Journal of Natural Gas Science and Engineering 36 (2016) 540–549

Contents lists available at ScienceDirect

Journal of Natural Gas Science and Engineering

journal homepage: www.elsevier.com/locate/jngse

An industrial Steam Methane Reformer optimization using response surface methodology

Mojtaba Sinaei Nobandegani [a, b], Mohammad Reza Sardashti Birjandi [c], Tayebeh Darbandi [b, d], Mir Mohammad Khalilipour [c], Farhad Shahraki [c, *], Davod Mohebbi-Kalhori [c]

[a] Department of Chemical Engineering, International Campus, University of Sistan & Baluchestan, Chabahar, Iran
[b] Department of Chemistry, University of Eastern Finland, 111, FI80101 Joensuu, Finland
[c] Department of Chemical Engineering, University of Sistan and Baluchestan, Zahedan 98164, Iran
[d] Department of Chemical Engineering, Marvdasht Branch, Islamic Azad University, Marvdasht, Iran

ARTICLE INFO

Article history:
Received 17 June 2016
Received in revised form
19 September 2016
Accepted 21 October 2016
Available online 22 October 2016

Keywords:
Steam methane reforming
Multiobjective optimization
Response surface methodology
Hydrogen production

ABSTRACT

Steam methane reforming is an endothermic reaction which is considered as one of the main processes in hydrogen and syngas production. This process has been modelled and optimized in the present study using design of experiment and response surface methodology. The hydrogen production and unreacted methane mole fractions are considered as two responses. Temperature, pressure and flowrate of input feed, tube wall temperature, steam to methane ratio, and hydrogen to methane ratio in the input feed are considered as the independent factors, and their effects on the responses have been studied. Finally, the optimum values of independent factors and responses are reported. The average error was about 7%, which shows the presented model has an acceptable validity.

1. Introduction

Finding potential sources of energy has become an indispensable challenge recently. In last decades, increasing the environmental pollution and reduction in fossil-fuel sources compel researchers to look for an alternative environmental-friendly fuel source. As a solution for the mentioned problems, hydrogen can be introduced as a suitable alternative energy source. Plenitude of hydrogen with unlimited access, no pollution emission and a reversible productive process are some other major reasons, which have introduced the hydrogen as a proper energy source in recent explorations. If we accept hydrogen as a new energy source, it is necessary to identify its production processes. There are different procedures and chemical processes for producing hydrogen, namely coal gasification and biomass, water electrolysis, photoelectrolysis, photodissociation and biological operation. Among these various processes, hydrocarbon reforming is one of the most promising ones (Liu et al., 2010; Sørensen, 2011).

Steam methane reforming is one of the main processes in hydrogen production, which has been used since 1930 (Byrne et al., 1932; Van Hook, 1980; De Deken et al., 1982; Aparicio, 1997; Rostrup-Nielsen, 2000, 2004). SMR is an endothermic process in which methane reacts with steam in presence of a catalyst in the temperature and pressure ranges of 800–1000 °C and 5–35 bar, respectively (Rydén and Lyngfelt, 2006; Chen et al., 2008; Mbodji et al., 2012). The SMR process can be described by three main reactions (Xu and Froment, 1989):

Steam reforming of methane:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H_r = -2.061 \times 10^5 \frac{kj}{kmol} \tag{1}$$

Water gas shift:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H_r = +4.11 \times 10^4 \frac{kj}{kmol} \tag{2}$$

Reverse methanation:

Abbreviations: ANOVA, Analysis of Variance; CCD, Central Composite Design; DOE, Design of Experiment; RSM, Response Surface Methodology; SMR, Steam Methane Reforming.

* Corresponding author.
E-mail address: fshahraki@eng.usb.ac.ir (F. Shahraki).

http://dx.doi.org/10.1016/j.jngse.2016.10.031

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \Delta H_r = -1.65 \times 10^5 \frac{kj}{kmol} \tag{3}$$

Large number of studies have been done on the SMR kinetics, modelling, simulation and optimization. Fischer and Tropsch studied steam methane reforming process over different catalysts. They reported nickel and cobalt as the best catalysts for SMR process (Van Hook, 1980). De Dekens et al. evaluated the temperature range of 550–675 °C and pressure range of 5–15 bar, and suggested a kinetic mechanism for SMR process (De Deken et al., 1982). One of the most acceptable kinetic mechanisms for SMR process has been suggested by Xu and Froment. They studied the SMR process on Ni/$MgAl_2O_3$ catalyst, and derived an intrinsic rate equation for this process (Xu and Froment, 1989). Ochoa-Fernandez et al. prepared and used a nickel catalyst in a fixed bed reactor, which was further employed for simulation of hydrogen production by a dynamic one-dimensional pseudo-homogenous model (Ochoa-Fernandez et al., 2005). Simpson and Lutz analysed the exergy of hydrogen production in the steam methane reforming process. They used a chemical equilibrium model and investigated the operating parameters' influences on the system performance (Simpson and Lutz, 2007). Hajjaji et al. applied a factorial design of experiment method and studied the operating parameters on the process exergy efficiency (Hajjaji et al., 2010). Sinaei et al. optimized the SMR process by the Genetic Algorithm in steady-state condition (Sinaei Nobandegani et al., 2014). Jeon et al. optimized a counter-flow reactor configuration using response surface methodology (Jeon et al., 2014).

In classic methods, to investigate the parameters' effects in a process, the value of one independent parameter is varied, while the other parameters are kept constant. In other words, only one parameter is optimized each time. This strategy increases the number of experimental runs. The parameters' interactions on each other are also ignored in the conventional methods (Khayet and Cojocaru, 2012).

Response surface methodology (RSM) is one of the most popular methods in which the interactions between operating parameters can be assessed simultaneously. In RSM, it is possible to obtain more data by a lower number of experiments. Moreover, the optimum value of each parameter can be calculated in this method. Indeed, RSM is an experimental methodology which is constructed based on mathematics and statistics. It is used to generate a model, analyse the effects of operating parameters, and to optimize the process conditions. This method can be used in each process which has a measurable criterion of effectiveness on a continuous scale and quantifiable independent variables that affect the system performance. To make the parabolic effects evaluation possible, each parameter should have at least three levels. In the design and statistical evaluation of experiments, the RSM can be used for process modelling and optimization (Manohar, 2014; Krishnaiah et al., 2015; Aksoy and Sagol, 2016).

RSM can be studied by different methods. CCD is one of the most common methods for designing the experiments, and making a second-order response surface model in optimization of processes. Full factorial is another popular method in this field, but it produces a large number of experiments when the goal of study is the evaluation of a high number of parameters. In compared to full factorial, CCD provides more data by a lower number of experiments. In central composite design, fractional factorial design is combined with additional axial or start point and at least one central point in the experimental region. This axial point, α, causes the discrimination property in CCD methods (Aksoy and Sagol, 2016; Naik et al., 2005; Ferreira et al., 2007).

Accordingly, in the present study, RSM based on central composite design (CCD) was used to design experiments, build models and determine the optimum modification conditions for desirable responses.

As it was mentioned, some studies have been done on optimization of steam methane reforming process. However, published reports on optimization of SMR process with RSM and CCD is very rare, especially in industrial scale. In spite of previous studies (Riaz et al., 2011; Pantoleontos et al., 2012; Sadooghi and Rauch, 2013), the objective of our study is considering a large group of variables and two objective functions in response surface methodology optimization of steam methane reforming. Furthermore, effects of modification parameters (temperature, input feed temperature, input feed pressure, feed flowrate, steam to methane ratio in feed and hydrogen to methane ratio) to decrease the unreacted methane and increase the hydrogen production in the SMR process, in an Iranian refinery company, has been considered in the present study.

2. Design of experiments

In each experiment, there are some controllable independent variables, which are called factors, and the amount or magnitude of factors is called the level (Easton and McColl, 1997). Design of experiment represents an experimental point by combining the levels of factors. Different DOE methods use different arrangements of these experimental points (Safizadeh and Thornton, 1984). The DOE methods reduce the number and cost of experiments, provide more information and determine the interactions between variables simultaneously. Consequently, these methods have received much attention as a powerful tool in process simulation and optimization. The response surface methodology is a statistical method in design of experiment, which has been used for optimizing experiments and determining the interactions with a minimum number of experiments (Hajjaji et al., 2010; Vicente et al., 1998; Berrios et al., 2009; Shafeeyan et al., 2012). Response surface methodology is also a reliable analysis tool in investigation of chemical processes (Aksoy and Sagol, 2016; Shafeeyan et al., 2012; Can et al., 2006; Körbahti and Rauf, 2008).

