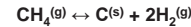


1. Introduction

Besides established hydrogen consumers in metallurgy such as the production of molybdenum and tungsten powder from their oxides, the iron and steel industry among others is now also considering the increased use of hydrogen as an energy carrier and reducing agent. Against this background, the production of hydrogen must be massively expanded and further developed to meet the increasing demand in metallurgy and other energy-intensive industries. Nowadays, more than 96 % of the global hydrogen production is done by Steam Methane Reforming of natural gas (SMR) and other processes based on fossil raw materials at an average environmental burden of about 10 t CO₂ per t H₂, accelerating the consequences of global warming. A more sustainable path to produce hydrogen from natural gas is via methane pyrolysis. Compared to SMR, significantly less CO₂ is produced due to the conversion of methane into hydrogen and solid carbon. Among other reactor concepts, the liquid metal bubble column reactor (LMBCR) represents a promising option for methane pyrolysis. Methane bubbles decompose mainly during their rise in the liquid metal column. For a high hydrogen yield, the residence time of methane in the liquid metal should be as long as possible. Important parameters in this context are the reactor dimensions, the applied bath height and the controlled introduction of turbulence into the liquid metal as well as the use of reactor inserts which can influence the bubble rising behaviour. Furthermore, the bubble size plays a decisive role for methane conversion rate in a LMBCR. The results presented in the following comprise the reactor performance of the current scale-up stage, and show the influence of process improvements aiming at reducing bubble diameter and thus increasing the surface available for the reaction.

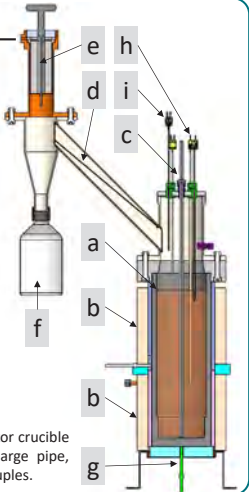
2. Method

Methane (CH₄) is introduced into the molten metal via purging lances (figure 1). Due to the high temperature of up to 1250 °C, methane decomposes inside the formed bubbles according to the following reaction equation.



The bubbles rise up through the liquid metal column and burst at the upper surface releasing carbon and hydrogen from the pyrolysis reaction but also unaffected methane and gaseous intermediates formed during decomposition. This product stream is then discharged via an inclined discharge pipe, in which macroscopic metal particles are gravimetrically separated. By means of a hot gas filter the product gas gets purified from carbon particles and is then passed on for gas analysis. The carbon produced is collected in a collection vessel.

Figure 1. Current experimental setup for methane pyrolysis: (a) reactor crucible with liquid metal, (b) induction coil, (c) purging lance, (d) discharge pipe, (e) hot gas filter, (f) carbon collection vessel, (g, h, i) Type N thermocouples.



3. Results and discussion

In the results presented, liquid tin and a metal bath height of 300 mm were applied in all experiments, while individual parameters were changed in a controlled manner, or certain process adaptations were made.

Influence of temperature and methane input rate

To evaluate the performance of the current reactor, the influence of temperature on methane conversion was investigated (figure 2). At the same time, the CH₄-flushing rate was varied between 1.0 and 4.0 standard liters per minute (SLM).

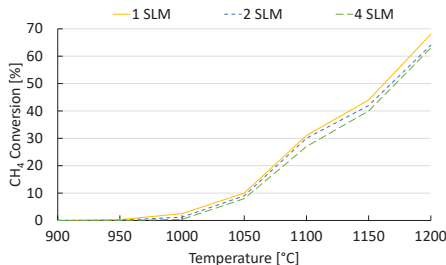


Figure 2. Methane conversion as a function of temperature and flushing rate for a tin-liquid metal column of 300 mm.

The conversion rate shows a strong temperature dependence in the considered range of 900 to 1200 °C. However, altering the methane input rate within the range of 1.0 to 4.0 SLM had only a small impact on the yield of methane pyrolysis. This limited effect of the flushing rate can be attributed to a maximum attainable bubble size in the LMBCR. Bubbles exceeding this threshold undergo instability, collapse, and subsequently form smaller bubbles. Consequently, the injection rates studied result in the formation of bubbles of similar sizes, which ascend at comparable rates. The observed slight variations in methane conversion can be attributed to the differing residence times within the gas space above the liquid metal column. It is important to note that the residence time in this reactor compartment strongly depends on the volumetric flow rate.

