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Final Report Reimagining Liquid Transportation Fuels: Sunshine to Petrol

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Final Report

Reimagining Liquid Transportation Fuels: Sunshine to Petrol

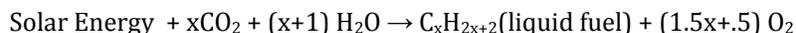
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Abstract

Two of the most daunting problems facing humankind in the twenty-first century are energy security and climate change. This report summarizes work accomplished towards addressing these problems through the execution of a Grand Challenge LDRD project (FY09-11). The vision of Sunshine to Petrol is captured in one deceptively simple chemical equation:



Practical implementation of this equation may seem far-fetched, since it effectively describes the use of solar energy to reverse combustion. However, it is also representative of the photosynthetic processes responsible for much of life on earth and, as such, summarizes the biomass approach to fuels production. It is our contention that an alternative approach, one that is not limited by efficiency of photosynthesis and more directly leads to a liquid fuel, is desirable. The development of a process that efficiently, cost effectively, and sustainably reenergizes thermodynamically spent feedstocks to create reactive fuel intermediates would be an unparalleled achievement and is the key challenge that must be surmounted to solve the intertwined problems of accelerating energy demand and climate change. We proposed that the direct thermochemical conversion of CO₂ and H₂O to CO and H₂, which are the universal building blocks for synthetic fuels, serve as the basis for this revolutionary process. To realize this concept, we addressed complex chemical, materials science, and engineering problems associated with thermochemical heat engines and the crucial metal-oxide working-materials deployed therein. By project's end, we had demonstrated solar-driven conversion of CO₂ to CO, a key energetic synthetic fuel intermediate, at 1.7% efficiency.

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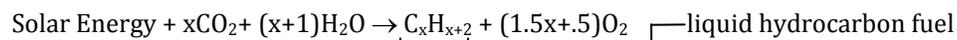
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1.0 Project Purpose

This project was conducted as the first steps towards a technological solution to two of the most daunting problems facing humankind: energy security and climate change. Our vision for the project is captured in one deceptively simple chemical equation:



Practical implementation of this equation seems far-fetched because it effectively describes using solar energy to reverse combustion. However, it also describes photosynthesis and, as such, summarizes the biomass approach to producing fuel. Regrettably, photosynthesis and consequently the biofuels approach have a very low sunlight-to-hydrocarbon conversion efficiency and suffer from a number of other shortcomings. Thus, developing an alternative approach that more-directly and -efficiently produces a liquid fuel is desirable. Developing a process that sustainably and cost-effectively reenergizes thermodynamically spent feedstocks to create reactive fuel intermediates would be an unparalleled achievement and is the key challenge that must be surmounted to solve the intertwined problems of accelerating energy demand and climate change. Our proposition was that the direct thermochemical conversion of CO_2 and H_2O to CO and H_2 , which are the universal building blocks for synthetic fuels, should serve as the basis for this revolutionary process. To realize this concept, we addressed complex chemical, materials science, and engineering problems associated with thermochemical heat engines and the crucial metal-oxide working materials deployed therein.

2.0 Context, the S2P Concept, and Thermochemical Cycle Introduction

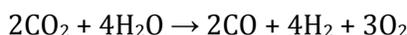
Energy resources are the foundation for developed economies and are inextricably linked to national security, social stability, and quality of life. The nation's increasing reliance on costly imported petroleum and fuels [1] and "peak oil" concerns create an increasing vulnerability to potentially high-consequence supply disruptions. Diversification of supplies, including developing additional independent, domestic sources of transportation fuel, is essential for the future security and economic well-being of the US. Additionally, the effect of unmitigated CO_2 releases on the global climate is a growing concern both here and abroad. Independence from energy imports can be achieved to a great degree through the utilization of less-conventional hydrocarbon resources such as coal, oil-shale and tar-sands. However, tapping into and converting these resources into liquid fuels only exacerbates green house gas emissions as they are carbon rich, but hydrogen deficient. Solving this conundrum requires us to adopt revolutionary thinking. We must recognize that hydrocarbon fuels are energy carriers, not energy sources. ***That is, with an***

appropriate persistent energy source, there is the potential to effectively reverse combustion and "re-energize" CO_2 and H_2O back into hydrocarbon form in a process analogous to, but more

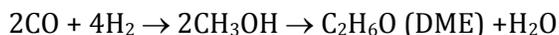
1. The U.S. imports almost 2/3 of the petroleum that it consumes; 2/3 of that is used in the transportation sector.

direct and efficient than, the one that produced fossil fuels. We call this process “Sunshine to Petrol” or S2P.

Solar insolation is a very attractive persistent energy source as it is by far the largest exploitable renewable resource and is technically capable of supplying all of the global energy needs utilizing only a few per cent of the world’s desert area. However, the efficient conversion of solar energy to stored chemical energy in the form of hydrocarbons is a significant challenge. Photosynthesis is the biological route for accomplishing this conversion, but the sunlight-to-stored chemical energy efficiency is limited by the photosynthetic step alone to only a few percent on average [2]. The most general and straightforward chemical approach to converting CO₂ and H₂O into a fuel is through the intermediate production of syngas. Syngas is roughly a 1:2 mixture of CO and H₂. That is, the key to chemically converting CO₂ and H₂O into fuel is the following “reenergizing” reaction:



Of course, the reduction of CO₂ and H₂O (carbon dioxide splitting, CDS, and water splitting, WS) may be carried out individually rather than in a single step or apparatus. Once syngas is obtained, there are numerous commercial processes for the subsequent production of liquid fuels, including alcohols, ethers (e.g., methanol and dimethyl ether as shown below), gasoline, jet fuel, diesel and other products.



The reactions leading to hydrocarbons from syngas are thermodynamically “downhill” at the applicable temperatures. Thus, the most challenging and energy-consuming chemical processes required for closed cycle hydrocarbon manufacture and use is syngas production, i.e. CDS and WS.

