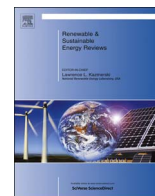




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An overview of the solar thermochemical processes for hydrogen and syngas production: Reactors, and facilities

H.I. Villafán-Vidales^{a,*}, C.A. Arancibia-Bulnes^a, D. Riveros-Rosas^b, H. Romero-Paredes^c,
C.A. Estrada^a

^a Instituto de Energías Renovables-Universidad Nacional Autónoma de México. Privada Xochicalco S/N, Col. Centro. Temixco, Morelos, Mexico

^b Instituto de Geofísica, Universidad Nacional Autónoma de México, Ciudad Universitaria, México D.F. 04510, Mexico

^c Universidad Autónoma Metropolitana-Iztapalapa. Área de Ingeniería en Recursos Energéticos, San Rafael Atlixco No. 186. Col. Vicentina, Iztapalapa, Mexico

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ABSTRACT

Hydrogen is a promising energy carrier for transportation, domestic and industrial applications. Nowadays hydrogen is consumed basically by the chemical industry, but in long term its demand is expected to grow significantly due to emerging markets. Hence production of hydrogen with sustainable methods is a relevant issue. This work presents a review of the different CSP- aided thermochemical processes for hydrogen and syngas production. For each process, some relevant solar-tested reactor prototypes are described. In a second part, the developed solar furnaces for investigation of thermochemical process are also discussed. In addition, relevant research on hydrogen or syngas production in solar tower installations is presented. Finally the current challenges of the technology and the process for its future commercialization are also analyzed.

1. Introduction

Hydrogen is the most abundant molecule in the universe; however on earth there is no natural source of this element. Hydrogen is found in the entire planet in a large number of molecules, like water and fossil fuels [1]. Nowadays, hydrogen production reaches around 300 billion of liters per year, where the chemical industry is the main consumer of this molecule [2]. Hydrogen is used mainly by the chemical industry for producing fertilizers, ammonia, and for petroleum refining. Nevertheless, its consumption is expected to increase in the next years due to emerging markets, like the fuel-cell applications (automobile and portable devices based on fuel-cells) [3].

Nowadays, 96% of hydrogen consumed worldwide is obtained by processes where fossil fuels are used both as raw material and energy source. The principal process for H₂ production is the steam reforming of natural gas, which produces 48% of the world's supply, whereas other methods like the partial oxidation of petroleum and carbon produce 30% and 18%, respectively. The remaining 4% of H₂ production comes from water electrolysis [4]. The main disadvantages of these processes, which make them unviable on the long term for hydrogen production, are the generation of important greenhouse gas emissions and the contribution to the depletion of fossil fuels. In this context, renewable energies, such as solar, constitute a viable option to mitigate both drawbacks. Solar energy in particular, is one of the most abundant

renewable sources on earth, and its usage for hydrogen production represents a virtuous combination: solar energy can be concentrated to high levels, allowing to obtain the high temperatures required to carry out solar thermochemical processes efficiently; on the other hand these processes constitute an alternative route to storage solar energy in a chemical form, helping to compensate the variability of this resource.

When solar radiation is used as the power source to produce energy carriers such as hydrogen or synthesis gas “syngas” (which is a mixture containing different amounts of H₂ and CO), they are denominated “solar fuels”. Solar fuels can be used to generate electricity through fuel cells, to produce heat or mechanical work, or to obtain “Synthetic Liquid Fuels”, by means of the Fischer-Tropsch process. This last process is a catalytic chemical method used to convert syngas to hydrocarbons of various molecular weights that are mainly liquids. Depending of operating conditions (catalyst, temperature, etc.) several hydrocarbons (from methane, to paraffin) are obtained [5].

These Synthetic Liquid Solar Fuels can be easily transported with current technology; still hydrogen transportation needs further research. The most promising liquid solar fuels are methanol, dimethyl-ether and Fischer-Tropsch diesel. For example methanol can be used in a mixture with unleaded gasoline (85% methanol, 15% gasoline) in a conventional engine with minor modifications. Dimethyl-ether is a compound that can substitute diesel, because it can be used without any modification on internal combustion engines [6].

* Corresponding author.

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Nomenclature

UNAM	Universidad Nacional Autónoma de México
PSI	Paul Scherrer Institute
WIS	Weizmann Institute of Sciences
SNL	Sandia National Laboratory
CIEMAT	Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas
PROMES	PRocédés, Matériaux et Energie Solaire
ETH	Eidgenössische Technische Hochschule Zürich
CNRS	Centre National de la Recherche Scientifique
ASTERIX	Advanced Steam Reforming of Methane
CSIRO	Commonwealth Scientific and Industrial Research

Organization

CAESAR	CATalytically Enhanced Solar Absorption Receiver
GAS	Solar-driven Gas-Cooled Solar Tower
SOLREF	Solar Steam Reforming of Methane Rich Gas for synthesis Gas Production.
TIT	Tokio Institute of Technology
SYNPET	Solar gasification of Petcoke
PDVSA	Petroleos de Venezuela S.A
SOLSYNCS	Solar Fuels for Cement Manufacturing
HYDROSOL	Solar Hydrogen via Water Splitting in Advanced Monolithic Reactors for Future Solar Power Plants
HoSIER	Horno Solar de Alto Flujo Radiativo
UNISON	Universidad de Sonora

Solar fuels can be produced basically by three different routes: electrochemical, photochemical, and thermochemical. Among these different options, the thermochemical route is a promising one for solar fuels production due to higher overall efficiencies ($\eta \sim 52\%$) [7]. The considered thermochemical reactions require high temperatures, which are reached by using concentrated solar energy as a heat source.

