

A study on methane coupling to acetylene under the microwave plasma

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By optimizing the microwave chemistry reactor made of the rectangular waveguide resonator, the methane conversion (the maximum 93.7%), the C₂ hydrocarbon yield (the maximum 91.0%) and the acetylene yield (the maximum 88.6%) were all greatly increased under the microwave plasma. Furthermore, for the optimal reactor, the change of the methane conversion and the C₂ hydrocarbon yield is little within the range of the pressures in the experiments. The C₂ hydrocarbon is mainly made up of acetylene, and the selectivity for acetylene is above 90%. Energy yield and space time yield of acetylene are also high. Optical emission spectroscopy (OES) was adopted for the diagnosis of methane coupling to acetylene under microwave plasma. The excited species (CH, C₂, H₂, H_α) were detected in the spectra range of 300–750 nm. Based on the products and the excited species, the reaction mechanism of methane coupling under microwave plasma was investigated, using the thermodynamics and kinetics of the chemical reaction.

microwave plasma, methane, acetylene

1 Introduction

In the world, the resource of existent petroleum tends to become indigent. However, the storage of natural gas is comparatively abundant. The foreground to develop chemical engineering of natural gas is affirmative. However, methane, the main component of natural gas, is one of the most inert organic compounds, and its direct conversion to useful products is well known to be a difficult process by conventional heating. Recently, methane coupling by unconventional method is getting more and more concerned [1–14]. Methane coupling by microwave plasma also attracted more and more attention [8–14]. Under low pressure, the maximum of the conversion of methane was 93.7%, and the maximum of the selectivity for acetylene 96.5% [8]. A selective, direct, continuous, and low-power catalytic conversion of methane to C₂ hydrocarbons via microwave

plasma method has been developed by Suib and Zerger [9]. Under the pressure of 1.133 kPa, the power of 60 W, and the catalyst of Ni, the methane conversion was 52%, and selectivity for ethylene was 25%, for ethane 50%, and for acetylene 25%. Without catalyst, the conversion of methane was 38%. With high power and low flow rates, coking was produced. A novel method to obtain high yield of C₂ hydrocarbons from methane conversion was proposed by Zhang *et al.* [10]. In that process, microwave heating and microwave-induced plasma were combined with C/SiC catalyst. Under the conditions of pulse power of 90 W, 1% duty and 20 s period, the acetylene yield was >60%. Under pulsed microwave, the effect of $n(\text{H}_2)/n(\text{CH}_4)$ on the methane conversion was investigated by Zhang *et al.* [11, 12]. With the pressure of 0.13 MPa, and $n(\text{H}_2)/n(\text{CH}_4)$ ratio of 2, the methane conversion and the acetylene yield had reached up to 59.2% and 42.7%. The methane decomposition and the formation of C₂ hydrocarbons, in particular acetylene, in a microwave plasma were studied by Heintze

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et al. [13, 14]. The effect of the operating parameters, including the pulse durations, the discharge power, flow rate and pressure, was investigated. The methane conversion and the selectivity for acetylene had reached up to 94.3% and 71.2%, respectively.

The microwave chemistry reactor, made of the rectangular waveguide resonator, was optimized with HFSS (High Frequency Structure Simulator). The effect of the reactor structure on methane coupling was studied, and the energy yield and the space time yield of acetylene were also investigated. Optical emission spectroscopy (OES) was adopted for the diagnosis of methane coupling to acetylene. Optical emission spectroscopy, which can be performed without any physical contact with the plasma, has become a very powerful technique for *in situ* diagnosis of the excitation of atomic and molecular species in the plasma [1–3, 13, 14, 16, 17]. Based on the products and the excited species, the reaction mechanism of methane coupling under microwave plasma was investigated, using the thermodynamics and kinetics of the chemical reaction.

