

Reactions in a mixture of CH<sub>4</sub> and CO<sub>2</sub> under the action of microwave  
discharge at atmospheric pressure

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**Abstract**

Reactions between CH<sub>4</sub> and CO<sub>2</sub> under the action of continuous microwave discharge at atmospheric pressure were studied in a special homemade reactor. The main products were CO and H<sub>2</sub>, while acetylene and ethylene were also found in the products. Experimental results show that conversions of CH<sub>4</sub> and CO<sub>2</sub> could be higher than 90% without the presence of any catalyst. Effects of CO<sub>2</sub>/CH<sub>4</sub> molar ratio and total flow rate of the feed gas on the reaction results were also investigated.

**Key words:** methane; carbon dioxide; action of microwave discharge

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**1. Introduction**

Studies on the conversion of natural gas are very important owing to the declining reserves of crude oil and the abundant resources of natural gas. Since methane, the main component of natural gas, is thermodynamically one of the most stable hydrocarbons, such that selective conversion of methane to more useful organic

chemicals is difficult. A number of promising methods for the conversion of natural gas are under extensive development, and one of them is the application of microwave technology for selective activation of methane [1--13]. Among these researches, the application of microwave discharge or plasma for the conversion of methane to higher hydrocarbons have been investigated, and certain important results were achieved in the experiments [8--13]. In the early stage, McCarthy reported that methane could be decomposed and converted mainly to acetylene under microwave plasma at low pressures [8]. In recent years, Suib et al. have reported a selective, direct, continuous and low-power-consuming catalytic conversion of CH<sub>4</sub> to higher hydrocarbons via microwave plasma methods in the pressure range 10--50 Torr [9]. In their experiments, CH<sub>4</sub> could be converted to ethane, ethylene and acetylene with different selectivities, depending on the power of the microwave plasma, the flow rate, the nature of the catalyst and the pressure of the system. Levanov et al. reported that formic acid was found to be the main product upon low-temperature (77 K) condensation in a CH<sub>4</sub> - CO<sub>2</sub> mixture which dissociated in the microwave discharge at a low pressure [10]. Oumghar reported methane conversion by an air microwave plasma, with 17%--62% of methane in the gas mixture and under pressures of 10-66 mbar and flow rates of 140--700 ml/min [11]. Zhang et al. synthesized carbon tubes by using microwave plasma-assisted chemical-vapor-deposition under low pressure [12].

The above investigations showed that methane conversion via microwave discharge or plasma was usually conducted under low pressures, namely, below

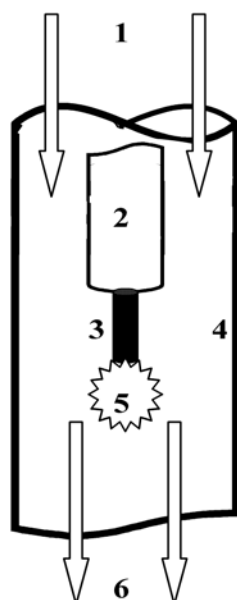
atmospheric pressure. Simon et al reported that atmospheric methane plasmas need to be stabilized by using argon as a diluent [13]. In the present paper, we report on the utilization of continuous microwave discharge at atmospheric pressure for the reforming of methane with carbon dioxide, without the presence of any diluent or catalyst, and the reaction was carried out in a special homemade reactor. In this study, the influence of feed gas flow rates and  $\text{CO}_2/\text{CH}_4$  molar ratios on the selectivity and conversion of methane was also explored.

