Review

Special articles: Leading-edge Technology for Energy Conversion of Solar Thermal Energy into Chemical Fuels
特集：太陽熱の化学燃料転換に関する最新動向

Current Status of Solar Thermochemistry in Spain

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(Received January 27, 2015)

Solar thermochemistry deals with the conversion of concentrating solar energy into chemicals. Its interest lays in the production of valuable energy carriers and chemicals with high solar-to-fuel conversion efficiencies that would help to decarbonising the transport and to produce cleaner fuels.

This manuscript reviews R&D activities on high-temperature solar chemistry in Spain in the last three-year period. It comprises solar fuels production by thermochemical cycles;solar gasification and reforming; high-temperature steam electrolysis and thermochemical heat storage. The legacy of Spain in this field started in 90's supported by unique experimental facilities that currently cover a wide power and flux densities range from low-to-medium power high-flux solar simulators to solar furnaces and MW-range central receiver systems. Most representative projects related to solar hydrogen production are the European HYDROSOL-Plant (750 kW_{th}) and the Spanish SOLH2 (200 kW_{th}). These activities have been reinforced by fundamental research on materials characterisation and kinetics as well as integration analyses in solar thermochemical plants.

Key Words
Solar fuels, High-temperature water electrolysis, Thermochemical energy storage, Solar chemistry

1. Introduction

Spain has diversified its national energy mix in the last two decades according to the objectives established by the European Union. In the last two years the penetration of renewable energy in the total electricity production has exceeded the 40% [1]. The growth has been particularly strong in solar and wind, representing 28% of the total electricity production in 2014. Solar thermal power plants are playing already a significant role in this transformation of the power generation sector. The total installed capacity of those solar plants is 2300 MW and they achieve 5% daily contribution to the power mix in summer time.

In addition to electricity generation, process heat for industry, co-generation of heating, cooling and power and water desalination, concentrating solar energy can also be applied to synthesis of energy carriers or solar fuels. Solar-generated hydrogen can help to decarbonising the transport (consumption of oil for transport is about 40 million toe at present) and other end-use sectors by mixing hydrogen with natural gas in pipelines and distribution grids, and by producing cleaner liquid fuels. The EU Directive 2009/28/EC requests a 10% share of renewable energy in the transport sector in every Member State by 2020.

Solar fuels could also be used as zero-emission back-up fuel for generating solar thermal electricity (STE). This application for STE is considered in various roadmaps concerning energy and transportation (i.e. IEA Technology Roadmap Solar Thermal Electricity 2014, EERA CSP Subprogramme Solar Thermochemical Production of Fuels).

In a previous article published in this journal, an overview on activities related to solar thermochemistry in Spain in 2011 was given [1]. This manuscript updates the information on solar thermochemistry in Spain as of 2014.

2. Thermochemical routes explored in Spain

Different pathways have been proposed to efficiently store the solar energy in liquid or gaseous fuels either indirectly by supplying the electricity for electrolysis or co-electrolysis or directly supplying the high-temperature

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heat for endothermic thermochemical processes [2]. The single-step thermal dissociation of water or CO_2, solar thermolysis, is a conceptually simple chemical reaction that has been discarded due to the high temperature required (above 2500 K) for achieving a reasonable degree of dissociation, and by the need of an effective technique for separating H_2 and O_2 or CO and O_2 at high temperatures to avoid ending up with an explosive mixture. Furthermore, the very high temperatures demanded by the thermodynamics of the process (e.g. 3000 K for 64% dissociation at 1 bar) pose severe material problems and can lead to significant re-radiation from the solar reactor, thereby lowering the absorption efficiency.

Water-splitting thermochemical cycles bypass the H_2/O_2 separation problem and further allow operating at relatively moderate upper temperatures. They consist of a series of chemical reactions, of which net result is the splitting of water in oxygen and hydrogen or water and CO_2 in syngas (a mixture of CO and H_2). They are believed to have the highest potential to achieve the massive production of clean hydrogen from solar energy sources, doubling the efficiency by making use of solar electricity, generated via PV or thermal, followed by electrolysis of water, which is nowadays a viable technical route.

Combining heat and electricity from solar, high-temperature solid oxide electrolysers can be used to generate hydrogen and synthesis gas. Solar-to-hydrogen efficiencies above 20% seem possible, which is higher than using solar electricity in low-temperature steam electrolysers (around 12%).

