DEVELOPMENT OF VALIDATION EXPERIMENTS FOR BUBBLING LIQUID METAL THERMAL REACTORS.

Alberto Abánades*, Elisa Alonso Romero, Luis F. González-Portillo, Francisco Cruz Mazo, María Isabel de Andrés García

Universidad Politécnica de Madrid, Thermal Energy for Sustainability (TE4S) group, Madrid, Spain

*Corresponding Author: alberto.abanades@upm.es

ABSTRACT

Liquid metals are usually pure chemical elements characterized by a very low degradation at very high temperature, low vapor pressure, high conductivity and diffusivity. However, the utilization of liquid metals for the design of chemical reactors has been scarcely tackled by the research community. Nevertheless, the application of liquid metal as media to hold high temperature processes is very promising. Processes as methane pyrolysis, dry reforming or metal oxide carbon-reduction are under development in our group. The numerical simulation of multiphase/multicomponent physical phenomena is a very challenging issue. For instance, a detailed 3-D CFD simulation of hydrocarbon pyrolysis requires the coupling of multiphase thermal-hydraulic physics (gas components, liquid metal and carbon particles) with chemical kinetics is not clearly validated with current available tools. We are developing experimental facilities and programs for analysis and validation of gas injection into liquid metal, either at micro-scale, as macro-scale. We have designed and built a 1.5 m liquid metal column for the validation of methane bubbling into a liquid metal bath, as well as small scale devices to evaluate the phenomena at the level of microbubble formation and chemical kinetics independently from other physical effects.

1 INTRODUCTION

Air and water, or other gaseous and liquid coolants as nitrogen, helium, molten salts or various types of oils has been used for heat transfer in every engineering design and practical applications. Technological evolution trends to broad the range, for instance, of temperature operation, to improve many chemical and energy processes. Many of new frontiers of thermal engineering is demanding coolant materials far exceeding the limitations of the thermal-physical properties of heat transfer fluids, either by their density and thermal diffusivity, or by limited operation temperature. Some chemical processes are also demanding higher temperatures and reaction environments. The need to extend beyond the current limits opens the door to consider alternatives as liquid metals (Lorenzin and Abánades 2016). They offer high density, thermal capacity and diffusivity; and many of them very high boiling temperatures and low vapor pressures. As drawback, high temperature operation amplifies their corrosion impacts on usual structural materials, mainly steels.

The utilization of liquid metals is acquiring an enormous potential for novel energy applications requiring ultra-high temperatures (exceeding 1000 ºC). Some of the processes interested in the use of liquid metals are energy storage (Pacio et al. 2013), nuclear energy (either fission or fusion) (Del Moral et al. 2014; Spencer 2000), and methane pyrolysis (Geißler et al. 2016; Leal Pérez et al. 2021), among others. Historically, the challenge of handling these extreme temperatures has hindered the advancement of these applications. However, recent advancements in several energy and chemical concepts have provided the necessary momentum for their development, and the increasing research interest in them has uncovered the limited understanding of liquid metals, for instance, related to the corrosion effect of some liquid metal in structural materials.

As described, their good cooling capabilities are the reason for their proposal of liquid metals in nuclear reactor engineering (Subbotin et al. 2002), aerospace, solar energy and industrial waste heat utilization. As an example, sodium has been tested as coolant/moderator in fast nuclear reactors (Spencer 2000), or as coolant of solar thermal central tower receivers (Arévalo and Abánades 2023). Other additional features of liquid metals are high volumetric expansion coefficient (high Grashoff number-strong natural convection), and low Prandtl number (turbulent effects have relatively less importance that heat conduction in the flow).

