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Highly efficient conversion of methane using microsecond and nanosecond pulsed spark discharges

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HIGHLIGHTS

- Microsecond and nanosecond pulsed spark discharges are conducted in CH_4 pyrolysis.
- Discharge property, CH_4 conversion, H_2 yield and *ECE* are synthetically analyzed.
- Highest 91.2% CH_4 conversion and 38.4% H_2 yield with an *ECE* of 44.3% are obtained.
- Three probable reaction approaches works synergistically for pyrolysis of CH_4.
- V-V and V-T relaxation processes play important roles in CH_4 spark discharge.

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ABSTRACT

Plasma-assisted methane (CH_4) activation is a promising way for a hydrogen (H_2) production. In this paper, we describe our studies of microsecond and nanosecond pulsed spark discharge plasmas use in a CH_4 pyrolysis for a H_2 production. The dependence of CH_4 conversion and gas discharge product composition on discharge power, discharge gap length and gas flow rate are studied. The electrical and optical characteristics of the discharges are also studied to reveal discharge plasma parameters and chemical reactions leading to CH_4 pyrolysis. Experimental results show that H_2 and acetylene (C_2H_2) are the major gas discharge products accompanied by trace gas discharge products, such as ethane (C_2H_6), ethylene (C_2H_4) and carbon. The highest CH_4 conversion and H_2 yield, 91.2% and 38.4%, respectively, are achieved with an energy conversion efficiency of 44.3% using the microsecond pulsed spark discharge at a gap length 6 mm and a gas flow rate 50 mL/min. The carbon balance under the studied operating parameters varies from 66.7% to 92.8%. The morphology of carbon deposition is presented by two crystal forms identified by SEM and Raman spectral analyses. Finally, comparatively low electron temperature and high vibrational molecular temperature are observed in our experiments, which suggests that V-V transition for CH_4 excitation process and V-T transition for CH_4 heating process play important roles in CH_4 pyrolysis sustained by the pulsed spark discharge.

1. Introduction

The rapid exhaustion of fossil fuel reserves (petroleum and coal) and the increased energy requirements cause serious energy and environmental problems associated with the greenhouse CO_2 emissions. The development of new and emerging clean energy technologies [1–3], such as use of a natural gas whose annual production grows up to 4.5×10^{12} m^3 worldwide [4], is essential and may play an important role in the future. Clean and efficient utilization of natural gas resources require a process wherein the CH_4 is selectively converted into a range of value-added sub-products, such as H_2, C_2H_4, C_2H_2 and methanol (CH_3OH) [5–7]. However, CH_4 is characterized by high C—H bond strength (435 kJ/mol), negligible electron affinity, high ionization energy, and weak polarizability [8]. In the last century, various chemical technologies had been developed for converting CH_4 into H_2 and other value-added chemicals [8–10]. In the beginning of this century, Guo et al. [11] developed a novel catalyst with single iron molecules embedded in a silica matrix at 1363 K for direct, non-oxidative conversion

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of CH_4 with maximum CH_4 conversion 48.4% and total hydrocarbon selectivity 99%. However, the high temperature of the process and high costs of manufacturing the highly active and stable catalyst remain the main challenges for that type of CH_4 conversion in a commercial scale [12].

Low-temperature plasma (LTP) provides a promising alternative route to tackle the challenges in CH_4 activation and conversion [13–15]. LTP systems can directly excite, dissociate and ionize CH_4 molecules [16–19] to create a range of reactive species, including vibrationally and electronically excited species and radicals [20–23], at a comparatively low-temperatures. In the past decades, various LTP systems, such as spark discharge [24,25], dielectric barrier discharge (DBD) [26], gliding arc discharge (GAD) [27–29], radio frequency (RF) discharge [30,31], microwave (MW) discharge [32,33], and corona discharge [22,34] had been used for the conversion of CH_4. Thanyachotpaiboon et al. [22] investigated the direct conversion of CH_4 to higher hydrocarbons using an AC LTP system and obtained a highest conversion efficiency 25% at an applied voltage 11 kV. Kado et al. [24] evaluated the direct conversion of CH_4 by comparing pulsed DC DBD, corona discharge and spark discharge and found that the energy efficiency of plasma process using the spark discharge, 32.3%, was three times as much as that if using DBD and corona discharge. Li et al. [25] developed a stable kilohertz spark discharge system for high energy-efficient conversion of CH_4 to H_2 and C_2H_2 and obtained the energy costs 6.6–10.7 eV per CH_4 molecule converted, 4.4–6.7 eV per H_2 molecule, and 16.9–27.6 eV per C_2H_2 molecule produced. Dae Hoon et al. [29] designed a rotating GAD system to evaluate the influence of arc length on C_2 selectivity and suggested that the arc length plays an important role in the controlling of ambient temperature and chemical reactions. Higher-energy LTP excited by RF and MW power sources were employed to CH_4 conversion for a better conversion performance, especially for the pyrolysis of CH_4 hydrate [30]. Jasiński et al. [32] converted CH_4 with MW power of few kilowatts at a gas flow rate of thousands L/h and obtained H_2 production rate and energy efficiency of H_2 production of about 600 NL [H_2]/h and 200 NL [H_2]/kWh, respectively. Putra et al. [31] and Rahim et al. [33] investigated CH_4 reforming using RF and MW plasmas and showed that H_2 content of 55% can be obtained in RF plasma at 150 W and that microwave plasma optimizes pyrolysis of CH_4 at a fast-emitted rate.

