

Optimisation of CH₄ and CO₂ Conversion and Selectivity of H₂ and CO for the Dry Reforming of Methane by a Microwave Plasma Technique Using a Box-Behnken Design

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Abstract

A microwave plasma was generated by N₂ gas. Synthesis gases (H₂ and CO) were produced by the interaction of CH₄ and CO₂ under plasma conditions at atmospheric pressure. The experimental pilot plant was set-up, and the gases were sampled and analysed by GC/MS. The Box-Behnken design (BBD) method was used to find the optimising conditions based on the experimental results. The response surface methodology (RSM) based on a three-parameter and three-level BBD has been developed to find the effects of independent process parameters, which were represented by the gas flow rates of CH₄, CO₂ and N₂ and their effects on the process performance in terms of CH₄, CO₂ and N₂ conversion and selectivity of H₂ and CO. In this work, four models based on quadratic polynomial regression have been determined to understand the connection between the limits of the feed gas flow rate and the performance of the process. The results show that the most important factor influencing the CO₂, CH₄ and N₂ conversion and the selectivity of H₂ and CO was *CO₂ feed gas flow rate*. At the maximum desirable value of 0.92, the optimum CH₄, CO₂ and N₂ conversion were 84.91%, 44.40% and 3.37%, respectively and the selectivity of H₂ and CO were 51.31% and 61.17%, respectively. This was achieved at a gas feed flow rate of 0.19, 0.38, and 1.49 L min⁻¹ for CH₄, CO₂ and N₂, respectively.

Keywords: Box-Behnken Design, Dry Reforming of Methane, Microwave Plasma, Optimisation, Syngas Production

1. Introduction

Due to the increasing demand for energy in recent years, there has been higher usage of fossil fuels. This has led to the release of greenhouse gases such as methane (CH₄) and carbon dioxide (CO₂), causing global warming and subsequent climate change [1]. Consequently, it has become imperative to depend on the modern and economical technologies using greenhouse gases as an alternative source for energy generation (such as synthesis gas production) [2]. Synthesis gas is an environmentally friendly fuel, which is synthesised from greenhouse gases. A mixture of hydrogen and carbon monoxide (H₂ + CO) has been used to produce a wide range of liquid fuels by the Fischer-Tropsch (F-T) process [3]. Additionally, this process can be used to synthesise a wide range of chemicals such as ammonia, ethanol, methanol, alcohol, acetic acid, dimethyl ether, methyl formate, diesel, and gasoline [4]. Methane is the

1 most commonly used gas for synthesis gas production. There are three major methods used to convert
2 methane (CH₄) into synthesis gas, and these include steam reforming of methane (SRM) [5, 6], partial
3 oxidation of methane (POM) [7, 8] and dry reforming of methane (DRM) [9-12] which are described
4 below;

5 **Steam Reforming of Methane (SRM)**

6 The most important technology for high syngas production is SRM. It produces a gas mixture with a high
7 H₂:CO ratio (Eq. (1)) [5]. This technology is an endothermic reaction and needs a high temperature
8 (higher than 700 °C) to activate the reforming reaction [6].



10 **Partial Oxidation of Methane (POM)**

11 POM, which is an exothermic reaction, is more suited to produce synthesis gas [7], as shown in Eq. (2).
12 The advantages of this process include high conversion rates of methane and carbon dioxide, and high
13 selectivity of hydrogen and carbon monoxide, all during a very short residence time [8].



15 **Dry Reforming of Methane (DRM)**

16 Recently, DRM has been used to produce synthesis gas from greenhouse gases (CH₄ and CO₂). leading
17 to the reduced emissions of these gases to the atmosphere [9, 10], as shown in Eq. (3). DRM yields a
18 lower syngas ratio (H₂/CO=1) [11], suitable for use as feedstock to produce a variety of liquid
19 hydrocarbons via the F-T process [12, 13].



22 Plasma dry reforming of methane technology is considered the best way to convert CO₂ and CH₄ to
23 synthesis gas [14]. Plasma, the fourth state of matter, is a partially ionised gas mixture consisting of ions,
24 atoms, electrons, molecules, free radicals, neutral by-products, and photons [15]. Generally, the plasma
25 process is divided into two main methods; the first is cold plasma (non-thermal plasma) discharge
26 including dielectric barrier discharge (DBD), corona discharge (CD), atmospheric pressure glow
27 discharge (APGD), gliding arc discharge (GAD), microwave discharge (MWD) and spark discharge
28 [16]. The second is thermal plasma including direct current (DC), alternating current (AC) arc torch and
29 radio frequency (RF) [17, 18].

30 In the nitrogen-plasma process, CO₂ and CH₄ conversion, selectivities and yields of H₂ and CO and
31 H₂/CO ratio are affected by many factors such as feed gas flow rate, CO₂:CH₄ ratio, reactor design,
32 residence time, and discharge power [19]. Several authors [15, 1 and 20] have proved that the effect of
33 feed gas flow rates of CO₂, CH₄, and N₂ is an effective factor in the performance of the plasma process.
34 Firstly, Cleiren, Emelie, et al. [15] reported that the feed flow rate affects the conversion, selectivity,

1 yield, and syngas (H_2/CO) ratio. They found that an increasing CH_4 flow rate leads to a decrease in the
2 conversions of CO_2 and CH_4 , selectivities, and yields of H_2 and CO . Secondly, Khoja, Asif Hussain et
3 al. [1] have pointed out that the $CO_2:CH_4$ ratio affects the plasma stability and performance of the process.
4 They noticed that the CH_4 and N_2 conversion, as well as the CO selectivity increase with increasing CO_2
5 flow rate, while CO_2 conversion, H_2 selectivity, H_2 and CO yields and H_2/CO ratio all decreased. Finally,
6 Serrano-Lotina, A., and L. Daza [20] found that the conversion of CO_2 and CH_4 , selectivity, yield of H_2
7 and CO , and H_2/CO ratio did not change with increasing N_2 flow rate. Pakhare and Spivey [21] pointed
8 out that the ratio of CO_2/CH_4 affects the plasma stability and the process performance. They found that
9 the CH_4 and N_2 conversion, along with the CO selectivity increase with increasing CO_2/CH_4 ratio, while
10 the CO_2 conversion, H_2 selectivity, H_2 and CO yields and H_2/CO ratio all decreased. Adris et al. [22]
11 concluded that the reactor design affects the plasma stability and process performance. Ashcroft et al.
12 [23] reported that the CO_2 , CH_4 and N_2 conversions, H_2 and CO selectivities and yields and H_2/CO ratio
13 decrease with increased residence time. Zhang, A. J. et al. [24] and Jiang, T. et al. [25] reported that
14 the discharge power affects the plasma stability and process performance. They found that the
15 conversions of CO_2 , CH_4 and N_2 , CO selectivity and H_2 , CO yields increase, while H_2 selectivity and
16 H_2/CO ratio decrease with increased power.

17 The influences of these parameters have not independently affected each other; therefore their
18 interactions must be taken into consideration. Identifying the optimum performance of the plasma
19 process using standard experiments is time-consuming and costly due to the need for multiple
20 experiments under different test conditions [26]. To reduce the difficulty in determining the optimum
21 performance of the plasma process, previous studies have used the chemical model [27-37]. It has been
22 found that the chemical model is useful in determining the optimum value for output responses. This
23 model requires a significantly lower number of experiments compared to using a traditional method [27].
24 The design of experiments (DoE) can be classified into a two main types Box-Behnken factorial design,
25 and Taguchi methods [28]. The ability to use more than one input factor is a significant advantage of
26 DoE. The most used methodology in DoE is the response surface methodology (RSM) [29]. This facility
27 assumes that various input variables and output responses to be connected. In this way, the impact of
28 single variables and their interactions on each response is more easily understood via 3D and contour
29 interpretations [30]. Two design methods, in response to the surface methodology, have been used to
30 determine the optimisation of the plasma process via the central composite design (CCD) and Box-
31 Behnken design (BBD) methods [31]. Fewer experiments are necessary when using the BBD method,
32 making this a more efficient choice than the CCD method [32]. During the 1950s, Box and collaborators
33 developed the response surface methodology (RSM) [33]. RSM is based on many mathematical and
34 statistical techniques which fit a polynomial equation that depends on the experimental data. [34].

35 Nitrogen is diatomic gas therefore it is usually used for generating a high energy plasma flame through
36 the dissociation and ionization process [16, 38-45]. However, the discussion about N_2 conversion is rare.
37 One of the more interesting findings that emerged from this study is that N_2 can be converted but only in
38 small percentage approximately 3%. Although, the nitrogen gas is considered as an inert gas, and it has
39 a triple strongest bond ($N\equiv N$) [46]. However, it exhibited a conversion ability in the present work. The

1 conversion of nitrogen could be attributed into the high temperature inside the plasma reactor and due to
2 the high energy from the microwave. There is another way to generate the plasma from nitrogen by using
3 eclectic-induced reactions. The plasma induced by electron beam has an energy much higher than the
4 energy needed for ionization and dissociation [47-50].

5 The temperature inside the plasma reactor is usually above 1600 °C, which is enough to breakdown the
6 triple bonds of nitrogen. Then, nitrogen is possible to consider, as some of this amount may be
7 contributed to produce ammonia and cyanide as a side reaction [43, 51].



11 The use of the DoE method to optimise the plasma chemical reactions in the microwave is still limited.
12 Therefore, this work focuses on the investigation and optimisation the effect of the different feed gas
13 flow rates upon the CH₄, CO₂ and N₂ conversions and selectivities of H₂ and CO to determine which gas
14 is most significant in terms of the process performance. The Box-Behnken design was employed to
15 design the experiments using RSM. In addition, the impact of different process parameters and their
16 interaction on CH₄, CO₂ and N₂ conversions and selectivities of H₂ and CO are investigated and
17 discussed.

