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Optimisation of catalytic system for tar mitigation in biomass producer gas

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ABSTRACT

The producer gas from biomass gasification is an upcoming power-generating technique for meeting the power requirements of the rural society. The performance of the biomass gasifier can be raised by mitigating tar in producer gas. Tar is highly carcinogenic and tends to condense at room temperature, which results in blocking and fouling of the downstream equipment. In this research, nano-structured SiO_2-supported Ni pellets are used as catalysts to reduce the tar content in producer gas from a biomass gasifier. Further, Cerium (Ce) and Praseodymium (Pr) are reinforced with Ni–SiO_2 pellets to improve the catalytic activity for tar mitigation. The Taguchi methodology is employed to rank and predict the optimal catalytic factor among the catalyst weight, gas feed rate (GF) and bed temperature (BT) for the tar cracking. The experimentation is done according to the L_9 design table and the mathematical model for tar concentration is developed with the adequacy (R^2) of 99.93%. The optimal catalytic system with 9 g of Pr, 0.01 l/s GF and 775°C of BT has reduced the tar concentration from 27 to 0.17 mg/Nm^3, i.e. the efficiency of tar mitigation achieved is around 99.3%.

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KEYWORDS
Taguchi; tar cracking; biomass gasifier; Ni-based catalysts

1. Introduction

Biomass gasification plays a vital role in generating off-grid green power in rural regions (Sreejith, Muraleedharan, and Arun 2013; Varshney, Bhagoria, and Mehta 2010). The biomass gasifiers are classified as downdraft, updraft and cross draft, which is based on the mode of fuel, air and gas flow. The crucial problem in biomass gasifiers is the formation of tar along with producer gas, since the tar is highly carcinogenic and creates significant environmental pollution (Vivanpatarakij, Rulerk, and Assabumrungrat 2014). In internal combustion engines, the maximum acceptable level of tar is less than 100 mg/m^3 as per norms of the pollution control board of India (Energy Statistics Report, Government of India 2015). The catalytic tar cracking method is the most effective method to reduce the tar in the producer gas. Therefore, the higher quality of producer gas can be achieved without any waste water or matter disposal (Yung, Jablonski, and Magrini-Bair 2009; Akia et al. 2014). Many researchers worked on the catalytic tar cracking problem and inferred that a Nickel (Ni)-based catalyst performs better in tar mitigation compared to other transition-metal-based catalysts (Shanmuganandam and Venkata Ramanan 2016). But still, the tar concentration in producer gas close to zero is not achieved as the tar formation is due to many factors such as gas flow rate, combustion zone (bed) temperature, catalyst content, feedstock size, etc. (Keche, Rao, and Tated 2015). Therefore, the requirement of high-performance optimal tar cracking system is raised to reduce the tar concentration.

In this current research work, Ce- and Pr-reinforced Ni-based catalysts are employed to improve the efficiency of the catalytic activity in tar mitigation. Further, the factors influencing tar formation in a downdraft gasifier and catalytic system are optimised using the Taguchi methodology.

2. Materials and methods

2.1. Synthesis of a nano-Ni-based catalyst

The silica gel is synthesised from condensation of tetraorthosilicates (TEOS), hydrochloric (HCl) acid and ethanol in the ratio 1:0.25:6, respectively, at 60°C for 1 h. The hydrated nickel nitrate (Ni $(NO_3)_2.6H_2O$) and silica are dissolved in deionised water in the mole fraction of 0.15:0.85. Further, cetyl trimethyl ammonium bromide (2.1×10^{-4} mol/l) is also dissolved and constantly stirred. After complete mixing, the possible absorbed ions and chemicals are removed. Then it is dried in a hot air oven at 120°C for 2 h at a heating rate of 10°C/min. Dried samples are calcined in a muffle furnace at 600°C for 6 h at a heating rate of 20°C/min. This process resulted in the formation of a Ni/SiO_2 nano-structured catalyst. The Ni $(NO_3)_2.6H_2O$ is replaced by cerium nitrate ($Ce(NO_3)_3.6H_2O$) and praseodymium nitrate ($Pr(NO_3)_3.6H_2O$) for obtaining Ni–Ce/SiO_2, and Ni–Pr/SiO_2 nano-catalyst. The obtained powders are pulverised and pelletised. The photographs of the Ni/SiO_2, Ni–Ce/SiO_2 and Ni–Pr/SiO_2 nano-catalyst pellets are shown in Figure 1(a–c), respectively.

