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DEVELOPMENT OF METHANE DECARBONISATION BASED ON LIQUID METAL TECHNOLOGY FOR CO₂-FREE PRODUCTION OF HYDROGEN

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ABSTRACT

The development of a low-carbon technique to produce hydrogen from fossils would be of great importance during the transition to a long-term sustainable energy system. Methane decarbonisation, the well-known transformation of methane into hydrogen and solid carbon, is a potential candidate in this regard. At the Institute for Advanced Sustainability Studies (IASS), a new alternative technology for methane decarbonisation applying liquid metal technology was proposed and an ambitious programme was set up in collaboration with the Karlsruhe Institute of Technology (KIT). The comprehensive programme included the following: conceptual design of a liquid metal bubble column reactor and material testing, process engineering incorporating carbon separation and hydrogen purification, and a socio-economic analysis. In the present paper, an overview of the programme along with some of the results, are presented. Results from the experimental campaigns show that the liquid metal reactor design works effectively in producing hydrogen and carbon separation. Other aspects of the technology such as socio-economics, environmental impact, and scalability also seem to be favourable making methane decarbonisation based on liquid metal technology a potential candidate for CO₂-free hydrogen production.

Keywords: methane decarbonisation, technology development, liquid metal, hydrogen, carbon.

INTRODUCTION

Energy is one of the basic needs of our society and a sustainable energy system is a must for the long term stability and development of humankind. This means that the energy demand should be met from technologies that are sustainable from an environmental, economic, and social point of view. A sustainable energy system should be based on renewable or long term available resources and should not cause major irreversible changes in our ecosystem.

To progress towards a sustainable society, the implementation of a low-carbon energy system is crucial and should be one of the pillars of the energy and environmental policies around the world. However, this aim should be compatible with the economic and social aspects as well. Hydrogen is one of the energy vectors that could play a role in the implementation, as it can be produced from most of the available energy sources. As pointed out by many authors before, a low-carbon energy system will likely be based on carbon-free renewable or nuclear energy sources. Nevertheless, the transition phase will require the CO₂-free utilisation of fossil fuels, in particular natural gas, most likely for decades from now, and this calls for innovative solutions. This issue also affects the current hydrogen production processes, such as steam reforming and gasification that generate CO₂ emissions. The development of a low-carbon technology to produce hydrogen from fossil-fuels would be of great importance during the transition to a long-term sustainable energy system [1]. The potential options are applying Carbon Capture and Sequestration (CCS) or Usage (CCU) to existing reforming and gasification processes, or developing alternative fossil-fuel decarbonisation pathways. However, the CCS technologies entail critical technical, economic, and safety-related challenges that are far from being resolved. There are also public acceptance and environmental concerns arising from CCS, ranging from the need to ensure suitable long-lasting storage to finding efficient, environmentally friendly CO₂ capture technologies.

The decarbonisation of fossil fuels, especially, natural gas, is an attractive alternative and offers certain advantages over the use of CCS technologies [2]. Methane decarbonisation by pyrolysis ('methane cracking') involves the splitting of methane (CH₄) into its molecular components: solid carbon (C) and hydrogen (H₂). Its main advantage lies in the lack of CO/CO₂ emissions, and in fact, in contrast to CCS and CCU, it replaces the management of CO₂ with a much lower amount of easier-to-handle solid carbon. Hydrogen represents an important clean energy carrier, with an already sizeable demand and promising prospects for the future energy system; it is also an important industrial commodity. Additionally, carbon is potentially marketable as a product for both current and envisaged usages (carbon fibres, materials, nanotechnology, etc.). On the other hand, the development of methane decarbonisation concepts has suffered drawbacks and an industrial process has not been deployed until now [3]. In this paper, we describe an approach to evaluate at laboratory scale a novel methane decarbonisation process that is capable of overcoming the obstacles and could lead to its industrial implementation. An overview of natural gas utilisation options in the light of CO₂ emissions is shown in Figure 1.

