

## Light years ahead

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Consider an area of less than 5 per cent of the Sahara desert, roughly 500km by 500km: a minute fraction of the Earth's surface. Even with solar collectors of a limited (20 per cent) efficiency, sunlight falling on this area would be sufficient to supply the current yearly energy needs ( $1.2 \times 10^{14}$  kWh) of the world's entire population. In practice, of course, it doesn't, because solar radiation reaching the Earth has some serious drawbacks: it is very dilute (only  $1\text{ kW m}^{-2}$ ), intermittent (available only during daytime and under clear sky conditions); and unequally distributed (mostly falling near the equator). But we can overcome these drawbacks by converting solar energy into solar fuels that can be stored over long periods of time, and transported over long distances, from the sunny regions of the Earth to the industrialised and populated centres, where much of the energy is needed. Solar fuels can be burnt to generate heat, further processed into electrical or mechanical work, or used directly to generate electricity in fuel cells and batteries, to meet customer's energy demands whenever and wherever needed.

There are three pathways for making solar fuels from solar energy:

- solar electrochemical path: solar-made electricity, from photovoltaic or solar thermal systems, followed by an electrolytic process;
- solar photochemical path: direct use of the photon energy; and
- solar thermochemical path: solar-made heat followed by a thermochemical process.

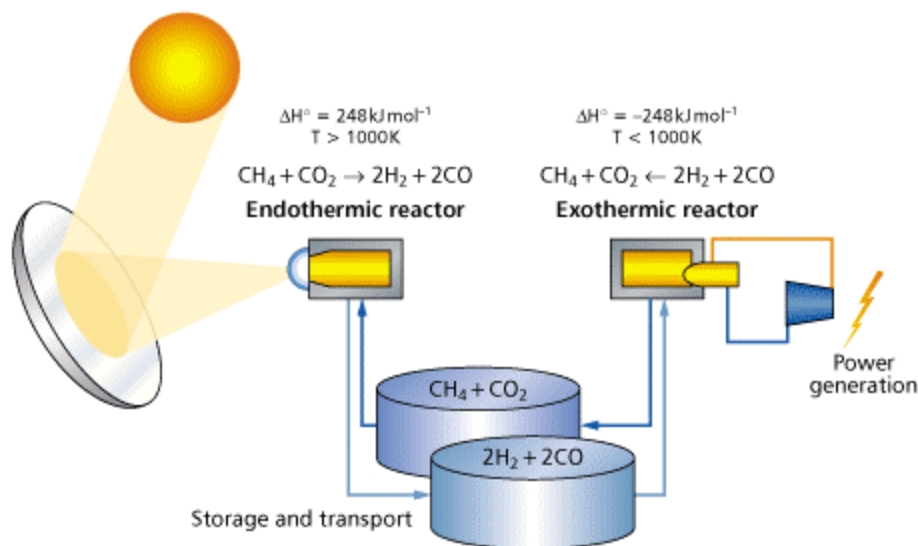
Combinations of these three pathways are possible, but the thermochemical path offers some intriguing thermodynamic advantages. It is this approach that is of most interest to a consortium of scientists, including ourselves, at the Paul Scherrer Institute (PSI)/Swiss Federal Institute of Technology (ETH), Switzerland and the Weizmann Institute of Science (WIS) in Israel.

Crucial to the solar thermochemical path are parabolic-shaped reflectors that concentrate the solar radiation by up to 5000 times. Solar receivers absorb this concentrated solar radiation and deliver it, in the form of high-temperature heat, to a chemical reactor wherein an endothermic reaction results in the production of solar fuels. These solar fuels ultimately store solar energy within their chemical bonds. Regardless of the fuel, the higher the temperature of the reaction process, the higher the efficiency of energy conversion. Higher temperatures, however, also lead to greater losses by re-radiation from the solar receiver. For a given solar concentration, there is an optimum temperature for maximum efficiency. For a solar concentration of 5000, the optimum temperature of a solar receiver is 1500K - giving a maximum theoretical efficiency of 75 per cent (the solar energy that could in principle be converted into the chemical energy of fuels). High efficiencies translate into smaller solar collection areas for the same chemical energy output and, consequently, lower costs.