Further, the catalyst pellets are analysed using High-Resolution Transmission Electron Microscopy (HR-TEM, Model: JOEL JEM 2100Plus) and formation of NiO, CeO_2, Pr_2O_3 and SiO_2 are evidenced (Figure 2). HR-TEM images show a spherical-like structure of nano-particles with a range of 10–20 nm in dia, which are self-assembled without agglomeration.

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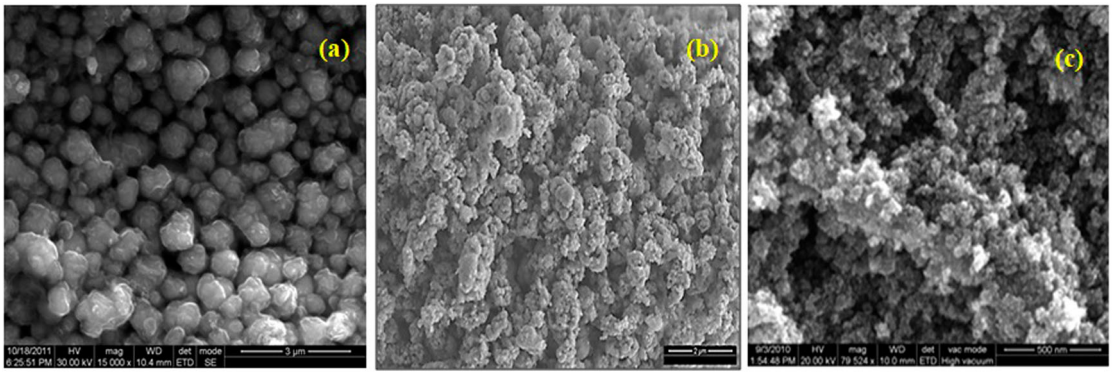

Figure 1. Photographs of synthesised nano-structured catalysts: (a) Ni/SiO_2; (b) $Ni–Ce/SiO_2$ and (c) $Ni–Pr/SiO_2$.

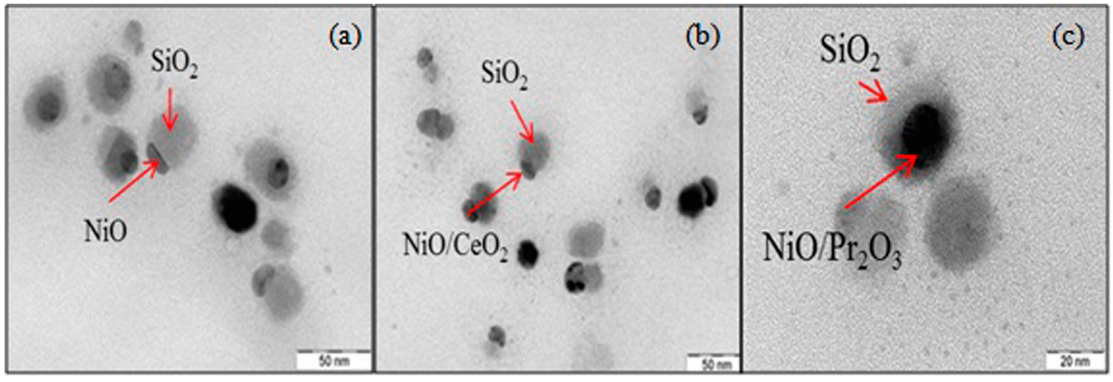

Figure 2. HR-TEM images of synthesised nano-structured catalysts: (a) Ni/SiO_2; (b) $Ni–Ce/SiO_2$ and (c) $Ni–Pr/SiO_2$.

2.2. Design of experimentation in the bio gasifier

The downdraft, dry bottom fixed bed gasifier and the catalytic tar cracking system are fabricated as shown in Figure 3.

Casuarina wood is used as the feedstock at the rate of 6 kg/h for 24 kg full-load capacity in the gasifier. The catalytic tar cracking unit is placed downstream of the gasifier. It consists of a guard bed containing 100 g of crushed dolomite ($CaMgCO_3$) stones and the main catalytic reactor containing synthesised nano-catalysts. Both the guard bed and main catalytic reactor are wound with electrical resistance heating coils to maintain the desired bed temperature. The tar content of producer gas is measured by the sampling unit as per the guidelines of the international protocol for measurement of organic contaminants in producer gas (CEN BT/TF 143, 2005).

