Reactions in a Mixture of CH\textsubscript{4} and CO\textsubscript{2} under the Action of Microwave Discharge at Atmospheric Pressure

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[Manuscript received February 6, 2002; revised April 26, 2002]

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

Key words: CH\textsubscript{4}, CO\textsubscript{2}, microwave discharge, atmospheric pressure

1. Introduction

Studies on the conversion of natural gas are very important because of the declining reserves of crude oil and the abundant resources of natural gas. Since methane, the main component of natural gas, is one of the most thermodynamically stable hydrocarbons, 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. One of these methods is the application of microwave technology for selective activation of methane [1–13]. In these studies, the applications of microwave discharge or plasma for the conversion of methane to higher hydrocarbons have been investigated and certain important results achieved [8–13]. In the early stages, McCarthy [8] reported that methane could be decomposed and converted mainly to acetylene under microwave plasma at low pressures. In recent years, Suib et al. [9] have reported a selective, direct, continuous and low-power-consuming catalytic conversion of CH\textsubscript{4} to higher hydrocarbons via microwave plasma methods in the pressure range 10–50 Torr. In their experiments, CH\textsubscript{4} 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. [10] reported that formic acid was found to be the main product upon low-temperature (77 K) condensation in a CH\textsubscript{4}-CO\textsubscript{2} mixture which dissociated in the microwave discharge at a low pressure. Oumghar et al. [11] reported methane conversion by an air microwave plasma, with 17\%–62\% of methane in the gas mixture, pressures of 10–66 mbar, and flow rates of 140–700 ml/min. Zhang et al. [12] synthesized carbon tubes by using microwave plasma-assisted chemical-vapor-deposition under low pressure.

The above investigations illustrated that methane conversion via microwave discharge or plasma was usually conducted under low pressures, specifically, below atmospheric pressure. Simon et al. [13] reported that atmospheric methane plasmas needed to be stabilized by using argon as a diluent. In this paper, we report on the utilization of continuous microwave discharge at atmospheric pressure for the reforming of methane with carbon dioxide, which was carried out in a special homemade reactor without the presence of any diluent or catalyst. The influence of

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the feed gas flow rate and CO₂/CH₄ molar ratio on the conversion of methane and selectivity of products was also explored.

2. Experiment

The CH₄ used in our experiments came directly from natural gas (98.5% methane, 1.3% ethane and 0.2% nitrogen) without further purification. CO₂ with a purity of 99% (containing 1% N₂) was used as another reaction gas for the experiments. Flow rates of CH₄ and CO₂ were controlled separately by mass flow meters. By adjusting the flow rates of each feed gas, different molar ratios of CO₂/CH₄ could be obtained. Microwave radiation was generated by a variable continuous microwave generator with a working frequency of 2,450 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. Its longitudinal axis was perpendicular to the length-wise side of the rectangular wave-guide. The schematic diagrams of the reactor and the experimental equipment are shown in Figure 1 and Figure 2, respectively.

![Figure 1. Schematic diagram of the microwave discharge reactor at atmospheric pressure.](image1)

(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 CH₄ and CO₂ conversion.](image2)

(1) CH₄; (2) CO₂; (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.

Usually, microwave discharge reactions of CH₄ and CO₂ mixtures were conducted under low pressures, because stable continuous microwave discharge of those gases was difficult to maintain under atmospheric pressure. Therefore, a 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 between CH₄ and CO₂ under 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$_4$ and CO$_2$ mixtures were mainly due to a metal initiator, which could produce a continuous discharge on its tip under microwave irradiation, in the center of the reactor as presented in Figure 2. The microwave discharge initiator used in this experiment was made of stainless steel (ϕ 3 mm). The diameter of the outside quartz tubular reactor was 15 mm.

To begin the experiment, the feed gas was fed into the reactor before being irradiated by the microwave. After the air in the reactor was completely replaced by the feed gas, 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, the size of which depended on the diameter of the metal initiator and the microwave incident power, about 6 mm in diameter was observed. Usually, a large diameter for the metal initiator and a high microwave incident power led to a large discharge plasma zone. The sound of microwave discharge could be heard immediately after 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 carbon molecular sieve columns for the separation of the gas species in the tail gas. CH$_4$, CO, and CO$_2$ were analyzed with TCD, while CH$_4$, acetylene, ethylene, and ethane were analyzed by FID. Conversions of CH$_4$ and CO$_2$, as well as selectivities towards CO$_2$, 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. Coke deposits were ignored because very little carbon deposits were found during the microwave discharge reactions. The selectivity towards H$_2$ was calculated based on the hydrogen and oxygen balance in the system.

3. Results and discussion

3.1. Reactions of CH$_4$ with CO$_2$ under discharge at atmospheric pressure

The atmospheric pressure microwave discharge produced in this work by the special homemade reactor could generate high temperatures in the discharge zone, though the temperature at the edge of the reactor was comparatively low. Accordingly, the continuous microwave discharge presented here is a high temperature plasma process. For this reason, the reactions of CH$_4$ with CO$_2$ that occurred at high temperatures and under energetic microwave discharge were quite complicated. From the data derived from the two online gas chromatographs we know that the main products of the discharge reactions were CO and H$_2$, while a certain amount of C$_2$ hydrocarbons such as acetylene, ethylene and ethane were also found in the tail gas. Therefore, we can visualize that the following reaction was the predominant reaction during the experiments:

$$\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2$$ (1)

This reaction is referred to as “reforming of methane with carbon dioxide”, which is a very promising way of producing syngas, because it can diminish the amount of the green-house gas CO$_2$ under mild conditions.

