

FUELS FROM SUNLIGHT AND WATER

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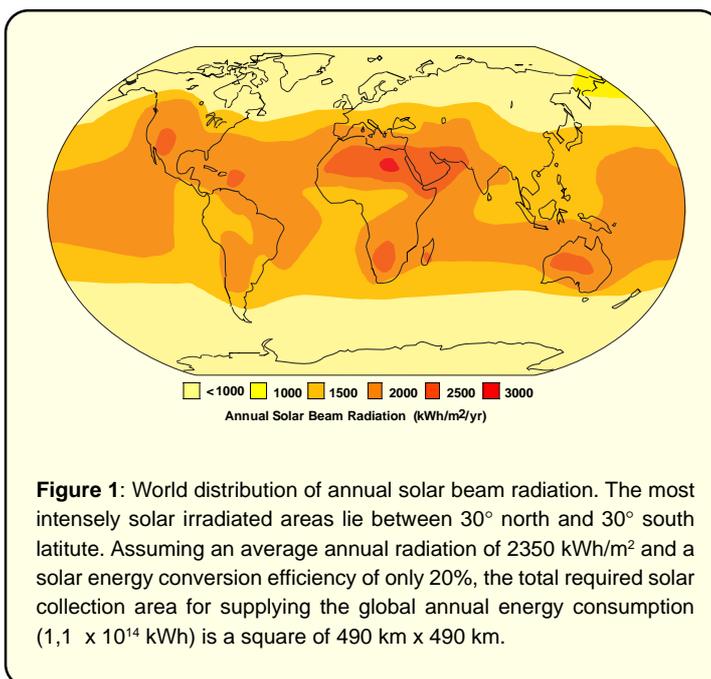
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INTRODUCTION

Two of the most abundant resources on the surface of the earth are sunlight and water. Yet we do not typically think of these resources as the solution to any upcoming energy crisis or as the fuel that will bring clean air to our cities. We just cannot see ourselves driving into the local gasoline station and filling our cars up with water or sunlight. Perhaps it is for this reason that these resources do not capture our imagination as the mix of ingredients that could help us deal with two of the most pressing problems that we will meet head on in the 21st century, namely: the impending shortage of crude oil and environmental pollution. None-the-less, a number of scientists and engineers from around the world are intrigued by a rather staggering fact: using only 0.1% of the earth's land space with solar collectors that operate with a collection efficiency of merely 20%, one could gather more than enough energy to supply the current yearly energy needs of all the citizens of the planet. Furthermore, the solar energy reserve is essentially unlimited. No particular individual or government owns it. And its utilisation is ecologically benign. Good enough reasons to expect the vast utilisation of solar energy, if it were not for some very serious drawbacks: solar radiation reaching the earth is very dilute (only about 1 kW per square meter), intermittent (available only during day-time), and unequally distributed (mostly by the equator, as seen in Figure 1). These scientists ask themselves how can we get hold of a sunbeam such that it can be stored and transported from the sunny and uninhabited regions of the earth's sunbelt to the world's industrialised and populated centers outside the earth's sunbelt, where much of the energy is required?

This question has motivated them to search for recipes that convert sunlight and water into a fuel that one can use to propel not only our cars but the entire world economy. In other words, these investigators are looking for processes (and reactors for conducting these processes) that can convert intermittent solar radiation falling in the deserts of the world into storable chemical energy, in the form of fuels, that can be transported to the population centres. Cars running on fuels produced from such a recipe would be, in fact, running on solar energy. These scientists can imagine the patrons of London's Shakespeare Theatre arriving on a sunbeam - even if it happens to be a rainy London evening. They see *solar energy in motion*.



THE ESSENCE OF THE RECIPE

The means by which sunlight can be used to produce fuels for the 21st century can be found in the writings of two of the prominent scientists of the 19th century, Carnot and Gibbs. They created the discipline of Thermodynamics, which is the study of how energy can be converted from one form to another, for example, from solar energy to chemical energy. In very simple terms, Thermodynamics tells us that the higher the temperature at which we supply solar energy to our process, the more creative we can be with what comes out as a final product. For example, if we use sunlight in a typical flat-plate solar collector, we can produce warm water that could be used for taking baths or supplying space heat. Although this type of device can make a great deal of sense for certain local conditions, it will not enable solar energy collected in Australia to be transported to Japan. But if we supply solar energy to a chemical reactor at very high temperatures, near 2300 K, we open up the possibility for such a feat: solar energy collected in Australia can heat homes, supply electricity, propel cars, and more ... in Tokyo!

