. (2020) reported similar findings that variation of reaction

temperature has a statistically significant impact on H_2 yield [26]. Nataj et al. (2018) also demonstrated a similar impact of temperature in their study over Ni-Cu bimetallic catalyst and reported that bimetallic catalyst has higher activity and stability when compared to mono-metallic catalyst [31]. Figure 1 b depicts the interaction impact of temperature and O_2/CH_4 ratio. The H_2 yield is significantly dependent on these parameters. The increases in O_2/CH_4 ratio resulted in increased H_2 yield and CH_4 conversion due to the synergetic effect of both partial oxidative and dry reforming. Similar trends of increasing CH_4 conversion and H_2 yield with increasing reaction temperature and O_2 proportion were reported by Rosha et al. (2018) [13]. Moreover, a drop in CO_2 conversion was reported with an increasing O_2/CH_4 ratio. The CH_4 reacts more favorably with oxygen (O_2) when compared to carbon dioxide (CO_2), and the presence of two oxidizing agent results in a higher conversion of CH_4. Figure 1 c demonstrates the interaction impacts of CH_4/CO_2 and O_2/CH_4 ratio. The impacts of O_2/CH_4 are more detrimental than CH_4/CO_2 ratio due to the higher reactivity between CH_4 and O_2. However, the yield of H_2 was improved by raising both the parameters. The highest H_2 yield of 44.04% was obtained at 850 °C with 1.5 and 0.5 CH_4/CO_2 and O_2/CH_4 ratio, respectively. The experimentation demonstrated that for dry oxidative reforming, the effective control of all discrete input parameters (temperature, CH_4/CO_2, and O_2/CH_4 ratio) is required for maximum H_2 enrichment of biogas. This model provided that optimum conditions for dry oxidative reforming are a temperature of 725.65 °C with 1.32 and 0.42, CH_4/CO_2, and O_2/CH_4 ratio, respectively. The optimum H_2 enrichment of 36.9% was attained under these reaction conditions.

3.2 Statistical analysis

Results obtained from experimentation were evaluated through BBD using statistical methods to establish a relationship between independent and dependent variables. The summary statistics of various models checked for data fitting has been shown in Table 3. The suitability of data fitting was determined by using standard deviation (SD), R^2, adjusted R^2, predicted R^2, and PRESS (predicted sum of square).

Table 3 shows that experimental values fit into the quadratic models with value of 0.44, 0.989, 0.976, 0.832, and 21.99 for SD, R^2, adjusted R^2, predicted R^2, and PRESS,

Table 3 Summary of statistics of various models

Source	Standard deviation	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	1.56	0.758	0.702	0.496	66.06	
2FI	1.74	0.770	0.632	− 0.171	153.69	
Quadratic	0.44	0.989	0.976	0.832	21.99	Suggested
Cubic	0.00	1.00	1.00			

Table 4 Sequential sum of squares

Source	Sum of squares	Degree of freedom	Mean square	F value	p value	
Mean vs. total	24,643.09	1	24,643.09			
Linear vs. mean	99.49	3	33.16	13.60	0.0003	
2FI vs. linear	1.55	3	0.5153	0.1709	0.9136	
Quadratic vs. 2FI	28.78	3	9.59	48.85	< 0.0001	Suggested
Cubic vs. quadratic	1.37	3	0.4582			
Residual	0.0000	4	0.0000			
Total	24,774.28	17	1457.31			

respectively. The high value of R^2 (0.989) shows the high proximity of input variables and response [26, 32]. The quadratic model infers that 98% fluctuations of responses are around their mean. Furthermore, current model is also satisfactory for forecasting H_2 yield as assigned through predicted R^2 value [25, 26]. This also implies that experimentally obtained values are in agreement with the predicted values. Additionally, the sequential model of sum of squares suggests that there is two-factor interaction between input variables and quadratic model. The p value of quadratic vs. 2FI is less than 0.0001 which demonstrates that both 2FI and quadratic models are statistically significantly (Table 4).

