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Methane conversion in pulsed corona discharge reactors

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Abstract

This work reports the effect of capacitance, cathode material, gas flow rate and specific energy input on methane conversion, energy efficiency and product selectivity in a co-axial cylinder pulsed corona discharge reactor. Ethane and acetylene appear to be formed from dimerization of CH_3 radicals and CH radicals, respectively, while ethylene is formed mainly from the dehydrogenation of ethane. At a given power input, low capacitance with high pulse frequency results in higher methane conversion and energy efficiency than operation at high capacitance with low pulse frequency. Platinum coated stainless steel cathodes slightly enhance methane conversion relative to stainless steel cathodes, perhaps due to a weak catalytic effect. As specific energy input increases, energy efficiency for methane conversion goes through a minimum, while the selectivity of acetylene has a maximum value. Comparison of methane conversion for different types of plasma reactors shows that the pulsed corona discharge is a potential alternative method for low temperature methane conversion.

Keywords: Pulsed corona discharge reactor; Methane conversion; Energy efficiency; Product selectivity

1. Introduction

The conversion of natural gas (typically 75% by weight methane) to hydrogen and more valuable higher hydrocarbons, including acetylene, is of great importance to the petrochemical industry. Gaseous plasma is a good source for generating chemically active species, including radicals, electronic excited states and ions. Direct conversion of methane using various plasma processing technologies, including thermal arc plasma, dielectric barrier discharge, microwave plasma and corona discharge, has been studied for many years and has received significant recent attention. Thermal arc plasma is the only plasma technology for converting methane to acetylene that has been demonstrated on an industrial scale [1]. This process, known as the Huels process, has been practiced for more than 50 years, but the energy consumption is high due to the extremely high temperature (about 2000 K) [1]. Although the selectivity for acetylene formation is high (72.9%), the gas contains a number of higher unsaturated hydrocarbons and extensive gas purification is required [2]. Nonthermal plasma technologies are characterized by low gas temperature and high electron temperature because high energy electrons are produced in the gas while the bulk temperature of the gas is unchanged. Nonthermal plasmas overcome the disadvantage of high temperature because the majority of the electrical energy goes into the production of energetic electrons rather than into gas heating. For reactions that are thermodynamically unfavorable and for which low equilibrium conversions are obtained at high reaction temperatures, nonthermal plasmas have an advantage over thermal processes because thermal equilibrium is not achieved. Therefore, nonthermal plasmas are currently being investigated as a promising alternative near ambient temperature method to convert methane to higher hydrocarbons [3].

Extensive recent research has shown that the hydrocarbon product distribution from a plasma reactor is determined by the type of nonthermal plasma discharge. For example, in a dielectric barrier discharge reactor, ethane is the most abundant reaction product and only small amounts of unsaturated hydrocarbons are formed [4,5]. In microwave plasma reactors, the product distribution shifts with increasing power input, from ethane to ethylene and finally to acetylene [6–9]. However, the energy efficiency of microwave driven methane conversion is

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very low, from 0.2 to 3.3%, as reported by Huang and Suib [9] and Onoe et al. [6] High selectivity for acetylene is reported only in pulsed corona discharge reactors (PCDR's). Yang [5] compared the acetylene selectivity between corona discharge and dielectric barrier discharge reactors. In a corona discharge, the acetylene selectivity reaches 60%, while the acetylene selectivity is less than 6% in a dielectric barrier discharge. In a co-axial cylinder (CAC) reactor configuration, Zhu et al. [10] reported about 70% selectivity to acetylene. Kado et al. [11] obtained acetylene with approximately 94% selectivity in a point-to-point (PTP) reactor. They also reported mechanistic pathways of methane conversion in a PTP reactor using isotopic tracer experiments [12].

The rate of methane conversion in pulsed corona reactors is consistently higher than that reported for microwave or silent discharge [13]. The combination of high methane reaction rates and high selectivity to acetylene has resulted in a number of recent research efforts on methane conversion in PCDR's. These systematic investigations of methane conversion in PCDR's [13–18] have included reports of over 85% acetylene selectivity in a pulsed corona discharge at high pulse frequency in a CAC reactor [15] and in a PTP reactor [17]. The effects of pulse voltage rise time, reaction temperature, pulse voltage, pulse frequency, gas flow rate, electrode arrangement and reactor configuration (CAC reactor and PTP reactor) on methane conversion and product selectivities were analyzed. Pulse frequency has been reported as the most important factor influencing acetylene selectivity and methane reaction rate [15]. A pulse power supply with a frequency up to 10 kHz with a PTP type reactor provided the optimum combination for acetylene and hydrogen production [14].