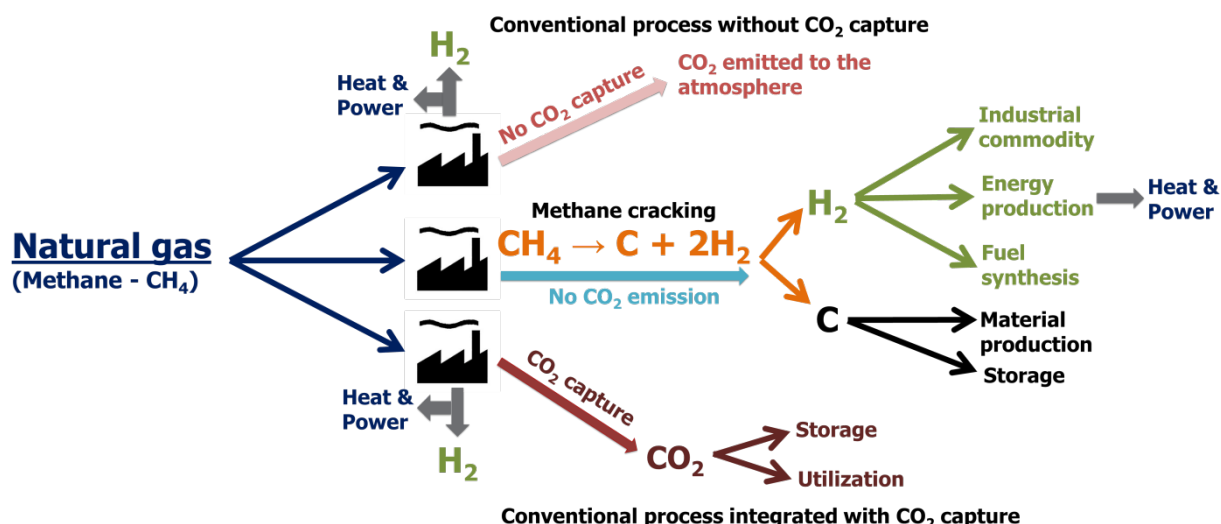


Figure 1 Overview of natural gas utilisation options in the light of CO₂ emissions.

METHANE DECARBONISATION

Methane is a rather stable molecule that has been widely studied due to its abundance and its extensive application as raw material for many industrial processes and its importance as an energy source. Apart of its direct combustion application, its high hydrogen to carbon ratio has converted methane into one of the main raw materials for hydrogen production integrated in important sectors such as ammonia production or fuel hydrogenation. The thermal dissociation of methane has been extensively studied from the 60s until now. Methane pyrolysis is an endothermic process (1) that requires high temperatures of the order of 1000 °C to obtain significant conversion of methane. Methane is known to be unstable with respect to its elements (C & H₂) from 527 °C. However, it is the most stable hydrocarbon up until 1027 °C [4].



The reaction is initiated with the formation of a free radical $\text{CH}_4 \rightarrow \text{CH}_3^* + \text{H}^*$ that dominates the kinetics of the reaction splitting the C-H bond (dissociation energy: 434.72 kJ/mol), which requires high temperature levels [5]. Our evaluation of the reaction thermodynamic equilibrium mole fraction with Cantera library [6] is depicted in Figure 2. It could be seen that above 1273 K (1000 °C), almost complete conversion of methane into hydrogen is theoretically feasible.

Significant effort has been previously dedicated to provide catalysts to the reaction in order to achieve a viable implementation below 1000 °C. In particular, metallic catalysts based on Ni and Fe have achieved quite interesting conversion rates at temperatures of the order of 600-700 °C [7]. Carbon-based catalysts such as black carbon or activated carbon have been also proposed [8]. Figure 3 gives a schematic view of the application range of the main catalyst types.

The practical industrial implementation in the case of catalysed reactions is limited by the deactivation of the catalyst and its cost. The deactivation of the catalyst is a process resulting from the formation of coke on the surface of the catalyst during its operation and its control is a very important challenge. In the case of carbonaceous catalysts, carbon from the pyrolysis process reduces the active surface, and finally

eliminating its catalytic effect [9]. A detailed review on the thermocatalytic decomposition of methane has been recently published by Ashik et al. [10]. The review has discussed in detail the effect of catalysts on the process of thermal decomposition of methane. Catalyst regeneration and co-feeding of methane with other hydrocarbons were proposed as solutions to the issue of catalyst deactivation.

