

Synthesis-Gas Production from CH₄-CO₂-Ar via Microwave Plasma Torch

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Abstract

In order to produce synthesis-gas from CH₄-CO₂-Ar system, a non-thermal plasma technology at atmospheric pressure will be used. This design enables us to produce syngas in the plasma reactor instead of the usual catalytic processes. In addition the gas phase composition of plasma species has been evaluated using the Gibbs free energy minimization method. Furthermore, for optimizing the production conditions of syngas production, the effects of CH₄/CO₂ gas flow rate and plasma power were investigated. Our results confirm our pre-estimation simulations and good agreement with existing literature data.

Keywords: CH₄ conversion, CO₂ reforming of methane, microwave plasma torch, Thermodynamics, modeling, synthesis-gas

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1 The State of Art on syngas

Large range of intermediate products such as syngas (CO, H₂), ethylene (C₂H₄), methanol (CH₃OH) and formaldehyde (CH₂O) are generally produced by CH₄ as a greenhouse gas [1]. Syngas is used mainly for production of pure H₂, ammonia and liquid products such as methanol, diesel fuel, jet fuel, gasoline, etc. The lack of sulphur or nitrogen compounds in the fuels made from syngas enables lower environmental pollution combustion [2]. For economic reasons natural gas (CH₄) conversion instead of coal as the primary source of carbon [2] is used in new technologies in partial oxidation and steam or CO₂ reforming methods which are the main routes in subsequent methanol production methods such as ammonia synthesis, or the Fischer-Tropsch synthesis [1].

The dominant applied method to produce syngas from CH₄ is the steam reforming technology. However, it is still unsuitable for methanol and Fischer-Tropsch synthesis due to its high energy consumption, poor CO selectivity and high H₂/CO ratio [3]. Using highly activated catalysts such as Ni, Co, Ir, Pd, Pt, or Ru metals supported on Al₂O₃, TiO₂ or other substrates such as oxidized diamond at 1000–1300 K under 15–30 atm enables researchers to convert CH₄ in to syngas through partial oxidation of it [1]. Thus, in the present study we are going to develop a more economic and environmentally friendly method to reduce the operation temperature and pressure while avoiding the catalyst poisons side effects based on the plasma abilities. It has been shown that the decomposition of carbon containing molecules such as CH₄, C₂H₂ and C₆H₆ mixed with O₂ or CO₂ (as the source of O) by ionized noble gases like Ar could produce syngas inside microwave discharge plasma reactors [1]. In these systems CH₄ provides the source of C and H, while ionized Ar helps the ionization of the working gas [4, 5]. Plasma is a high energy medium where various kinds of chemical reactions effectively could lead to CH₄ conversion while overcomes the drawback of the high temperature requirement in conventional catalytic processes.

The conversion of CH₄ (or its mixture with O₂) into higher hydrocarbons, syngas and organic oxygenate liquid recently has been made through non-equilibrium plasma methods [6] as non-catalytic conversion technologies. Usually the discharge in the plasma reactors is carried out by high pulse frequency [7], corona [8], radio-frequency “RF” [9], microwave “MW” [10], or dielectric barrier discharges “DBDs” [11]. Such plasma environments initially lead to the formation of C₂ hydrocarbons, methanol, or diamond-like carbon films instead of syngas [7–11]. However, in preliminary studies of low-pressure RF plasma the ability of this method to convert CH₄-O₂ into syngas has been demonstrated [12]. Although it has been shown that the RF plasma reactor in [12] is able to produce high CH₄ conversion and syngas selectivity, but such a system requires low pressure of 4 kPa along with low flow rate of 200 sccm for operation which is not practical in industry. However, high plasma density and electron mean energy can be achieved in MW plasma at a wide range of pressures and gas flow rates [1, 5, 13].

In the previously reported results by same authors in [13] the atmospheric pressure plasma methane conversion running by low MW power has been demonstrated. Analytical analysis along with thermodynamics and simulation evaluations has been used to investigate the plasma gas phase species produced and study the plasma chemistry phenomena inside the CH₄-O₂-Ar gas mixture [13]. These results proved that the designed plasma reactor in [13] is suitable for syngas production from the CH₄-O₂-Ar system at atmospheric pressure in the absence of catalytic or thermal processes. Therefore, in continuing our research work on CH₄-O₂ MW plasma conversion in to syngas [13], in this report the constructed MW plasma reactor operating at atmospheric pressure will be investigated for CO₂ reforming of methane in to syngas. As CO₂ gas is a green house gas, by the help of this study we could be able to convert CO₂ in to valuable products such as syngas. In addition by studying the effect of CH₄/CO₂ ratio and plasma power we are able to explain the main plasma chemistry phenomena occurring in this system which could lead to optimum production conditions. In this work in addition to CO₂ conversion through CO₂ reforming of methane in to syngas, by comparing the results of previously studied CH₄-O₂-Ar system [13] we expect more CH₄ conversion ratio and CO selectivity while using CO₂ instead of O₂ as the source of oxygen.