The SMR process has been optimized using response surface methodology. In this line of work, the following steps have been done. Firstly, the process responses were obtained by designing and conducting a series of experiments. Secondly, a mathematical model has been developed with the best fittings. As the third step, the optimal values for the variables have been found (the values which cause the optimum value of both responses). Finally, the main effects of the process variables on the responses have been studied by 2D and 3D plots (Khayet and Cojocaru, 2012).

For RSM, the experimental data was fitted with a common second-order polynomial equation:

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ij} X_i X_j + \sum \beta_{ii} X_{ii}^2 \tag{4}$$

Where Y is the predicted response, β_0 is a constant, β_i is linear coefficient, β_{ii} is quadratic coefficient, and β_{ij} is interaction coefficient (Pooralhossini et al., 2017; Papaneophytou and Kyriakidis, 2012). The unreacted methane and hydrogen production are two objective functions in the optimization. The effects of the operating variables were also studied in the SMR process.

Fig. 1 shows a simple process flow diagram of the steam methane reforming, in which the most important operating parameters can be observed (Rajesh et al., 2001). Among these variables, tube wall temperature (X_1), input feed temperature (X_2), input feed pressure (X_3), input steam to methane ratio (X_4), hydrogen to methane ratio (X_5) and feed flowrate (X_6) have been considered in the present study. The coded and actual steam methane reforming process designed variables, which are used for

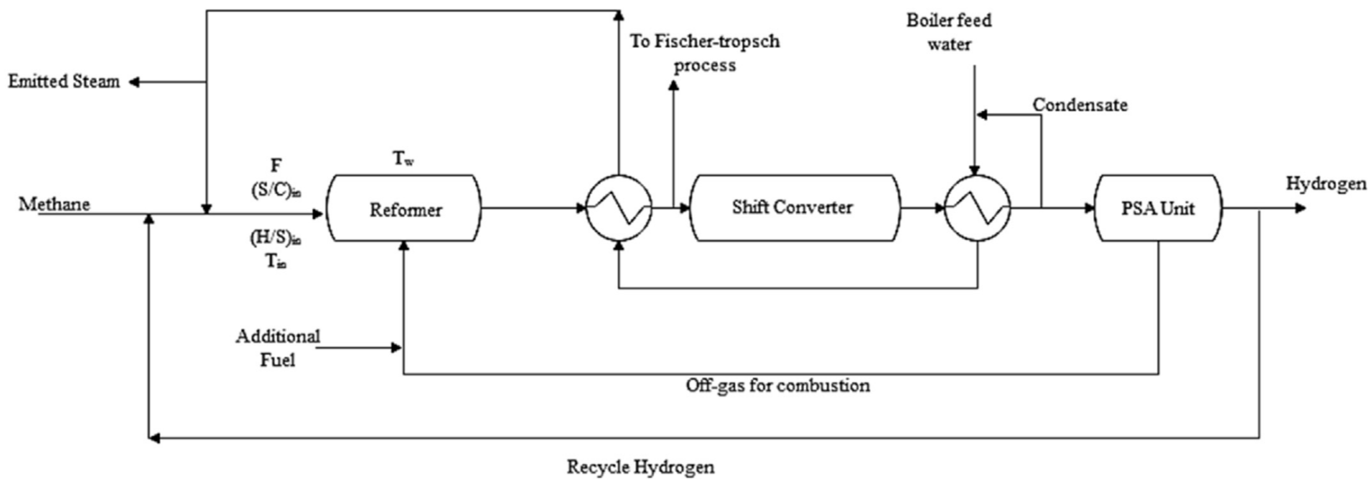

Fig. 1. Simplified process flow diagram for the steam methane reforming (Rajesh et al., 2001).

Table 1
Low and high values of operating variables in actual and codec forms.

Variable	Actual Values	Low Codec	High Codec	Variable Symbols
Tube Wall Temperature	$800\ k < T_w < 1100\ k$	−1	1	X_1
Input Feed Temperature	$650\ k < T_{in} < 815\ k$	−1	1	X_2
Input Feed Pressure	$23\ bar < P_{in} < 27\ bar$	−1	1	X_3
$(S/C)_{in}$	$3.15 < (S/C)_{in} < 7$	−1	1	X_4
$(H/C)_{in}$	$0.15 < (H/C)_{in} < 0.5$	−1	1	X_5
Feed Flowrate	2800 kmol/h < F < 9000 kmol/h.	−1	1	X_6

experimental design, can be seen in Table 1. All the experimental values which are used in this study were obtained from the Bandar Abbas Refinery Company, Iran (Sinaei Nobandegnai, 2014).

The DOE has been done by RSM method, and the best fitting was obtained for six variables (which were named as X_1 to X_6) with each at three levels. The studied ranges of operating variables in this article are those which are used in the Bandar Abbas Refinery Company, Iran. The DOE has been done using Design of Expert 7.0.0 software, with the quadratic design model. The value of α was taken as 1.57 in calculation of axial points, which was proposed by the software for orthogonal quadratic design.

3. Results and discussion

In this study, the central composite design (CCD) was employed. According to this method, a total of 86 runs have been done (10 central points, 64 factorial points, and 12 axial points). The first 10 runs have been reported in Table 2. The whole runs can be found in the appendix A. The identical runs, like run 7 and run 10, are replication of central points, which is needed to estimate the method error.

According to the experimental results which are reported in Table 2, and equation (4), the response surface models with codec variables have been written for both responses as:

$$H_2 = +0.35 + 0.098X_1 + 0.046X_2 - 0.042X_4 - 0.019X_6 - 0.023X_1X_2 - 0.021X_1X_4 - 0.033X_1X_6 - 6.887 \times 10^{-3}X_2X_4 + 0.033X_2X_6 - 0.037X_1^2 - 0.015X_2^2 - 0.018X_6^2 \quad (5)$$

$$CH_4 = +0.046 - 0.039X_1 - 0.018X_2 - 0.032X_4 + 5.361 \times 10^{-3}X_5 + 0.01X_6 + 8.109 \times 10^{-3}X_1X_2 + 0.012X_1X_4 + 0.017X_1X_6 + 4.591 \times 10^{-3}X_2X_4 - 0.013X_2X_6 - 3.363 \times 10^{-3}X_4X_6 + 0.014X_1^2 + 6.347 \times 10^{-3}X_2^2 + 9.348 \times 10^{-3}X_4^2 + 8.266 \times 10^{-3}X_6^2 \quad (6)$$

Table 2
The first 10 runs according to CCD in experiment design.

Run	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response 1	Response 2
	$A{:}T_w$	$B{:}T_{in}$	$C{:}P_{in}$	$D{:}(S/C)_{in}$	$E{:}(H/C)_{in}$	F:F	H_2	CH_4
1	950	732.5	25	5.08	0.05	5900	0.3480	0.0373
2	800	815.0	23	7.00	0.50	2800	0.1903	0.0737
3	800	815.0	27	3.15	0.15	9000	0.3748	0.0896
4	800	650.0	23	7.00	0.50	2800	0.1209	0.0966
5	800	650.0	27	3.15	0.50	9000	0.1067	0.2107
6	800	650.0	23	7.00	0.15	9000	0.0753	0.1041
7	950	732.5	25	5.08	0.33	5900	0.3489	0.0446
8	1100	650.0	27	7.00	0.50	2800	0.3550	0.0110
9	1100	650.0	23	3.15	0.50	9000	0.3220	0.1317
10	950	732.5	25	5.08	0.33	5900	0.3489	0.0446