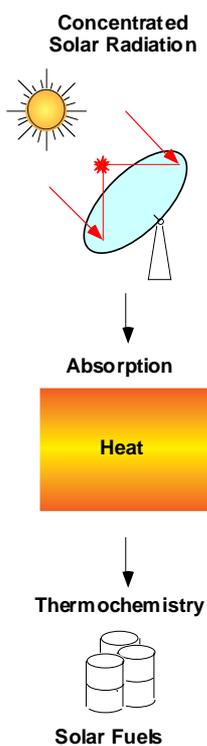


Figure 2: Solar energy conversion into solar fuels: concentrated solar radiation is used as the energy source of high-temperature process heat for driving chemical reactions towards the production of storable and transportable fuels.

Figure 2 illustrates the basic idea: If we concentrate the diluted sunlight over a small area with help of parabolic mirrors, and then capture that radiative energy with help of suitable receivers, we would be able to obtain heat at high temperatures for driving a chemical transformation and producing a storable and transportable fuel. Regardless of the nature of that fuel, the theoretical maximum efficiency of such an energy conversion process is limited by the Carnot efficiency of an equivalent heat engine: with the sun's surface as a 5800 K thermal reservoir and the earth as the thermal sink, 95%

of the solar energy could in principle be converted into the chemical energy of fuels. It is up to us to design and develop the technology that approaches this limit.

We all have experienced hot sunny summer days where cement and black top surfaces get warm. Some of us can even recall using a magnifying glass to ignite leaves and twigs, but it is likely difficult for most people to imagine that sunlight can drill a hole the size of a football through a quarter inch thick piece of steel in less than 10 seconds. But it can be done. The principle is the same one governing the behaviour of the magnifying glass, but rather than using a lens to focus the light, it is focused with a large parabolic mirror. Figure 3 is a photograph of the solar concentrator at the Paul Scherrer Institute, in Switzerland. This parabolic dish follows the sun as it moves across the sky, and reflects and concentrates the sun rays to essentially a small circle. The energy impinging on this small surface is equivalent to the surface seeing 5,000 suns! With this technology one can easily achieve the very high temperatures required for producing solar fuels [1].

SOLAR HYDROGEN - SOLAR ZINC

One possible and certainly very attractive chemical process is the solar production of hydrogen from water. At high-temperatures, and depending on the pressure, water splits into hydrogen and oxygen. Although conceptually simple, the direct splitting of water is impeded by the lack of an effective technique for separating the hydrogen from the oxygen while avoiding an explosion. One way to bypass the separation problem is via a 2-step thermochemical cycle in which hydrogen and oxygen are derived in different steps. For example, a 2-step cycle based on metal oxide "red-ox" systems (reduction-oxidation systems) was proposed for splitting water [2].



Figure 3: The solar parabolic dish at the Paul Scherrer Institute, Switzerland, tracks the sun and concentrates the sun rays 5,000 times into a small circle at its focus.

Figure 4 is a schematic of how the idea works using the zinc oxide red-ox system. In a sunny region of the world, zinc oxide can be brought to the focus of a solar concentrator. If it reaches a temperature near 2300 K, it will decompose to metallic zinc. One could collect the oxygen that is liberated or simply vent it to the atmosphere. In a second step, and without the sun, zinc can be reacted with water to produce hydrogen. Zinc will again become ZnO, which in turn will be recycled back to zinc in the solar step. Hydrogen can be further processed to make other fuels or it can be used directly for producing electricity or other forms of power. Once the hydrogen is expended, it will convert back to water. In this figure you notice a cyclic process. No material is consumed. No material is discharged. The only energy that enters into the process is sunlight. The energy available in the hydrogen used to produce electricity or power is solar energy in disguise.

The reduction of zinc oxide is one example of an energy-intensive process that proceeds at high temperatures and which could be conducted using concentrated solar energy. In fact, many other metal oxides could be thermally reduced using solar process heat. The products are metals which are usable as fuels for generating either high-temperature heat via combustion or electricity via fuel cell and batteries, or for producing