2 Thermodynamics of Chemical Reactions

Before studying the different plasma species inside the designed reactor, we can analysis the overall balance chemical reactions which are more possible to be the dominant phenomenon inside the CH₄ and CO₂ gas mixture. For this reason the main possible chemical reactions along with their Gibbs free energy have been calculated which are listed in table 1 regarding the data in [14]. The overall conclusions can be categorized as follows:

Formation of syngas in different conditions (CH₄/CO₂ ratio):

- The formation of syngas from CH₄ and CO₂ can only be possible with CH₄/CO₂ ratio of (=1) at very high temperature (reaction no. 2).
- Comparing the reactions no. 1-4 shows that only at the high ratio of CO₂/CH₄ the syngas can be formed at very high temperatures. In addition the undesired species like H₂O and O₂ are also formed.
- Also, at very low ratio of CO₂/CH₄ (=1/2) no syngas can be formed.

Effect of undesired molecules such as H₂O and O₂:

- Comparing reaction no. 5-7 shows that CH₄ can use undesired species like H₂O and O₂ in a chain reaction to form more syngas (although the ratio of H₂ in these syngas are quite high) (reactions no. 5-6).
- Also the reaction no. 7 shows that the combination of CO₂ and H₂O for a self-production (spontaneous reaction) of syngas is not a probable phenomenon.
- Reaction no. 8-9, shows that at least small amount of O₂ as a side-production can reduce the amount of H₂ or CO according to reactions no. 8 and 10.

Table 1. Main reactions in CH₄-CO₂ gas mixture and their correspondence change of Gibbs free energy of reaction.

no.	reactions ***	$\Delta_r G_{298}^0$ *	$\Delta_r G_{1000}^0$ *	$\Delta_r G_{2000}^0$ *	remark
1	CH ₄ +1/2CO ₂ → 3/2CO+2H ₂ O+7O ₂	-415.071	-507.484	-633.395	
2	CH ₄ +CO ₂ →2CO+2H ₂	170.761	14.860	-306.747	probable above 1000 K
3	CH ₄ +2CO ₂ →3CO+2H ₂ +1/2O ₂	427.945	171.265	-196.539	probable above 1500 K
4	CH ₄ +3CO ₂ →4CO+H ₂ +2H ₂ O	227.889	-18.612	-357.875	probable above 1000 K
5	CH ₄ +1/2O ₂ →CO+2H ₂	-86.423	-180.689	-416.955	but here O ₂ << CH ₄
6	CH ₄ +H ₂ O→CO+3H ₂	142.197	12.024	-281.183	probable above 1000 K
7	CO ₂ +2H ₂ O→CH ₄ +2O ₂	800.847	761.664	798.707	for 1 mole of CO ₂
8	H ₂ +1/2O ₂ →H ₂ O	-228.620	-192.713	-135.772	for 1 mole of H ₂
9	2H ₂ +CO ₂ →CH ₄ +O ₂	343.607	376.238	527.163	for 2 mole of H ₂
10	CO+1/2O ₂ →CO ₂	-257.184	-195.549	-110.208	for 1 mole of CO
11	CO+2H ₂ O→CH ₄ +3/2O ₂	543.663	566.115	688.499	for 1 mole of CO
12	CH ₄ +CO ₂ →C ₂ H ₂ +H ₂ +O ₂	654.322	545.882	382.483	not probable
13	CH ₄ +CO ₂ →C ₂ H ₂ +H ₂ O+1/2O ₂	425.702	353.169	246.711	not probable
14	CH ₄ +2CO ₂ → C ₂ H ₂ +CO+H ₂ +3/2O ₂	911.506	741.431	492.691	not probable
15	CH ₄ +1/2CO ₂ → 1/2C ₂ H ₄ +1/2CO+H ₂ +1/4O ₂	213.559	137.803	-29.845	probable above 2000 K
16	CH ₄ +1/2CO ₂ → 1/2C ₂ H ₄ +1/2CO+1/2H ₂ O+1/2H ₂	99.249	41.446	-42.627	probable above 2000 K
17	CH ₄ +CO ₂ →C ₂ H ₄ +O ₂	513.541	495.439	467.472	not probable
18	CH ₄ +3CO ₂ →C ₂ H ₄ +5/2O ₂ +CO	-1201.095	-1086.798	973.903	probable under 1500 K and when CO ₂ >> CH ₄
19	CH ₄ +1/2CO ₂ → 1/2C ₂ H ₆ +1/2CO+1/2H ₂ +1/4O ₂	162.934	132.981	**	not probable
20	CH ₄ +CO ₂ → 1/2C ₂ H ₆ +CO+1/2H ₂ +1/2O ₂	291.526	230.755	**	not probable
21	CH ₄ +1/2CO ₂ → 1/2C ₃ H ₆ +1/2H ₂ +1/2O ₂	300.078	357.566	**	not probable
22	CH ₄ +CO ₂ →1/3C ₃ H ₆ +2CO+H ₂	205.520	48.313	**	not probable
23	CH ₄ +1/2CO ₂ →1/2C ₃ H ₈ +1/2O ₂	236.254	274.064	**	not probable
24	CH ₄ +CO ₂ → 1/2C ₃ H ₈ +1/2CO+3/4O ₂	364.846	371.838	**	not probable

