

Liquid Metal Based Bubble Column Reactor Solving Coking Issues for High Reaction Temperatures

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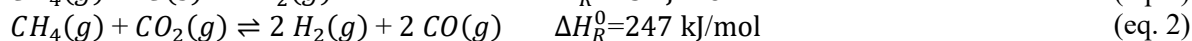
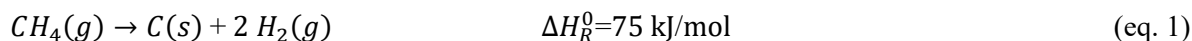
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Highlights

- Overcoming coking problems due to constant surface renewing in liquid metal bubbles
- Excellent heat transfer supports high conversion and hydrogen yields
- Reactor can be steadily operated and long-term applicability has been shown

1. Introduction

Methane pyrolysis (eq. 1) is a promising route for producing CO₂-neutral hydrogen from natural gas and has been intensively studied in for years. Key challenges include the high temperatures required (~1000 °C for non-catalytic decomposition), uniform energy supply for the endothermic reaction, and effective management of solid carbon formation to prevent coking inside of the reactor.



To address these challenges, one of the proposed reactor concepts is a liquid metal bubble column reactor (see fig. 1). This approach has been under investigation for several years and offers distinct advantages in terms of heat management and carbon handling. At the Karlsruhe Liquid Metal Laboratory (KALLA), extensive research has been conducted by Geißler et al.¹, Hofberger et al.², and Uhlenbruck et al.³ contributing significantly to the development and understanding of this technology.

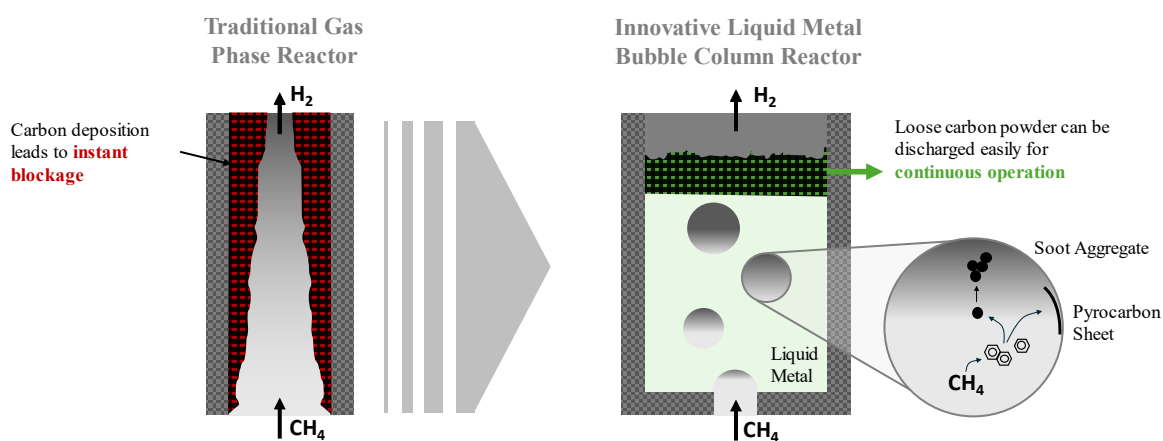


Figure 1. Visualization of the disadvantages of a traditional gas phase reactor for carbon producing reactions (left) in contrast to the working principle of a continuously operable liquid metal based bubble column reactor (right).

The innovative, continuously operable methane pyrolysis reaction in a liquid metal bubble column reactor produces a nanoscale carbonaceous powder. The solid carbon is formed in the gas phase of the bubble and at the gas metal interface as the bubble rises. The carbon is released as a powder at the top of the liquid column due to the density difference. In contrast to classic gas phase reactors, the deposition at the heated wall is suppressed by the liquid metal.

2. Methods

All experiments were conducted using liquid tin with a bath height of 500 – 1050 mm in quartz glass reactors or Al₂O₃ crucibles, which were placed in a resistance-heated tube furnace. This allows tin temperatures between 950 °C and 1175 °C to be reached. The pressure is close to ambient at the reactor head and increased toward the gas inlet due to hydrostatic effects. The educt gas flow rate was varied between 50 and 800 mL_N min⁻¹. Gas-phase analysis of CH₄, H₂, CO₂, CO, Ar, N₂, C₂-species, and C₃H₈, was performed using a MS, while H₂O content was quantified with a P₂O₅ sensor. Carbon discharge was carried out either gravimetrically or pneumatically using an argon flow of 6 to 16 L_N min⁻¹. The main focus was on methane pyrolysis, with recent experiments extending toward dry reforming of methane (eq. 2). Initial work employed pure methane and nitrogen-diluted methane in a quartz-glass reactor and involved testing different reactor inventories to increase residence time¹. Further studies addressed the pyrolysis of synthetic methane derived from atmospheric CO₂, emphasizing proof-of-concept⁴ and detailed carbon analysis⁵ using SEM, TEM, Raman spectroscopy, HNC elemental analysis, XRD, EDX, and HAADF. Additional research targeted the production of turquoise hydrogen² using methane, ethane, and propane mixtures, as well as natural gas, and included reactor-design improvements such as evaluating reactor materials and implementing a pre-chamber⁶.

3. Results and discussion

Over the past years, several design options for the educt-gas inlet have been developed and tested at KALLA^{1,4,6} (see Fig. 2). These designs exhibited varying levels of durability and process performance. The latest configuration consists of an Al₂O₃ tube (ID = 3 mm, L = 1500 mm) inserted from the top into the reactor. This design demonstrated excellent long-term stability, enabling continuous reactor operation for more than six months.

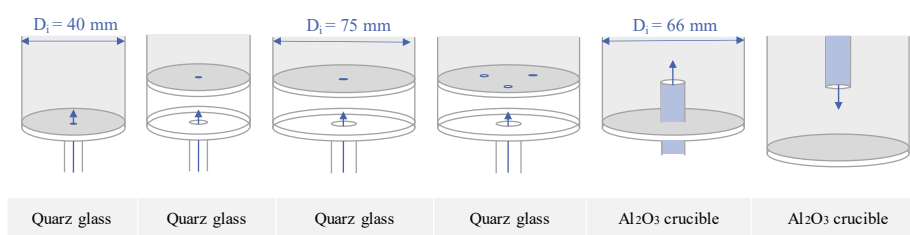


Figure 2. Schematic representation of the developed educt gas inlet concepts at the KALLA, see also ^{1,4,6}.

4. Conclusion

Substantial progress has been achieved in the development of liquid-metal-based reactor designs; nevertheless, current challenges under investigation include efficient scale-up of the technology, further energy and process optimization, and comprehensive characterization of the resulting carbon to assess its suitability for industrial applications.

References

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Keywords

Liquid Metal, Bubble Column, Methane Pyrolysis, Scale-up