The catalytic system is influenced by the catalyst, catalyst weight (CW), gas feed rate (GF) and bed temperature (BT) in optimising the tar concentration. Design of experimentation (DOE) is framed and optimised using the Taguchi methodology. The factors and their levels are tabulated in Table 1. Based on Table 1, the orthogonal (L_9) design table is selected and it is shown in Table 2.

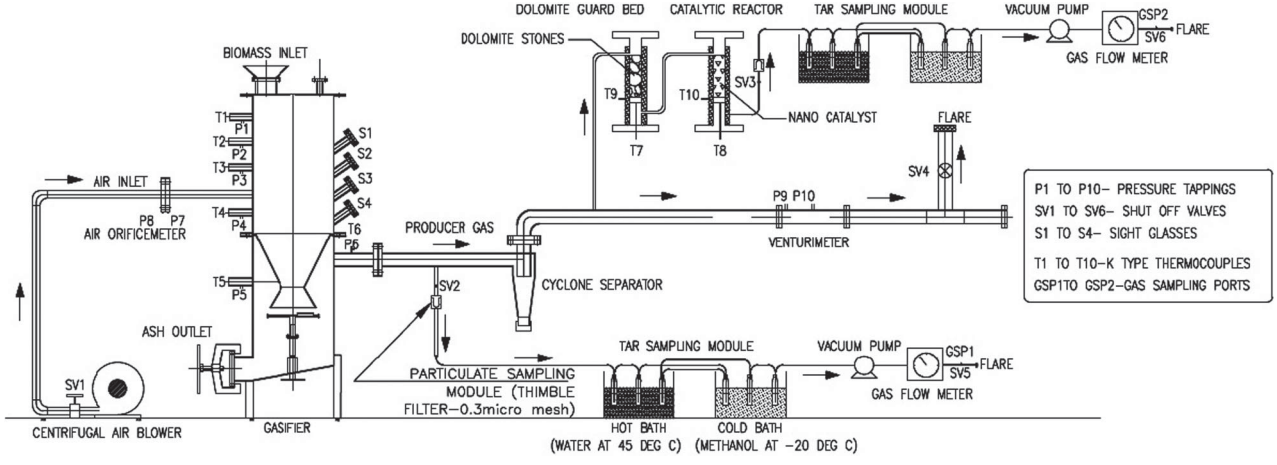

Figure 3. Schematic of the catalytic tar cracking system with the downdraft gasifier.

Table 1. Factors influencing the catalytic system.

Variable	Factor	Unit	Level		
			Low (−1)	Middle (0)	High (+1)
A	Catalyst (Ni/SiO_2)		Neat	Ce	Pr
B	Bed temperature (BT)	(°C)	700	775	850
C	Catalyst weight (CW)	(g)	3	6	9
D	Gas feed rate (GF)	(l/s)	0.01	0.02	0.03

Table 2. Statistical analysis of influencing factors as per the L_9 design table.

Run	Catalyst	BT	CW	GF	Catalyst	BT (°C)	CW (g)	GF (l/s)	Tar concentration (mg/Nm^3)
1.	1	1	1	1	Neat	700	3	0.01	0.628
2.	1	2	2	2	Neat	775	6	0.02	0.562
3.	1	3	3	3	Neat	850	9	0.03	0.488
4.	2	1	2	3	Ce	700	6	0.03	0.281
5.	2	2	3	1	Ce	775	9	0.01	0.205
6.	2	3	1	2	Ce	850	3	0.02	0.231
7.	3	1	3	2	Pr	700	9	0.02	0.242
8.	3	2	1	3	Pr	775	3	0.03	0.274
9.	3	3	2	1	Pr	850	6	0.01	0.174

3. Results and discussion

3.1. Statistical analysis on tar concentration

The statistical analysis of the catalytic system on tar concentration is done and tabulated in Table 2 as per the L_9 design table. The residuals of the run are plotted in Figure 4 to estimate the normality of the selected runs/trails. The normality plot falls on a linear trend, which reveals that the selected data are uniformly distributed with respect to the catalyst.