An example of a thermochemical process for producing fuels using solar power involves thermally reducing a metal oxide at elevated temperatures using concentrated solar energy. The product metal can be used to generate power directly in metal-air batteries or fuel cells, or it can

be reacted with water to form hydrogen that can be further processed for heat and electricity generation. The chemical byproduct from either the power generation process or the water-splitting reaction is the original metal oxide, which is recycled to the solar reactor. The cycle is completely closed and there are no emissions to the environment. We are currently investigating the solar thermal dissociation of ZnO into its elements<sup>1,2</sup> at temperatures above 2000K. The ZnO-Zn redox pair is an attractive candidate for this solar thermochemical cycle because of its potential high efficiency and because of the versatility of zinc as an energy vector and as a material commodity.

Another thermochemical process, known as the closed-loop chemical heat pipe (*Fig 1*),<sup>3</sup> uses high-temperature solar heat to drive the endothermic CO<sub>2</sub>-reforming of methane. The product of this reversible reaction is synthesis gas (syngas), a mixture of hydrogen and carbon monoxide that can be stored at ambient temperatures and transported to where energy is needed. By the reverse exothermic reaction, stored solar energy is released in the form of high-temperature heat, which can be used for whatever purpose the customer has in mind, eg for generating electricity via a Rankine cycle. The products of this reverse reaction are again recycled to the solar reactor, where the process is repeated. In 1999, researchers at WIS and the German Aerospace Centre (DLR) demonstrated this closed-loop chemical pipe experimentally at a solar power level of about 0.5MW.



**Fig 1. Closed-loop chemical heat pipe based on the CO<sub>2</sub>-reforming of methane**

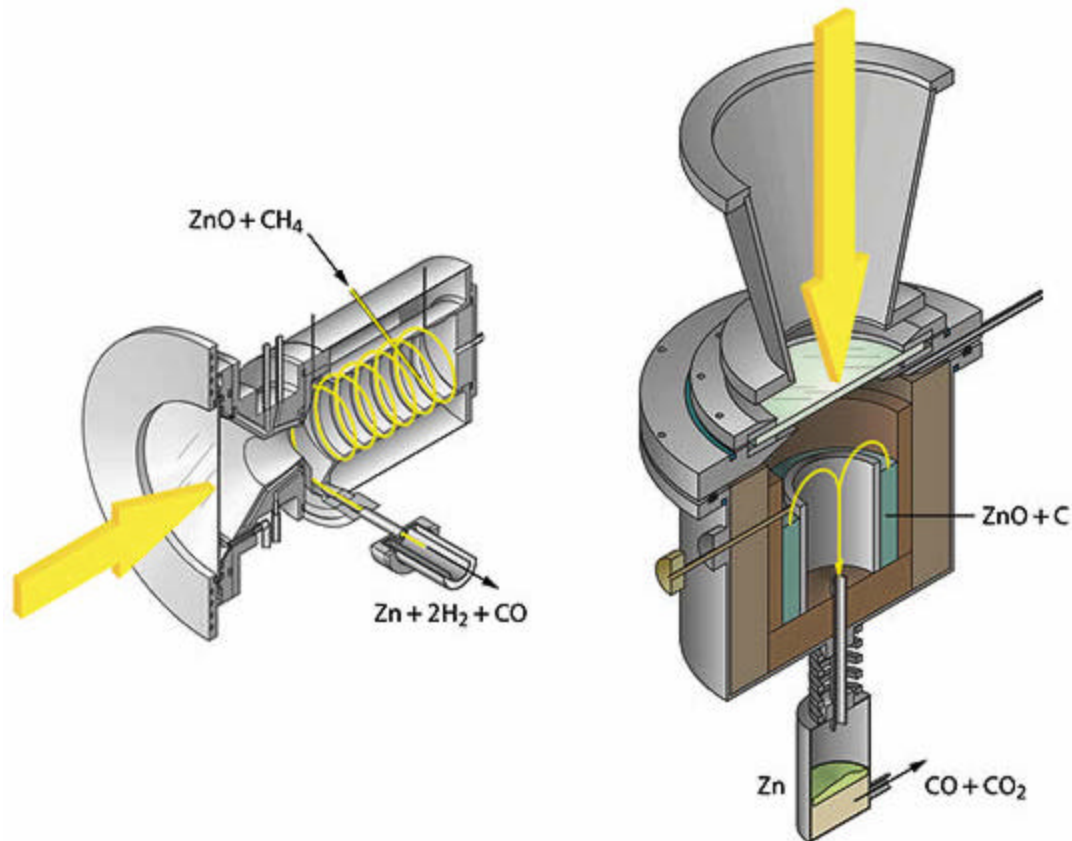
We can also apply the solar process shown in *Fig 1* in an open scheme in which the product syngas is used as a 'solar-upgraded' fuel, because its calorific value is increased above the value of methane by the solar input. Fossil fuels can similarly be solar-upgraded via endothermic processes, such as solar reforming or cracking of natural gas, or solar gasification of coal, in which fossil fuels are not combusted, but used exclusively as reactants in processes fuelled by concentrated solar energy. Solar-upgrading fossil fuels in this way avoids greenhouse gas emissions and conserves fossil fuels. This 'chemical hybridisation' of solar and fossil energies creates a bridge between today's fossil fuel-based technology and tomorrow's solar chemical technology.