Hydrogen can of course be produced electrolytically from water. Selective electrochemical reduction of CO₂ is not yet a realistic alternative, but CO can be produced from H₂ and CO₂ with additional energy input via the endothermic Reverse Water Gas Shift (RWGS) reaction:



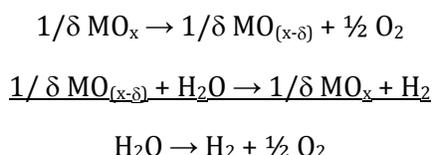
A reasonable annual average estimate for the photovoltaic-powered water electrolysis step is 7% efficiency. In this case, the primary factor limiting solar-to-chemical efficiency is the conversion of sunlight to electricity, as electrolytic system efficiencies of 73% have been reported [3].

Avoiding the solar to electric conversion altogether is a potentially attractive avenue for further improving the efficiency. However, thermolysis of water is not thermodynamically favorable even at the impractically high temperature of 3000 °C. Furthermore, if direct dissociation were to be accomplished, it would remain to perform a difficult high temperature quench and H₂/O₂ separation. The elegant work-around for these problems is to couple two or more chemical reactions that sum to WS, and then perform these reactions in a cyclic manner, recycling all the

2. J.S. Dukes, Climatic Change 61 (2003) 31.

3. J. Ivy, National Renewable Energy Laboratory Report NREL/MP-560-36734 (2004).

reactants and products other than H₂O, H₂, and O₂. Conceptually, thermochemical cycles are heat engines that drive endothermic chemical reactions and that have the potential to be more efficient than electrolytic approaches. The basic thermodynamic principles are described elsewhere [4]. Concentrating solar power (CSP) provides efficient utilization of solar energy and access to temperatures in excess of 1500 °C. This allows the consideration of CSP-driven ultra-high temperature two-step metal oxide based cycles. An example of a thermochemical WS cycle based on a hypothetical metal oxide working material (MO_x) is shown below. CDS is entirely analogous. Thermodynamics requires that the two chemical reactions of the cycle be carried out at different temperatures: the endothermic thermal reduction of the metal oxide (TR) at a high temperature, and the exothermic H₂-producing oxidation step (WO) at a lower temperature. It is necessary therefore to cycle the temperature of the oxide as well as the gaseous environment.



From a design standpoint, the relatively simple two-step metal oxide cycles are particularly attractive as they involve only gas-solid reactions and the two reactions comprising the cycle can be

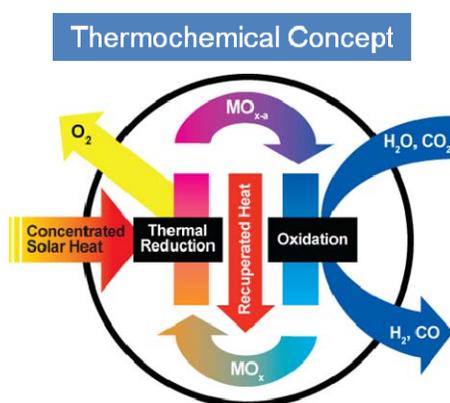


Fig. 2. Schematic representation of an operating 2-step metal-oxide thermochemical cycle.

temporally or spatially separated from one another, eliminating cause for difficult gas phase separations. However, the required temperature cycling introduces large efficiency losses into the system unless the heat is recuperated between the two steps. Further, until very recently, metal oxide thermochemical cycles were a laboratory curiosity, made impractical by the fact that the materials required processing between each successive step to ensure reactivity.

3.0 Project Goals, Structure, and Participants

Briefly, at the highest level the goal of this project was to establish credibility for the S2P approach to fuels from sunlight. This was understood to mean that the effort needed to demonstrate that the approach is technically sound, that there is a realistic pathway to economic and commercial viability, and that the approach is scalable to the extent that it could potentially meet a large fraction of U.S. liquid fuel demand. Specific high level goals derived

4. See for example J.E. Funk and R.M. Reinstrom, *Ind. Eng. Chem. Process Des. & Dev.* 5 (1966) 336 and B.A. Abraham and F. Schreiner, *Ind. Eng. Chem. Fundam.* 13 (1974) 305. As a caution, note the derivations were carried out for WS in the context of nuclear hydrogen production assuming stoichiometric reactions of pure compounds and upper temperature limits of < 1100 °C. Prior to our own efforts, thermochemical CDS had not been addressed.

from this vision included demonstrating the thermochemical conversion of CO₂ to CO at a solar-to-fuel efficiency of 2%, demonstrating a pathway for 5% efficiency, and defining an approach to 20%. In other words, it was understood from the beginning that the three-year time frame of the project would be insufficient to produce a commercial product given the immaturity of the associated science and technology. However, the time frame would allow for the development of the underlying science and tools needed to provide a very strong basis to move the field of thermochemistry forward. Keeping an eye towards larger systems and economics issues was deemed vital as well so that the work would be relevant and so that a community of interest and support could be built with confidence.

To summarize, the high-level goals included:

- Demonstrating the thermochemical conversion of CO₂ to CO at a solar-to-fuel efficiency of 2% and a pathway for 5% efficiency, and defining an approach to 20% efficiency.
- Developing thermodynamic models of active oxides.
- Quantifying the fundamental transport and reaction rates and mechanisms.
- Developing and validating kinetics models.
- Defining optimum material composition and geometry.
- Modeling heat engines at multiple scales.
- Designing and constructing a next generation heat engine.
- Implementing full “Sunshine to Petrol” systems and economics models.
- Communication of results and building a community of interest and support.