In spite of their good thermal-physical properties, the utilization of liquid metals for the design of chemical reactors has been neglected by the research community (Daeneke et al. 2018). The reasons may be based on the difficulties for reactor integrity due to due to high corrosion rates (Shin et al. 2012) between liquid metals and steels. Nevertheless, the application of liquid metals in chemical engineering as reaction media is being proposed as an alternative for high temperature processes for their potential for a stable performance in a wide range of temperatures. Indeed, temperature upgrades suggest the utilization of non-steel materials, as alumina or SiC. As a result, there are a number of liquid metals and liquid metal alloys that has been considered. For instance, tin has a low vapor pressure (5,78·10-21 Pa @ 505 K) and large liquid-phase temperature range (232-2602 ºC), or even Lead and Sodium. One of the process that would play a role in the transition towards a decarbonized future is hydrocarbon pyrolysis (Clarke and Abánades 2021), that transform hydrocarbons into solid carbon and hydrogen in the absence of oxygen.

Corrosion issues have to be addressed for the evaluation of the lifetime of large-scale chemical reactors. Recent experiences with liquid tin at high temperatures and making use of ceramic materials did minimize corrosion concerns (Zhang et al. 2018). Previous work (Abánades-Velasco and Martínez-Rodríguez 2023) has concluded that some technological uncertainties should be solved for the reliable up-scaling of the liquid-metal pyrolysis process as fluid-mechanical models. Another key area of uncertainty is the interfacial interaction between liquid metals and gases in the form of bubbles. The fluid dynamics of these mechanisms have been preliminarily explored, drawing on metallurgical expertise. However, validating these models is challenging due to the opaque nature of the materials involved, and the challenges related to the implementation of useful instrumentation to monitor their behavior. New knowledge is still needed to qualify engineering design and control of such processes. Furthermore, the thermal behavior in these processes still needs to be explored. In addition, reaction kinetics must be investigated separately from transport phenomena, which implies reducing the reactor scale to minimize thermal and mass transfer limitations. The separate understanding of fluid-mechanics and chemical kinetics should be coupled to generate scaling laws for engineering design of reactors for pyrolysis based on this technology. Although methane thermal decomposition kinetics have been widely studied, they have not been characterized in the presence of molten tin. This gap limits our understanding of intrinsic reaction rates under realistic reactor conditions and hinders the validation of coupled kinetic–fluid dynamic models.

In this communication, we will describe the status of a facility that we are building to evaluate the whole process of methane pyrolysis in liquid tin, which includes fluid-mechanic models for gas bubbling into liquid metals, thermal transfer and chemical kinetics. Key parameters such as liquid metal hold up, bubble ascending velocity or methane residence time in molten tin are being assessed, as they are critical for the scale-up of liquid metal reactors. In parallel, smaller-scale investigations and experimental set-ups are being conducted to deepen the understanding of individual phenomena, which are also reported in this work.

2 EXPERIMENTAL VERIFICATION OF BUBBLING REACTORS

The reactor consists of an alumina column measuring 1.5 meters in height, with an internal diameter of 17 cm and an external diameter of 20 cm. The lower section includes a gas inlet equipped with a flow meter operating in the 0–10 L/min range, along with sensors for pressure and temperature. The gas first enters a pre-chamber, from which it is distributed into the main column through a diffuser featuring 40 orifices, each 0.5 mm in diameter.

The column is filled with tin which is molten and heated to the CH_4 dissociation temperature, and a ceramic filler material, which increases the residence time of the gas within the molten medium. The reactor is designed so that up to one meter of the column can be filled with tin and ceramic filler, leaving an upper free region for the accumulation of solid carbon produced during operation.

Temperatures inside the molten tin are monitored at four different heights using K-type thermocouples enclosed in a ceramic sheath. Additionally, temperatures are measured on the external surface of the ceramic column, aligned with the position of each heating zone. The column is enclosed in a split-body electric heater that can be opened and closed. The heating system consists of three independently controlled resistive heaters, each rated at 5 kW and located at different heights along the column. This configuration allows flexible and localized thermal management.

