



Research article

Low energy cost conversion of methane to ethylene in a hybrid plasma-catalytic reactor system

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ARTICLE INFO

Keywords:

Methane coupling
Non-thermal plasma
Hybrid plasma-catalytic reactor
Nanosecond pulsed discharge
Ethylene

ABSTRACT

In this work, we report on low energy cost methane conversion to ethylene in a hybrid plasma-catalytic reactor system. Methane is first converted to acetylene, reaching up to 23.5% yield per pass, by a nanosecond pulsed discharge (NPD), and subsequently, acetylene is hydrogenated to ethylene using a Pd-based catalyst, which is placed in the post-plasma zone. Overall, ethylene is formed as major product at 25.7% yield per pass, consuming 1642 kJ/molC₂H₄, which is the lowest energy cost reported for plasma-assisted methane-to-ethylene conversion so far. The two-step process is carried out in a single reactor volume that aside from the discharge energy does not require any heat or hydrogen input since both are provided by methane cracking in the plasma zone itself.

1. Introduction

Methane, the major compound in natural gas, is deemed a promising alternative feedstock for fuels and chemicals [1,2] due to its wide availability and low cost. Recent hydrocarbon explorations worldwide have revealed an abundance of conventional and unconventional rich-in-methane (CH₄) gas reserves such as tight gas, shale gas, methane hydrate and coalbed methane [3–6]. However, about half of the natural gas reserves are located in remote areas, far away from any sizeable market [7,9]. Those decentralized gas reserves have low commercial interest due to costly transportation, unless they can efficiently be converted to added value products on site.

CH₄ can be converted into added value products either in two steps, via synthesis gas [10], or directly to C₂ hydrocarbons in one step. Pyrolysis [11,12], partial oxidation [13,14], dry [15,16] and steam reforming [17] constitute CH₄ valorization processes of great commercial interest [18]. Non-oxidative CH₄ coupling has also attracted attention [19] since the formed C₂ hydrocarbons have high market value. In view of ethylene (C₂H₄) and acetylene (C₂H₂) production from CH₄, various catalysts have been studied. Recently, Guo et al. synthesized an iron-based catalyst (Fe/SiO₂) that enables direct non-oxidative CH₄ coupling at 1363 K with 23.4% ethylene yield [20]. However, the high energy demand due to the high pyrolysis temperatures (> 1100 °C) and the shortcomings associated with the pyrolytic furnaces, such as long start-up/shut-down periods, high volumetric footprints and gas emissions, are considered as important process limitations [21,22].

Plasma-assisted CH₄ cracking and particularly non-thermal plasma (NTP) may be a promising alternative solution [23–26]. High energy electrons created in the plasma zone can effectively generate a high concentration of chemically active species such as radicals, excited species and ions through electron-molecule collisions. The generated active species can rapidly undergo several chemical reactions [26] at atmospheric pressure and low temperatures. Low reaction volumes are needed due to the fast electron-induced reactions. The technology is also compatible with the renewable energy sources, which electricity may be drawn from, leading to gas emissions elimination. Undesirably, plasma is not selective and results in wide product distribution. C₂ yields strongly depend on the discharge energy density. High energy density discharges (i.e. microwave, gliding arc, spark and corona) reach up to 71% CH₄ conversion at 1861 kJ/mol_{CH₄} energy input [27]. C₂H₂ is the dominant product (60.3% selectivity), while C₂H₄ is formed in small amounts (6.3% selectivity) [27]. Low energy density discharges (i.e. DBD) reach up to 7.5% CH₄ conversion at 482 kJ/mol_{CH₄} energy input [27]. Ethane (C₂H₆) is the dominant product (42.9% selectivity), while C₂H₄ selectivity is significantly lower, 2.4% [27]. The product distribution variation observed among the different plasma sources is due to different plasma characteristics that drive the plasma chemistry.