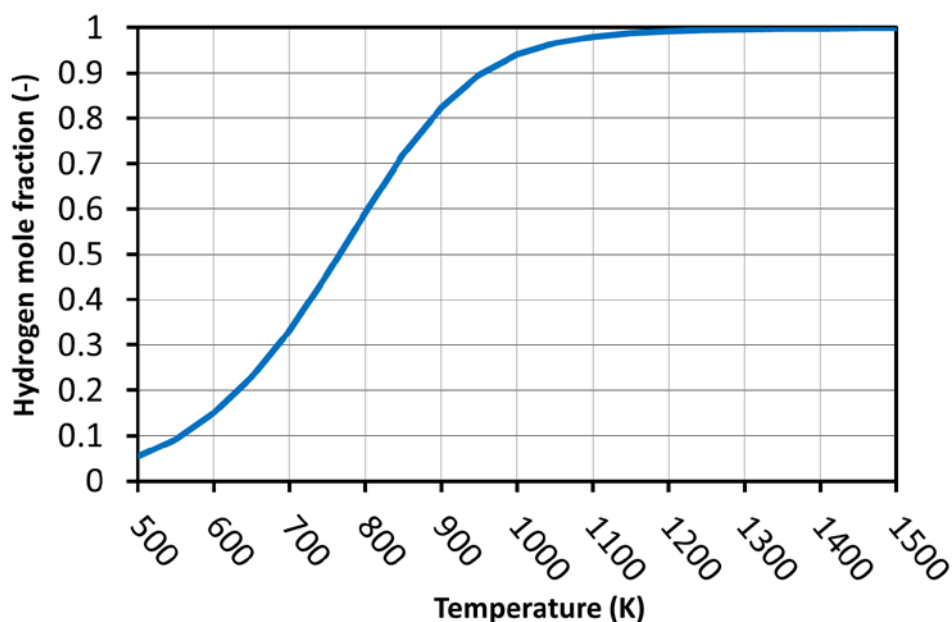


Figure 2 Hydrogen mole fractions (in the gas phase excluding solid carbon) attained during thermodynamic equilibrium of the methane cracking reaction at various temperatures and 1 bar pressure.

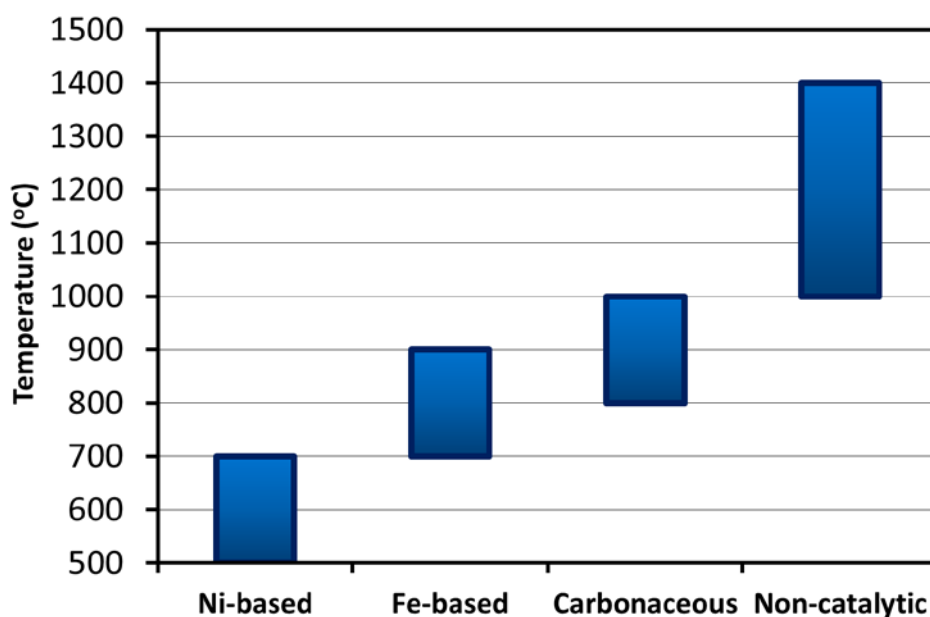


Figure 3 Catalyst types used for methane cracking and their temperature range of applicability.

In spite of these problems, methane decarbonisation was implemented in the HYPRO project by Universal Oil Products in the 1960s, based on a fluidized bed reactor with Ni-Fe-Co catalyst in Al_2O_3 support [11]. The system with two fluidized bed was too complex and expensive and hence not viable.

Another major challenge is the regeneration of the spent catalyst that is mainly done with air or steam. Air regeneration is able to produce energy that will cover part of the energy demand for the methane cracking process, but has as main drawbacks: catalyst oxidation, production of hot spots, sintering and disintegration of the catalyst leading to its destruction [12]. Steam regeneration is more promising from the point of view of the catalyst integrity, as many regeneration cycles have been reported for Ni-based catalysts, although small amounts of filamentous carbon remained, reducing the catalyst performance slightly [13].

One more major issue associated with the current technological proposals can arise from the scale-up of the process. The step forward from the experimental device, based generally on a tubular reactor in the case of direct methane cracking, to an industrial scale system is not trivial. An industrial system might not be a result of a simple multiplication of tubes to reach a reasonable amount of hydrogen production, for instance, a few MW. The economic viability of the system may require the design of reactors with higher volumes that need to be heated by an external source to reach the operating temperature. A device based on a gaseous volume is limited by the thermo-physical properties of the gas itself if it is required to maintain a stable high temperature. Thermal conductivity, for instance, and thermal diffusivity will limit the volume of a temperature controlled process in which an endothermic reaction is taking place. The utilization of carbon particles for a better thermal homogeneity is a potential good option to overcome this problem.

From the analysis of previous work on the topic, it could be realized that the technological development of methane decarbonisation has apparently been slowed down by some technical difficulties. The main technical issues are the production of carbon and the subsequent reactor clogging and catalyst deactivation. In Figure 4, carbon agglomeration inside the reactor from carbon seeds attached to the reactor wall is shown [14].



Figure 4 Carbon clogging in a tubular experimental reactor [14].

