A drop-tube particle-entrained flow solar reactor applied to thermal methane splitting for hydrogen production

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

HIGHLIGHTS

- A particle-flow solar reactor was designed and operated for continuous H_2 production.
- Feeding of carbon black catalyst was used to study the effect on methane decomposition.
- The entrained-flow drop-tube reactor was based on the indirectly-irradiated concept.
- Particle injection slightly improved the performances of the solar chemical reactor.
- CH_4 conversion of 80% and solar-to-chemical efficiency of 5% were reached at 1350 °C.

GRAPHICAL ABSTRACT
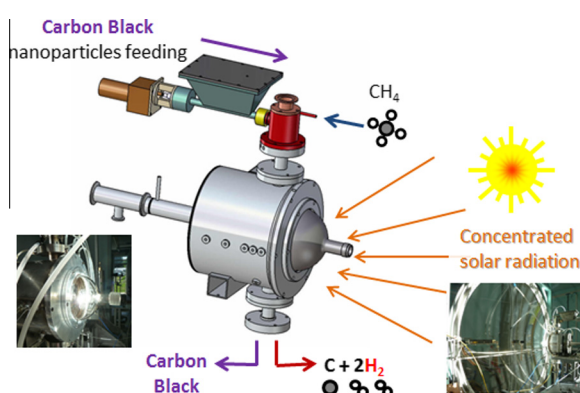
ABSTRACT

A solar chemical reactor with continuous particle feeding in a tubular absorber has been designed and tested for CO_2-free hydrogen production from thermal methane decomposition. The entrained-flow reactor was operated on sun with carbon black particle injection in a stream of methane diluted in argon. The carbon particles are expected to act as a catalyst for the dissociation reaction and the indirect irradiation via an intermediate opaque tubular absorber results in a more uniform heating of the reactor volume and thus an easier reaction temperature control and determination. The effect of particle injection on the reactor performance was investigated as a function of the type of carbon black catalyst and characteristics, reaction temperature (1150–1400 °C), total volumetric gas flow rate and methane content in the feed gas (10–40%). Key measured performance outputs were CH_4 conversion and H_2 yield, C_2H_2 outlet concentration, and solar-to-chemical reactor efficiency. The particle feeding did not drastically improve the methane decomposition rate and hydrogen yield, which can presumably be attributed to kinetic limitation due to short particle residence time in the high-temperature region. Likewise, the inlet methane mole fraction was not a primary influencing parameter. In contrast, the temperature and the gas flow rate strongly affected the methane decomposition rate.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The thermo-catalytic decomposition (TCD) of methane, as the main component of natural gas (NG), is a very interesting alternative to mitigate the CO_2 emissions commonly associated with 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).

conventional hydrogen production processes (i.e., steam reforming, partial oxidation, autothermal reforming, coal or biomass gasification) [1–9]. The moderately endothermic methane decomposition reaction $(CH_4 \rightarrow C(s) + 2H_2, \Delta H^0 = 74.6$ kJ/mol) yields a carbon-rich condensed phase (carbon black, CB) and a hydrogen-rich gas phase. The carbonaceous solid product can either be sequestered without CO_2 release or used as a material commodity in various industrial applications (e.g., tire and rubber product manufacturing industry or high-value conductive CB for polymers and batteries) or as a metallurgical reducing agent under less severe CO_2 restraints (if CO production is targeted as a key component of syngas) [10,11]. Hydrogen is currently considered as a promising energy vector in both transport and power generation sectors, if it is produced from renewable energy, because water is the only product generated during hydrogen fuel combustion. In most current fossil-based hydrogen production methods, the thermal energy required by the endothermic processes of hydrogen production is supplied by the combustion of a portion of the same fossil fuel feedstock. This increases the fossil fuel consumption and greenhouse gas emissions.

For a transition period, solar-aided decomposition of methane-containing gaseous feedstocks, with NG being the first choice due to the elevated H:C ratio, can offer a viable route for fossil fuel decarbonization and CO_2 avoidance with potential to create a transition path towards a "solar hydrogen-solar fuels" economy [12–14].

Thermal NG cracking has been applied for the production of carbon-rich hydrocarbons and carbon black [15,16]. Industrial process has already been employed for CB production with hydrogen being a supplementary fuel for the process (Thermal Black process [10]). More recent studies have considered this process for H_2 production as an alternative route to steam-reforming, using metallic or carbonaceous catalysts [17–30]. Catalysts are used to reduce the operation temperature in contrast with the thermal decomposition of methane that typically requires temperatures in excess of 1300 °C.

