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Hydrogen production from CO_2-free thermal decomposition of methane: Design and on-sun testing of a tube-type solar thermochemical reactor

Stéphane Abanades [a,*], Hiroyuki Kimura [b], Hiroyuki Otsuka [b]

[a] Processes, Materials, and Solar Energy Laboratory, PROMES — CNRS, 7 Rue du Four Solaire, 66120 Font-Romeu, France
[b] Research Laboratory, Heat & Fluid Dynamics Department, IHI Corporation, 1, Shin-Nakahara-Cho, Isogu-ku, Yokohama 235-8501, Japan

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ABSTRACT

This study addresses the development of a solar thermochemical reactor for CO_2-free production of hydrogen from solar-aided methane decomposition. The developed lab-scale solar reactor basically pertaining to the indirect heating concept is chiefly based on a tube-type configuration in tandem with a cavity receiver. The reactor design and performance prediction were first appraised via 3-dimensional CFD thermal simulation as a function of internal geometry. The model including coupled heat/mass transfer and chemical reaction aimed to simulate the reactor in order to determine the temperature distribution and the conditions for maximum reactor efficiency. The designed 1 kW solar reactor was then constructed and installed for reaction testing at the focus of a 2 m-diameter parabolic solar concentrator. Solar CH_4 decomposition experiments were performed between 1300 and 1400 °C to demonstrate the feasibility of hydrogen production and the reliability of the solar process using the developed reactor concept, and the results were used to validate simulations. Regarding the estimated kinetic parameters, the best fitting was obtained for an activation energy of 320 kJ/mol and a pre-exponential factor of 10^{11} s^{-1}. The chemical conversion was improved when increasing the temperature or decreasing the inlet gas flow rate or the CH_4 mole fraction. A maximum CH_4 conversion (resp. H_2 yield) of 90% (resp. 85%) was achieved at 1400 °C and the thermochemical reactor efficiency reached 5% for the highest CH_4 content in the feed.

1. Introduction

The main source of hydrogen is currently methane due to its high hydrogen to carbon ratio and its abundant reserves. Natural gas steam reforming (SMR) is the largest and most economical process to produce hydrogen [1]. The main drawback of this process is the formation of CO_2 as a reaction product, which contributes to the growth of anthropogenic greenhouse emissions. Capture and storage of the produced CO_2 have thus to be implemented, but the economic, environmental and energy cost of these additional operations reduce the overall energy efficiency and the economic interest of this process [2]. Consequently, the thermal decomposition of methane (TDM) appears as an interesting alternative process for CO_2-free production of hydrogen along with a marketable high-value nano-material called "Carbon Black" (CB) [1–6]:

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H^\circ = 75.6 \text{ kJ/mol}. \tag{1}$$

The carbonaceous solid product can be either sequestered without CO_2 release or used as a valuable material commodity in different applications. It can also be applied as reducing agent in metallurgical industry. The generated H_2-rich gas mixture can be directly used as fuel for internal combustion engines or further processed to high-purity H_2 for being used in fuel cells.

TDM (non-catalytic) typically requires temperatures higher than 1300 °C in order to achieve reasonable reaction rates. Consequently, the use of catalysts (either metallic or carbonaceous catalysts) was investigated in order to operate at lower temperature and improve the process kinetics [3–10], but the catalyst regeneration issue after deactivation due to carbon deposition is the main process constraint.

The TDM process yielding hydrogen and solid carbon is an endothermic reaction that can benefit from concentrated solar energy to circumvent the use of fossil fuels for providing high-temperature process heat [11,12]. The reaction must take place in a reactor powered by solar energy that must achieve both efficient solar radiation absorption and heat transfer to the reactant flow. Substituting concentrated solar energy in place of carbonaceous fuels, as the source of high-temperature process heat, is a means to reduce the dependence on conventional energy resources and to avoid emissions of CO_2 and other pollutants.

The proposed solar reactor concepts for TDM process include directly irradiated particle-laden flows and indirectly irradiated graphite/ceramic absorber tubes [13–18]. Regarding solar reactors featuring continuous particle flow directly exposed to concentrated solar irradiation, the main drawback relates to the protection of the

* Corresponding author. Tel.: +33 4 68 30 77 30; fax: +33 4 68 30 77 99.
E-mail address: stephane.abanades@promes.cnrs.fr (S. Abanades).