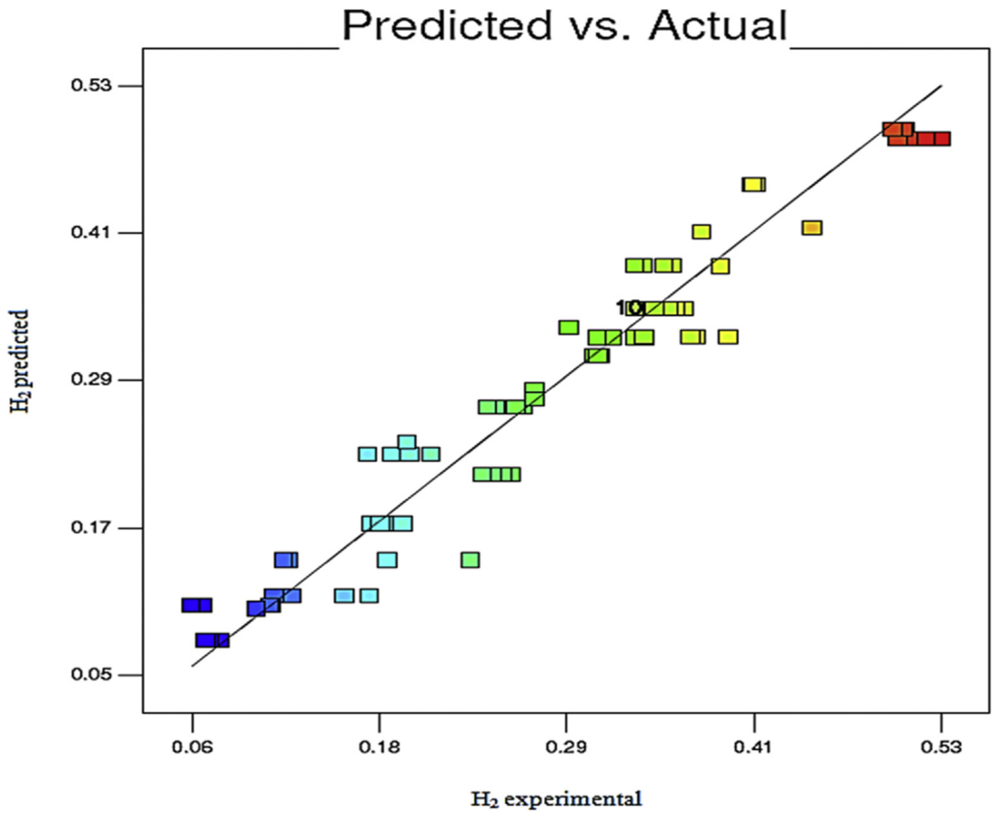

Fig. 2. Comparison between the experimental and the predicted SMR performance index (H_2) determined by the RSM model.

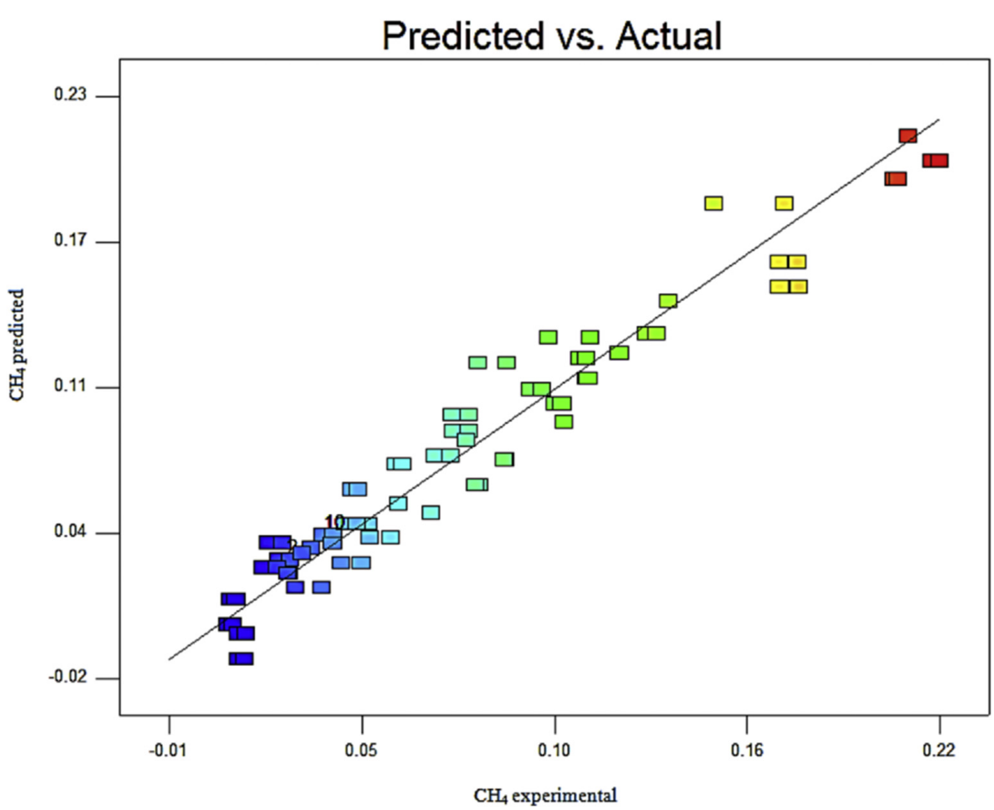

Fig. 3. Comparison between the experimental and the predicted SMR specific performance index (CH_4) determined by the RSM model.

Table 3
Analysis of variance (ANOVA) of the RSM model corresponding to the response: performance index (H_2).

Source	DF[a]	SS[b]	MS[c]	F-value	P-value	R^2	R^2_{adj}
Model	12	1.22	0.10	110.32	<0.0001	0.9477	0.9392
Residual	73	0.067	9.234e-004				
Total	85	1.29					

[a] Degree of freedom.
[b] Sum of squares.
[c] Mean square.

Table 4
Analysis of variance (ANOVA) of the RSM model corresponding to the response: performance index (CH_4).

Source	DF[a]	SS[b]	MS[c]	F-value	P-value	R^2	R^2_{adj}
Model	15	0.270	1.800e-002	91.14	<0.0001	0.9513	0.9409
Residual	70	0.014	1.981e-004				
Total	85	0.280					

[a] Degree of freedom.
[b] Sum of squares.
[c] Mean square.

These models can be written as a function of actual variables as follow:

$$H_2 = -4.927 + 5.944 \times 10^{-3} Z_1 + 5.038 \times 10^{-3} Z_2 + 0.078 Z_4 - 1.021 \times 10^{-5} Z_6 - 1.894 \times 10^{-6} Z_1 Z_2 - 7.117 \times 10^{-5} Z_1 Z_4 - 7.146 \times 10^{-8} Z_1 Z_6 - 4.33 \times 10^{-5} Z_2 Z_4 + 1.288 \times 10^{-7} Z_2 Z_6 - 1.642 \times 10^{-6} Z_1^2 - 2.202 \times 10^{-6} Z_2^2 - 1.884 \times 10^{-9} Z_6^2 \quad (7)$$

$$CH_4 = +2.402 - 2.348 \times 10^{-3} Z_1 - 2.059 \times 10^{-3} Z_2 - 0.100 Z_4 + 0.031 Z_5 - 2.220 Z_6 + 6.553 \times 10^{-7} Z_1 Z_2 + 4.157 \times 10^{-5} Z_1 Z_4 + 3.655 \times 10^{-8} Z_1 Z_6 + 2.891 \times 10^{-5} Z_2 Z_4 - 4.988 \times 10^{-8} Z_2 Z_6 - 5.635 \times 10^{-7} Z_4 Z_6 + 6.205 \times 10^{-7} Z_1^2 + 9.325 \times 10^{-7} Z_2^2 + 2.523 \times 10^{-3} Z_4^2 + 8.601 \times 10^{-10} Z_6^2 \quad (8)$$

As it was mentioned, X_1 to X_6 are tube wall temperature, input feed temperature, input feed pressure, input steam to methane ratio, hydrogen to methane ratio, and feed flowrate, respectively. As a result, it can be concluded that Eqns. (5) and (6) are the correlations between the objective functions of H_2 and CH_4 in form of codec variables, while Eqns. (7) and (8) show these correlations on the basis of actual variables.

Figs. 2 and 3 typically represent the results of a comparison between the values of the responses, which are determined by the regression equations, and the obtained experimental data. As it has been shown, the models have a good reliability in prediction of the experimental data.