Table 5 shows the analysis of variance (ANOVA) of discrete as well as linked impacts of independent variable (temperature, and CH_4/CO_2 and O_2/CH_4 ratio). Based on ANOVA analysis, the reaction temperature and O_2/CH_4 ratio have more dominant effect on hydrogen production as depicted by the very low p value (< 0.0001). The reforming reaction and methane (CH_4) cracking reactions are responsible for H_2 production, and both reactions are favored at higher temperature.
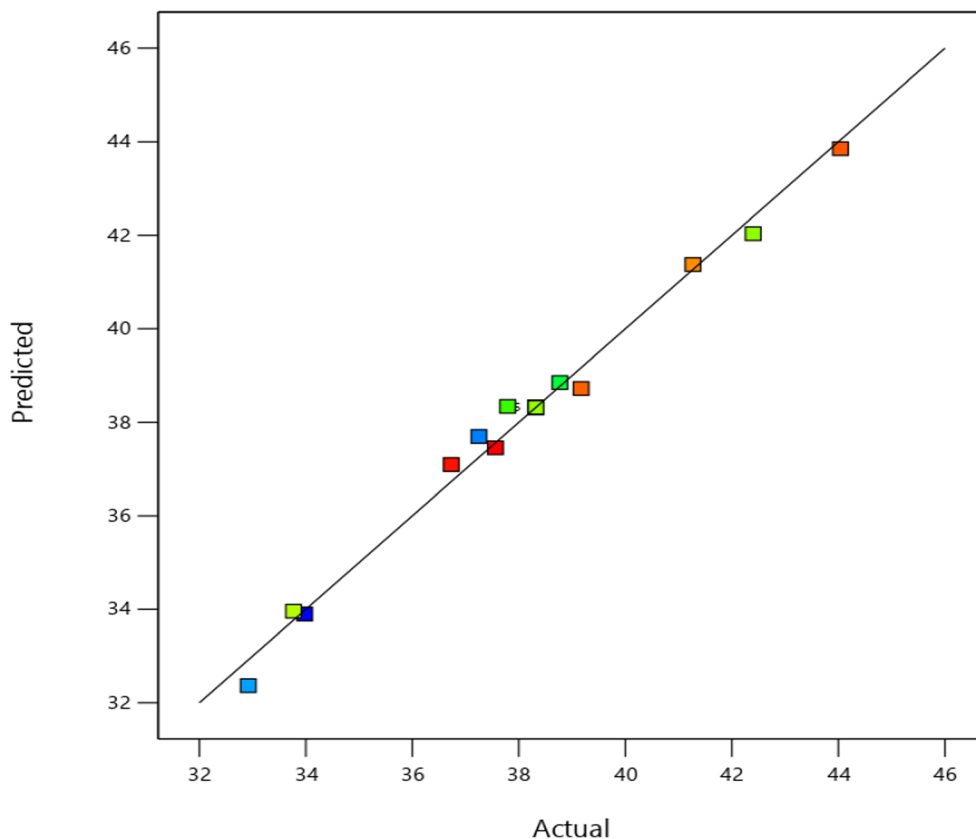
It is evident form ANOVA table that reactant ratio (CH_4/CO_2) is statistically insignificant of H_2 production demonstrated by the p value (0.1476) higher than 0.05. The CH_4/CO_2 ratio has substantial impact on the syngas or product ratio (H_2/CO). The interaction among inlet parameters, temperature and CH_4/CO_2 ratio, temperature and O_2/CH_4 ratio, and CH_4/CO_2 ratio and O_2/CH_4 ratio, is not statistically much significant as their p values are higher than 0.05. The quadratic effects of all distinct variables are statistically critical as their p values are less than 0.05 and these results can be seen in the Fig. 1. The complete analysis of RSM models shows that modes having very low p value (0.0001) have significant impact on the H_2 production with good data fitting.

The final expressions of quadratic model concerning coded and actual factors are represented in Eqs. 8 and 9, respectively. The positive value in the equation shows increases with corresponding parameters results in increased H_2 yield. It is evident form the equations that increasing both temperature and O_2/CH_4 ratio has dominant impact on H_2 yield as compared to CH_4/CO_2 ratio.

