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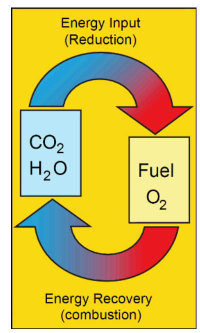
Solar Recycling of Carbon Dioxide into Hydrocarbon Fuels

Sandia National Laboratories seeks to address two of the most daunting problems facing humankind in the twenty-first century: energy security and climate change. The vision for achieving this is captured in one deceptively simple chemical equation for solar fuels production:

$$\text{Solar Energy} + xCO_2 + (x+1)\,H_2O \rightarrow \underbrace{C_xH_{2x+2}}_{\text{(liquid hydrocarbon fuel)}} + (1.5x+.5)\,O_2.$$

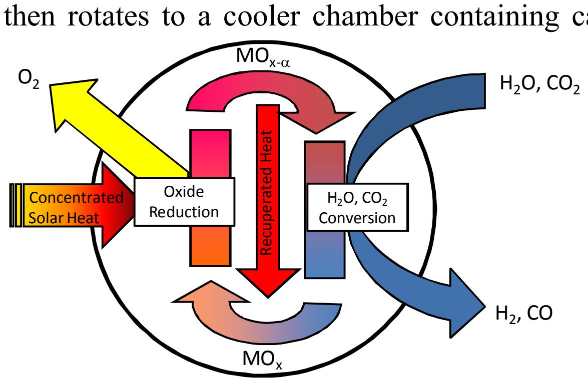
The equation above can be thought of as a simplified depiction of photosynthesis, the low-temperature biological process that is at the heart of the biomass approach to fuel production. Regrettably, photosynthesis and, consequently, biofuels, currently have a very low sunlight-to-hydrocarbon conversion efficiency. Thus, an alternative approach that is not limited by the inefficiency of photosynthesis and that more directly and much more efficiently leads to a liquid fuel is highly desirable.

The Sandia "Sunshine to Petrol" (S2P) team is developing technology based on concentrating solar power (CSP) to provide high temperatures for driving chemical reactions. In this case, it is helpful to view the equation shown above as depicting "reverse combustion." To accomplish this, Sandia is developing a novel thermochemical heat engine driven by concentrated solar irradiation. The engine converts either carbon dioxide or water to carbon monoxide or hydrogen, respectively. Of course CO and H_2 are the precursors to high-quality synthetic fuels. Although significant progress has been made, much of the work has, by design, been focused on demonstrating the promise of the approach with the expectation that this would open the door to opportunities to make the required advances in the underlying science and technology. Indeed it is fair to say that significant gaps in scientific knowledge and technology remain in the critical areas of active metal oxide materials, integrating these materials into reactor concepts, and in providing a complete systems context to these processes and devices.



The Metal-Oxide Thermochemical Cycle

At the heart of the S2P process is a metal-oxide-based thermochemical cycle, currently being implemented in a unique thermochemical heat engine, the Counter-Rotating-Ring Receiver Reactor Recuperator, or CR5. Within the engine, reactive solid rings are continuously thermally and chemically cycled to produce oxygen and carbon monoxide (or hydrogen) from carbon dioxide (or water) in separate and spatially isolated steps (see schematic). A parabolic solar concentrator heats a metal-oxide (MO_x) on a rotating ring to ~1500 °C, causing it to release oxygen ($MO_{x-\alpha}$). The ring then rotates to a cooler chamber containing carbon dioxide (or steam). At this lower temperature, thermodynamics favors re-oxidation of the reduced material back to its original state. This cycles repeats in a continuous fashion. A key feature of the CR5 is the counter-current recuperation of heat between the high-temperature oxygen-generating thermal reduction and the lower-temperature hydrogen- or carbon monoxide-producing step. This recuperation is key to achieving high efficiencies.



