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Research article

Methane to acetylene conversion by employing cost-effective low-temperature arc

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ABSTRACT

A plasma process for methane conversion into acetylene is proposed. Acetylene is one of the basic materials used in the chemical industry and its production is predominantly based on chemical processing of naphtha and CaC_2. The recent increase in shale gas production makes acetylene production from methane a feasible expectation. This study provides data on the lowest cost of acetylene production from methane by a plasma process. The proposed plasma process is based on an effective rotating arc reactor. The rotating arc provides a relatively low reaction temperature, achieving a high carbon balance. Through a study of reaction parameters and the effect of H_2 as a reactant additive, the mechanism of methane conversion was analyzed. The proposed process showed a high efficiency with a minimum process cost of approximately 9 kWh/kg-C_2H_2.

1. Introduction

Acetylene is an important precursor of chemical products such as tetrachloroethane, acetaldehyde, and diverse plastics [1]. Acetylene is produced through thermal cracking of hydrocarbon species (e.g., naphtha), oxidative or non-oxidative coupling of light hydrocarbons, hydration of calcium carbide, and other processes [2,3]. Among these, the hydration of calcium carbide has the longest history of application. In this method, calcium carbide that is produced from the reaction of calcium oxide and coke (coal) reacts with water to produce acetylene. This process is generally located in places where coal is available at low cost. In spite of high production costs and possible environmental problems, it has been adopted as the method to produce acetylene as the precursor of the vinyl chloride monomer in the production of polyvinyl chloride (PVC) [3–6].

Production of acetylene via partial oxidation or combustion uses hydrocarbon and oxygen preheated to above 1400 °C as reactants. The reactants are fed into a burner with a rather short reaction time scale of 10^{-2}–10^{-3} s. Fast quenching and low acetylene partial pressure are also beneficial reaction conditions. Possible feedstocks for the method are natural gas, ethane, LNG, naphtha, LPG, etc. [2,6–8]. Meanwhile, an electric arc can produce a thermal plasma with temperatures of up to 20,000 K. Reactants can be fed directly into the arc region and indirectly into the post arc plume. The method is applicable to reactants with any phase [9–11].

The optimal method of acetylene production often varies geographically, being dependent on varying regional costs of the feedstock for production [3]. The recent increase in shale gas production has the potential to promote a change from petroleum base energy and chemical industries to gas base industries [12–15]. Current acetylene production, which is mostly based in bulk plants, may also be influenced by shale gas availability. The possibility of distributed production or on-site production of acetylene at shale wells may invoke consideration of the relative costs of transport of feedstock to bulk acetylene production sites and transport of acetylene produced on-site to the site of application.

With this background, plasma processing can be tentatively considered as a cost-effective method of acetylene production. Plasma processes that utilize electric energy are not suitable for bulk production, but their simple design makes them candidates for medium- and small-scale production schemes, such as at shale gas wells.

Plasma processing for the conversion of natural gas (or methane) into other hydrocarbons has been considered for decades, with practical research into the Huels process having begun in the 1940s [16]. In the Huels process, an arc with high temperature (15,000–20,000 K) is produced by conversion of electric energy to thermal energy. Within this arc, methane is converted to acetylene. Water and liquid hydrocarbons are applied to the quenching of the product, to prevent the reverse reaction and subsequent reactions [9–11,16].

High temperature chemistry of methane conversion can be found in publications from Dr. Laurent Fulcheri and his coworkers [17–19]. The effect of temperature and pressure on thermal cracking and formation of monodispersed carbon black particle has been addressed.

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The mechanism of most of plasma processes is, in principle, no different from that of the Huels process [9]. A high-temperature environment, which is beneficial for the conversion of methane, is produced in a discharge gas. The composition of the product is mainly determined by the temperature of the reaction, which is dependent on the nature of the discharge gas. In this study, with the optimal design of plasma reactor and discharge gas system, a cost-effective method of acetylene production is introduced.

2. Experiment

Discharge parameters are among the reaction parameters of methane conversion by plasma processing. In general, the discharge gas and the electric field imposed determine the breakdown condition of the discharge process. Ar and N_2 were compared as discharge gases, based on the conversion of methane and selectivity of acetylene. The effect of hydrogen as an additive on the characteristics of reaction was also investigated. The efficiencies of energy usage in all of the tested conditions were compared.

The experimental apparatus is shown schematically in Fig. 1. It is essentially comprised of a plasma generation section (reactor and power supply), a gas supply system (cylinders and mass flow controllers (MFC)), and a measurement system (gas chromatograph, oscilloscope, and probes for voltage and current measurement).