The purpose of this paper is to present a review of the Concentrated Solar Power (CSP)-aided thermochemical processes for hydrogen and syngas production. First, the different thermochemical routes are described, followed by the description of relevant solar reactors developed for carrying out each of them. Then, solar concentrating systems developed for performing research on these processes and the relevant pilot-scale tests realized are described. Finally, the current challenges that exist to implement this technology in a commercial-level are discussed.

2. Thermochemical solar-aided hydrogen or syngas production

The use of solar energy and its effective conversion into hydrogen and syngas is possible thanks to the development of new concepts and the creation of new facilities for the conversion of solar radiation into heat, with temperatures ranging from 200 to 3000 °C [4]. Some of these techniques are subject of research, and constitute an important technological challenge. Nowadays it is possible to obtain these two energy carriers essentially with three different solar processes: electrochemical, photochemical and thermochemical.

The solar electrochemical method consists in water electrolysis for hydrogen or syngas production, where the electricity needed to carry out this process can be obtained either by means of photovoltaic panels or by solar thermal power plants. The second option, solar photochemical method uses a part of the solar spectrum which can be absorbed by a photocatalyst or sensitizer to split steam/CO₂ mixtures or water molecules to produce syngas or H₂, respectively. Finally, solar thermochemical methods use concentrated solar energy provided by CSP systems to carry out high-temperature reactions that allow obtaining these chemical commodities.

All of these three methods are feasible and promising alternatives for the storage of solar energy [4], however thermochemical processes feature more interesting thermodynamic advantages [7–9]. Fig. 1 conceptually illustrate the thermochemical solar processes, in which solar radiation is concentrated through high concentration systems, i.e. mirror structures that track the sun and concentrate it in one point, for example parabolic dishes, solar furnaces or solar power tower systems. This energy is captured in a receiver or solar reactor, where high temperatures are obtained in order to carry out the endothermic or exothermic reactions involved in the processes to obtain “solar fuels”. In this manner, concentrated solar energy is stored in their chemical bonds.

Thermochemical solar fuels production has five main routes [9]:

thermolysis, thermochemical cycles, reforming, cracking, and gasification (Fig. 2). Water thermolysis and thermochemical cycles are emission-free routes, due to the fact that they use only water or a mixture of water and CO₂ and concentrated solar energy. However, both processes have challenges that need to be addressed before a large-scale implementation can be accomplished. On the other hand, the last three routes (reforming, cracking, and gasification) use fossil fuels, or a mixture of fossil fuels and water or CO₂, as raw materials for obtaining hydrogen or syngas. (Fig. 3). The main disadvantages of these processes are that they they contribute to the depletion of fossil fuels and produce greenhouse gas emissions. However, these emissions are considerably mitigated if concentrated solar energy is used as an energy source to carry out the processes, compared to the conventional heating systems.

Because they are not 100% clean, the routes involving fossil fuels are seen as transition processes; it is expected that their associate costs can be competitive with the current costs of conventional hydrogen production, but with lower environmental impacts. For instance, steam reforming of methane is a well-known process that can be easily coupled to CSP- technology [6].

All the above thermochemical processes for solar fuels production must be performed in devices called “solar reactors”. The design of these reactors is different from their conventional counterparts. However, it is possible to combine concepts of traditional reactor engineering, with the aim of reaching a uniform heating in the reactive particles, for instance, as in conventional catalytic reactors. In this case there are two important categories depending of the distribution of the reacting material inside the reactor. In the first category, particles are randomly distributed, e.g. packed beds and fluidized beds. The second category includes structured systems, e.g. catalytic membrane reactors, foams and honeycomb structures. Both reactor concepts have been tested in thermochemical solar processes with satisfactory results [6].

Solar reactors are classified in two groups according to the way

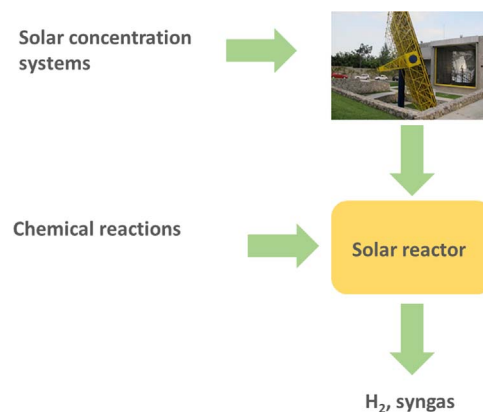


Fig. 1. Scheme of thermochemical solar processes general performance.

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