Smaller bubbles by using porous lance tip

To achieve the formation of smaller bubbles, porous flushers are used in the metallurgical industry. The impact of gas injection through a porous structure in the applied lance purging was investigated by attaching a porous tube to the lance tip, as illustrated in the provided figure 3a. When utilizing lances with inner diameter of 0.8 mm, relatively large bubbles of 10 – 15 mm are generated (figure 3b). This can be determined either through empirical formulas or qualitatively assessed using a water model (figures 3b, 3c).

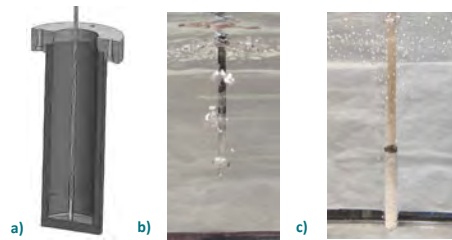


Figure 3. (a) Schematic representation of the reactor vessel with porous lance tip, (b) water model with standard lance, (c) water model with porous cap on the lance tip.

However, with the implementation of the porous lance attachments, the resulting bubbles are reduced in size by a factor of 10. This significant reduction leads to enhanced conversion rates, as a greater surface area becomes available for the decomposition reaction of methane (figure 4)

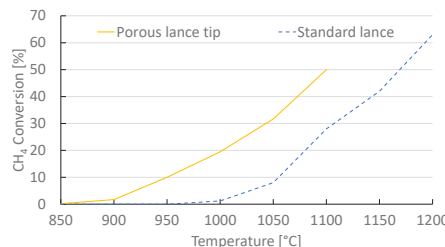


Figure 4. Methane conversion as a function of temperature using two different lances: a standard lance with an inner diameter of 0.8 mm and a lance equipped with a porous cap

Influence of perforated disc inserts

In addition to the use of porous flushers, another approach to enhance both residence time and bubble size is the implementation of reactor inserts. Initially, experiments were conducted with a perforated disc insert positioned at various heights within the reactor (figure 5a – 5c).

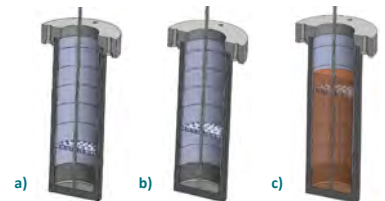


Figure 5. Schematic representation of the reactor vessel with a perforated disc insert at (a) 100 mm, (b) 150 mm and (c) 250 mm.

When a perforated disc was installed 100 mm above the bottom of the reactor, only a marginal improvement in conversion was observed. However, as the disc was inserted further up the reactor, their positive influence became increasingly evident (figure 6).

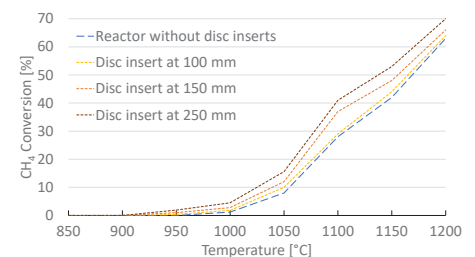


Figure 6. Methane conversion as a function of temperature with perforated discs installed at different heights.

This phenomenon can be attributed to the behavior of gas bubbles, which tend to grow in size significantly due to decomposition reactions and coagulation with other bubbles. However, when encountering the perforated discs, these larger bubbles are disrupted, leading to the creation of additional surface area for the reaction to occur. As a result, the positive influence of the perforated discs becomes more pronounced with increasing height within the reactor.

4. Conclusion

The anticipated rise in hydrogen demand in the upcoming decade has driven increased research endeavors towards developing production processes with minimal CO₂ emissions. Among the other technologies, methane pyrolysis has gained attention due to its low energy requirements and significantly reduced carbon dioxide emissions in comparison to conventional fossil fuel-based methods such as steam methane reforming (SMR). For the presented results, the production of hydrogen and solid carbon via the thermal decomposition of methane was investigated within a liquid metal bubble column reactor. Liquid tin served as the heat transfer medium, while induction coils were employed to introduce energy into the molten metal. Experimental investigations demonstrated that the use of porous structures for gas introduction could effectively reduce the primary bubble size. This reduction in bubble size resulted in an approximate 20% increase in conversion efficiency. Furthermore, the integration of perforated disc inserts within the reactor system is assumed to reduce secondary bubble size, consequently resulting in an increased yield. Achieving continuous carbon discharge is crucial for further process development, necessitating the optimization of the entire discharge system, including the tube reactor segment above the melt.