APPLICATION OF LIQUID METAL TECHNOLOGY TO METHANE DECARBONISATION

In 1930, Tyrer [15] had proposed and patented a process for producing hydrogen from methane or methane containing gases using molten iron (1200-1300 °C). More recently, Steinberg [16] has also proposed a methane decomposition process using liquid metal technology for producing hydrogen from natural gas; molten tin was recommended for the process. The proposed process for hydrogen production was part of an overall process for producing methanol by combining the produced hydrogen later with CO₂. Serban et al. [17] proposed a process for utilising the heat generated in Generation IV nuclear reactors for direct contact pyrolysis of natural gas to produce hydrogen and carbon without any greenhouse gas emissions. The reproducibility of the results from their experimental work in the presence of tin and lead and very low flow rates (less than 10 ml/min) needs to be confirmed [17]. Martynov et al. [18] proposed a methane pyrolysis process for hydrogen production by direct-contact heat transfer from heavy liquid metal coolants (Pb-Bi). Paxman et al. [19] have presented their preliminary experimental and theoretical investigations on methane cracking for hydrogen production with a molten metal reactor. Their ultimate goal is to build and test a prototype solar reactor with molten metal for methane cracking.

A process for producing hydrogen from methane using liquid metal (tin) and methane flowing through a capillary reactor in slug flow has been proposed and studied by researchers at the Technical University of Dortmund [20]. Their initial experiments at 1100 °C revealed that an average methane conversion of 32% was possible without carbon depositions. The continuous thin liquid metal film that is formed on the capillary reactor wall avoids carbon deposition and also the reverse reactions. The capillary reactor was operated continuously for over 5 h and found no carbon deposits in the reaction zone after draining the

liquid tin. The authors claim that the residence times in the reactor could be varied by changing the gas and liquid flows independently or in unison according to the requirements. This feature offers a significant advantage over liquid metal bubble column reactors. They concluded that residence times higher than 10 s and reaction temperatures lower than 1200 °C could be achieved without any difficulty in the capillary molten metal reactor resulting in high methane conversions.

The preferred option, in most of the previous studies, for liquid media is based on molten metals, as carbon separation seems more achievable during the process due to the density difference between the liquid metal and the carbon. In our point of view, the use of molten media to host the methane cracking reactions is promising, although preliminary experimental work is necessary to confirm if a continuous operation scheme may be feasible at industrial scale. A reasonable range for the reaction temperature for a methane cracking process applying liquid media should be determined as well. The main source of problems might be the compatibility between hydrogen, carbon and the molten media and their thermal stability should be evaluated at the reaction conditions, as well as the kinetics and rates versus temperature of the reaction. The application of molten media should avoid the problems associated with reactor clogging due to carbon agglomeration, but opens new questions related to corrosion, especially when steel-based materials are used. Nevertheless, carbon separation processes from the liquid media should be developed from additional experimental evaluation.

In this direction, we have initiated a research project in which we try to shed some light about the feasibility of using liquid metal reactors to develop a technology for methane decarbonisation. This paper provides an overview of the project and its current status.

PROJECT DEVELOPMENT OVERVIEW

A collaborative R&D project between the Institute for Advanced Sustainability Studies (IASS) and the Karlsruhe Institute of Technology (KIT) was initiated to design and develop a reactor based on liquid metal technology in order to overcome the technological uncertainties associated with the industrial implementation of methane cracking. The outcome of the project will be three fold:

- The evaluation of the technical feasibility of a liquid metal bubble column reactor concept for methane decarbonisation.
- The proposal of the reference process engineering for a methane decarbonisation facility.
- Realization of the socio-economic analysis of the technology.

The 30-month project with a fast track approach to develop an industrial methane cracking process commenced in December 2012. Figure 5 shows the relationship between different tasks of the project.

Our first task was the realization of a conceptual design of a bubble column reactor for preliminary methane cracking experiments [21]. In parallel to the reactor concept, material testing was also carried out to confirm the material choice for the reactor. The improvements and feedbacks from the reactor experiments and material compatibility tests will produce a final reactor configuration. The requirements for additional equipment for auxiliary tasks such as carbon removal and hydrogen/hydrocarbon purification will be established and a process will be proposed.

As a support to the technological development, a socio-economic analysis which also includes a life cycle assessment is being performed to evaluate the benefits and the chance of success of the technology in the current socio-economic context and in relation to potential competitors, existing and alternative technologies for hydrogen production, such as steam reforming and electrolysis with wind energy.