## 2. Experimental

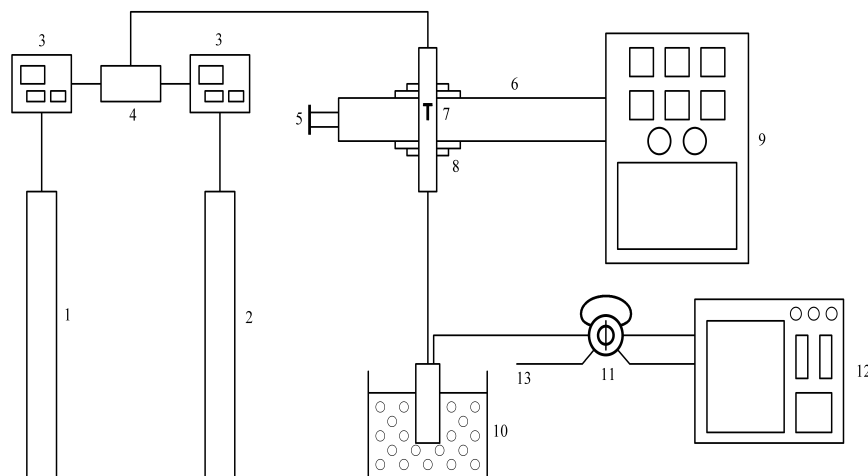
$\text{CH}_4$  used in our experiments was directly from natural gas (98.5% methane, 1.3% ethane and 0.2% nitrogen) without further purification.  $\text{CO}_2$  with a purity of 99% (containing 1%  $\text{N}_2$ ) was used as another reaction gas for the experiments. Flow rates of  $\text{CH}_4$  and  $\text{CO}_2$  were controlled separately by mass flow meters. By adjusting the flow rates of each feed gas, different molar ratios of  $\text{CO}_2/\text{CH}_4$  could be obtained. Microwave radiation was generated by a variable continuous microwave generator with a working frequency of 2450 MHz and a total power of 10 kW. The reaction cavity was a modified section of the wave-guide where a special homemade reactor for producing continuous microwave discharge at atmospheric pressure was inserted, and its longitudinal axis was perpendicular to the length-wise side of the rectangular wave-guide. The schematic diagram of the reactor and the experimental equipment are shown in Figures 1 and 2.

Usually, microwave discharge reactions of  $\text{CH}_4$  and  $\text{CO}_2$  mixtures were conducted under low pressures, because stable continuous microwave discharge of

those gases was difficult to maintain under atmospheric pressure. Therefore, vacuum technique has to be employed to control the microwave discharge reactions in those studies, which is, however, a disadvantage for the commercialization of the process. In the present study, the reactions of CH<sub>4</sub> and CO<sub>2</sub> mixtures microwave discharge were conducted in a special homemade reactor, which could easily initiate continuous microwave discharge under atmospheric pressure by continuous microwave irradiation. The initiation and maintenance of the microwave discharge for the reactions of the CH<sub>4</sub> and CO<sub>2</sub> mixtures were mainly due to a metal initiator in the center of the reactor, as presented in Figure 2, which could produce continuous discharge on its tip under microwave irradiation. The microwave discharge initiator used in this experiment was made of stainless steel.



**Figure 1.** Schematic diagram of the microwave discharge reactor at atmospheric Pressure. 1---reagent gas feed in, 2---quartz tube for connecting 3, 3---microwave discharge initiator, 4---outside quartz tubular reactor, 5---microwave discharge zone, 6---tail gas to chromatographs



**Figure 2.** Diagram of equipment of atmospheric pressure microwave discharge for CH<sub>4</sub> and CO<sub>2</sub> conversion. 1---CH<sub>4</sub>, 2---CO<sub>2</sub>, 3---mass flow meter, 4--- feed gas mixing tank, 5--- plunger, 6--- rectangular wave-guide, 7--- atmospheric pressure microwave discharge reactor, 8--- water-sleeve, 9--- microwave generator, 10--- condenser, 11--- six-pole valve, 12--- gas chromatographs, 13--- tail gas let out

At the start of an experiment, the feed gas was fed into the reactor before it was irradiated by microwave. After the air in the reactor was replaced by the feed gas completely, the reaction zone was subjected to continuous microwave irradiation with an appropriate power of about 500 W. By varying the position of the plunger, the microwave cavity could be made to resonate at the working frequency, and the discharge was initiated on the tip of the microwave discharge initiator. During the microwave discharge reactions a spherical bright plasma zone could be observed, and the size of which depended on the diameter of the metal initiator and the microwave incident power, which was about 6 mm in diameter. Usually, a large diameter for the metal initiator and a high microwave incident power could lead to a bigger discharge plasma zone. The sound of microwave discharge could be heard as soon as the discharge reaction took place.

The products were analyzed by two online gas chromatographs equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) respectively, and both were equipped with carbon molecular sieve columns for the separation of the gas species in the tail gas. CH<sub>4</sub>, CO and CO<sub>2</sub> were analyzed with the thermal conductivity detector (TCD), whilst CH<sub>4</sub>, acetylene, ethylene and ethane were analyzed by the flame ionization detector (FID). Conversions of CH<sub>4</sub> and CO<sub>2</sub>, as well as selectivities towards CO<sub>2</sub>, acetylene, ethylene and ethane were calculated on carbon bases with respect to normalized total species in the tail gas, detected by both of the online gas chromatographs with TCD and FID, and the coke deposits were ignored because very little carbon deposits were found during the microwave discharge reactions. The selectivity towards H<sub>2</sub> was calculated basing on the hydrogen and oxygen balance in the system.