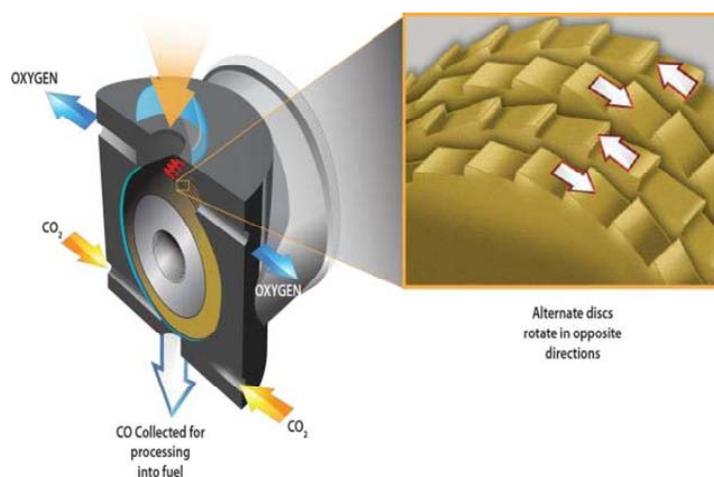


Fig. 3. Simplified drawing of the Counter-Rotating-Ring Receiver Reactor Recuperator (CR5) prototype.

The high-level technical and programmatic goals and outcomes led to a natural structuring of the project around three principle interconnected focus areas: Reactors, Materials and Systems. The Reactors component was further subdivided into three areas: 1) Reactor development and operation (mainly the CR5 prototype – see publications list for details,) 2) Reactive structures, and 3) Reactor Modeling. Similarly, the Materials area was subdivided into 1) Materials characterization and development, 2) Thermodynamics and reaction kinetics, and 3) Surface reactions and bulk transport. The Systems area largely focused on efforts in plant design and

economics but also included an effort in separations. Although details are not provided here, each of these sub-areas was further organized with well-defined goals and tasks.

Leads and principal staff for the focus areas over the course of the project included:

Principal Investigator: James E. Miller

Program Manager: Ellen B. Stechel

Director Champion: Carol L. Adkins

Programmatic Director Champion: Margie L. Tatro

Reactor:

Reactor Design: Richard B. Diver, Nathan P. Siegel

Reactive Structures: Nathan P. Siegel, Terry J. Garino,

Reactor Modeling: Roy E. Hogan, Ken S. Chen

Materials:

Characterization and Development: Andrea Ambrosini, Eric N. Coker

Thermodynamics and Kinetics: Mark D. Allendorf, Anthony H. McDaniel

Surface Reactions: Gary L. Kellogg, Ivan Ermanoski

Systems:

Design and Economics: Daniel E. Dedrick, Terry A. Johnson

Separations: Chad L. Staiger

University collaborators were also prominent and an important part of the project. These included:

Darryl James, Texas Tech University – reactor modeling and validation

Christos Maravelias, University of Wisconsin – system modeling and economics

Al Weimer, University of Colorado – materials kinetics and development

Chris Wolverton, Northwestern University – computational materials science

During the final year of the project fabrication of a large number of reactive ring structures at an increased rate was necessary and a strong team was formed around this need. Leaders in this effort included:

Overall coordination, tape casting and lamination of ceria fins: Lindsey R. Evans

Tape casting lead: Christopher B. DiAntonio

Fabrication and assembly: John Stuecker – Robocasting, LLC

Numerous others beyond these leads provided valuable contributions and insight. Please refer to the publications and presentations lists and the acknowledgements for a fuller accounting.

The project also benefitted greatly from the contributions and recommendations of a distinguished and committed external advisory board (EAB):

George W. Crabtree, Argonne National Laboratory – Board Chair

Gary Dirks, Arizona State University – Associate Chair

Mike A. Aimone, Battelle's National Security Global Business

Charlie Campbell, University of Washington

Martha Krebs, University of California, Davis

Tom Kreutz, Princeton University

Terry Mazanec, Consultant, T-MAZ LLC

Bill Schneider, University of Notre Dame

4.0 Project Risk/Reward

Our statement of the Sunshine to Petrol project's purpose, "a technological solution to two of the most daunting problems facing humankind: energy security and climate change," speaks to the nature of the impact we seek to have nationally and, in fact, globally. That is, the technical hurdles and the potential reward are both consistent with the definition of Grand Challenge, and merit the attention of a National Laboratory. Of course an important hallmark of LDRD programs, and of Grand Challenge projects in particular, is that they by nature embody a significant risk. This project also met that expectation. It was the goal of the project team to anticipate the risks and mitigate them whenever possible. Some of the risks and possible mitigating factors that were identified in the proposal stages are provided below by focus area. With the benefit of hindsight, the second materials risk proved to be the most challenging to overcome.

- The active materials must have favorable thermodynamics and rapid kinetics.
 - There is leeway to put additional work into the system (e.g. reduced pressure) to drive reactions at conditions where kinetics may be more favorable, but thermodynamics are less favorable.
 - Much of the project focus is on elucidating rate limiting steps so that improvements may be made.
 - Applying new quantitative models of actual processes should improve material utilization.
- The active materials must be fabricated into parts that remain chemically and physically stable under extreme conditions.
 - Results for known complex materials are positive, reactivity increases with time-on-stream.
 - New single-phase active materials should be more physically and chemically robust.
- The heat engine is a complex device that must efficiently integrate transient heat and mass transport and chemical reaction across multiple scales.
 - These two-step cycles are amongst the simplest thermochemical cycles ever devised.
 - This team has unparalleled experience and tools to design new and unique solar heat engines
- S2P may be uneconomical
 - Numerous models show approaches with less efficient use of sunlight (e.g. electrolytic H₂ + CO₂ to methanol) than our projections are approaching viability.
 - Experience with H₂ production, for example, suggests costs will fall as technology matures.

