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Research article

Numerical analysis of methane pyrolysis in thermal plasma for selective synthesis of acetylene

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ABSTRACT

Thermal plasma pyrolysis can realize direct synthesis of acetylene and carbon black from methane, while the yields of products vary according to the reaction conditions. In the present work, a pre-proposed detailed kinetic mechanism is applied to investigate the efficiency and product distribution of methane pyrolysis in thermal plasma. The kinetic mechanism is validated with experiments, which proves the reliability of the mechanism under the conditions of thermal plasma. From simulation results, higher temperature and residence time in millisecond are beneficial for higher acetylene yield, while long residence time is beneficial for the production of carbon black. To be specific, when the temperature is higher than 2100 K, conversion of methane is above 99 wt % and the yield of acetylene is above 80 wt%, which is referred to as the selective synthesis of acetylene from methane. When temperature increases, the proper residence time for the maximum acetylene yield would decrease to within one millisecond.

1. Introduction

Methane is one of the most important fossil fuels and is abundant in natural gas, shale gas, coalbed methane, and so on. There has been sustained interest in the efficient utilization of methane in chemical industry for decades [1]. A representative converting route is thermal plasma pyrolysis of methane, which uses electricity to ionize gas and produce jet with ultra-high temperature, and then directly pyrolyzes methane into acetylene, hydrogen and carbon black under inert or reductive atmosphere [2]. The earliest record of the realization of this process was claimed by Hüel Corp. in 1940s [2,3]. Since then, this process has been widely investigated both experimentally [4–9] and numerically [10,11]. Table 1 gives a summary of the representative researches on methane pyrolysis in thermal plasma [2,9,12–16], in which argon and hydrogen are widely used as the plasma gas and the reaction temperature is generally among 1400–3000 K. The products of the reported processes include acetylene, hydrogen and carbon black, while the yields of these products vary a lot from one another. For example, when the pyrolysis temperature was 1550–2600 K and the residence time was 3.0–3.5 ms, methane conversion in argon and hydrogen plasma was reported to approach 100 wt% with the yield of acetylene between 90–95 wt% (Fincke et al. [15]). However, when the residence time was extended to above 200 ms, carbon black would be the dominant product (Kim et al. [12]). So the products of methane pyrolysis in thermal plasma are remarkably affected by the reaction conditions.

In the thermal plasma process, methane undergoes complex gaseous reactions to form light hydrocarbons (e.g., acetylene), also including deep dehydrogenation and polymerization reactions of hydrocarbons to form benzene and higher aromatics [15]. With increased residence time, the aromatic species would form precursors of carbon black through aggregation, which leads to the remarkable formation of carbon particles [17]. The temperature requested for the decomposition reactions and the intrinsic sequence of carbon formation after decomposition implies that the products of methane pyrolysis in thermal plasma would be significantly affected by the reaction temperature and residence time, which is illustrated in Table 1. The trend in Table 1 shows that higher temperature and shorter residence time are favorable for higher acetylene yield, while longer residence time is favorable for higher yield of carbon black. This point was also addressed by Fincke et al. [14]. However, researchers usually focus on the product analysis at their own specific conditions. Few reports focus on analyzing the common ground of different studies. Thus it would be meaningful to conclude the relationship between the wide range of reaction conditions and the products yields, and provide guidance to the selective synthesis of acetylene and carbon black, from the perspective of basic reaction conditions, namely temperature and residence time.

In this work, methane pyrolysis is investigated using a numerical approach based on a pre-proposed detailed kinetic mechanism [14]. Besides the validation in our previous work [17], the kinetic mechanism is further validated with the results of experiments. The

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Table 1
Representative researches on methane pyrolysis in thermal plasma.

Year/reference	Power	Plasma gas	Volume ratio of plasma gas/CH_4	Residence time[a]	Temperature (average)	Conversion	C_2H_2 yield	Carbon yield
	kW			ms	K	wt%	wt%	wt%
2008 [9]	50	Ar/H_2	–	–	–	96	86.2	1.3–3.9
2005 [12]	40	Ar	2:1	> 200	1500–2548	~100	Little	Dominant
2003 [13]	120	N_2	2:1	Millisecond	2100–2300	97.1	–	43
2002 [14]	60	Ar/H_2	1.98:1	~2.5	~3000	99.1	85.5	4.67
	60		1.88:1	~20.3	1400–2400	99.4	47.5	30.5
2002 [15]	75	Ar/H_2	2:1	3.0–3.5	1550–2600	~100	90–95	2–4
1986 [16]	4.2	Ar	–	–	900–1200	> 90	50	> 40
1962 [2]	8000	CH_4	–	–	–	70.5	72.9	2.7

[a] Residence time is estimated from the reported reactor length and velocity, respectively.

mechanism is then used to simulate the product evolution under a series of reaction conditions. The effects of reaction temperature and residence time on the yields of acetylene and carbon black are concluded. The relationships of different processes are well explained. Furthermore, quantitative guidance is suggested regarding the selective synthesis of acetylene or carbon black from methane.