To check the significance of the model coefficients, the analysis of variance (ANOVA) has been done. Tables 3 and 4 summarise the ANOVA results for both responses H_2 and CH_4, respectively. Among the reported values in these tables, the determination coefficient (R_2) is used for evaluation of the quality of the polynomial fitting, and the statically significance can be checked by the F-value. As it can be seen in Tables 3 and 4, the P-value is smaller than 0.0001, the F-values are so high, and the coefficient of multiple determinations (R^2) and the adjusted statistic coefficient (R^2_{adj}) are in agreement for both responses. According to the R^2 values, in Tables 3 and 4, the model explains 95% of the variability of these responses. As a result of data comparison (Figs. 2 and 3) and based on the statistical tests (Tables 3 and 4), the mentioned models can be considered as a reliable model for SMR simulation and optimization.

The effects of the tube wall temperature and input feed temperature on the hydrogen production have been illustrated in Fig. 4, both in 2 and 3-dimensional plots of the surfaces. As it can be observed in Fig. 4, the hydrogen production increased with an increase in the tube wall temperature. The input feed temperature has the same effect on the hydrogen production. This is because of the endothermic nature of the SMR process. Increasing the temperature provides more heat for the process, and leads the reactions to move forward, which results to more hydrogen production. This fact is in consistency with our previous study (Sinaei Nobandegani et al., 2014).

The tube wall temperature and input feed temperature have opposite effects on the unreacted methane, which is considered as the second response in optimization. As it is demonstrated in Fig. 5, the unreacted methane reduced by increasing both tube wall temperature, and input feed temperature. Increasing the heat

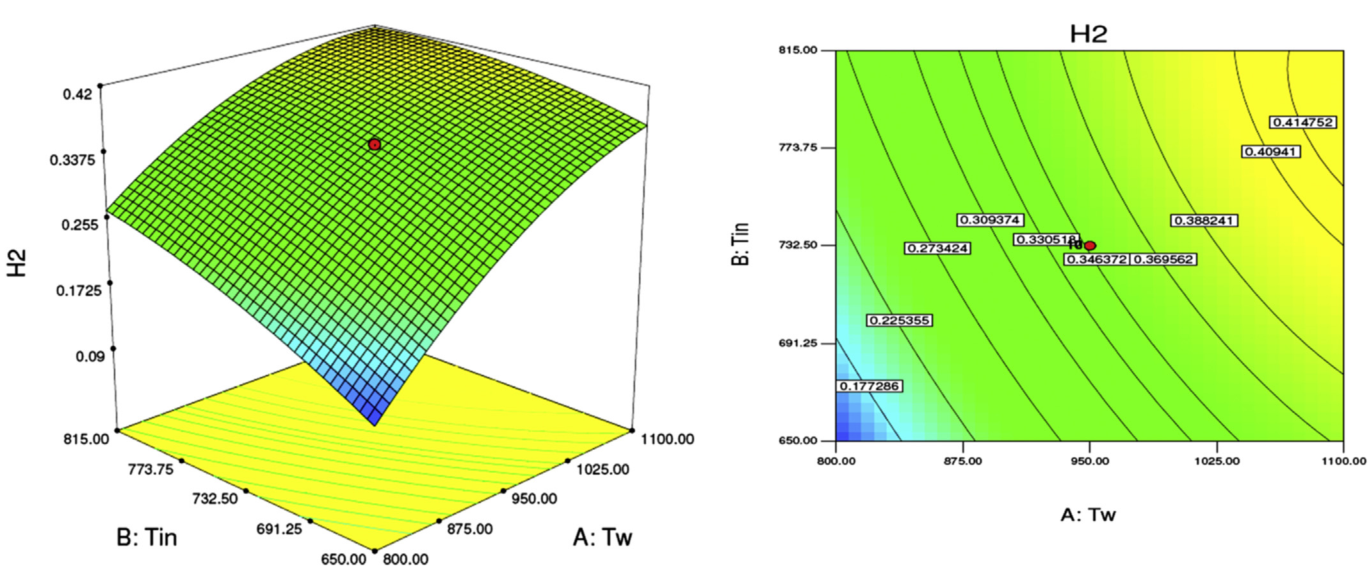

Fig. 4. Response surface plot and contour-lines showing the SMR performance index (H_2) as a function of T_{in} and T_w for P_{in} = 25.00; $(S/C)_{in}$ = 5.08; $(H/C)_{in}$ = 0.33; F = 5900.00.

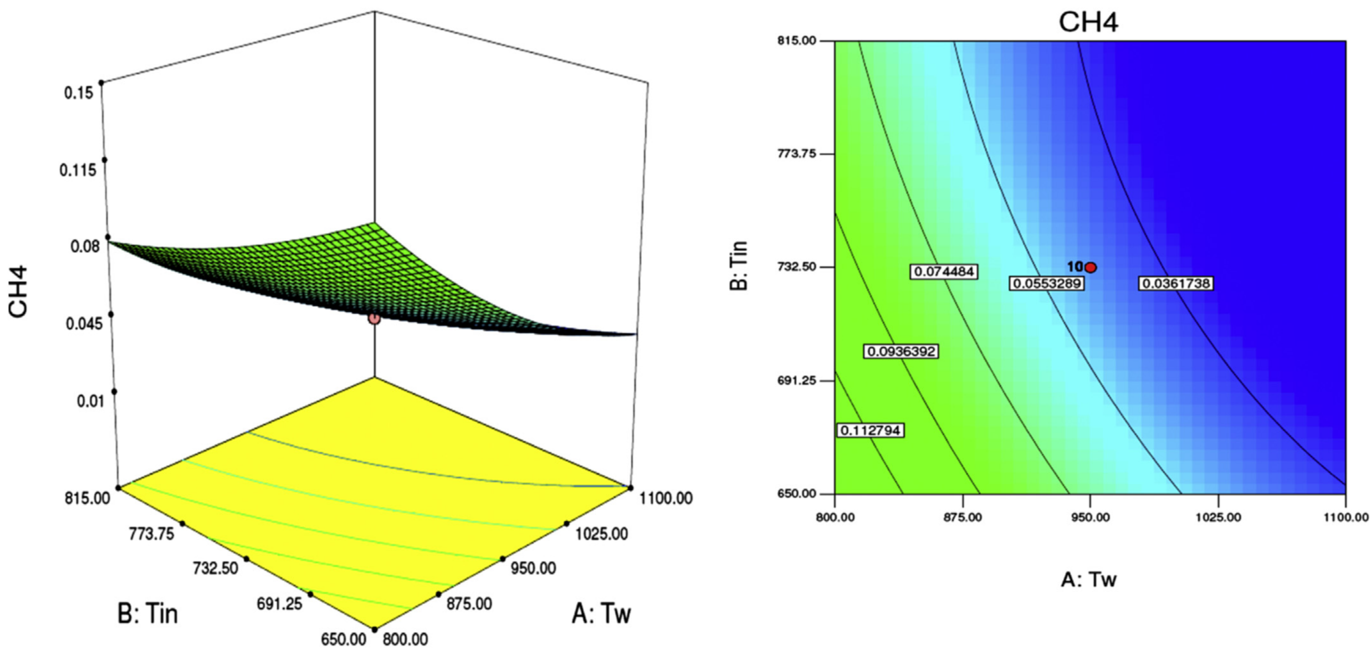

Fig. 5. Response surface plot and contour-lines showing the SMR performance index (CH_4) as a function of T_w and T_{in} for $P_{in} = 25.00$; $F = 5900.00$; $(H/C)_{in} = 0.33$; $(S/C)_{in} = 5.08$.