*: in [kJ/mol] calculated from Gibbs free energy of the formation of gas state species from [14]

** : there is no thermodynamics data for C₂H₆, C₃H₆ and C₃H₈ at 2000 K.

***: in all reactions H₂O is considered in its gaseous state, also the values were calculated for 1 mole of CH₄ in all reactions except those which were written as remarks.

Formation of higher C containing molecules:

- Also regarding reactions no. 12-24, the formation of C₂H₂, C₂H₄, C₂H₆ and C₃H₈ seems to be not very probable except reaction no. 18 which indicates the possibility of formation of C₂H₄ at the high CO₂/CH₄ ratio.

Overall conclusions from table 1:

- In all ratios of CO₂/CH₄ (especially= 1, 2, 3), we can expect the formation of CO₂, H₂O and C₂H₄ in addition to H₂ and CO in two or three step reactions, if the conditions of high temperature environment will be available.

The above conclusions show similar behavior of CH₄-CO₂ and CH₄-O₂ system regarding their capabilities to produce H₂ and CO in a proper ratio as a syngas at

high temperatures. In this case, CH₄-CO₂ mixture requires the higher ratio (almost twice) of CO₂ to methane input than that of the similar CH₄-O₂ system [13]. However, in the case of CH₄-CO₂ the process of CO₂ greenhouse conversion into valuable products is the additional aspect of such a technology.

However, regarding the temperature condition for the aforementioned chemical reactions to produce a syngas, in a plasma reactor instead of producing high temperature environment, the existence of ionized molecules and atoms along with high energy electrons makes the electron impact ionization and dissociation reactions dominated compared to the neutral-neutral reactions. Therefore, the existence of those high energy electrons will produce the conditions at which the mentioned chemical reactions and phenomenon required for the syngas production will take place.

The Gibbs energy function is the quantity defining the criteria of equilibrium in a system undergoing chemical reactions. Therefore, in order to predict more precisely the possibility of such a plasma environment at which the required chemical reactions (mentioned above) take place, in the following, the concentrations of the plasma gas phase species during the production of syngas from CH₄-CO₂-Ar system will be calculated in a microwave plasma torch using a thermodynamic modeling. Pre-estimated simulation results on concentrations and dominant existing type of species enable us to predict the expected species and their ratio in our experimental investigations.

3 Compositions of Plasma Species inside CH₄-CO₂-Ar Gas System (simulation study)

The macroscopic properties of our plasma system are determined by the nature of main chemical reactions taken place inside the plasma reactor. This information can be extracted by knowing the dominant species and their concentrations regarding the plasma chemical reactions inside our system, which enables us to understand the nature of the main plasma phenomena. Therefore, here using the Gibbs free energy minimization method the equilibrium concentrations of the plasma gas phase species have been calculated. In these calculations the pressure was kept constant and calculations were independent of the reactor volume. Since in arc plasmas or burning flames the collision frequency between electrons and gas molecules increases when the gas temperature exceeds some thousand degrees, regarding our reaction zone temperature (see below) the plasma can be considered to be at nearby thermal equilibrium ($T_e \approx T_g$) [15]. Therefore, we were able to apply the conditions of Gibbs free energy minimization method in our CH₄-CO₂-Ar gas mixture.