Based on the data plot, the mathematical models are developed for the Ni/SiO_2, $Ni–Ce/SiO_2$ and $Ni-Pr/SiO_2$ catalysts (Equations (1–3)). From the first-order equations, the regression models are derived with adequacy of 99.32% i.e. 99.93% of R^2 and 99.81% of R^2_{adj} values,

$$\text{Neat}_{\text{Tar Concentration}} = 1.0577 - 0.000573\ \text{BT} - 0.01100\ \text{CW} + 0.600\ \text{GF}, \quad (1)$$

$$\text{Ce}_{\text{Tar Concentration}} = 0.7373 - 0.000573\ \text{BT} - 0.01100\ \text{CW} + 0.600\ \text{GF}, \quad (2)$$

$$\text{Pr}_{\text{Tar Concentration}} = 0.7283 - 0.000573\ \text{BT} - 0.01100\ \text{CW} + 0.600\ \text{GF}. \quad (3)$$

Analysis of variance (ANOVA) is carried out and tabulated in Table 3 for the data. It evidences the level of contribution

Table 3. Analysis of variance.

Source	DF	Adj SS	Adj MS	*F*-value	*P*-value	Contribution (%)
Regression	5	0.228999	0.045800	824.40	0.000	
BT	1	0.011094	0.011094	199.69	0.001	4.84
CW	1	0.006534	0.006534	117.61	0.002	2.85
GF	1	0.000216	0.000216	3.89	0.0143	0.09
Catalyst	2	0.211155	0.105577	1900.39	0.000	92.21
Error	3	0.000167	0.000056			
Total	8	0.229166				

Table 4. Response for SN ratio.

Level	Catalyst	BT	CW	GF
1	5.093	9.130	9.338	10.998
2	12.506	10.005	10.407	10.019
3	12.919	11.383	10.773	9.501
Delta	7.827	2.253	1.436	1.497
Rank	1	2	4	3

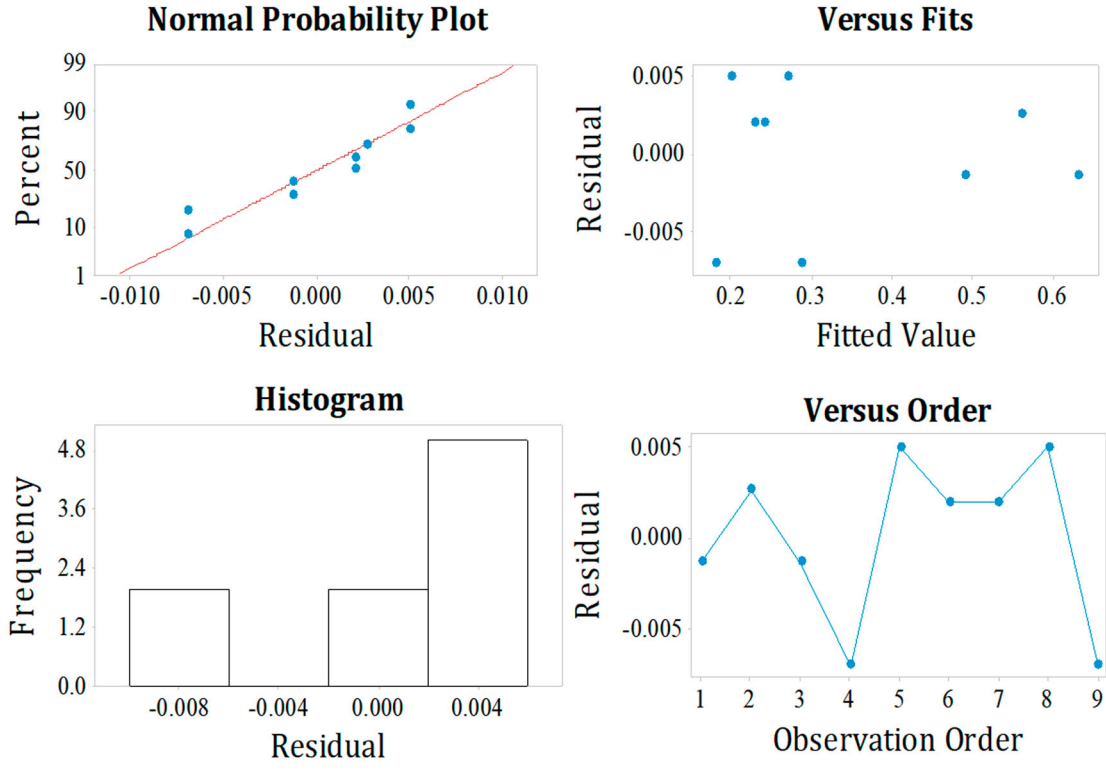

Figure 4. Residual plots on tar concentration.

