

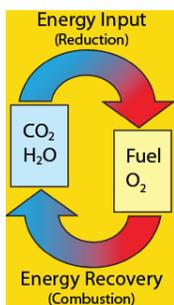
Sunshine to Petrol



Solar Recycling of Carbon Dioxide into Hydrocarbon Fuels

Sandia 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 that defines solar fuels production: Solar Energy + $x\text{CO}_2 + (x+1)\text{H}_2\text{O} \rightarrow \text{C}_x\text{H}_{2x+2} + (1.5x+0.5)\text{O}_2$ (liquid hydrocarbon fuel)

Solar irradiation is a sustainable energy source of a magnitude sufficient to meet projections for global energy demand, provided it is used efficiently. The equation 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 alternate approach, not limited by the inefficiency of photosynthesis-, and that more directly and much more efficiently leads to a liquid fuel-, is highly desirable.



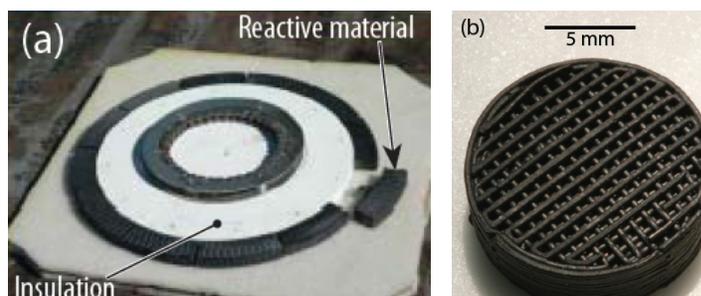
The development of a process that efficiently, cost effectively, and sustainably re-energizes thermodynamically spent feedstocks to produce reactive fuel intermediates would be a game-changing, unparalleled achievement. This is the key challenge that must be surmounted to solve the intertwined problems of accelerating energy demand and climate change.

The S2P process incorporates CO₂ into the vision for the hydrogen economy powered by the sun.

The Sandia "Sunshine to Petrol" (S2P) team is developing technology based on concentrating solar energy that provides high temperatures to drive chemical reactions. In this case, it is helpful to view the equation as depicting "reverse combustion." To accomplish this,

Sandia is developing a novel thermochemical heat engine. The engine converts either carbon dioxide or water to carbon monoxide or hydrogen, respectively. Carbon monoxide and hydrogen are the universal energy-rich

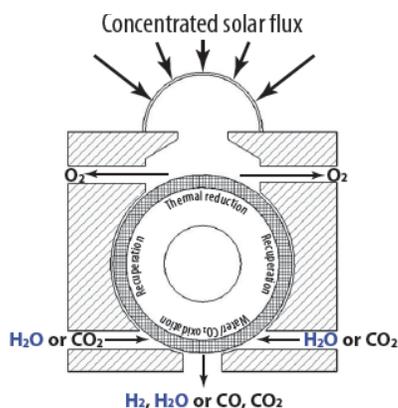
building blocks for producing synthetic fuels. These synfuels can be equivalent to today's fossil-derived liquid products that remain the "gold standard" of transportation fuel. To realize this concept, the team is addressing and solving complex chemical, materials science, and engineering challenges associated with advanced thermochemical heat engines and the crucial enabling metal-oxide working-materials.



(a) The CR5 device employs a mixed valent metal oxide, arranged around the perimeter of a rotating ring. Shown here are iron oxides supported in a yttria stabilized zirconia (YSZ) matrix that exploit the "ferrite" thermochemical cycle in which Fe^{+3} reduces to Fe^{+2} and reoxidizes back to Fe^{+3} . (b) A monolithic test sample fabricated from a cobalt ferrite/YSZ composite. Its lattice structure provides high geometric surface area.

The Metal-Oxide Thermochemical Cycle

The heart of the S2P process is a unique metal-oxide-based thermochemical heat engine, the Counter-Rotating-Ring Receiver Reactor Recuperator, or CR5. Within the engine, reactive solid rings are continuously cycled thermally and chemically to produce oxygen and carbon monoxide or hydrogen from carbon dioxide or water in separate and spatially isolated steps (see figure on next page). High temperatures are required to drive this process. A solar concentrator heats the ceramic oxide reactant material on a rotating ring to $\sim 1500\text{ }^\circ\text{C}$ ($2700\text{ }^\circ\text{F}$), causing it to give up some of its oxygen. The ring then rotates to a colder chamber containing carbon dioxide. At this lower temperature, the oxygen-deficient reactant material is chemically able to 'steal' an oxygen atom from the carbon dioxide, leaving behind carbon monoxide. The cycle described here repeats continuously.



Side view of the CR5 showing a single ring. In the top chamber, concentrated solar irradiation heats the ferrite to ~1500 °C and thermally reduces the iron, driving off some oxygen. In the opposite chamber, the oxygen-deficient reduced ferrite is exposed to either water vapor or carbon dioxide at a lower temperature to produce either hydrogen or carbon monoxide. Heat is recuperated between the ceramic oxide materials as they leave the two reactant chambers by counter rotating the reactive rings relative to one another.

monoxide-producing re-oxidation of the metal oxide. This recuperation is key to achieving high overall efficiency of the thermochemical process.

Materials Challenges

The thermochemical process that occurs within the CR5 engine creates extreme demands on the ceramic ring materials. The reactive rings must maintain structural integrity and high reactivity after extensive thermal cycling. In addition, the monolithic ring structures must have high geometric surface area for effective gas-solid contact and reaction rates and for uniform adsorption of the concentrated solar radiation.

The S2P team found that directly fabricating structures from the active components e.g. Fe oxide composites with yttria-stabilized zirconia, or cerium oxides, yields robust and reactive monolithic parts that maintain productivity over hundreds of cycles of laboratory and solar testing. Furthermore, they demonstrated for the first time that carbon dioxide splitting to carbon monoxide and oxygen could be accomplished cyclically with both iron- and cerium-based materials.

The same thermochemical cycle can be used to remove oxygen from water vapor to produce hydrogen. The carbon monoxide and hydrogen are mixed to make syngas, which can be turned into methanol, gasoline, jet fuel, or almost any type of hydrocarbon fuel. A key feature of the CR5 is the counter-current recuperation of heat between the high-temperature oxygen-generating thermal reduction of the metal oxide and the lower-temperature hydrogen- or carbon

The Path Forward

The S2P team, assembled from many organizations across Sandia in both New Mexico and California and including collaborators in a number of universities across the country and a distinguished board of external advisors, has proven out the CR5 concept and continuous solar driven production of CO and O₂ in isolation from one another has been demonstrated in a first-generation prototype CR5.

Ongoing work is focused on materials and reactor improvements and on demonstrating steady state operation and establishing record efficiencies. The team believes that they are still probably 15 to 20 years away from a market-ready device. Success will consist of continuously improved generations of prototypes and S2P systems, a new generation every three years with significant improvements in performance (measured as the amount of solar energy converted into the fuel), greater durability, and reduced cost.

The genuine possibility of making real the promise of economically and sustainably creating liquid fuels from combustion products dries this effort and the team forward.



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 in front of Rich Diver) and onto the reactive rings. Above, the CR5 device is in place at the solar furnace. The parabolic reflector of segmented mirrors can concentrate the sun's energy up to 6750 times ambient solar radiation—the CR5 easily achieves ~1500 °C on the reactive rings.

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