Another hybrid fossil-solar energy process is the carbothermic reduction of metal oxides, using fossil fuels as reducing agents. Of special interest is the production of zinc by carbothermic reduction of zinc oxide, with solid carbonaceous materials (such as coke) or gaseous hydrocarbons (such as natural gas) as reducing agents. Such reducing agents allow the reduction of zinc oxide at more moderate and technically feasible temperatures (about 1300K) than the pure thermal dissociation. The reducing agent can also come from biomass sources, with zero net CO<sub>2</sub> emissions to the environment. If low-grade fossil fuels are used, eg lignite, shale, or residual oil, endothermic or carbothermic reduction results in gaseous products that can be used for producing electricity at higher efficiencies than by just burning the low-grade fossil fuels.

Using natural gas as a reducing agent combines, in a single process (the SynMet process), the reduction of zinc oxide with the reforming of methane for the co-production of zinc and syngas. The advantages of the SynMet process are three-fold.

- Methane is reformed in the absence of catalysts and, with proper optimisation, may be made to produce high-quality syngas with an H<sub>2</sub>:CO molar ratio of two, which is especially suitable for synthesising methanol - a potential substitute for petrol.
- The evolved gases are sufficiently valuable to justify collection, avoiding the CO<sub>2</sub> emissions from the traditional carbothermic ZnO reduction.
- Concentrating solar process heat avoids the discharge of greenhouse gases from the combustion of fossil fuels. This is particularly important because current industrial processes for producing zinc and syngas are extremely environmentally unfriendly. A recent life cycle assessment on the conventional fossil fuel-based production of zinc by electrolysis, and of syngas by natural gas reforming, indicates total greenhouse gas emissions\* of over 2kg CO<sub>2-equiv</sub>·kg<sup>-1</sup> for primary zinc and 0.8kg CO<sub>2-equiv</sub>·kg<sup>-1</sup> for syngas respectively.<sup>4</sup> The SynMet process can reduce substantially, or even completely eliminate, these emissions.
- The amount of CH<sub>4</sub> and N<sub>2</sub>O emitted over the entire process is converted into CO<sub>2</sub> equivalents by using the Global Warming Potential factor of 21 for CH<sub>4</sub> and 310 for N<sub>2</sub>O.