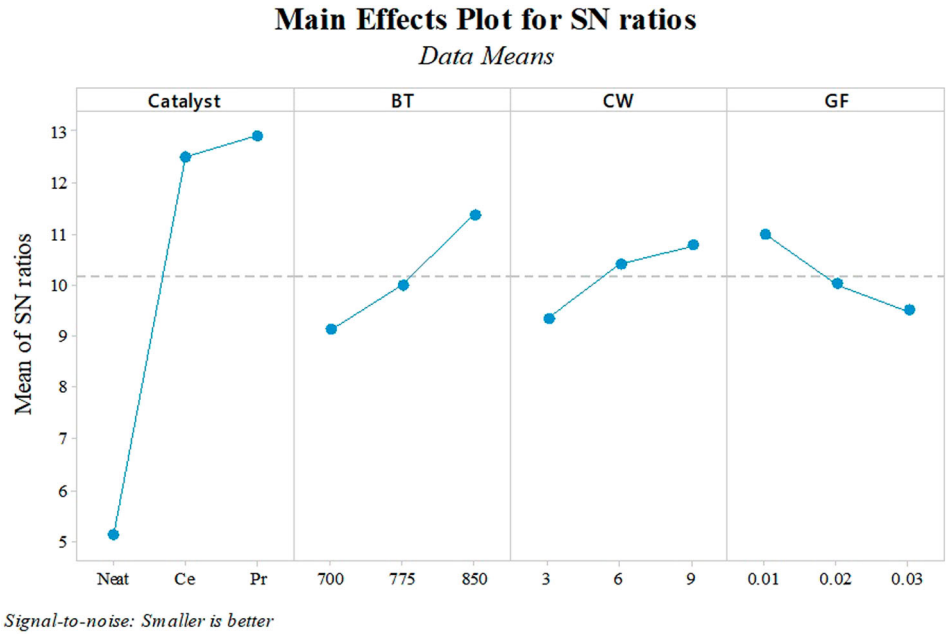

Figure 5. Main effects plot for SN ratios.

and confidence of factors (Saravanan et al. 2015). The student trail error (*P*-value) is less than the *F*-value and also it is lesser than 0.05 (5%), which states that the level of confidence is 95%. The contribution of the categorical factor (catalyst) is the most predominant factor compared to other factors as its level of contribution is 92.21%.

Table 5. Response for mean.

Level	Catalyst	BT	CW	GF
1	0.5593	0.3837	0.3777	0.3357
2	0.2390	0.3470	0.3390	0.3450
3	0.2300	0.2977	0.3117	0.3477
Delta	0.3293	0.0860	0.0660	0.0120
Rank	1	2	3	4

3.2. Taguchi methodology for optimisation of the catalytic system

The Taguchi methodology works on the principle of ranking the influencing factors based on their levels and contribution towards the response (Baradeswaran, Elayaperumal, and Issac 2013). The major approaches to identify the contribution rate of the factors to response are mean and signal-to-noise ratio (SN ratio). The response table for signal-to-noise ratios is tabulated in Table 4 and graphically represented in Figure 5 considering the 'smaller is better' ideology.

Similarly, the response table for means is tabulated in Table 5 and graphically represented in Figure 6. Both the approaches state that the catalyst and bed temperature are the most