Metal catalysts (e.g. transition metals such as Ni, Fe, Co, etc.) exhibit the highest activities in methane decomposition and generally promote the formation of carbon nanostructures as long filaments (carbon nanofibers or nanotubes), but they present the disadvantage of being rapidly deactivated by the carbon deposits on the catalyst surface due to blocking of surface active sites [17–21]. Furthermore, regeneration of metal catalysts by burning those carbon deposits is not an attractive option since it would lead to undesirable CO_2 emissions. Alternatively, the use of carbon-based catalysts offers several advantages over metal catalysts: (i) high thermal stability; (ii) resistance to sulfur poisoning and other potentially harmful impurities present in the feedstock; (iii) no metal carbides formation, (iv) availability, durability and low cost, (v) regeneration step is not needed; (vi) the carbon formed can be used as catalyst precursor, so that the process could become autocatalytic, and (vii) the co-produced carbon may be more easily marketable (that could substantially reduce the net cost of hydrogen production) [22,23]. Numerous types of carbonaceous materials have been tested as catalysts for methane decomposition [22–35], and the catalytic performance of carbons is mostly determined by their crystallinity and surface properties. Thus, amorphous carbons (e.g. activated carbons or CB) are more active catalysts than crystalline ones, this fact being attributed to a higher amount of surface active sites. Carbons having a high external surface area or mesoporosity offer a higher accessibility to the methane molecules and usually exhibit a higher resistance to deactivation by carbon deposits [29–33].

Current processes are practiced at an industrial scale for H_2 and CB production but they are not combined, with the process heat being supplied by burning a significant portion of the feedstock. These processes are characterized by their high energy consumption and the concomitant emission of pollutants, derived mainly from the combustion of fossil fuels for heat generation. Internal combustion results in the contamination of the gaseous products while external combustion results in a lower thermal efficiency because of the irreversibility associated with indirect heat transfer via heat exchangers. Alternatively, using solar energy as external source for supplying the process heat offers several advantages: (1) the discharge of pollutants and greenhouse gases is avoided; (2) the gaseous products are not contaminated by combustion by-products; and (3) the calorific value of the feedstock is solar-upgraded in an amount equal to the reaction enthalpy.

During the last years, significant research has been conducted in development of different solar reactor designs for methane decomposition. These designs employ different heating concepts and flow patterns [36–43]. The solar chemical reactors for effecting the high-temperature gas–solid transformations usually feature directly-irradiated reacting particles (e.g. particle suspension fed in a cavity), or indirectly-irradiated graphite/ceramic tubes or other opaque surfaces serving as absorbers and heat conductors. For example, an indirectly-irradiated fluid–wall aerosol flow solar reactor was studied and approximately 90% of methane conversion was obtained at a wall temperature of 1860 °C and an average residence time of 0.01 s [36]. The reactor was chiefly composed of concentric tubes with an inner porous graphite tube (12 mm i.d.) and a radial forced Ar flow through the porous tube wall (that served to protect the inner tube wall from carbon particle deposition). It was also evidenced that feeding particles (fine acetylene black particles with an average primary size of 30 nm suspended in argon) did not increase methane conversion over the values obtained with no co-feed conditions, this result being attributed to the small reactor tube size. It is expected that the effect of particle feed will become more important when the reactor is scaled-up and the volume to surface area ratio is significantly increased.

A 20 kW prototype and a 50 kW pilot-scale solar reactor based on multi-tube reaction zones inserted in a cavity-receiver were built and tested at CNRS-PROMES (SOLHYCARB EU project) [37–41]. A complete CH_4 conversion and H_2 yields above 80% were reached without particle injection for operating temperatures between 1400 °C and 1800 °C.

A directly-irradiated 5 kW particle-flow solar chemical reactor featuring a continuous flow of CH_4 laden with μm-sized CB particles, was tested in a solar furnace in the 1027–1327 °C range [42]. The reactor performance was examined for varying operational parameters, namely the solar power input, seed particle volume fraction, gas volume flow rate, and CH_4 molar concentration. However, the effect of CB particle addition was not investigated in detail compared to no-feed studies. Methane conversion and hydrogen yield exceeding 95% were obtained at residence times of less than 2.0 s. For the direct heating concept, the particle temperature strongly depends on the particle suspension's optical properties, especially its extinction coefficient, which in turn is a function of the particle volume fraction and determines the penetration and absorption of concentrated solar radiation. High particle loading implies higher attenuation and, consequently, a more efficient absorption, resulting in the gas/particle flow being hotter than the reactor walls, as the optically-thicker particle cloud serves as a radiation shield. It further augments the reaction rate due to a larger specific surface area available for the heterogeneous reaction. The carbon particles thus theoretically serve the functions of both radiant absorbers and nucleation sites for the heterogeneous reaction, enhancing the chemical kinetics. For the indirect heating concept, the particle temperature is limited by the absorber wall temperature because particles are heated mainly by IR radiation from the wall.

Hence, chemical reactors based on the concept of direct irradiation of particle suspensions provide efficient energy transfer