Additional risks were identified during the course of the project by both the team and by the EAB and corrective actions were taken as possible. These risks mainly fell in the category of threats to the project schedule due to equipment outages and the physical durability of reactor components. The distribution of resources between activities aimed at developing materials to meet long-term (post-project) goals (e.g. new classes of thermochemical materials), and developing and understanding materials from known classes to facilitate completion of the shorter-term demonstration goals and provide a learning platform was a particular and ongoing challenge. The phrase "the paradox of materials that are good enough, but not good enough" was adopted as a brief description of the challenge being managed. That is, it was important to provide materials to demonstrate key concepts and to establish a platform for testing and validation. However, it was equally important that a credible case be made that variations on existing materials, or alternate

materials, would eventually be able to meet the long-term goals needed for the technology to be commercially viable.

5.0 High Level Summary of Accomplishments

This section provides an overview of progress over the course of the project (FY09 and 10) with emphasis on some of the major accomplishments at the conclusion of the project (FY11). More detailed information is available in the publications and presentations documented below.

Fiscal Year 2009

Materials

The promising iron oxide/zirconia or yttria-stabilized zirconia (Fe/YSZ) system was the focus of the materials effort in FY09. The overall strategy was to provide characterization of this material for reactor demonstration and modeling efforts, while also working to develop a deep fundamental understanding of why and how the particular combination of these materials functions so well, when individually they cannot be effectively cycled for H₂ or CO production. An important insight was that Fe is soluble in YSZ and in fact appears to be highly mobile within the material. The team demonstrated and characterized thermally-driven iron oxide transformations and migration in and out of YSZ substrates via in-situ x-ray diffraction, microscopy, etc. The team developed procedures for analyzing and imaging YSZ samples by low-energy electron diffraction (LEED) and low-energy electron microscopy (LEEM) and expanded our ultrahigh vacuum surface science capabilities. We collected kinetic data for model materials in a stagnation flow reactor (SFR) and correlated the results with the presence of a spinel phase to develop a first-generation kinetic model of redox materials. In addition, we collected kinetic data for CO₂ and H₂O splitting over ceria/zirconia monoliths.

In the subarea of thermodynamics and computational materials science, the team evaluated density functional theory (DFT) functionals as a mechanism for filling gaps in the thermodynamic database for metal-substituted ferrites, and a path forward was identified for modeling most materials of interest. We also developed a computational method to predict iron solubility in yttria-stabilized zirconia (YSZ) that correlated to our empirical findings.

Metal volatility was identified as a potential problem with the ferrite-based chemistries. We thus evaluated metal oxide volatility as function of temperature and steam exposure to guide operations and prioritize materials. We also experimentally evaluated iron loss from model materials and constructed a materials durability apparatus.

Reactor

In FY09, the team updated the solar test facility including controls and data acquisition and mounted the counter-rotating-ring receiver/reactor/recuperator (CR5) prototype to begin operations. After initial experimentation, we developed and mounted our second-generation CR5 rings. It became clear that increasing ring durability was going to be an important and difficult

challenge. As result of testing, key attributes for the reactive materials and associated hardware were better known and better defined. By the end of the year we had identified and fabricated three promising monolithic structures. During this process we developed new techniques for fabrication. During this year we also developed and implemented a 2D, 2-phase model of our CR5 and developed concepts for a simplified apparatus designed to facilitate characterizing heat transport within the CR5.

Systems

Our systems team established a baseline architecture using ASPEN process modeling software that includes water gas shift, separations, and methanol synthesis and assembled an ASPEN flow sheet to represent the CR5. We also performed a comparative analysis of methanol production via two different pathways: (CO + H₂O) and (CO₂ + H₂) to determine if the potential advantage of splitting CO₂ rather than H₂O might be realized. This established a break-even price for the CO or H₂. With this systems analysis in hand, we were able to identify the major cost drivers for the complete sunshine to petrol (S2P) system. These studies clearly pointed to the separation and recovery of CO and CO₂ as a major contributor to the cost and energy burden. Experimental work directed at minimizing these costs led to the creation of new CO₂ absorbers with demonstrated capacities >1.5 mmol/g.

Fiscal Year 2010

Materials

During this second year, we continued to build a scientific foundation around ferrites, while also transitioning to include more effort on ceria-based materials. We characterized in detail the solubility of iron in YSZ as a function of loading, oxidation state, and temperature. This solubilized iron is highly mobile and very accessible to redox chemistry. That is, we determined that in the Fe/YSZ system, the solubilized iron is responsible for the bulk of the redox capacity, while iron in excess of the solubility limit is present as “bulk” ferrite particles that provide virtually no additional capacity. In the surface science laboratory, we grew ultrathin films of iron oxide on YSZ. Using LEEM, we observed real-time transformations including structuring, phase change, and what was tentatively identified as mixing and de-mixing phenomena.

In order to choose the optimal material for the CR5 demonstrations, we measured global rate parameters for peak H₂ and CO production for numerous ferrite and ceria materials. Our team demonstrated that the full rate expression is dependent on sample geometry and preparation and identified likely mechanisms. We demonstrated high activity for monolithic ceria materials and characterized the reaction via various in situ probes including high-temperature x-ray diffraction and ambient-pressure x-ray photoelectron spectroscopy. A potential shortcoming of ceria is its poor compatibility with many other refractory materials, and also its relatively small redox capacity under practical conditions. We directed our computational materials resources to address these issues as well as to the question of reaction mechanisms.

Reactor

Using ferrites, we demonstrated key features of the CR5 design including continuous production and separate recovery of CO and O₂. Following this success, we transitioned the CR5 to the next-generation ceria materials and new reactive metal-oxide rings were fabricated. Our laboratory evaluations indicated ceria should perform sufficiently to meet the project goals, although we continued to evaluate the potential for loss of the reactive material through volatilization.

Our computational model for energy recuperation was improved as was the geometric fidelity of the reactor model, thereby allowing for assessment of more-realistic flow conditions. In addition, the distribution of solar flux for operating conditions expected during CR5 testing was calculated. These modeling/simulation efforts began to bear fruit when we modified the CR5's reactant rings to reduce thermal stresses and improve durability.

