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Hydrogen production via methane pyrolysis in a liquid metal bubble column reactor with a packed bed

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HIGHLIGHTS

- Methane pyrolysis in a liquid metal bubble column with a packed bed.
- 78% maximum hydrogen yield at 50 ml_n/min methane volume flow rate and 1175 °C.
- Influence of different packed bed designs and feed gas dilution.
- Carbon separation on the liquid metal interface.
- No clogging issues due to solid carbon deposition.

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ABSTRACT

Methane pyrolysis experiments using a quartz glass-steel bubble column reactor filled with liquid tin and cylindrical quartz glass rings serving as a packed bed were conducted at various liquid metal temperature levels in the range of 930–1175 °C. Besides the liquid metal temperature, special attention was paid to the influence of the feed gas volume flow rate in the range of 50–200 ml_n/min and the inlet feed gas dilution with nitrogen. Increasing liquid metal temperatures resulted in increasing hydrogen yields, leading to a maximum hydrogen yield of 78% at 1175 °C and 50 ml_n/min methane volume flow rate. Within all experimental runs, less than 1.5 mol-% intermediate products were detected in the product gas. The produced carbon appeared as a powder consisting of flake shaped agglomerations in the size range of 15–20 μm, wherein the particle size varied from 40 nm to 100 nm. During the experiments, the produced carbon was completely separated and accumulated at the top surface of the liquid metal. Only minor quantities were transported with the off gas stream. Within the liquid metal inventory, a thin carbon layer of about 10 μm, probably partly showing the formation of nanotubes, in the hot reaction zone, had been deposited on the quartz glass reactor wall.

1. Introduction

A low-carbon energy system and economy is the ultimate goal of developing renewable energy technologies. Nevertheless, the transition to such a low-carbon economy will require not only the development of innovative solutions but also a continued utilization of fossil fuels for decades to come. We are hereby developing an alternative solution—specifically applicable to the energy generation with natural gas (NG)—in which NG is transformed into hydrogen without any CO_2 emissions. The studied endothermic process with a standard reaction enthalpy of 74.85 kJ/mol is the well-known pyrolysis of methane (representing natural gas in a first approximation), also called thermal methane cracking or simply methane decomposition.

$$CH_4(G) \rightarrow C(S) + 2H_2(G) \quad \Delta H_R^0 = 74.85\ \frac{kJ}{mol} \tag{1}$$

The H_2 from the reaction will be in gaseous form under all considered conditions, while the C is produced in solid form, which will permanently eliminate direct CO_2 emission by using the solid carbon as raw material for further purposes such as color pigments

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Nomenclature

d	equivalent bubble diameter [mm]
ΔG^0	standard Gibbs free energy [J/mol]
ΔH_R^0	standard reaction enthalpy [J/mol]
$\dot{N}$	molar flow rate [mol]
p	absolute pressure [Pa]
R_g	universal gas constant [J/mol/K]
T	temperature [K]
X	conversion [–]
y	mole fraction in the gas phase [–]
Y	yield [–]

Greek letters

τ	mean residence time [s]

Subscripts

B	bubble
CH_4	methane
G	gas
H_2	hydrogen
LM	liquid metal
N_2	nitrogen
n	standard conditions
S	solid
UP	upper part
0	inlet condition
1	outlet condition

Abbreviations

GC	gas chromatograph
QG	quartz glass

or tires. Potential intermediate products known to be formed during the decomposition process are ethane, ethylene and acetylene, considering the proposed step-wise dehydrogenation mechanism [1], whereas Polycyclic Aromatic Hydrocarbons (PAH) might be formed as by-products.