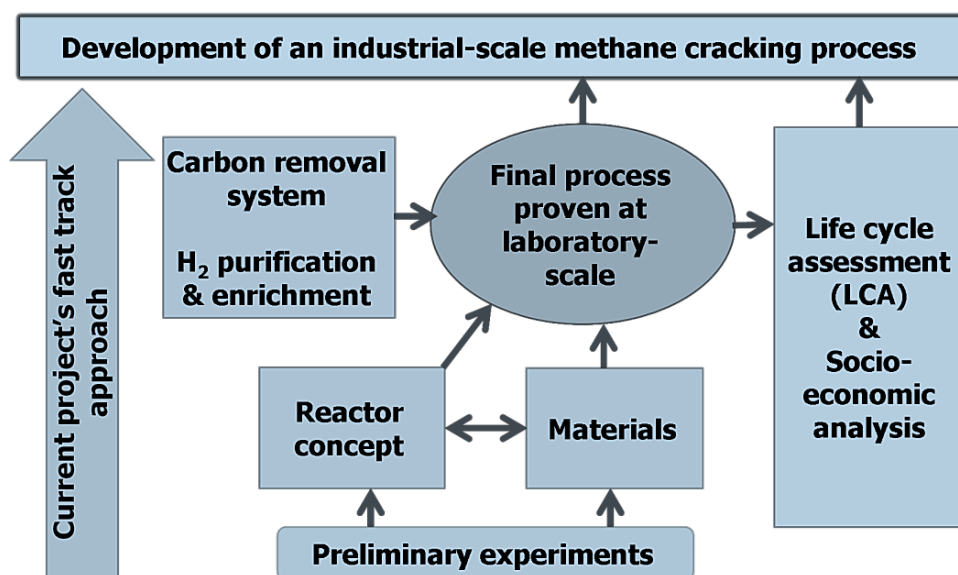


Figure 5 Main tasks of the project to develop a process for methane decarbonisation based on liquid metal technology.

Technical feasibility

The basic operational parameters, such as, reaction temperature and inlet methane flow rate, significantly influence the conversion of methane to hydrogen, and hence the hydrogen production rate. A dedicated experimental facility is currently in place to investigate the performance of the methane cracking reaction in a liquid metal bubble column reactor and study the evolution of the reaction rates versus temperature and to test additional technological features as well. Previous effort has also been made to evaluate the need of a catalyst for the reaction.

The design of the experimental reactor should serve to check the absence of critical technological show-stoppers in the scale-up of the system to an industrial device and the possibility of operating the reactor continuously without any issues, and be able to answer some questions related to the type of carbon that is produced. A tubular reactor design with a methane bubble injection mechanism has been proposed. Information on the carbon formed and its location obtained from the experiments would shed some light on the options for its removal from the reactor.

The technical feasibility of a methane cracking reactor based on liquid metal technology is dependent on material compatibility as well. In that sense, suitable materials should be selected for its long-term structural integrity with liquid metals, such as, tin or lead, at the operating temperatures (likely up to 1200 °C) in the presence of hydrogen. This analysis includes corrosion, erosion, and chemical attack that can

lead to the formation of carbides and hydrides, as well as alloys or compounds derived from the corrosion products.

Process engineering

The engineering of a methane decarbonisation process is one of the objectives of the project. The process engineering integrates all the information obtained from the experimental verification to propose a reliable scheme for the industrial implementation of the technology. The steps in the development of the process are the following:

- Determination of the basic functional units required for the process in view of the experimental results. Possible units include: carbon and hydrogen separation, gas stream filtering, methane conditioning or any other ancillary units.
- Evaluation of the technological options for the functional units.
- Integration of the technological options to form the process scheme.
- Evaluation of the mass and energy balances.

The preliminary process engineering will produce important data that could be used to evaluate the technical and economic feasibilities of the technology.

Socio-economic analysis

Potential benefits to society and people welfare, without compromising the sustainable development of future generations, should be among the major driving forces fostering new technological developments. For this reason one of the main cornerstones in the evaluation of new chemical processes is the socioeconomic analysis, which encompasses a cost/benefit study based on the technical performance of the process and its broader effects in relation to society and market economy. Within the energy industry, socio-economic analysis acquires even more relevance, since this sector is facing paramount challenges worldwide, because of progressively increasing environmental concerns and the need for securing stable and sustainable energy resources in the long term.

The socio-economic analysis will endeavour to make an assessment of the benefits and drawbacks of methane decarbonisation in comparison with existing hydrogen production processes and will be complemented with a life cycle assessment (LCA) analysis to evaluate its environmental impact. The results of the LCA are also envisioned to be used as feedback to the design phase of the process definition to optimise the process from an environmental point of view; this could affect the material choice for the reactor and technological options for auxiliary tasks. The socio-economic analysis is expected to show some aspects related to the sustainability of the process as a whole.