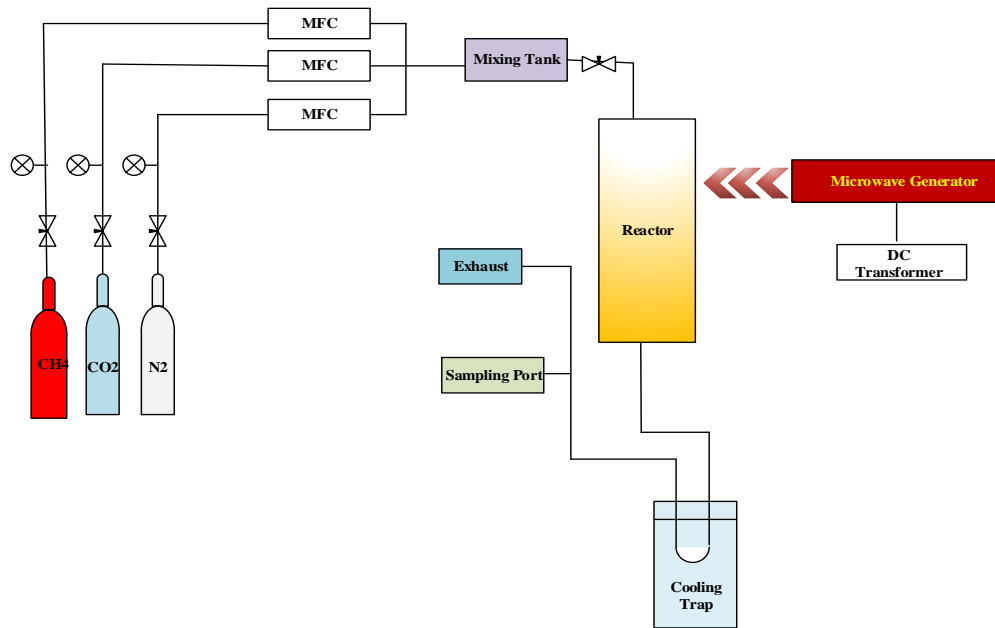
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19 **2. Experimental Work**

20 **2.1. Experimental Design**

21 Figure 1 shows the schematic diagram of the experimental set up for syngas production by plasma
22 generation. It consists of six essential units:- gas cylinders, mass flow controllers (MFC Alicat Scientific,
23 MCS-Series), gas mixer, plasma reactor (microwave generator [power supply SM1150x and magnetron
24 GA4313] and quartz glass tube), water cooling system, gas sampling unit and gas chromatography/mass
25 spectrometry unit (GS/MSD). More specifically, CH₄ (99.99%), CO₂ (99.99%) and N₂ (99.99%) were
26 supplied to experiment while the flowing of gasses were controlled by the mass flow controllers. After
27 that, the gases were mixed by a gas mixer to achieve the desired composition before entering the plasma
28 reactor. Inside the plasma reactor, the plasma flame was generated by nitrogen gas to provide the
29 condition of gas reaction. The thermocouples of type k were located at different locations in all parts of
30 the experimental apparatus to observe and control the temperatures during the reaction. The gas sample
31 was first drawn by syringe then injected into the GC detector. The cooler trap was set up outside the
32 plasma reactor to distinguish the produced gases from water which may be produced as a side product.

33



1

2

Fig 1. Schematics Flow Diagram of the Experimental Process

3

2.2. Gas Analysis

4

The sampled gas was analysed by GC which is gas chromatography combined online with a mass selective detector (MSD). GC can separate and identify the gases such as CH₄, CO₂, H₂, CO, and N₂ by using the thermal conductivity detector (TCD) detector. On the other hand, the structure information was determined by using the MSD. The conversion of CH₄ and CO₂ (C); and the selectivity of H₂ and CO (Y) are presented by the following equations:

9

$$C_{CH_4}(\%) = \frac{\text{moles of } CH_4 \text{ converted}}{\text{moles of } CH_4 \text{ introduced}} \times 100 \quad (8)$$

10

$$C_{CO_2}(\%) = \frac{\text{moles of } CO_2 \text{ converted}}{\text{moles of } CO_2 \text{ introduced}} \times 100 \quad (9)$$

11

$$C_{N_2}(\%) = \frac{\text{moles converted of } x}{\text{moles introduced of } x} \times 100 \quad (10)$$

12

$$Y_{H_2}(\%) = \frac{\text{moles of } H_2 \text{ produced}}{2 \times \text{moles of } CH_4 \text{ converted}} \times 100 \quad (11)$$

13

$$Y_{CO}(\%) = \frac{\text{moles of } CO \text{ produced}}{[\text{moles of } CH_4 + \text{moles of } CO_2] \text{ converted}} \times 100 \quad (12)$$

14

Where x indicates one of the chemicals from N₂ conversion.

15

1 **2.3. Approximate Model Function**

2 The response surface method (RSM) is a set of mathematical and statistical tool that is helpful for the
 3 modelling and analysis of problems [32]. RSM refers to a function of independent parameters described
 4 as [35]:

5
$$y = f(x_1, x_2, x_3, \dots, x_i) \tag{13}$$

6 Where y is the response variable, f is the response function, and x_1, x_2, \dots, x_i are the independent input
 7 parameters. RSM is a very beneficial and helpful method to control variables in experiments and optimise
 8 the operating parameters with as few errors as possible [36]. The relationship between the independent
 9 parameters and the response surface is essential because it gives the real functional relationship.
 10 Additionally, the second-order model is used in RMS [37].

11 In this study, three factors in the three-level Box-Behnken design (BBD) were utilised to investigate the
 12 interaction impact among these factors on the performance process of CO₂ and CH₄ conversions and H₂
 13 and CO **yields**. In this work, the flow rates of CH₄ (x_1), CO₂ (x_2), and N₂ (x_3) have been identified as the
 14 three independent variables affecting the conversions of CH₄, CO₂ and N₂ and the selectivities of H₂ and
 15 CO. Therefore, they were selected as the input parameters for the BBD, while conversions of CH₄ (Y_1),
 16 CO₂ (Y_2) and N₂ (Y_3), and selectivities of H₂ (Y_4) and CO (Y_5) are identified as responses. Either
 17 independent process variable contains three different levels, which are coded as low (-1), centre (0) and
 18 high (+1), as shown in Table 1.

19 **Table 1. Experimental range and levels of the independent input variables in the Box-Behnken**
 20 **design.**

Independent Variables	Symbols	Level and Range		
		Low [-1]	Centre [0]	High [+1]
CH ₄ [L/min.]	x_1	0.1	0.2	0.3
CO ₂ [L/min.]	x_2	0.2	0.4	0.6
N ₂ [L/min.]	x_3	1.4	1.5	1.6

21

22 The BBD, the regression (quadratic) model describes the relationship between the input process variables
 23 and each response. The quadratic model used to predict the optimal values is presented by the following
 24 equation [52]:

25
$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_i^k \beta_{ii} x_{ii}^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} x_i x_j \tag{14}$$

26 where Y is the response; β_0 is the constant coefficient; β_i is the coefficient for linear; x_i is the initial input
 27 parameters; β_{ii} ($i = 1, 2, \dots, k$) are the quadratic coefficients, and β_{ij} ($i = 1, 2, \dots, k; j = 1, 2, k$) are the
 28 coefficients that represent the interactions of x_i and x_j [53]. The reaction performance can be predicted at
 29 different process conditions by this model [54].

1 Analysis of variance (ANOVA) is used to estimate the indication of adequacy and modelling fitting.
 2 Response surfaces were generated by JMP statistical discovery™ software from SAS (version 13.1.0),
 3 which was used in the regression analysis and to plot the contour and 3-dimensional surface figures. The
 4 multiple coefficients of determination (R^2) values were found by the variance of variables and identified
 5 the interaction between the parameters within the particular experimental boundary conditions. The
 6 interaction between parameters was obtained by using the model equation to determine the optimum
 7 response values.

8

9 **3. Results and Discussion**

10 In this research, H_2 and CO were found to be the main two gas products that result from the CH_4 and
 11 CO_2 conversion. The $CO_2:CH_4$ molar ratio was kept at 2:1, and the microwave power at 700 W. The
 12 conversions of CH_4 , CO_2 and N_2 were within the ranges of (94.67-79.35%), (65.24-44.82%) and (11.67-
 13 3.22%), respectively. Meanwhile, the selectivities of H_2 and CO were (70.85-50.12%) and (75.32-
 14 58.42%), respectively. The conversion of CH_4 was always higher than those of CO_2 and N_2 . That can be
 15 attributed to the nature of the gas molecules, where these gases have a different molecular structure with
 16 different chemical bonds. Methane has covalent bonds, and a large amount of energy may be released
 17 when they are broken [55]. Additionally, the rate of dissociation of methane molecule depends on the
 18 initial supplied energy. On the other hand, the rate of thermal dissociation of CO_2 was lower due to its
 19 dependence on both temperature and the initial concentrations of CO_2 [56] which adversely affect the
 20 conversion of CO_2 . N_2 gas is dissociated due to applied microwave energy, as shown in Eq. (15) which
 21 produces the plasma flame. Moreover, the produced N atoms may adhere to the wall of the quartz tube
 22 and lead to recombination of nitrogen atoms again, as shown in Eq. (16) [57]. This mechanism leads to
 23 the reproduction of N_2 gas and reduces the conversion rate in the product.