Table 5 Analysis of variance (ANOVA) of H_2 enrichment for quadratic model

Source	Sum of squares	Degree of freedom	Mean square	F value	p value	
Model	129.81	9	14.42	73.46	< 0.0001	Significant
A-Temperature	59.68	1	59.68	303.92	< 0.0001	
B-CH_4/CO_2 ratio	0.5202	1	0.5202	2.65	0.1476	
C-O_2/CH_4 ratio	39.29	1	39.29	200.11	< 0.0001	
AB	1.04	1	1.04	5.30	0.0548	
AC	0.4830	1	0.4830	2.46	0.1608	
BC	0.0225	1	0.0225	0.1146	0.7449	
A^2	12.08	1	12.08	61.51	0.0001	
B^2	2.44	1	2.44	12.43	0.0097	
C^2	15.70	1	15.70	79.98	< 0.0001	
Residual	1.37	7	0.1964			
Lack of fit	1.37	3	0.4582			
Pure error	0.0000	4	0.0000			

Fig. 2 Predicted and actual values for hydrogen yield

$$H_2 \text{ yield } (\%) = 38.32 + 2.73125A + 0.255B$$
$$+ 2.21625C - 0.51\,AB + 0.3475AC$$
$$+ 0.075BC - 1.69375A^2 - 0.76125B^2$$
$$+ 1.93125C^2$$

$$(8)$$

$$H_2 \text{ yield } (\%) = -370.524 + 1.07368A$$
$$+ 24.345B - 186.713C - 0.0204\,AB$$
$$+ 0.0695AC$$
$$+ 1.5BC - 0.0006775A^2 - 3.045B^2$$
$$+ 193.125C^2 \qquad\qquad (9)$$

For further testing the predictability of the model, the results of experimentation were fitted to predict the values of H_2 produced. The relationship of actual and predicted values of H_2 yield is shown in Fig. 2. The adjusted R^2 value is obtained by fitting of data demonstrated the goodness of empirical models. The addition of input parameters that have significant impact on the response results in the increased value of adjusted R^2 and vice versa. The adjusted R^2 value for H_2 yield is 0.976 which indicates that only 2.4% variations of model were not illustrated by input parameters.

4 Conclusion

In the present study, response surface methodology using Box-Behnken DoE was employed for evaluating the domination of input parameters and optimizing the process for H_2 enrichment of biogas over nickel-cobalt bimetallic catalyst. The Ni-Co/TiO$_2$ catalyst has been observed to demonstrate suitable catalytic properties for the dry oxidative reforming of synthetic biogas. The following conclusions were drawn from the study:

1. The experimental data obtained from BBD showed that all inlet parameters have a predominant effect on H_2 yield under dry oxidative reforming. Moreover, reforming temperature and O_2/CH_4 ratio have a statistically significant impact on reforming reaction as shown by p value ($p < 0.0001$).

2. The study manifested that maximum H_2 enrichment was obtained at 800 °C along 1.5 and 0.5 CH_4/CO_2 and O_2/CH_4 ratio, respectively. The maximum product ratio (H_2/CO) was obtained at 800 °C with 1.5 and 0.3 CH_4/CO_2 ratio and O_2/CH_4 ratio, respectively.

3. The statistical model predicted that a temperature of 725.68 °C with ratios of 1.32 and 0.42 CH_4/CO_2 and O_2/CH_4, respectively, are the optimum conditions for the dry oxidative reforming. The optimum H_2 enrichment of 36.9% and product (H_2/CO) ratio of 0.93 was obtained under optimum conditions.

4. The experimentation also demonstrated that CH_4 conversion and H_2 yield escalated with increasing temperature and O_2/CH_4 ratio due to the endothermic nature of reforming reaction and the presence of two oxidative agents (O_2 and CO_2). However, the conversion of CO_2 was found to decline with escalating O_2/CH_4 ratio due to higher affinity of CH_4 towards O_2 when compared to CO_2 and manifestation of RWGS (reverse water gas shift reaction).

5. The study ascertained that RSM and BBD statistical experimental design give statistically significant results as well as optimum conditions for improved catalytic performance as evident from the close agreement of predicted and experimental data.