Figure 1 shows two views of the reactor setup with the heating system in both the open and closed positions, with key components indicated by red arrows. Figure 2 presents three different filler materials tested to induce distinct gas flow patterns inside the liquid tin

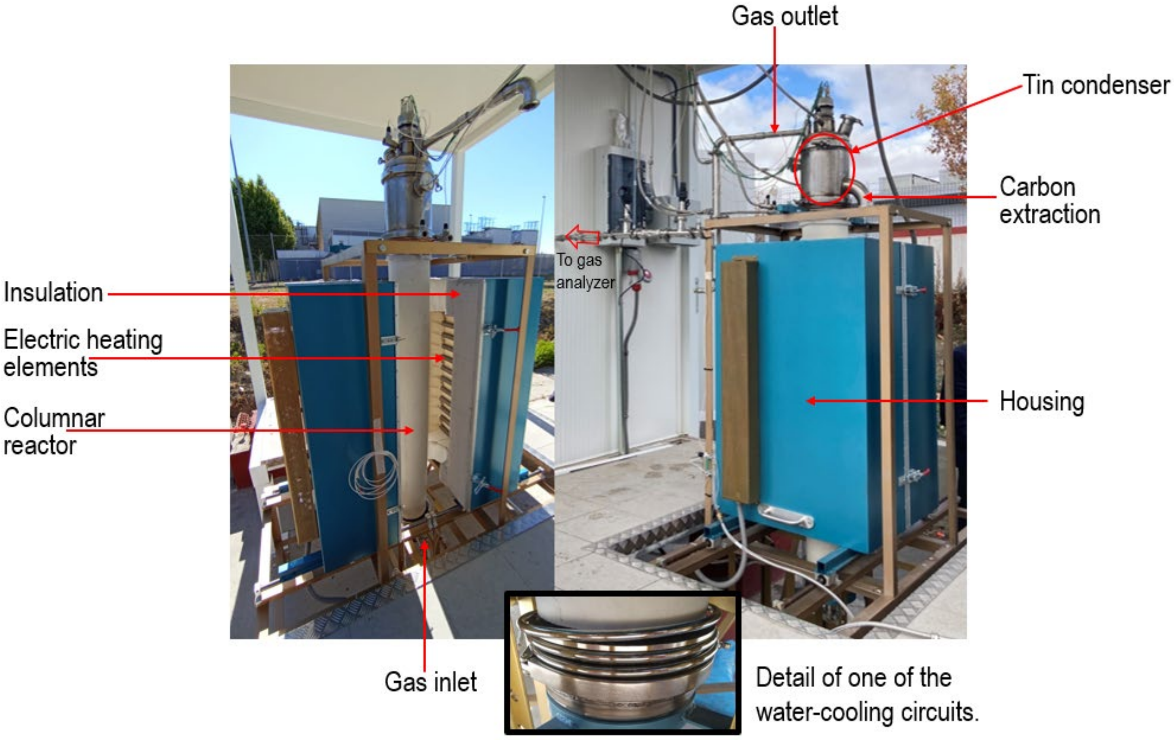

Figure 1. General views of the reactor facility with the heating system open and closed.

Water-cooling circuits are installed at four zones of the system: at the joints between the ceramic column and the metal housing (top and bottom), at the gas outlet, and at the connection between the central thermocouple sheath and the outer casing. Figure 1 also shows a detailed view of one of the refrigeration systems to avoid sealing joints overheating.

The gas exiting the reactor is initially cooled before being directed to a gas analyser capable of measuring H_2, CH_4, CO, and CO_2 concentrations. Temperature, flow rate, and pressure are also monitored at the gas outlet. Additionally, a filter prevents the gas from carrying particles or liquid compounds (such as aromatic compounds). A number of valves and bypasses enable precise control over the flow rate and pressure of the gas stream entering the analyser, while also providing essential safety features and operational flexibility. Figure 3 illustrates the gas line configuration located at the reactor outlet, with the valves used to regulate flow rate and pressure before entering the gas analyzer.

Figure 2. Different shape filler to increase residence time within the liquid metal column.