26

27 **3.1 Analysis of Multiple Regressions**

28 Fifteen experimental samples were selected randomly for the BBD, including triplicate experimental
 29 runs, as shown in Table 2. The real relationships between the input and output values are presented in
 30 four equations based on the DoE analysis. The CH_4 , CO_2 and N_2 conversion (Y_1 , Y_2 and Y_3), and the
 31 selectivity of H_2 and CO (Y_4 , Y_5) are presented in Equation (17)-(21).

32 $Y_1 = 77.80 + 6.41x_1 - 32.32x_2 + 2.63x_3 + 0.64x_1x_2 + 7.13x_1x_3 - 0.91x_2x_3 - 9.84x_1^2 -$
 33 $36.08x_2^2 - 8.93x_3^2$ (17)

34 $Y_2 = 43.38 - 2.43x_1 - 12.19x_2 - 0.84x_3 + 1.28x_1x_2 - 0.32x_1x_3 - 0.85x_2x_3 - 4.35x_1^2 -$
 35 $25.54x_2^2 - 6.94x_3^2$ (18)

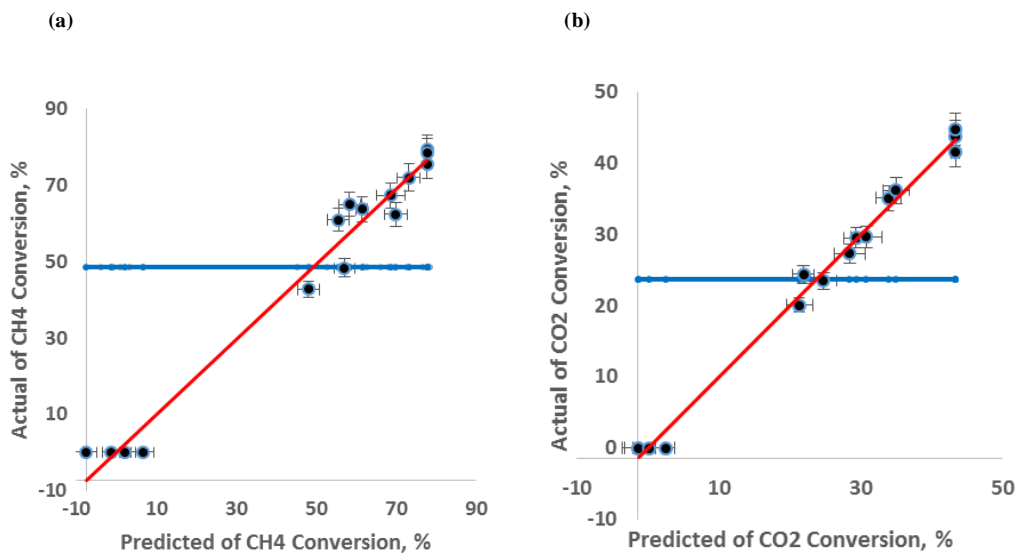
36 $Y_3 = 3.08 + 0.04x_1 - 1.33x_2 - 0.04x_3 + 0.04x_1x_2 - 0.08x_1x_3 + 0.065x_2x_3 - 0.26x_1^2 - 1.45x_2^2 -$
 37 $0.32x_3^2$ (19)

$$Y_4 = 48.78 + 0.58x_1 - 16.24x_2 + 0.26x_3 + 0.107x_1x_2 + 1.005x_1x_3 - 0.38x_2x_3 - 5.03x_1^2 - 25.75x_2^2 - 8.54x_3^2 \quad (20)$$

$$Y_5 = 57.35 + 0.23x_1 - 21.1x_2 + 0.05x_3 + 0.02x_1x_2 + 0.28x_1x_3 - 0.38x_2x_3 - 6.05x_1^2 - 29.09x_2^2 - 8.26x_3^2 \quad (21)$$

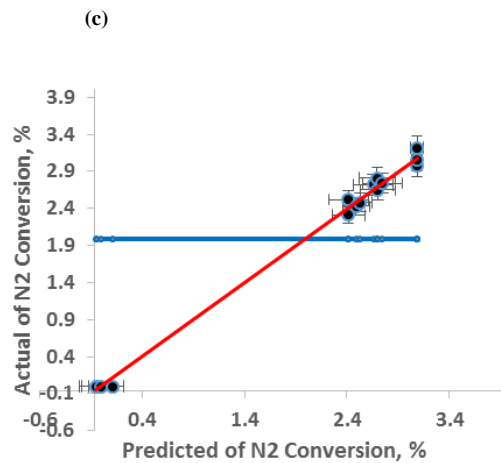
ANOVAs were used to determine the significance and adequacy of the quadratic models (Tables 2-7). The coefficient of determination (R^2) of the regression equations for the process parameters (CH_4 , CO_2 and N_2 conversions) and process performances (H_2 and CO selectivities) were 0.97, 0.99, 0.97, 0.99 and 0.99, respectively. The relationship between the variables and responses is described by the second order equation and this shows a good agreement between the experimental and predicted values because R^2 is close to 1, as shown in Figure 2. These results indicate that the quadratic models are statistically significant also able to predict and optimise the CH_4 , CO_2 and N_2 conversions and yields of H_2 and CO due to minimum error bar, as shown in Figure 2. Moreover, leverage residuals values were 47.74, 23.73, 1.2, 27.81 and 34.2 for the conversions CH_4 , CO_2 , N_2 , H_2 and CO which measures of how of the variables have a significant effect on the process performance. As shown in Figure 2, CO_2 is identified as a significant factor because the more of values were pass close to the leverage residuals line.

16



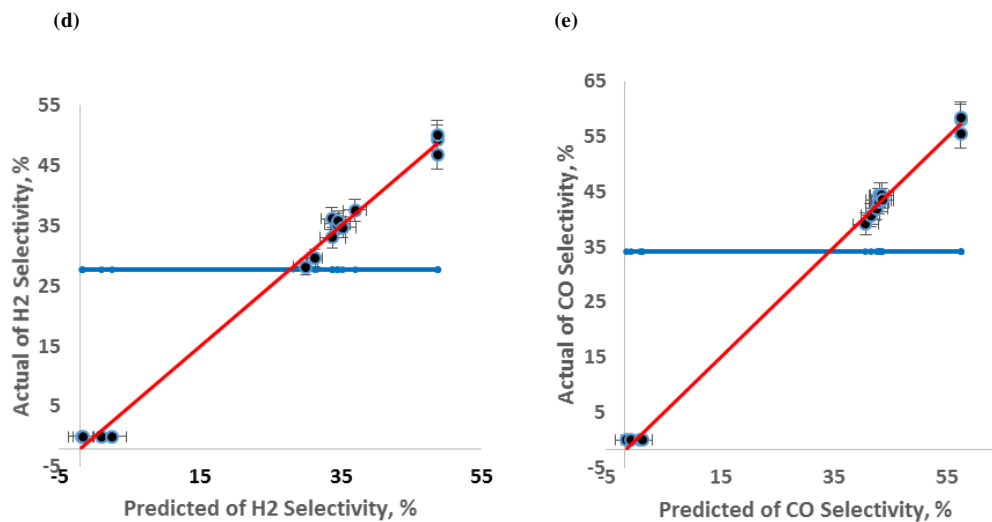
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1



2

3 **Fig 2. Comparison between actual and predicted values; (a) Conversion of CH₄; (b) Conversion**
 4 **of CO₂; (c) Conversion of N₂; (d) Selectivity of H₂; (e) Selectivity of CO [(•) experimental points,**
 5 **(•••) confidence bands > (95%), (–) fit line, Eqs. (17)-(21), (–) mean of the Y leverage residuals].**
 6

6

7 3.2 Effects of Plasma Process Parameters

8 3.2.1 CH₄, CO₂ and N₂ Conversions

9 The coefficient (β), standard error (ST), the squares sum (SS), the degree of freedom (DF), f-values and
 10 p-values are created by ANOVA, as presented in Table 3. The importance of this factor is indicated by
 11 its f-value and the p-value which indicates the level of significance of the parameter. The influence is
 12 considered significant on the performance of process if the p-value of a term (individual parameter x_i or
 13 interaction of two parameters $x_i x_j$) is below 0.05, while it is not significant if the p-value is above 0.05.

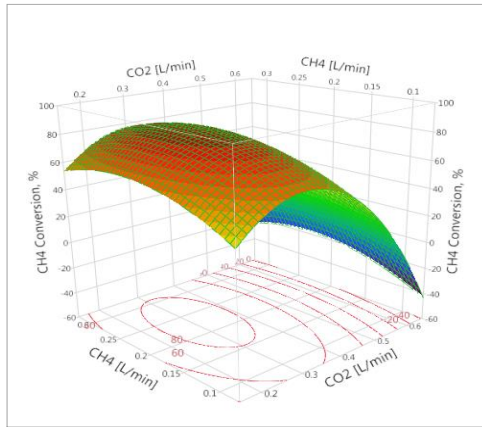
14 In the CH₄, CO₂ and N₂ conversion, the variables x_2 , x_1^2 , x_2^2 and x_3^2 are identified as significant factors
 15 ($p < 0.005$), while the variables x_2 , x_1^2 , x_2^2 and x_3^2 are not significant ($p > 0.005$), as shown in Tables 3-7.
 16 These results suggest that the term of CO₂ is the most significant impact on conversions of CH₄ and CO₂
 17 compared to the other parameters because it has the highest f-value among the CH₄, CO₂ and N₂
 18 conversion which are 96.78, 200.87 and 745.96, respectively (shown in Tables 3-5). The 3D response
 19 surface and 2 D contour lines are based on Equations (9)-(11) plots in Figures 3-5, respectively with one
 20 independent factor kept at a constant level (coded zero level), while the other two factors were changed
 21 within the experimental ranges.

