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Solar thermal reforming of methane feedstocks for hydrogen and syngas production—A review

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A B S T R A C T

It is currently accepted that at least for a transition period, solar-aided reforming of methane-containing gaseous feedstocks with natural gas (NG) being the first choice, can offer a viable route for fossil fuel decarbonization and create a transition path towards a "solar hydrogen- solar fuels" economy. Both industrially established traditional reforming concepts, steam and dry/carbon dioxide reforming, being highly endothermic can be rendered solar-aided and thus offer in principle a real possibility to lower the cost for introducing renewable hydrogen production technologies to the market by a combination of fossil fuels and solar energy. They also share similar technical issues considering linking of their key thermochemistry and thermodynamics to efficient exploitation of solar energy. In this perspective, the current article presents the development and current status of solar-aided reforming of gaseous methane-containing feedstocks, focussing in particular on the reactor technologies and concepts employed so far to couple the heat requirements of the methane reforming process to the underlying principles, intricacies and peculiarities of concentrated solar power (CSP) exploitation. A thorough literature review is presented, addressing practically the whole scale of solar reactors employed so far: from small-scale reactor prototypes often tested under simulated solar irradiation up to scaled-up reformer reactors tested on solar platform sites at the level of few hundreds of kilowatts. Having presented the current state-of-the-art of the technology, topics for future work are suggested and issues to help further commercialization are addressed.

Contents

1. Introduction

Hydrogen (H_2) has a long tradition as an energy carrier and as an important "raw material" in chemical industries and refineries. Hydrogen can be produced from a variety of feedstocks, gaseous, liquid and solid, including fossil fuels such as natural gas, oil and coal respectively, as well as renewable such as biomass and

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water [1]. Virtually all hydrogen produced today is sourced from fossil fuels, with the principal method employed being the catalytic reforming of methane (CH_4, the principal component of natural gas and other gaseous fuels such as landfill or coal seam gas). Two different reactions can be distinguished in the methane reforming process: steam methane reforming (SMR) and CO_2 (or dry) methane reforming (DMR), represented by the following Eqs. (1) and (2), respectively:

$$CH_4 + H_2O \leftrightarrows 3H_2 + CO \quad \Delta H^0_{298\ K} = +206\ \text{kJ/mol} \tag{1}$$

$$CH_4 + CO_2 \leftrightarrows 2H_2 + 2CO \quad \Delta H^0_{298\ K} = +247\ \text{kJ/mol} \tag{2}$$

Both these reactions are highly endothermic, therefore the heating value of the product is greater than the heating value of the reactants and both reactions are favored by high temperatures (industrial reforming processes are carried out between 800 and 1000 °C) [1]. The required energy is supplied by combustion of additional natural gas and process waste gas (tail gas) from the downstream hydrogen purification step. The share of natural gas, consumed as fuel, varies from 3% to 20% of the total natural gas consumption of the plant, depending on the subsequent energy requirements of downstream processes (e.g. CO_2 removal) [2]. The reaction gas product mixture is known with the name Synthesis Gas (syngas). Syngas is a gas mixture that contains varying amounts of CO and H_2 whose exothermic conversion to fuel and other products has been commercially practiced since a long time ago e.g. via the Fischer–Tropsch technology and which can be also used as a source of pure hydrogen and carbon monoxide [3,4]. In fact Hydrogen and syngas are the basic raw materials to produce synthetic liquid fuels (SLF) and chemicals via industrially available processes.

There are additional ways to produce hydrogen and/or syngas; e.g. from biomass processing, coal gasification, other hydrocarbons, etc. Whilst reforming is likely to remain the technology of choice for some time, hydrogen is ultimately seen to be the clean fuel of the future and will need to be produced entirely from renewable or carbon-neutral energy i.e. with energy input from sunlight, wind, hydropower or nuclear energy [5]. In this perspective, the harnessing of the huge energy potential of solar radiation and its effective conversion to hydrogen becomes a subject of primary technological interest. There are basically three pathways for producing Hydrogen with the aid of solar energy [6,7]: electrochemical, photochemical and thermochemical. The latter is based on the use of concentrated solar power (CSP) radiation as the energy source for performing high-temperature reactions that produce Hydrogen – in many cases first via syngas – from transformation of various fossil and non-fossil fuels via different routes such as water splitting (to produce