Systems

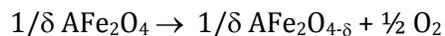
During FY10, the systems team improved the fidelity of the CR5 reduced-order model and developed a Fischer-Tropsch (FT) reactor model to replace the methanol reactor. The model indicates the FT process offers potential efficiency gains over methanol production. Analysis of mixed CO₂ and H₂O splitting was performed and it was shown that the mixed pathway is significantly more energy- and cost-efficient than earlier architectures.

Major Accomplishments Over Course of Project FY09-11

The focus of the project during the third year was applying all the lessons and tools of the previous two years to achieve the reactor efficiency goals. Additionally, the team worked to bring the materials and systems activities not to a point of conclusion, but rather to a point of fulfillment, where they can provide confidence for the world at large and serve as the basis for the further advancement of the field of thermochemistry both at Sandia and in the larger community. Here we summarize the state of the three focus areas after the three years of effort.

Materials

Our analysis indicates that numerous ferrites meet the thermodynamic criteria to be utilized in thermochemical cycles. We found that it was quite important to consider the role of solution phases in evaluating candidate materials. It is also important to account for the occurrence of non-stoichiometric phases. That is, complete reduction should not be the expected result. Rather, quite often, an oxygen deficient material of the same phase as the starting material will result, e.g.



Nickel ferrite of the composition NiFe₃O₄ in particular is an attractive candidate to perform thermochemical water or carbon dioxide splitting. However bulk ferrites, and especially those formed or sintered into larger monolithic shapes, do not perform as anticipated from the thermodynamics, i.e. they are not cyclable. Co-mingling the ferrites with YSZ yields a cyclable material that has even been observed to improve with time on stream.

The materials effort elucidated and convincingly demonstrated that the iron oxide is rendered cyclable by YSZ via the dissolution of iron into the zirconia crystal lattice. The dissolved iron is redox active (i.e. it readily cycles between +2 and +3 oxidation states) and may be utilized to a high degree (i.e. a large fraction of the iron participates in the redox chemistry). The YSZ matrix further facilitates the process as it is an effective oxygen ion carrier. Iron present in excess of the solubility limit contributes only minimally to the redox capacity of the material. This is quite simply due to fact that oxygen transport (oxygen ion diffusion rates) within the ferrite are very small relative to YSZ for example. Hence the interior of “bulk” particles is unavailable to perform the desired chemistry. TOF-SIMS imaging of isotopically labeled (^{18}O) composites provides a definitive illustration of this fact. The solubility of Fe in YSZ varies as a function of oxidation state and temperature and the transport of Fe into and out of the YSZ matrix is facile at the relevant temperatures. Unfortunately under all conditions the solubility of Fe is relatively small and therefore although Fe utilization is high, the total capacity averaged over the composite is small.

Work with model materials demonstrated that the above statement regarding the inability of bulk ferrites to participate in the redox chemistry to an appreciable extent should be qualified. As the ferrites are limited by oxygen transport, they may in fact be utilized to a very high degree, provided the size scale of the material is well matched to a transport dimension. For example, it was demonstrated that thin ferrite films on zirconia particles may be utilized to a very high degree. Additionally it was determined that these thin films exhibit reaction rates as much as 100 times greater than their Fe/YSZ counterparts. The challenge in this approach arises from the limited thermal stability of thin ferrite films. Under thermal stress they evolve to produce structures and results mirroring those of the Fe/YSZ. Nonetheless, this system provides important insights into the design of new and improved materials as does the Fe/YSZ composite. In addition to providing these insights, our work has also provided a foundation to advance the fundamental science behind the interactions of iron oxides and zirconia surfaces.

Regarding ceria materials, these materials were shown to be appropriate for achieving the goals of the project. For unadulterated ceria, the reaction rates are quite high as is oxygen transport. However the utilization remains relatively small under practical conditions, i.e. typically $\delta < 0.05$ ($1/\delta \text{ Ce}_2\text{O}_3 \rightarrow 1/\delta \text{ Ce}_2\text{O}_{3-\delta} + 1/2 \text{ O}_2$). Thus far, attempts to improve upon this via substitution with other elements, e.g. zirconia, have generally been unsuccessful as improvements are offset by new issues such as poor reaction kinetics.

Reactor

The most significant reactor accomplishment was continuously producing CO from CO₂ at a peak efficiency of 1.7% in two separate tests conducted late in FY11. These successes followed a long series of on-sun tests, each of which provided valuable operating experience. Design refinements were typically made in response to difficulties encountered during the test procedure. In order to minimize the cost and time required to carry out each set of modifications we adopted a philosophy of conducting partial tests to evaluate the effect of modifications prior to conducting a full test. In

practical terms this meant that thermal tests were carried out without sealing the CR5 and providing gas flows and without the full complement of ring segments. Only after success was achieved in a partial test was additional complexity added.

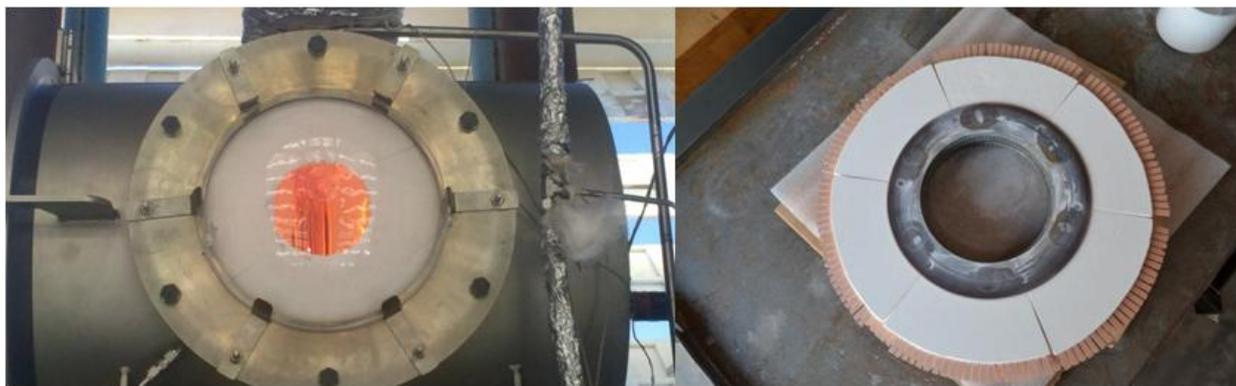


Fig. 4. (Left) Photo of the CR5 taken shortly after the conclusion of a successful 4-ring test (ceria) conducted on July 20, 2011. (Right) Ring segments recovered after the test showing ceria fins (pink), zirconia carrier segments (white), and metallic central hub (gray).