2 Experimental

A schematic diagram of experimental arrangement is shown in Figure 1. The microwave chemistry reactor, made of the rectangular waveguide (BJ22, 109.2 mm × 54.6 mm) resonator, is shown in Figure 2. One end of the rectangular waveguide coupled to an iris is origin ($z=0$) for the z -axis coordinate, and the other end is the short-circuit plunger from the iris to L_i ($i=0, 1$). By adjusting the short-circuit plunger, the resonator would be at the resonant state. There is a hole from the iris to z_i ($i=0, 1$) in the center line of upper and lower surfaces. A quartz tube, with outer diameter of 20 mm and inside diameter of 16 mm, was positioned

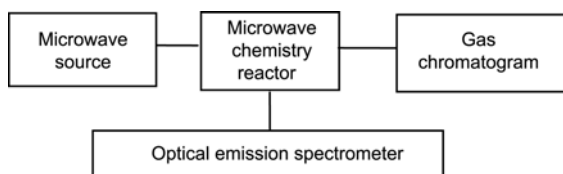


Figure 1 A schematic diagram of experimental arrangement.

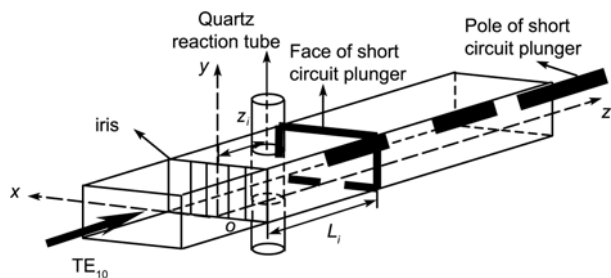


Figure 2 The microwave chemistry reactor made of the rectangular waveguide resonator.

vertically through the hole. The quartz reaction tube was filled with methane. Microwave was generated by magnetron, which was supplied to 400 W power at 2450 MHz. Microwave energy was transmitted to the rectangular waveguide resonator through the microwave transmission system. With the aid of microwave energy, methane was discharged to plasma. Flow of methane (purity > 99.99%) was controlled and read through the mass flow controller and flow totalizer (Beijing Seven Star Electronics Co., Ltd.). The system pressure is different at the different flow, such as the system pressure of 16160 Pa at methane flow of 500 mL/min. Product analysis was done with an on-line SC-6 gas chromatogram and a chromatograph station of type 3000. The optical emission spectrometer (EPP2000, StellarNet Company of USA) was adopted for the diagnosis of methane coupling to acetylene. The wavelength scanning range of the optical emission spectrometer (EPP2000) is 300–750 nm.

3 Results and discussion

3.1 The effect of the reactor structure on methane coupling

HFSS (High Frequency Structure Simulator) was used to calculate the S_{11} parameter (This parameter can show the reflection of power.) of the microwave chemistry reactor with different positions z_i of reaction tube. The simulation results showed that the positions z_i had a great effect on the S_{11} parameter. When the position reaction tube z_0 is 106 mm, the scattering parameter S_{11} would reach the minimum. Figure 3 gives the field structure distribution inside the reactor tube for two different positions. As can be seen from Figure 3, when the reaction tube position $z_0 = 106$ mm, and the short-circuit plunger position $L_0 = 146$ mm, methane gas inside the tube is in the location of the strongest electric field and uniform field distribution, which is conducive to methane discharge. When the reaction tube position $z_1 = 150$ mm, and the short-circuit plunger position $L_1 = 292$ mm, the field structure distribution inside the reactor tube is very uneven, which is not conducive to the reaction of methane gas. The first half of the field is weak, and the second half is strong. It can be regarded as a response to the reaction tube position z_0 of 106 mm, and the microwave chemistry reactor is of the best characteristics of electromagnetic resonance.

Based on this theory simulation, the effect of the reactor structure on methane coupling was investigated by experiments. When the reaction tube location for $z_0 = 106$ mm (optimized) and $z_1 = 150$ mm (before optimization), the methane conversion (Conv) and the C_2 hydrocarbon yield (Y_{C_2}) at different pressures (p) were shown in Figure 4. Figure 4 showed that both the methane conversion (Conv) and the C_2 hydrocarbon yield (Y_{C_2}) increased as the pressure decreased in the range of experiments, when the reaction tube position $z_1 = 150$ mm. While the reaction tube position