High-temperature solar-driven processes can also be used to upgrade carbonaceous materials such as natural gas, biogas, low-grade coals, biomass or carbon-containing wastes through solar cracking, reforming or gasification. Solar-to-fuel conversion efficiency could achieve 55% assuming carbon sequestration and 71% for hydrocarbon thermal decomposition and steam-gasification of coal, respectively.

3. Main R&D centers and institutions

The number of R&D institutions and companies related to solar-driven thermochemistry in Spain is very small. The Spanish National Laboratory on Energy Research (CIEMAT) is the institution with a long lasting tradition in solar chemistry. CIEMAT has been active in solar fuels for decades since early nineties, being engaged in various projects on solar thermochemistry; projects mainly on solar reforming and gasification and hydrogen production, with focus on carbonaceous materials of low quality and also in pre-commercial demonstration scale of the technical and economic feasibility of water splitting for hydrogen production using thermochemical cycles with concentrated solar power. The unique research platform that CIEMAT has in Almeria (the Plataforma Solar de Almería or PSA) allows analysing solar processes at pre-commercial demonstration scale (http://www.psa.es).

At regional level, the most important research programme is conducted in Madrid by the Instituto IMDEA Energía or IMDEA Energy institute (http://www.energy.imdea.org). IMDEA Energía has various indoor solar facilities such as the high-flux solar simulators (7 and 42 kW) and has established a research programme on solar thermochemistry addressing processes such as energy storage, thermochemical cycles for hydrogen production or solar upgrading of carbonaceous materials.

Regarding Universities, it is remarkable the Group of Chemical and Environmental Engineering of the University Rey Juan Carlos (URJC) (http://www.urjc.es) that has been involved in the study of thermochemical cycles based on manganese and cerium oxides, mainly focused on kinetics and thermodynamics.

Other stakeholders and research entities with significant activity in solar-driven thermochemistry in Spain are CIDAUT (http://www.cidaut.es), the Institute of Catalysis and Petrochemistry ICP-CSIC (http://www.icp.csic.es) and the company Abengoa, through the subsidiaries Abengoa Research and Abengoa Hidrógeno (http://www.abengoa.com)

4. Regional and national projects

The national project SOLH2 is a Spanish collaborative program involving the University of Seville, the research centres IMDEA Energy Institute and CIEMAT-PSA, and the company Abengoa Hidrógeno, established within the framework of the INNPACTO Initiative promoted by the Spanish Ministry of Science and Innovation [3].

The project started in June 2011 and ended in December 2014 and dealt with the development of clean technologies for solar hydrogen production based on water splitting by mixed-ferrites thermochemical cycle in central receiver systems (CRS) and bioethanol steam reforming using solar dishes. Two independent installations (one for each hydrogen production route) were designed, constructed, and commissioned.

The first facility was mounted in the Small Solar Power System central receiver System (SPSS-CRS) at

Fig. 1 SSPS-CRS tower at CIEMAT-PSA, Almeria. Solar reactors from SYNPET, SOLH2 and HYDROSOL are installed in different height platforms from top to bottom (courtesy: Abengoa Hidrógeno)

PSA, a CRS facility used to test solar receivers and reactors in the 200-350 kW range. It has an autonomous north solar field of 91 40-m^2 heliostats distributed in 16 rows. The SPSS-CRS tower has been recently modified in order to allocate various test platforms at three different levels. The 200 kW_{th} SOLH2 solar receiver is located in the 2nd level at 28 m height and consists of a cavity receiver in which 80 vertically oriented ceramic tubes containing commercial ferrite. Experimental tests of reaction performance in one tube have been already tested in the 42 kWe-high-flux solar simulator at IMDEA Energy Institute. The plant includes auxiliary services, nitrogen inert gas supply, water, steam generator, compressed air and electricity supply and communications wiring. Besides new functionalities of the heliostat control program have been implemented.

Fig. 2 View of the bio-ethanol solar reforming facility developed in SOLH2 project (courtesy: Abengoa Hidrógeno)

The second one is a solar bioethanol reforming parabolic dish facility that was located in the R&D platform that Abengoa has in Sanlucar La Mayor, Seville (see Fig. 2).