22 These figures show the effects of CH₄ and CO₂ feed flow rates on CH₄ and CO₂ conversions at a CO₂:CH₄
 23 ratio of 2:1 and the microwave power at 700 W. Figures 3 and 4 show that the responses enhanced as
 24 corresponding factors (flow rate of CH₄, CO₂ and N₂) peaked, and after that, they decreased when it (the
 25 corresponding factor) increased to more than 0.19, 0.38 and 1.49 L min⁻¹, respectively. Figure 3a
 26 indicated that the CH₄ conversion increased rapidly when the CH₄, CO₂ and N₂ flow rates ranged from
 27 0.1 to 0.19, 0.2 to 0.38 and 1.4 to 1.49 L min⁻¹, respectively, and then declined when the flow rate

1 increased to greater than 0.19, 0.38 and 1.49 L min⁻¹, respectively. This is because the reduction in the
 2 conversion of CH₄, CO₂ and N₂ could be related to the residence time of gases in the microwave discharge
 3 zone, and it is reduced with the increase in gas feed flow rate; this led to the shorter treatment time [21].

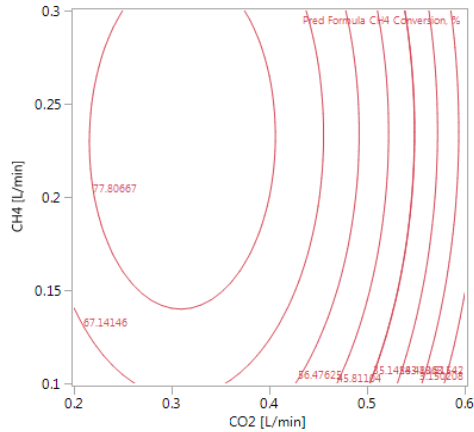
4 Maximum CH₄, CO₂ and N₂ conversions of 84.91%, 44.40% and 3.37%, respectively were achieved at
 5 the highest gas feed flow rates of 0.19, 0.38 and 1.49 L min⁻¹ for CH₄, CO₂ and N₂, respectively. The
 6 conversion of CH₄ and CO₂ decreased with increasing the feed flow rates for CH₄, CO₂ and N₂ from 0.05
 7 to 0.19, 0.1 to 0.38 and 0.3 to 1.49 L min⁻¹, respectively. This is due to the reduction in conversions of
 8 CH₄, CO₂ and N₂ which could be related to the residence time in the microwave discharge zone.
 9 Moreover, its value was reduced with the increasing of gas feed flow rate, which led to the shorter
 10 treatment time [20], as plotted in Figures 3, 4 and 5(b, d, and f). These results indicate that the interactions
 11 of the conversion of CH₄ (0.1083, 0.4590, 0.8950, 0.1852 and 0.8513) as shown in Table 3 i.e., the terms
 12 x₁, x₃, x₁x₂, x₁x₃ and x₂x₃ are not significant. Likewise, the interaction of the two parameters on the
 13 plasma process is not considered significant on the CO₂ and N₂ conversion as shown by the high p-values
 14 (0.0365, 0.3692, 0.3401, 0.8015 and 0.5160) and (0.4243, 0.3207, 0.5879, 0.2994 and 0.3902), of the
 15 terms x₁, x₃, x₁x₂, x₁x₃ and x₂x₃, respectively, as listed in Tables 4 and 5.

16 (a)

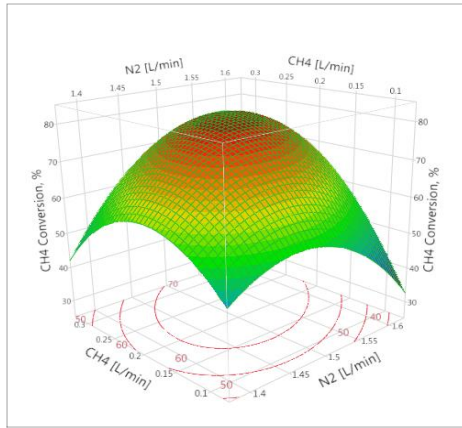


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(b)

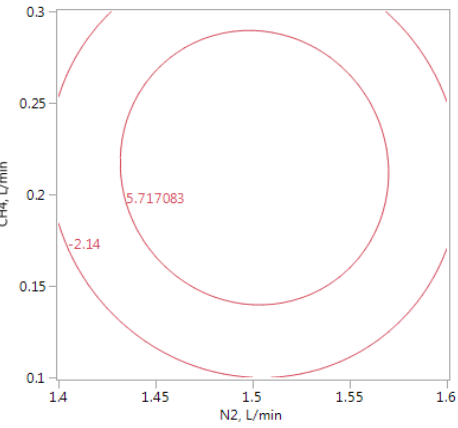


18 (c)



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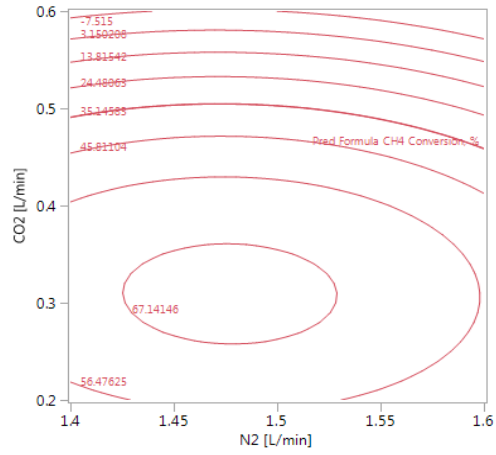
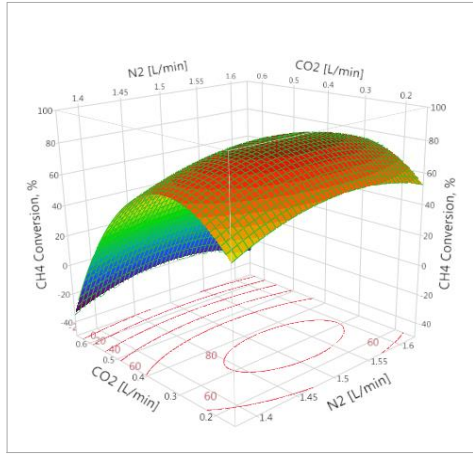
(d)



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21 (e)

(f)

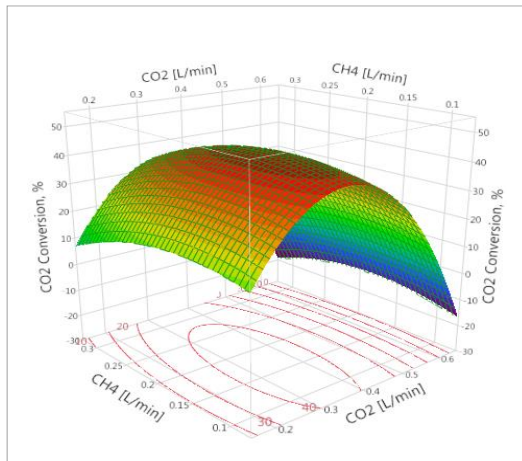


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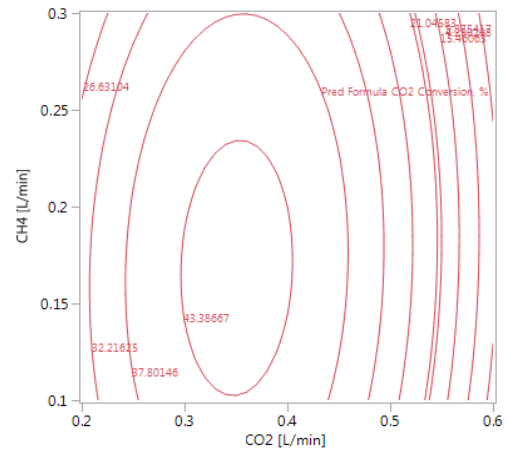
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3 **Fig. 3. Effect of feed gas flow rates and their interaction on CH₄ conversion at a CO₂:CH₄ ratio of**
 4 **2:1 and microwave plasma of 700 W (a, c, and e) three-dimensional surface plot; (b, d, and f)**
 5 **projected contour plot.**

6 (a)

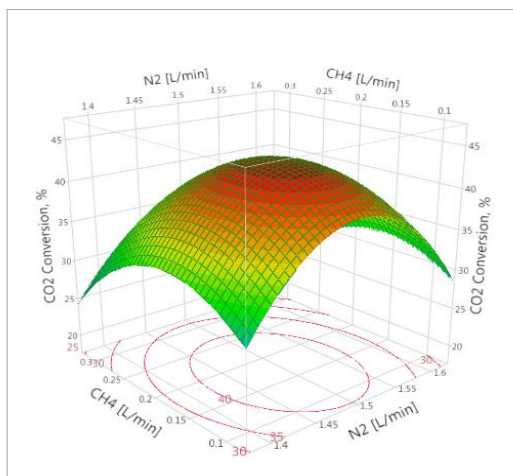


(b)

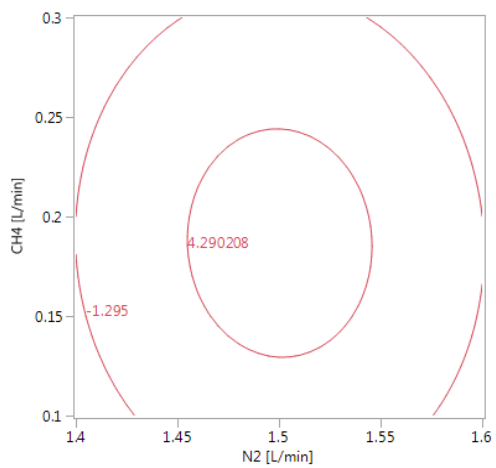


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8 (c)