On July 20, the thermochemical heat engine continuously operating with 4 ceria rings produced carbon monoxide for several hours with a peak concentration of $>0.7\%$ and a peak rate of >100 sccm (standard cubic centimeters per minute). Peak efficiency was 1.7% (accounting for light impinging on the substrate) and $\sim 0.3\%$ for light at the aperture. Importantly, the test was stopped, not because of a materials or mechanical failure, but because the pumps were unable to keep up with the flows when the gas flows were intentionally increased. On August 1st, the team conducted a follow-up test with 12 rings that demonstrated $\sim 0.9\%$ efficiency at the aperture, >500 sccm of CO with a peak concentration of $\sim 1.0\%$, and a peak efficiency of $\sim 1.7\%$ accounting for light impinging directly on the rings (Figure 5). Discounting the efficiency to account for parasitic losses such as energy to run the pumps and inert gas flows gives a value of 1.5% . Accounting for the differences in the number of rings, the results for the two tests are consistent with one another. Furthermore, the apparent reaction rates and degree of utilization appear to be consistent with laboratory data at least to the degree that can be measured in the CR5.

The most significant factor in achieving these results was the continual improvement we achieved in ring durability over the course of this project. The current generation of ring segments features thin ceria fins fabricated by a casting/lamination/laser cutting methodology. These ceria fins are captured within a zirconia-based carrier ring that is in turn captured by a metal hub (Figure 4). During the July system test, our team could see (via camera) dark segments leaving the reduction zone and light segments entering the zone—indicating both reactions were proceeding well. When we disassembled the device after that test, the rings appeared to be in nearly pristine condition, with only a slight indication of metal-on-metal contact between rings. The ceria fins in particular were in excellent condition. A similar result for the ceria was realized in the 12-ring test although the zirconia carrier showed evidence of damage, for example delamination. Next generation designs include modifications to relieve some of the stresses in the zirconia.

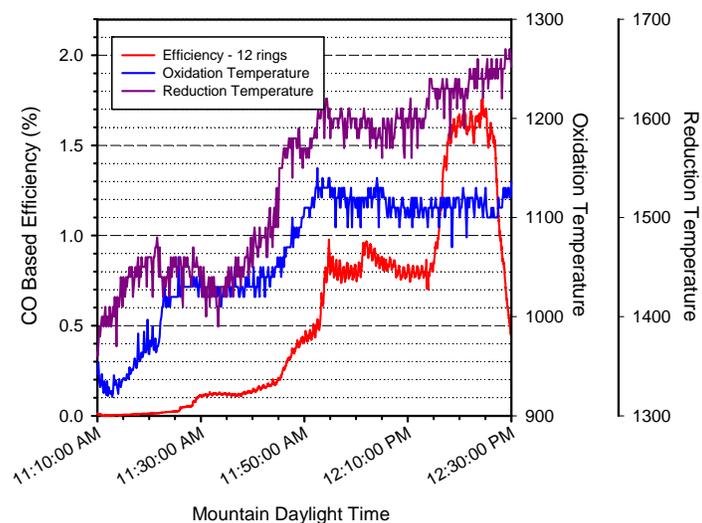


Fig. 5. Efficiency, Reactor Reduction and Oxidation Temperatures in a 12-ring on-sun test conducted on August 1, 2011. The CO yield and efficiency responded strongly to the CO₂ flow rate and reduction temperature.

The reactor team accomplished many things in addition to the success with the prototype CR5. Of particular note, the team was able to refine and better quantify key attributes for achieving high efficiency in a thermochemical reactor. Amongst these are continuous on-sun operation, sensible energy recovery (recuperation), minimal work input, pressure separation between reaction chambers, direct solar absorption, chemical and mechanical durability, and inherent reaction product separation. In addition, the team was able to demonstrate the interconnected nature of reactor and reactive material and defined a new figure of merit that combines properties of the two and that is called the utilization factor. Also of significance was the development of reactor models that incorporate measured parameters (e.g. reaction rates) and that have been partially validated against the CR5, and that can now begin to be used in something of a predictive fashion. Already these models have revealed details of the redox behavior in this complex, highly-coupled system that are non-intuitive. A related accomplishment was the development and fabrication of a validation reactor, the CR5v, that allows more direct characterization of heat flows within the system. Finally, team members developed two alternative reactor designs, a particle bed reactor and a hybrid system that offer potential advantages over generation-1 CR5 concept.

System

The systems team established a methodology for evaluating efficiencies, economics, and lifecycle impacts for the system and also established a baseline system design. In doing so we demonstrated that the details of the balance of system design can have significant impact on the full system efficiencies, which also strongly affected both the economics and lifecycle impacts. This methodology was then extended to evaluate the efficiencies and economics of several alternate S2P configurations for producing either methanol or Fischer-Tropsch hydrocarbons. These options

each begin with CO₂ capture, but vary in the initial thermochemically produced chemically energized intermediate, the subsequent downstream processing, and the final product. In all cases, the primary contributor to the minimum selling price (MSP) was the cost of capital for the solar thermochemical component; therefore utilizing the captured sunlight at the highest possible efficiency and obtaining favorable financing are shown to be vital factors for minimizing costs. Furthermore, we found that the choice of separations technologies can yield significant system improvements. It was determined that emerging technologies for recovering CO from CO₂ (as opposed to recovering the CO₂ from CO) should provide significant advantages. Sensitivity analysis was also performed to determine the effects of a number of key system and economic parameters on the MSP. The most optimistic case considered resulted in an encouraging MSP for methanol of \$4.24/GGE. Hence the systems team demonstrated the potential for thermochemistry to be a viable option for fuel production.

