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# Experimental investigation and thermo-chemical modeling of methane pyrolysis in a liquid metal bubble column reactor with a packed bed

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## ABSTRACT

The decomposition of methane in a bubble column reactor, filled with tin, in combination with a packed bed, was investigated at different liquid metal temperature levels. All experiments were conducted with a methane feed gas volume flow rate in the range of 50–200 ml<sub>r</sub>/min at temperatures up to 1273 K. The maximum hydrogen yield was 30% at 50 ml<sub>r</sub>/min methane volume flow rate and a temperature level of 1273 K. The main components measured in the product gas were methane and hydrogen, intermediates were detected only in small amounts of less than 1.6 mol-%. The produced carbon was mainly accumulated as powder on top of the liquid metal interface. Within the liquid metal, only a thin carbon layer was deposited on the reactor wall. During the experiments, clogging issues due to solid carbon layers at the reactor wall did not occur. A thermo-chemical model was developed and implemented, taking into account the influence of the adjustable operating conditions as well as an experimentally determined gas residence time. Using the thermo-chemical model, a sensitivity analysis of the most dominant process parameters was performed, indicating that temperature and gas residence time have the strongest influence on the process. The model predictions were compared with the experimental results.

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## Introduction

Close to 50% of the global hydrogen production is based on steam reforming of natural gas which produces significant amounts of CO<sub>2</sub> as a byproduct [1]. Hydrogen production from other fossil sources causes even higher specific CO<sub>2</sub> emissions. With the motivation to mitigate the worldwide CO<sub>2</sub> emissions, alternative hydrogen production technologies without direct CO<sub>2</sub> emissions, e.g. PEM [2], alkaline [3] or high temperature [4] water electrolysis, water photolysis [5] or thermochemical water splitting [6,7], and also the dehydrogenation of ammonia [8], are under investigation. One way to avoid the formation of CO<sub>2</sub> while reforming fossil hydrocarbons for hydrogen production is the direct thermal or thermo-catalytic decomposition, also known as cracking or pyrolysis. Especially the decomposition of natural gas with its main component methane is a promising process in this field.

The methane pyrolysis reaction, as described by the simplified reaction equation



is endothermic with a standard reaction enthalpy of 74.8 kJ/mol. Investigating the reaction mechanism, Back et al. [9] proposed an advanced reaction scheme for the decomposition of methane by assuming a stepwise dehydrogenation starting from methane producing ethane, ethylene and acetylene as intermediate products and ending with solid carbon and gaseous hydrogen. Investigations about the formation of the mentioned intermediates by using the standard Gibbs free energy of formation as a function of the reaction temperature showed that high temperatures and long residence times, which favor equilibrium compositions, reduce the probability of producing intermediates as hydrocarbons are known to be unstable at higher temperatures [10], [11]. For these operating conditions, the overall reaction would preferably lead to hydrogen and carbon. While early investigations about methane decompositions were most likely conducted in shock tube or tubular reactors, summarized in a literature survey from Khan and Crynes [12], recent reactor designs are based on fluidized bed [13,14], fixed bed [15] or vortex flow reactors [16]. These reactor concepts are basically investigated for the application of catalysts, which increase the reaction rate and enable lower reaction temperatures by decreasing the activation energy. Potential investigated catalysts are metals (e.g. Ni, Fe, Cu, Co) with resulting reaction temperatures between 773 K and 973 K or carbon, respectively activated carbon, with appropriate reaction temperatures between 1123 K and 1273 K, summarized in reviews from Abbas et al. [17] and Amin et al. [18]. Nevertheless, all catalysts suffer from deactivation [19–21], due to carbon deposition on the active sites or even mechanical abrasion of the catalyst [22]. Besides the deactivation of catalysts, the formation of solid carbon during the decomposition reaction, could result in reactor clogging [23,24]. An approach for the continuous decomposition of hydrocarbons avoiding these limitations is the utilization of liquid metals as a heat transfer fluid in a bubble column reactor. Even with a simple mechanistic model of the bubbles which continuously renew their interface serving as micro reactors, releasing the formed solid carbon

and gaseous hydrogen on top of the liquid metal column, the above mentioned disadvantages of reactor clogging might be circumvented. Continuous carbon removal from the liquid metal surface due to density differences could be possible for instance. Additionally the liquid metal and/or the produced carbon could serve as a potential catalyst for the reaction. One of the first experimental investigations of methane cracking in liquid metal was published by Steinberg [25] and later followed by Serban et al. [26], who conducted experiments using a stainless steel feed tube or a porous metal sparger, injecting the methane gas from the top into liquid tin or lead, with or without SiC serving as a packed bed. With a packed bed/tin combination and a porous metal sparger, Serban et al. [26] achieved 57% methane conversion at 1023 K. Recent work has been presented by Plevan et al. [27], who injected the gas from the bottom via a single-hole orifice into a stainless steel bubble column reactor filled with tin, without applying a packed bed. With this setup, they achieved a maximum methane conversion of 18% at 1173 K, although most of the conversion likely occurred in the gas phase above the liquid metal part. Due to the presence of liquid tin at temperatures up to 1173 K in combination with a stainless steel reactor concept, corrosion dominated their experiments. While Serban et al. [26] claimed a strong catalytic effect of tin and lead, Plevan et al. [27], including the authors of this paper, have not found this effect in their experiments so far.

The current study focuses on experimental investigation and thermo-chemical modeling of hydrogen production in a liquid metal bubble column reactor with a packed bed inventory using pure methane as feed gas for the pyrolysis process. In contrast to Plevan et al. [27] a new reactor material selection enabled higher and various liquid metal temperatures without corrosion issues. The utilization of a packed bed inventory instead of pure tin enhanced the gas residence time in the reactor and thus led to higher hydrogen yields. In order to identify the process limitations, the influence of varying process parameters were investigated experimentally and an according thermo-chemical model was implemented. Within the model, kinetic data from the literature were implemented and the results of model predictions have been compared to the experimental findings, forming the basis for a thorough discussion. The thermo-chemical model was complemented by a third partial differential equation for the absolute gas pressure inside of the reactor and additionally, the gas and liquid metal properties were implemented as a function of local temperature, pressure and species fraction. The new reactor design also improved the temperature distribution along the reactor and thus dividing the reactor in different subsystems for process modeling was not necessary anymore. Instead of using different subsystems, the measured experimental temperature profile was fitted and implemented as a boundary condition in the thermo-chemical model.

## Experimental setup

Considering the strong corrosion of almost all conventional structural materials, particularly all steels, by liquid tin at the required high temperatures, proper material selection was one of the key issues in the reactor design. The resulting

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