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Experimental evaluation of a heat pipe cooled structured reactor as part of a two-stage catalytic methanation process in power-to-gas applications

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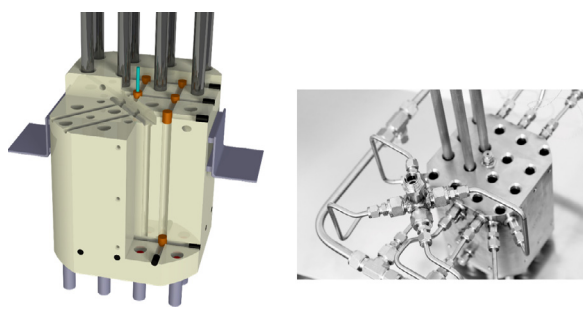
HIGHLIGHTS

- Literature review on recent demonstration projects concerning structured and micro-structured reactors.
- Novel and innovative integration of heat pipes in a structured reactor for methanation.
- Extensive experimental work and proof-of-concept.
- Grid-injectable SNG in lab-scale two-stage experimental setup.

GRAPHICAL ABSTRACT



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ABSTRACT

Establishing the power-to-gas process as a suitable energy storage in future energy systems requires process simplification in order to make it competitive. An intensified methanation reactor concept could contribute to this overall goal. The present work suggests a new catalytic methanation reactor with heat pipe integration into a structured reactor. This approach benefits from the highly industrial maturity of the methanation process and simultaneously addresses the requirements of new applications in power-to-gas processes. The concept comprises a metallic body, which is perforated by channels for internal gas preheating, reaction channels and spaces for the incorporation of heat pipes. Calculation of the radial temperature profiles provided the limits for the channel geometry. Three layers of internal manifolds at different heights distribute, collect and divert the gas. Heating cartridges integrated at the bottom of the reactor enable rapid start up from cold conditions. The metallic block structure facilitates the sealing of the pressurized reaction space and the scaling. First experiments with a 5 kW prototype prove that the maximum temperature is kept more than 100 K below calculated adiabatic synthesis temperatures. Furthermore, the integration in a lab-scale two-stage test rig with intermediate water removal demonstrates the Substitute Natural Gas (SNG) production with grid-injectable quality.

1. Introduction

The power-to-gas (PtG) process is one of the most discussed concepts within the past few years for long-term storage of renewable electricity, particularly for the energy transition in Germany [1]. A remarkable progress of the process maturity can be stated. The reviews of Bailera et al. [2] and Götz et al. [3] give an excellent overview on the development of recent pilot projects in Europe.

A promising approach to reduce further the complexity of the overall PtG-process consists of process intensification of the methanation step. All common definitions cover less complex auxiliary systems and an increase in the ratio of converted gas per reactor volume [4]. In

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Nomenclature

D	diameter of a single reaction channel [mm]
d_p	equivalent particle diameter of a catalyst pellet [mm]
H_l	lower volumetric heating value [kWh/m^3]
H_u	upper volumetric heating value [kWh/m^3]
$\lambda_{rad,eff}$	effective radial heat conductivity [W/(m K)]
MLRD	Multi Level Reactor Design
OP	operating point
PtG	power-to-gas
$P_{th,l}$	thermal power based on lower heating value [kW]
$P_{th,u}$	thermal power based on upper heating value [kW]
$\dot{q}'''$	volumetric averaged constant heat source [W/m^3]
$\dot{Q}_{sensible}$	sensible heat of a of fluid flow [kW]
$\dot{Q}_{th}$	chemical energy of a fluid flow [kW]
r	radial coordinate in a single reaction channel [mm]
R	radius of a single reaction channel [mm]
Se	Semenov number
SNG	substitute natural gas
T_{HP}	operating temperature of heat pipe [°C]
T_{in}	inlet temperature of educt gas to reactor [°C]
T_{max}	maximum temperature of axial temperature profile [°C]
T_{out}	outlet temperature of product gas from reactor [°C]
$T_{preheating}$	temperature after internal preheating channels [°C]
$W_{u,n}$	upper Wobbe Index [kWh/m^3]
X_{H2}	hydrogen conversion
$Y_{CH4,CO2}$	methane yield related to CO_2

