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Detailed kinetic modeling of chemical quenching processes of acetylene-rich gas at high temperature

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HIGHLIGHTS

- Introduced an integrated detailed kinetic mechanism for acetylene decomposition at high temperature.
- Revealed the general requirements in preserving acetylene during quenching processes.
- Discussed the co-production of acetylene and ethylene and energy re-utilization of chemical quenching method.
- Proposed a detailed propane-quenching optimization for pilot-plant acetylene production by plasma coal pyrolysis.

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ABSTRACT

Quenching of acetylene-rich gas at high temperature is an essential step in most acetylene production processes. Different from traditional physical quenching methods (e.g., water spray), chemical quenching has the advantage of reusing the gas heat content and producing co-products while preventing acetylene from decomposing. In this work, a detailed kinetic mechanism was proposed to theoretically describe and reveal the chemical quenching process. Reactions of small hydrocarbons, PAHs growth and soot formation were taken into consideration to build the model, which was validated by reported data. Afterwards, an ideal PFR model was used to investigate the effects of different operating conditions, including temperature after quenching, quenching time, and quenching media. Furthermore, the proposed model was used to optimize the chemical quenching operation for a pilot-plant acetylene production process based on thermal plasma technique. The results showed that chemical quenching could effectively realize both energy re-utilization and ethylene co-production, while maintaining a satisfactory yield of acetylene.

1. Introduction

Acetylene is a versatile intermediate used in the production of various chemicals including vinyl chloride [1], 1,4-Butanediol [2], and acetylene black [3]. Industrial processes to produce acetylene include the calcium carbide method[2], partial oxidation of natural gas [4], steam cracking of petroleum fractions [2], and thermal plasma pyrolysis (Fig. 1) of carbonaceous materials (e.g., coal [5,6]). In thermal plasma pyrolysis, acetylene-rich gas is formed under high temperature. The Gibbs energy of acetylene formation becomes the lowest among C1-C3 hydrocarbons when the temperature is above 1500 K and further decreases at higher temperatures [7,8], which makes it possible to produce acetylene under high temperature conditions. However, acetylene will decompose into carbon black and hydrogen during quenching, leading to acetylene loss. In order to maintain efficient yields of the targeted product and prevent acetylene decomposition, effective quenching is essential. Another key factor regarding the quenching process is the need to reutilize energy. If no energy reutilization is applied, the quenching process would also cause massive energy dissipation owing to irreversible heat transfer from product gases to the quenching media. Therefore, the quenching process must be appropriately designed to ensure less acetylene loss and more energy reuse for better profit of the whole process.

Quenching is typically performed by physical or chemical methods. Physical quenching utilizes a cold inert medium to rapidly cool the system via mixing and phase transition. A prime example of physical quenching is in industrial oxidation processes, where quenching is realized by a water spray [9]. However, this operation causes complete dissipation of the heat contained in the product fluid. In chemical quenching, the heat is removed by both physical

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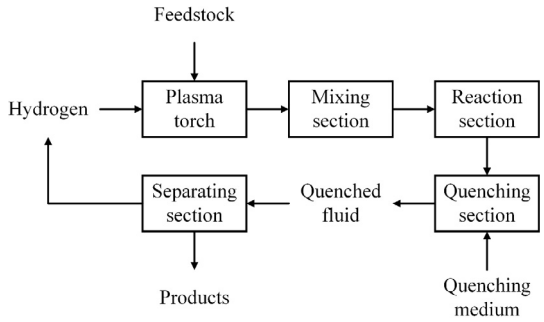

Fig. 1. Sketch of acetylene production via thermal plasma process.

cooling and endothermic chemical reactions of the quenching media itself. In chemical quenching, cold media, typically hydrocarbons, is injected and then mixed with the hot fluid. Heated by the product stream, the hydrocarbons in the quenching media will undergo endothermic decomposition reactions. Consequently, the system is cooled while producing value-added co-products from the decomposition of hydrocarbons. In this way, the system energy is partially recovered. One practical example of chemical quenching was reported by Patrick et al. [5] in which propane was adopted as the quenching medium after thermal plasma pyrolysis of coal by AVCO Corp. The propane quenching brought a remarkable increase of ethylene yield from almost zero (using water spray quenching) to about 20 wt.% according. In addition, the specific energy decreased from 10.5 kWh/kg ($C_2H_2 + C_2H_4$) to 6.1 kWh/kg ($C_2H_2 + C_2H_4$). The above-mentioned quenching methods in thermal plasma processes for acetylene production are summarized in Table 1 [5,10]. While, the results of the AVCO study indicate that the chemical quenching of acetylene-rich gas is a promising method for energy re-utilization and ethylene co-production, there are still very few studies in the literature.