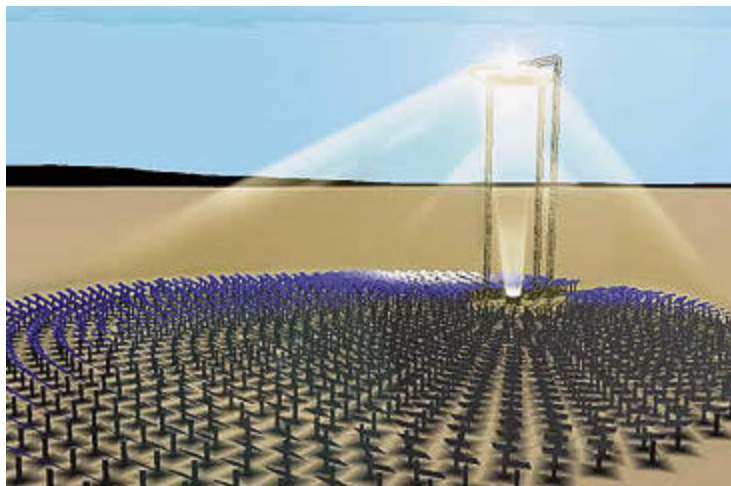
For the past four years, we and our coworkers at PSI/ETH and WIS have been developing the solar chemical reactor technology for the solar carbothermic reduction of ZnO. *Fig 2* shows the proposed solar reactor configurations, with natural gas (SynMet process) and with solid carbonaceous materials as reducing agents. The SynMet reactor consists of an insulated cylindrical cavity made of heat-resistant steel that contains a windowed aperture to let in concentrated solar energy.<sup>5</sup> Particles of ZnO, conveyed in a flow of natural gas, are continuously injected into the reactor's cavity via a tangential inlet port located at the back of the cavity. As they flow towards the reactor along a helical path, the particles of ZnO are directly exposed to the high-flux solar irradiation, providing efficient heat transfer directly to the reaction site. Energy absorbed by the reactants raises the reactor temperature to above 1300K and drives the simultaneous reduction of ZnO and reforming of natural gas. The products, zinc vapour and syngas, continuously exit the cavity via a tangential outlet port at the front of the cavity, behind the aperture, and flow into a quenching device for zinc condensation and separation.



**Fig 2. Solar reactor configurations for (a) the SynMet process and (b) the carbothermic reduction of ZnO**

The ZnO+C reactor (*Fig 2b*) consists of an annular cavity receiver, made of silicon carbide, with concentrated solar energy entering at the top through a windowed aperture and being absorbed by the inner walls. Heat is conducted into the annular gap filled with the solid reactants in the form of powder, grains, or pellets. The reaction proceeds above 1500K and the main gaseous reaction products are zinc vapour, CO, and CO<sub>2</sub>. The window is kept clean by means of inert gas flow at the window flange, which also carries away the gaseous products through an outlet port at the cavity bottom into a quencher for zinc condensation and separation. At PSI, ETH and WIS, we have recently demonstrated the technical feasibility of both reactor concepts with several 10kW prototypes, and our current work involves scaling them up to 0.5MW.

Meanwhile, recent improvements in large-scale solar energy collection and storage will have a major impact on the rate of uptake of solar fuel technology by industry. *Figure 3* illustrates the new 'beam down' Cassegrain optical configuration:<sup>6</sup> a surrounding field of heliostats (parabolic-shaped mirrors) track the sun and concentrate its rays onto an hyperboloidal reflector at the top of a tower, which re-directs the sunlight onto a solar receiver-reactor on the ground. In contrast to the traditional tower-top systems, major hardware associated with the chemical plant is therefore located on the ground, which is helpful for operations such as continuous feeding of solid reactants and removing solid products. With further development, this solar concentrating technology, along with the solar chemical reactor, may one day be implemented on a much larger scale, to provide power at the MW level.



**Fig 3. Illustration of a large-scale solar energy concentrating system delivering high-flux solar radiation to a solar chemical reactor on the ground**

Solar thermochemical processes have favourable long-term prospects because they avoid or reduce costs for CO<sub>2</sub> mitigation and pollution abatement. The products are renewable fuels and material commodities for delivering clean and sustainable energy services. Our ultimate goal is the substitution of fossil fuels with solar fuels. However, a continuous programme of research, development and demonstration is needed to bring about the large-scale implementation of solar chemical technologies. Such a programme will repay the next generation with a renewable energy supply for sustainable world development.

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