case of highly exothermal methanation, the latter one is accompanied by an increase of the volumetric heat production source. Since power-to-gas processes will be likely smaller and decentralized units, the process complexity has to be low to make investment costs reasonable [5]. Apart from other methanation concepts (e.g. biological methanation [6], three-phase slurry [7] or fluidized-bed methanation [8]) the catalytic process in a fixed-bed possesses the highest industrial maturity. On the other hand, the use of a product gas recycle compressor as done in most of established methanation systems (e.g. TREMP [9]) is considered as a drawback in terms of costs and plant complexity [10]. Krier et al. from *AirLiquide* emphasized the necessity of a reduced product gas recycle since this contributes to improved economics [11]. The authors suggested an increased conversion in each stage at the expense of harsher reaction conditions at the outlet of each adiabatic reactor. For industrial relevant forecasts a kinetic rate expression based on a Langmuir-Hinshelwood mechanism as well as a deactivation model has been developed [11]. The development of catalytic once-through processes without product gas recycle is one step beyond and gives the chance to improve further economics. This development has been recently pushed forward to commercialization by *Amec Foster Wheeler* and *Clariant* as VESTA technology but still using a series of adiabatic reactors [12]. A first pilot-plant with 100 Nm^3/h capacity of SNG has been erected and commissioned 2014 in Nanjing, China, and grid-injectable SNG was produced. Furthermore, Koytsoumpa et al. discussed the ideal placement of the gas compression step in a series of adiabatic reactors without product gas recycle. For bulk methanation at moderate pressures and only trim methanation in the last reactor at elevated pressures, the authors calculated a reduction of 72% for the electrical power consumption related to the gas compressor [13]. This gas compression at a later stage is particularly of interest, when hydrogen supply is accomplished at moderate pressure, e.g. by pressurized electrolysis. In contrast to established methanation systems, concepts without product gas recycle need to apply other measures for cooling in order to keep the maximum synthesis temperature of a stoichiometric feed below the adiabatic one. In case of the aforementioned VESTA technology, split feed injection, CO_2 as thermal ballast (CO_2 separation downstream of methanation) and a high steam content are responsible for temperature control of the series of adiabatic reactors. Obviously, only non-adiabatic reactor concepts offer the possibility to increase the conversion per reaction stage. Hence, "e-gas", the first commercial power-to-gas plant in the world, located in Werlte, Germany, applies a non-adiabatic cooled reactor. The 6 MW plant comprises a tube-bundle reactor manufactured by MAN, which is cooled through molten salt and applies staged feed injection to avoid hot-spot formation [14]. When aiming for non-adiabatic concepts, structured and micro-structured reactor concepts gained attraction within the last decade. In the near future, several pilot plants in the 1 MW range will be erected at different European locations as part of the European project STORE&GO [15]. Particularly, for highly exothermal synthesis (e.g. Fischer-Tropsch synthesis with micro-structured foils [16] or with a structured reactor [17] as well as methanation with individual catalyst felt [18] or commercial Ni-catalyst powder [19]) they are attractive due to their superior heat removal capability. In both concepts, reaction zones (heat source) next to cooling zones (heat sink) form a regular pattern, but with different scales of the characteristic length. Commonly, a characteristic size of 1 mm is considered as the threshold between micro-structured and structured concepts. A comprehensive overview about (micro-) structured reactor concepts for endothermic reforming and exothermal reactions like Fischer-Tropsch and methanol synthesis is given by Kolb [20]. The same author contributed also more recently to a review dedicated to the use of micro-structured reactors in selective oxidation reactions [21]. Micro-structured reactors allow for very high process intensification but require advanced technologies for manufacturing (e.g. etching [22]) and catalyst treatment (e.g. coating of reaction channels [23]). Nevertheless, their superior heat transfer capability makes them a suitable alternative for CO_2 methanation under harsh conditions of a stoichiometric feed. A very recent joint publication of *Karlsruhe Institute of Technology (KIT)* and *ThyssenKrupp Industrial Solutions* demonstrated in a model-based approach how the combination of catalytic layers with varying thickness over the axial coordinate improves thermal management within the cooled, micro-structured catalytic wall-reactor [15]. The authors could show, that an increase of the catalytic layer thickness in the second part produces again a tolerable hot spot resulting in much smaller reactor dimensions due to enhanced reaction kinetics. This approach of locally adapted ideal boundaries is further elaborated in the so called Multi Level Reactor Design (MLRD) and has been already successfully applied to ethylene oxidation [24] as well as to SO_2 oxidation [25].

From a technical point of view, the use of foams is very promising due to a low pressure drop and enhanced radial heat transport. Visconti et al. combined the superior heat transport characteristics with the high catalytic inventory of catalyst pellets that have been placed in the void space of the foam structure [26]. The thermal characteristics of three common foam structure materials, SiC, Alumina, Aluminium have been studied by in-situ infrared thermography in [27]. Foams improve significantly the radial heat transport in comparison to fixed-bed or monolithic structures as long as the solid-solid contact of the foam's struts at the wall is above a certain level. Razza et al. demonstrated that even in case with only 20% of the struts of a foam connecting directly to the wall, the radial heat transfer improves tremendously and is close to full and ideal one hundred percent wall contact [28]. The possibilities for direct additive manufacturing of catalysts and reactors are reviewed recently by Parra-Cabrera et al. [29]. Unfortunately, nowadays the maturity of these concepts is still low.

In opposite to this, the manufacturing of micro-channel reactors by means of welding technologies (e.g. laser-welding) is already close to industrial applications and its commercialization is pushed forward by different actors like INERATEC [30], Velocys [31] or Atmostat [32].