Series of experiments mentioned above are mostly conducted with DC, AC, RF or MW power sources, when the injected power is used for heating CH_4 molecules in the discharge area, which results in considerable energy losses [35]. In recent years, however, pulsed discharge plasma has become an important subject of academic research and applications [36–39]. Especially, the ultra-fast repetitive pulsed discharges have been rapidly developed and used in many applications, such as H_2 generation [40–42], surface modification [43], heavy oil catalytic-cracking [44] and VOC degradation [45]. The repetitive pulses initiate discontinuous discharge that prevents remarkable heat losses between pulses and improves, by such a way, the discharge stability and the energy efficiency without overheating effect. Nishida et al. [46] investigated the influence of a pulse power source on efficient H_2 production from CH_4, and showed that the microsecond pulses can effectively enhance the conversion efficiency. Khalifeh et al. [47,48] studied the pyrolysis of CH_4 using a nanosecond pulsed plasma in a cylindrical DBD reactor and found that the maximum CH_4 conversion 87% and H_2 yield 80% can be achieved at the average input power 268 W. Scapinello et al. [49] employed a nanosecond pulsed plasma for CH_4 and CO_2 reforming and achieved an energy efficiency up to 40%. Rousso et al. [50] developed a nanosecond pulsed discharge system for a low-temperature conversion processes of *n*-heptane and found that argon dilution induced by higher argon concentration enhanced the oxidation and pyrolysis of *n*-heptane by increasing the electron energy and electron density.

Thus, a high efficient and energy saving direct conversion of CH_4 to value-added chemicals is still considered to be a challenge. Although the thermal processes have demonstrated excellent conversion performances at high temperatures and high pressures, long cycle times, harsh conditions, and complicated reprocessing of these technologies can't be neglected. The LTP technology is also considered as a potential direct CH_4 conversion method because of its easy operation, efficient reaction process and mild condition. It should be noted that the conversion and energy efficiency of cold plasmas (such as corona and DBD) are not as high as it is with warm plasmas (i.e. gliding arc, spark, MW, and RF) because of their low reaction temperature, stability, controllability, and other factors. However, the severe overheating effect in warm plasmas can result in coking processes, which may attenuate and terminate the reaction.

The pulsed plasma can be used to obtain excellent conversion performances and mitigate the coking problems. The stability and controllability of a discharge also may be enhanced larger duty cycle of a pulsed plasma. Moreover, the higher average electron energy induced by short-pulsed plasmas is more favorable to excite and dissociate CH_4 molecules and further improve energy efficiency.

In our previous work, we verified the advantage of repetitively pulsed discharge plasma produced by microsecond and nanosecond duration pulse power sources for flow control and material modification [51–54]. It was also showed that the electro-thermal coupling effect played a dominated role in plasma chemical reactions. The pulse power sources are more favorable in controlling electro-thermal coupling effect comparing to the traditional DC, AC, RF, and MW power sources.

The core issue of CH_4 non-oxidation is to find an optimum condition to investigate the balanced relation between the conversion degree of reactant, energy efficiency and coking. The average electron temperature in electric-field and the gas temperature can be efficiently improved using pulse power sources. The coking process is also well suppressed when a considerable energy efficiency is achieved.

In this paper, we describe the experimental results of CH_4 non-oxidative conversion for H_2 production in a needle-to-plate discharge reactor using nanosecond and microsecond pulse power sources. The voltage-current characteristics and optical emission spectra of the plasmas, as well as CH_4 conversion and gas product distributions are evaluated using different pulse power sources, gap lengths and gas flow rates. The power consumption, plasma parameters, carbon and hydrogen balances and energy efficiency are estimated and the possible reaction approaches of CH_4 pyrolysis are explored.

2. Experimental setups and methods

2.1. Experiment

Fig. 1 shows the experimental setup consisting of a pulse power source, a needle- plate discharge reactor, an electrical measurement system, a gas supply with a flow control system, an optical emission spectrometer and a gas chromatograph. The microsecond (peak voltage 0–40 kV, rising time 500 ns and FWHM 300 ns) and nanosecond (peak voltage 0–30 kV, rising time 350 ns and FWHM 150 ns) pulse power sources are triggered with a repetition frequency varied from 1 to 5 kHz.

In the needle-to-plate discharge reactor, two PTFE connectors and O rings are used to fix and seal a quartz tube with an outer diameter 60 mm and wall thickness 4 mm. A stainless-steel plate (diameter 50 mm) and a rod (length 120 mm, diameter 4 mm) with a needle-head (radius of curvature 0.5 mm) are placed inside the quartz tube and used as ground and high voltage electrodes, respectively. The gap length between the needle and the plate electrode may be varied from 0 to 10 mm. The gap lengths of the nanosecond pulsed spark discharge are 4 mm, 6 mm, 8 mm and 10 mm, while those of the microsecond pulsed spark discharge are 2 mm, 4 mm and 6 mm. The applied voltage and the discharge current are measured by a high voltage Tektronix probe P6015A and a current Pearson probe 6595, respectively, and recorded