

Methanol Optimization in a DBD Plasma Reactor: Using RSM Method and Variables Survey

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ABSTRACT: In this study, direct conversion of methane to methanol in the plasma process was attended. Besides, RSM modeling for the optimization and evaluation of parameters likewise voltage, the flow rate of CH_4 , Ar, and external electrode length was used. RSM prediction model by the desired condition include minimized Ar (20 mL/min), O_2 (2 mL/min), CH_4 (2 mL/min), voltage (4 kV) was used to determine the effect of Ar and CH_4 in reactions. The results showed that growing up the Ar flow from 20 to 100 mL/min led to less methanol mole percent. On the other hand, enhancement in methane flow rate from 2 to 12 mL/min was the reason of raising the methanol mole percent at the outlet of the reactor. To determine how modifying the length of the external electrode affected the mole percent of methanol, the length was lowered from 12.5 to 2 cm, clearly reducing the amount of methane converted. However, it was effective to raise the methanol mole percent to 3% in E.EFF 0.13 mmole/kJ and length of electrode 4 cm. As well as the methanol mole percent in the least energy efficiency E.EFF 0.045 mmole/kJ detected at 2.27%. To summarize, in DBD plasma reactor by direct conversion of methane, increasing in voltage and Ar flow rate had a significant influence on the progress of the process which had an unfavorable effect on methanol mole percent. Meanwhile, the enhancement of CH_4 flow rate had an impressive effect on the raising of methanol. Furthermore, influence of oxygen flow was negligible.

KEYWORDS: Plasma DBD reactor; Methanol production; RSM modeling; Direct conversion of methane.

INTRODUCTION

These days, owing to environmental issues, the suitable combustion systems with the least amount of CO_2 emission were focused [1–5]. Besides, there are industrial ways to convert natural gas to valuable hydrocarbons likewise methanol, which are using the combustion systems to produce the energy for endothermic reactions.

Steam reforming, dry reforming and partial oxidation of methane are industrially used. Moreover, the plasma process and direct conversion of methane were recently studied as an eco-friendly process [6–11]. The direct conversion of methane by partial or total oxidation is one of the newest methods for the methanol production [12, 13].

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The problems of traditional methane reforming are many. Following CO₂ emission, these processes have substantial temperature and pressure issues [14]. Free radicals are essential to methane oxidation processes, and their chemistry is well recognized. Other researchers' low-pressure tests suggested that methane may be directly oxidized in plasma reactors to make methanol. However, the ability of a plasma-based methanol production process depends on its ability to convert large quantities of methane near the atmospheric pressure to increase the amount of the products [15]. On the other hand, the direct conversion of methane into methanol is not cost-effective, and the conventional methods of partial and total oxidation of methane have poor yields. Despite the fact that, the kinetics of reactions, and side reactions at each step of methanol production in the plasma process is not known yet. But, this process could be controlled and optimized by impressive parameters include applied voltage, power supply, the flow rate of gases, and the length of the electrode [2,16-18]. Active entities including electrons, ions, and radicals are created during the plasma process. Changes in voltage, plasma carrier gas, and feedstock flow rates are used to regulate these active forms. An important kind of plasma in which background gases have more energy than the average electron energy is known as non-equilibrium plasma [19]. Energized electrons collide with the background gases, neutral atoms, or molecules and they are ionized or dissociated. For this purpose and for the generation of plasma, the AC(alternative current), DC(direct current), or microwaves sources are used [20]. Among the present plasma reactors, dielectric barrier discharge (DBD) plasma reactor for special characteristics such as facility of using, lower cost, less possibility of sparks and dielectric materials is frequently used. Besides, it was confirmed for experimental simulation of chemical processes and for CH₄ reforming process [21–24]. Another point is, the physical properties of DBD reactors are so substantial. One of the characteristics which are seriously noticeable in studies is the residence time distribution, which is the function of various parameters same as reactor length, the roughness of the inner wall, and the shape of inner electrode [25]. In 2001, *Namihira et al.* showed that the energy of the discharge grows up by enhancement of reactor length. Furthermore, at the fixed gas flow rate and a fixed pulse repetition rate, the final concentrations

of feed gas were decreased by rising reactor length [26]. The study of, *Bahri et al.* demonstrated that rising in the residence time by utilizing a larger length of the inner electrode, could cause earlier plasma ignition, as well as the formation of larger amounts of ozone for given specific input energy[27]. In 2012, *Wang et al.* explored the impact of reactor length in the DBD for ambient temperature non-thermal plasma processing of NO to N₂. They demonstrated how conversion efficiency decreases as the inner electrode diameter becomes smaller. In order to convert CH₄ into higher hydrocarbons, *Wang et al.* demonstrated the impact of external electrode length in a micro-DBD plasma reactor. He examined six different electrodes (10, 12, 14, 16, 20 cm).He showed that the most conversion of methane is provided while the length of external electrode is equal to 10 cm [28].

Nevertheless, besides experimental methods, the computation techniques for illustration of effective parameters on plasma, including control of non-inductive scenarios, fast ion instabilities, plasma boundary physics, heat load management, and disruption prediction, are noticeable [29]. Moreover, numerical methods to solve problems in the plasma process were explored in recent searches [29]. In 2019, *Wehner et al.* showed that numerical optimization methods can be used for the plasma-control problems and optimization [30]. Furthermore, researchers used computation methods that could give the stability to any equilibrium solution, uniquely specified by the plasma boundary shape, as well as pressure and safety factor profiles [31]. Methods that are assisted by computers have found multiple applications in tokamak research, including nonlinear regression for the energy confinement scaling, neoclassical transport, rapid determination of equilibria, electron temperature profiles, and charge exchange spectra, classification of disruption, and L-H transition onsets [32].

The major disadvantage of some computation techniques is that it does not include the interactive effects among the variables and, eventually, it does not show the complete effects of parameters on the process [33]. To overcome this problem, optimization studies can be carried out using Response Surface Methodology (RSM). RSM is a collection of statistical and mathematical techniques useful for developing, improving, and optimizing processes in which a response of interest is affected by several variables

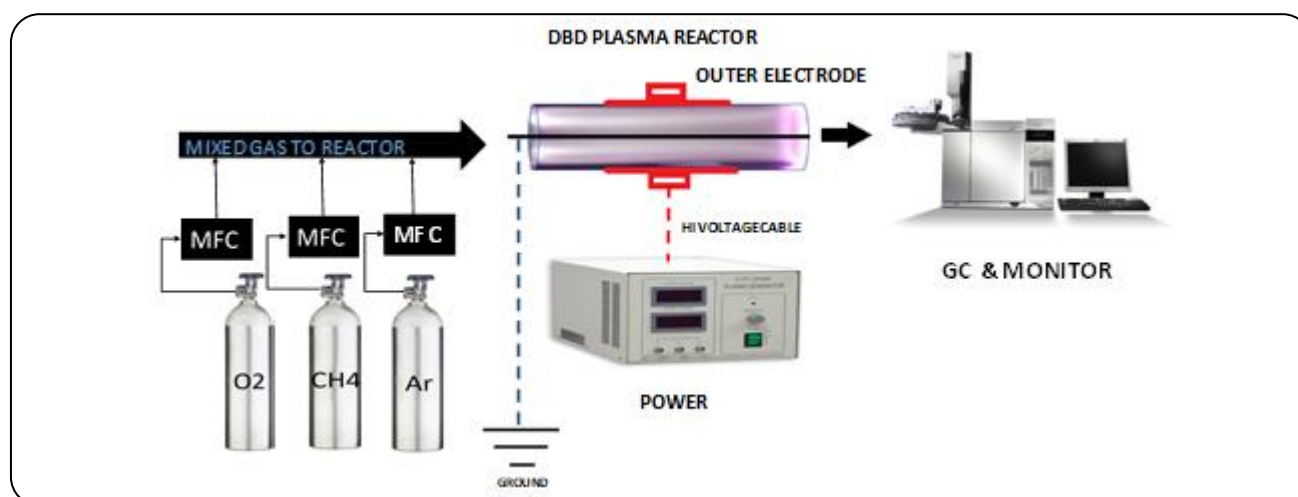


Fig1: Schematic diagram of system and DBD reactor

and the objective is to optimize this response [33]. RSM has important application in the design, development and formulation of new products, as well as in the improvement of existing product design. The response of surface describes the effect of the independent variables, alone or in combination, on the processes. Besides analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which explains the chemical or biochemical processes [33]. Arguably, RSM was very popular for optimization studies in recent years. Some examples of the RSM applications performed for optimization of the chemical process are studying the catalytic performance in plasma [34], degradation of toluene [35], packed bed plasma reactor [36], energy efficiency improvement [37] dry reforming of methane [38], photocatalytic process [39]. RSM is used for kinetic constant calculation and research kinetics in addition to optimization. RSM was used by *Beg et al.* to calculate the kinetic constants for enzyme kinetics. Additionally, RSM was used to assess the alcohol dehydrogenase simple enzyme kinetics [33].

