HYDROGEN AND CARBON BLACK PRODUCTION FROM CRACKING IN MOLTEN MEDIA (HAMMER)

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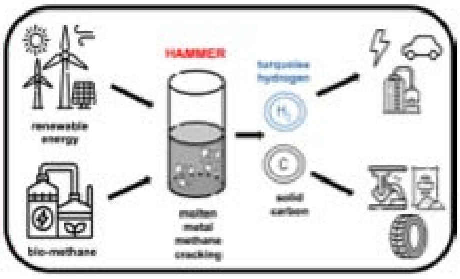
Background

Methane cracking is a prominent method for producing hydrogen and carbon nanomaterials. This process, occurring at high temperatures in the absence of catalysts, leads to the thermal decomposition of methane (CH_4) into hydrogen (H_2) and solid carbon.

$$CH_4 \rightarrow C_{(s)} + 2H_2 \qquad \Delta H^0 = 74.91\ kJ/mol$$

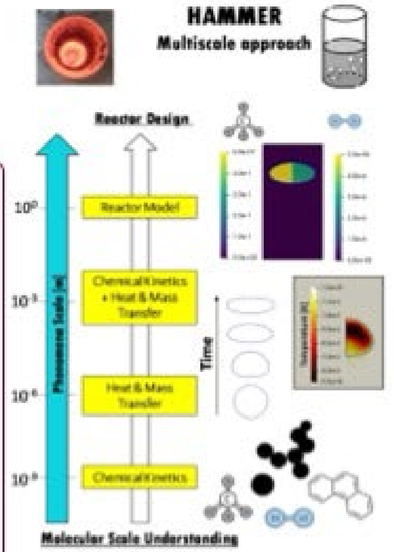
The production of **solid carbon** represents a **value-added aspect** of the process, as it allows for the generation of high-value materials (e.g., carbon black, graphene, activated carbon) and avoids CO_2 emissions. However, the formation and accumulation of carbon also pose significant engineering challenges. In this context, **the use of molten metals** as thermal medium represents a promising solution. Deep knowledge of the occurring kinetic/fluid-dynamic is missing and application is still largely limited to empirical lab-scale approaches. The lack of detailed experimental data on the reaction intermediates and carbon precursors, on bubbles motion in the molten media and on solid carbon characterization inhibits the development of reactor models, hindering a careful assessment of the impact of operating conditions for design and optimization purposes.



Objectives

The goals of HAMMER require the combination of high-quality experimental data (UNIROMA1) and advanced numerical models (POLIMI)

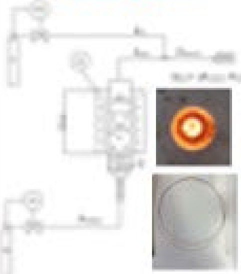
1. Development of a lab-scale bubble molten metal reactor aiming at validating an experimental procedure to decouple kinetics and fluid-dynamics aspects.
2. Definition of a comprehensive kinetic model describing in detail the homogeneous gas-phase cracking as well as the heterogeneous formation of solid carbon
3. Development of a multiscale reactive CFD-based model able at providing deep insights into the interactions between the fluid dynamics and the chemistry



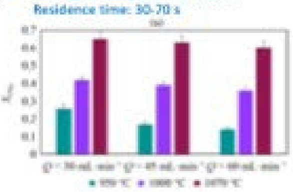
1 Experimental work

1) Homogeneous gas-phase tests for validation of kinetic model
2) Molten tin methane tests for validation of the reactor model
3) Carbon characterization: Raman, SEM, BET

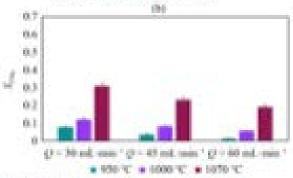
Experimental Apparatus:
Reactor diameter: 1.5-6 cm
Injection capillary diameter: 0.1-0.53 mm
T=950-1070 °C
Flow rate 10-60 ml/min

