

Hydrogen and Hydrocarbon Fuels from Abundant Resources and Solar Energy: Current Activities and Perspectives in DLR's Institute of Future Fuels

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Abstract. Chemical energy carriers, centralized around Hydrogen products, will play an essential role in the energy system of the future. The advantages of comparable power density and reliability to fossil fuels, as well as their versatile applications, make them an important component of the energy transition. DLR is conducting research on technologies that ensure the efficient production of chemical energy carriers. De-carbonizing the energy system and of industry needs not only electricity from carbon-neutral sources but also green fuels. DLR's Institute of Future Fuels steps in at that point by developing and investigating production methods for hydrogen and synthetic hydrocarbon fuels. Those are mostly based on the utilisation of concentrated sunlight but in additionally also on other renewable resources. The development goes all along the way of identifying and qualifying suitable functional materials, over integrating them in specific components allowing to introduce renewable energy into the process, towards the demonstration of a representative overall process along the chain from raw materials to the targeted fuel. Hydrogen plays a key role in this context, either as the fuels itself or as a core building block of synthetic hydrocarbon fuels and chemicals. The institute has a specific focus on thermochemical processes, in particular for water and CO₂ splitting, but also on air separation, thermochemical heat storage and upgrading of biomass and other hydrocarbons.



1. Introduction

Climate-friendly generated hydrogen and derivatives like synthetic hydrocarbon and ammonia will be core elements of a transition towards a greener energy economy. Hydrogen and its derivatives can act as a central energy vector, since they exhibit high energy storage densities, they can be combusted cleanly and they allow to store energy over longer periods of time, even over seasons. Various sectors, including industry and mobility, are getting prepared to adapt to hydrogen technologies and to the use of vast amounts of hydrogen.

Especially, in the cement, steel, and chemical industry new technologies need to be introduced to replace the need of fossil fuels and reductants to achieve lower greenhouse gas emissions.

Hydrogen can be transported over long distances and its use therefore opens up opportunities for international cooperation in energy supply. There are still significant challenges linked to the introduction of such fuel, such as the cost of producing green hydrogen, building sufficient production capacity and developing suitable infrastructure for transportation, storage and distribution.

There are various methods for producing hydrogen, which differ in terms of cost and greenhouse gas emissions. Currently, hydrogen is mainly produced from fossil fuels, which causes high CO₂ emissions. New technologies based on renewable energies are being developed to make production more environmentally friendly.

Many countries in Europe have set themselves ambitious targets in terms of increasing the share of renewable energies in gross final energy. In order to achieve this, energy imports will still be essential, but from now on rather based on clean energy vectors like hydrogen to replace the previously used fossil fuels. How fast and to what extent the transition to a hydrogen economy will materialise depends not only on technical innovations, but also on the future conditions in terms of political and social frameworks.

Hydrogen is available on earth almost exclusively in chemically bound form. There are two main sources: Water and organic substances (fossil resources and biomass). In order to use it as an energy carrier, it must be extracted from these compounds. Water, which contains the majority of terrestrial hydrogen, is particularly attractive because the only products of its splitting are hydrogen and oxygen. Extracting hydrogen from hydrocarbons produces CO₂ emissions - unless the carbon is captured and stored in such a way that it cannot escape into the atmosphere. On the basis of sustainable biomass and biowaste, hydrogen can be produced in an almost CO₂-neutral way, but the availability of such resources for industrial use is limited, in particular in highly populated areas. The main methods for generating hydrogen from water are

- Electrolysis
- Solar thermochemical processes
- Photo-electrochemical and photocatalytic processes

The former route, electrolysis, is the most advanced of those three production routes. This is in particular true for room temperature water electrolysis. Apart from some activities in the field of photo-electrochemical methods the main focus of DLR's Institute of Future Fuels is on Thermochemical Routes as an alternative method for water splitting due to its high efficiency potential [1]. Beyond this several thermochemical routes also offer the option to generate

syngas from water and CO₂ and, thus, open pathways to CO₂-neutral synthetic hydrocarbon fuels. There are thermochemical pathways that use high-temperature heat provided by concentrating solar thermal energy to produce green hydrogen. Water splitting using high-temperature heat promises particularly high efficiencies and therefore low hydrogen production costs. Among the different processes, there are several that consist of a number of process steps, which is higher than 2, allowing the required maximum operation temperature to be reduced. However, as additional process and conversion steps are associated with energy losses, the two-step cycle processes are considered to have the highest efficiency potential. [2, 3] The processes were initially developed in connection with waste heat from high-temperature nuclear reactors. [4, 5] However, the focus is now primarily on concentrating solar technology as a source of renewable and cost-effective high-temperature heat.