Other activities related to solar fuels production by solar thermochemical process are being driven at regional level. The R&D programme SOLGEMAC (Modular, Efficient and Dispatchable High Flux Solar Thermal Power Systems) (2009-2013), funded by Regional Government of Madrid, aimed at establishing the scientific and technological foundations to address the development of new systems of thermal and chemical utilization of concentrated solar power more efficient, manageable and modular way, drawing the outline of what would the second generation solar thermal power plants. For this research it will be focused on the development of components and systems to provide a new generation of power plants and solar thermal systems to open the range of applications for new thermodynamic cycles and more efficient power plants and endothermic chemical processes at high temperature. The concept is based upon a modular design that allows distributed generation in semi-urban locations with lower environmental impact and greater manageability of the thermal energy produced by storage systems and solar fuel production. The consortium was composed by the IMDEA Energy Institute (coordinator), INTA (Instituto Nacional de Técnica Aeroespacial or National Institute of Aerospace Technology), University Autonoma of Madrid (UAM), University Rey Juan Carlos (URJC) and CIEMAT. Activities on solar thermochemistry were mainly focused on particle solar reactors and thermo-chemical cycles based on manganese oxides and ferrites, and limiting the study of doped cerium oxides $M_xCe_{1-x}O_2$ (M = Zr, Co, Fe or Mn) due to the higher temperature required for reduction. The project allowed analysing kinetic and structural properties of commercial ferrites ($NiFe_2O_4$) [5], studying the recyclability of the complete three-steps manganese oxide thermochemical cycle [6], and the kinetics of the two reduction chemical reactions required in the step driven by solar energy:

$$3Mn_2O_3 \leftrightarrow 2Mn_3O_4 + 1/2\ O_2, \quad (1)$$

$$Mn_3O_4 \leftrightarrow 3MnO + 1/2\ O_2, \quad (2)$$

Kinetics for eq. (1) and (2) were obtained making use of conventional and solar-driven thermogravimetric analysis [7) 9) 11]. Simultaneous measurement of sample weight and gas analysis at reactor downstream indicated that thermal desorption under highly concentrated light could be applied in kinetics determination if the solar chemical reactor behaviour is described by a plug-flow reactor [9]. As result, a chemical reactor was specifically design for determining kinetics under high radiation fluxes [10].

The regional program AlcConES (the acronym in Spanish stands for Storage and Conversion of Concentrated Solar Power) (2014-2017) focusses its R&D objectives onto the heart of concentrating solar technologies, that is the loop involving conversion from high flux solar to thermal energy, including the storage system needed to optimized dispatch on demand for further use of energy in the production of electricity, solar fuels or chemicals. This project enlarges the material synthesis to include new materials such as perovskite type $La_{1-x}B_xMO_3$ (B = Sr, Co, Ca, Cr, M = Mn, Fe; x = 0; 0.3; 0.7; 1) and develops new reactor concepts in order to increase the heat and mass transfer.

Although redox reactions are usually applied in thermochemical cycles for solar fuels production, it can be also considered the use of cycles at high and low temperature in order to produce other chemicals. The national project SOLARO2 (awarded in the Subprogram of fundamental not-oriented research of the National Plan of Scientific Research, Development and Technological Innovation 2008-2011) analyses the use of this approach using the redox chemical reactions (eq. 1 and 2) in order to generate oxygen. The process is composed by two reactors, one at high temperature in which the reduction takes place and a second one at low temperature in which the oxidation proceeds. The manganese oxide circulates transporting the oxygen from one reactor to the other.

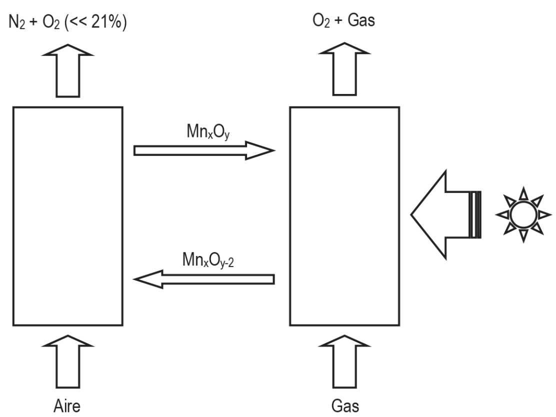

Fig. 3 Scheme of solar process for oxygen production analysed in SOLARO2

5. International projects

Spain has been involved in various international initiatives addressing the production of solar fuels (mainly hydrogen) by means of solar gasification (SYNPET, EU FP7 STAGE-STE), thermochemical cycles (EU FP7 HYDROSOL, STAGE-STE) and high-temperature steam electrolysis (EU FCH-JTI ADEL) and thermochemical heat storage (EU FP7 TCSPower).