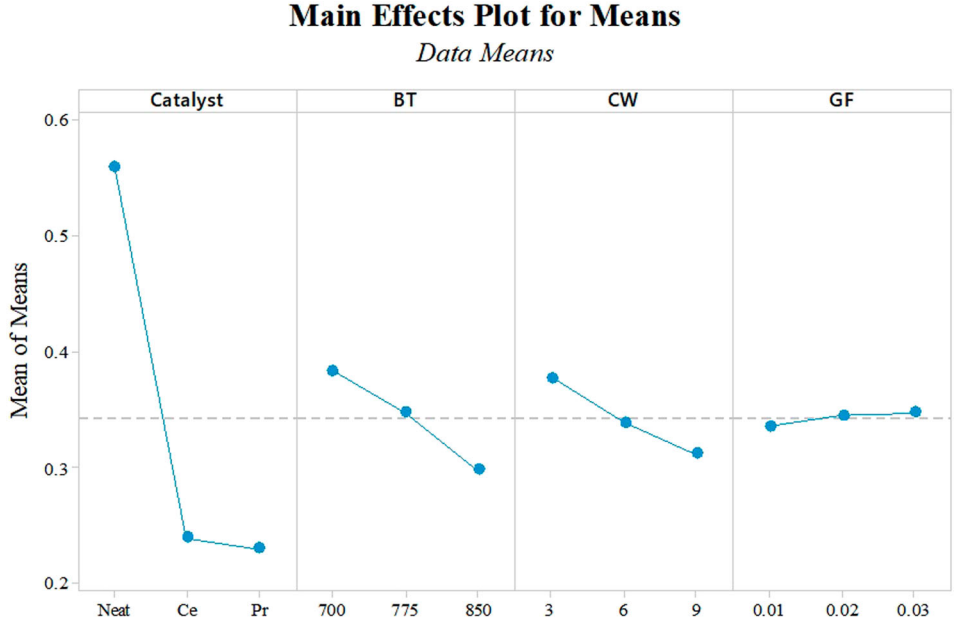

Figure 6. Main effects plot for means.

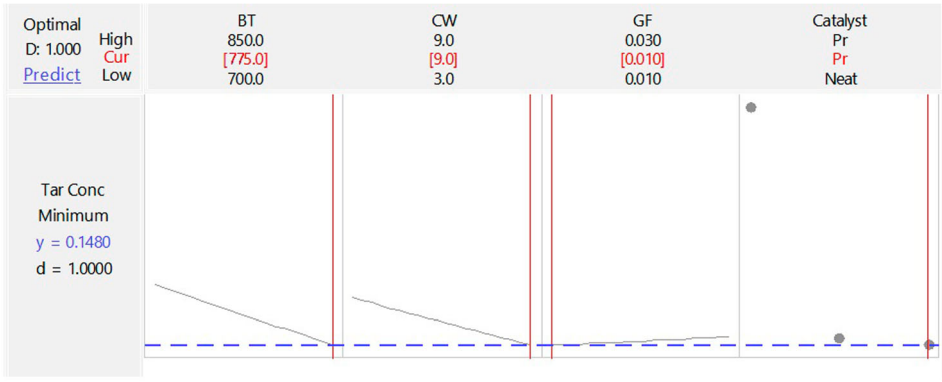

Figure 7. Optimal configuration of the catalyst system.

Table 6. Optimal configuration for catalyst.

Catalyst	Tar concentration (mg/Nm^3)	Tar mitigation efficiency (%)	Bed temperature (°C)	Catalyst amount (g)	Gas feed rate (l/s)
Ni/SiO_2	1.8	93	850	9	0.01
$Ni–Ce/SiO_2$	0.2	99.2	775	9	0.01
$Ni–Pr/SiO_2$	0.17	99.3	775	9	0.01

influencing factors on the response tar concentration. This result agrees with the ANOVA result. The other two factors, catalyst weight and gas feed rate, mutually contribute to a significant extent.

The optimal configuration of the catalyst system for the reducing the tar concentration is shown in Figure 7. The