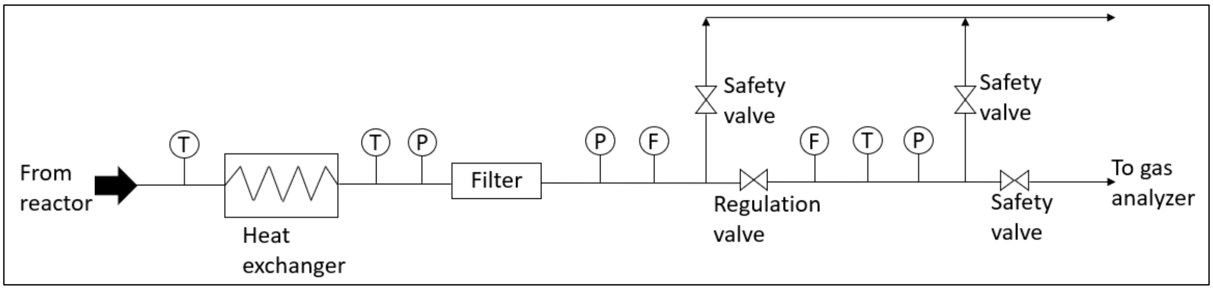

Figure 3. Schematic of the gas outlet line, including regulation and safety valves, flow meters, and pressure and temperature sensors used to condition and control the gas stream exiting the reactor before it enters the gas analyzer.

3 EXPERIMENTAL KINETIC EVALUATION

A custom-built experimental setup has been developed to investigate the chemical kinetics of methane pyrolysis in molten tin. The system was deliberately miniaturized to minimize interference from external physical phenomena, while ensuring that the reaction occurs entirely within the liquid metal phase. The reactor consists of a compact quartz cylinder, 2.5 cm in internal diameter and 3 cm in height, partially filled with tin to allow space for carbon deposition. It is introduced in a small refractory furnace where heating is provided by a direct flame whose velocity—and thus the energy input—can be controlled.

The quartz cylinder is equipped with gas inlet and outlet tubes, enabling methane to be introduced and the resulting gas mixture to be extracted for analysis using a gas analyzer. The temperature of the molten tin is estimated by a thermocouple in contact with the external wall of the quartz cylinder.

Isothermal experiments are conducted starting at 800 °C, with subsequent tests performed in 100 °C increments. The kinetic mechanism governing the reaction is identified by applying the Arrhenius equation and comparing the experimental results with the primary kinetic models for methane pyrolysis reported in the literature. A schematic of the apparatus is represented in Figure 4.

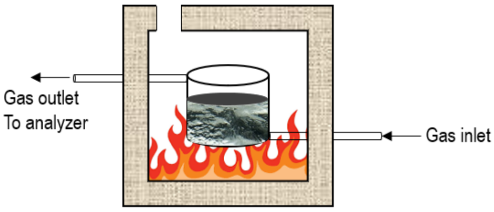

Figure 4. Kinetic parameters experimental set-up

Several complex, multi-step mechanisms have been proposed to explain the thermal cracking of CH_4. However, in most cases, a global reaction mechanism is assumed for modeling purposes, neglecting other byproducts.

$$\mathrm{CH_4 \rightleftharpoons C{+}2H_2} \tag{1}$$

Under this assumption, the reaction rate is typically described by the Arrhenius law to capture the temperature dependence, while the concentration dependence is modeled using expressions as the following extracted from the literature review by Becker (Becker, 2023) and presented in Table 1.

Table 1. Some typical kinetics mechanisms for methane pyrolysis.

Kinetic Mechanism	Reaction orders (n, m)
$r = k \cdot C_{CH4}^{n}$ (reverse reaction neglected)	n=1 / n=4.4
$r = k \cdot C_{CH4}^{n} - \dfrac{k}{K_{eq}} \cdot C_{H2}^{m}$	n=1.123, m=0.9296
$r = k \cdot C_{CH4}^{n} - \left(1 - \dfrac{C_{H2}^{2}}{cC_{CH4} \cdot K_{eq}}\right)$	n=1 / n=1.0809

where, *r* is the reaction rate [mol/($m^3 \cdot s^1$)], *k* is the rate constant and C_i [mol/m^3] the concentration of the specie i. K_{eq} [mol/m^3] is the equilibrium constant for the reverse chemical reaction defined as

$$K_{eq} = e^{\frac{-\Delta G_R^{\circ}}{RT}} \tag{2}$$

with ΔG_R° [J/mol] the standard Gibbs free energy change of reaction, *R* [J/mol·K] the ideal gas constant, and *T* [K] the temperature.