The main drawback of former attempts to realize this decomposition process – mainly in tubular reactors – is the deposition of solid carbon layers on the heated reactor walls, subsequently leading to complete reactor blockage [2]. Removing these carbon layers has been a severe problem, which has so far prevented continuous large scale industrial application of this process. An alternative approach for the continuous decomposition of hydrocarbons is the utilization of liquid metals as a heat transfer fluid in a bubble column reactor. The liquid metal is chemically stable and applicable at temperatures above 1200 °C. In the investigated process, methane gas is injected into a liquid metal bubble column and decomposes inside of the formed bubbles which are rising up in the reactor. The bubbles open at the upper interface of the liquid metal, releasing the produced carbon and hydrogen but also the remaining methane gas and the formed gaseous intermediates. The energy efficiency for such a methane pyrolysis process in a liquid metal bubble column reactor cannot be reliably established, based on existing laboratory scale experiments as the design for a large scale facility is not yet clear. In general, depending on the feed gas stream, energy is necessary for the endothermic reaction as well as for heating the methane gas and to maintain the liquid tin at reaction temperature, while the hot product gases and the produced carbon leave the reactor. Additionally, the application of carbon and product gas separation technologies consume an unknown amount of energy, whereas heat recuperation could counteract. Also the energy needed to cover the heat loss of the liquid bubble column strongly depends on the insulation and finally on the future reactor design. In general and in comparison with other hydrogen production technologies, such as steam reforming (74%) and coal gasification (60%), the energy efficiency in transformation for methane pyrolysis processes is about 55%, whereas the application of potential carbon capture and storage (CCS) technologies reduces the energy efficiency to 54% for the steam reforming process, respectively 43% for coal gasification [3]. In this scenario, hydrogen production by methane pyrolysis could become competitive.

After a patent from Tyrer et al. [4] in 1931, one of the first authors who proposed the decomposition of natural gas for hydrogen production by applying liquid tin as heat transfer fluid was Steinberg [5]. Martynov et al. [6] and Gulevich et al. [7] proposed a hydrogen production process by using heavy liquid metal coolants (Pb–Bi) while the methane for the pyrolysis reaction is fed to the lower section of a reaction vessel. Paxman et al. [8] published theoretical investigations of methane cracking in a bubble column reactor with different injector designs (6 mm and 3 mm tube, 7 μm and 0.5 μm porous sparger). In their most recent study they presented preliminary experimental runs in a blank tubular reactor without applying liquid metal. The concept published by Schultz et al. [9] for hydrogen production in liquid metals is based on the utilization of a capillary reactor. In their first experiment at 1100 °C, they achieved an average methane conversion of 32%. After 5 h of operation, no carbon deposition on the hot wall of the capillary reactor was found. So far, methane pyrolysis experiments in liquid metal bubble column reactors were conducted by Serban et al. [10], Schultz et al. [9], Plevan et al. [11] and Geißler et al. [12]. Serban et al. [10] operated a heated stainless steel vertical microreactor, 355.6 mm long with a diameter of 25.4 mm and placed a stainless steel cup of diameter 12.7 mm inside. The cup was either filled with tin or lead or a tin/packed bed combination at a filling level of 101.6 mm. Natural gas was injected from the top inside of the reactor either by a 5.33 mm or a 0.51 mm stainless feed tube or a porous metal sparger. With this setup, they achieved a maximum methane conversion of 57% at 750 °C and volume flow rates around 10 ml/min using tin and SiC as a packed bed while injecting the gas via a porous metal sparger. Plevan et al. [11] conducted experiments in a stainless steel reactor, 1150 mm heating length with a diameter of 35.9 mm and a pure tin filling level of 600 mm, injecting the methane gas from the bottom using a 1 mm single orifice and applying volume flow rates in the range of 5–200 ml_n/min. With this setup, they reported a maximum methane conversion of 18% at 900 °C. Most recent experiments in a liquid metal bubble column reactor were presented by Geißler et al. [12]. They conducted experiments in a quartz glass reactor, filled with quartz glass fragments and tin, 1150 mm heating length and 1100 mm filling level, injecting the methane gas from the bottom using a 0.5 mm single orifice. Within the investigated temperature levels between 820 °C and 1000 °C and volume flow rates between 50 ml_n/min and 200 ml_n/min, they reached a maximum hydrogen yield of around 30%.

With regards to the reactor design, both in Serban et al. [10] and Plevan et al. [11] the main part of the reaction most likely could have taken place in the heated tubular part above the liquid metal interface, which implied 71% of the total heated reactor volume in