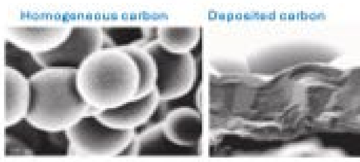


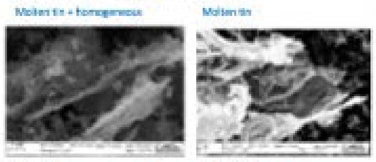
Homogeneous gas-phase tests:
Residence time: 30-70 s



Molten tin tests:
Residence time: 0.9-1.4 s







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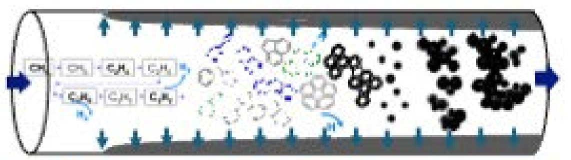
Carbon produced in a homogeneous reactor show spherical stacked carbon particles (~300-500 nm).
In contrast, a sheet-like structures were the predominant form observed in the carbon samples produced in the reactor with tin. This morphology seems to be due to the bubbling configuration implying that carbon particles were formed preferably at the liquid-gas interface

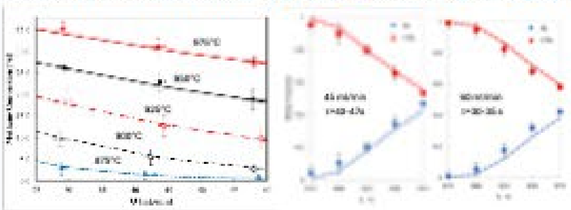
2 Kinetic modeling

Challenges: Heterogeneous chemistry



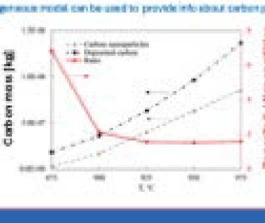
Validation of kinetic model developed by CRECK Model in homogeneous gas phase

OpenSMOKE++

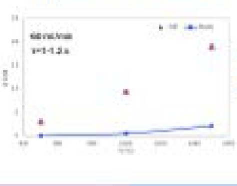


Model was validated succesfully in homogeneous gas phase

Homogeneous model can be used to provide info about carbon production



Experimental vs. model in molten tin

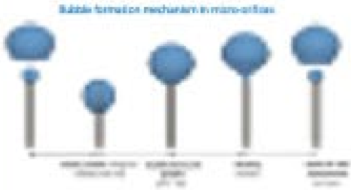


The model is not validated in molten tin
Effect of the carbon at the bubble surface should be take into consideration

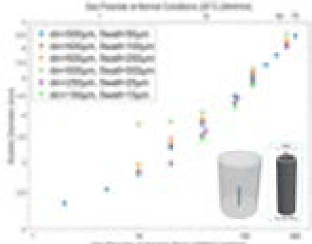
3 CFD modeling

1) Development of a multiscale multiphase CFD-based model of pyrolysis in molten metals
2) Fundamental investigation of bubble formation from micro-orifices and rise due to buoyancy in molten metals and the interactions with the chemistry

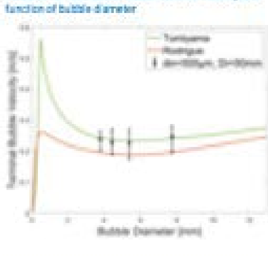
Bubble formation mechanism in micro-orifices



Bubble diameter as a function of flow rate and injection capillary diameter



Validation of simulations: Bubble terminal velocity as a function of bubble diameter



Bubble trajectories

- Bubble formation follows a four steps mechanism characterized by an initial growth around the injection cannula due to capillary forces and cannula non-wettability
- Bubble diameter is mostly influenced by gas flowrate. At low flowrate, the ratio between outer and internal cannula diameter is a critical parameter. The larger is the ratio the larger are the bubbles that asymptotically tend to Tate's law that is not followed at small ratios due to the initial growth around the cannula.
- In large containers, once formed, the bubbles rise following a spiral or zig-zag trajectory depending on the diameter. Wall effect can be important in small reactors.
- Terminal bubble velocity can be well described by literature correlations enabling to predict the residence time in the reactor.

Finanziato dall'Unione europea NextGenerationEU
Ministero dell'Università e della Ricerca
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