By this background, the present research was aimed at the comprehension of valuable hydrocarbons production with a focus on methanol in the partial oxidation of methane. Some factors, such as the discharge power, external electrode length, and catalyst that may influence the plasma reaction, were investigated. Various parameters were optimized by the objective of achieving the best methanol mole percent and reducing the specific input energy.

EXPERIMENTAL SECTION

DBD tubular reactor

Fig.1 shows the schematic diagram of the system and DBD reactor. Conversion of methane into products has happened at a quartz glass tube with an outer diameter of 14 mm, 1 mm wall thickness, and 25 cm reactor length. The dielectric material (glass) has been used for the separation of inner and outer electrodes. The inner electrode was stainless steel and the outer one was from the copper that was wrapped around the quartz tube and fixed at the length of 12.5 cm for experimental design and RSM prediction. Moreover, the reactor's length was decreased from 12.5 to 8, 4, and 2 cm, respectively, in order to study the impact of length on the products and energy consumption. The plexiglass supports that held the inner electrode in place. These supports help to prevent the localization of the electric region and to provide a consistent discharge zone. The outer electrode was connected to the earth because the inner electrode was connected to a high voltage. The vital tests for the examination occurred in two levels of feedstock methane, 6, 12 mL/min, and for testing the software. The final tests took place by 9 mL/min methane as feed.

Circuit setup

A high voltage generator has been used to produce the required voltage up to 12 kV. By raising the voltage and falling it from 2 kV up to 10 kV, the experiments were performed. The applied voltage and current are measured using a high voltage probe (Tektronix, P6015A, 1000:1) and a current probe (Pearson 150, 2A/V), respectively. The output

Table 1: experimental parameters for RSM prediction

parameter	value/characteristic
frequency(kHz)	20
High voltage electrode diameter (mm)	2
High voltage electrode material	stainless still
Ground electrode material	copper
CH ₄ flow rate (mL/min)	2,6,12
O ₂ flow rate (mL/min)	2,4,6,12
Electrode length (cm)	12.5

signals are transmitted to a high-speed oscilloscope (Tektronix TDS 1012B-SC, bandwidth of 100 MHz, and a time resolution of 1 GS/s). The average power delivered to the reactor can be calculated using Eq. (1):

$$P_{av} = V_e \cdot I \cdot \cos(\phi) \quad (1)$$

Where (V_e) is the effective voltage that read from the monitor, (I) is the current that showed by the monitor and (ϕ) is equal to 0.1 for plasma generator. Five different applied voltages, including 2,4,6,8 and 10 kV are selected to analyze the effect of applied voltage on plasma performance and RSM prediction. In order to evaluation of the effect of Ar, O₂ and CH₄ flow rate on reactions, the frequency was fixed at 20 kHz in this study.

Experimental parameters and product analysis

The carrier gas was Argon (99.999 %) and it combined with CH₄ (99.999%) and O₂ (99.999%). The gas was analyzed by a Gas Chromatograph (G.C) and three mass flow controllers measured the flow of gases. A volumetric flow controller detected the gas flow in the reactor's output. The conversion of reactants, selectivity, and yield of products was calculated as follows:

Conversion % =

$$\left(\frac{\text{mmole flow of CH}_4 \text{ input} - \text{mmole flow of CH}_4 \text{ output}}{\text{mmole flow of CH}_4 \text{ input}} \right) * 100 \quad (2)$$

Moreover, mole flow of CH₄ is calculated using the Equation (3):

$$\text{mmole flow of CH}_4 = \left(\frac{P \cdot V}{M_w} \right) \quad (3)$$

E. EFF = Energy efficiency $\left(\frac{\text{mmole}}{\text{kJ}} \right) =$

$$\frac{\text{CH}_4 \text{ Converted} \left(\frac{\text{mole}}{\text{min}} \right)}{P(W)} * \left(\frac{1000}{60} \right) \quad (4)$$

SIE = System internal energy $\left(\frac{J}{\text{mL}} \right) =$

$$\frac{60 * P(W)}{\text{Total gas flow rate} \left(\frac{\text{mL}}{\text{min}} \right)} \quad (5)$$

In which ρ , v , and M_w are the density of CH₄, the volumetric flow of CH₄ (mmole/min), and the molecular weight of CH₄. For measuring the applied power and determination of the effects of frequency, voltage, and carrier gas, the experimental conditions were adjusted to fix the situation according to Table 1.

The experimental design and procedure of RSM

Experimental design for RSM prediction and modeling

Statistical optimization used to evaluate and optimize the effect of factors on product concentration in the reactor. Among the statistical optimization methods, RSM has a significant efficient tool. For investigating the effect of variables on functions or quality characteristics of a process and determining the optimal conditions of a multivariate system [40], [41]. First of all, six different levels of Ar flow including 20, 30, 40, 50, 60, and 100 mL/min were selected to be analyzed. In addition, the CH₄ and O₂ flow rates changed from 2 to 12 mL/min, respectively. In some tests, to control the reaction toward precious products, the ratio (CH₄/O₂) fixed to 3/1. This ratio controls higher hydrocarbon production (including C₂ and C₃). Larkin et al. showed that variation of CH₄/O₂ ratio from pure methane to 3:1 led to enhancement of the methane reaction rate by a factor of three [15, 42, 43].

The tests occurred in 6 mL/min methane, 2 mL/min O₂ for level (1). The fixed flow rate of CH₄ used for analyzing the effect of the carrier gas, methane gas, and power. It determined that by mounting Ar flow from 20 to 50 mL/min, the conversion of methane increased sharply and from 50 to 60, it is steadily. Furthermore, the variation of voltage from 2 to 10 utilized for demonstrating the effect of this parameter on products.

In the second step, experiments in level (2) took place at 100 mL/min Ar, 12 mL/min methane, and 4 mL/min O₂. Furthermore, in terms of the enhancement in experimental points for the design of experiment software, the tests performed in a different situation and illustrated in Table 2. owing to, Minimum allowable voltage that plasma existed and maximum voltage which all the methane was disappeared, were respectively 2 and 10 Kv and mass flow meter of argon worked between 0 to 100 mL/min, there were limitations for the adjustment in voltage and flow. Therefore, the manual mode used for the design of experiment software. Table 2 show 25 exams that were possible for analysis by Design-Expert 7.0.0 software.

Table 2: manual experimental design

	Factor 1	Factor 2	Factor 3	Factor 4		Factor 1	Factor 2	Factor 3	Factor 4
Std	A:Flow of O2	B:Flow Of Ar	C:voltage	D:Flow of CH4	Std	A:Flow of O2	B:Flow Of Ar	C:voltage	D:Flow of CH4
	ml/min	ml/min	KV	ml/min		ml/min	ml/min	KV	ml/min
1	3	30	6	6	14	2	50	6	6
2	2	20	6	6	15	2	50	6	6
3	2	40	6	6	16	2	50	6	6
4	2	30	6	6	17	2	50	6	6
5	2	50	6	6	18	4	50	6	12
6	2	60	6	6	19	4	50	6	12
7	2	50	8	6	20	6	50	6	12
8	2	50	10	6	21	6	100	10	12
9	4	100	10	12	22	12	100	10	12
10	2	50	2	6	23	4	100	12	12
11	2	50	6	6	24	2	100	10	6
12	2	50	4	6	25	6	50	2	2
13	2	50	6	6					