- *Species to be considered:*

Next step before simulation of a complex system is to know all possible species existing in the plasma gas phase during the main reactions. Regarding table 1, the formation of CO, H₂, CO₂, H₂O, C₂H₄ along with some remaining CH₄ in all CO₂/CH₄ input flow rate is expected. In addition, the research reported in [16] indicates the formation of H₂O₂ species (OH + OH → H₂O₂) in CH₄ (90%)-O₂ (1%) mixture in a MW plasma reactor where the formation of H₂O₂ was believed to be related to the formation of other species such as OH, C₃H₈O and C₂H₆O₃. Also considering the previous section, we use the ratio of CO₂/CH₄ (= 1 or 1/2). Therefore, comparing it to [16], we do not expect the formation of OH, C₃H₈O or C₂H₆O₃ in our system. In addition, for pure CH₄ MW plasma conversion experiments, authors in [6] reported the possibility of existence of C₂H₂, C₂H₄, C₂H₆ and small amount of C₃H₆ and C₃H₈ species in the final product. Thus, regarding the selected analysis in [1,6,16] along with our pre-assumption (table 1) carried out for the CH₄-CO₂-Ar MW plasma reactor all considerable species for the simulation could be listed as: Ar, CO, H₂, H₂O, Ar⁺, CO₂, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈. However, comparing this list to the list reported for the CH₄-O₂-Ar system [13] one can find the lack of O₂, CH₃OH and CH₂O molecules. However, in this case, species like C₃H₆ and C₃H₈ appears as the new type of molecules which are possible to be formed in CH₄-CO₂-Ar system due to its different nature with respect to the CH₄-O₂-Ar gas mixture.

- *Thermodynamics Model:*

The total Gibbs energy of the system can be evaluated as the sum of the partial molar Gibbs energy of all species regarding their molar weight in the gas mixture. Therefore, we may write:

$$G_{\Sigma} = \sum_{N_g=1}^{N_g^t} G_{N_g} n_{N_g}, \quad (1)$$

$$G_{N_g} = G_{N_g}^{\circ}(T, P) + RT \ln(X_{N_g}), \quad N_g = 1, \dots, N_g^t, \quad (2)$$

where G_{Σ} is the total Gibbs energy function of the system in J, G_{N_g} is the partial Gibbs energy of N^{th} specie in J.mol⁻¹, n_{N_g} is the number of the mole of N^{th} specie, N_g^t is number of the total species in the gas phase of the plasma, $G_{N_g}^{\circ}$ is the standard partial Gibbs energy of N^{th} specie in J/mol, R is universal gas constant in J.mol⁻¹.K⁻¹, X_{N_g} is the mole fraction of N^{th} specie, T is temperature in absolute scale, and P is pressure in atm.

The value of $G_{N_g}^{\circ}$ has been evaluated from the standard partial enthalpy and entropy of specie ($G_{N_g}^{\circ} = H_{N_g}^{\circ} - TS_{N_g}^{\circ}$). In our simulation the pressure is kept constant and the temperature dependency of $S_{N_g}^{\circ}$, $H_{N_g}^{\circ}$ and $G_{N_g}^{\circ}$ (used in Eqs. (1, 2)), has been calculated by a simple polynomial form for heat capacity as:

$$\frac{C_{p,N_g}^\circ}{R} = \sum_{i=1}^I \alpha_{N_g,i} T^{(i-1)} = \alpha_{N_g,1} + \alpha_{N_g,2} T + \alpha_{N_g,3} T^2 + \alpha_{N_g,4} T^3 + \alpha_{N_g,5} T^4, \quad (3)$$

where $\alpha_{N_g,1}, \alpha_{N_g,2}, \alpha_{N_g,3}, \alpha_{N_g,4}, \alpha_{N_g,5}$ are the coefficients of the temperature dependence of the heat capacity and C_{p,N_g}° is heat capacity in constant pressure in J.mol⁻¹.K⁻¹.

The coefficients of the heat capacity (Eq. (3)) for all species have been taken from [17]. Furthermore, the atomic population constrain of all basic elements (O, H, Ar, e and C) should be considered as:

$$p_j = \sum_{N_g=1}^{N_g^I} n_{j,N} n_{N_g}, \quad (4)$$

where $n_{j,N}$ is the number of the j -type atom in N^{th} specie (here j : H, Ar, e and C), p_j is the total population of the j -type atom in mol.

The mathematical equilibrium solution at a given temperature and pressure is the distribution of all n_{N_g} which minimizes the total Gibbs function of the system (Eq. (1)), together with considering atomic population constrains (Eq. (4)) along with a non-negative n_{N_g} condition in the system.

- Input Parameters (macroscopic quantities):

In our simulation the pressure has been kept at 1 atm for the plasma gas phase along with considering the initial mole fraction of Ar, CO₂ and CH₄ by 0.9873, 0.0093 and 0.0033, respectively, where these data are equivalent to CH₄/CO₂ ratio of 1 in 5000 sccm Ar gas.

