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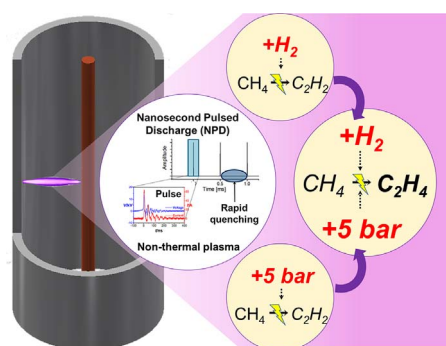
Direct methane-to-ethylene conversion in a nanosecond pulsed discharge

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GRAPHICAL ABSTRACT



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ABSTRACT

We report that gas phase plasma-assisted non-oxidative methane coupling can lead to formation of ethylene as major product at ~20% yield per pass. This is attained by using a nanosecond pulsed discharge (NPD) reactor, featuring rapid product quenching rates, (recyclable) hydrogen co-feeding ($\text{CH}_4:\text{H}_2 = 1:1$) and elevated pressures (5 bar) at which NPD is ignited.

1. Introduction

The societal and industrial importance of methane, as a source of energy and chemicals, in the coming decennia will be significant. The enormous reserves found (proven world natural gas reserves were $187 \times 10^{12} \text{ m}^3$ for the year 2016 [1] in addition to 10^{15} to 10^{18} m^3 of methane stored in hydrates [2]), environmental sustainability and lower overall costs point to natural gas as the primary source for energy and chemicals in the near future. The great variety of methane sources, including existing gas networks, small natural gas fields, shale gas, coal beds, agricultural biogas and deep-sea methane hydrates creates an urgent need to develop modular and flexible reactor systems able to valorize methane to chemicals or liquid fuels and to operate with changing methane feedstock in various environments.

Methane can be converted to methanol and synthetic fuels via syngas, or directly to olefins. These processes are not directly competitive; depending on the location, the available process and transportation infrastructure, the magnitude of available methane resources, the presence of other chemical feeds (e.g., CO_2) and current market value of relevant products, different valorization routes may be selected. Considering the products above, ethylene has the highest market value since it is the basic building block for a very broad range of chemicals ranging from plastics to solvents. Therefore, simple, scalable and efficient processes to convert methane to ethylene are highly desired. Direct methane transformation to ethylene may occur via oxidative or non-oxidative coupling. Oxidative coupling is exothermic and occurs at 1000–1200 K in presence of catalyst (metal oxides) and oxygen. However, the low single-pass C_2 yields of 18–26% [3] (while commercial

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viability requires ethylene yields > 25%), high purity O₂ demand and by-products formation (CO₂, CO, H₂ and H₂O), which necessitate intensive downstream processing, have limited the exploitation potential of the technology so far. Non-oxidative methane coupling results in light hydrocarbons (mainly C₂ species), hydrogen, carbon, benzene and other aromatics depending on the process conditions (mainly temperature and catalyst type). Carbon and hydrogen are thermodynamically the most stable products in the temperature range 1000–3300 K. In addition, benzene is formed in the temperature range 1100–1500 K while mainly acetylene is formed at higher temperatures [4]. Ethylene formation is maximized in the range 1300–1800 K [4]. Recently, Guo et al. synthesized an iron-based catalyst (Fe/SiO₂) that enables direct non-oxidative methane coupling at 1363 K and yield of 23.4% [5].

Alternative technologies for methane processing at low temperatures have also been investigated aiming at improved energy efficiency, catalyst stability and process safety. Among them, non-thermal plasma can activate methane coupling and reforming reactions at lower temperatures, overcoming the thermal losses in gas heating [6]. Concerning methane coupling, plasma is not selective to ethylene. Ethane is mainly formed in dielectric barrier discharges (DBD) [7], or other low energy density discharges, while acetylene and carbon are the dominant products in high energy density discharges (MW [8], GA [9], spark [10] and corona [11]). Long chain hydrocarbons can also be formed under specific conditions (in batch DBD) [12]. Relatively high ethylene selectivity, comparable to that of acetylene and ethane, can only be obtained in glow discharges [13]. The reason of the different product distributions obtained from different types of plasma discharges is essentially the different plasma chemistries that are determined by the plasma characteristics. In DBD and low energy density discharges, electron impact reactions drive the reactivity, leading to CH₃ radical formation in the discharge [14] and consequently to ethane and propane after CH₃ radical recombination reactions at low temperatures [15]. By increasing the reduced electric field, the fragmentation pattern is shifted from CH₃ to CH₂, CH and C radicals [16]. Since the energetic thresholds of these electron impact reactions are comparable, no remarkable enrichment of CH₂ radicals (ethylene precursors) is attained and thus, ethylene formation is limited. In high energy density discharges, or “warm” discharges, apart from the electron impact reactions, high temperatures (from hundreds to thousands of degrees Celsius) can further promote methane conversion and dehydrogenation reactions to acetylene and carbon [17]. It is possible to kinetically control carbon formation since methane coupling and dehydrogenation reactions proceed sequentially (methane → ethane → ethylene → carbon). Ethylene formation requires 10⁻⁶–10⁻⁵ s, while acetylene 10⁻⁵–10⁻⁴ s [18]. Conventional quenching systems cannot achieve very fast quenching rates to suppress ethylene

dehydrogenation to acetylene. A relatively new plasma technology in the field of chemical processing, the Nanosecond Pulsed Discharge (NPD) technology can achieve higher quenching rates; Lotfalipour et al. [19] has calculated the quenching rate to be ~20 K μs⁻¹, that is 20 times higher than in conventional systems (i.e. Hüls process). Martini and coworkers measured the quenching rate in CO₂ splitting (7.5 K μs⁻¹) using LIF spectroscopy [20].