Each experiment was repeated three times to assure the adequacy of the proposed model. Subsequently, analysis of variance (ANOVA) was performed to evaluate the significance and adequacy of the proposed model, as summarized in Table 3. The model proved significant and accurate in fitting the actual experimental results with “F-values” of 3.61, 38.49, and 3.66 for methanol, C₂, and C₃ at a “P-value” of less than 0.0287, 0.0001, and 0.0276, respectively. The “Lack of Fit P-value” are 0.2546, 0.6611, and 0.3456 for methanol, C₂, and C₃, implying that the lack of fit is not significant, and the proposed model is proved to have the capability of high predictable. Furthermore, the results of R² values of 0.8574, 0.9847, and 0.8651 demonstrate the acceptable correlation between predicted and experimental results of models. The empirical model summarized as a function of coded factors for methanol, C₂, and C₃, as presented in Equations (6), (7), and (8):

$$M = -0.41 - 0.25A + 5.89B - 6.27C - 4.63D + 3.89AB - 6.83AC - 2.47AD + 8.72BC + 7.35BD - 15.4CD - 0.18A^2 - 2.82B^2 + 3.64C^2 - 2.56B^3 + 3.97A^3 \quad (6)$$

$$C_2 = 0.25 - 0.51A + 2.01B - 0.046C - 0.12D + 2.02AB - 0.89AC + 1.49AD + 5.05BC - 2.97BD - 0.22CD - 1.75A^2 - 0.51B^2 + 0.57C^2 - 0.82B^3 + 0.61C^3 \quad (7)$$

$$C = -0.58 - 1.2A + 2.91B - 3.38C - 0.84D + 3.75AB - 4.34AC + 0.64AD + 2.9BC - 0.27BD -$$

$$4.23CD - 1.39A^2 - 0.039B^2 + 2.92C^2 - 0.63B^3 + 3.36C^3 \quad (8)$$

In above equation, M, C₂, and C₃ represent methanol, C₂, and C₃ mole percent, A, B, C, and D stand for flow of O₂, the flow of Ar, voltage, and flow of methane, respectively. The signs (+) and (-) represent the positive and negative effects from the point of view of the plasma degradation process.

It obviously showed that the methanol mole percent has most considerably affected by voltage compared to other variables in DBD plasma (Table 3). Besides, the flow of methane and argon has a significant effect on methanol mole percent by comparison with the F values. Similar to how oxygen flow rate was shown to have a more dominating influence than other factors for C₂ and C₃ concentration, with the accompanying F-values. Finally, the results of modeling as three-dimensional surface plots of methanol, C₂, and C₃ as a function of four independent variables (flow of O₂, flow of Ar, voltage, and flow of methane) presented Fig. 2, Fig.3, and Fig.4.

Test the results of RSM modeling

For testing the models provided by RSM software for mole percent of methanol and C₂, C₃ the experiments performed in different levels. In level (3) by 9 mL/min methane, 3 mL/min O₂ as feed, and 90 mL/min Ar as a carrier gas in DBD plasma reactor. The results of changing the voltage in level (3) demonstrate that by the decline of voltage,

Table 3: ANOVA results of response surface cubic models

Source	Methanol			C2			C3		
	Sum of Squares	F Value	p-value	Sum of Squares	F Value	p-value	Sum of Squares	F Value	p-value
Model	1.12	3.61	0.0287	6.08	38.49	<0.0001	2.2	3.66	0.0276
A-Flow of O2	2.43E-03	0.12	0.7397	0.01	0.97	0.3511	0.055	1.37	0.2712
B-Flow Of Ar	0.041	1.99	0.1915	4.79E-03	0.46	0.5167	0.01	0.25	0.6285
C-voltage	0.07	3.4	0.0981	3.86E-06	3.67E-04	0.9851	0.02	0.51	0.493
D-Flow of CH4	0.039	1.89	0.2023	2.45E-05	2.33E-03	0.9625	1.30E-03	0.032	0.8613
AB	0.08	3.88	0.0803	0.022	2.06	0.1846	0.075	1.87	0.2051
AC	0.069	3.32	0.1017	1.16E-03	0.11	0.7474	0.028	0.69	0.4274
AD	0.039	1.88	0.2039	0.014	1.35	0.2749	2.62E-03	0.065	0.8041
BC	0.021	1	0.3425	6.96E-03	0.66	0.437	2.31E-03	0.057	0.8159
BD	0.038	1.81	0.2109	6.14E-03	0.58	0.4643	5.13E-05	1.28E-03	0.9723
CD	0.044	2.15	0.177	9.31E-06	8.85E-04	0.9769	3.34E-03	0.083	0.7793
A^2	4.45E-03	0.21	0.654	0.43	41.27	0.0001	0.27	6.84	0.0281
B^2	0.026	1.26	0.2898	8.60E-04	0.082	0.7815	5.13E-06	1.28E-04	0.9912
C^2	0.13	6.41	0.0321	3.27E-03	0.31	0.5909	0.085	2.12	0.179
B^3	0.02	0.98	0.3491	2.05E-03	0.2	0.669	1.23E-03	0.031	0.8651
C^3	0.12	5.95	0.0374	2.89E-03	0.27	0.6129	0.088	2.2	0.1719
Residual	0.19			0.095			0.36		
Lack of Fit	0.06	1.67	0.2546	0.011	0.44	0.6611	0.094	1.24	0.3456
Pure Error	0.13			0.084			0.27		
Cor Total	1.31			6.17			2.56		

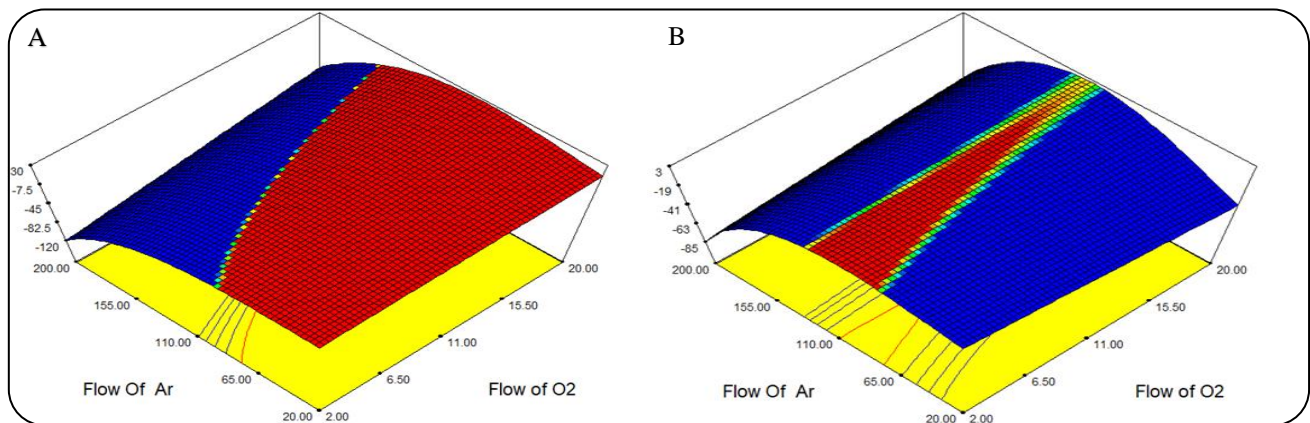
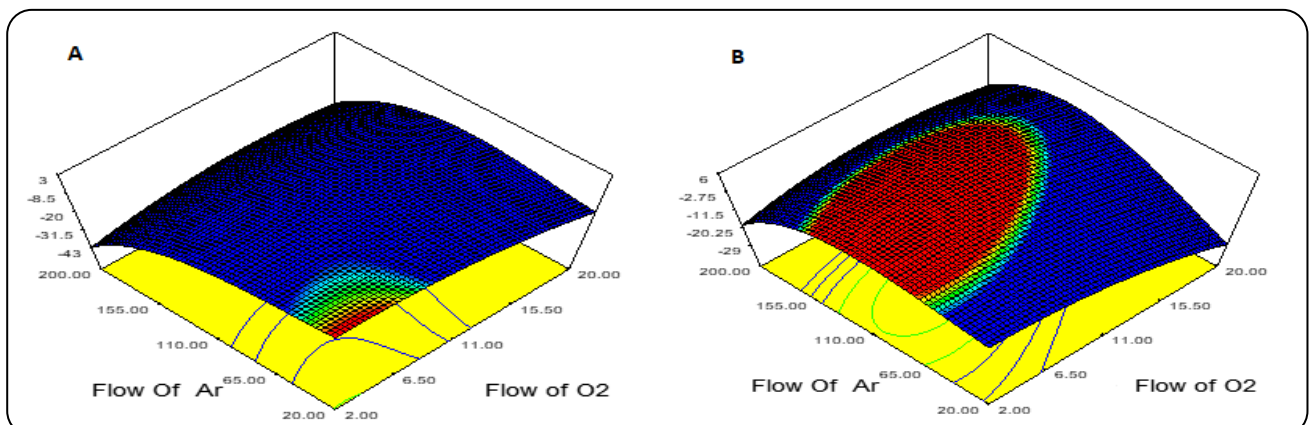