The typical MW plasma torch operated at 2.45 GHz and 2000 W power produced the maximum temperature of 6000 K at atmospheric pressure [18]. Also the thermocouple and optical emission spectroscopy in Ar MW plasma at 1 atm with power range of 650-950 W showed the temperature of 1030-2200 K [19]. In other references, below 600 W MW power, a lower temperature plasma zone of 500-1000 K at low pressure near the discharge volume has been estimated [1]. However, regarding our experimental setup running with maximum MW power of 300 W, regarding [18] at atmospheric pressure we expect the maximum temperature of 2000-3000 K for our plasma flame. Obviously, far from the flame, the temperature decreases drastically, where at the distance of 2 cm we measured only 299, 303 and 308 K at 100, 200 and 300 W, respectively. Therefore, the temperature zone for these simulations was set to be varied in the range of 298-3000 K.

- *Simulation Results:*

The output of the total Gibbs free energy minimization energy (running at an in-house programming) presents the equilibrium molar concentration of all possible species existing in our plasma reactor zone as presented in figure 1. The results of figure 1 represent the calculated concentration of CO, CO₂, H₂, e, H₂O, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆ and C₃H₈ at different plasma reactor temperature.

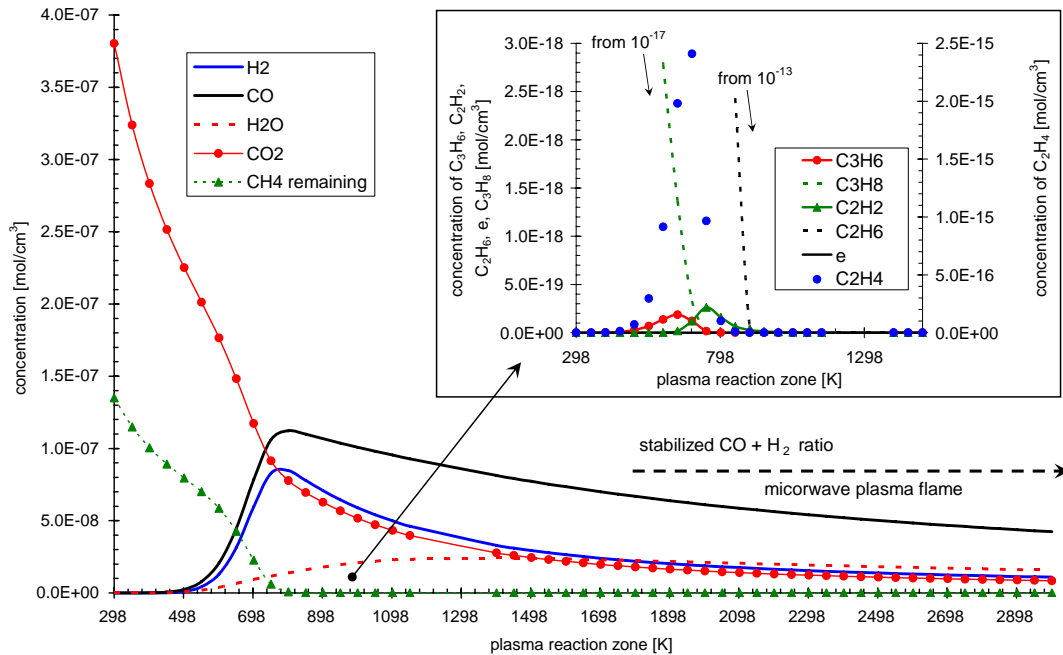


Figure 1. Calculated concentration of the CO, CO₂, H₂, e, H₂O, CH₄, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈ species as a function of plasma reaction zone temperature.

As it can be seen, H₂ and CO are the most stable species above 800 K and by increasing the amount of CO and H₂ the amount of CH₄ remaining concentration decreases. Also by increasing the temperature the amounts of H₂O and CO₂ decrease slowly and are flattened. This is in favor of reactions no.8 and no.10-11 in table 1. Furthermore, the concentrations of atomic species such as H, O, and electrons increase at higher plasma temperature due to the higher rate of electron impact ionization and dissociation reactions.

- *Overall Conclusion from Simulation Results:*

In our system, complex hydrocarbons (like C₂H₄, CH₃OH, C₂H₆, CH₂O and C₂H₂) reported in [1, 6] have very low concentrations, and their probability decreases drastically at higher temperature near our plasma reaction zone. Therefore, in simulations of the CH₄-CO₂-Ar plasma reactor at atmospheric pressure for low MW power along with mole fraction of CH₄/CO₂ of 1 in 5000 sccm Ar, we expect

to detect the high amount of CO and H_2 , while we do not expect to have very high concentrations of complex hydrocarbons such as CH_3OH , C_2H_6 , CH_2O and etc. Obviously, some CH_4 remaining concentration will be detectable too. In addition, H_2O and CO_2 , as undesired species, are expected to be found in our experimental samplings.

Therefore, the non-thermal microwave plasma reactor can be an efficient system for the plasma chemistry reactions such as electron-impact, neutral-neutral and ionic-molecules phenomena needed for the formation of synthesis-gas species from the inlet CH_4 , CO_2 and Ar gas mixture in the absence of catalytic or thermal processes.