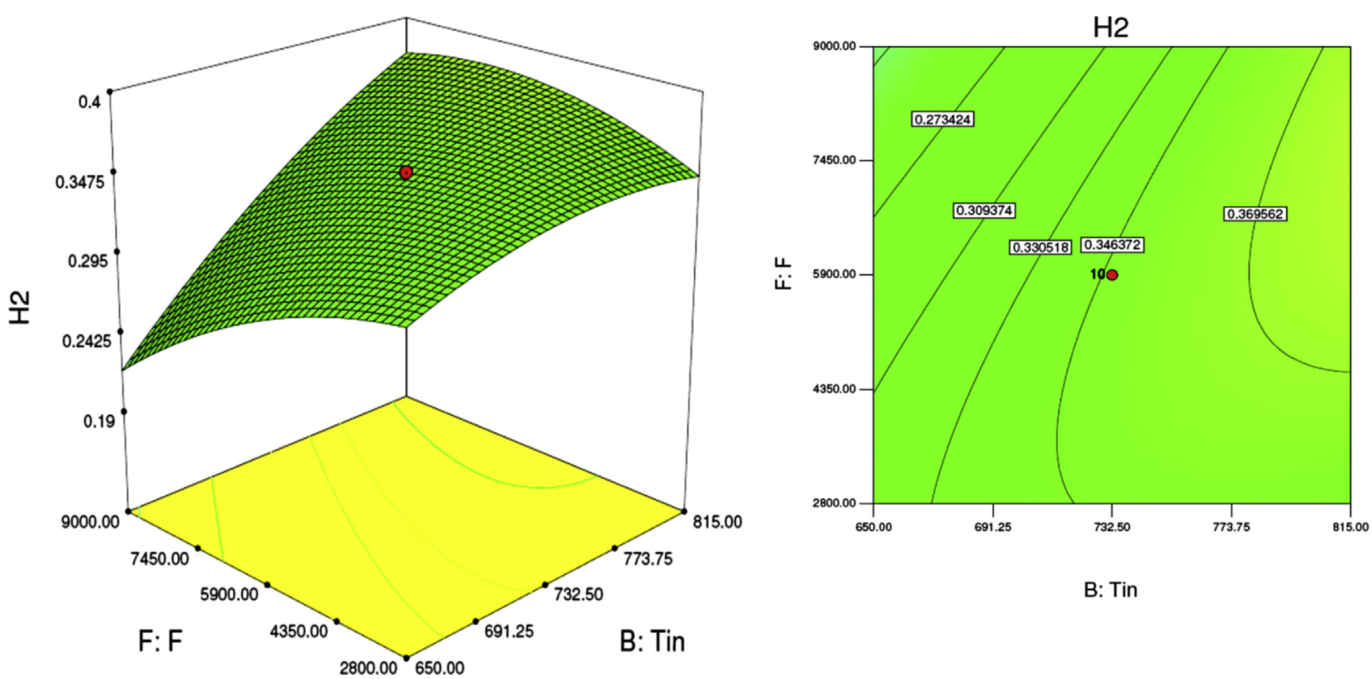

Fig. 6. Response surface plot and contour-lines showing the SMR performance index (H_2) as a function of F and Tin for $P_{in} = 25.00$; $T_w = 950.00$; $(H/C)_{in} = 0.33$; $(S/C)_{in} = 5.08$.

causes the reaction to be done more completely, therefore; more methane will be converted, and the unreacted methane will reduce.

Fig. 6 represents the influence of input feed temperature and flowrate on the hydrogen production. As it can be seen, the hydrogen production decreased while the input feed flowrate increased. The main effect of the input flowrate is greater than the main effect of the input feed temperature. On the contrary, the unreacted methane will increase by increasing the input feed flowrate. This fact is implied in Fig. 7. This is due to the reaction time reduction, which would not favour for the reactions and leads to higher unreacted methane and lower hydrogen production.

Effects of $(S/C)_{in}$ and T_{in} on the response CH_4 are represented in Fig. 8. As it is shown, the unreacted methane decreased as the $(S/C)_{in}$ increased. Increasing the steam will be desirable for all forward reactions 1–3, and it will cause more methane conversion in the process.

Fig. 9 illustrates effects of $(S/C)_{in}$ and T_{in} on the hydrogen production. As it is shown in this figure, the hydrogen production increased by decreasing the $(S/C)_{in}$ ratio. Increasing the $(S/C)_{in}$ can be caused by either increasing the steam, or reducing the methane amount in the input feed. Increasing the amount of steam is a favoured for the forward reaction, while decreasing the methane

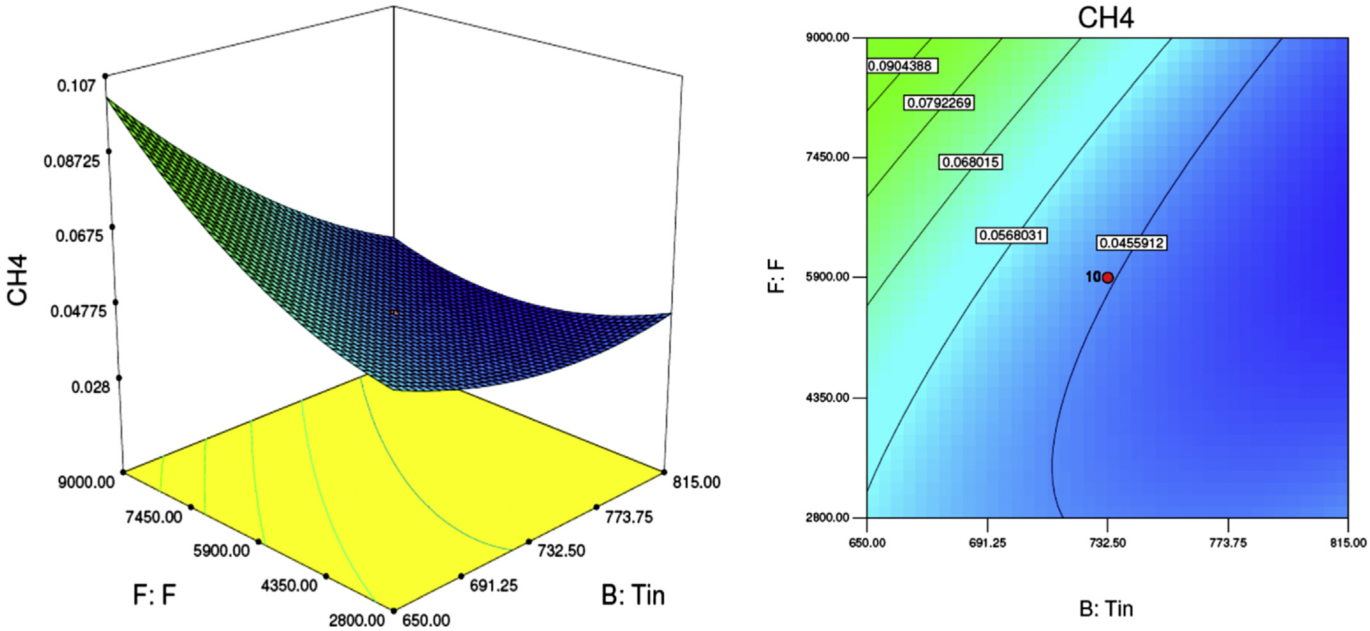

Fig. 7. Response surface plot and contour-lines showing the SMR performance index (CH_4) as a function of F and T_{in} for $P_{in} = 25.00$; $T_w = 950.00$; $(H/C)_{in} = 0.33$; $(S/C)_{in} = 5.08$.