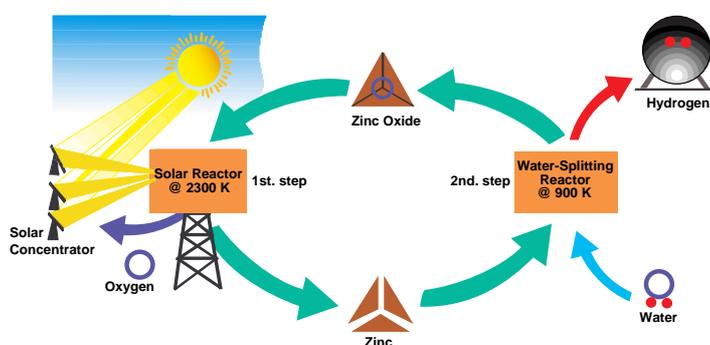


Figure 4: A 2-step thermochemical cycle for the solar production of hydrogen from water. In the first, solar step, zinc oxide is reduced at 2300 K using solar process heat. In the second step, zinc is reacted with water to produce hydrogen. Zinc will again become ZnO, which in turn will be recycled back to zinc in the solar step. The net reaction is $\text{H}_2\text{O} = \text{H}_2 + 0.5 \text{O}_2$; hydrogen and oxygen are derived in different steps, eliminating the need for high-temperature gas separation.

hydrogen and other fluid fuels from water. One such versatile metal is, of course, zinc. Today, metallic zinc is employed primarily as a raw material in the galvanising industry for protecting iron and steel from corrosion. However, zinc exhibits various intriguing advantages when considered, not as a chemical commodity, but rather as a solid fuel. It can be safely handled in air, may be easily transported, and can be efficiently converted either to hydrogen with a water-splitting reactor (and the hydrogen further processed to electricity), or used directly to generate electricity with a zinc/air battery.

BUILDING BRIDGES

As we examine other metals that could be used as fuels, it is of no surprise that the most attractive ones are those requiring high temperatures and lots of energy for winning them from their oxides. That is also the reason why the extractive metallurgical industry is one of the major consumers (if not the major consumer) of industrial process heat, and, consequently, a major producer of greenhouse gases and other pollutants derived from the combustion of fossil fuels for heat and electricity generation. Yet, these emissions can be significantly reduced if the high-temperature process heat were to be supplied by an alternative clean energy source, e.g. concentrated solar energy. A quick look at the economics will show that the large investment associated with the solar collection plant prohibits concentrated solar energy from competing with today's prices of fossil fuels. But this competition is unfair: the price of oil and coal does not account for the cost of pollution abatement. When we start accounting for the externalities of fossil fuel burning, solar energy will become competitive. But we should not wait too long. If the environmental damage associated with increasing greenhouse gas levels reaches the point where rising oceans flood homes in low-lying areas (in developing and developed countries alike), it will be then too late for any remedy.

While working intensively on processes that produce solar fuels from sunlight and water, we are aware that it will take time before this technology will be ready for large-scale commercialisation. It is clear that one should start developing now if one wishes to be ready in 30 years. Nobody likes crash programs; they are expensive and riddled with mistakes. One can avoid them by supporting a continuous program of research, development, and demonstration. The transition from today's fossil-fuel-based technology to tomorrow's solar chemical technology can occur smoothly with the help of processes that mix both fossil fuels and solar energy. Such a mixture can help create a link between present and future technologies. It also can build bridges between present and future energy economies because of the potential of solar to become a viable economic path once the cost of energy will account for the environmental externalities from burning fossil fuels, such as depletion, CO₂ mitigation, and pollution abatement. Figure 5 depicts a process for accomplishing such an energy mixture [3]. It is an example of an important intermediate solution towards a sustainable energy supply system.

You notice in Figure 5 that the input is not only water and sunlight, but also includes natural gas. Notice also that the natural gas is not burned for supplying process heat; that job is being fulfilled by solar energy. Instead, natural gas is being used exclusively as a reactant to serve simultaneously the functions of the reducing agent of zinc oxide and the feed stock for synthesis gas (syngas). Syngas, a gas mixture of primarily hydrogen and carbon monoxide, is the building block of a wide variety of organic chemical commodities, including methanol, which happens to be a promising substitute of gasoline for fuelling our cars. Zinc serves as a recyclable fuel in which the solar energy is stored and can be transported, as we discussed it in a previous paragraph. The chemical products of the overall process are methanol and hydrogen; they have been energetically upgraded with solar energy and therefore are cleaner fuels than the starting fossil fuel. Compared to the heating value of natural