Fig 2: Response of surface for methanol mole percentage with increasing voltage from 2Kv (A) to 12Kv (B) and 6 mL/min methane feed

Fig3: Response of surface for C₂ mole percentage with increasing voltage from 2Kv (A) to 12Kv (B) and 6 mL/min methane feed

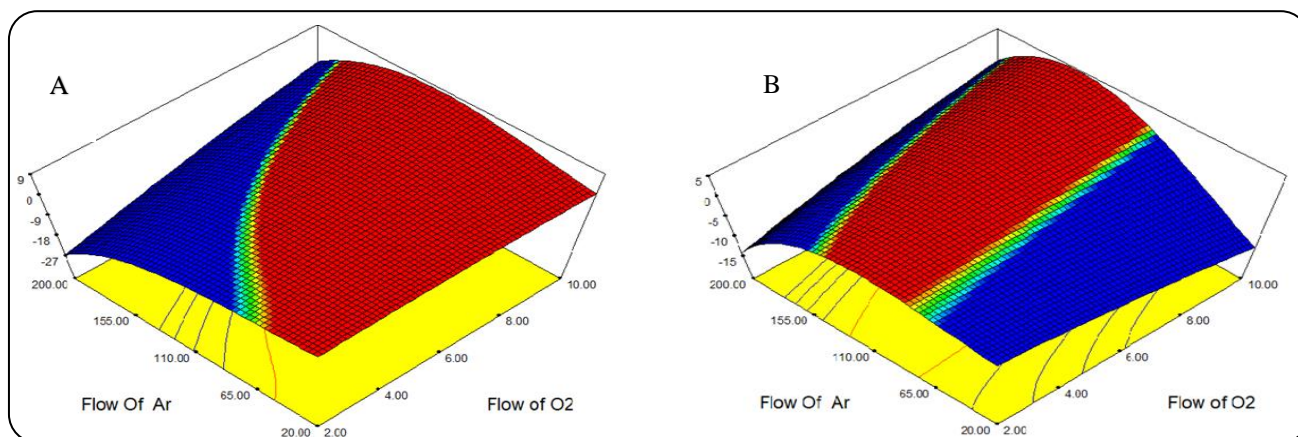


Fig4: Response of surface for C3 mole percentage with increasing voltage from 2Kv (A) to 12Kv (B) and 6 mL/min methane feed

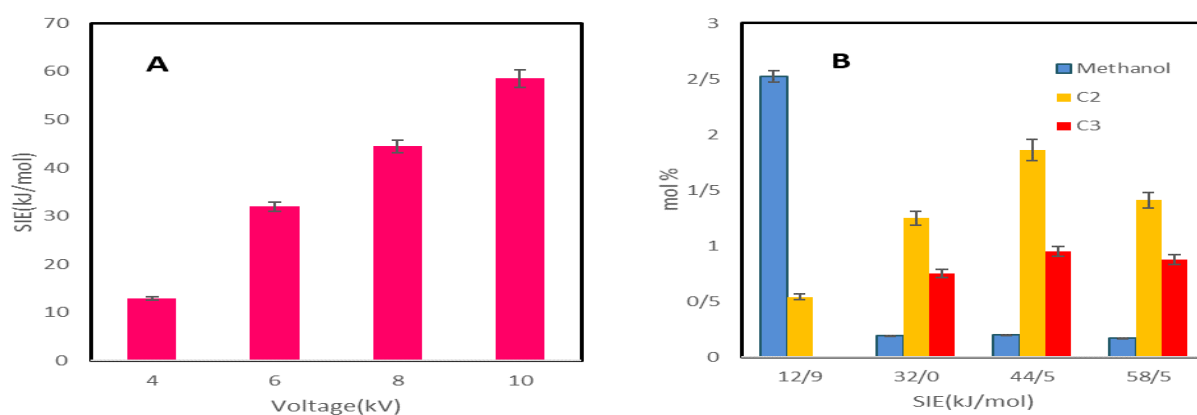


Fig 5: Effect of voltage in SIE (A), variation of products percentage (B)

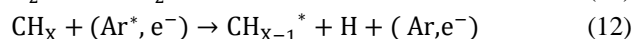
the concentration of methanol rises (Fig 4). Moreover, the results of the Table 1 that was prepared by RSM modeling show that low voltages have a major effect on the enhancement of methanol concentration. On the other hand, increasing voltage has a negative effect on C₂, C₃ concentration in RSM modeling (Fig 2, 3, and Fig 4), if the situation of level (3) is considered. Consequently, as mentioned before the prediction model is reliable.

RESULTS AND DISCUSSION

The effect of applied voltage on power supply and products

Based on what Fig5A shows, the voltage has a significant effect on the power supply, and SIE parameter that represent power per volume unit of total gas. Four different applied voltages, including 4, 6, 8, and 10 kV tested in the plasma system. It is observed that generally by increasing in the applied voltage from 4 to 10 kV, the SIE raised from 12.88 to 58.53 J/mL, consequently. Because of enhancement in the voltage and different

potential between the anode and cathode electrode, the number of electrons increased in the electrical field. Furthermore, based on Equation 5 rising the power and consumption of energy, it can be a reason of growing the SIE [25]. Thus, stronger electric field in the discharge zone, leading to high density of electrons with more energy, high temperature and it produces more species with higher activity. These highly energetic electrons can transform the discharge energy to the reactant gas molecules *via* none elastic collisions. In general, the following reactions are probable for metastable forms and reactive species [44]:



To determine the effects of voltage on methanol, C₂, and C₃ at 9mL/min CH₄, 3mL/min O₂ (CH₄/O₂=3) and Ar flow 90mL/min, the voltage was increased from 4kV up to 10kV (Fig.5B).

Table 4: the dissociation energy of connection bonds [49]

Bond	D.E(kj/mol)	Bond	D.E(kj/mol)
O-O	498.34	CH ₃ -CH ₃	368
H-CH ₃	431	CH ₂ =CH ₂	682
CH ₃ -OH	372	CH=CH	962
C ₂ H ₄ =CH	490	C ₂ H ₅ -CH ₃	356

The bar chart (Fig.5B) illustrates that, the mole percentage of methanol rose to 2.52 in the lowest voltage 4kV, and SIE 12.9 kJ/mole. When the voltage increases from 4 to 10 kV, the SIE parameter enhances from 12.9 to 58.5 kJ/mole as well as the methanol (mole percentage) decline dramatically from 2.52 to 0.17. This matter has been shown in Fig 2A, B. RSM model for methanol obviously showed that in the test point (9 mL/min CH₄, 3 mL/min O₂); the effect of raising the voltage on methanol mole percentage is converse. Regarding the exciting pieces containing high-temperature electrons and meta states are dramatically descended in the reactor when the voltage is reduced, the dissociation of methanol is less than conditions that reactor work with more SIE [45]. Consequently, when SIE increase from 12.9 kJ/mole to 58.5 kJ/mole, the mole percentage of methanol is a decline from 2.5% to 0.17%.

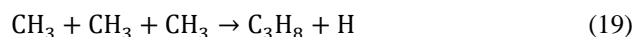
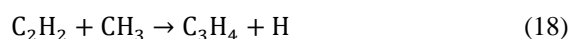
To explain why lower applied voltage leads to lower conversion, and consequently lower exited pieces density, it is undeniably evident that increase in applied voltage directly increases the discharge power, which is followed by intensification in the number of electrons and active species. The mixture of active species is include exited Ar (e.g., Ar⁺ and Ar*), exited O₂ (e.g., O₂^{*}, O₂ and O₂₋) and CH₄ radicals (e.g., CH_x) in the discharge zone[46]. In fact, providing higher discharge power via increasing the applied voltage can strengthen the electric field intensity that induces the presence of high-temperature electrons with higher density, which is in favor of electron impact, dissociation reactions, including ionization, excitation, and dissociation of feed gas molecules. Thus, not only the carrier gas (Ar) can be transformed into reactive species, such as Ar⁺ and Ar* which can contribute to higher conversion of CH₄ and O₂ molecules (equation 9-12), but also the energetic electrons can directly boost the conversion of reactant gases via the electron effect dissociation reactions [47], [48]. Based on these dissociation energies (Table 4), it is expected that CH₃-OH single bonds

to be broken more easily (372 kJ/mole) than C-C bonds for the C₂ group in the high voltages [49]. Hence, the result of lower voltage is less dissociation of molecules same as methanol.