References

1. Verma S, Das LM, Kaushik SC (2017) Effects of varying composition of biogas on performance and emission characteristics of compression ignition engine using exergy analysis. Energy Convers Manag 138:346–359. https://doi.org/10.1016/j.enconman.2017.01.066

2. Jindal M, Rosha P, Mahla SK, Dhir A (2015) Experimental investigation of performance and emissions characteristics of waste cooking oil biodiesel and n-butanol blends in a compression ignition engine. RSC Adv 5:33863–33868. https://doi.org/10.1039/c4ra14431g

3. Rosha P, Dhir A, Mohapatra SK (2018) Influence of gaseous fuel induction on the various engine characteristics of a dual fuel compression ignition engine: a review. Renew Sust Energ Rev 82:3333–3349. https://doi.org/10.1016/j.rser.2017.10.055

4. Das S, Kashyap D, Kalita P, et al (2020) Clean gaseous fuel application in diesel engine: a sustainable option for rural electrification in India. Renew. Sustain. Energy Rev.

5. Rosha P, Ibrahim H, Nanda AK, et al (2020) Effect of hydrogen-enriched biogas induction on combustion, performance, and emission characteristics of dual-fuel compression ignition engine. Asia-Pacific J Chem Eng 1–10. https://doi.org/10.1002/apj.2435

6. Singh R, Dhir A, Mohapatra SK, Mahla SK (2019) Dry reforming of methane using various catalysts in the process: review. Biomass Convers. Biorefinery

7. Usman M, Wan Daud WMA (2016) An investigation on the influence of catalyst composition, calcination and reduction temperatures on Ni/MgO catalyst for dry reforming of methane. RSC Adv 6:91603–91616. https://doi.org/10.1039/c6ra15256b

8. Usman M, Wan Daud WMA, Abbas HF (2015) Dry reforming of methane: influence of process parameters - a review. Renew Sust Energ Rev 45:710–744

9. Chen L, Zhu Q, Wu R (2011) Effect of Co-Ni ratio on the activity and stability of Co-Ni bimetallic aerogel catalyst for methane Oxy-CO2 reforming. Int J Hydrog Energy 36:2128–2136. https://doi.org/10.1016/j.ijhydene.2010.11.042

10. Lau CS, Tsolakis A, Wyszynski ML (2011) Biogas upgrade to syngas (H2-CO) via dry and oxidative reforming. Int J Hydrog Energy 36:397–404. https://doi.org/10.1016/j.ijhydene.2010.09.086

11. Rosha P, Mohapatra SK, Mahla SK, Dhir A (2019) Catalytic reforming of synthetic biogas for hydrogen enrichment over Ni supported on ZnO[sbnd]CeO2 mixed catalyst. Biomass

12. Rosha P, Mohapatra SK, Mahla SK, Dhir A (2018) Biogas reforming for hydrogen enrichment by ceria decorated over nickel catalyst supported on titania and alumina. Int J Hydrog Energy 43:21246–21255. https://doi.org/10.1016/j.ijhydene.2018.09.187

13. Rosha P, Singh R, Mohapatra SK, Mahla SK, Dhir A (2018) Optimization of hydrogen-enriched biogas by dry oxidative reforming with nickel nanopowder using response surface methodology. Energy and Fuels 32:6995–7001. https://doi.org/10.1021/acs.energyfuels.8b00819

14. Rosha P, Mohapatra SK, Mahla SK, Dhir A (2019) Hydrogen enrichment of biogas via dry and autothermal-dry reforming with pure nickel (Ni) nanoparticle. Energy 172:733–739. https://doi.org/10.1016/j.energy.2019.02.006

15. Alves HJ, Bley Junior C, Niklevicz RR, et al (2013) Overview of hydrogen production technologies from biogas and the applications in fuel cells. In: International Journal of Hydrogen Energy. pp. 5215–5225

16. Abdullah B, Abd Ghani NA, Vo DVN (2017) Recent advances in dry reforming of methane over Ni-based catalysts. J Clean Prod 162:170–185

17. San-José-Alonso D, Juan-Juan J, Illán-Gómez MJ, Román-Martínez MC (2009) Ni, Co and bimetallic Ni-Co catalysts for the dry reforming of methane. Appl Catal A Gen 371:54–59. https://doi.org/10.1016/j.apcata.2009.09.026