4 Plasma Reactor

The experimental setup for synthesis gas production is shown schematically in figure 2 that is similar to the one used in the previously reported system of $\text{CH}_4\text{-O}_2\text{-Ar}$ [13].

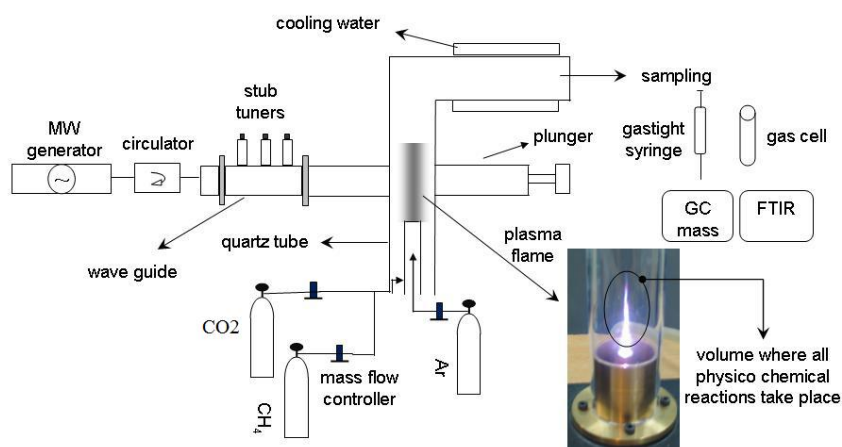


Figure 2. Schematic representation of our experimental setup.

This atmospheric pressure plasma reactor designed for the production of syngas and other byproducts, consists of MW plasma torch as a field applicator, 2.45 GHz MW generator, waveguide components including an isolator and a 3-stubtuner and also a quartz tube for the reaction of carbon and oxygen containing gases with inner diameter of 4 cm and length of 15 cm intersected perpendicularly to the waveguide.

In order to lower the temperature of reactant gases, a cooling tube is located after the quartz tube in which the water passes in the opposite direction to the flow of

the reactant gases. For transporting the produced gas sample to GC and FTIR apparatus, we use a gastight syringe and a gas cell, respectively.

5 Experiments

Experimental Processes and Set-Up:

In the present research the flow rate of high purity reactants Ar (99.999%), CH₄ (99.5%) and CO₂ (99.5%) (supplied from Technical Gas Services Co., UAE), were adjusted with calibrated mass flow controllers (Apex, AX-MC-5SLPM-D). The plasma reactor was cleaned with Ar gas before each experiment. All experiments were done under 1 atm while the reaction time of the inlet gases was about 30 s.

The GC (Thermo Finnigan, column type) equipped with a mass detector for identifying CH₄, CO, CO₂ and C₂H₄ was used to identify the compositions of the products. In addition, FTIR spectrometer (Bruker, Tensor 27) was also used to check the accuracy of GC analysis and to identify the trace amount of byproducts such as CO, CO₂, and CH₄. During the experiment, Ar gas was passed through the quartz tube. This passage through the axial discharge zone of the reactor enables us to stabilize of the plasma torch. Then, working gases (here CH₄ and CO₂) are directly swirled to the plasma zone.

When plasma chemical reactions were been finished, the gas products were passed through a cooling tube before the sampling section. After lowering the temperature of gas, the produced gas mixtures were collected with a 10 ml gastight syringe (SGE) for GC and with a Bruker gas cell (Strom 10, ZnSe windows, Specac Co.) for further FTIR analysis.

Results of Chemical Analysis:

The existence of H₂ molecules as the produced gas was detected by examining the samples prepared at 200 W MW power and CH₄/CO₂ flow rate of 1 through the single ion monitoring "SIM" analysis with the GC system. These results proved the existence of H₂ species formed due to the reaction of CH₄ with CO₂. Also using GC mass detector in total ion chromatograph "TIC" condition species such as CH₄, CO, CO₂ and H₂O were detected. These results confirm our pre-estimated simulation in figure 1 and table 1.

For quantitative investigation of gas samples the conditions of FTIR analysis were set for resolution of 2 cm⁻¹, number of background scans of 32, number of scans of 50, and spectral range of 4000–400 cm⁻¹. The FTIR absorbance spectroscopy for plasma-on and -off state for the inlet CH₄/CO₂ molar ratio of 1 and MW power of 250 W is shown in figure 3. Ar, CH₄ and CO₂ flow rates for this sample were kept at 5000, 180 and 180 sccm, respectively. As it can be seen from figure 3, by applying the plasma discharge the intensity of CO increases in the favor of syngas production.