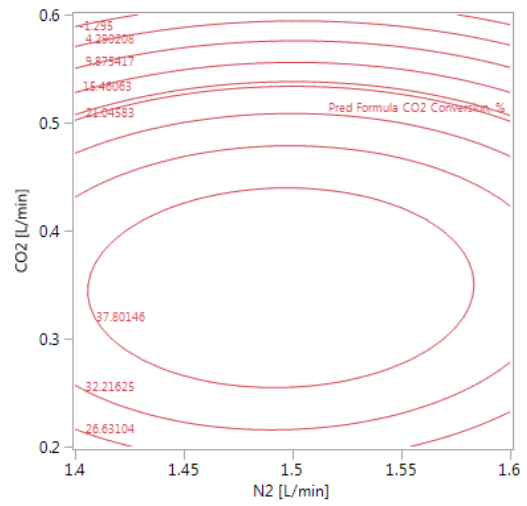
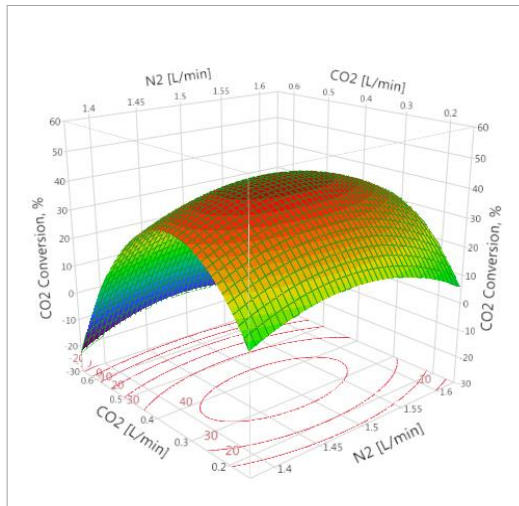
(d)



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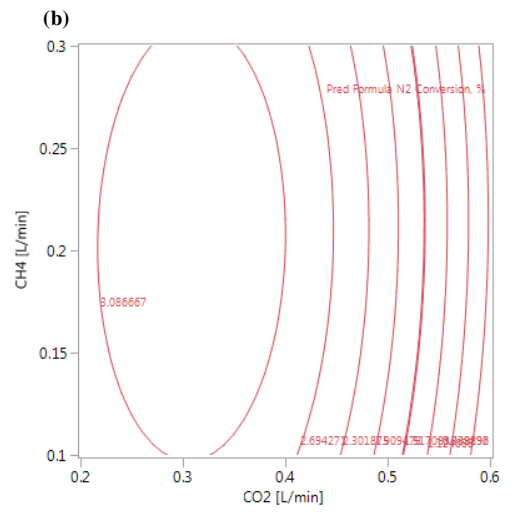
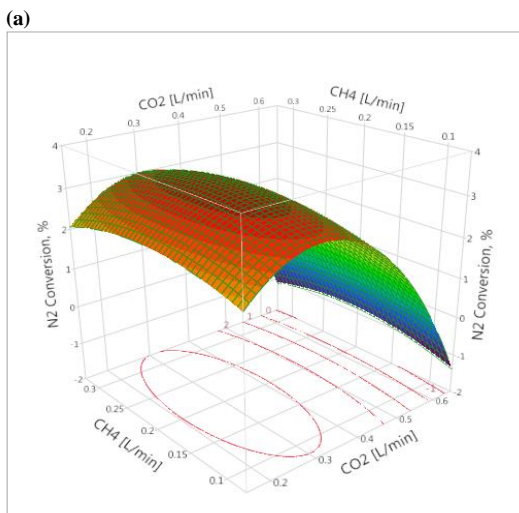
10 (e)

(f)

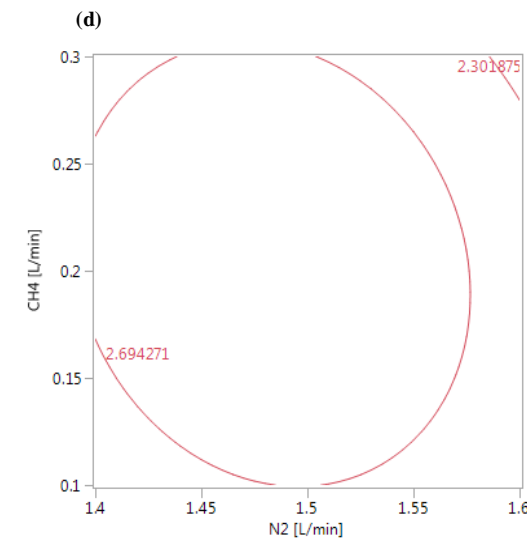
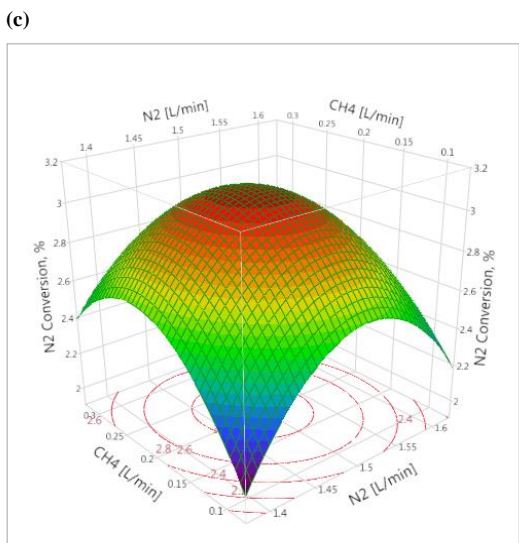


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Fig. 4. Effect of feed gas flow rates and their interaction on CO₂ conversion at a CO₂:CH₄ ratio of 2:1 and microwave plasma of 700 W (a, c and e) three-dimensional surface plot; (b, d, and f) projected contour plot.



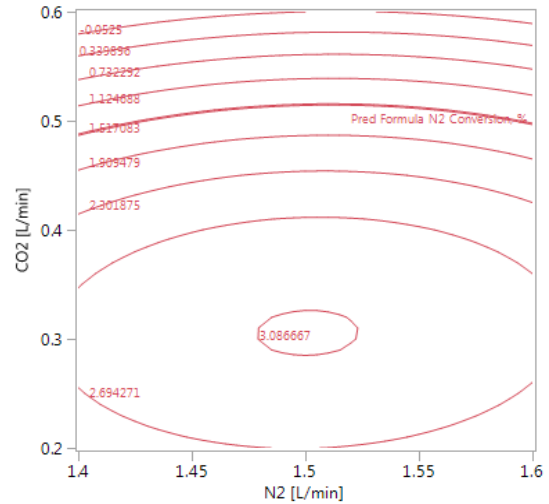
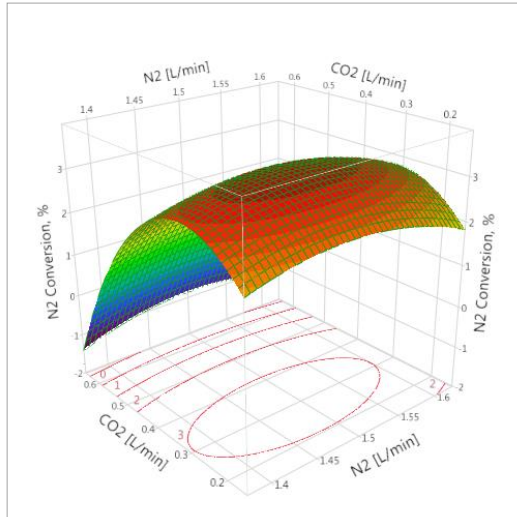
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(e)

(f)



1

2 **Fig. 5. Effect of feed gas flow rates and their interaction on N₂ conversion at a CO₂:CH₄ ratio of**
 3 **2:1 and microwave plasma of 700 W (a, c and e) three-dimensional surface plot; (b, d, and f)**
 4 **projected contour plot.**

5

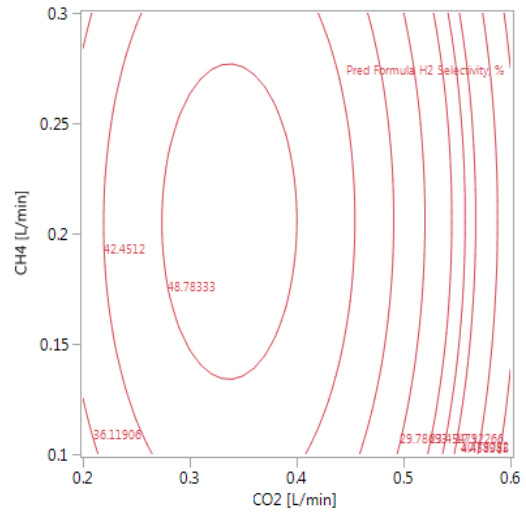
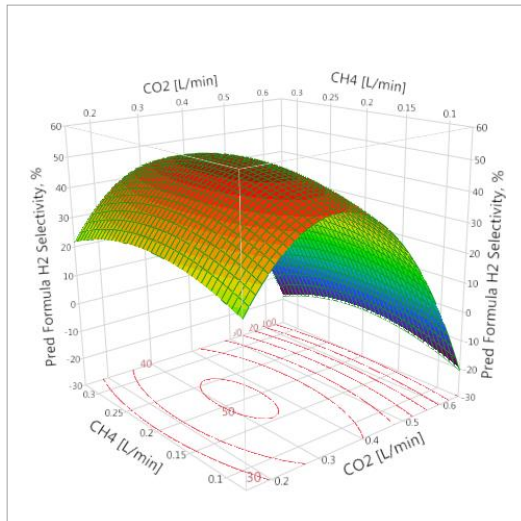
6 3.2.3 H₂ and CO Selectivity