The following reactions are considerable for C₂, C₃ production[44]:



With C₂ hydrocarbons, the CH₃^{*} radical can form C₃ hydrocarbons[50]:



Moreover, by changing SIE from 12.9 to 44.5 kJ/mole, C₂, C₃ concentrations in products rose from 0.54, 0.0 to 1.86, and 0.95, respectively. There is a pick in SIE 44.5 kJ/mole and after that from 44.5 to 58.5 kJ/mole the percentage of C₂, C₃ decreases to 1.41 and 0.88. In general, although, increasing the voltage have a reverse effect on methanol mole percent; it raises the concentration of C₂, C₃. Since the pathway pattern in plasma changes easily under different conditions and the plasma, reactions are very sensitive to the population of active species. Therefore the mechanism of reactions under plasma conditions are very complex and remain unclear[25], but the cracking of a single carbon-carbon and carbon-hydrogen bonds and the recombination of produced fragments (e.g., radicals, hydride ions, carbonation fragments) are involved to form products according to equations 13 to 19. Hydrocarbon interactions occur with electrons, other molecules or radicals, or surfaces inside the reactor. Only the collisions with sufficient energy may break a molecule at bond sites. Therefore, the Dissociation of C-H bonds leads to hydrogen production. As result, based on the differences between dissociation energy of C-H and C-C bonds major products of the plasma process are C₂ and H₂, when the voltage is increased[25]. The R-CH₃ bonds in C₃ are weaker than C₂. For instance, in the case of propane, C-CH₃ bond dissociation is 356 kJ/mole, and for ethane C-CH₃ bonds is 368 kJ/mole [49, 51-53].

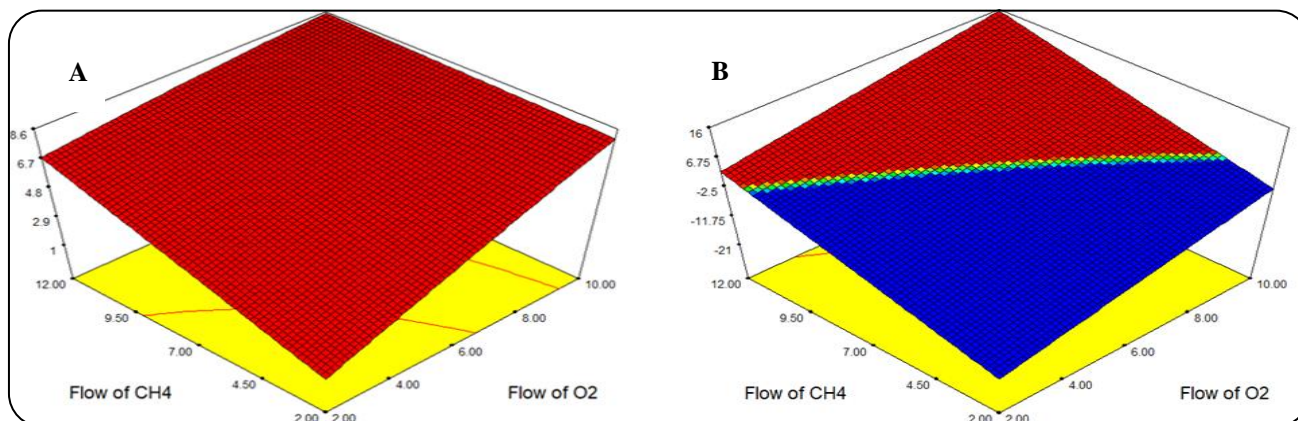


Fig 6: Effect of Ar flow from 20mL/min (A) to 100mL/min (B) on methanol

The C_3 products may not be formed in higher electric field and the concentration of C_2 is more than C_3 in the mixture while the voltage is raised.

The effect of Argon, Methane flow rate on methanol

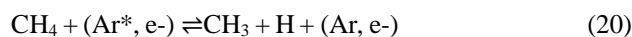
To show the effects of other significant parameters RSM models and facility of optimization by the software used. To survive the influence of other parameters in the desired conditions include minimized Ar (20 mL/min), O_2 (2 mL/min), CH_4 (2 mL/min), voltage (4 kV) as an optimum condition (results of Fig. 5A) for saving energy and material, investigated. The results illustrated that in fixed and optimized term while the Ar flow rate is enhanced from 20 to 100 mL/min (fig 6 A, B) the concentration of methanol decline severely. Thus, the raise in Ar flow rate has a negative effect on methanol mole percent. The cause of this is that increased Ar flow rates and power consumption also result in increased electric field intensity and effective collisions. Ar's plasma-phase electrons have kinetic energy. This energy may be the cause of the dissociation of methane and oxygen molecules as well as the excitation of argon to metastable states (Ar^*)[54]. Therefore, active species in the reactor grow up [25]. More species that are active lead to enhancement of methane conversion. Increasing in Ar flow rate could have both positive and negative effects on methane conversion [55]. One of the advantages is that Ar molecules are not only a balancing agent but also can function as an energy-transferring medium in the discharge zone. Ar molecules can receive the plasma electric field energy easier than methane molecules. Leading to a better possibility of collisions between Ar molecules and energetic electrons to transform Ar to its metastable state of Ar[56]. As a result,

more Ar molecules in the discharge zone lead to a higher possibility of a collision between (Ar^*) and CH_4 molecules, which helps to more CH_4 conversion.

Although high flow rate of Ar declines the methane concentration in the reactor, it has two negative effects on methanol mole percent, accordingly. First of all, it raises the power, and secondly, it causes diminishing the residence time of material in the plasma zone[25]. Because of using the fixed minimum voltage (4kV), growing up of residence time is the major reason for decreasing the methanol concentration.

Furthermore, by considering that Ar molecules have low heat capacity, the flow of Ar increased. As a result, the temperature of the zone raised and it could be the reason for more conversion of CH_4 [55], [56]. On the other hand, when Ar flow increased, the residence time decreased. Thus, collision opportunity between CH_4 molecules and reactive species diminishes, followed by less CH_4 conversion [57–59].

On the other hand, modeling by RSM shows that methane as a feed of reaction has a significant effect on methanol mole percent in a DBD plasma reactor. Fig 7(A, B) demonstrates that by growing up the flow of CH_4 from 2 to 12 mL/min, the concentration of methanol in DBD plasma reactor rose. Thus, the enhancement of methane has a positive effect on the mole percentage of methanol. Considering the possibility of presence methyl group, CH_3OH is produced at the vicinity of excited electrons, Ar^* , OH, H and active radicals of oxygen. These process considerably as following reactions and mechanisms [13, 43, 60–62]:



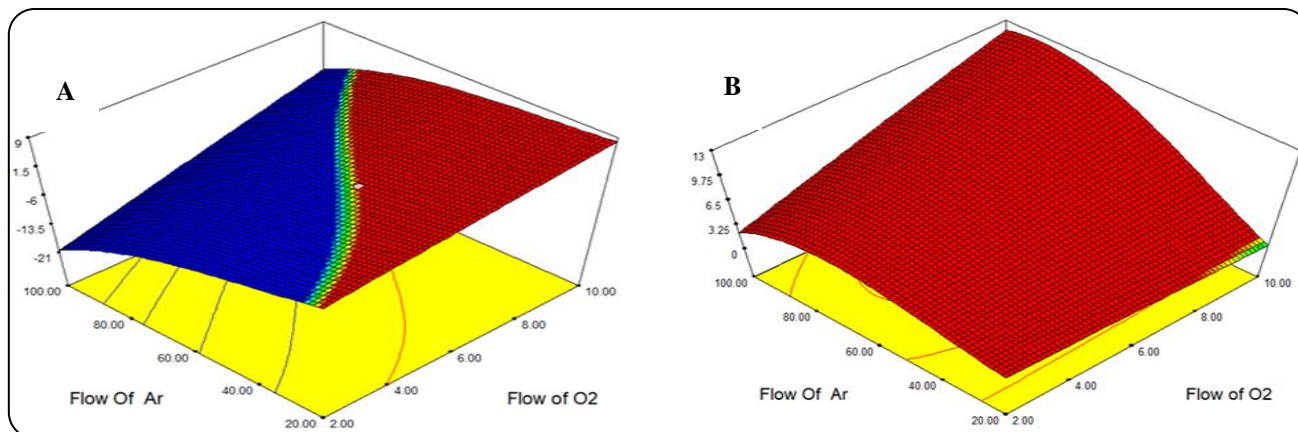
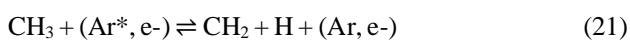