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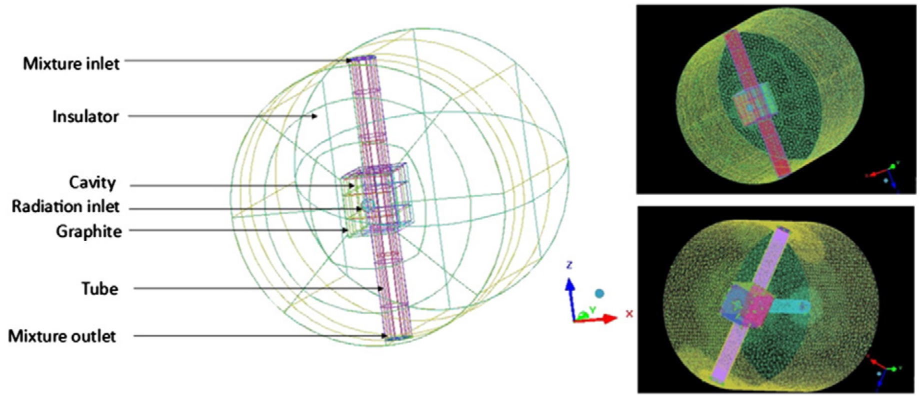

Fig. 1. Geometry of the reactor (left) and scheme of the meshed reactor configurations (right).

optical window against particle deposition. In the European project SOLHYCARB, a novel indirect-irradiation 50 kW_{th} multi-tubular cavity-type solar reactor was developed based on a first 20 kW_{th} solar reactor prototype, which was successfully tested at high temperatures (1400–1800 °C range), yielding complete CH_4 conversion and up to 90% H_2 yield without particle injection [19–22]. The main technical challenge for this reactor came from the formation of a dense carbon deposit (pyrolytic carbon) strongly adhering to the inner wall surfaces in the high-temperature region. The carrying of carbon product was also facilitated by low pressure operation, thus inducing additional process constraint. Decreasing the operating process temperature is thus of great interest for eliminating the formation of undesirable carbon deposit inside the reactor while favoring the carrying of product to the reactor outlet, thereby improving the reactor reliability for on-sun operation over extended duration.

In this study, a new lab-scale tube-type solar chemical reactor based on the indirect heating concept was thus developed for studying TDM at moderately low temperatures (between 1300 and 1400 °C) and at atmospheric pressure. The work first focused on the CFD thermal simulation of the solar reactor in order to predict the temperature distribution, assess the energy losses, and predict the reactor performance as a function of the operating conditions. One of the key objectives of the simulation was also to size/design the demonstrator reactor before its construction and on-sun continuous operation at the focus of a dish concentrator.

The development of the demonstrator reactor included the design and construction of the reactor components, the assembling at the focus of a solar concentrator, and the implementation of the subsystems (gas injection, filtering system, and gas analysis). Solar experiments related to TDM were performed to demonstrate hydrogen production potential and reactor performances were determined as a function of the main operating parameters (temperature, gas flowrate, CH_4 mole fraction). Reliable on-sun reactor operation at high temperature was demonstrated for long period of solar irradiation.

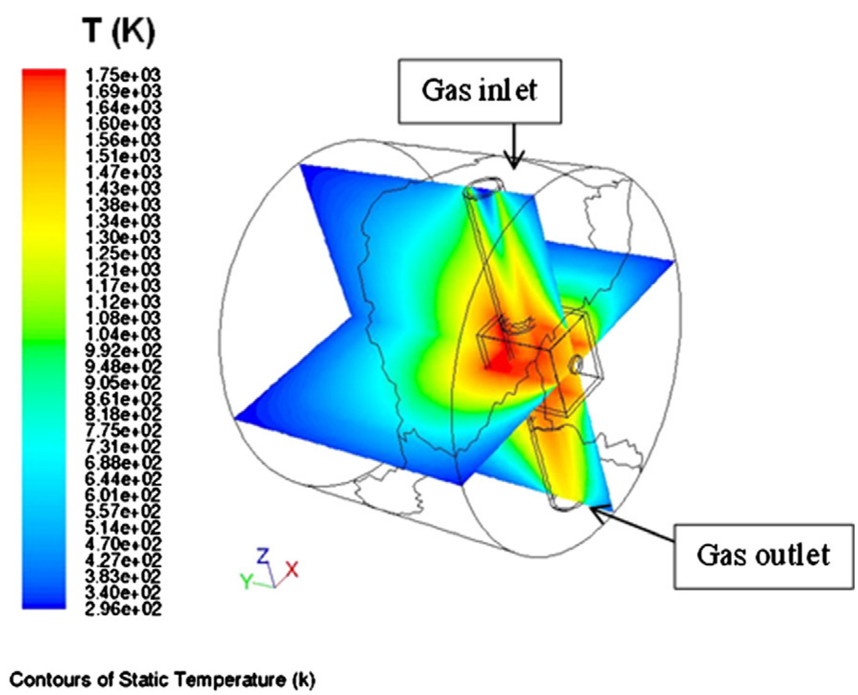

Fig. 2. Global contour of temperature.