7 The ANOVA results for the quadratic model are shown in Tables 6 and 7. In H₂ and CO selectivity, the
 8 terms x_2 , x_1^2 , x_2^2 and x_3^2 are identified as significant, while the terms x_1 , x_3 , x_1x_2 , x_1x_3 and x_2x_3 are not
 9 considered significant. These results indicate that the CO₂ term is more important than the interactions
 10 between various parameters in term of selectivities of H₂ and CO. As shown in Tables 6 and 7, the CO₂
 11 flow rate has the highest F-value while it is 307.7060 and 1141.848 for CH₄ and CO respectively, so it
 12 reflected the most significant effect on selectivities of H₂ and CO. The highest H₂ and CO selectivities
 13 of 51.31% and 61.17% were achieved at the optimal gas feed flow rate of CH₄ (0.19 L min⁻¹), CO₂ (0.38
 14 L min⁻¹) and N₂ (1.49 L min⁻¹), respectively. The effect of different factors and their interaction on
 15 selectivities of H₂ and CO are shown by the 3D response surface plots and 2 D contour lines and
 16 represented by Eqs. (13) and (14), as shown in Figures 6 and 7. The reduction in selectivities of H₂ and
 17 CO could be related to the consumed time for gases inside the microwave discharge zone, which was
 18 reduced with increasing flow rates of the gases [58], as shown in Figures 6 and 7(b, d, and f).

19 This behaviour is similar to that reported previously [38, 40-43, 45, 59, 60]; these studies have shown
 20 that the conversions of CH₄ and CO₂ and selectivities of H₂ and CO were decreased with increasing gas
 21 feed flow rates. The interactions between the two parameters on the selectivities of H₂ and CO are not
 22 considered significant as illustrated in Tables 6 and 7 respectively. This was confirmed when high p-
 23 values (p-values for x_1 , x_3 , x_1x_2 , x_1x_3 and x_2x_3) for H₂ and CO selectivity were obtained. It was 0.5561,
 24 0.7881, 0.9378, 0.4774 and 0.7833 for H₂ and 0.7263, 0.9378, 0.9828, 0.7579 and 0.6810 for CO.

25 (a)

(b)

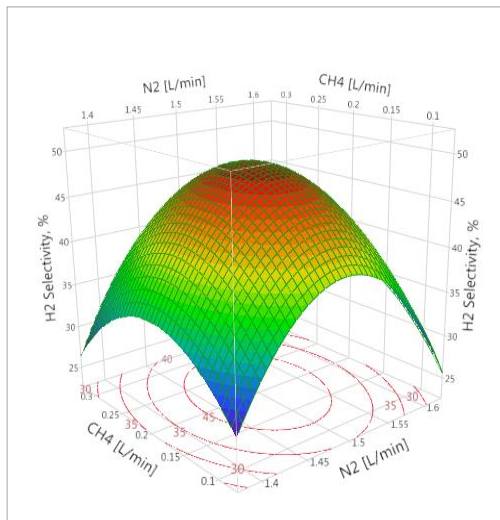


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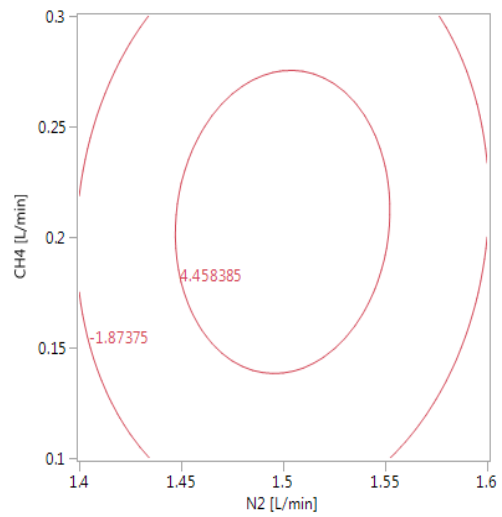
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(c)



(d)



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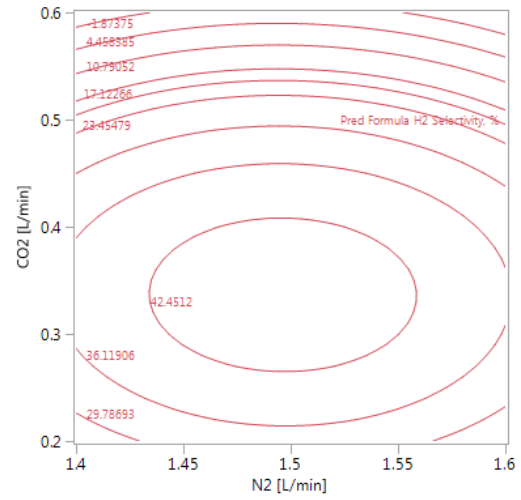
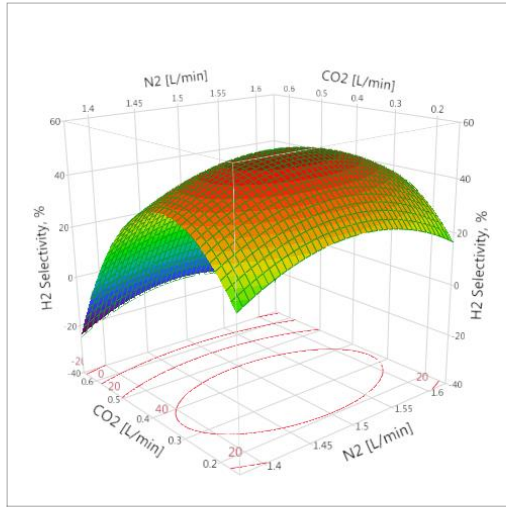
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(e)

(f)



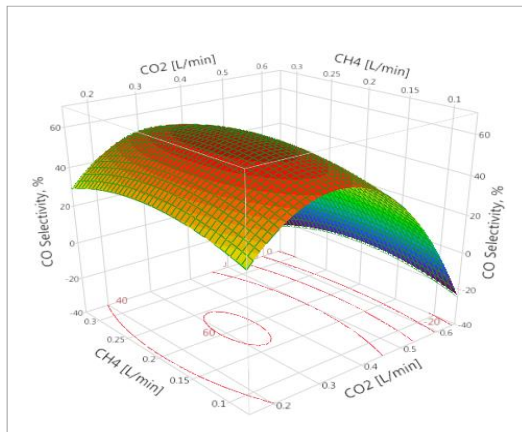
1

2 **Fig. 6. Effect of feed gas flow rates and their interaction on H₂ selectivity at a CO₂:CH₄ ratio of**
 3 **2:1 and microwave plasma of 700 W (a, c, and e) three-dimensional surface plot; (b, d, and f)**
 4 **projected contour plot.**

5

6

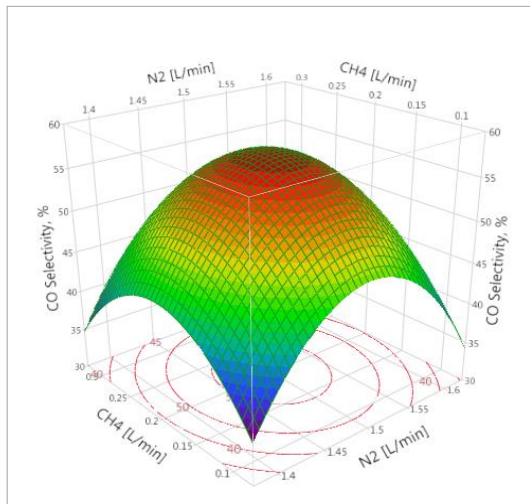
(a)



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8

(c)

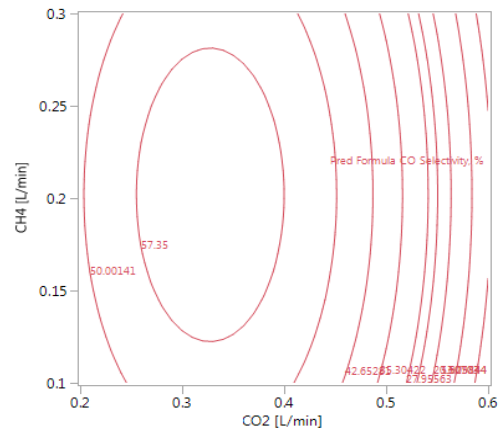


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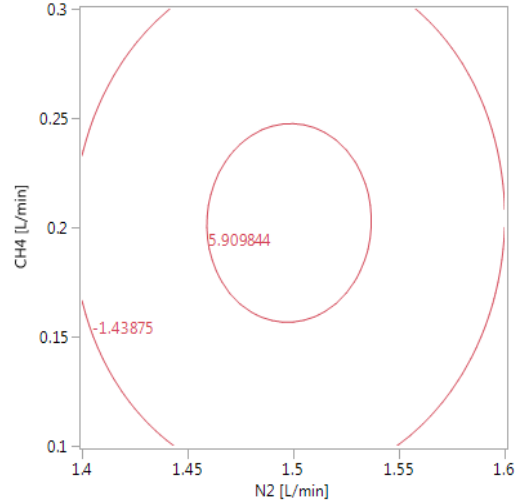
10

(e)