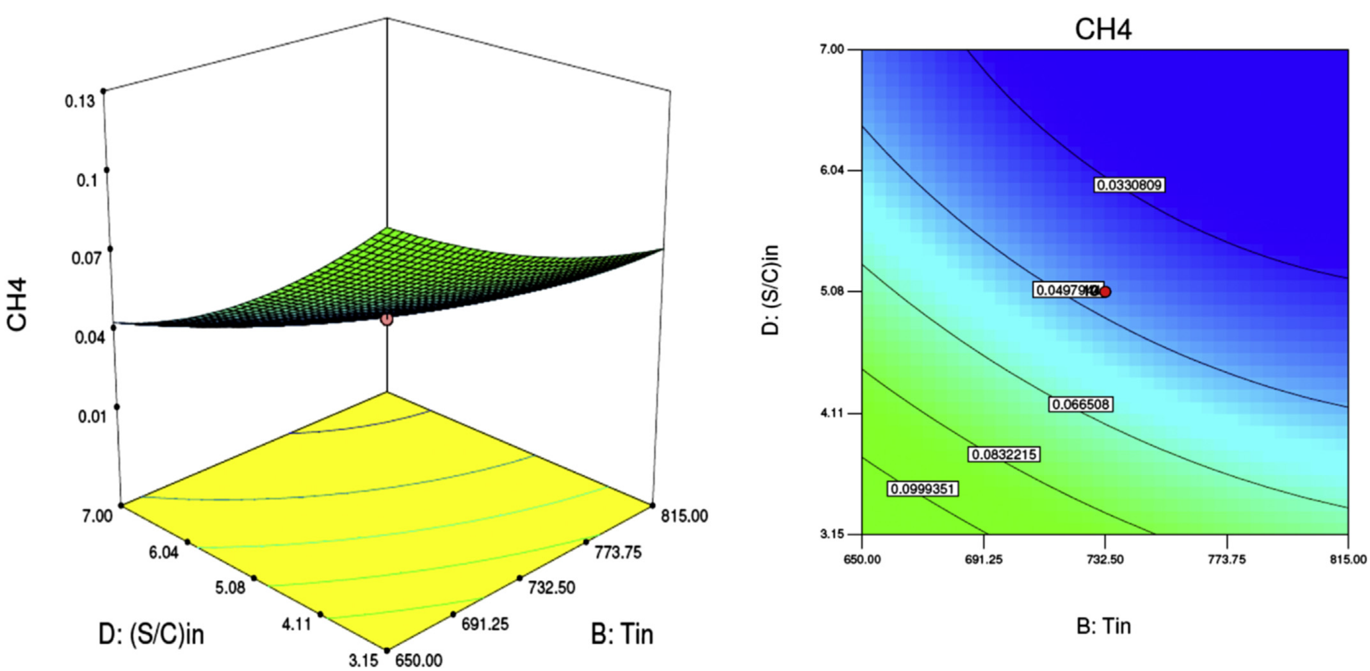

Fig. 8. Response surface plot and contour-lines showing the SMR performance index (CH_4) as a function of $(S/C)_{in}$ and T_{in} for $P_{in} = 25.00$; $T_w = 950.00$; $(H/C)_{in} = 0.33$; $F = 5900.00$.

amount is undesirable for this reaction. In other words, there is a conflict between input methane decrement and input steam increment, which causes an optimal point be formed. The same result has been obtained in other studies (Chen et al., 2012).

In the optimization study, two responses were considered as the objective functions. Minimization of unreacted methane and maximization of hydrogen production are the two objective functions. Therefore, the optimization problem can be expressed as follow:

$$\text{1st Objective Function}: \min CH_4\ (X_1, X_2, X_3, X_4, X_5, X_6) \quad (9)$$

$$\text{2nd Objective Function}: \max H_2\ (X_1, X_2, X_3, X_4, X_5, X_6) \quad (10)$$

The optimum values of independent variables and responses are reported in Table 5.

As it can be seen in Table 5, the average error in the model predictions is about 7.24%, which is obtained from the following equation:

$$Error(\%) = \frac{|Experimental - Calculated|_{Value}}{Experimental_{value}} \times 100 \quad (11)$$

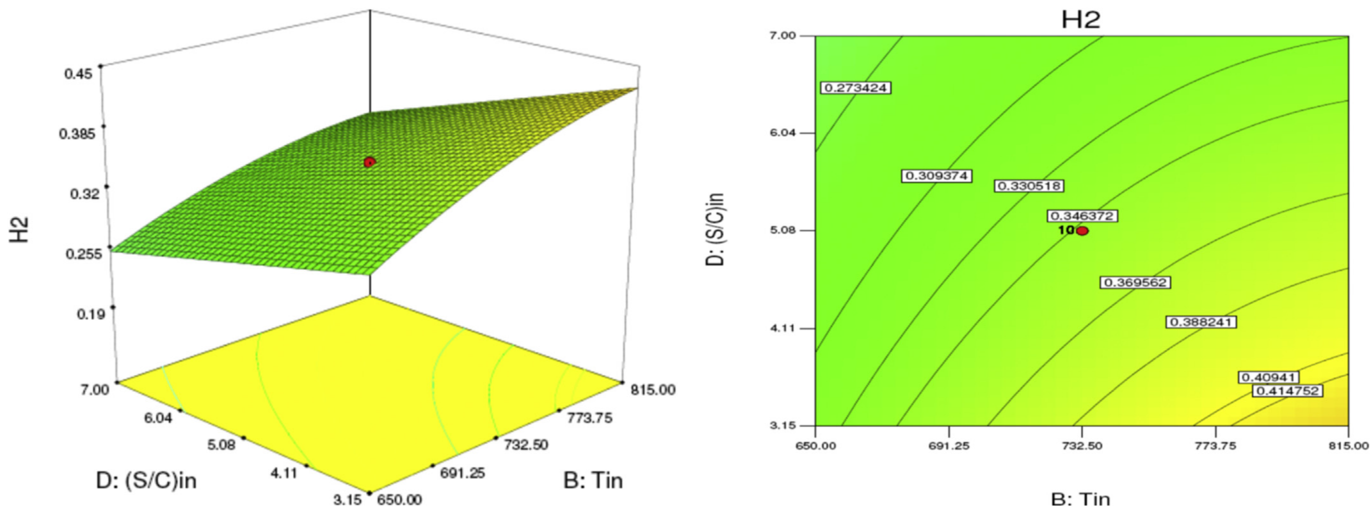

Fig. 9. Response surface plot and contour-lines showing the SMR performance index (H_2) as a function of $(S/C)_{in}$ and T_{in} for $P_{in} = 25.00$; $T_w = 950.00$; $(H/C)_{in} = 0.33$; $F = 5900.00$.

Table 5
Optimum values of variables obtained from the SMR performance.

Parameter	Optimum value
Input flowrate (F)	2800.07 kmol/h.
Steam to methane ratio in input feed $(S/C)_{in}$	4.03
Input feed pressure (P_{in})	26.32 bar
Tube wall temperature (T_w)	1100.00 K
Hydrogen to methane ratio in input feed $(H/C)_{in}$	0.15
Input feed temperature (T_{in})	725.12 K
Response	**Optimum value**
Experimental mole fraction of unreacted methane $(CH_4)_{experimental}$	0.0095
Predicted mole fraction of unreacted methane $(CH_4)_{predicted}$	0.0086
Experimental mole fraction of hydrogen $(H_2)_{experimental}$	0.4507
Predicted mole fraction of hydrogen $(H_2)_{predicted}$	0.4775

4. Conclusion

The steam methane reforming has been modelled and optimized using the design of experiment and response surface methodology. The unreacted methane and hydrogen production were considered as two responses, and the effects of six independent variables have been investigated upon the mentioned responses. Among the said variables are: input feed temperature, input feed pressure, tube wall temperature, input feed flowrate, input steam to methane ratio and the hydrogen to steam ratio.

It was concluded that the input feed pressure has a very small effect on responses, and it was neglected in the presented model. Moreover, it was shown that the hydrogen mole fraction increased when the input feed temperature and tube wall temperature increased. On the other hand, the unreacted methane mole fraction decreased when the input feed temperature and tube wall temperature increased. Furthermore, the hydrogen production decreased, while the input feed flowrate increased. On the contrary, the unreacted methane will increase by increasing the input feed flowrate. Besides, the unreacted methane decreased as the $(S/C)_{in}$ increased. On the other hand, increase in the $(S/C)_{in}$ ratio caused the hydrogen production to reduce.

Last but not least, the process has been optimized by RSM methodology, and the optimum values of independent variables have been reported, which causes the maximum hydrogen production and minimum unreacted methane.

Acknowledgment

Hereby, we tend to extend our hearties gratitude to the Bandar Abbas Refinery Complex Company in Iran, for their financial support. Mohammad Mohsen Sarafraz and Mohammad Jafar Mousavi are also appreciatively acknowledged for technical support and collaboration on data gathering.

Nomenclature

Symbols

DF	Degree of Freedom
F	[kmol h^{-1}], Reformer Feed Rate
F-value	Ratio of Variance (ANOVA test)
$(H/C)_{in}$	Recycle Hydrogen/Methane Molar Ratio in Feed
P	[bar], Pressure
P-value	Probability in Statistical Significance Testing (ANOVA test)
MS	Mean Squares (ANOVA test)
$(S/C)_{in}$	Steam/Methane Molar Ratio in Feed
SS	Sum of Square (ANOVA test)
T	[K] Temperature
X	Coded Levels of Variables
Z	Actual Values of Variables
ΔHr	[kJ $kmol^{-1}$], Reaction Enthalpy

Indices
in. Reformer Input
W Wall

Appendix A

In this study, the central composite design (CCD) was employed. According to this method, a total of 86 runs have been done, which are reported in Table A1.