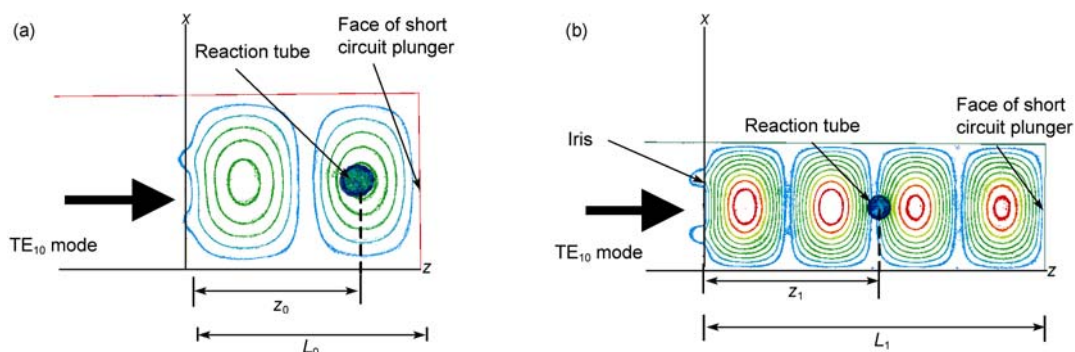


Figure 3 The field structure distribution inside the reactor tube for two different positions. (a) The reaction tube position $z_0 = 106$ mm, and the short-circuit plunger position $L_0 = 146$ mm; (b) the reaction tube position $z_1 = 150$ mm and the short-circuit plunger position $L_1 = 292$ mm.

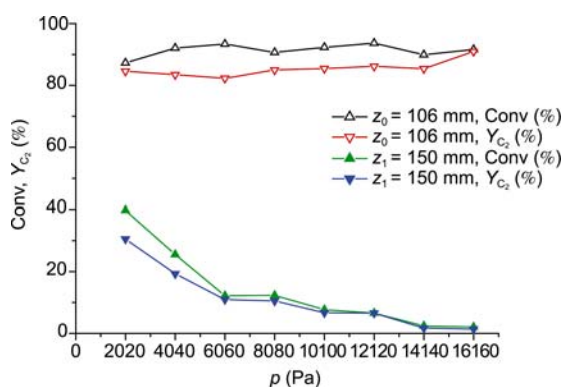


Figure 4 Methane conversion (Conv) and C_2 hydrocarbon yield (Y_{C_2}) vs. pressure (p).

$z_0 = 106$ mm, both the methane conversion (about 90.0%) and C_2 hydrocarbon yield (about 85.0 %) were higher, and the change was little with the change of the pressure in the range of experiments. Experiments show that both the methane conversion (the maximum of 93.7%) and the C_2 hydrocarbon yield (the maximum of 91.0%) were greatly increased under microwave plasma, by optimizing the microwave chemistry reactor made of the rectangular waveguide resonator. When the reaction tube position $z_0 = 106$ mm, methane gas inside the tube is in the location of the strongest electric field and uniform field distribution. It is conducive to methane discharge, so as to enhance the methane conversion and C_2 hydrocarbon yield. The experimental results verify the theoretical calculation results.

3.2 The effect of pressure on methane coupling

Figure 4 shows that both the methane conversion and C_2 hydrocarbon yield were higher, and the change was little with the change of the pressure in the experimental scope, when the reaction tube was at the optimized location (i.e., $z_0 = 106$ mm). At 12120 Pa, the methane conversion was up to 93.7%, while at 16160 Pa, C_2 hydrocarbon yield was up to 91.0%, and the acetylene yield was up to 88.6%. Selectivity of reaction products at different pressures (p) is shown in Figure 5. At 2020–6060 Pa, acetylene was only the pro-

duct of C_2 hydrocarbons. While at 8080–16160 Pa, acetylene was the major product of C_2 hydrocarbons, and there was a small amount of ethylene. At 10100 Pa, the ethylene selectivity reached up to the maximum (9%).

3.3 Energy yield and space time yield of acetylene for methane coupling under the microwave plasma

In the study of methane coupling under microwave plasma, the process is significant for its conversion and selectivity parameters, energy yield (EY, the amount of acetylene per unit of consumed energy) and space-time yield (STY, the amount of acetylene per unit time and unit volume of plasma cavity), which is expressed as

$$EY(C_2H_2) = 0.5 \times Y(C_2H_2) \times F(CH_4) / P \quad (1)$$

$$STY(C_2H_2) = 0.5 \times 10^{-3} \times Y(C_2H_2) \times F(CH_4) / V \quad (2)$$

where $EY(C_2H_2)$ is the energy yield of C_2H_2 (mmol/kJ), $STY(C_2H_2)$ is the space-time yield of C_2H_2 (mol/s m³), $Y(C_2H_2)$ is the yield of C_2H_2 , $F(CH_4)$ is the flow rate of CH_4 (mmol/s), P is the input power (kW) and V is the volume of plasma cavity (m³). Formula (2) multiplied by 10^{-3} is for unit conversion.