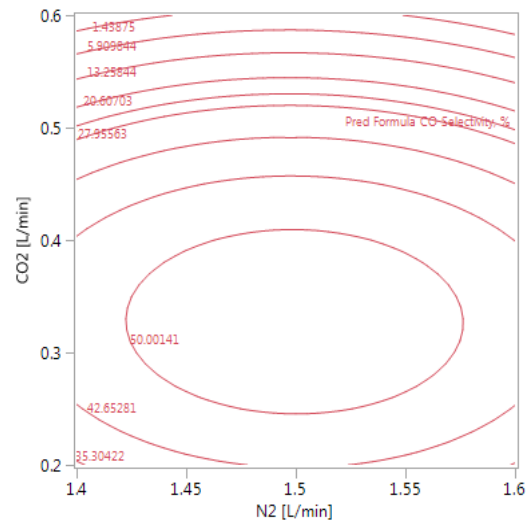
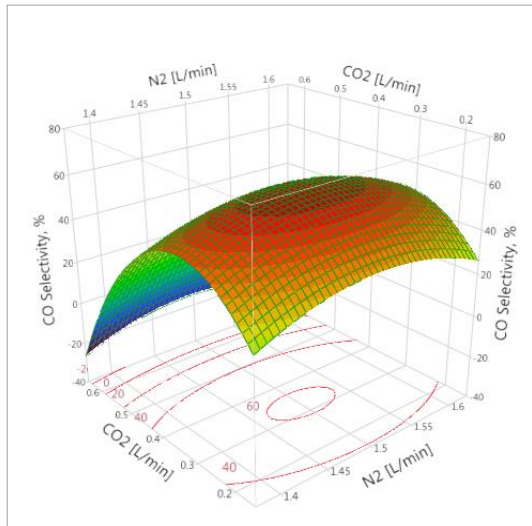
(b)



(d)



(f)



1

2 **Fig. 7. Effect of feed gas flow rates and their interaction on CO selectivity at a CO₂:CH₄ ratio of**
 3 **2:1 and microwave plasma of 700 W (a, c and e) three-dimensional surface plot; (b, d and f)**
 4 **projected contour plot.**

5

6 **4. Desirability and Optimum conditions**

7 The optimum operating conditions were determined for several input variables, which led to obtaining
 8 the desirable output response values. Desirability Function (DF) method is used to prove the optimal
 9 approaches of multiple responses. Also, the values of DF are dimensionless and ranged from zero to one
 10 (zero means the unacceptable response value while one represents gaining the goal) [61]

11 In this research, the maximised desirability flow rates of CO₂, CH₄ and N₂ is 0.92. This value for the
 12 desirability gives strong supporting to the fitting model. The optimal experimental conditions were
 13 achieved at CH₄ = 0.19 L/min, CO₂ = 0.38 L/min and N₂ = 1.49 L/min, respectively. The validity of the
 14 equations of the model (Eqs. 17-21) is good with a reasonable error, as shown in Table 8.

15 Therefore, the balance between conversions (CH₄, CO₂ and N₂) and selectivities (H₂ and CO) is important
 16 in the development of an active plasma process for CH₄ and CO₂ conversions. Thus, the performance of
 17 the plasma process generally depends on a wide range of operating conditions and especially on the flow
 18 rates. It is necessary and fundamental for optimising the performance plasma process with multiple
 19 inputs and multiple responses. This study aims to optimise the process to find the plasma process
 20 variables (various parameters) that jointly optimise the CH₄, CO₂ and N₂ conversions and selectivities
 21 of H₂ and CO (various responses).

22

23 Table 9 summarises the results of conversions and selectivities in the previous studies compared with
 24 those in this work. It has been demonstrated that this study obtained acceptable results amongst others.
 25 All previous reports were done a different operating conditions which are higher than those used in this
 26 study including the flow rate, CO₂/CH₄ ratio and microwave power. In this research, the total feed flow
 27 rate of 2.04 L min⁻¹, CO₂/CH₄ ratio of 2/1 and microwave power of 700 W were used for producing

1 microwave plasma with a good performance. The conversions of CH₄, CO₂ and N₂ were 84.91%, 44.40%
2 and 3.37%, in sequence while the selectivities of H₂ and CO were 51.31% and 61.17%, respectively.
3 Hwang [40] claimed that the highest selectivities can be achieved at high feed flow rate and input power.
4 Although they used an input power of 1000 W and total flow rate of 20 L min⁻¹ which were higher than
5 those in the present work, the conversion in this study is greater than their conversion. In addition, Long,
6 Shang [38] found that the conversions of CH₄ and CO₂ and selectivities of H₂ and CO were changed with
7 increasing flow rate also the optimum flow rate and input power were 16.667 L min⁻¹ and 770 W
8 respectively. However, as shown in Table 9, the present conversions were higher than their conversions.
9 Moreover, Chun and Lim [62] reported that the microwave discharge affected the stability of plasma and
10 the process performance. It can be shown in Table 9, that their conversions of CH₄ and CO₂ at a low total
11 flow rate (2.25 ml. min⁻¹) and a high microwave energy (2000W) was lower than the conversions of CH₂
12 and CO₂ in this study.

13 Furthermore, Fidalgo and Menéndez [63] investigated how the flow rate and microwave energy affected
14 the CH₄ and CO₂ conversions and selectivities of H₂ and CO. They claimed that the maximum CH₄ and
15 CO₂ conversions and the selectivities of H₂ can be obtained at high total flow rate of 33.34 L min⁻¹ and
16 microwave power of 83000 W. Their results were higher than the present results although they used
17 lower specific energy which was due to using a microwave laboratory pilot plant with CO₂ gas as the
18 plasma generation gas. Eventually, Chun, Hong [64] pointed out that microwave power affected the
19 plasma stability and performance of the process. They noticed that the CH₄ and CO₂ conversions and the
20 H₂ and CO selectivities were improved at the total flow rate of 30 L min⁻¹ and the high microwave power
21 of 6000 W. They used feed flow rates and power a higher than this work but the results in term
22 conversions and selectivities were fairly close, as shown in Table 9. It seems that the results of this
23 research are more reliable for conversion of CO₂ and CH₄ and producing CO and H₂ with high
24 selectivities.

25

Table 2. Actual values of the independent variables with the experimental and predicted values in the Box-Behnken Design

Run order	Actual Values			Response Values, CH ₄ Conversion [%]		Response Values, CO ₂ Conversion [%]		Response Values, N ₂ Conversion [%]		Response Values, H ₂ Selectivity [%]		Response Values, CO Selectivity [%]	
	X ₁	X ₂	X ₃	^d Experimental of CH ₄ Conversion	Predicted of CH ₄ Conversion	^d Experimental of CO ₂ Conversion	Predicted of CO ₂ Conversion	^d Experimental of N ₂ Conversion	Predicted of N ₂ Conversion	^d Experimental of H ₂ Selec.	Predicted of H ₂ Selec.	^d Experimental of CO Selec.	Predicted of CO Selec.
1^a	0.2	0.4	1.5	70.29	72.36	38.65	40.35	2.77	2.87	43.61	45.36	51.75	53.33
2^b	0.2	0.4	1.5	72.1	72.36	40.71	40.35	2.84	2.87	45.88	45.36	53.92	53.33
3	0.1	0.4	1.6	39.77	44.74	32.69	31.63	2.25	2.31	30.75	31.49	39.04	39.58
4	0.1	0.2	1.5	60.49	54.33	27.47	27.35	2.61	2.51	33.67	31.39	41.33	40.07
5	0.2	0.2	1.6	62.68	63.85	18.69	19.89	2.31	2.35	27.64	29.16	37.91	38.62
6	0.3	0.2	1.5	58.09	65.07	22.71	20.43	2.46	2.52	33.27	32.28	41.26	40.46
7	0.2	0.6	1.6	0	-2.01	0	-1.21	0	-0.08	0	-1.73	0	-1.33
8	0.1	0.4	1.4	44.94	53.11	33.67	32.62	2.14	2.24	32.35	32.88	40.11	40.01
9	0.2	0.6	1.4	0	-1.17	0	-1.21	0	-0.04	0	-1.52	0	-0.71
10	0.3	0.4	1.6	68.81	69.94	25.41	26.48	2.34	2.24	34.99	34.46	40.47	40.55
11^c	0.2	0.4	1.5	73.79	72.36	41.68	40.35	2.99	2.87	46.61	45.36	54.33	53.33
12	0.1	0.6	1.5	0	-6.98	0	-2.27	0	-0.04	0	-0.98	0	-0.79
13	0.2	0.2	1.4	59.27	57.24	21.85	23.05	2.54	2.55	26.23	27.98	36.47	37.81
14	0.3	0.6	1.5	0	-6.14	0	0.13	0	0.11	0	2.27	0	1.26
15	0.3	0.4	1.4	56.74	51.77	27.59	30.83	2.52	2.66	32.85	34.52	40.46	42.92

^{a-c}Replicated experimental runs (Run order 1, 2, and 14); ^dResponses are shown as the means of three replicates with a standard deviation

Table 3. ANOVA results for the quadratic regression model of CH₄ conversion

Model Terms	B^a	SE^b	SS^c	DF^d	F-Value	P-Value
<i>Intercept</i>	77.806667	5.366206	-	-	-	-
<i>X₁</i>	6.41625	3.286116	329.3461	1	3.8124	0.1083
<i>X₂</i>	-32.32875	3.286116	8361.1846	1	96.7859	<.0001*
<i>X₃</i>	2.635	3.286116	55.5458	1	0.6430	0.4590
<i>X₁ X₂</i>	0.645	4.64727	1.6641	1	0.0193	0.8950
<i>X₁ X₃</i>	7.1375	4.64727	203.7756	1	2.3588	0.1852
<i>X₂ X₃</i>	-0.9175	4.64727	3.3672	1	0.0390	0.8513
<i>X₁²</i>	-9.845833	4.837032	357.9339	1	4.1433	0.0974
<i>X₂²</i>	-36.08583	4.837032	4808.0764	1	55.6564	0.0007*
<i>X₃²</i>	-8.938333	4.837032	294.9925	1	3.4147	0.1239