The project SYNPET (Hydrogen Production by Steam-Gasification of Petcoke) involved the Venezuelan state-owned oil and natural gas company PDVSA (Petróleos de Venezuela S.A.), CIEMAT and the Swiss Federal Institute of Technology in Zurich ETH Zürich. SYNPET started on January 1, 2003 and finished on December, 31 2012. It focused on solar steam-gasification of petroleum derivatives and residues using concentrated solar radiation in a 500 kW solar reactor. The facility was commissioned in 2009 at the SSPS-CRS tower of the Plataforma Solar de Almería. CIEMAT took over the construction of the whole installation.

Three testing campaigns were carried out from 2009 to 2012 which main objective was to obtain operating experience with the system at power levels approaching the maximum load and to solve some structural problems, such as resistance of conical aperture and thermal behaviour of an innovative design of a segmented window.

Fig. 4 shows the refrigerated quartz window specially designed in the SYNPET project. It has a diameter of 1400 mm and represents a technical challenge for advancing in CRS. The design window would be able to withstand the needed pressure inside the reactor and high temperatures (up to 1400 °C). Inner and outer frames were stiff and equipped with water cooling channels. Reliability of window configuration during thermal tests up to 1000 °C was checked performing some tests using air as heat

Fig. 4 SYNPET500 reactor receiver window

transfer fluid. Final solar chemical testing in 2012 demonstrated the unfeasibility of the present design to operate with steam as carrier gas. Next solar testing has been scheduled for 2015, once identifying possible solutions and determining critical parameters. A final decision is not already taken. New proposals are being considered based on economics and/or constructive aspects.

The EU FCH-JU-2012 HYDROSOL-Plant aims at developing and operating a plant for solar thermo-chemical hydrogen production from water at 1 MW scale using the HYDROSOL technology. The consortium is composed by APTL (Greece), the German national research center for aeronautics and space DLR (Germany), Total (France), Hygear (Netherlands) and CIEMAT-PSA (Spain). The project has been funded with 2.5 M€ and will be carried out in the period comprised between January 1, 2014 and December 31, 2016. The HYDROSOL-Plant project is a follow-up of the HYDROSOL projects, HYDROSOL (2002-2005), HYDROSOL II (2006-2009) and HYDROSOL-3D (2010-2013) and will required an upscaling of current solar reactor technology from 100 kW to 750 kW and develop all aspects in the central solar tower plant such as heliostat field, monitoring and control or feedstock conditioning and hydrogen storage. The project targets to operate the plant and demonstrate hydrogen production and storage on site (at levels > 3 kg/week).

ADEL (ADvanced ELectrolyser for Hydrogen Production with Renewable Energy Sources) is a European project co-funded by 7th Framework Programme of the European Union (FP7) and Fuel Cells and Hydrogen Joint Undertaking (FCH-JU) and gathers 13 partners. This project was developed between 2010 and 2013 and aimed at developing a new steam electrolyser concept, the so-called Intermediate Temperature Steam Electrolysis (ITSE), based on solid oxide electrolysis technology (SOEC), and to analyse how to integrate these devices with non-greenhouse emitting energy sources to use clean heat and electricity in steam generation, electrolyser heating and electricity feeding [12) 13)]. By decreasing operating temperature, optimization of the electrolyser lifetime and shrinkage of constraints on specific system components (heat exchangers for instance) are expected while maintaining satisfactory performance level and high energy efficiency at the complete system level including the heat and power sources and the electrolyser unit. The relevance of this ITSE was studied both at the stack level based on performance and durability tests and at the system level based on flow sheets and energy efficiency calculations. When coupled with renewable energy sources and depending on the electricity demand and storage, the electrolyser is operated in transient conditions which were also considered in the ADEL project.