Therefore, experimental data on temperature and species concentrations are used to verify these kinetic models when methane cracking is carried out in an isothermal liquid tin medium.

4 EXPERIMENTAL EVALUATION OF BUBBLE THERMO-FLUID-DYNAMICS

The objective of this part is to determine the extent to which CH_4 can be converted into H_2, which is influenced by the interplay of fluid dynamics, heat transfer, and reaction kinetics. The kinetics are directly affected by the heat transfer between the liquid tin and the gas, which in turn depends on the fluid dynamic and thermodynamic characteristics of the bubbles, which are themselves influenced by the reaction kinetics due to volume changes during the reaction. To better understand this process, we have developed a smaller setup dedicated to bubble characterization.

The study focuses on characterizing the interaction between gas and liquid tin, addressing challenges such as bubble formation, heat transfer and chemical reaction. It is structured into three phases: (1) characterization of bubble fluid dynamics in liquid metals at high temperatures, (2) characterization of heat transfer, and (3) analysis of the interaction with reaction kinetics. Current efforts are concentrated on the first phase, where we are developing a probe to measure bubble size and velocity within the reactor. Since tin is opaque, the probe's performance is first validated in water-air experiments, where high-speed imaging can provide a benchmark for calibration. Once validated, the probe is deployed in a tin-N_2 setup to analyze fluid dynamics, with results compared to numerical models developed in parallel (beyond the scope of this paper).

Electro-Resistivity Probe

Since direct observation of bubbles in high-temperature experiments is not feasible due to tin's opacity, alternative methods are required. This project is developing an electro-resistivity probe to introduce in the reactor with tin and measure bubble size and velocity within the tin reactor. Initially, the probe will be tested and calibrated using a high-speed camera in a transparent setup in water. The calibration data will guide the design of a probe for the high-temperature setup with tin.

The probe consists of three wires connected to a power supply: two detect bubble flow by opening and closing the circuit, while the third serves as the ground. A resistor and voltmeter, connected to an Arduino board, record bubble size and speed. The probe leverages the significant resistivity difference between air and water: when no bubbles are present, the circuit remains closed, and voltage is measured. As a bubble passes through the uncovered wire tip, the circuit opens, and the voltmeter registers 0V. With wire tips positioned at different heights, two distinct signals are received, allowing bubble speed and size estimation.

At high temperatures, chemical reactions between the liquid tin and the probe may occur. To mitigate this, noble metal electrodes such as tungsten are used, enclosed in a heat-resistant alumina cylinder tube to maintain stability and minimize overheating, as illustrated in Figure 5.

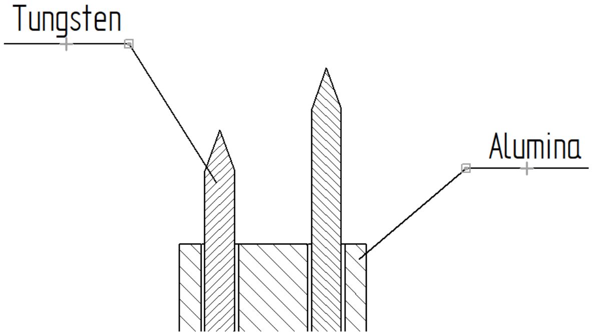

Figure 5. Diagram of the electro-resistivity probe

Bubbles in Water

The electro-resistivity probe is first tested in water allowing comparison of its results with high-speed camera images. The water setup (Figure 6) consists of a transparent methacrylate tube with a removable 3D-printed plate at the lower end and an open top. An O-ring provides sealing, enabling nozzle changes to test different geometries and hole configurations. Air is introduced from the bottom through the nozzle, with a flowmeter and manometer measuring pressure and flow rate, which are regulated via a valve. The system operates with an air compressor providing gauge pressures from 0 to 8 bar.