NPD is generated using a nanosecond pulsed power supply unit, with voltage rise rate in the order of kV ns⁻¹ or higher and pulse duration in the range of tens of ns [21]. At these conditions, arc is prevented and non-equilibrium plasma is sustained. In the case of methane coupling, the streamer-to-spark regime may be significant; the discharge includes a streamer that propagates between the electrodes followed by a spark in the active channel. The temperature of the active channel during the discharge rapidly increases and reaches thousands of degrees Kelvin in few tens of ns, activating also thermally driven reactions. This fast heating rate is not a requirement in methane coupling but the ability to reach high temperatures does affect the chemistry; methane can be dehydrogenated by H radicals at 1000 K and dehydrogenation of ethane to ethylene and then to acetylene can be activated by H radicals at 1300 K [17]. Collectively, both methane conversion and unsaturated hydrocarbons selectivity increase. Higher temperatures are avoided as they lead to significant amounts of carbon.

In this work, we present the results of methane coupling using a nanosecond pulsed discharge in a coaxial reactor. We particularly investigate, for first time, the combined effect of the hydrogen content in the feed and the plasma reactor pressure and we show that proper selection of these parameter values in combination with the unique features of the NPD technology can lead to remarkable ethylene yields through single-step plasma processing, unlike previous important works in the field in which acetylene was the major product [19,22]. Since the aim of the work is the production of ethylene as main product, we have focused on determination of the C₂ species, which represent the products of the main reactivity at the studied experimental conditions. The results of the current work are also compared to other pioneering works, in which ethylene was produced from methane and considerable yields were attained.

2. Materials and methods

A detailed schematic representation of the experimental setup used is presented in Fig. 1. The plasma reactor is a coaxial shaped reactor that comprises an inner axial wire and an outer co-axial tube. The inner axial wire constitutes the high voltage (HV) electrode of the reactor; it

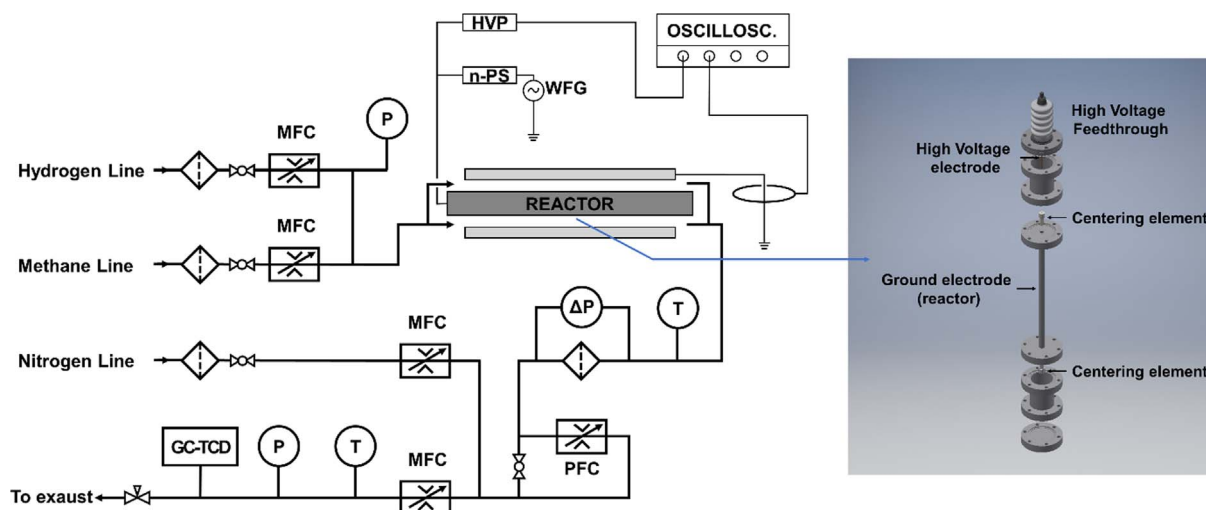


Fig. 1. Representative drawing of the experimental setup: MFC, mass flow controllers; PFC, pressure flow controller; WFG, waveform generator; n-PS, nanosecond pulsed generator; HVP, high voltage probe; OSCILLOSC., oscilloscope; GC-TCD, gas chromatography with thermal conductivity detector; P, pressure probes; ΔP, differential pressure meter; T, thermocouples.

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