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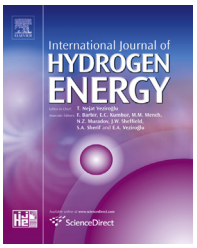

Kinetic modeling and experimental validation of the pyrolysis of propane in hydrogen plasma

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ABSTRACT

Acetylene is one basic raw material for the production of valuable chemicals. The non-oxidative pyrolysis of hydrocarbons in plasma arc provides one direct way to produce acetylene. In this work, the propane pyrolysis was simulated by a plug flow reactor model, and the model was validated by the experimental data of a pilot-scale magnetically rotating hydrogen plasma reactor. Effects of H/C ratio and energy input were investigated. The propane pyrolysis was an ultra-fast process and completed with less than 1.0 ms. The acetylene yield was affected by both the reaction temperature and the carbon black produced from the degradation of the acetylene. The CH_4 yield decreased dramatically with the increase in temperature, which was consistent with results of the thermodynamic equilibrium analysis. The calculated value of the kinetic model correlated well with the experimental data, and the mathematical model was proved to be a viable way to study the plasma pyrolysis process.

Introduction

Acetylene is one basic raw material for the production of vinyl chloride monomer, acetaldehyde, 1, 4-butanediol and so on [1]. Depending on the feed types, acetylene is mainly produced from coal by calcium carbide method [1,2] or from hydrocarbons by the partial oxidation (POX) method [3]. The POX method focuses on the conversion of various hydrocarbons, such as methane, LPG and naphtha [4,5]. Also the hydrocarbons can be pyrolyzed under non-oxidative atmosphere in plasma arc [6]. Thermal plasma with the unique features of high temperature, abundant reactive species [7,8], provides an effective way to convert fossil resources [9–11] or biomass [12–14] to valuable chemicals. Also the plasma could be used in the waste to energy process such as the utilization of municipal solid waste (MSW) [15–17]. The plasma gas medium can be easily changed to meet the need of product gas compositions varying from hydrogen rich gas, syngas [18–25] or C_2 (C_2H_2, C_2H_4) hydrocarbons [13,14,26,27].

Since the hydrocarbon pyrolysis is an energy-intensive process, the energy needed in the POX process is supplied with partial oxidation or combustion of the hydrocarbon feed, while the plasma arc process is supplied with electric power. The common mechanism of the POX process and the electric arc process lies in the fact that acetylene is the most stable light hydrocarbon when the temperature is above 1600 K [7,28,29]. It has been acknowledged that element carbon and hydrogen are more stable than hydrocarbons. Acetylene will decomposed to carbon black and hydrogen under high temperature. However, the decomposition of acetylene to carbon and hydrogen is kinetically controlled [30], which is a quasi-second order

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reaction. In order to keep acetylene as the target product, the product stream should be quenched efficiently [31].

Plasma conversion of hydrocarbons have been widely studied in lab-scale reactors, mainly focusing on various operating parameters, such as feed rate [30–32], energy input [4,32,33], reactor geometry [33] and feed type [33,34]. Generally, high energy input is favorable for the conversion of hydrocarbons, and C_2H_2 yield is sensitive to reaction temperature, thus a compatible feed rate with the energy input is critical for the pyrolysis process. Since the residence time is closely related to the yield of carbon black (C(S)) from the degradation of C_2H_2, the reactor geometry such as reactor length, diameter and quenching position are also important parameters for the pyrolysis process. Even though the plasma pyrolysis of hydrocarbon is in quasi-equilibrium state, the process is also affected by the feed type and operating conditions. Bitter [34] investigated the pyrolysis of different feeds with the same H/C ratio and energy input, and the product compositions differed from each other with different feeds. As for the feed type, both the gaseous and liquid hydrocarbons show a good performance with the reaction time less than 1.0 ms in the reported operating conditions [33,34]. However, longer residence time is suggested for the liquid hydrocarbons at larger feed rate due to an extra vaporization process [35]. Furthermore, the paraffin hydrocarbons usually have a higher C_2H_2 yield than that of the aromatic hydrocarbons with a higher coking tendency [33,36]. Few data are concerned with pilot-scale or industrial scale plasma reactors, DuPont [37]reported a 9 MW scale magnetically rotating plasma reactor, with the CH_4 as feed and the C_2H_2 yield of 70%, and the SER is 8.8 kWh/kg-C_2H_2. However, details of the operating conditions in the DuPont process were not disclosed. As discussed above, the pyrolysis of hydrocarbon is affected by both the feed type and operating conditions [3,31,38–42], thus it is necessary to study the kinetics of the pyrolysis process.