In the most recent research, two pathways to water splitting have emerged that are particularly promising in terms of their efficiency: One is metal oxide redox cycles and the other one is sulphur cycles. Both pathways are being intensively researched at DLR. Exemplarily, current research on redox cycles is presented in the following section.

2. Thermochemical Hydrogen and Syngas Production

Two-step thermochemical redox cycles utilize a metal oxide-based redox material that is endothermally reduced and exothermally oxidized alternately. The oxidation can take place with water or carbon dioxide or a mixture of both. The reduction and oxidation reactions take place at different temperatures; while the reduction proceeds at the maximum process temperature above 1000 °C, the oxidation proceeds at lower temperatures. For that purpose, specific redox materials with dedicated properties need to be developed and qualified.

2.1 Materials thermodynamics and oxygen transport

Transition metal redox systems in an oxidic matrix are central components in high-temperature functional materials for very different technical applications. In solar thermal fuel production, a transition metal oxide is initially reduced at high temperatures and low oxygen partial pressures to form an oxide phase with an oxygen deficit. In the subsequent step, re-oxidation takes place at lower temperatures using water vapor or CO₂, whereby the gas molecules are split and H₂ or CO, i.e. the basic building blocks for synthetic fuels, are built.

The most important prerequisite for the targeted further development of redox ceramics is reliable quantitative information on the thermodynamic variables of the redox reactions and precise knowledge of fundamental kinetic parameters for oxygen incorporation and removal such as surface exchange coefficients and diffusion coefficients as a function of the process variables.

One of the core tasks, which has arisen in the course of investigations carried out so far, is related to the question which doping concepts or surface modification strategies can be used to further optimize the thermodynamic and kinetic parameters of cerium dioxide-based redox systems since ceria is one of the most promising material for solar thermal water and CO₂ splitting but still not reaching the ultimate performance target.

So, the influence of the ionic radii and the valence of the dopant ions in $\text{Ce}_{0.9}\text{La}_x\text{Yb}_y\text{Zr}_{0.1-x-y}\text{O}_{2-\delta}$ ($x = 0, 0.05, 0.1, y = 0, 0.05, 0.1$) on the oxidation kinetics was investigated by thermogravimetric analysis in synthetic air and compared with undoped ceria. The analysis of the oxidation kinetics of different doped ceria compositions showed that the oxidation of undoped ceria as well as 10 % Ytterbium-doped and 10 % Lanthanum-doped ceria is much faster than that of 10 % Zirconia-doped ceria at all oxidation temperatures. The addition of Yb^{3+} and La^{3+} to Zr-doped ceria significantly improved the oxidation kinetics due to the formation of extrinsic vacancies. The calculated activation energies also prove that the slow diffusion of oxygen ions in Zr-doped ceria at low temperatures is improved by additional doping with Yb^{3+} or La^{3+} [6].

2.2 Particle Based Approach for Solar Thermal Water splitting

Particles made of materials like functional ceramics have proven in recent years to be an interesting alternative to other forms of solar absorbers. They can be used both in receivers, where they directly absorb solar radiation, and as storage materials. In such case the particles themselves represent the material to be treated and converted to the desired product if the particles are made from the water and CO_2 splitting redox material itself

Ermanoski et al. presented a receiver concept based on moving particles, which enables continuous operation and which ensures efficient heat transfer to the redox material. Beyond this the redox material can be easily accessed and replaced [7]. The reduction of the metal oxide is foreseen to be carried out in two solar reactors exhibiting different vacuum pressure levels. The concept was transferred into a small demonstration, in which one reduction reactor was successfully operated and the capability of generating hydrogen was proven [8]. Since then, the design of the solar reduction reactors has been revised. A two-reactor system demonstrated a stable and reliable operation at different pressure levels [9].