Fig 7: Effect of CH₄ flow from 2mL/min (A) to 12mL/min (B) on methanol



The reason of that is, enhancement in the CH₄ feeding concentration resulted in the generation of more CH_x radicals and led to the formation of CH₃O, CH₃O and increasing the probability of the formation of CH₃OH[63]. Another idea is, when the CH₄ flow rate is raised, because of constant power (4kV), the electric field intensity descends and similar low power discharge effects on methanol concentration, the amount of CH₃OH grows considerably. In fact, because of the dissociation energy of O-O, the level of energy at the plasma zone must be close to (498.3 kJ/mol). In this condition, formation of oxygen radicals that are significant for methanol production is begun. Despite, CH₃-OH bonds in high voltages are unstable due to low dissociation energy (372 kJ/mol) [25, 49], the C2 and C3 components are formed by follow up the pathway of reactions 13 to 19. In conclusion, the model prof that by raising the CH₄ flowrate, the CH₃OH is increased as well as the previous studies.

The effect of electrode length on methanol mole percent

The effect of changing the electrode length on energy efficiency (E.EFF) illustrated in (Fig. 8A) and effects of variation of energy efficiency on methanol revealed in Fig. 8B. To complete the optimization of the process, the length of the external electrode descended from 12.5 to 8, 4, and

2 cm respectively. The results showed that by decreasing in the electrode length from 12.5 to 8 cm, the energy efficiency declined modestly from 0.08 to 0.045 mmole/kJ, and after that, it rose dramatically from 0.045 to 0.242 mmole/kJ while the electrode length reduce from 8 to 2cm (fig 8A). The reason is, when the length of the electrode is declined, the residence time decreases for all components, such as Ar, O₂ and CH₄. Further, electric field intensity and effective collisions descended certainly[25] it could lead to weaker electron cloud and less active species that are produced by equation of 9-12. Accordingly, by changing the length from 12.5 to 8 cm in terms of lower residence time and electric field intensity, in presence of constant power the conversion of CH₄ and energy efficiency decrease from 19.5% to 5.6% and 0.08 to 0.045 mmole/kJ eventually (Equation (4)). Furthermore, despite the fact that is diminishing in length from 8 to 2 cm lead to less residence time, but also because of constant power supply (19.5 W), the electric field intensity and density of electron cloud dramatically raise. Thus, the conversion of methane increase from 5.6% to 61.6% and the energy efficiency raises from 0.045 to 0.242 mmole/kJ rapidly (Equation (4)) [25, 27].

On the other hand, a decrease in length from 12.5 to 8cm is caused by a decline in methanol mole percentage from 2.52 to 2.27 owing to less conversion of methane and reducing of residence time, electric field intensity, and effective collisions[16, 25, 27]. Besides, changing the length from 8 to 4cm lead to a pick in the methanol mole percentage to 3 because of high density of electron cloud, the possibility of more collision and formation of active species (Ar⁺, Ar^{*}, exited O₂ and CH₄ radicals), the conversion of methane raise from 5.6% to 28.9% [17, 25].

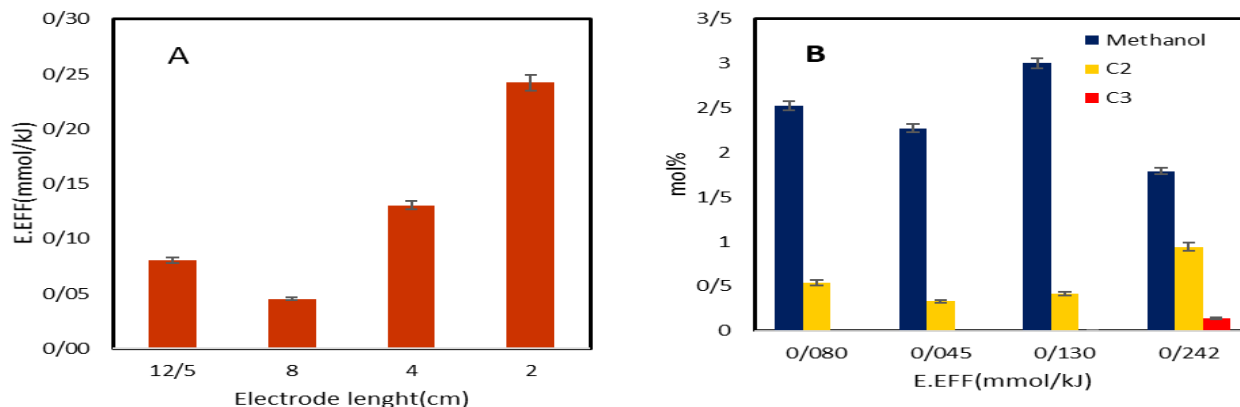


Fig 8: Effect of electrode length on E.EFF (A), variation of products percentage (B)

In the following, it descended sharply to 1.79 because of high intensity of electron field and more collision in reaction zone, the probability of dissociation in $\text{CH}_3\text{-OH}$ bonds is enhanced [17, 25]. The results of Table 4 show that methanol molecules do not have suitable stability at the plasma zone because of dissociation energy of $\text{CH}_3\text{-OH}$ connection is (372 kg/mole). Although the level of energy at the plasma zone must be close to (498.3 kJ/mol) for the production of oxygen radicals. In this situation, methanol molecules are unstable and enhancement in collisions could be the reason of decline in methanol mole percentage [49].

CONCLUSIONS

The optimization of direct conversion of methane at a DBD plasma reactor to methanol in presence of oxygen by detecting the influences of voltage, Ar gas, and methane and external electrode length studied. Furthermore, by the RSM modeling method, the effective parameters same as apply voltage, methane, and Ar flow rate on methanol production detected. It is inevitable that when the applied voltage was raised, it would be beneficial for more conversion of methane at the system. Besides, not only do exams illustrate that enhancement in the voltage from 4kV up to 10 kV is the reason for the decline in methanol mole percentage from 2.52 to 0.17, but also RSM model for methanol in the voltages from 2 to 12 kV proofed the fact. The RSM prediction model by the desired condition include minimized Ar (20 mL/min), O_2 (2 mL/min), CH_4 (2 mL/min), voltage (4 kV) was utilized for determining the effect of Ar and CH_4 on reactions. It showed that despite the fact that, growing up the Ar flow from 20 to 100 mL/min led to less methanol concentration, on the other hand,

enhancement in the methane flow rate from 2 to 12 mL/min was the reason of methanol concentration in the outlet of DBD reactor.

To determine the consequence of changing the length of the external electrode on methanol percentage, the length descended from 12.5 to 2 cm. consequently, the conversion of methane enhanced from 5.6% to 61.6%. It was effective to raise the methanol mole percent to 3% in E.EFF 0.13 mmole/kJ and optimum length equal 4 cm, although optimum methanol (mole percent) in minimum E.EFF 0.045 mmole/kJ was detected 2.27%.

To summarize, in the DBD plasma reactor by direct conversion of methane, increasing in voltage and Ar flow rate had significant effect in the process and had unfavorable effect for methanol production. Meanwhile, the CH_4 flow rate detected is impressive for the intensification of methanol. On top of that, fragile influence of oxygen flow is negligible.