Owing to the high temperature gradient in the plasma reactor [31], plasma pyrolysis process usually suffers from poor mixing when the feed is injected downstream of the plasma jet. And the mixing efficiency could be substantially improved in the magnetically rotating arc with the feed injected upstream in the reactor.

In our previous work [43], a simplified black box model considering only one global reaction was established, focusing on the energy and material balance to assess the plasma pyrolysis process. In this paper, the kinetic modeling of the propane pyrolysis was investigated and the model was validated by the experimental data of a pilot-scale magnetically rotating hydrogen plasma reactor. Effects of H/C ratio and energy input were investigated, results were used to evaluate the process and optimize the reactor geometry.

Mathematical model and experimental setup

The plasma pyrolysis was modeled with a plug flow reactor (PFR) model with the Chemkin program [44]. Generally, the plasma could be implemented by assuming an inlet temperature [30,42,45] based on the gas enthalpy, or by applying a plasma zone with heat source [46,47]. In this work, the energy source was applied in the plasma zone below the tip of the cathode. The C_1–C_4 reaction mechanism [48] was used to simulate the pyrolysis of propane, and the Holmen mechanism [7] was used to simulate the formation of carbon black C(S).

The experimental investigation was carried out with a 1 MW-scale magnetically rotating plasma reactor. The diameter of the anode is 0.10 m, and 0.40 m in length. Propane and hydrogen were injected upstream of the rotating plasma. Pyrolysis gas was quenched in the reactor outlet. The product yield, specific energy (SE) input of hydrogen, specific energy requirement (SER) and conversion rate are presented in Equations (1)–(4).

$$Y_i = \frac{m_{i,c}}{m_{C_3H_8} \times \frac{36}{44}} \times 100\% \quad (1)$$

$$SER\left(\frac{kWh}{kg}\right) = \frac{P}{m_{C_2H_2}} \quad (2)$$

$$SE\left(\frac{kWh}{Nm^3}\right) = \frac{P}{Q_{H_2}} \quad (3)$$

$$Conversion = \left(1 - y_{p,C_3H_8}\right) \times 100\% \quad (4)$$

Where Y_i represent the carbon yield of species i, and $m_{i,c}$ represents the carbon mass in species i, and m_{C3H8} is the mass flow rate of C_3H_8; SER is the specific energy requirement (SER) in kWh/kg-C_2H_2, P is the input power in kW, SE is the specific energy (SE) input of hydrogen in kWh/Nm^3, Q_{H2} is the flow rate of hydrogen in Nm^3, $y_{p,C3H8}$ is the mole fraction of C_3H_8 in the pyrolysis gas.

In this work the chemically inert Argon is used as an inner standard (Equation (5)) to calibrate the gas flow rate and product yield.

$$Q_i = Q_{Ar} \times \frac{y_i}{y_{Ar}} \quad (5)$$

Where Q is the gas flow rate, and y is the mole fraction.

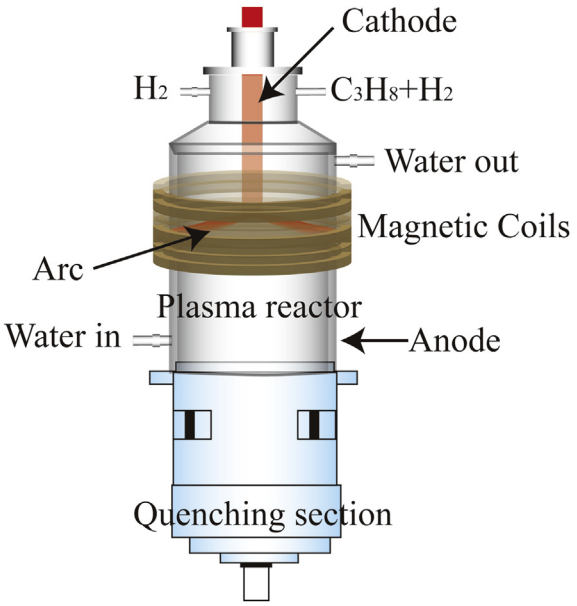

Fig. 1 – Schematic view of the plasma pyrolysis reactor.

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