Current Status

A first of its kind CR5 prototype has been designed, built and operated on-sun and CO_2 has been split to CO and O_2. Materials with sufficient kinetics and capacity have been identified that should allow this device to achieve several % solar to CO efficiency within the coming months. Our models suggest an eventual pathway to high efficiency and viability. New materials as well as advances to reactor designs will be needed to achieve our long-term goals of 25% or greater thermal and 9+% sun to fuel efficiency. Thermochemical reactors are by necessity a complex non-steady state environment with coupled heat transfer, mass transfer, and chemical reaction. Many of the processes occurring on and within the critical metal oxide working materials during actual operating conditions are only understood at a very superficial level. Only with greater knowledge and understanding of the fundamental processes and materials will we be able to apply the most rational design process for both the materials improvements and reactor and system designs.

The CR5 device (left) contains the counter-rotating ceramic rings. The solar energy from the concentrator passes through the aperture (hole in the white disk and onto the reactive rings. At right, the CR5 device in place at the solar furnace test facility.

The Path Forward

A concerted scientific and engineering effort is needed to translate the possibility of solar thermochemical fuels into a reality. In our view any successful effort must consist of at least three focus areas: materials, reactor design and engineering, and systems and economics. The materials effort must be formulated to meet two critical ends: developing the science base to design advanced metal oxides for thermochemical conversions, and developing the quantitative knowledge and models of reactions and transport processes on and within these materials required to produce a unique, highly efficient thermochemical heat engine. Specifically, we require quantitative knowledge of current and prospective materials regarding phases expected as a function of temperature and reaction environment, and kinetics (rates and pathways) of the transformation of interest including surface reactions, and bulk transport and transformation. Additional challenges that must be given significant consideration include fabrication of oxides into durable and optimal shapes, and characterizing and managing the effects of aging (phase segregation, migration, creep, flow, cracking, breaking, volatilization, etc.)

The materials science effort must be closely associated with a reactor design and build effort. A principal reason for this is that the reactor design sets quantitative targets for materials performance; often these performance standards cannot be defined outside of the specific reactor context. Additionally, constructing and operating the reactor helps to validate and refine these requirements and leads to the discovery of other issues that may well otherwise go unidentified. As an example, one may define a conversion rate of CO_2 or H_2O required relative to a solar flux to achieve a desired efficiency. In the CR5 concept there are numerous parameters that can be manipulated to achieve this rate including oxide composition, mass loading of oxide, rotation rate of the oxide, surface area of the oxide, temperature of the reaction, flow rate of the gas, and so on. However, these parameters are not independent. For example, if the mass loading and/or rotation speed is changed, then the temperature of the metal oxide (heat transfer from solar flux and from ring to ring) will vary as well and so on. Hence the required rate targets are intimately tied to the context within which they will be applied. The reactor also defines the additional physical and chemical challenges that the materials must meet such as the stress of high energy fluxes and rapid temperature variation. Thus, it is critical then that the reactor context be understood and characterized at least as well as the materials. Characterizing and modeling the behavior of these processes is challenging because the problem is inherently multi-physics and multi-scale. The multi-physics challenges include coupled analysis of transient heat and mass transfer of multiple species with chemical reaction, all additionally coupled with radiative exchange and moving parts. The multi-scale challenges include the multi-component heat/mass transfer between the gas phase and the solid phase with chemical reaction occurring on the surfaces and diffusion within the solid phase on the small-scale or localized level. These localized physics must be coupled to or integrated with a much larger-scale analysis that addresses the system-level physics and the bulk heat/mass transfer processes.

Finally, any credible effort to develop fuels from sunlight must include an analytical effort to place the emerging technology within the context of the larger systems and world. The effort should define overall systems targets and the optimum deployment strategies and scales. This in turn will define performance targets and scales for system components such as the thermochemical reactor (in our case), identify the critical technology gaps and components to target for improvement, and also establish the overall fuel from sunlight economics. We must develop models at both at the unit-op and at the plant level as well as an associated economic analysis. A unique part of this challenge is that we must develop credible models for evolving components that do not as yet exist in their final form and that can be validated only in part. An additional challenge is presented by the fact that the system is powered by solar energy, an intermittent resource that requires consideration of dynamic operation.

Sandia has already made significant investment in S2P and is well-situated from both a technology and facilities standpoint to be a world leader in thermochemical fuels. The laboratory has recently committed to funding the effort for the coming fiscal year. We are interesting in developing relationships with customers who can partner with us during this final project year and leverage that work by supporting further efforts to develop and refine future generations of solar thermochemical heat engines.

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