Table A1
Total of 86 runs according to CCD in experiment design

Run	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response 1	Response 2
	A:T_w	B:T_{in}	C:P_{in}	D:$(S/C)_{in}$	E:$(H/C)_{in}$	F:F	H_2	CH_4
1	950.00	732.50	25.00	5.08	0.05	5900.00	0.3480	0.0373
2	800.00	815.00	23.00	7.00	0.50	2800.00	0.1903	0.0737
3	800.00	815.00	27.00	3.15	0.15	9000.00	0.3748	0.0896
4	800.00	650.00	23.00	7.00	0.50	2800.00	0.1209	0.0966
5	800.00	650.00	27.00	3.15	0.50	9000.00	0.1067	0.2107
6	800.00	650.00	23.00	7.00	0.15	9000.00	0.0753	0.1041
7	950.00	732.50	25.00	5.08	0.33	5900.00	0.3489	0.0446
8	1100.00	650.00	27.00	7.00	0.50	2800.00	0.3550	0.0110
9	1100.00	650.00	23.00	3.15	0.50	9000.00	0.3220	0.1317
10	950.00	732.50	25.00	5.08	0.33	5900.00	0.3489	0.0446
11	1100.00	650.00	23.00	7.00	0.15	2800.00	0.3418	0.0087
12	1100.00	650.00	27.00	7.00	0.50	9000.00	0.2406	0.0584
13	950.00	732.50	25.00	5.08	0.33	10751.76	0.2735	0.0775
14	800.00	650.00	23.00	3.15	0.15	9000.00	0.0648	0.2175
15	1100.00	815.00	27.00	3.15	0.50	9000.00	0.3130	0.1348
16	800.00	650.00	23.00	3.15	0.15	2800.00	0.2330	0.1521
17	800.00	815.00	23.00	7.00	0.15	9000.00	0.2657	0.0397
18	800.00	650.00	27.00	7.00	0.50	9000.00	0.0569	0.1142
19	1100.00	815.00	23.00	3.15	0.15	2800.00	0.5126	0.0164
20	1100.00	815.00	27.00	7.00	0.50	2800.00	0.3625	0.0082
21	950.00	732.50	25.00	5.08	0.33	5900.00	0.3489	0.0446
22	950.00	732.50	25.00	5.08	0.33	5900.00	0.3489	0.0446
23	950.00	732.50	25.00	5.08	0.33	5900.00	0.3489	0.0446
24	1100.00	815.00	27.00	3.15	0.50	2800.00	0.5204	0.0221
25	950.00	732.50	25.00	8.09	0.33	5900.00	0.2736	0.0260
26	1100.00	650.00	23.00	7.00	0.15	9000.00	0.2589	0.0431
27	950.00	732.50	25.00	2.06	0.33	5900.00	0.4487	0.1236
28	950.00	732.50	25.00	5.08	0.60	5900.00	0.3369	0.0571
29	800.00	815.00	23.00	3.15	0.50	9000.00	0.3718	0.1022
30	800.00	815.00	27.00	7.00	0.15	9000.00	0.2486	0.0459
31	1100.00	815.00	23.00	3.15	0.15	9000.00	0.4103	0.0815
32	1100.00	650.00	23.00	7.00	0.50	9000.00	0.2473	0.0563
33	1100.00	815.00	23.00	7.00	0.50	9000.00	0.3146	0.0307
34	1100.00	650.00	23.00	3.15	0.50	2800.00	0.5062	0.0345
35	715.24	732.50	25.00	5.08	0.33	5900.00	0.0977	0.1382
36	1100.00	650.00	27.00	7.00	0.15	2800.00	0.3363	0.0109
37	1100.00	815.00	27.00	7.00	0.15	9000.00	0.3113	0.0238
38	950.00	732.50	21.87	5.08	0.33	5900.00	0.3582	0.0409
39	950.00	732.50	25.00	5.08	0.33	5900.00	0.3489	0.0446
40	1100.00	650.00	23.00	3.15	0.15	9000.00	0.3432	0.1117
41	800.00	815.00	27.00	7.00	0.15	2800.00	0.1711	0.0727
42	950.00	603.38	25.00	5.08	0.33	5900.00	0.1932	0.1069
43	950.00	732.50	28.13	5.08	0.33	5900.00	0.3399	0.0482
44	950.00	732.50	25.00	5.08	0.33	5900.00	0.3487	0.0448
45	950.00	732.50	25.00	5.08	0.33	5900.00	0.3483	0.0445
46	1100.00	815.00	23.00	7.00	0.50	2800.00	0.3674	0.0064
47	800.00	815.00	23.00	7.00	0.15	2800.00	0.1855	0.0680
48	1100.00	815.00	23.00	7.00	0.15	9000.00	0.3123	0.0241
49	800.00	815.00	27.00	3.15	0.15	2800.00	0.1682	0.1775
50	950.00	732.50	25.00	5.08	0.33	5900.00	0.3487	0.0448
51	800.00	815.00	27.00	3.15	0.50	9000.00	0.3425	0.1149
52	1184.76	732.50	25.00	5.08	0.33	5900.00	0.3787	0.0340
53	800.00	650.00	27.00	7.00	0.15	9000.00	0.0674	0.1064
54	1100.00	650.00	27.00	3.15	0.50	2800.00	0.4992	0.0374
55	1100.00	815.00	23.00	3.15	0.50	9000.00	0.4133	0.0891
56	1100.00	815.00	23.00	3.15	0.50	2800.00	0.5299	0.0179
57	1100.00	815.00	27.00	3.15	0.50	9000.00	0.4114	0.0890
58	1100.00	650.00	27.00	3.15	0.15	2800.00	0.4989	0.0246
59	1100.00	650.00	27.00	3.15	0.15	9000.00	0.3372	0.1137
60	800.00	815.00	23.00	3.15	0.50	2800.00	0.2083	0.1717
61	800.00	650.00	27.00	3.15	0.50	2800.00	0.1152	0.2076
62	800.00	815.00	23.00	3.15	0.15	2800.00	0.1831	0.1719
63	800.00	815.00	27.00	7.00	0.50	9000.00	0.2436	0.0549
64	800.00	815.00	27.00	7.00	0.50	2800.00	0.1763	0.0783

Table A1 (*continued*)

Run	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Response 1	Response 2
	A:T_w	B:T_{in}	C:P_{in}	D:$(S/C)_{in}$	E:$(H/C)_{in}$	F:F	H_2	CH_4
65	800.00	815.00	27.00	3.15	0.50	2800.00	0.1944	0.1771
66	1100.00	815.00	27.00	7.00	0.15	2800.00	0.3464	0.0072
67	1100.00	815.00	27.00	3.15	0.15	2800.00	0.5025	0.0206
68	800.00	650.00	27.00	3.15	0.15	2800.00	0.1804	0.1732
69	950.00	861.62	25.00	5.08	0.33	5900.00	0.3908	0.0280
70	1100.00	815.00	27.00	7.00	0.50	9000.00	0.3132	0.0307
71	800.00	815.00	23.00	7.00	0.50	9000.00	0.2616	0.0484
72	800.00	650.00	23.00	3.15	0.50	9000.00	0.1073	0.2105
73	1100.00	650.00	23.00	7.00	0.50	2800.00	0.3606	0.0088
74	950.00	732.50	25.00	5.08	0.33	5900.00	0.3492	0.0450
75	800.00	650.00	27.00	7.00	0.15	2800.00	0.1535	0.0783
76	1100.00	815.00	23.00	7.00	0.15	2800.00	0.3511	0.0055
77	800.00	650.00	23.00	7.00	0.50	9000.00	0.0682	0.1135
78	800.00	650.00	23.00	7.00	0.15	2800.00	0.1691	0.0732
79	800.00	650.00	23.00	3.15	0.50	2800.00	0.1187	0.2063
80	800.00	815.00	23.00	3.15	0.15	9000.00	0.3956	0.0811
81	1100.00	815.00	27.00	3.15	0.15	9000.00	0.4099	0.0804
82	950.00	732.50	25.00	5.08	0.33	1048.24	0.2952	0.0668
83	1100.00	650.00	23.00	3.15	0.15	2800.00	0.5075	0.0210
84	1100.00	650.00	27.00	7.00	0.15	9000.00	0.2531	0.0450
85	800.00	650.00	27.00	7.00	0.50	2800.00	0.1093	0.1003
86	800.00	650.00	27.00	3.15	0.15	9000.00	0.0573	0.2201

References

Aksoy, D.O., Sagol, E., 2016. Application of central composite design method to coal flotation: modelling, optimization and verification. Fuel 183, 609–616.