Nanosecond pulsed discharges (NPD) show higher energy efficiency than other plasma sources [28]. By applying electrical pulses of high voltage rise rate (in the order of kV ns⁻¹) and short duration (tens of ns [29]), the electrical energy is channeled into the electrons, promoting electron-induced chemical reactions. Transition to arc regime is prevented and NTP is sustained at these conditions. Collectively, electrical

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energy is predominantly channeled into chemical energy rather than into gas heating. Recent studies using NPD in CH₄ reforming have reported 23.5% [30] – 50% [31] CH₄ conversion, at 73 kJ/mol_{CH₄}–250 kJ/mol_{CH₄} energy input. In all studies, C₂H₂ is formed as dominant product at 72% [31] – 85% [30] selectivity while C₂H₄ selectivity is limited, about 2% [31] – 4% [30], as in other high energy density plasmas.

Formation of C₂H₄ in the plasma zone can be enhanced via enrichment of CH₂ radicals which serve as C₂H₄ precursors. Although the reduced electric field increase may benefit CH₂ radicals formation by shifting the CH₄ fragmentation pattern from CH₃ to CH₂ [32], CH₂ cannot be the dominant species since the energetic thresholds of the electron-induced CH₄ to CH₃, CH₂, CH and C cracking reactions are close [26] and inevitably, all CH_x radicals are contemporarily present. Therefore, no significant C₂H₄ yields in plasma-driven processes have been reported so far and so, direct CH₄ coupling to C₂H₄ in plasma is still a challenge. However, C₂H₄ can be formed indirectly; C₂H₂, which is majorly formed in the plasma zone, can be catalytically hydrogenated to C₂H₄ beyond the plasma zone; the H₂ required for C₂H₂ hydrogenation is produced by CH₄ cracking in the plasma zone. Gordon et al. [33] introduced a Ag-Pd-Y zeolite catalyst in a DC plasma reactor, equipped with an external heating/cooling system to precisely maintain the reactor temperature at values suitable for catalyst operation. A global C₂H₄ yield of 19.3% was reported. Kado et al. [34] placed a Lindlar catalyst between the electrodes of a DC plasma reactor and achieved 47% global C₂H₄ yield. However, they questioned the economic feasibility of the process due to the extremely high energy consumption. Wang et al. [35] employed two reactors, an AC plasma reactor and a catalytic one to first couple CH₄ to C₂H₂ and then hydrogenate, in a second step, C₂H₂ to C₂H₄. They reported 52.1% global C₂H₄ yield. Working the same way, Wang and Guan [36] optimized this system further by introducing recycle streams and reached 55% global C₂H₄ yield. In these works, the significantly high energy cost of C₂H₄ production was the major disadvantage of the process.

In the current work, a hybrid plasma-catalytic reactor system is proposed for low energy cost C₂H₄ production. An NPD reactor is first optimized with respect to feed flowrate, feed composition and discharge gap in order for C₂H₂ production at minimum energy cost. Then, integration of plasma with highly selective hydrogenation catalysts, placed individually in the post plasma zone, is carried out and optimized. Specifically, three hydrogenation catalysts, all supplied by Johnson Matthey (JM), were tested; a commercial palladium (Pd)-based catalyst, a Pd/Al₂O₃ catalyst and a Au/TiO₂ catalyst. The two-step process takes place in the same reactor volume while neither extra source of hydrogen, nor heat, are required; both are provided by CH₄ cracking in the plasma zone. The global C₂H₄ yield of this self-sustained hybrid plasma-catalytic reactor system reaches 25.7% at significantly lower energy cost, 1642 kJ/molC₂H₄, compared to previous works.

2. Material and methods

2.1. Experimental setup

The experimental setup used for the experiments performance is presented in Fig. 1. The discharge was initiated by a nanosecond pulsed power supply (n-PS) (NPG-24/2500, Megaimpulse Ltd.) which was triggered by a waveform generator (WFG) (33220A, Keysight Technology) at frequencies up to 3 kHz. A high-voltage probe (P6015A, Tektronix) and an I/V converter (CT-D-1.0, Magnelab) were employed to measure the applied voltage and discharge current, respectively, which were recorded over the course of the experiment by a digital oscilloscope (Wavesurfer 10, Teledyne Lecroy) with a sampling frequency of 10 GS/s. The discharge energy input was estimated as in other work [37]. The integral of the instantaneous power ($V \times I$), corrected by the voltage (V) and current (I) signals time delay, constitutes the pulse energy. Voltage and current signals time delay was

calculated by zeroing the $V \times I$ product time integral under absence of discharge, managed by filling the plasma reactor with SF₆ [38].