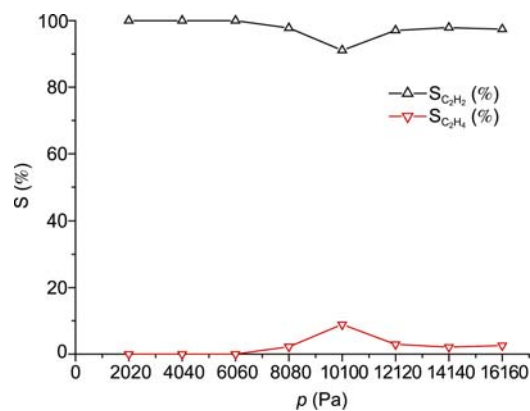


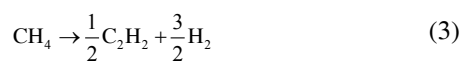
Figure 5 Selectivity of reaction products vs pressure (p), when the reaction tube location $Z_0 = 106$ mm.

Compared with the results under other kinds of discharges shown in Table 1, both the energy yield and the space-time yield are higher basically in the case of microwave plasma discharge. Compared with the results under microwave plasma discharge, both the energy yield and the space-time yield are the highest in ref. [14]. However, acetylene yield is only 67.1% in ref. [14]. In our experiment, both the energy yield and the space-time yield are the second highest, but acetylene yield is relatively high (88.6%), showing that our result of methane coupling to acetylene is better integrated after optimizing the structure of the experimental reactor.

3.4 Thermodynamic analysis for methane coupling under the microwave plasma

Because acetylene was the major product of C₂ hydrocarbons, the reaction of methane coupling to acetylene under microwave plasma was investigated, using the thermodynamics theory.

Chemical reaction equation of methane coupling to acetylene is



Without non-expansion work, Gibbs-Helmholtz equation shows Gibbs free energy change of a chemical reaction with temperature T .

$$\left[\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right]_p = \frac{-\Delta H}{T^2} \quad (4)$$

where ΔH is the thermal effect for the chemical reaction, and the effect of temperature on ΔH follows Kirchhoff's Law.

$$\Delta H = \int \Delta C_p dT + \Delta H_0 \quad (5)$$

where ΔH_0 is an integral constant, and ΔC_p is the isobaric

heat capacity difference between products and reactants of a chemical reaction. The effect of temperature on isobaric heat capacity follows:

$$C_p = a + bT + cT^2 + \dots \quad (6)$$

Based on formulae (4)–(6), the function of ΔG with T for a chemical reaction can be expressed as:

$$\Delta G^\ominus(T) = \Delta H_0 - \Delta aT \ln T - \frac{1}{2}\Delta bT^2 - \frac{1}{6}\Delta cT^3 + \dots + IT \quad (7)$$

where superscript “ \ominus ” indicates the pressure as $p^\ominus = 100$ kPa, and I is an integral constant. The isobaric heat capacity with temperature, the standard enthalpy of formation, and the standard Gibbs free energy were taken from ref. [18].

The thermodynamic equilibrium constants K^\ominus were calculated from ΔG^\ominus .

$$\ln K^\ominus = -\Delta G^\ominus / RT \quad (8)$$

The maximum thermodynamic yields of acetylene Y (C₂H₂) were calculated from the equilibrium constant K^\ominus .

$$K^\ominus = \frac{[(Y/2)/(1+Y)]^{0.5} [(3Y/2)/(1+Y)]^{1.5}}{(1-Y)/(1+Y)} \times \frac{p}{p^\ominus} \quad (9)$$

$$Y(\text{C}_2\text{H}_2) = [K^\ominus / (K^\ominus + 1.299p/p^\ominus)]^{0.5} \times 100\% \quad (10)$$