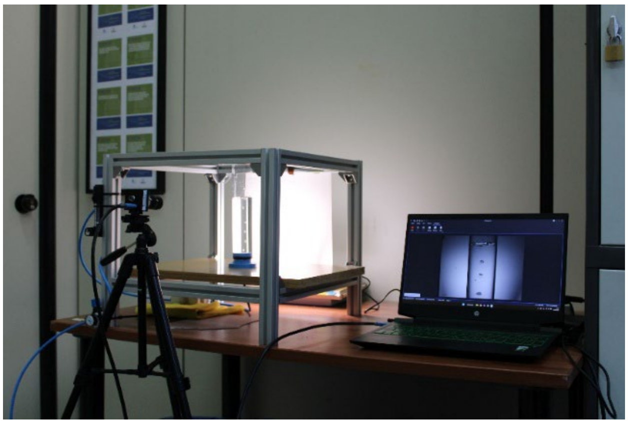

Figure 6. Water setup for bubble experiments

For visualization, a high-speed camera captures bubble formation. The camera is equipped with a 16 mm focal length lens and mounted on a tripod for precise focus on the bubble column. A backlit LED panel with a diffuser ensures even lighting, enhancing bubble outline visibility through diffraction.

MATLAB-based image processing software identifies bubble size and speed. Frames are converted to binary images to distinguish bubbles from the background. Bubble size is measured by scaling pixel dimensions along the major axis, while speed is determined by tracking bubble movement across consecutive frames and calculating the time interval between appearances.

Bubbles in Tin

After calibrating the electro-resistivity probe in the water setup, it is deployed in a tin-based setup. The setup (Figure 7) consists of a 50-mm quartz crucible featuring a pierced entry point for N2 gas flow. The gas is introduced via a 2-mm internal diameter tube connected to flow and pressure regulators, forming bubbles in the molten tin. A stainless-steel tube facilitates gas exit. The crucible is enclosed in a band heater and insulated with ceramic coatings and stacked bricks. Thermocouples monitor temperature, with a 300 W power supply heating the quartz walls to approximately 500°C to ensure tin melting (melting point: 231.9°C). To prevent oxidation, a nitrogen atmosphere is maintained throughout the experiment. This study provides a structured approach to understanding bubble behavior in liquid tin, laying the foundation for optimizing CH_4-to-H_2 conversion processes.

