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Co-generation of hydrogen and carbon aerosol from coalbed methane surrogate using rotating gliding arc plasma

Angjian Wu [a], Xiaodong Li [a], Jianhua Yan [a,*], Jian Yang [a], Changming Du [b], Fengsen Zhu [a], Jinyuan Qian [a]

[a] State Key Laboratory of Clean Energy Utilization, Institute for Thermal Power Engineering, Zhejiang University, 38# Zheda Road, Hangzhou, Zhejiang 310027, China
[b] School of Environmental Science and Engineering, Sun Yat-sen University, Guangzhou 510275, China

HIGHLIGHTS

- Rotating gliding arc (RGA) is proposed in coal bed methane (CBM) conversion.
- The performance of CBM surrogate conversion in RGA is comprehensively evaluated.
- 2D graphene sheets are formed in CBM surrogate conversion by RGA discharge.

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ABSTRACT

A novel atmospheric pressure non-thermal plasma, i.e., rotating gliding arc (RGA), is developed to upgrade coal bed methane (CBM) into hydrogen and carbon aerosol simultaneously. CH_4 is used as a CBM surrogate. In present work, the V-I characteristics of RGA discharge in CH_4 conversion are monitored with different gases (N_2, Ar and CO_2) as carrier gas, while the active species (such as OH, CH, CN, C_2, excited molecules and ions) involved in the plasma reactions are identified by optical emission spectroscopy (OES). According to the sensitivity analysis of specific energy density (SED), the importance of operating conditions on SED sensitivity is in a sequence of CH_4 concentration > applied voltage > residence time. The performance of CH_4 conversions are comparatively evaluated based on the variation of operating conditions. In general, the enhancement of applied voltage and residence time effectively increases the CH_4 conversions, selectivity of hydrogen, as well as the energy efficiency, while the augment of CH_4 concentration has a negative effect in contrast. The carbon aerosol obtained in CH_4/N_2 and CH_4/Ar discharge are comparatively investigated. Transparent crumped-like graphene sheets and spherical nanostructure carbon are observed in both obtained carbon aerosol, with relative high I_D/I_G ratios (~0.62) indicated in Raman spectroscopy. High C/O ratios (>14) are obtained in the XPS survey spectra, with the intensity ratios of sp^2 C=C/sp^3 C-C occupy about 80%. However, the BET surface area of carbon obtained from CH_4/N_2 is almost 3 times larger than that from CH_4/Ar discharge. In addition, super hydrophobic and oleophilic properties are observed in both carbon samples. The contact angles of water droplets are above 130°, while the contact angle of oil is less than 4°.

1. Introduction

Widely distributed from coal basins throughout the world, Coalbed methane (CBM) manifests great potential to compensate aggressive necessity in the expanding energy market due to its huge reserve [1]. In China, the CBM area within the buried depth of 2 km is 41.5×10^4 km^2, with the reserve of approximately 36.8×10^{12} m^3 [2]. However, large amount of CBM is emitted directly into the atmosphere along with the increasingly exploitation of coal for lack of effective technologies, which leads to a waste of energy and the emission of greenhouse gas [3] Recently, several investigations have been conducted towards the effective utilization of CBM. Wu et al. [4] proposed to combine coal gasification with CH_4 reforming in a fluidized-bed reactor at a heating temperature above 1000 °C, resulting in the carbon conversion and hydrogen selectivity of 68–70% and 35–39%, respectively. Zhang et al. [5] applied nanocomposite Ni/ZrO_2 catalyst in reforming of the mixture gas of CH_4 and CBM at 1073 K, achieving about 80% conversion of CH_4 by regulating the H_2/CO ratio. Yang et al. [3] converted CBM in a bubbling fluidized-bed reactor with a mixture

* Corresponding author.
E-mail address: yanjh@zju.edu.cn (J. Yan).

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of limestone and crushed catalyst as bed material, which required a harsh operating condition.

However, the existing thermal or thermal catalytic efforts in CBM utilization inevitably encounter common challenges, such as high operating temperature, large-size equipment, catalyst poisoning and greenhouse gas emission. Furthermore, unlike ordinary natural gas, CBM usually contains different levels of N_2 and CO_2, which is hard to be removed by the common purification technologies [6–8]. Distinct from conventional thermal process, non-thermal plasma (NTP) techniques have the advantages of high chemical selectivity, instantaneous start-up time and low energy cost [9,10]. In addition, N_2 and CO_2 are common carrier gases used in NTP to generate active species for the conversion of hydrocarbons [11,12]. Hence, NTP techniques, such as gliding arc plasma [13], radio-frequency plasma [14], dielectric barrier discharge (DBD) [15,16], corona discharge [17] and microwave discharge [18], have been widespread employed in various researches [19]. Fulcheri et al. [20] used arc plasma to synthesize hydrogen and wide broad carbon nanoparticles such as furnace-carbon black, crumpled carbon sheets and carbon rods. Schmidt-Szalowski et al. [21] used DBD to convert CH_4 into C_2 hydrocarbons and carbon black. Until now, seldom have researches focused on the direct conversion of CBM to valuable chemicals (hydrogen and carbon materials) using NTP technologies. In present work, we proposed to use atmospheric pressure rotating gliding arc (RGA) to convert CBM directly. CH_4 is used as a CBM surrogate, while different carrier gases are used to investigate the influence of common components in CBM. Benefits with both thermal and non-thermal plasma characteristics [9,22], gliding arc (GA) is attempted to exhibit better performance in synthesis of hydrogen and carbon nanoparticles when compared with other NTP. By combining high electron energy (1–10 eV) and active species with moderate gas temperature (translational temperature in a scope of 2200–2500 K), GA could easily break strong C—H bond (E = 436 kJ/mol) and promote the electrical-chemical energy transformation. Zhang et al. [23] converted CH_4 in nitrogen RGA plasma, and achieved hydrogen selectively of 80.7% when CH_4/N_2 is 0.05. Yuan et al. [24] used gliding arc to produce carbon black from propane, and obtained spherical carbon with an average diameter of 50 nm and a high oil absorption number of 136 mL/100 g.