R², 0.97; ^aCoefficient; ^bStandard error; ^cSum of Squares; ^dDegrees of freedom; f-values and p-values

Table 4. ANOVA results for the quadratic regression model of CO₂ conversion

Model Terms	B^a	SE^b	SS^c	DF^d	F-Value	P-Value
<i>Intercept</i>	43.386667	1.404953	-	-	-	-
<i>X₁</i>	-2.4375	0.860354	47.5312	1	8.0267	0.0365
<i>X₂</i>	-12.19375	0.860354	1189.5003	1	200.8722	<.0001*
<i>X₃</i>	-0.84875	0.860354	5.7630	1	0.9732	0.3692
<i>X₁ X₂</i>	1.2825	1.216725	6.5792	1	1.1110	0.3401
<i>X₁ X₃</i>	-0.3225	1.216725	0.4160	1	0.0703	0.8015
<i>X₂ X₃</i>	0.85	1.216725	2.8900	1	0.4880	0.5160
<i>X₁²</i>	-4.353333	1.266407	69.9748	1	11.8167	0.0185*
<i>X₂²</i>	-25.54583	1.266407	1109.5616	1	106.9052	<.0001*
<i>X₃²</i>	-6.940833	1.266407	177.8775	1	30.0384	0.0028*

R², 0.99; ^aCoefficient; ^bStandard error; ^cSum of Squares; ^dDegrees of freedom; f-values and p-values

Table 5. ANOVA result for the quadratic regression model of N₂ conversion

Model Terms	B^a	SE^b	SS^c	DF^d	F-Value	P-Value
<i>Intercept</i>	3.0866667	0.079819	-	-	-	-
<i>X₁</i>	0.0425	0.048879	0.014450	1	0.7560	0.4243
<i>X₂</i>	-1.335	0.048879	14.257800	1	745.9609	<.0001*
<i>X₃</i>	-0.0425	0.048879	0.014450	1	0.7560	0.3207
<i>X₁ X₂</i>	0.04	0.069125	0.006400	1	0.3348	0.5879
<i>X₁ X₃</i>	-0.08	0.069125	0.025600	1	1.3394	0.2994
<i>X₂ X₃</i>	0.065	0.069125	0.016900	1	0.8842	0.3902
<i>X₁²</i>	-0.265833	0.071948	0.260926	1	13.6515	0.0141*
<i>X₂²</i>	-1.455833	0.071948	7.825664	1	409.4348	<.0001*
<i>X₃²</i>	-0.325833	0.071948	0.392003	1	20.5094	0.0062*

R², 0.97; ^aCoefficient; ^bStandard error; ^cSum of Squares; ^dDegrees of freedom; f-values and p-values

Table 6. ANOVA result for the quadratic regression model of H₂ selectivity

Model Terms	B^a	SE^b	SS^c	DF^d	F-Value	P-Value
<i>Intercept</i>	48.783333	1.511944	-	-	-	-
<i>X₁</i>	0.58375	0.925873	2.7261	1	0.3975	0.5561
<i>X₂</i>	-16.24125	0.925873	2110.2256	1	307.7060	<.0001*
<i>X₃</i>	0.2625	0.925873	0.5513	1	0.0804	0.7881
<i>X₁ X₂</i>	0.1075	1.309382	0.0462	1	0.0067	0.9378
<i>X₁ X₃</i>	1.005	1.309382	4.0401	1	0.5891	0.4774
<i>X₂ X₃</i>	-0.38	1.309382	0.5776	1	0.0842	0.7833
<i>X₁²</i>	-5.032917	1.362848	93.5271	1	13.6378	0.0141*
<i>X₂²</i>	-25.75292	1.362848	1448.7854	1	257.0736	<.0001*
<i>X₃²</i>	-8.545417	1.362848	269.6276	1	39.3162	0.0015*

R², 0.97; ^aCoefficient; ^bStandard error; ^cSum of Squares; ^dDegrees of freedom; f-values and p-values

Table 7. ANOVA result for the quadratic regression model of CO selectivity

Model Terms	B ^a	SE ^b	SS ^c	DF ^d	F-Value	P-Value
<i>Intercept</i>	57.35	1.019677	-	-	-	-
X_1	0.23125	0.624422	0.4278	1	0.1372	0.7263
X_2	-21.1	0.624422	3561.6800	1	1141.848	<.0001*
X_3	0.05125	0.624422	0.0210	1	0.0067	0.9378
$X_1 X_2$	0.02	0.883066	0.0016	1	0.0005	0.9828
$X_1 X_3$	0.2875	0.883066	0.3306	1	0.1060	0.7579
$X_2 X_3$	-0.385	0.883066	0.5929	1	0.1901	0.6810
X_1^2	-6.05375	0.919125	135.3153	1	43.3811	0.0012*
X_2^2	-29.09125	0.919125	3124.8031	1	1001.788	<.0001*
X_3^2	-8.26375	0.919125	252.1461	1	80.8361	0.0003*

R², 0.99; ^aCoefficient; ^bStandard error; ^cSum of Squares; ^dDegrees of freedom; f-values and p-values

Table 8. Comparison between the experimental and predicted data at optimum conditions

Parameters [L/min]	Response [%]	Experimental Data [%]	Predicted Data [%] (Eqs. (17-21))	Error [%]
CH ₄ = 0.19	CH ₄ Conversion	79.35	80.64	1.59
CO ₂ = 0.38	CO ₂ Conversion	44.82	43.15	3.72
N ₂ = 1.49	N ₂ Conversion	3.22	3.08	4.34
	H ₂ Selectivity	50.12	50.24	0.23
	CO Selectivity	58.42	57.33	1.86

Table 9. Comparison between previous studies with the current study

Production method	Feed Gas Flow Rate [L min ⁻¹]			CO ₂ /CH ₄ Ratio	Total Flow Rate [L min ⁻¹]	*Specific energy [kJ L ⁻¹]	Power [W]	Conversion [%]			Selectivity [%]		Refs
	CO ₂	CH ₄	N ₂					CH ₄	CO ₂	N ₂	H ₂	CO	
Arc Jet Plasma (AJP)	2	2	16	1/1	20	0.00083	1000	50.74	35.55	NA	80.98	78.31	[40]
Cold Plasma Jet (CPJ)	3.334	5	8.334	2/3	16.667	0.0008	770	45.68	34.03	NA	78.11	85.41	[38]
Microwave reformer	1.5	0.75	NA	2/1	2.25	0.00148	2000	79.41	41.7	NA	NA	NA	[62]
Microwave pilot plant	16.67	16.67	NA	1/1	33.34	0.00415	8300	88.13	93.36	NA	75.37	69.72	[63]
Microwave plasma torch	15	15	NA	1/1	30	0.00334	6000	86.84	48.41	NA	54.61	65.92	[64]
Microwave Plasma	0.38	0.17	1.49	2/1	2.04	0.00571	700	84.91	44.40	3.37	51.31	61.17	This study

Not Available (NA)

5. Conclusions

The effect of the feed gas flow rates (CO_2 , CH_4 , and N_2) and their interactions on process performance to produce syngas (H_2 and CO) has been investigated by a microwave plasma reactor at atmospheric pressure. The conversions of CH_4 , CO_2 and N_2 and selectivities of H_2 and CO were determined and optimised. The Behnken-Box design and response surface methodology have been used to determine the interactions of feed flow rate variables in the dry reforming of methane technology. Regression models have been developed to describe the relationships between the feed flow rate variables and reaction performance (conversions and selectivities). ANOVAs were applied to estimate a significant interaction flow rates of CO_2 with CH_4 to produce H_2 and CO via the plasma process. The results show that the CO_2 and CH_4 conversion and selectivity of H_2 and CO decrease with the increasing the gas feed flow rate. The most significant effect on process parameters and process performances was had by the flow rate of CO_2 (x_2) compared with other parameters CH_4 (x_1) and N_2 (x_3). The interactions of different process parameters have a very weak effect on CH_4 , CO_2 and N_2 conversions and on H_2 and CO selectivities. The optimum coefficient of determination (R^2) of the regression equations for the CH_4 , CO_2 and N_2 conversion were 0.97, 0.99 and 0.97, respectively, while those of the selectivity of H_2 and CO were 0.98 and 0.97, respectively. The optimal CH_4 , CO_2 and N_2 conversion were 84.91%, 44.40% and 3.37%, respectively, and the selectivity of H_2 and CO were 51.31% and 61.17%, respectively. The optimal plasma condition was achieved when the gas feed flow rates of CH_4 , CO_2 and N_2 were 0.19, 0.38, and 1.49 L min^{-1} , respectively. The experimental results under the theoretical optimal conditions have explained the ability and reliability of the DoE for understanding the effect of process variables and their interaction on the process parameters and performances.

Competing financial interests

The authors declare no competing financial interests.

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Nomenclature

Abbreviations

BBD	Box-Behnken Design
RSM	Response Surface Methodology
ANOVA	Analysis of Variance

Y Response

Symbol Description and units

CH₄ Methane Gas, L min⁻¹

CO₂ Carbon Dioxide Gas, L min⁻¹

N₂ Nitrogen Gas, L min⁻¹

H₂ Hydrogen Gas, L min⁻¹

CO Carbon Monoxide, L min⁻¹

Greek Characters

β Coefficient

Subscripts

β_0 Constant coefficient

β_i Coefficient for linear

x_i Initial input parameters

β_{ii} Quadratic coefficient

β_{ij} Coefficient for interactions

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