The maximum thermodynamic yields of acetylene Y (C₂H₂) at various temperatures and pressures were calculated and are listed in table 2. When the temperature is constant, the maximum thermodynamic yield of acetylene increases with decreasing pressure, because $\Delta \nu = 0.5 + 1.5 - 1 = 1 > 0$ for this reaction. At the same pressure, the maximum thermodynamic yield of acetylene increases with increasing pressure, because the reaction is an endothermic reaction. At 14140 Pa and 1000 K, the maximum thermodynamic yield of acetylene is only 4.04%. The very low thermodynamic yield of direct conversion of methane is an obstacle difficult to overcome by utilizing conventional method. Re-

Table 1 The energy yield and space-time yield under kinds of discharges

Discharge method	$F(\text{CH}_4)$ (mmol/s)	P (kW)	V (m ³)	$Y(\text{C}_2\text{H}_2)$ (%)	$EY(\text{C}_2\text{H}_2)$ (mmol/kJ)	$STY(\text{C}_2\text{H}_2)$ (mol/s m ⁻³)
Micro-arc [7]	0.00279	0.0300	— ^{a)}	6.68	0.00311	— ^{a)}
RF [6]	0.00372	0.0500	1.06×10^{-6}	16.3	0.00606	0.286
Pulsed corona [4]	0.0186	0.0153	1.41×10^{-6}	13.3	0.0808	0.877
Microwave discharge [8]	0.0347	0.200	1.17×10^{-5}	90.4	0.0784	1.34
Pulsed microwave [11]	0.0743	0.060	— ^{a)}	42.7	0.264	— ^{a)}
Microwave discharge [14]	0.112	0.070	2.83×10^{-7}	67.1	0.537	133
This research	0.372	0.400	1.10×10^{-5}	88.6	0.412	15.0

a) denotes that the reference did not give specific data.

Table 2 Gibbs free energy change ΔG^\ominus , thermodynamic equilibrium constants K^\ominus and maximum thermodynamic yields of acetylene $Y(\text{C}_2\text{H}_2)$ for methane coupling to acetylene

T (K)	ΔG^\ominus (J/mol)	K^\ominus	$Y(\text{C}_2\text{H}_2)$ (%)			
			2020 Pa	6060 Pa	10100 Pa	14140 Pa
298	155320	6.13×10^{-28}	1.53×10^{-11}	8.83×10^{-12}	6.84×10^{-12}	5.78×10^{-12}
300	155116	9.79×10^{-28}	1.93×10^{-11}	1.12×10^{-11}	8.64×10^{-12}	7.30×10^{-12}
400	143677	1.73×10^{-19}	2.56×10^{-7}	1.48×10^{-7}	1.15×10^{-7}	9.69×10^{-8}
500	131630	1.77×10^{-14}	8.22×10^{-5}	4.74×10^{-5}	3.67×10^{-5}	3.10×10^{-5}
600	119179	4.21×10^{-11}	4.00×10^{-3}	2.31×10^{-3}	1.79×10^{-3}	1.51×10^{-3}
700	106455	1.14×10^{-8}	6.58×10^{-2}	3.80×10^{-2}	2.94×10^{-2}	2.49×10^{-2}
800	93549	7.79×10^{-7}	5.45×10^{-1}	3.15×10^{-1}	2.44×10^{-1}	2.06×10^{-1}
900	80527	2.12×10^{-5}	2.84	1.64	1.27	1.07
1000	67436	3.00×10^{-4}	10.6	6.16	4.78	4.04
1100	54314	2.64×10^{-3}	30.2	18.0	14.0	11.9
1200	41190	1.61×10^{-2}	61.7	41.2	33.1	28.4
1300	28085	7.44×10^{-2}	86.0	69.7	60.2	53.7
1400	15018	2.75×10^{-1}	95.6	88.2	82.3	77.4
1500	2001	8.52×10^{-1}	98.5	95.7	93.1	90.7

cently, methane coupling by unconventional method is getting more and more concerned [1–14]. Methane coupling by microwave plasma also attracted more and more attention [8–14].