### **3. Results and discussions**

#### **3.1. Reactions of CH<sub>4</sub> with CO<sub>2</sub> under discharge at atmospheric pressure**

The atmospheric pressure microwave discharge produced in this work by the special homemade reactor could generate high temperature in the discharge zone, though the edge temperature of which was comparatively low. Accordingly, the continuous microwave discharge presented here is a high temperature plasma process. For this reason, the reactions of CH<sub>4</sub> with CO<sub>2</sub> occurred at high temperatures and under energetic microwave discharge were quite complicated. From the data determined by the two online gas chromatographs we know that the main products of the discharge reactions were CO and H<sub>2</sub>, while a certain amount of C<sub>2</sub> hydrocarbons

such as acetylene, ethylene and ethane was also found in the tail gas. So we can visualize that the following reaction was the predominant reaction during the experiments:

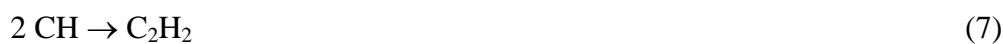


This reaction is referred to as “reforming of methane by carbon dioxide”, which is a very promising way for producing syngas, because it can diminish the amount of the green-house gas  $\text{CO}_2$ , and the reaction conditions are rather mild.

Under similar reaction conditions, the decomposition of methane can also happen [9]:



These reactions can lead to the formation of acetylene, ethylene and ethane by the following reactions:

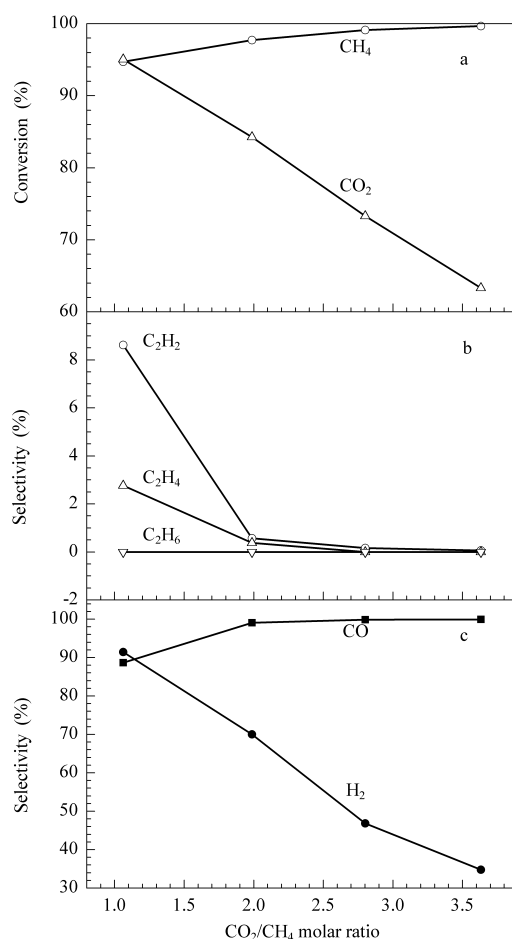


These reactions for producing  $\text{C}_2$  hydrocarbons are competing with the reforming reaction (1) during the microwave discharge, as will be evidenced by the results of the following sections.

### **3.2. Effect of the $\text{CO}_2/\text{CH}_4$ molar ratio**

Effect of the  $\text{CO}_2/\text{CH}_4$  molar ratio on the reactions of methane with  $\text{CO}_2$  under

microwave discharge at atmospheric pressure were investigated. As shown in Figure 3 and Table 1, conversion of CH<sub>4</sub> increased slightly to higher than 95% with the increasing of the CO<sub>2</sub>/CH<sub>4</sub> molar ratio, while CO<sub>2</sub> conversion decreased sharply from 95% to about 60%. The reason is as follows: The main reaction of CH<sub>4</sub> and CO<sub>2</sub> under microwave discharge at atmospheric pressure was the reforming reaction (1). The stoichiometric ratio of CO<sub>2</sub>/CH<sub>4</sub> in this reaction was 1, while the molar ratio of CO<sub>2</sub>/CH<sub>4</sub> employed in our experiments was above 1, so that when CO<sub>2</sub> exceeded the reaction stoichiometry of the main reaction, the conversion of CO<sub>2</sub> will decrease.