6.0 Beyond the LDRD Grand Challenge

As acknowledged from the beginning, the ultimate vision for thermochemical fuels was never going to be achievable in a three-year LDRD Grand Challenge project. Rather we set out to demonstrate a prototype device at a level of maturity that would provide evidence as to the achievability of our ultimate purpose and provide additional support for the credibility of this claim through scientific study and engineering analysis. Furthermore we set out to develop a research community with a “critical mass” of expertise, interest, and passion for this research that would sustain it beyond the three-year LDRD project limit. It is our contention that we have achieved these broad objectives. In addition we have also created a unique legacy for the laboratory in the form of new experimental and computational tools, capabilities, and expertise. We also believe we have established the laboratory as a national and international leader in the field of thermochemistry.

If thermochemistry is to achieve its promise, much work remains to be done. We propose a path forward that addresses the three principle topics areas: Reactors, Materials, and Systems.

Materials: Current materials are incapable of supporting efficiencies high enough for the thermochemical technology to outpace other approaches (e.g. electrochemistry). However, looking forward, our material efforts have laid the groundwork for a new generation of thermochemical materials. As metrics, one must consider not only the thermodynamics, but broader principles as well. Publications currently being prepared will present a comprehensive set of criteria for the design these materials, supported by an experimental approach, and informed by a set of reactor criteria. The strategy we advocate is to pursue multiple complementary routes in parallel to yield a drastically improved material. The three legs of our strategy include: 1) exploring new classes of thermochemical redox systems; 2) building on current knowledge to improve on mixed and composite systems that combine functionalities such as ion transport with a high density of redox centers; and 3) structuring materials so that characteristic dimensions are matched to transport dimensions. This approach is required, yet it is unique in that it will be among the first in this field to be guided by materials design considerations extending beyond the simplest thermodynamics

and the need to do a proof of principle demonstration of a functioning thermochemical heat engine in a first-generation reactor.

Reactors: We advocate two principle focal points for reactors. The first is continued operation and collection of valuable data for the existing Gen1 platform, the CR5. The CR5 embodies the critical design attributes with the exception that the total operating pressures of each half-cycle are closely coupled. Operating experience is priceless in developing new technologies such as this, and the data will be applied to validate and further refine computational models of the TC environment, including thermal and chemical profiles. These models and experience will be applied to the second focus, developing, building and testing a Gen2 platform with the goals of demonstrating 12.5% efficiency. One strong concept that embodies all the key attributes is a particle reactor that is the subject of an upcoming publication.

Systems: The most basic metric for success is sustained efficiency in a thermochemical reactor system. An initial systems foundation is in place. However, it is necessary to continue to provide a systems context for the reactor and materials work so that measurements and projections of efficiency and other important parameters such as cost and environmental impacts can be made confidently and credibly.

7.0 Presentations

This section comprises a list of presentations concerning the S2P project. Internal presentations (e.g. advisory board meetings, corporate visits, etc) and minor presentations may not be included. Invited presentations are denoted with an *.

Calendar Year 2011

E. N. Coker, J. E. Miller and E. B. Stechel, "Transforming carbon dioxide into carbon-neutral liquid fuels," presented at *Sustainable methanol: an alternative green fuel for the future*, Institute for Advanced Sustainability Studies e.V., Potsdam, Germany, Nov. 24-25, 2011.

I. Ermanoski and G. L. Kellogg, "Iron oxide growth on YSZ(001) and YSZ(111)," presented at the 58th American Vacuum Society (AVS) International Symposium, Nashville, Tennessee, October 30-November 4, 2011.

J. Kim, T. A. Johnson, J. E. Miller, E. B. Stechel and C. T. Maravelias, "Liquid fuel production using solar-thermal energy: Process development and techno-economic evaluation," presented at the 2011 Annual Meeting of the American Institute of Chemical Engineers, Minneapolis, Minnesota, October 16-21st, 2011.

E. N. Coker, A. Ambrosini, M. A. Rodriguez, J. A. Ohlhausen, J. E. Miller, and E. B. Stechel, "In operando characterization of Ferrite-YSZ materials for solar-thermochemical fuels synthesis," presented at Hi-Temp 2011, Boston, MA, September 20th-22nd, 2011.

I. Ermanoski, and N. P. Siegel, "Packed bed reactor for solar-thermochemical fuel production," presented at SolarPACES 2011 (Solar Power and Chemical Energy Systems), Granada, Spain, September 20-23, 2011.

N. P. Siegel, R. B. Diver, G. J. Kolb, J. E. Miller, I. Ermanoski, E. Stechel, "System Performance Estimation of Two-Step Thermochemical Fuel Production Processes," presented at SolarPACES 2011 (Solar Power and Chemical Energy Systems), Granada, Spain, September 20-23, 2011.

J. A. Ohlhausen, E. N. Coker, A. Ambrosini and J. E. Miller, "ToF-SIMS analysis of iron oxide particle oxidation by isotopic and multivariate analysis," presented at the 18th International Conference on Secondary Ion Mass Spectrometry, Riva del Garda, Italy, Sept. 18 – 23, 2011.

J. R. Scheffe, A. H. McDaniel, M. D. Allendorf, E. N. Coker, and A. W. Weimer, "Thin film ferrites by ALD for solar redox cycles," presented at EuroCVD 18, Kinsale, County Cork, Ireland, September 4–9, 2011.