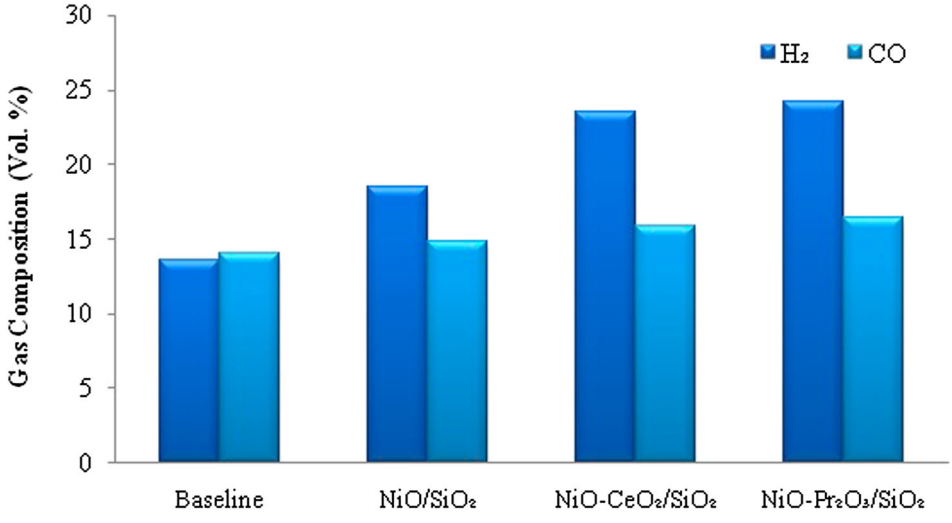

Figure 8. Gas compositions of producer gases.

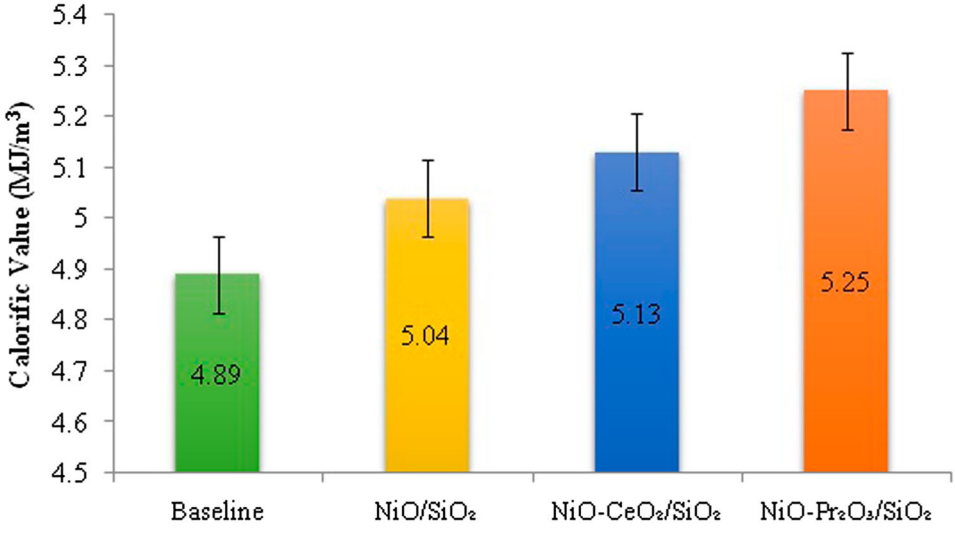

Figure 9. Calorific values of producer gases.

optimal configuration for tar reduction using Ni–Pr/SiO_2 of 9 g in 775°C of bed temperature with 0.01 l/s gas feed rate. These identified optimal factors are experimented and obtained the optimal tar concentration about 0.17 mg/Nm^3, which deviates about 5% from the computational result. Similarly, for other Ni/SiO_2 catalysts, values are tabulated in Table 6.

3.3. Emission and performance of the producer gas

The gas composition and the calorific value of the producer gas produced by the thermal method (baseline) and under optimal configuration are compared in Figures 8 and 9, respectively. The producer gas obtained using Ni–Pr/SiO_2 is better in all the discussed aspects compared to others.

4. Conclusion

The new Ni/SiO_2, Ni–Ce/SiO_2 and Ni–Pr/SiO_2 catalysts are synthesised and characterised using HR-TEM and its oxide spherical particle size is determined in the nano-range of 10–20 nm. The baseline study is done by the thermal method and the insignificant factors are fixed. Based on this analysis, the levels of significant influencing factors, design table and the optimisation methodology are framed. The regression models of tar concentration are derived with an adequacy of 99.32%, and the most predominant factor is the catalyst with a 92.21% level of contribution, which is inferred through ANOVA. The optimal configuration for tar reduction using Ni–Pr/SiO_2 of 9 g in 775°C of bed temperature with 0.01 l/s gas feed rate is identified by the Taguchi methodology. This configuration is experimented with and the obtained optimal tar concentration is 0.17 mg/Nm^3, which deviates about 5% from the computational result. The producer gas obtained using Ni–Pr/SiO_2 for the optimal configuration is better in emission and calorific values also when compared to others. This work can be further extended to the study of engines for the obtained producer gas with its diesel blends.

Disclosure statement

No potential conflict of interest was reported by the authors.

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