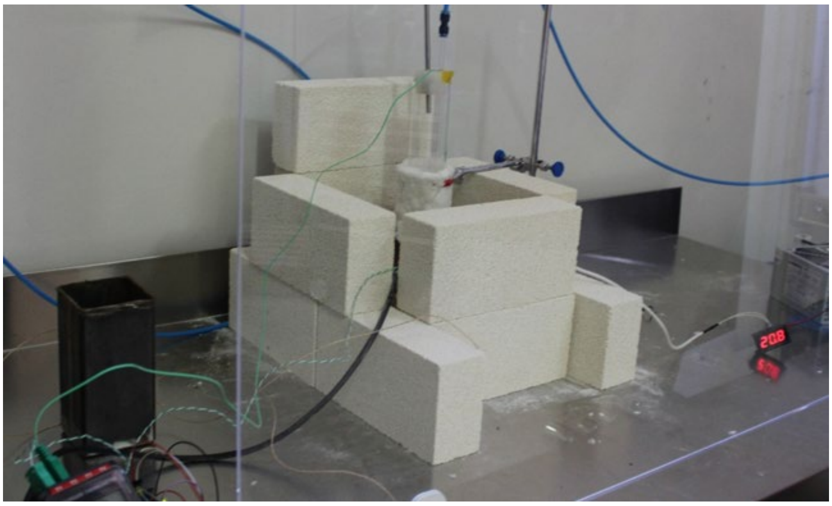

Figure 7. Molten tin setup for bubble experiments

5 MICROBUBBLES IN LIQUID METALS: ADVANCING THEORETICAL AND EXPERIMENTAL APPROACHES.

In this section, we propose the need of conceptualization and design of innovative methodologies for the injection of methane bubbles into a liquid metal environment, such as tin, with the objective of optimizating the methane pyrolysis reaction for hydrogen production. Given a specified mass flow rate of methane intended for conversion, we postulate that the efficiency of the chemical reaction can be significantly enhanced by creating interaction surfaces between the methane phase and the liquid metal, which improves heat transfer. This approach aims to reduce the bubble diameter from the millimeter scale, commonly utilized in previous studies, to the targeted micrometer scale. Indeed, the surface-to-volume ratio of a bubble scales as 1/D, where D is the bubble diameter. Consequently, the decrease in diameter results in a over three order of magnitude in the interaction area per unit volum for microbubbles compared to their millimeter-sized counterparts. The development of a novel device capable of producing such tiny bubbles while maintaining a required mass flow rate and the lack of studies on this matter, naturally leads us to extensive investigation into the underlying physical processes, chemical interactions, and heat transfer mechanisms that governs microbubble formation, instability, fragmentation, at subsequent ejection at these tiny scales. These factors are also critical in determining the collective bubbly phenomena downstream and also matching the much larger scales phenomena explored in the previous section.

Our ongoing research innovate methodologies to effectively address these complex challenges:

- Theoretical research: exploration of novel physical-mathematical modeling that elucidate the interfacial dynamics between liquid metals and gases, including considerations of chemical reactions and heat transfer phenomena at the microscale level
- Experimental research: development of a specialized microscopic high-speed set-up aimed at visualizing the micro-formation, micro-instability, and micro-fragmentation of microbubbles within an opaque environment, such as that of liquid metals (see Figure 8).

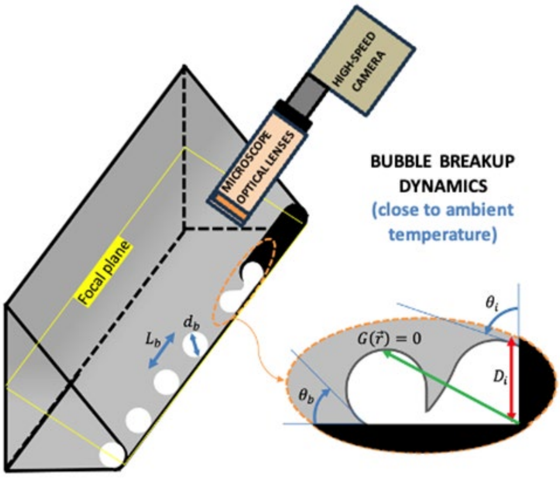

Figure 8. Sketch on the challenges for microscopic high-speed visualization of microbubbles during their micro-generation, micro-instability and micro-fragmentation.

6 CONCLUSIONS

At the group “Thermal Energy for Sustainability” (TE4S) of the UPM, we are developing a program for the development of chemical reactors based on gas bubbling into a liquid metal bath. Our commitment is a deep understanding of the chemical and fluid mechanics involved in the technology for the generation of engineering tools that could be useful for the engineering scaling and design of the concepts. Our experimental program includes: a) a dedicated experimental set-up for the analysis of gas-liquid metal interaction at microscale, b) lab scale apparatus for the analysis of bubble dynamics on a liquid metal column, c) a low scale test-bench for the study if kinetic parameters and finally d) a large scale model for the evaluation and validation of engineering models integrating chemical kinetic and fluid-dynamic phenomena.