2. Kinetic mechanism and experiments

In this work, attention is paid to acetylene and carbon black formation during methane pyrolysis. So the mechanism [17] consists of two parts: (1) gas-phase mechanism, which describes the evolution of light hydrocarbons and could be obtained from reported works [18,19]; (2) carbon black formation model, which describes the nucleation and growth processes of carbon black [20–22]. By this means, the kinetic mechanism could give predictions on the yields of both gas species (especially acetylene) and carbon black. In our previous work [17], the kinetic mechanism was validated under a wide range of conditions from the literature [23–25], including (i) atmospheric pressure, 873–1323 K and 1–3 vol% acetylene; (ii) 8 kPa, 1000–1300 K and 60–100 vol% acetylene; (iii) 8 atm, 1200–2400 K and ~1 vol% acetylene. The mechanism has been proved capable to provide reliable predictions for both gas species and carbon black under the mentioned conditions.

Furthermore, methane pyrolysis experiments were carried out in a tube reactor to further validate the mechanism under thermal plasma conditions. As shown in the upper half of Fig. 1, the plasma torch was powered by an insulated gate bipolar transistor (IGBT) rectifier power. The torch was protected with cooling water. The temperature change of cooling water was monitored with thermocouples to calculate the heat loss. At the jet outlet, methane was injected into the reactor through two pores on the reactor wall. Reactions took place along the downstream of the reactor, and were quenched by argon to prevent further decomposition. The gas products were then collected and analyzed with two gas chromatography (GC) analyzers. Please refer to ref. [26] for more information about the analytical instruments.

The geometric size of the reactor is shown in Fig. 1, and the working parameters are listed in Table 2, which provides the boundary conditions for simulation. The heat loss through the water jacket was calculated from the temperature change of cooling water with the set flow rate. Then, the total input power was modified with the heat loss to derive the actual energy ended-up in the reactor, which was used to calculate the temperature boundary conditions of plasma torch. The heat loss and temperature boundary conditions are given in Table 3. The wall of reaction section was set as 500 K with a heat transfer coefficient of 1.0×10^2 W/m^2·K according to our experiments. The reactor is assumed to be an ideal plug flow reactor (PFR). The simulations are performed in CHEMKIN 4.1 with the Particle Tracking Module.

3. Results and discussion

3.1. Validation of the kinetic mechanism

In the present work, the kinetic mechanism is further validated with thermal plasma experiments using different input power and methane feeding rate. The simulation parameters are set according to the experiments. As shown in the lower half of Fig. 1, the temperature would decrease after the injection of methane and then keep decreasing along the axial direction of reactor. The residence time of methane in the reaction section is within milliseconds, and will change slightly at different operating conditions.

Fig. 2 compares the gas concentration at different methane feeding rate with a constant input power of 1164 W. With the increase of methane feeding rate, the estimated temperature before quenching (x = 24 mm) would decrease, and methane concentration would increase, which results in a relatively low conversion. Fig. 3 compares the gas concentration at different input power with a constant methane feed of 3.56 l/min. With the increase of input power, the pyrolysis temperature would increase, leading to higher methane conversion and higher acetylene concentration. As shown in both Figs. 2 and 3, the simulation could give satisfactory predictions of the experimental results. So the kinetic mechanism could be used to further investigate methane pyrolysis under thermal plasma conditions. In the following discussion, the temperature range is set within the validated conditions in our previous work [17] to ensure the reliability of the kinetic mechanism.

3.2. Methane pyrolysis at different temperatures

As discussed above, reaction conditions would significantly affect acetylene and carbon black yields during methane pyrolysis. To investigate the effects of reaction temperature and residence time, pyrolysis of a hypothetical gas is simulated at different temperatures to reveal the evolution of main products. The hypothetical gas consists of 26 vol% CH_4 and 74 vol% Ar, in accordance with the gas components of our experiments (see Table 2). Figs. 4 and 5 give the evolution of the products at two typical temperatures, i.e., 2300 K and 1500 K, respectively.

As shown in Fig. 4, when pyrolyzed at 2300 K, methane is converted to acetylene at the beginning and the concentration of acetylene would maintain before decreasing due to further decomposition. Quantitatively, methane would be consumed within 0.40 ms and acetylene concentration would reach a maximum of 8.5 vol% at 0.34 ms correspondingly. The residence time corresponding to the maximum acetylene concentration is marked with t_{max}. As the residence time is prolonged, acetylene concentration would gradually decrease and carbon black would be produced. It is worth mentioning that the time for considerable formation of carbon black is much delayed compared with t_{max}. Therefore, if the products are quenched before carbon black