2.1. Plasma generation section

The plasma reactor is based on a rotating arc reactor design. An arc column is generated between a conical high-voltage electrode and a cylindrical ground electrode [20–23]. In the course of arc generation, an extended arc is anchored at the high-voltage electrode tip and expands into the earthed straight reactor tube. The capability of length control for extension of the arc is what the rotating arc differs from other types of arc generation [20,24,25]. Extension of arc string enables more flexible control of temperature condition in wide range. For the expansion of the arc string, a contracting part (diameter from 40 mm to 12 mm) and a straight tube (50 mm length with constant diameter of 12 mm) are connected to the basic rotating arc reactor. The procedure for generation and development of the arc in a rotating arc reactor can be found in the literature [20–24]. The contracting part and straight tube are designed to promote heat transfer and fixation of the arc string length. Contraction of the flow path results in rather enhanced heat transfer with anchoring of the arc, and generates a more uniform high-temperature volume inside the contracted tube, which is beneficial for the thermal conversion of methane. The reactor was made of stainless steel with a copper electrode. The tip of the high-voltage electrode was made of zirconium to minimize possible erosion. Discharge power was supplied by an AC high-voltage transformer with a frequency of 20 kHz, which delivered up to 20 kW. The power supply has designed to have limit of current supply. Once the condition for electric power was set, the current level is determined by the voltage condition of the discharge. In the case Ar alone balance, discharge voltage is lower than that of other gas composition resulting in higher current at the same designed electric power condition. So, in some condition of experiment (Ar balance, $H_2 = 0\%$), SED condition was limited up to 1.7 kJ/L while other composition has higher SED limit up to about 3 kJ/L.

2.2. Gas supply system

Discharge gases were argon (Ar, 99.999%) and nitrogen (N_2, 99.9%). Reactants are methane (CH_4, 99.95%) and hydrogen (H_2, 99.9%). The methane fraction was fixed at 10% of the total flow rate of 50 liters per minute (LPM). Table 1 shows the test condition matrix.

The flow rates of gases are controlled by mass flow controllers (MFCs, Brooks) calibrated with a flow calibrator (Defender 530, BIOS International). Discharge gas was fed through the bottom hole, generating a swirling flow inside the reactor. Methane is fed via the contracting tube that is downstream of the arc string.

2.3. Measurement system

Electric power supplied for the reactor was measure by an oscilloscope with a 1000:1 high-voltage probe and a current probe (Tektronix TDS 5054B; 1000:1 voltage probe, Tektronix TCP 303 current probe &

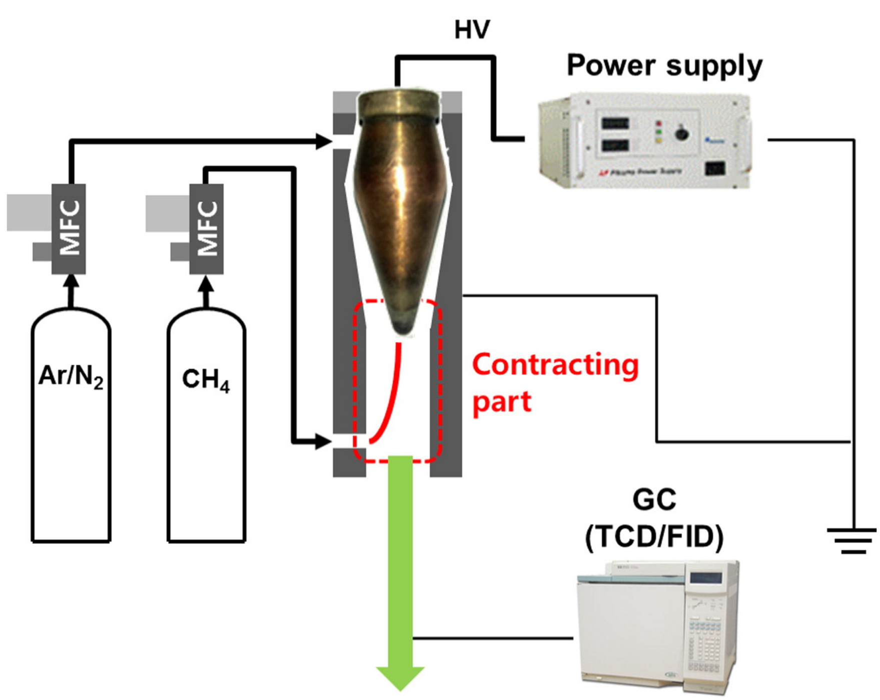

Fig. 1. Schematic of the experimental setup, used electrode does not show any tar-like deposition or degradation.