RESULTS AND DISCUSSION

Technical feasibility

Preliminary experiments were conducted using stainless steel reactors in order to verify the liquid metal bubble column reactor concept [21]. Regarding material compatibility, corrosion (Figure 6) was a very important issue when metallic materials are used for the construction of the reactor. In the case of tin, the preferred material from its chemical and fluid-mechanics behaviour [16] [17] [19] [21], the corrosion rates

for steels at the temperature of the process are very high, of the order of 30 $\mu\text{m/h}$ at 700 $^{\circ}\text{C}$ [22]. More sophisticated materials such as tungsten and molybdenum have been identified as structural materials, as well as quartz or alumina.

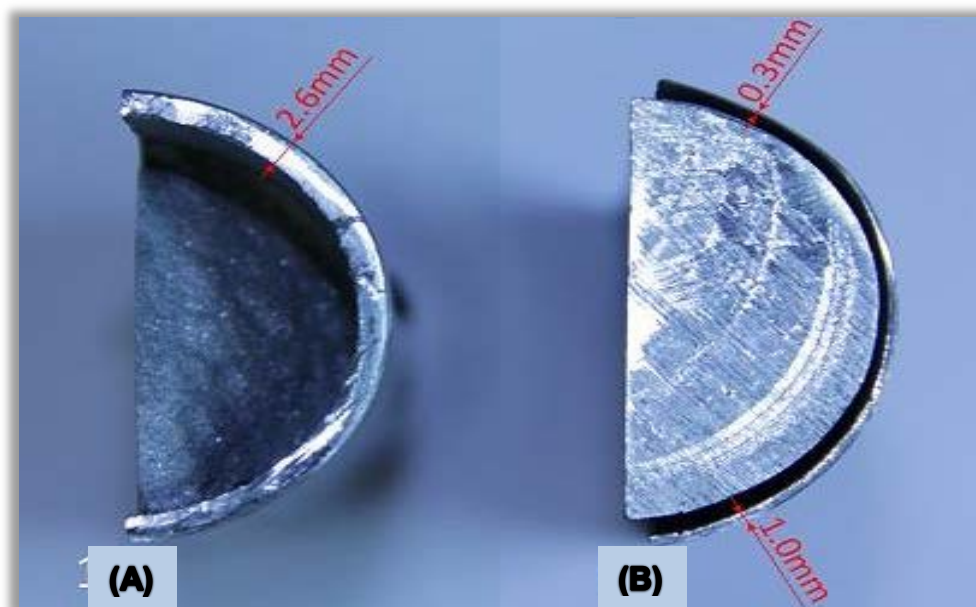
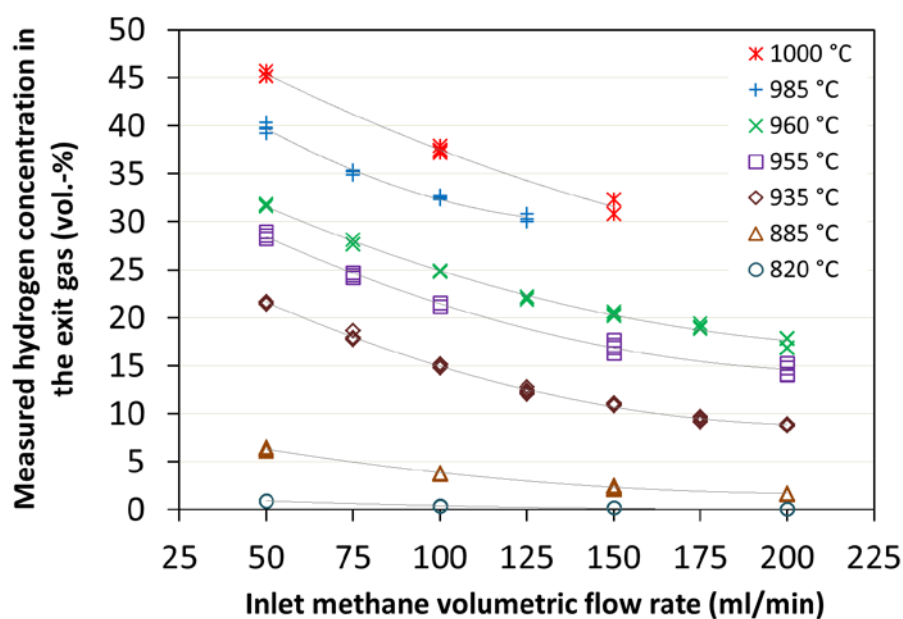


Figure 6 Cross-sections of the stainless steel reactor tube at different heights: (A) from a low-temperature lower section and (B) from a high-temperature upper section showing reduced wall thickness due to corrosion by liquid tin.