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

$$\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$$ (2)

$$\text{CH}_3 \rightarrow \text{CH}_2 + \text{H}$$ (3)

$$\text{CH}_2 \rightarrow \text{CH} + \text{H}$$ (4)

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

$$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$$ (5)

$$2\text{CH}_2 \rightarrow \text{C}_2\text{H}_4$$ (6)

$$2\text{CH} \rightarrow \text{C}_2\text{H}_2$$ (7)

These processes for producing C$_2$ hydrocarbons are competing with the reforming reaction (1) during the microwave discharge, as will be demonstrated by the results in the following sections.

3.2. Effects of CO$_2$/CH$_4$ molar ratio

Effects of the CO$_2$/CH$_4$ molar ratio on the reactions of methane with CO$_2$ under microwave discharge at atmospheric pressure were also investigated. As shown in Figure 3a, the conversion of CH$_4$ slightly
increased to higher than 95% with an increase in the CO$_2$/CH$_4$ molar ratio, while CO$_2$ conversion decreased sharply from 95% to about 60%. This can be explained because the main reaction of CH$_4$ and CO$_2$ under microwave discharge at atmospheric pressure was the reforming reaction (1) in which the stoichiometric ratio of CO$_2$/CH$_4$ was 1, while the molar ratio of CO$_2$/CH$_4$ employed in our experiments was above 1, so that when CO$_2$ exceeded the reaction stoichiometry of the main reaction, the conversion of CO$_2$ decreased.

This is because the increasing amount of CO$_2$ in the reacting gas can facilitate the formation of CO from CH$_4$, as shown in reaction (1), and at the same time lead to the deep dehydrogenation or oxidation of C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$ and H$_2$ as shown below:

$$C_2H_2 + 2CO_2 = 4CO + H_2$$  \hspace{1cm} (8)
$$C_2H_4 + 2CO_2 = 4CO + 2H_2$$  \hspace{1cm} (9)
$$C_2H_6 + 2CO_2 = 4CO + 3H_2$$  \hspace{1cm} (10)
$$H_2 + CO_2 = CO + H_2O$$  \hspace{1cm} (11)

3.3. Effects of the total flow rate

Figure 3b and Figure 3c show the effect of CO$_2$/CH$_4$ molar ratio on the selectivity of the products. From Figure 3b and Figure 3c, we can see that the selectivity to CO increased with increasing CO$_2$/CH$_4$ molar ratio, but the selectivities to C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$ and H$_2$ changed in the opposite way.

Effects of total flow rate on the reactions of methane and CO$_2$ under microwave discharge at atmospheric pressure were also investigated, and the re-
results are shown in Figure 4. It can be seen from Figure 4a that the conversions of CH$_4$ and CO$_2$ slightly changed with an increase in the total flow rate of the feed gas when it was below 300 ml/min, whereas they sharply decreased with an increase in the total flow rate when it was above 300 ml/min. This phenomenon indicated that the resident time of the CH$_4$ and CO$_2$ reacting gases in the microwave discharge zone had an effect on the degree of discharge reactions. When the resident time was high enough so that the reactions could take place to a considerable extent, the conversions of CH$_4$ and CO$_2$ did not change much with increasing the flow rate of feed gas. While it was insufficient, the conversions would rely on the resident time and obviously decreased with increasing the flow rate.

Figure 4b and Figure 4c show that the variation of the flow rate of feed gas had considerable effect on the selectivity of the products. The CO selectivity decreased while increasing the feed gas flow rate, and the H$_2$ selectivity only slightly decreased in comparison with that of CO. On the other hand, the selectivities for C$_2$H$_2$ and C$_2$H$_4$ increased with increasing flow rate, but the C$_2$H$_6$ selectivity did not noticeably change because the value was too small. We can conclude that a short resident time would lead to the quenching of the C$_2$H$_2$ and C$_2$H$_4$ products while avoiding their further decomposition and oxidation. As a result, the selectivities for C$_2$H$_2$ and C$_2$H$_4$ increased, while the productions of CO and H$_2$ were inhibited.

4. Conclusion

Reactions of CH$_4$ and CO$_2$ were conducted under microwave discharge at atmospheric pressure in a special homemade reactor. Conversions of CH$_4$ and CO$_2$ could be higher than 90% without the presence of any catalyst. The main products were CO and H$_2$, while C$_2$H$_2$, C$_2$H$_4$ and C$_2$H$_6$ were also produced during the reactions. The main reaction in this process was the reforming of methane with CO$_2$. Variations in selectivity and conversion with the feed gas flow rate as well as CO$_2$/CH$_4$ molar ratio were all explored. Conversion of CH$_4$ increased and CO$_2$ conversion decreased with the increase of the CO$_2$/CH$_4$ molar ratio. The selectivity for CO increased with increasing CO$_2$/CH$_4$ molar ratio, but the selectivities for C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$ and H$_2$ changed in the converse way. Conversions of CH$_4$ and CO$_2$ slightly changed with increasing the total flow rate of feed gas when it was below 300 ml/min, whereas they sharply decreased with increasing the total flow rate when it was above 300 ml/min. The CO selectivity decreased with increasing feed gas flow rate, and the H$_2$ selectivity decreased very little as compared with that of CO. On the other hand, selectivities for C$_2$H$_2$ and C$_2$H$_4$ increased with increasing flow rate, but C$_2$H$_6$ selectivity did not obviously change.

References