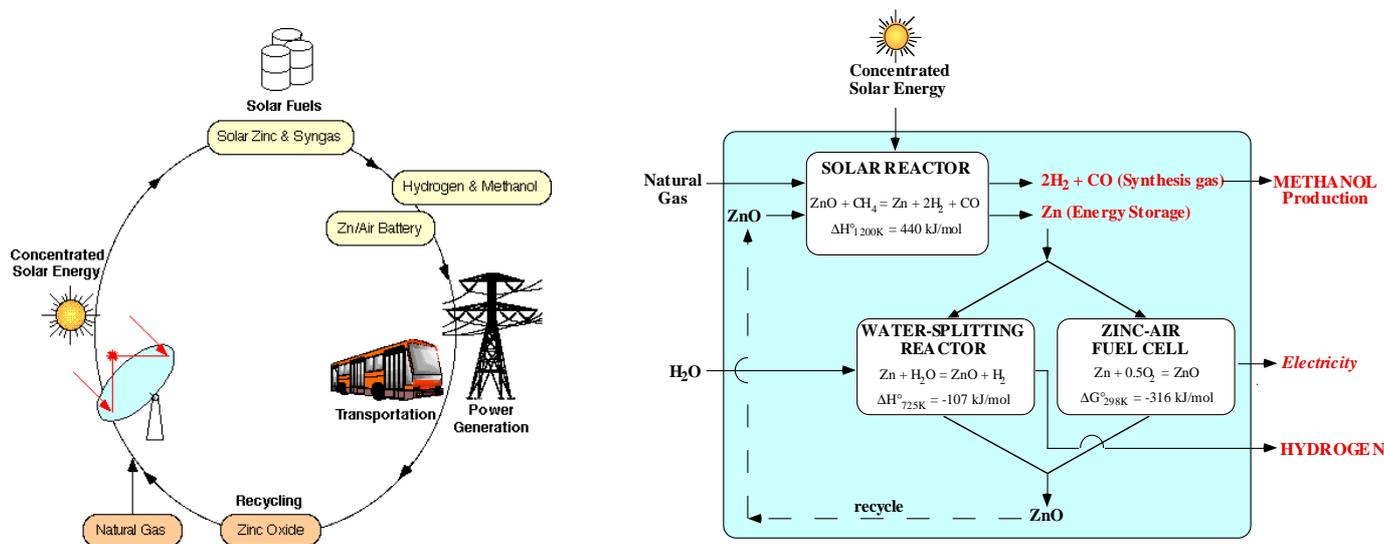


Figure 5: Scheme of a solar process for the production of zinc, syngas/methanol, and H₂/electricity, using natural gas and water as feedstock and solar energy as the source of high-temperature process heat. It consists of two main steps: 1) In a highly endothermic solar step, zinc oxide is reduced with natural gas to form zinc and syngas; syngas is further processed to methanol. 2) In a slightly exothermic step, zinc is used to split water and form hydrogen (not contaminated with carbon oxides) or, alternatively, zinc is used in a zinc/air fuel cell or battery to generate electrical work. In either case, the chemical product is zinc oxide which, in turn, is recycled to the solar step. By this process, solar energy can be converted to solar fuels for storage and transportation.

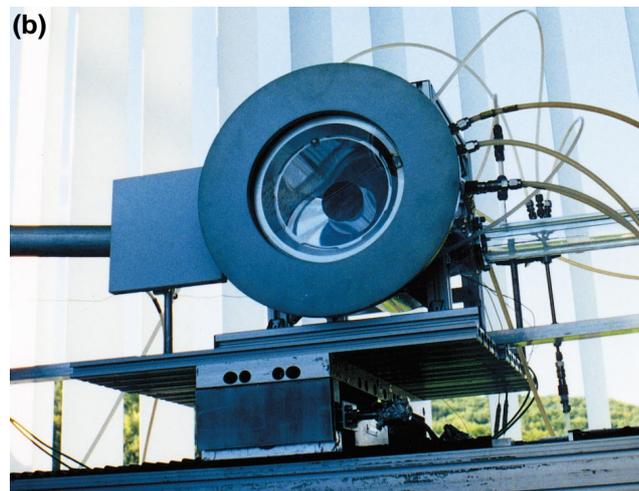
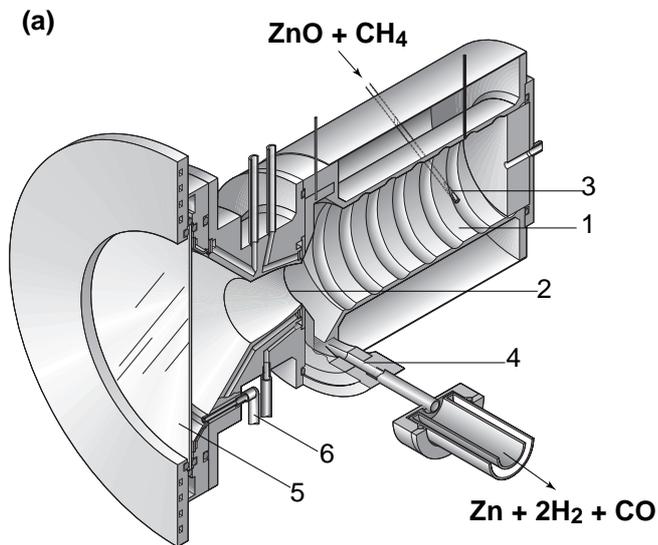