18. Xu J, Zhou W, Li Z, Wang J, Ma J (2010) Biogas reforming for hydrogen production over a Ni-Co bimetallic catalyst: effect of operating conditions. Int J Hydrog Energy 35:13013–13020. https://doi.org/10.1016/j.ijhydene.2010.04.075

19. Sharma H, Dhir A (2020) Hydrogen augmentation of biogas through dry reforming over bimetallic nickel-cobalt catalysts supported on titania. Fuel 279:118389. https://doi.org/10.1016/j.fuel.2020.118389

20. Takanabe K, Nagaoka K, Nariai K, Aika KI (2005) Titania-supported cobalt and nickel bimetallic catalysts for carbon dioxide reforming of methane. J Catal 232:268–275. https://doi.org/10.1016/j.jcat.2005.03.011

21. Takanabe K, Nagaoka K, Aika KI (2005) Improved resistance against coke deposition of titania supported cobalt and nickel bimetallic catalysts for carbon dioxide reforming of methane. Catal Letters 102:153–157. https://doi.org/10.1007/s10562-005-5848-4

22. Xu J, Zhou W, Li Z, Wang J, Ma J (2009) Biogas reforming for hydrogen production over nickel and cobalt bimetallic catalysts. Int J Hydrog Energy 34:6646–6654. https://doi.org/10.1016/j.ijhydene.2009.06.038

23. Ayodele B V., Abdullah S (2018) An overview of response surface methodology approach to optimization of hydrogen and syngas production by catalytic reforming of greenhouse gases (CH4 and CO2). In: Statistical Approaches With Emphasis on Design of Experiments Applied to Chemical Processes

24. Braga TP, Santos RCR, Sales BMC, da Silva BR, Pinheiro AN, Leite ER, Valentini A (2014) CO2 mitigation by carbon nanotube formation during dry reforming of methane analyzed by factorial design combined with response surface methodology. Cuihua Xuebao/Chinese J Catal 35:514–523. https://doi.org/10.1016/s1872-2067(14)60018-8

25. Fan MS, Abdullah AZ, Bhatia S (2011) Hydrogen production from carbon dioxide reforming of methane over Ni-Co/MgO-ZrO2 catalyst: process optimization. Int J Hydrog Energy 36:4875–4886. https://doi.org/10.1016/j.ijhydene.2011.01.064

26. Mageed AK, Ayodele BV, Mustapa SI (2020) Response surface optimization of hydrogen-rich syngas production by greenhouse gases reforming. Chem Eng Technol 43:742–751. https://doi.org/10.1002/ceat.201900475

27. Ayodele BV, Khan MR, Nooruddin SS, Cheng CK (2017) Modelling and optimization of syngas production by methane dry reforming over samarium oxide supported cobalt catalyst: response surface methodology and artificial neural networks approach. Clean Techn Environ Policy 19:1181–1193. https://doi.org/10.1007/s10098-016-1318-5

28. Rao JS, Kumar B (2012) 3D blade root shape optimization. In: institution of mechanical engineers - 10th international conference on vibrations in rotating machinery

29. Das AK, Dewanjee S (2018) Optimization of extraction using mathematical models and computation. In: Computational Phytochemistry

30. Turap Y, Wang I, Fu T, Wu Y, Wang Y, Wang W (2020) Co–Ni alloy supported on CeO2 as a bimetallic catalyst for dry reforming of methane. Int J Hydrog Energy 45:6538–6548. https://doi.org/10.1016/j.ijhydene.2019.12.223

31. Nataj SMM, Alavi SM, Mazloom G (2018) Modeling and optimization of methane dry reforming over Ni–Cu/Al2O3 catalyst using Box–Behnken design. J Energy Chem 27:1475–1488. https://doi.org/10.1016/j.jechem.2017.10.002

32. Roshan N, Ghader S, Rahimpour MR (2018) Application of the response surface methodology for modeling demulsification of crude oil emulsion using a demulsifier. J Dispers Sci Technol 39:700–710. https://doi.org/10.1080/01932691.2017.1385480