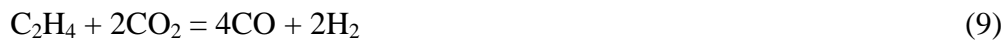


**Figure 3.** Effect of CO<sub>2</sub>/CH<sub>4</sub> molar ratio on the reactions of methane and CO<sub>2</sub>. Reaction conditions: atmospheric pressure, microwave power input 500 W, total flow rate 160 ml/min (STP)

**Table 1. Effect of CO<sub>2</sub>/CH<sub>4</sub> molar ratio on the conversion of CO<sub>2</sub> and CH<sub>4</sub>**

CO <sub>2</sub> /CH <sub>4</sub> molar ratio	Conversion (%)	
	CO <sub>2</sub>	CH <sub>4</sub>
1.05	95.0	95.0
1.95	84.1	97.8
2.85	73.0	99.5
3.65	63.8	99.8

Figure 3b shows the effect of CO<sub>2</sub>/CH<sub>4</sub> molar ratio on the selectivities of the products. From Figure 3b we can see that the selectivity of CO increased with increasing CO<sub>2</sub>/CH<sub>4</sub> molar ratio, but the selectivities of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> changed in the converse way. This is because that the increasing amount of CO<sub>2</sub> in the reacting gas can facilitate the formation of CO from CH<sub>4</sub>, as shown in reaction (1), while at the same time lead to the deep dehydrogenation or oxidation of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub>. These processes can be described as follows:

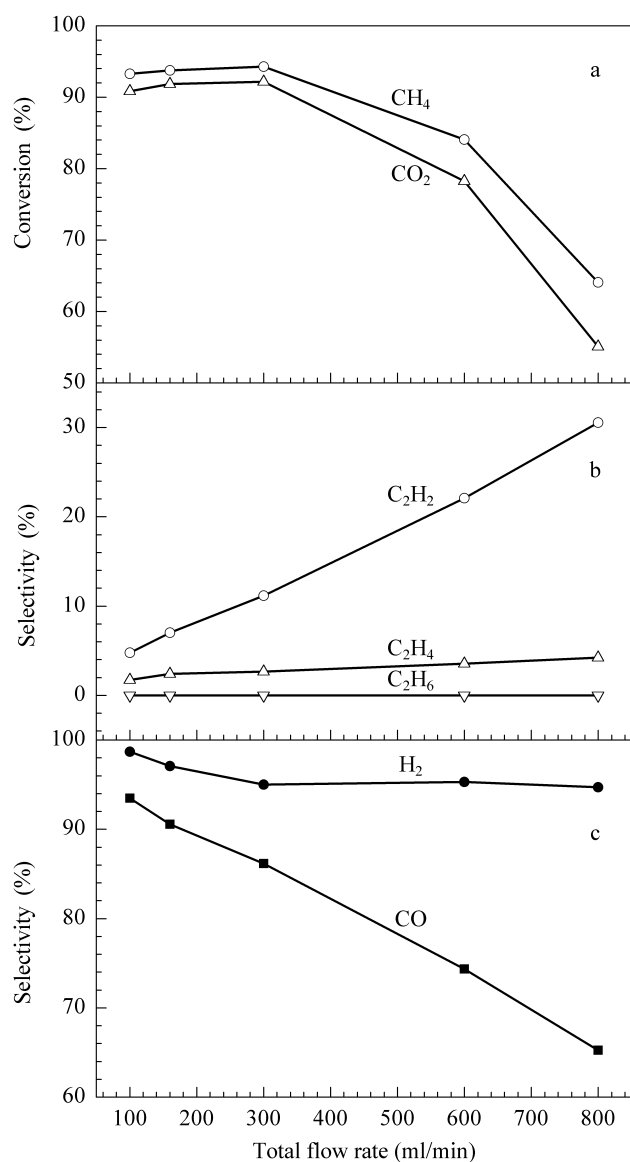


### 3.3. Effect of the total flow rate

Effect of total flow rate on the reactions of methane and CO<sub>2</sub> under microwave

discharge at atmospheric pressure were also investigated, and the results are shown in Figure 4a and 4b. It can be seen from Figure 4a that the conversions of CH<sub>4</sub> and CO<sub>2</sub> changed slightly with the increasing in total flow rate of the feed gas when it was below 300 ml/min, whereas they decreased sharply with the increasing of the total flow rate when it was above 300 ml/min. This phenomenon indicated that the resident time of the CH<sub>4</sub> and CO<sub>2</sub> reacting gases in the microwave discharge zone had an effect on the degree of discharge reactions. When it was enough so that the reactions could take place in a considerable extent, the conversions of CH<sub>4</sub> and CO<sub>2</sub> did not change much with increasing the flow rate of feed gas; while it was insufficient, the conversions would be relied on the resident time and decreased obviously with increasing the flow rate.

