CO_2-Free Hydrogen and Syngas Production from Methane Pyrolysis Using Electrothermal Fluidized Bed Technology

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Highlights

- Zero-emission hydrogen production from methane without downstream purification in ETFB reactor.
- Carbon deposition can be mitigated through continuous catalyst replacement or CO_2 regeneration .
- Syngas with tailored H_2/CO ratios can be obtained via cyclic methane pyrolysis and CO_2 gasification

1. Introduction

Methane pyrolysis is emerging as a promising low-carbon pathway for hydrogen production, generating H_2 and solid carbon without direct CO_2 emissions. Compared with conventional technologies such as steam methane reforming or coal gasification, this "turquoise hydrogen" route offers lower emissions and the potential for valuable carbon by-products [1]. However, catalyst deactivation due to carbon accumulation remains a major challenge for continuous operation. In this work, an electrothermal fluidized bed (ETFB) reactor is investigated as an electrified and energy-efficient system for methane pyrolysis over carbon catalysts. Two strategies to overcome catalyst deactivation are evaluated: (i) continuous replacement of deactivated catalyst with fresh material and (ii) cyclic operation involving methane pyrolysis followed by CO_2-based catalyst regeneration via gasification. The latter approach enables partial CO_2 utilization while restoring catalyst activity. The proposed concept aims to achieve sustained hydrogen production with zero direct CO_2 emissions, while also enabling flexible syngas generation for downstream applications such as methanol synthesis or iron reduction.

2. Methods

A one-dimensional steady-state model of an electrothermal fluidized bed (ETFB) reactor, with central electrode and conductive reactor wall, operating in the bubbling regime was employed [2] to simulate methane pyrolysis and catalyst regeneration. The model assumes adiabatic operation at atmospheric pressure with conductive carbon particles heated by the Joule effect through an applied electric potential. Fluidized-bed hydrodynamics are described using two-phase theory, separating the bubble and dense phases to account for gas flow distribution. Mass and energy balances are solved along the reactor height, incorporating heat generation from electrical resistance and reaction heat effects. Methane pyrolysis and CO_2-based carbon gasification are described using literature kinetic models adapted to reactor conditions. The model enables prediction of reactor behavior during both hydrogen production and catalyst regeneration

3. Results and discussion

The simulations demonstrate that the electrode position strongly affects heat generation and reactor behavior. Figure 1 shows the power density and methane conversion profile for pyrolysis at a space time amounting to 1 kg h Nm^{-3}. A deeper electrode immersion increases the Joule heating, resulting in higher bed temperatures at a constant applied voltage of 12.3 V. In the analyzed configuration, the electrical power supplied to the reactor increases from 178 W to 332 W when the electrode tip is moved from 10 cm to 3.5 cm above the reactor base. This additional heat input enhances methane conversion,

and complete conversion is obtained when the electrode is fully immersed, allowing the production of hydrogen without CO_2 generation and therefore eliminating the requirement for downstream separation processes.

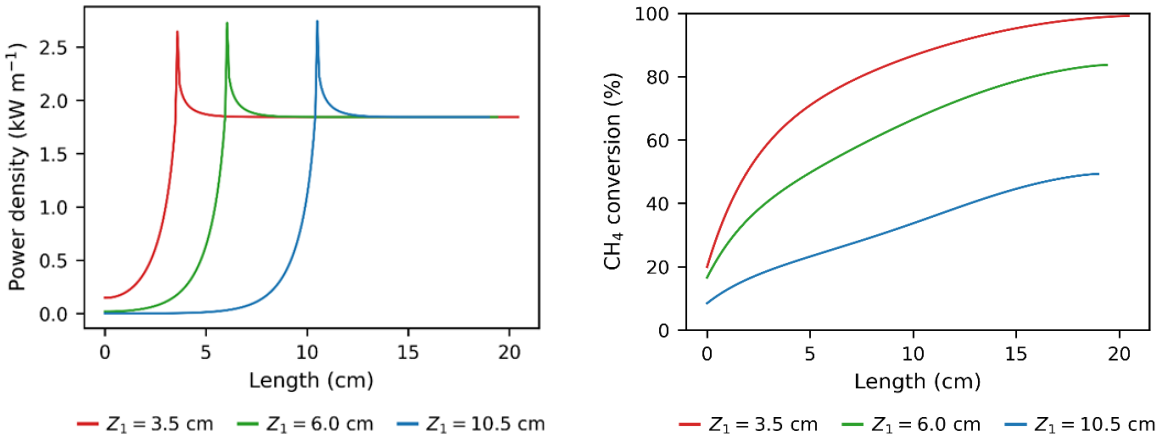

Figure 1 Temperature and conversion profile of methane pyrolysis along the ETFB reactor at different submersion depth of central electrode. ΔV=12.3 V, $Q_{CH4,in} = 4.5Nl.min^{-1}$.

To mitigate catalyst deactivation caused by carbon accumulation, two operational strategies were assessed. The first relies on a continuous catalyst makeup stream, where fresh catalyst is periodically introduced while a portion of the deactivated material is simultaneously removed, ensuring a stable average catalyst activity. Model predictions show that maintaining a bed activity above 80 % requires feeding fresh catalyst at roughly 1.4 % of the initial bed mass per second, with spent catalyst removed at a rate approximately 50 % higher. The extracted solid contains deposited carbon, which can potentially be valorized in applications such as energy storage materials, composites, or construction products. The second approach consists of regenerating the catalyst through CO_2 gasification via the reverse Boudouard reaction. This treatment generates a CO-rich gas stream that can be combined with hydrogen produced during methane pyrolysis to form syngas. Simulation results indicate that nearly complete CO_2 conversion can be reached at about 18 V for an H_2/CO ratio of 1 and 14 V for an H_2/CO ratio of 2, effectively removing deposited carbon while enabling adjustment of the resulting syngas composition.

4. Conclusions

Methane pyrolysis offers a low-carbon pathway for hydrogen production, generating H_2 and solid carbon without direct CO_2 emissions. In this work, an electrothermal fluidized bed (ETFB) reactor enables complete methane conversion through Joule heating, avoiding downstream purification. Catalyst deactivation remains a key challenge; model results show that maintaining >80 % bed activity requires continuous catalyst renewal with fresh catalyst fed at ~1.4 % of the initial bed mass s^{-1}. Alternatively, catalyst regeneration via CO_2 gasification can remove deposited carbon and produce syngas, achieving near-complete CO_2 conversion at ~18 V (H_2/CO = 1) and 14 V (H_2/CO = 2). In both strategies, CO_2 emissions are minimized while carbon or syngas is valorized in downstream processes.

References

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Keywords

Methane pyrolysis, electrothermal fluidized bed reactor, carbon catalyst regeneration, Boudouard reaction .