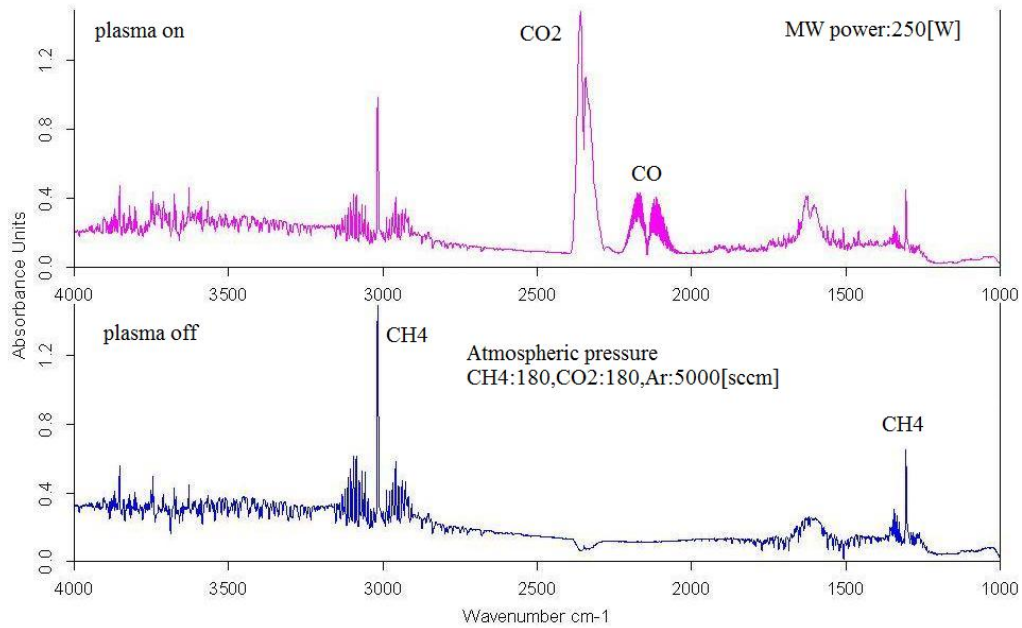


Figure 3. FTIR spectrum comparison of gas sample for plasma-off and plasma-on state.

In order to optimize the production conditions we need to study the effect of main parameters determining the conditions of experiments (here MW power and CH₄/CO₂ flow rate ratio) on CH₄ conversion and CO selectivity as the best quantitative scales which enable us to investigate the overall experimental environment.

Therefore, similar to our previous work [13], for quantitative investigations of the CH₄ conversion and CO selectivity a linear relationship between absorbance and concentration of species regarding Beer's law [20] has been considered, as:

$$A_i(\nu) = a_i(\nu)bc_i, \quad (5)$$

where A_i is the absorbance of i^{th} species, ν is the wavenumber, a_i is the absorptivity, b is the pathlength, and c_i is the concentration.

Considering Eq. (5) using our FTIR absorbance peak at different experimental conditions, the CH₄ conversion and CO selectivity have been evaluated by following relations regarding [20];

$$\text{conversion of } CH_4 \quad \% = \frac{CH_4 \text{ converted}}{CH_4 \text{ fed to the reactor}} \times 100. \quad (6)$$

$$CO \text{ selectivity} \quad \% = \frac{CO \text{ formed}}{CH_4 \text{ converted}} \times 100. \quad (7)$$

6 Variation of Microwave Power and its Effect on syngas Production

The effect of the variation of MW power from 100 to 300 W on plasma chemistry reactions at 1 atm has been investigated by fixing the CH_4/CO_2 ratio to 1 while Ar flow rate was 5000 sccm. The diagrams of CH_4 conversion and CO selectivity from the quantitative FTIR analysis are presented in figure 4.

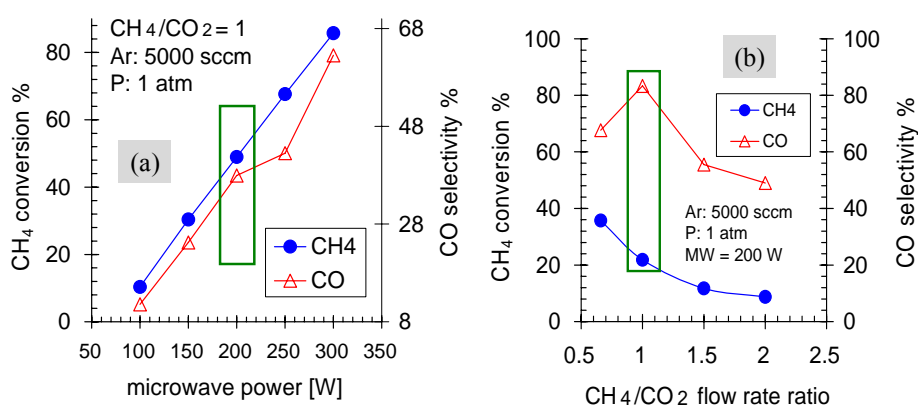


Figure 4. CH_4 conversion and CO selectivity, a. as function of MW power, b. as function of CH_4/CO_2 ratio.