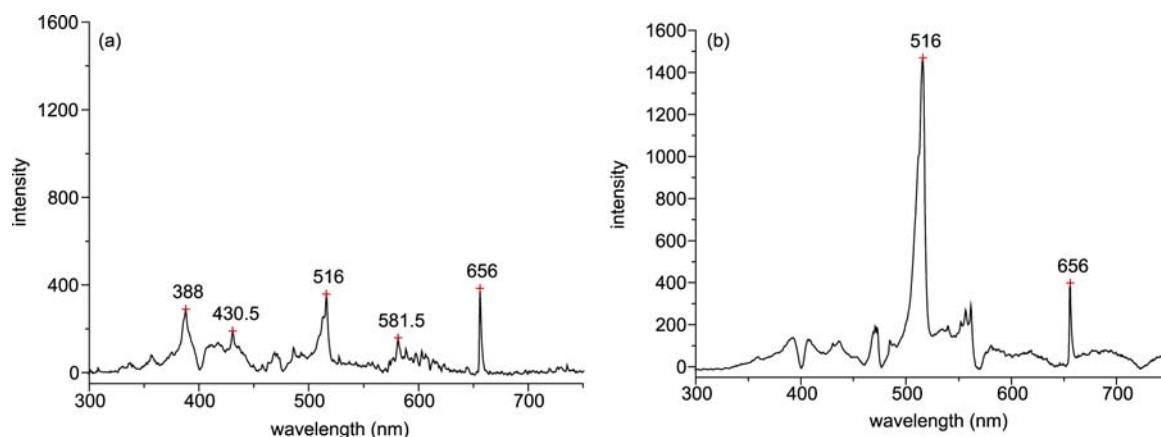
The temperature was about 1000 K for methane coupling under microwave plasma [19]. At 14140 Pa, the acetylene yield of 83.6% is much higher than the maximum thermodynamic yield of acetylene. This phenomenon was referred to as “beyond-thermal-equilibrium” by Zhu Aimin. It may be understood from the conditions of the basic thermodynamic relationship. In this paper, formula is deduced without non-expansion work. By heating, the chemical reaction is in line with the laws of this equilibrium. However, in the microwave plasma system, there is non-expansion work, generated from the movement of electronic with a certain speed. Because of the role of non-expansion work, the acetylene yield for methane coupling under microwave plasma is much higher than the maximum thermodynamic

yield of acetylene.

3.5 Kinetic analysis for methane coupling under the microwave plasma

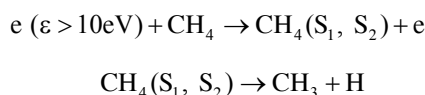
In order to further explore the reaction mechanism of methane coupling under microwave plasma, optical emission spectroscopy (EPP2000) was adopted for the diagnosis of excited species of methane coupling.

Figure 6 shows an optical emission spectrum of methane microwave plasma, when the reaction tube is at the optimized location. Excited species can be identified, based on optical emission spectrum [20]. The emission lines of CH_2 (141.5 nm) and CH_3 (216 nm) are not shown in Figure 6, because these wavelengths are not in the range of EPP2000 spectrometer. At 2020 Pa, there are mainly emission lines: CH (388 nm, 430.5 nm), C_2 (516 nm), H_2 (581.5 nm), and H_α (656 nm). At 10100 Pa, there are mainly two emission

**Figure 6** (a) Optical emission spectrum of methane microwave plasma at 2020 Pa; (b) optical emission spectrum of methane microwave plasma at 10100 Pa.

lines: C₂ (516 nm) and H_α (656 nm). Moreover, it is strong for the emission line of C₂ (516 nm). To compare the two different pressures, the ratio of the intensity of the emission lines of H_α and C₂ is greater at 2020 Pa, which shows that H is relatively much, and the degree of dissociation of methane is relatively high. Therefore, acetylene is only the product of C₂ hydrocarbons at 2020 Pa. While at 10100 Pa, H is relatively little, acetylene is the major product of C₂ hydrocarbons, and there is a small amount of ethylene. Because at the same temperature and the same cavity, density of methane molecules is lower at lower pressure, and each methane molecule accepts higher energy at a certain power. Therefore, three C–H bonds are ruptured easily and the concentration of CH and H is relatively large at lower pressure. By contrast, H is relatively little at higher pressure.

From the above spectrum analysis, it can be seen that methane coupling under microwave plasma is carried out through free radical reactions. Under microwave plasma, the inelastic collision of methane and high-energy electronic occurs to produce electronically excited CH₄ [S₁ (9.6 and 10.4 eV) and S₂ (11.7 eV)], which can be the precursor of radicals CH₃ and H [21]:



With the aid of hydrogen radicals, the reactions can occur as listed in Table 3. Table 3 also shows the relationship between reaction rate constant k and temperature [13, 22, 23]. Because the temperature was about 1000 K for methane coupling under microwave plasma [19], reaction rate constants k at 1000 K were calculated and are listed in Table 3.