NOMENCLATURE

The nomenclature should be located at the end of the text using the following format:

n	reaction order	(-)
m	reaction order	(-)
r	reaction rate	(mol/m^3-s)
k	kinetic constant	(m/s)
K	equilibrium constant	(mol/m^3)
C	Concentration	(mol/m^3)
R	Ideal gas constant	(J/mol-K)
ΔG_R°	Gibs free energy	(J/mol)

Subscript

CH4	methane
H2	hydrogen
eq	equivalent

REFERENCES

Abánades-Velasco, Alberto, and Ángel Martínez-Rodríguez. 2023. “Challenges for the Development of Numerical Models for Methane Pyrolysis With Liquid Metal Reactors.” *Dyna (Spain)* 98(4): 413–19.

Arévalo, R., and A. Abánades. 2023. “Thermal Evaluation of a Solar Power Tower External Receiver With Liquid Metal As Heat Transfer Fluid in Northern Chile.” *Heat Transfer Research* 54(2): 57–72.

Becker, T. et al. 2023. “Methane pyrolysis: Kinetic studies and mechanical removal of carbon deposits in reactors of different materials.” *International Journal of Hydrogen Energy* 48: 2112–2129.

Clarke, Richard, and Alberto Abánades. 2021. “Briefing: Pyrolysis of Natural Gas to Hydrogen: A Key Energy Transition Tool.” *Proceedings of the Institution of Civil Engineers - Energy* 174(3): 98–102. https://doi.org/10.1680/jener.20.00063.

Daeneke, T et al. 2018. “Liquid Metals: Fundamentals and Applications in Chemistry.” *Chemical Society Reviews* 47(11): 4073–4111. http://dx.doi.org/10.1039/C7CS00043J.

Geißler, T. et al. 2016. “Hydrogen Production via Methane Pyrolysis in a Liquid Metal Bubble Column Reactor with a Packed Bed.” *Chemical Engineering Journal* 299: 192–200.

Leal Pérez, Brandon José et al. 2021. “Methane Pyrolysis in a Molten Gallium Bubble Column Reactor for Sustainable Hydrogen Production: Proof of Concept & Techno-Economic Assessment.” *International Journal of Hydrogen Energy* 46(7): 4917–35.

Lorenzin, Nikola, and Alberto Abánades. 2016. “A Review on the Application of Liquid Metals as Heat Transfer Fluid in Concentrated Solar Power Technologies.” *International Journal of*

Hydrogen Energy 41(17): 6990–95.

Del Moral, O.G. et al. 2014. "Conceptual Design of Lithium Laboratory in the TechnoFusión Project." In *Physics Procedia*,.

Pacio, J. et al. 2013. "Performance of Molten Sodium vs. Molten Salts in a Packed Bed Thermal Energy Storage." *Nuclear Engineering and Design* 254: 194–217. https://www.sciencedirect.com/science/article/pii/S1359431117373027.

Shin, Sang Hun et al. 2012. "A Study on Corrosion Behavior of Austenitic Stainless Steel in Liquid Metals at High Temperature." *Journal of Nuclear Materials* 422(1): 92–102. http://www.sciencedirect.com/science/article/pii/S0022311511010439.

Spencer, Bruce W. 2000. "The Rush to Heavy Liquid Metal Reactor Coolants – Gimmick or Reasoned." *Proc. of the 8th International Conference on Nuclear Engineering (ICONE-8)*.

Subbotin, V I, M N Arnol'dov, F A Kozlov, and A L Shimkevich. 2002. "Liquid-Metal Coolants for Nuclear Power." *Atomic Energy* 92(1): 29–40. https://doi.org/10.1023/A:1015050512710.

Zhang, J B et al. 2018. "K2CO3-Promoted Methane Pyrolysis on Nickel/Coal-Char Hybrids." *J. Anal. Appl. Pyrolysis* 136: 53.

ACKNOWLEDGEMENT

This work has been carried out within the BrainEn Missions project with exp. MIG-20211033 in the framework of the Recovery, Transformation and Resilience funded by CDTI. The work is part of the grant PID2023-151272OA-I00, funded by the Ministry of Science, Innovation and Universities, the State Research Agency and the European Social Fund Plus.