Figure 4 shows the increase tendency of both CH_4 conversion and CO selectivity by increasing the MW power which confirms other literature observations [21]. Also when the MW power increases from 100 to 300 W, CH_4 conversion increases 75.33% along with 51.42% increase of CO selectivity. By comparing these results to previously reported results of the $\text{CH}_4\text{-O}_2$ system [13], while the flow ratio of O_2/CH_4 was 1:2, under similar conditions in the case of $\text{CH}_4\text{-CO}_2$ system we find an almost 1.8 times higher CH_4 conversion value along with more than 4.4 times higher CO selectivity.

7 Effect of CH_4/CO_2 Flow Ratio

In order to analyze the effect of CH_4/CO_2 on syngas production this ratio has been varied by 0.66 (180sccm / 270sccm), 1 (180sccm / 180sccm), 1.5 (180sccm / 120sccm), 2 (180sccm / 90sccm) and 2.57 (180sccm / 70sccm) while the Ar flow rate was set to be 5000 sccm and the experiments were investigated under atmospheric pressure with 200 W MW power.

Figure 4 shows the value of CH_4 conversion and CO selectivity extracted from FTIR analysis regarding Eqs. (6-7). Thus, as it can be seen the CH_4 conversion

decreases by 30.68% while the CH₄/CO₂ ratio increases from 0.66 to 2.57. It shows similar behavior if we compare it to behavior of the previously reported system CH₄-O₂ [13] which showed an increase of 29.6% of CH₄ conversion when O₂/CH₄ ratio increases from 0.4 to 1. This means that in both systems by increasing the CH₄ inlet ratio from the optimum thermodynamics estimation the CH₄ conversion quantity decreases.

Moreover, the value of CO selectivity in CH₄-CO₂ system increases by 15.65% while the CH₄/CO₂ ratio increases from 0.66 to 1 and decreases by 43.08% while the CH₄/CO₂ ratio increases from 1 to 2.57. However, at CH₄/CO₂ ratio of 1, the maximum value of CO selectivity can be reached, indicating that, reaction no.1 in table 1 dominates other CH₄ partial oxidation reactions in the plasma medium. This also was confirmed by other literature experiences [1] and our thermodynamic estimation. Such behavior is also detectable in the CH₄-O₂ [13] system where at the ratio of 1:2 of O₂/CH₄ this system shows the maximum CO selectivity.

Therefore, we can conclude that at low MW power up to 200-300 W at 1 atm with CH₄/CO₂ flow ratio of 1, the maximum CO selectivity can be reached as the optimum syngas production condition. However, by increasing the MW power the value of CO selectivity can be increased by almost 20% for each 100 W step. Obviously, one should also consider the fact that at higher MW power the number of the other undesired species increases too.

8 Conclusions

In this study the conversion of CH₄ from CH₄-CO₂-Ar gas mixture to syngas and other valuable products at 1 atm using the MW plasma torch reactor without catalysis process has been investigated experimentally and theoretically.

In comparison with similar works, lower power of MW plasma torch along with low flow rate of the reactant gases was used. In addition, a thermodynamic modeling using the Gibbs energy minimization method has been used to simulate the concentrations of all species formed in the gas phase plasma medium. In this simulation the presented model quantitatively predicts the concentration of plasma activated species and the most expected species at our experimental environment. The predicted results confirm the existing literatures and our experiments.

For experimental investigation Ar gas has been chosen as the carrier gas while CH₄ and CO₂ were the feed stock gases. GC and FTIR methods were used for characterizing and analyzing the produced gases. The effects of gas flow rate ratio defined by CH₄/CO₂ and MW power on CH₄ conversion and CO selectivity quantities have been investigated.

Our experimental results in addition to our theoretical pre-estimation proved that at low MW power under atmospheric pressure, the conversion of CH₄-CO₂ to syngas can be performed. Moreover, optimum value of CH₄/CO₂ flow rate ratio was found to be 1 in order to achieve maximum value of CO selectivity. Comparison our result to the previously reported system CH₄-O₂-Ar confirms the expected higher CH₄ conversion ratio in CH₄-CO₂-Ar system while the microwave power of plasma reactor increases. In conclusion, non-thermal plasma reactor is found to be an efficient system for plasma chemistry reactions needed for the formation of syngas from the CH₄-CO₂-Ar gas mixture in the absence of catalytic or thermal processes.

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