Because of the role of hydrogen radicals, CH₃, CH₂ and CH radicals may be generated from reactions 1, 2, 3. CH radicals have been detected by spectroscopy experiments (Figure 6(a)). These active particles can generate C₂H₄ through reactions 4–7, and can generate C₂H₂ through reactions 8–10. Compared with reaction rate constants for C₂H₄, reaction rate constants for C₂H₂ are greater. For example,

both reactions 7 and 8 are the reactions of two CH₂ radicals. Reaction 8 is almost two orders of magnitude faster than reaction 7. C₂H₂ may be also generated from C₂H₄ through reactions 11 and 12. Therefore, in this experiment for methane coupling under microwave plasma, acetylene is the major product of C₂ hydrocarbons, but the amount of ethylene is little or almost none.

4 Conclusions

By optimizing the microwave chemistry reactor made of the rectangular waveguide resonator, the methane conversion (the maximum 93.7%), the C₂ hydrocarbon yield (the maximum 91.0%) and the acetylene yield (the maximum 88.6%) all were greatly increased under microwave plasma. Furthermore, for the optimal reactor, the change of the methane conversion and the C₂ hydrocarbon yield is little with the change of the pressure in the experiments. In the C₂ hydrocarbon, acetylene is the main component, and selectivity to acetylene is above 90%. Compared with the results of references, the energy yield and space time yield of acetylene are also high.

Optical emission spectroscopy was adopted for the diagnosis of methane coupling to acetylene under microwave plasma. The excited species (CH, C₂, H₂, H_α) were detected in the spectra range of 300–750 nm. Based on the products and these excited species, the reaction mechanism of methane coupling under microwave plasma was investigated, using the thermodynamics and kinetics of the chemical reaction. The acetylene yield of methane coupling under microwave plasma is much higher than the maximum thermodynamic yield of acetylene. This phenomenon may be understood from the conditions of the basic thermodynamic relationship. Gibbs-Helmholtz equation is deduced without non-expansion work. However, there is non-expansion work in the microwave plasma system. Methane coupling under microwave plasma was carried out through free radical reactions.

Table 3 Reaction rate constants k for methane coupling [13, 22, 23]

No.	Reaction	k (cm ³ molecule ⁻¹ S ⁻¹)	K (1000 K) (cm ³ molecule ⁻¹ S ⁻¹)
1	H + CH ₄ → CH ₃ + H ₂	$2.2 \times 10^{-20} \text{T}^3 \exp(-4045/\text{T})$	3.8×10^{-13}
2	H + CH ₃ → CH ₂ + H ₂	$1.0 \times 10^{-10} \exp(-7600/\text{T})$	5.0×10^{-14}
3	H + CH ₂ → CH + H ₂	$1.0 \times 10^{-11} \exp(900/\text{T})$	2.4×10^{-11}
4	CH ₄ + CH → C ₂ H ₄ + H	1.0×10^{-10}	1.0×10^{-10}
5	CH ₃ + CH ₃ → C ₂ H ₄ + H ₂	$1.7 \times 10^{-8} \exp(-16000/\text{T})$	1.9×10^{-15}
6	CH ₃ + CH ₂ → C ₂ H ₄ + H	7.0×10^{-11}	7.0×10^{-11}
7	CH ₂ + CH ₂ → C ₂ H ₄	1.7×10^{-12}	1.7×10^{-12}
8	CH ₂ + CH ₂ → C ₂ H ₂ + H ₂	$2.0 \times 10^{-10} \exp(-400/\text{T})$	1.3×10^{-10}
9	CH ₂ + CH → C ₂ H ₂ + H	6.6×10^{-11}	6.6×10^{-11}
10	CH + CH → C ₂ H ₂	2.0×10^{-10}	2.0×10^{-10}
11	H + C ₂ H ₄ → C ₂ H ₃ + H ₂	$9.0 \times 10^{-10} \exp(-7500/\text{T})$	5.0×10^{-13}
12	H + C ₂ H ₃ → C ₂ H ₂ + H ₂	2.0×10^{-11}	2.0×10^{-11}

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