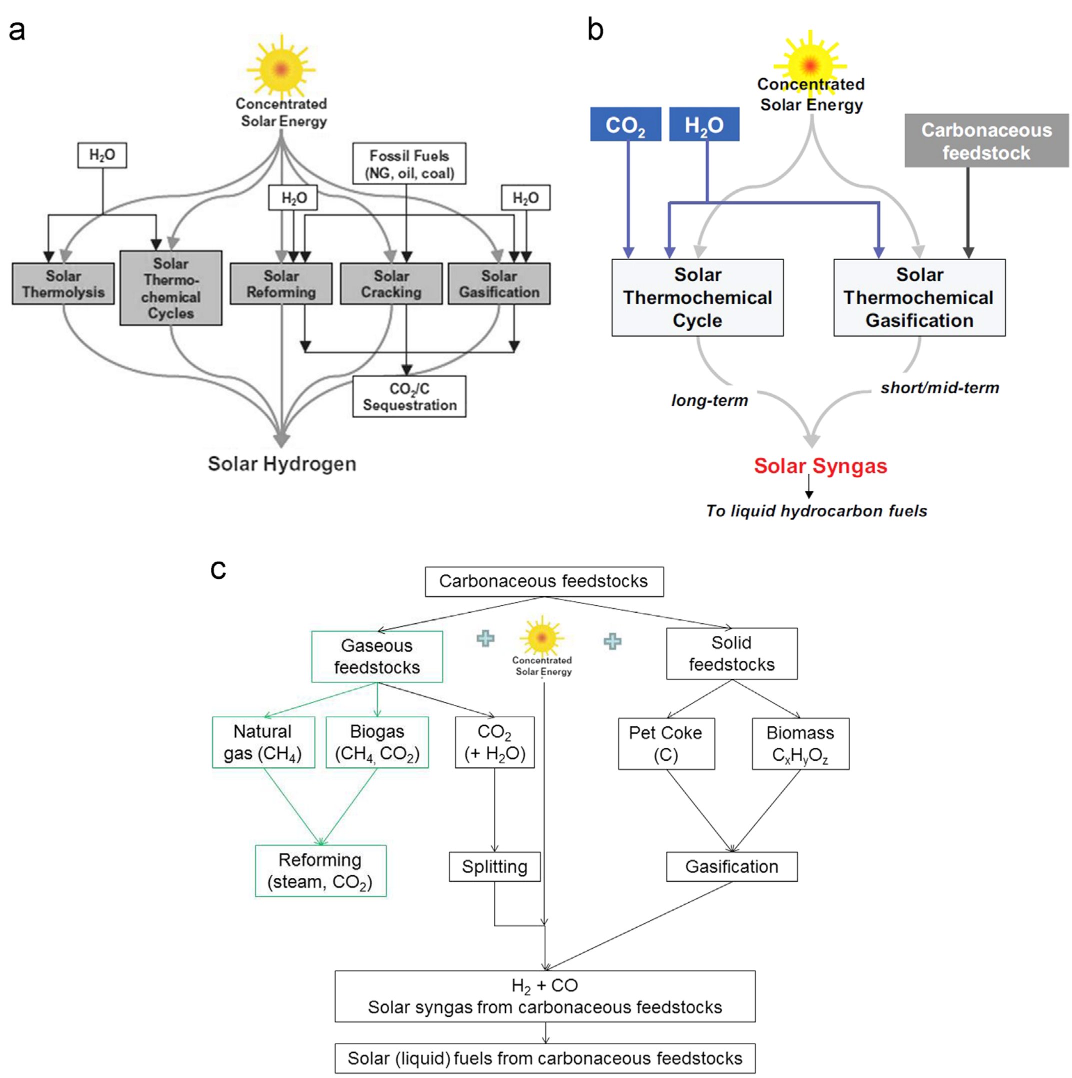

Fig. 1. CSP-aided routes for the production of (a) "solar hydrogen" [6]; (b) "solar syngas" [22]; (c) technologies and raw materials for the production of "solar syngas" from carbonaceous feedstocks (in green: topics covered in this work). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)