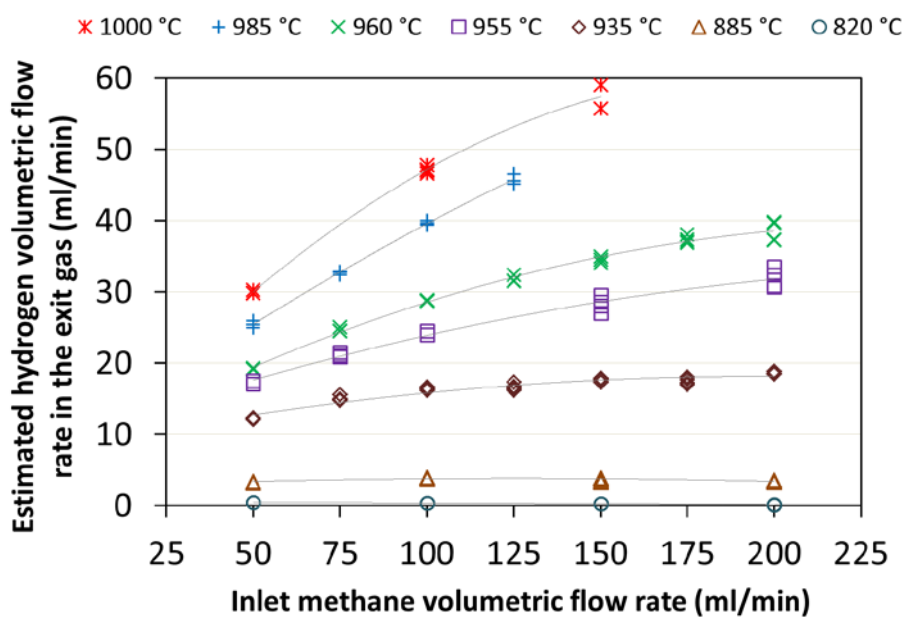
Based on the experience from the preliminary experimental campaigns [21], a liquid metal-packed bed reactor was designed and fabricated using a combination of quartz glass and stainless steel and operated at temperatures between 820 and 1000 $^{\circ}\text{C}$ in a dedicated facility set up at KIT (Figure 7); a detailed description of the recent reactor design and the resulting experimental setup is available in [23]. It could be seen from Figure 8 (A) that the hydrogen mole fraction in the exit gas increased with the decrease in the inlet methane flow rate. The decrease in the inlet methane flow rate corresponds directly to an increase in the gas residence time which in turn leads to a higher methane to hydrogen conversion. A maximum hydrogen mole fraction in the product gas of around 45 vol.-% was measured at 1000 $^{\circ}\text{C}$ and 50 ml/min inlet methane flow rate (Figure 8 (A)). The inlet methane flow rates that we have used, 50 to 200 ml/min, are an order of magnitude higher than previous works in the field [17]. The hydrogen flow rates have been estimated from the measured hydrogen mole fractions and presented in Figure 8 (B). It is evident that higher hydrogen flow rates are produced when the inlet methane flow rates are higher, especially at higher temperatures. No significant amounts of intermediate products such as ethane or ethylene have been detected. Nevertheless, scope for further improvement in the reactor design still exists and extended experimental effort in this direction is in progress. Regarding the carbon, it was found within the experimental apparatus in the form of fine powder mainly in the free space at the top of the liquid metal surface without blocking the reactor during its operation. This carbon was completely separated from the liquid metal and the reactor wall (Figure 9).



Figure 7 Photograph of the methane cracking experimental facility at KIT showing the insulated liquid metal reactor in the bottom.



(A)



(B)

Figure 8

Hydrogen production as a function of inlet methane flow rate and temperature in our experimental reactor: (A) measured hydrogen mole fraction in the product gas and (B) estimated hydrogen flow rates.



Figure 9 Carbon powder accumulated on top of the surface of the liquid metal along with quartz glass pieces that formed the packed bed.

Process scheme

The results of the experimental work have shed some light about the characteristics of the process that should be implemented for an industrial development of this technology. A basic process scheme (Figure 10) has been formed from the following functional units:

- Feed preparation: The raw natural gas may need a preparation unit to increase the methane content and to remove impurities.
- Reactor: The liquid metal bubble column reactor is envisaged to be made of quartz glass and operated at temperatures above 1000 °C.
- Heating: The heating to provide the energy for the reactor is based on two options for an industrial implementation: a hydrogen burner or a methane burner. Additionally, the integration with solar technology is envisaged for further stages, but that will imply higher capital costs.
- Carbon removal from the reactor: The carbon obtained from our experiments has been characterized [23] and work is in progress for the conceptual design of a carbon removal process.
- Carbon separation from the gas stream: A filter is proposed to remove small quantities of carbon particles from the gas stream.
- Hydrogen separation from the process stream: There are two main options under consideration: pressure swing absorption (PSA), a mature technique applied for CO₂ sequestration, and metallic membranes. Unreacted methane after separation from the process stream will be recycled back to the reactor.