Figure 6: Configuration (a) and photograph (b) of a solar chemical reactor for the co-production of zinc and synthesis gas (syngas). It consists of a cavity-receiver (#1) with a circular aperture (#2) to let in concentrated solar energy. Particles of zinc oxide, conveyed in a flow of natural gas, are continuously injected into the reactor's cavity via a tangential inlet port (#3). The gas-particle stream forms a vortex flow that progresses towards the front following an helical path. The chemical products continuously exit the cavity via a tangential outlet port (#4). The window (#5) is actively cooled and kept clear of particles by means of an auxiliary flow (#6). With this arrangement, the particles of zinc oxide are directly exposed to the high-flux solar irradiation. Such concept provides efficient radiation heat transfer directly to the reaction site where the energy is needed, by-passing the limitations imposed by indirect heat transport via heat exchangers. Energy absorbed by the reactants is used to raise their temperature to 1300 K, and to drive the simultaneous reduction of zinc oxide and reforming of natural gas. The chemical products exiting the reactor are zinc vapor and syngas. (Extracted from Ref. [3]).

gas for electricity generation, this solar process releases half as much CO₂ to the atmosphere. The key reaction of this scheme is the one occurring in the solar reactor, that is, the combined reduction of zinc oxide and reforming of natural gas for the co-production of zinc and syngas. Figure 6 shows a solar chemical reactor prototype designed for conducting such a reaction at about 1300 K. This solar reactor is being tested and developed further at the high-flux solar furnace of the Paul Scherrer Institute, Figure 7.

CONCLUSION

Whether research in high-temperature solar chemistry is forging the connections between old and new technology by mixing fossil fuels and sunlight or developing the scientific and technological know-how for a radically new recipe that mixes sunlight and water to produce fuels from solar energy, the ultimate goal is the same—development of the means by which we can be supplied by a clean, universal, sustainable energy resource. We know enough about the human condition to unequivocally state that we need to avoid the turmoil of a major world-wide energy crisis or the turmoil of major natural disasters associated with man induced climatic changes. One can almost hear in these words an echo from Macbeth that reverberates through the theatre,

*„Double, double toil and trouble,
Fire burn and cauldron bubble.”*

We hope to avoid these bubbling cauldrons by riding out of the 21st century on a sunbeam.

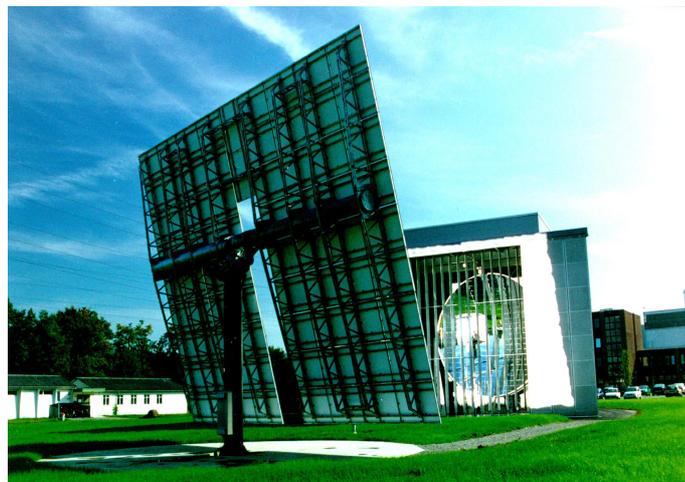


Figure 7: The high-flux solar furnace at the Paul Scherrer Institute, Switzerland, consists of a sun-tracking heliostat on axis with a parabolic dish concentrator. It can deliver 40 kW solar thermal power at peak solar concentrations exceeding 5,000 suns. The solar concentrating research facilities are used for testing high-temperature solar chemical reactors.

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