Aparicio, L., 1997. Transient isotopic studies and microkinetic modeling of methane reforming over nickel catalysts. J. Catal. 165, 262–274.

Berrios, M., Gutiérrez, M., Martín, M., Martín, A., 2009. Application of the factorial design of experiments to biodiesel production from lard. Fuel Process. Technol. 90, 1447–1451.

Byrne Jr., P., Gohr, E., Haslam, R., 1932. Recent progress in hydrogenation of petroleum. Ind. Eng. Chem. 24, 1129–1135.

Can, M.Y., Kaya, Y., Algur, O.F., 2006. Response surface optimization of the removal of nickel from aqueous solution by cone biomass of Pinus sylvestris. Bioresour. Technol. 97, 1761–1765.

Chen, Z., Po, F., Grace, J.R., Lim, C.J., Elnashaie, S., Mahecha-Botero, A., Rakib, M., Shirasaki, Y., Yasuda, I., 2008. Sorbent-enhanced/membrane-assisted steam-methane reforming. Chem. Eng. Sci. 63, 170–182.

Chen, B., Liao, Z., Wang, J., Yu, H., Yang, Y., 2012. Exergy analysis and CO_2 emission evaluation for steam methane reforming. Int. J. Hydrogen Energy 37, 3191–3200.

De Deken, J., Devos, E., Froment, G., 1982. Steam Reforming of Natural Gas: Intrinsic Kinetics, Diffusional Influences, and Reactor Design, pp. 181–197.

Easton, V.J., McColl, J.H., 1997. Statistics Glossary, Steps.

Ferreira, S.L.C., Bruns, R.E., da Silva, E.G.P., dos Santos, W.N.L., Quintella, C.M., David, J.M., de Andrade, J.B., Breitkreitz, M.C., Jardim, I.C.S.F., Neto, B.B., 2007. Statistical designs and response surface techniques for the optimization of chromatographic systems. J. Chromatogr. A 1158, 2–14.

Hajjaji, N., Renaudin, V., Houas, A., Pons, M.N., 2010. Factorial design of experiment (DOE) for parametric exergetic investigation of a steam methane reforming process for hydrogen production. Chem. Eng. Process. Process Intensif. 49, 500–507.

Jeon, S.W., Yoon, W.J., Jeong, M.W., Kim, Y., 2014. Optimization of a counter-flow microchannel reactor using hydrogen assisted catalytic combustion for steam reforming of methane. Int. J. Hydrogen Energy 39, 6470–6478.

Khayet, M., Cojocaru, C., 2012. Air gap membrane distillation: desalination, modeling and optimization. Desalination 287, 138–145.

Körbahti, B.K., Rauf, M., 2008. Response surface methodology (RSM) analysis of photoinduced decoloration of toludine blue. Chem. Eng. J. 136, 25–30.

Krishnaiah, D., Bono, A., Sarbatly, R., Nithyanandam, R., Anisuzzaman, S., 2015. Optimisation of spray drying operating conditions of Morinda citrifolia L. fruit extract using response surface methodology. J. King Saud Univ. Eng. Sci. 27, 26–36.

Liu, K., Song, C., Subramani, V., 2010. Hydrogen and Syngas Production and Purification Technologies. Wiley Online Library, New Jersey.

Manohar, B., 2014. Optimization of supercritical carbon dioxide extraction of phenolic compounds from mango ginger rhizome (Curcuma Amada Roxb.) using response surface methodology. Biomed. Biotechnol. 2, 14–19.

Mbodji, M., Commenge, J.-M., Falk, L., Di Marco, D., Rossignol, F., Prost, L., Valentin, S., Joly, R., Del-Gallo, P., 2012. Steam methane reforming reaction process intensification by using a millistructured reactor: experimental setup and model validation for global kinetic reaction rate estimation. Chem. Eng. J. 207, 871–884.

Naik, P., Reddy, P.S.R., Misra, V., 2005. Interpretation of interaction effects and optimization of reagent dosage for fine coal flotation. Int. J. Mineral Process. 75, 83–90.

Ochoa-Fernandez, E., Rusten, H.K., Jakobsen, H.A., Rønning, M., Holmen, A., Chen, D., 2005. Sorption enhanced hydrogen production by steam methane reforming using Li 2 ZrO 3 as sorbent: sorption kinetics and reactor simulation. Catal. Today 106, 41–46.

Pantoleontos, G., Kikkinides, E.S., Georgiadis, M.C., 2012. A heterogeneous dynamic model for the simulation and optimisation of the steam methane reforming reactor. Int. J. Hydrogen Energy 37, 16346–16358.

Papaneophytou, C.P., Kyriakidis, D.A., 2012. Optimization of polyhydroxyalkanoates production from thermusthermophilus HB8 using response surface methodology. J. Polym. Environ. 20, 760–773.

Pooralhossini, J., Ghaedi, M., Zanjanchi, M.A., Asfaram, A., 2017. The choice of ultrasound assisted extraction coupled with spectrophotometric for rapid determination of gallic acid in water samples: central composite design for optimization of process variables. Ultrason. Sonochemistry 34, 692–699.

Rajesh, J.K., Gupta, S.K., Rangaiah, G.P., Ray, A.K., 2001. Multi-objective optimization of industrial hydrogen plants. Chem. Eng. Sci. 56, 999–1010.

Riaz, A., Farsi, A., Zahedi, G., Manan, Z.A., 2011. Investigation of inert gas injection in steam reforming of methane: energy. IIB 1, 1.

Rostrup-Nielsen, J.R., 2000. New aspects of syngas production and use. Catal. Today 63, 159–164.

Rostrup-Nielsen, J., 2004. Steam reforming of hydrocarbons. A historical perspective. Stud. Surf. Sci. Catal. 147, 121–126.

Rydén, M., Lyngfelt, A., 2006. Using steam reforming to produce hydrogen with carbon dioxide capture by chemical-looping combustion. Int. J. Hydrogen Energy 31, 1271–1283.

Sadooghi, P., Rauch, R., 2013. Pseudo heterogeneous modeling of catalytic methane steam reforming process in a fixed bed reactor. J. Nat. Gas Sci. Eng. 11, 46–51.

Safizadeh, M.H., Thornton, B.M., 1984. Optimization in simulation experiments using response surface methodology. Comput. Ind. Eng. 8, 11–27.

Shafeeyan, M.S., Daud, W.M.A.W., Houshmand, A., Arami-Niya, A., 2012. The application of response surface methodology to optimize the amination of activated carbon for the preparation of carbon dioxide adsorbents. Fuel 94, 465–472.

Simpson, A.P., Lutz, A.E., 2007. Exergy analysis of hydrogen production via steam methane reforming. Int. J. Hydrogen Energy 32, 4811–4820.

Sinaei Nobandegani M, S.B.M. Shahraki F, Darbandi T, H. B, Steam methane reforming modeling and optimization. In: 13th Mediterranean Congress of Chemical Engineering, Spain, 2014.

Sinaei Nobandegnai, M., 2014. Optimization of Steam Reformer Reactor in Bandar Abbas Refinery (master thesis). University of Sistan and Baluchestan, Iran.

Sørensen, B., 2011. Hydrogen and Fuel Cells: Emerging Technologies and Applications. Academic Press, Burlington.

Van Hook, J.P., 1980. Methane-steam reforming. Catal. Rev. Sci Eng. 21, 1–51.

Vicente, G., Coteron, A., Martinez, M., Aracil, J., 1998. Application of the factorial design of experiments and response surface methodology to optimize biodiesel production. Ind. Crops Prod. 8, 29–35.

Xu, J., Froment, G.F., 1989. Methane steam reforming, methanation and water-gas shift: I. Intrinsic kinetics. AIChE J. 35, 88–96.