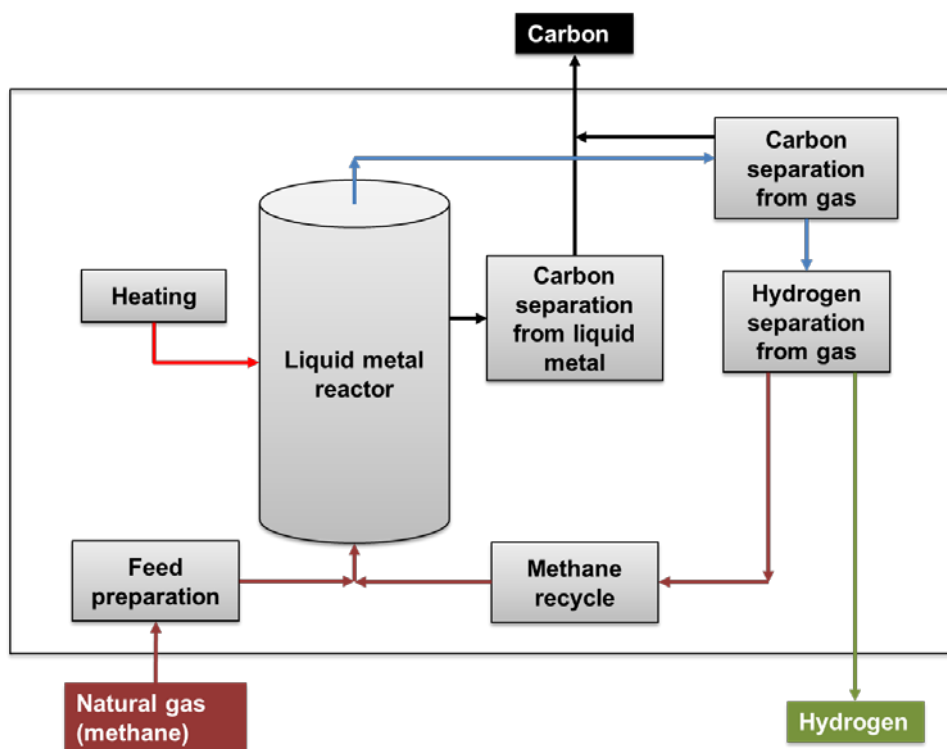


Figure 10 Basic methane decarbonisation process definition.

Socio-economic analysis

The comparison of methane pyrolysis with other developed methods for hydrogen production from fossil-fuels is displayed in Table 1. From this theoretical comparison, that should be checked in a demo facility, the production of 100 Mtoe (toe=ton of oil equivalent) of hydrogen will produce 103.8 Mton of carbon with methane cracking, avoiding the production of 255.18 Mton of CO₂ with Steam Methane Reforming, or 626.85 Mton CO₂ in comparison with coal gasification. The volume of CO₂ to be sequestered and managed in supercritical state will be 10 times larger than the volume of carbon produced for the same hydrogen energy generation, substituting the management of carbon dioxide with solid carbon, which may have additional applicability as well. The application of methane decarbonisation can be especially convenient in industrial sectors, as in the case of ammonia production, in which huge amounts of hydrogen are required.

Table 1 Comparison of hydrogen production technologies from fossil-fuels [16] [1].

Process	Methane Steam Reforming	Coal Gasification	Methane pyrolysis
Reaction	$\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$	$\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$	$\text{CH}_4 = \text{C} + 2\text{H}_2$
Heat of reaction (kJ/mol-H ₂)	63.25	89.08	37.43
Energy efficiency in transformation (%)	74	60	55
Energy efficiency with CCS (%)	54	43	55
CO ₂ emission (mol-CO ₂ /mol-H ₂)	0.34	0.83	0.05
Carbon production (mol-C/mol-H ₂)	0	0	0.5

From the preliminary economic analysis, the H₂ production cost that can be expected from industrial methane cracking could be of the order of 1.5 \$/kg, but this would be confirmed by the end of the project. In a previous analysis of methane decarbonisation [2], a H₂ cost of around 3.0 \$/kg for solar methane pyrolysis was reported; the higher cost was mainly due to the solar field, which represents a significant capital cost of the facility.

CONCLUSIONS

The up-to-date status of the collaborative project between IASS and KIT aimed at the development of a technology to produce CO₂-free hydrogen from methane based on liquid metal technology in a bubble column reactor has been described. Some advances regarding the technical feasibility of the liquid metal reactor concept based on the experimental work, progressing in parallel to the design of the process engineering for its implementation, have been reported. Until now, no critical technological show-stoppers have been found. Experimental measurements have shown that significant quantities of hydrogen can be produced continuously using the liquid metal bubble column reactor. Further work focused on improving the reactor design and optimising the operating conditions to increase the hydrogen production rate is in progress. The scale-up of the reactor from the experiment to an industrial size will be done to assess the technical viability of the concept. The socio-economic analysis predicts a reasonable hydrogen production cost that should be confirmed with additional comprehensive economic analysis.

ACKNOWLEDGEMENT

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