The two-receiver system is equipped with a particle feed chamber, in which 80 kg of ceria particles are preheated by resistive heaters to a temperature of 900°C . The particles are moved by gravity and led to the first receiver, where a linear actuator adjusts their flow onto a horizontal motion conveyor. A ceramic plate acts as the horizontal motion conveyor, which moves with a low forward acceleration and a high backward acceleration. Through this a net forward motion of the particles is realised by consecutive sticking and sliding as described in [10]. Different acceleration profiles introduced by a stepper motor controls the transportation speed and with it the particle film thickness on the ceramic plate. The redox material is then introduced into the cavity, where concentrated radiation heats it up to a temperature of about 1450°C . The radiation is provided by DLR's solar simulator Synlight in Julich, reflected by a beam-down mirror and further concentrated by a secondary concentrator at the aperture of the receiver. Since a low pressure of 100-1000 Pa is applied to the chamber, the redox material particles are being reduced and thereafter leave the ceramic plate, fall into a buffer container and entirely fill the tube connecting the first receiver to the second one, thereby ensuring a pressure separation [11]. The two receiver have identical designs, but the second one operates at a lower pressure of about 25 Pa, so that the particles are reduced further. After leaving the 2nd receiver, a water-cooled tungsten sheet quenches the particles. Finally, samples are taken for thermogravimetric analysis to measure the reduction extent.

Particle based thermochemical processes are also useful for the generation of other fuels and commodities. Nitrogen is required as a feedstock for the production of ammonia and nitrat

based fertilizers. Nitrogen can be industrially produced by filtering it out of the air using cryogenic air separation. The process requires cooling to very low temperatures, which consumes a lot of energy and is associated with high CO₂ emissions. Alternatively, there is thermochemical air separation, for which solar heat is used. In the SESAM project, a team from the Institute for Future Fuels has shown how the efficiency of such thermochemical process can be increased for industrial feasibility: Using pressure swing adsorption (PSA), nitrogen of low purity is produced at first hand. In a following step the remaining oxygen is removed by a thermochemical reaction to such an extent that the resulting nitrogen quality is suitable for the production of ammonia using the Haber-Bosch process. Ammonia is also under consideration as a potential low-carbon energy vector for the operation of ships, as an alternative to liquid gas, diesel, heavy fuel oil and biofuels.

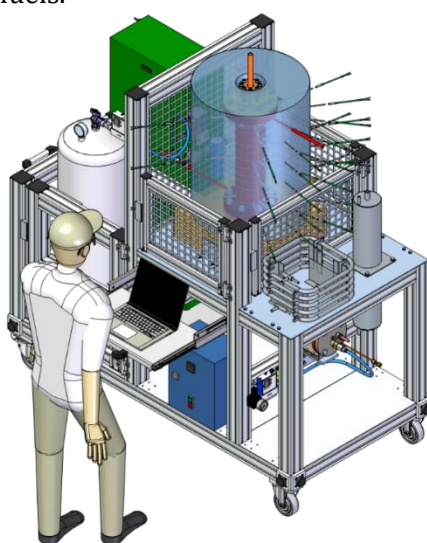


Figure 1. Scheme of thermochemical air separation device operated at DLR, Cologne, Germany.

The core of such process is the thermochemical reactor, in which the air separation takes place. It contains a redox material that can bind and release oxygen without changing its crystalline structure significantly. When it is heated oxygen is released. This oxygen is flushed out of the reactor with a carrier gas. When then air is fed into the reactor, the oxygen oxidizes the oxygen-lean redox material and pure nitrogen remains as the gas phase. Lastly, the material is heated again, the oxygen is released and the process starts all over again [12].

The family of materials used within this project are perovskites. These are ceramic materials with the same crystalline structure but exhibit extremely diverse properties depending on the choice of elements constituting the compound. In order to pre-select a short list of candidate materials, we first made a computer-based pre-selection. In addition to physical and chemical parameters, it was also important to us that the material was non-toxic and inexpensive. Through systematic testing in the lab we identified some materials that turned out to be promising in the laboratory. In the end, we opted for a perovskite granulate made of calcium-strontium manganate ($\text{Ca}_x\text{Sr}_{1-x}\text{MnO}_3$) which is used in a vertically aligned fixed bed reactor integrated in the final test set-up shown in figure 1.