Mass flow controllers (GF40 Series, Brooks Instrument) controlled the feed flowrate of the reactants (CH₄, Airliquide 99.995% purity, and H₂, Airliquide 99.999% purity). A filter (SS-4TF-7, Swagelok) with 7- μ m pore size was installed at the plasma reactor outflow to retain the formed carbon. A differential pressure meter (Model 700.02, WIKA) was used to monitor the differential pressure across the filter cloth, which was cleaned when the differential pressure exceeded a certain value. A second clean identical filter was used while the first one was under cleaning. A third mass flow controller (GF40 Series, Brooks Instrument), which was operated as flowmeter, continuously recorded the volumetric flowrate of the plasma reactor outflow. However, the readout value depends on a gas factor, which varied with the gas composition. Since the gas composition was not constant over the course of the plasma reaction, N₂ (Airliquide, 99.999% purity) was used as internal standard to accurately measure the value of the volume of the plasma reactor outflow. A known amount of N₂ (20 sccm) was fed into the plasma reactor outflow (not inside the plasma zone) [39]. The outflow rate was obtained by multiplying the initial total flowrate (CH₄ + H₂ + N₂) by the ratio of the chromatographic area of N₂ before and during the discharge. A fourth mass flow controller (4800 series, Brooks Instrument) was used to set the internal standard N₂ flow. Pressure probes (P1600 and P1650, Pace Scientific) and thermocouples (PT 900 Pace scientific) were employed to monitor the reactor operating conditions.

The analysis of the plasma reactor product stream was performed by an on-line GC (3000 MicroGC, Inficon). Detection of H₂, N₂ and CH₄ was done by a molesieve column (10 m) with backflush (3 m, Plot U); detection of C₂H₄, C₂H₆, C₂H₂, C₃H₈, C₃H₆ and C₃H₄ was done by a Plot U column (10 m) with backflush (1 m, Plot Q), while an Alumina column (10 m, 0.32 mm) with backflush (1 m, 0.32 mm, Alumina) was used for detection of higher species, i.e. C₄–C₆ hydrocarbons.

The nanosecond pulsed (co-axial) plasma reactor is presented in Fig. 1. Minor adaptations to the plasma reactor, which regard the outer (ground) electrode diameter, were carried out to enable the investigation of the discharge gap impact on CH₄ conversion and product distribution. The following four tubes with different internal (ID) and external (OD) diameters were used: 7 mm ID, 10 mm OD; 10.4 mm ID, 13 mm OD; 12.2 mm ID, 18 mm OD and 22.4 mm ID, 25.4 mm OD, which correspond to 2.4 mm, 4.2 mm, 6 mm and 10.1 mm discharge gap, respectively. The length of the outer electrode was constant (25 cm) in all tested gaps.

2.2. Catalyst preparation and utilization

To maximize the global C₂H₄ yield, three different hydrogenation catalysts were tested individually in the post-plasma zone. One commercial and one “for-research-purpose” Pd-based catalyst, both supplied by Johnson Matthey (JM) (Pd load < 0.1% w/w), were selected due to the Pd superior hydrogenation ability and its common use in industrial hydrogenation processes. Hereafter, the first (commercial) catalyst will be referred to as Johnson Matthey-developed Pd-based catalyst (JM catalyst) and the second one simply as Pd/Al₂O₃ catalyst. The latter catalyst in particular consisted of Pd (0.05% w/w) impregnated into α -alumina (Pd/Al₂O₃). This catalyst was prepared according to the following procedure; Pd(NO₃)₂ was added to alumina powder and mixed thoroughly; the mixture was dried at 120 °C and calcined at 300 °C to promote conversion of Pd(NO₃)₂ into PdO. Subsequently, it was compressed, crashed and sieved, resulting in granulates of 0.85–1.4 mm size. The third catalyst, also prepared by JM, consisted of Au (1% w/w) impregnated into titanium dioxide and is further referred to as Au/TiO₂ catalyst.

The plasma-catalyst integration was studied in the same experimental setup. All three hydrogenation catalysts were placed inside the co-axial plasma reactor, right beyond the plasma zone (post plasma

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