In this work, RGA is firstly proposed to convert CBM to synthesize hydrogen and carbon aerosol simultaneously. The electrical and spectroscopic parameters in CBM conversion are investigated based on V-I waveforms and OES diagnostics [25]. The influence of several operating conditions (applied voltage, residence time, types of carrier gas and reactant proportion) on the performance of CBM conversion are comprehensively evaluated in terms of CH_4 conversion, gas product selectivity, specific energy consumption of H_2 and energy conversion efficiency. Moreover, the carbon aerosol synthesized in RGA is characterized by its surface area, morphology, structure and chemical bonding. And the wettability of carbon aerosol is concluded from the contact angle measurement. This study aims to provide an innovative and facile approach to upgrade CBM into high-value chemicals.

2. Materials and methods

2.1. Materials

CH_4 (purity: 99.9%) is used as the surrogate of CBM. Argon (Ar, purity: 99.9%,), nitrogen (N_2, purity: 99.9%) and Carbon dioxide (CO_2, purity: 99.9%) are selected as the carrier gas. All the gas is purchased from JinGong, Inc. Using N_2 and Ar as the carrier gas, energy transformation is favored by generation of excited N_2 molecules and metastable Ar molecules induced by electron collisions. In addition, N_2 and Ar also provides an inert atmosphere for CH_4 reforming in plasma reaction. CO_2 is a soft oxidant and can provide extra carbon atom for CH_4 conversion. Moreover, N_2 and CO_2 are also common components in raw CBM. Ethanol (>99.7%, Sinopharm Chemical Reagent Co., Ltd) is used to purify output gases and collect carbon deposited along the system.

2.2. RGA system

The RGA system is schematically illustrated in Fig. 1, mainly consisting of a DC power supply (Teslaman TLP 2040), mass flow controllers (MFC, Sevenstar D07), home-made RGA reactor and a 40 k Ω resistance. The cylindrical RGA reactor is made of stainless steel (18/8 Cr–Ni) with a Teflon base. An inner cone-shape electrode is mounted in the center of the reactor and connected to a DC power supply. The base diameter and height of the cone electrode are 36 mm and 55 mm, respectively. An outer cylindrical electrode, with a dimeter of 42 mm and a height of 135 mm, is connected to the ground. The narrowest gap between two electrodes is 3 mm, which could realize the optimal breakdown voltage gradient for 3 kV/mm. CH_4 with carrier gas is sufficiently mixed in a tank, and then tangentially injected at the vicinity of narrowest gap through four inlets, resulting into a swirling flow field in the reactor. Permanent magnetic rings are mounted around the outer electrode by providing a perpendicular magnetic filed to the radial component of current, with a flux density of 2000 G. Co-driven by a tangential flow and magnetic force, RGA is elongated and propelled upward along the electrodes, and finally stabilizing at the tip of the inner electrode. The exhaust carbon aerosol is trapped by a cyclone collector, while the gas products are analyzed chromatographically [21]. The whole experimental system is operated at atmospheric pressure (1.01×10^5 pa), while the inlet gas temperature is kept at room temperature (25 °C). All the experiments were repeated 3 times to ensure reproducibility and accuracy of results.

2.3. Characterization

The waveforms of voltage and current are monitored by a high-voltage probe (Tektronix P6015A) and a current probe (Tektronix TCP303), respectively. All of the electrical signals are transmitted to a time-resolved oscilloscope (Tektronix DPO4034B) and recorded. The OES data are recorded by a spectrometer (Ocean Optics USB-4000 UV–VIS). The optical detector is set perpendicular to plasma zone with a distance of 20 cm to receive averaged spatial signals. Gas products are sampled and quantitatively estimated using a gas chromatograph (GC9790A, Fuli Analytical Instrument) equipped with a thermal conductivity detector (TCD) for H_2 and CO measurement, and a flame ionization detector (FID) for CH_4 and C_2 hydrocarbon measurement [26].

Carbon aerosol is collected from the cyclone collector and connecting lines along the system. After washed by ethanol and deionized water twice, the obtained carbon is dried at 100 °C under N_2 for weighing and characterization. The microscopic structure and morphology is evaluated by an emission scanning microscopy (SEM, Utral 55) and a transmission electron microscopy (TEM, Tecnai G2 F20 S-TWIN, FEI). Raman spectroscopy (Labor Raman series, HR-800, 514 nm laser) is used to investigate the graphitized degree of carbon aerosol. Chemical constituent and valence bonding on the surface of carbon is analyzed by X-ray photoelectron spectroscopy (XPS, Escalab 250Xi). The surface area is measured by nitrogen adsorption-desorption isotherms at 77 K (Tristar 3020) and calculated with Brunauer-Emmett-Teller (BET) method. A digital goniometer (DropMete, A-200) is used to measure the contact angles of water and oil on carbon surface.