2.3 Solarthermal Syngas Production based on volumetric receiver reactors

The main alternative to using particles in solar receivers is applying volumetric receiver-reactors containing porous functional ceramics as the absorber material and acting at the same time as reaction bed. The project series HYDROSOL has been making use of this concept to demonstrate solar-thermochemical water splitting in the several 100 kW range [13]. Again, the core process is a two-step thermochemical cycle for splitting H_2O and CO_2 using metal oxide redox materials. A variety of redox-active materials have been considered as suitable to be used in this technological approach [14]. There are advantages and disadvantages of both stoichiometric (i.e. iron oxide-based cycles) and nonstoichiometric (i.e. ceria-based cycles) materials in the context of thermodynamics, chemical kinetics, and material stability. Non-stoichiometric cerium oxide (ceria) has emerged as an attractive redox active material because of its high oxygen ion conductivity and cyclability, while maintaining its fluorite-type structure and phase. 3-Dimensional porous structures can be fabricated from such material by extrusion, by replica methods or in computer-aided designs as 3D printed structures.

In the frame of the EU project Sun2Liquid the respective reactor configuration consists of a cavity-receiver containing a reticulated porous ceramic (RPC) foam-type structure made of pure CeO_2 that is directly exposed to concentrated solar radiation. The production of H_2 from H_2O , CO from CO_2 , and high-quality syngas suitable for Fischer Tropsch (FT) synthesis by simultaneously splitting a mixture of H_2O and CO_2 has been demonstrated (see figure 2).

A total of about 102 stable redox cycles using H_2O and CO_2 were performed, yielding syngas which was compressed to 100 bar and further processed via FT synthesis to a mixture of naphtha and kerosene. To the best of our knowledge, this was the first integrated demonstration of solar fuels production from H_2O and CO_2 . FT-processed kerosene, derived from H_2O and CO_2 , is approved for commercial aviation by the ASTM specification D7566 for synthesized hydrocarbons [15].

Most recently the follow-up project SUN-to-LIQUID II has started. It aims at realising a carbon-neutral way of sustainable production of aviation fuel. For that purpose renewable liquid fuel ideally with the same properties as state-of-the-art fuel is directly generated from water and CO_2 through the integration of concentrated solar radiation. The project primarily seeks to increase the solar reactor energy efficiency to more than 15%. This is meant to be achieved by increasing the effective radiative absorption using 3D-printed redox materials rendering the absorber structure more effective and by more effective means to recover sensible heat while carrying out the temperature swing water and CO_2 splitting process. Besides, this project will seek to achieve cost-effective >80% GHG emission reduction, in particular for the aviation sector. At the same time emphasis is put on technical scalability to production potentials in industrial scale. The planned efforts will be based on the outcomes of the preceding SUN-to-LIQUID project with a successful 50-kW scale on-sun demonstration of synthetic hydrocarbon fuels generation through a cyclic thermochemical process.



Figure 2. Sun-to-Liquid Test Plant at site of IMDEA Energía, Mostoles, Spain.

3. Outlook

Focus of current work is the scale-up of the technology to the next level. Existing demonstrations operated with solar thermochemical reactors in the several hundred kWth range. But their operation was limited in time, with a peak reactor efficiency of less than 5 %. The challenge is to enhance the reactor and overall plant efficiency, while keeping the robustness and stability of operation in mind at the same time. Continuous operation of the solar reactor and the integration of heat recovery to the overall plant design have shown to be crucial for enhancing the overall process efficiency. In summary, it can be said that solar-thermochemical metal oxide redox cycle processes represent a promising way of producing hydrogen economically and on a large scale. The processes and the components and materials required for this have been significantly further developed in recent years. With regard to the core components required for the solarization of such processes, adjustments are still necessary in order to achieve further increases in efficiency. Approaches for this have been introduced and are being realized by research and industry. The wide range of possible redox materials and process concepts suggests that further increases in efficiency and an associated reduction in costs are also possible in the future.

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