Although extensive investigations have been reported for methane conversion in PCDR's, further study is necessary to clarify several issues. First, the effect of the pulse-forming capacitance (the capacitance of the charging capacitor) on methane reaction rate and product selectivities is of interest. For NO_x conversion in pulsed corona discharges, many investigations [19–22] have concluded that the pulse-forming capacitance affects energy transfer efficiency from the external circuit to the reactor. However, there are no studies that explore the effect of the pulse-forming capacitance on methane conversion. Second, the effect of the cathode material on methane reaction rate and product selectivities has not received attention. The role of electrode material in plasma-induced reactions is disputed, specifically whether metal electrodes serve simply as conductors of electricity or exhibit a catalytic effect [23]. Tanaka et al. [24] and Luo et al. [23] found that the metal surfaces of the anode have clear catalytic effects for ammonia synthesis and NO decomposition, respectively. However, there are no results that illustrate the effect of cathode material on methane conversion. Third, the effect of gas flow rate or residence time on methane reaction rate is important. Yao et al. [15] found that gas flow rate did not significantly affect methane conversion rate in a very small CAC reactor (0.01 m diameter × 0.15 m long). Although Yao et al. [17] reported that a PTP reactor with high pulse frequency (up to 10 kHz) can provide high methane reaction rate, scale-up of such PTP reactors is not straightforward. All pulsed corona discharge reactors used for methane conversion have been small, with low flow rates ($<2 \times 10^{-4}$ mol s^{-1}) that are far from practical for commercial operation [13–18]. The design and characterization of larger reactors that can accommodate high throughput are critical if these reactors are to be applied successfully in commercial operations.

The goals of this work are to investigate the effect of pulse-forming capacitance, cathode materials, gas flow rates and specific energy input on methane conversion and product distribution in large-scale co-axial cylinder PCDR's.

2. Experimental

Fig. 1 shows a diagram of the experimental system. The system consists of a reactor with an electrical system built around a thyratron switch, a flow control and distribution system, and a gas sampling system. The reactor is oriented vertically, with the gas flow from bottom to top. Experiments were conducted using three different metal tubes as the cathode: stainless steel, stainless steel coated with a 100 nm thick layer of platinum, and niobium. The cathode is 0.024 m in diameter and 0.914 m in length for the stainless steel and platinum coated stainless steel tubes and 0.60 m in length for the niobium tube, while the anode is a stainless steel wire 1 mm in diameter passing axially through the center of the tube. The wire is positively charged, while the tube is grounded. The gas flowing through the reactor tube is converted to plasma by high voltage discharge from the reactor anode.

Fig. 2 contains an electrical circuit diagram of the discharge reactor. The electrical circuit of the plasma reactor and the processes of charging and discharging used in this work are quite similar to previous plasma reactor designs used for NO_x conversion in nonthermal plasma [25]. The only difference is that a thyratron switch is used to initiate the corona discharge in this work, while a hydrogen switch was used in the previous work. The electrical system can deliver charge voltages from 10 to 25 kV at pulse frequencies from 0 to 1000 Hz. The capacitor bank provides space for four "doorknob" capacitors, in increments of 640 pF. The capacitance of the rest of the electrical system is negligible. The thyratron switch element is cooled with compressed air. The capacitors are charged to the desired voltage using a 40 kV oil-cooled high voltage power supply. A thyratron switch is connected directly to the anode of the reactor. On triggering the thyratron, the stored energy in the capacitors is discharged in a few nanoseconds to the anode, giving rise to a high rate of change of voltage (dV/dt) on the anode. This process of charging and discharging the capacitors is repeated based on the thyratron trigger frequency leading to sustained current streamers or plasma. Once triggered, the thyratron will shut off only if the cathode potential becomes higher than the anode potential or the current reaches zero. The anode potential is always higher than the cathode potential and the cathode potential is near zero once the corona is produced. After the corona begins, the current reaches zero only after the capacitor discharges completely. In this way, the energy released by the capacitors per pulse can be calculated from $1/2CV_c^2$, where C is the pulse-forming capacitance as shown in Table 1 and V_c is the