High temperature steam electrolysis with Solid-Oxide cells shows great advantages versus conventional alkaline and PEM electrolyser. These advantages stem from on its high operational temperature, among 600 to 1000 °C. From a thermodynamic point of view, hydrogen generation reaction can be described by the Gibbs function,

$$\Delta G = \Delta H - T\Delta S, \quad (3)$$

where ΔH is the overall energy needed, ΔG is the electrical energy and $T{\cdot}\Delta S$ is direct heat. As can be seen in Fig. 5, the electrical requirement decreases and heat energy demand increases with increasing temperature. Even though total energy demand increases, the decrease in electrical energy demand is more noticeable. Operation at high temperature can therefore decrease the electricity

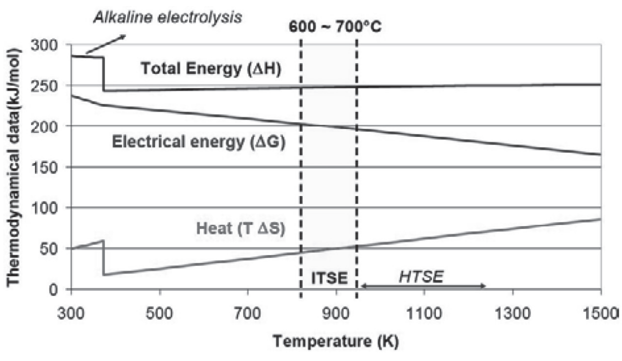

Fig. 5 Free energy water split diagram. Temperature interval 600-700 °C would apply to Intermediate Temperature Steam Electrolysers (ITSE). Temperatures above 700 °C are used by High Temperature Steam Electrolysers (HTSE)

consumption and projects less generation cost. Cost reduction can be greater if the heat energy demand can be fulfilled by industrial waste heat source.

From the kinetic point of view, high temperature helps to promote electrode activity and reduce cell overvoltage. It means that power density can be increased, reducing the size of the electrolyser for a given production. On the other hand, lower cell overvoltage can lead to lower energy losses, thus more electric efficient process. Additionally, Solid-Oxide systems are able to work either as electrolyser (SOEC) or as fuel cell (SOFC), reducing the number of units and their auxiliary elements.

IMDEA Energy participated in the ADEL project taking over the flowsheeting and analysis of integration of the SOEC stack in different solar thermal power plants.

The use of high-temperature redox chemical reactions in thermochemical heat storage has been explored in the framework of the European FP7 project TCSPower (2011-2015) [12]. DLR, Siemens AG, Bühler AG, Eramet et Comilog Chemicals SA, IMDEA Energy, Paul Scherrer Institut (PSI) and the University of Siegen participate in this initiative, that will culminate with an experimental 10kW reactor with about 10 hours charging time installed at DLR. Within TCSPower, IMDEA Energy conducts the activities on manganese oxides as storing material. This material provides an excellent trade-off between thermodynamics, energy storage density, material costs, reaction kinetics, toxicity and cyclability compared with other metal oxides such as Co_3O_4, BaO, or CuO. Besides of this, oxide based systems have an advantage compared to carbonates or hydroxides since air might be used as both the heat transfer fluid and the reactant, which removes the requirements to store CO_2 or water and to handle steam [15) 16)].

In addition to the on-going projects aforementioned (National SOLH2 and SOLARO2, Regional ALCCONES and European HYDROSOL-Plant and TCSPOWER), Spain is also involved in the Integrated Research Project STAGE-STE (Scientific and Technological Alliance for Guaranteeing the European Excellence in Concentrating Solar Thermal Energy). This project covering the full spectrum of current concentrating solar energy research topics and gathers 40 partners including the major European research centres and industry involved into concentrating solar technologies. Solar fuels are addressed in one of the work packages (coordinated by PSI, Switzerland) that counts on the participation of CIEMAT and IMDEA Energy as Spanish research members. Here the main contributions are related to solar fuels from carbonaceous feedstock and from thermochemical cycles, innovative materials for next generation solar chemical reactors and technology assessment of solar thermochemical production.

Acknowledgments

The European Commission is acknowledged for the research grant trough STAGE-STE Project "Scientific and Technological Alliance for Guaranteeing the Eurpean Excellence in Concentrating Solar Thermal Energy" (FP7, Project No. 609 837). The authors wish to thank "Comunidad de Madrid" and "European Social Fund" for financial support through the ALCCONES project by the program of activities between research Groups (S2013/MAE-2985). JGA wishes to thank the Spanish Ministry of Science and Innovation (grant Plan Nacional ENE2011-29293).

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