This work aims to investigate the chemical quenching process of acetylene-rich gas at high temperature. A detailed gas-phase kinetic mechanism coupled with the soot formation mechanism is proposed to quantitatively simulate the gas species evolution during quenching. The kinetic model consists of C1-C5 gas reactions, PAH (polycyclic aromatic hydrocarbon) growth and a simplified soot formation mechanism. The acetylene and soot yield results are then compared and validated with published data. In order to elucidate the factors influencing the yields of product gases, including temperature after quenching, quenching time and quenching medium are investigated. The reaction sequences of hydrocarbon quenching are established and justified. Based on the investigations discussed above, theoretical optimization of the chemical quenching process is performed for an on-going industrial practice.

2. Kinetic mechanism

In this study, the gas phase and soot formation mechanisms are evaluated. As reported in the literature [11], soot formation is a general phenomenon due to acetylene decomposition at high temperature. Fau et al. [12,13] emphasized the importance of soot formation during cracking reactions of hydrocarbons. Thus, this process cannot be ignored in modeling of the chemical quenching process of acetylene-rich gas.

2.1. Gas-phase mechanism

In thermal plasma pyrolysis of carbonaceous materials (e.g., coal), gas products include acetylene, hydrogen, methane, and carbon monoxide, among others. Kinetics of small hydrocarbons are adopted to develop the gas-phase kinetics in this work. In addition, PAH molecules should be considered in gas-phase reactions to further couple with the soot formation model. Fau [13] gave a comprehensive review on the mechanisms of pyrolysis and oxidation for C1-C3 hydrocarbons. Regarding acetylene evolution, the typical gas-phase kinetic mechanism includes GRI 3.0 [14], Wang-Frenklach [15], Curran [16], Appel-Bockhorn-Frenklach (ABF) [17], USC [18] and so on. GRI 3.0 is widely used in methane/natural gas combustion, and is the basis for many other mechanisms. However, GRI 3.0 does not consider PAH species, which limits its application to larger molecules and soot formation. Table 2 gives a comparison among different kinetic schemes. The number of reactions regarding acetylene is relatively small in GRI-Mesh 3.0 and Curran; Wang-Frenklach and ABF do not include propane. On the other hand, USC has a proper reaction framework regarding pro-

Table 1
Operation results of quench processes in thermal plasma pyrolysis [5,10].

Corp.	Unit	Tianye	AVCO	AVCO
Power	kW	1800	807	690
Coal Feed rate	kg/h	1300	205	221
Quenching media		Water	Water	Propane
C_2H_2 output	kg/h	139.0	77.0	66.3
C_2H_4 output	kg/h	20.0	0.2	47.3
Energy consumption	kWh/kg C_2H_2	12.9	10.5	10.4
	kWh/kg $C_2H_2 + C_2H_4$	11.3	10.5	6.1

Table 2
Comparison of five typical detailed gas-phase kinetic mechanisms.

Mechanism name	GRI-Mech 3.0	Wang-Frenklach	Curran	ABF	USC
Elements	C H O N Ar	C H O N Ar	C H O N Ar He	C H O N Ar	C H O N Ar
Species	53	99	118	101	71
Gas-phase reactions	325	527	665	544	469
C_2H_2 formation reactions	12	30	15	30	26
C_2H_2 oxidation reactions	7	7	8	7	7
C_2H_2 recombination reactions	1	39	3	40	29
C_3H_8 formation reactions	5	0	4	0	5
C_3H_8 oxidation reactions	2	0	22	0	8
C_3H_8 recombination reactions	2	0	13	0	4