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REFERENCES

- [1] Taghvaei H., Kheirollahivash M., Ghasemi M., Rostami P., Rahimpour M.R., **Noncatalytic Upgrading of Anisole in an Atmospheric DBD Plasma Reactor: Effect of Carrier Gas Type, Voltage, and Frequency**, *Energy and Fuels*, **28(4)**: 2535–2543 (2014).
- [2] Liu C., Marafee A., Hill B., Xu G., Mallinson R., Lobban L., **Oxidative Coupling of Methane with AC and DC Corona Discharges**, *Industrial & Engineering Chemistry Research*, **35(10)**: 3295–3301 (1996).
- [3] Liu C. J., B Xue., Eliasson B., He F., Li Y., Xu G.H., **Methane Conversion to Higher Hydrocarbons in the Presence of Carbon Dioxide Using Dielectric-Barrier Discharge Plasmas**, *Plasma Chem. Plasma Process.*, **21 (3)**: 301–310 (2001).
- [4] Nishida Y., H. Chiang C., T. Chen C., Cheng C.Z., **Efficient Production of Hydrogen by DBD Type Plasma Discharges**, *IEEE Trans. Plasma Sci.*, **42(12)**: 3765–3771 (2014).
- [5] Kim S.S., Kim J., Lee H., Na B.K., Song H.K., **Methane Conversion over Nanostructured Pt/ γ -Al₂O₃ Catalysts in Dielectric-Barrier Discharge**, *Korean J. Chem. Eng.*, **22(4)**: 585–590 (2005).
- [6] Liu C.-J., Mallinson R., Lobban L., **Nonoxidative Methane Conversion to Acetylene over Zeolite in a Low Temperature Plasma**, *Journal of Catalysis*, **179(1)**: 326–334 (1998).
- [7] Malik M.A. Jiang X. Z., **The CO₂ Reforming of Natural Gas in a Pulsed Corona Discharge Reactor**, *Plasma chemistry and Plasma Processing*, **19**: 505–512 (1999).
- [8] Yao S.L., et al., **Selective Oxidation of Methane Using a Non-Thermal Pulsed Plasma**, *Energy and Fuels*, **14(2)**: 459–463 (2000).
- [9] Eliasson B., Liu C.J., Kogelschatz U., **Direct Conversion of Methane and Carbon Dioxide to Higher Hydrocarbons Using Catalytic Dielectric-Barrier Discharges with Zeolites**, *Ind. Eng. Chem. Res.*, **39(5)**: 1221–1227 (2000).
- [10] Gesser H.D., Hunter N.R., **A Review of C-1 Conversion Chemistry**, *Catalysis Today*, **4(3)**: 183–189 (1998).
- [11] Larkin D.W., Caldwell T.A., Lobban L.L., Mallinson R.G., **Oxygen Pathways and Carbon Dioxide Utilization in Methane Partial Oxidation in Ambient Temperature Electric Discharges**, *Energy & Fuels*, **12 (4)**: 740–744 (1998).
- [12] Balopi B., Agachi P., Danha, **Methanol Synthesis Chemistry and Process Engineering Aspects - A Review with Consequence to Botswana Chemical Industries**, *Procedia Manuf.*, **35**: 367–376 (2019).
- [13] Indarto A., Choi J.W., Lee H., Song H.K., **The Kinetic Studies of Direct Methane Oxidation to Methanol in the Plasma Process**, *Chinese Sci. Bull.*, **53(18)**: 2783–2792, 2008.
- [14] Aziznia A., Bozorgzadeh H.R., Seyed-Matin N., Baghalha M., Mohamadizadeh A., **Comparison of Dry Reforming of Methane in Low Temperature Hybrid Plasma-Catalytic Corona with Thermal Catalytic reactor over Ni/ γ -Al₂O₃**, *J. Nat. Gas Chem.*, **21(4)**: 466–475, 2012.
- [15] Khoshtinat M., Amin N.A.S., Noshadi I., **A Review of Methanol Production from Methane Oxidation via Non-Thermal Plasma Reactor**, *World Acad. Sci. Eng. Technol.*, **62(2)**: 354–358 (2010).
- [16] Tang L. Huang H., **Biomass Gasification Using Capacitively Coupled RF Plasma Technology**, *Fuel*, **84 (16)**: 2055–2063 (2005).
- [17] Wang B., Yan W., Ge W., Duan X., **Methane Conversion into Higher Hydrocarbons with Dielectric Barrier Discharge Micro-Plasma Reactor**, *J. Energy Chem.*, **22(6)**: 876–882 (2013).
- [18] Fazeli S.M., Bozorgzadeh H.R., Ravari F., Sadeghzadeh Ahari J., **Dry reforming of Methane Using Cold Plasma; Kinetic Model Study**, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **39(1)**: 257–265 (2020).
- [19] Huang A., Xia G., Wang J., Suib S. L., Hayashi Y., Matsumoto H., **CO₂ Reforming of CH₄ by Atmospheric Pressure ac Discharge Plasmas**, *J. Catal.*, **189(2)**: 349–359 (2000).
- [20] Istadi, Amin N.A.S., **Co-generation of Synthesis Gas and C²⁺ Hydrocarbons from Methane and Carbon Dioxide in a Hybrid Catalytic-Plasma Reactor: A Review**, *Fuel*, **85(5–6)**: 577–592 (2006).
- [21] Indarto A., Choi J.-W., Lee H., Song H.K., **A Brief Catalyst Study on Direct Methane Conversion Using a Dielectric Barrier Discharge**, *Journal of the Chinese Chemical Society*, **54(4)**: 823–828 (2007)
- [22] Chen L., Zhang X W., Huang L., Lei L.C., **Partial Oxidation of Methane with air for Methanol Production in a Post-Plasma Catalytic System**, *Chem. Eng. Process. Process Intensif.*, **48(8)**: 1333–1340 (2009).

- [23] Kogelschatz U., Dielectric-barrier Discharges: Their History, Discharge Physics, and Industrial Applications, *Plasma Chemistry and Plasma Processing*, **23**(1): 1-46 (2003).
- [24] Kolb T., Voigt J.H., Gericke K.H., Conversion of Methane and Carbon Dioxide in a DBD Reactor: Influence of Oxygen, *Plasma Chem. Plasma Process.*, **33**(4): 631–646 (2013).
- [25] Khalifeh O., Mosallanejad A., Taghvaei H., Rahimpour M. R., Shariati A., Decomposition of Methane to Hydrogen Using Nanosecond Pulsed Plasma Reactor with Different Active Volumes, Voltages and Frequencies, *Appl. Energy*, **169**: 585–596 (2016).
- [26] Namihira T., *et al.*, Influence of Gas Flow Rate and Reactor Length on NO Removal Using Pulsed Power, *IEEE Trans. Plasma Sci.*, **2**(4): 592–598 (2001).
- [27] Bahri M., Haghighat F., Rohani S., Kazemian H., Impact Of Design Parameters On The Performance Of Non-Thermal Plasma Air Purification System, *Chem. Eng. J.*, **302**: 204–212 (2016).
- [28] Wang T., *et al.*, Effect of Reactor Structure in DBD for Nonthermal Plasma Processing of NO in N₂ at Ambient Temperature, *Plasma Chem. Plasma Process*, **32**(6): 1189–1201 (2012).
- [29] Boyer M. D., *et al.*, Toward Fusion Plasma Scenario Planning for NSTX-U Using Machine-Learning-Accelerated Models, Boyer, Mark. In "Learning for Dynamics and Control", 698-707 (2020).
- [30] Wehner W. P., Schuster E., Boyer M. D., Poli F. M., TRANSP-Based Optimization Towards Tokamak Scenario Development, *Fusion Eng. Des.*, (2019).
- [31] Piccione A., Berkery J.W., Sabbagh S.A., Andreopoulos Y., Physics-Guided Machine Learning Approaches to Predict the Ideal stability Properties of Fusion Plasmas, *Nucl. Fusion*, **60**(4): (2020).
- [32] Citrin, Jonathan, Sarah Breton, Federico Felici, Frederic Imbeaux, Aniel T., J Artaud. F., Baiocchi B., Bourdelle C., Camenen Y., Garcia J., Real-Time Capable First Principle Based Modelling of Tokamak Turbulent Transport, *Nuclear Fusion*, **55**(9): 092001 (2015).
- [33] Ba D., Boyaci I.H., Modeling and Optimization i: Usability of Response Surface Methodology, *J. Food Eng.*, **78**(3): 836–845 (2007).
- [34] Jiang] N. *et al.*, Enhanced Catalytic Performance of CoOx-CeO₂ for Synergetic Degradation of Toluene in Multistage Sliding Plasma System through Response Surface Methodology (RSM), *Appl. Catal. B Environ*, **259**: (2019).
- [35] Jiang N., Zhao Y., Shang K., Lu N., J. Li, Wu Y., Degradation of Toluene by Pulse-Modulated Multistage DBD Plasma: Key Parameters Optimization Through Response Surface Methodology (RSM) and Degradation Pathway Analysis, *J. Hazard. Mater.*, **393**: (2020).
- [36] Tian Y., Zhang X., Wang Y., Cui Z., tang J., SF₆ Abatement in a Packed Bed Plasma Reactor: Role of Zirconia Size and Optimization Using RSM, *J. Ind. Eng. Chem.*, **94**: 205–216 (2021).
- [37] Mansouri F., Khavanin A., Jafari A. J., Asilian H., Ghomi H.R., Mousavi S.M., Energy Efficiency Improvement in Nitric Oxide Reduction by Packed DBD Plasma: Optimization and Modeling Using Response Surface Methodology(RSM), *Environ. Sci. Pollut. Res.*, **27**(14): 16100–16109 (2020).
- [38] Khoja A.H., Tahir M., Saidina Amin N.A., Process Optimization of DBD Plasma Dry Reforming of Methane Over Ni/La₂O₃[Sbnd]MgAl₂O₄ Using Multiple Response Surface Methodology, *Int. J. Hydrogen Energy*, **44**(23): 11774–11787 (2019).
- [39] Galedari M., Mehdipour M. Ghazi, Rashid S., Mirmasoomi, Photocatalytic Process for the Tetracycline Removal under Visible Light: Presenting a Degradation Model and Optimization Using Response Surface Methodology (RSM), *Chem. Eng. Res. Des.*, **145**: 323–333 (2019).
- [40] Hosseinzadeh A., *et al.*, Application of Response Surface Methodology and Artificial Neural Network Modeling to Assess Non-Thermal Plasma Efficiency in Simultaneous Removal of BTEX from Waste Gases: Effect of Operating Parameters and Prediction Performance, *Process Saf. Environ. Prot.*, **119**: 261–270 (2018).
- [41] Teknologi J., Faraliana N. Shazwani, Nor Azmi, Mohammed Evuti A., M. Ariffin Abu Hassan, Raja Ibrahim R.K., J. Bahru, Optimization of Non Thermal Plasma Reactor Performance for the Decomposition of Xylene, *Jurnal Teknologi*, **78**(8): 165-171 (2016).
- [42] Aghamir F.M., Nasser M., Amir-Hossein J., Mohammad-Ali E., Methanol Production in AC Dielectric Barrier Discharge, *J. Plasma Fusion Res. SERIES*, **6**: 696-698 (2004).