Figure 4b and 4c shows that the variation of flow rate of the feed gas had considerable effect on the selectivities of the products. The CO selectivity decreased with increasing feed gas flow rate, and the H<sub>2</sub> selectivity decreased a little as compared with that of CO. On the other hand, the selectivities of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> increased with increasing flow rate, but the C<sub>2</sub>H<sub>6</sub> selectivity did not change obviously, as the value of which was too small. So we can conclude that a short resident time would lead to the quenching of the C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> products and the avoiding of their further decomposition and oxidation, and as a result, the selectivities of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> increased, while the productions of CO and H<sub>2</sub> were inhibited.



**Figure 4.** Effect of total flow rate on the reactions of CH<sub>4</sub> and CO<sub>2</sub>. Reaction conditions: atmospheric pressure, microwave power input 500 W, molar ratio CO<sub>2</sub>/CH<sub>4</sub>=1

#### 4. Conclusions

Reactions of CH<sub>4</sub> and CO<sub>2</sub> were conducted under microwave discharge at atmospheric pressure in a special homemade reactor. Conversions of CH<sub>4</sub> and CO<sub>2</sub> could be higher than 90% without the presence of any catalyst. The main products

were CO and H<sub>2</sub>, while at the same time C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> were also produced during the reactions. The main reaction in this process was the reforming of methane with CO<sub>2</sub>. Variations in selectivity and conversion with feed gas flow rates as well as CO<sub>2</sub>/CH<sub>4</sub> molar ratios were explored. Conversion of CH<sub>4</sub> increased and CO<sub>2</sub> conversion decreased with the increasing of the CO<sub>2</sub>/CH<sub>4</sub> molar ratio. The selectivity of CO increased with increasing CO<sub>2</sub>/CH<sub>4</sub> molar ratio, but the selectivities of C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and H<sub>2</sub> changed in the converse way. Conversions of CH<sub>4</sub> and CO<sub>2</sub> changed slightly with the increasing of the total flow rate of feed gas when it was below 300 ml/min, whereas they decreased sharply with the increasing of the total flow rate when it was above 300 ml/min. The CO selectivity decreased with increasing feed gas flow rate, and the H<sub>2</sub> selectivity decreased very little as compared with that of CO. On the other hand, selectivities of C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> increased with increasing flow rate, but C<sub>2</sub>H<sub>6</sub> selectivity did not change obviously.

## References

- [1] Tanashev Y Y, Fedoseev V I, Aristov Y I, Pushkarev V V, Avdeeva L B, Zaikovskii V I, Parmon V N I. *Catal Today*, 1998, **42**: 333
- [2] Bond G, Moyes R B, Whan D A. *J Catal*, 1993, **17**: 427
- [3] Roussy G, Thiebaut J M, Souiri M, Marchal E, Kiennemann A, Maire G. *Catal Today*, 1994, **21**: 349
- [4] Chen C, Hong P, Dai S, Kan J. *J Chem Soc, Faraday Trans*, 1995, **91**(7): 1179
- [5] Marun C, Conde L D, Suib S L. *J Phys Chem A*, 1999, **103**(22): 4332
- [6] Fedoseev V I, Aristov Y I, Tanashev Y Y, Parmon V N. *Kinet Catal (Transl Kinet*

- Katal*), 1996, **37**(6): 808
- [7] Ioffe M S, Pollington S D, Wan J K S. *J Catal*, 1995, **151**: 349
- [8] McCarthy R L. *J Chem Phys*, 1954, **22**(8): 1360
- [9] Suib S L, Zenger R P. *J Catal*, 1993, **139**: 383
- [10] Levanov A V, Gromov A R, Antipenko E E, Lunin V V. *Russ Chem Bull*, 2000, **9**(5): 823
- [11] Oumghar A, Legrand J C, Diamy A M. *Plasma Chem Plasma Process*, 1995, **15**(1): 87
- [12] Zhang Q, Yoon S F, Ahn J, Gan B, Rusli M B Yu. *J Mater Res*, 2000, **15**(8): 1749
- [13] Simon M W, Rozak J R, Suib S L, Harrison J, Kablauoi M. *Res Chem Intermed*, 2000, **26**(6): 529