- [43] Nozaki T., Hattori A., Okazaki K., [Partial Oxidation of Methane Using a Microscale Non-Equilibrium Plasma Reactor](#), *Catal. Today*, **98(4)**: 607–616 (2004).
- [44] Shareei M., Taghvaei H., Azimi A., Shahbazi A., Mirzaei M., [Catalytic DBD Plasma Reactor for Low Temperature Partial Oxidation of Methane: Maximization of Synthesis Gas and Minimization of CO₂](#), *Int. J. Hydrogen Energy*, **44(60)**: 31873–31883 (2019).
- [45] Tsuchiya T. Iizuka S., [conversion of Methane to Methanol by a Low-Pressure Steam Plasma](#), *J. Environ. Eng. Technol.*, **2(3)**: 35–39, (2013).
- [46] Taghvaei H., Jahanmiri A., Rahimpour M. R., Shirazi M.M., Hooshmand N., [Hydrogen Production Through Plasma Cracking of Hydrocarbons: Effect of Carrier Gas and Hydrocarbon Type](#), *Chem. Eng. J.*, **226**: 384–392 (2013).
- [47] Hammer T., Kappes T., Baldauf M., [Plasma Catalytic Hybrid Processes: Gas Discharge Initiation and Plasma Activation of Catalytic Processes](#), *Catal. Today*, **89(1–2)**: 5–14 (2004).
- [48] Zhou L.M., Xue B., Kogelschatz U., Eliasson B., [Partial Oxidation of Methane to Methanol with Oxygen or Air in a Nonequilibrium Discharge Plasma](#), *Plasma Chem. Plasma Process.*, **18(3)**: 375–393 (1998).
- [49] Patra A.K., Afshar R.K., Rowland J. M., Olmstead M.M., Mascharak P.K., [Thermally Induced Stoichiometric and Catalytic O-Atom Transfer by a Non-Heme iron\(III\)-Nitro complex: First Example of Reversible {Fe-NO} 7 ↔ FeIII-NO₂ Transformation in the Presence of Dioxide](#), *Angew. Chemie - Int. Ed.*, **42(37)**: 4517–4521 (2003).
- [50] Zanthoff H. Baerns M., [Kinetics And Catalysis Oxidative Coupling of Methane in the Gas Phase. Kinetic Simulation and Experimental Verification](#), *Industrial & Engineering Chemistry Research*, **29(1,2-10)**: 1990.
- [51] Ouellette R. J Rawn. J. D., [Alkanes and Cycloalkanes](#), in "Organic Chemistry Study Guide: Key Concepts, Problems, And Solutions", Elsevier (2014).
- [52] Genco J. I., Duke F.R., ["The \(C-H\) Bond Dissociation Energy in the Methyl Group of Toluene"](#), 746: United States Atomic Energy Commission, Technical Information Service (1956).
- [53] Goebbert D.J., Velarde L., Khuseynov D., Sanov A., [C-H Bond Dissociation Energy of Malononitrile](#), *J. Phys. Chem. Lett.*, **1(4)**: 792–795 (2010).
- [54] Taghvaei H., Jahanmiri A., Rahimpour M.R., Shirazi M.M., Hooshmand N., [Hydrogen Production through Plasma Cracking of Hydrocarbons: Effect of Carrier Gas and Hydrocarbon Type](#), *Chem. Eng. J.*, **226**: 384–392 (2013).
- [55] Khalifeh O., H. Taghvaei, Mosallanejad A., Rahimpour M.R., Shariati A., [Extra Pure Hydrogen Production through Methane Decomposition Using Nanosecond Pulsed Plasma and Pt-Re Catalyst](#), *Chem. Eng. J.*, **294**: 132–145 (2016).
- [56] Te Hsieh L., Lee W.J., Chen C.Y., Chang M.B., Chang H.C., [Converting Methane by Using an RF Plasma Reactor](#), *Plasma Chem. Plasma Process.*, **18(2)**: 215–239 (1998).
- [57] Kim T.K. Lee W.G., [Reaction between Methane and Carbon Dioxide to Produce Syngas in Dielectric Barrier Discharge System](#), *J. Ind. Eng. Chem.*, **18(5)**: 1710–1714 (2012).
- [58] Kasinathan P., Park S., Choi W.C., Hwang Y.K., Chang J.S., Park Y.K., [Plasma-Enhanced Methane Direct Conversion Over Particle-Size Adjusted MOx/Al₂O₃\(M = Ti and Mg\) Catalysts](#), *Plasma Chem. Plasma Process.*, **34(6)**: 1317–1330 (2014).
- [59] Xu C., Tu X., [Plasma-Assisted Methane Conversion in an Atmospheric Pressure Dielectric Barrier Discharge Reactor](#), *J. Energy Chem.*, **22(3)**: 420–425 (2013).
- [60] Lee H., Kim D.H., [Direct Methanol Synthesis from Methane in a Plasma-Catalyst Hybrid System at Low Temperature Using Metal Oxide-Coated Glass Beads](#), *Scientific. Reports*, **8(1)**: 1–8 (2018).
- [61] Chawdhury P., Ray D., Vinodkumar T., Subrahmanyam C., [Catalytic DBD Plasma Approach for Methane Partial Oxidation to Methanol under Ambient Conditions](#), *Catal. Today*, **337**: 117–125 (2019).
- [62] Chawdhury P., Ray D., Subrahmanyam C., [Single Step Conversion of Methane to Methanol Assisted by Nonthermal Plasma](#), *Fuel Process. Technol.*, **179**: 32–41 (2018).
- [63] Wang Y.-F., Tsai C.-H., M Shih., Hsieh L.-T., Chang W., [Direct Conversion of Methane into Methanol and Formaldehyde in an RF Plasma Environment II: Effects of Experimental Parameters](#), *Aerosol Air Qual. Res.*, **5(2)**: 211–224 (2005).