*A. H. McDaniel, J. R. Scheffe, V. J. Aston, D. Arifin, E. N. Coker, J. E. Miller, M. D. Allendorf, and A. W. Weimer, "High temperature splitting of water and carbon dioxide using complex oxides as a route to solar fuels," presented at the 242nd Annual Meeting of the American Chemical Society, Denver, Colorado, USA, August 28–September 1, 2011, Sandia National Laboratories document SAND2011-6244C.

*A. Ambrosini, E. N. Coker, M. A. Rodriguez, J. A. Ohlhausen, J. E. Miller, and E. B. Stechel, "Synthesis and characterization of supported ferrites for thermochemical CO₂ splitting using concentrated solar energy," presented at the Fall 2011 Meeting of the American Chemical Society (Division of Fuel Chemistry), Denver, Colorado, USA, August 28–31, 2011, Sandia National Laboratories document SAND2011-6209C.

*A. Ambrosini, E. N. Coker, M. A. Rodriguez, J. E. Miller, and E. B. Stechel, "Synthesis and characterization of oxide materials for thermochemical CO₂ splitting using concentrated solar energy," presented at the Fall 2011 Meeting of the American Chemical Society (Division of Physical Chemistry—Marie Curie Symposium), Denver, Colorado, USA, August 28–31, 2011, Sandia National Laboratories document SAND2011-6278C.

A. Ambrosini, E. N. Coker, M. A. Rodriguez, N. P. Siegel, T. Garino, L. R. Evans, B. D. Ehrhart, J. E. Miller, and E. B. Stechel, "Sunshine to petrol: Oxide materials for thermochemical CO₂ splitting using concentrated solar energy," presented at the 5th International Conference on Energy Sustainability hosted by the American Society of Mechanical Engineers, Washington, D.C., August 8-11, 2011.

A. H. McDaniel, D. Arifin, J. Scheffe, N. Siegel, M. Allendorf, and A. Weimer, "Kinetics of H₂O and CO₂ splitting chemistry on reactive structures suitable for concentrated solar power Application," presented at the 5th International Conference on Energy Sustainability hosted by the American Society of Mechanical Engineers, Washington, D.C., August 8-11, 2011.

L. J. Mayer and D. L. James, "Thermal recuperation modeling of a solar thermochemical reactor," presented at the 5th International Conference on Energy Sustainability hosted by the American Society of Mechanical Engineers, Washington, D.C., August 8-11, 2011.

K. S. Chen and R. E. Hogan, "Three-dimensional modeling of solar thermochemical splitting of CO₂ in a CR5," presented at the 5th International Conference on Energy Sustainability hosted by the American Society of Mechanical Engineers, Washington, D.C., August 8-11, 2011.

*E. N. Coker, M. A. Rodriguez, A. Ambrosini, and J. E. Miller, "Using in-situ techniques to probe high temperature reactions: thermochemical cycles for the production of synthetic fuels from CO₂ and water," presented at the 60th annual Denver X-ray Conference, Colorado Springs, CO, August 1-5, 2011.

*M. D. Allendorf and J. E. Miller, "Solar fuel production using thermochemical cycles: a challenging materials problem," presented at the School for Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, April 2011.

A. Ambrosini, E. N. Coker, M. A. Rodriguez, J. A. Ohlhausen, B. Ehrhart, L. R. Evans, J. E. Miller, and E. B. Stechel, "Synthesis and characterization of supported ferrites for thermochemical CO₂ splitting using concentrated solar energy," presented at 2011 MRS Spring Meeting, San Francisco, California, April 25-29, 2011.

*J. E. Miller, "Sunshine to petrol: Solar recycling of carbon dioxide into hydrocarbon fuels," presented at 2011 MRS Spring Meeting, San Francisco, California, April 25-29, 2011.

*H. Hansen, B. Meredig, and C. Wolverton, "Metal oxides for solar thermochemical H₂O- and CO₂-splitting cycles," presented at the 241st National Meeting of the American Chemical Society, Anaheim, California, March 27-31, 2011.

*J. E. Miller "Sunshine to petrol: Solar thermochemistry for liquid fuels," presented in Chemical Carbon Mitigation: A Physicochemical Approach, 241st National Meeting of the American Chemical Society, Anaheim, California, March 27-31, 2011.

*E.B. Stechel, "Sunshine to petrol: Achieving scale," presented in Solar Power as an Alternative Energy Source, 241st National Meeting of the American Chemical Society, Anaheim, California, March 27-31, 2011.

*A. Ambrosini, E. N. Coker, M. A. Rodriguez, T. Ohlhausen, S. Carroll, E. B. Stechel and J. E. Miller, "Sunshine to petrol: thermochemical CO₂ splitting using concentrated solar energy and related materials issues", presented at New Mexico Tech, March 2011.

E. N. Coker, M. A. Rodriguez, A. Ambrosini, and J. E. Miller, "In situ characterization of high temperature reactions," presented at the 25th Annual Western States Catalysis Club Symposium (WSCC 2011), Albuquerque, New Mexico, USA, February 18, 2011, Sandia National Laboratories document SAND2011-1452A.

A. Ambrosini, E. N. Coker, M. A. Rodriguez, J. A. Ohlhausen, B. Ehrhart, L. R. Evans, J. E. Miller, and E. B. Stechel, "Synthesis and characterization of supported ferrites for thermochemical CO₂ splitting using concentrated solar energy," presented at the 2011 Spring Meeting of the Materials Research Society,

San Francisco, California, USA, April 25–29, 2011, Sandia National Laboratories document SAND2011-2901C.

I. Ermanoski and G. L. Kellogg, “Ultrathin film growth of iron oxides on YSZ(001) and (111),” presented at the 2011 March Meeting of the American Physical Society, Dallas, Texas, USA, March 21–25, 2011.

G. L. Kellogg and I. Ermanoski, “Ultrathin oxide growth on YSZ single-crystal surfaces,” presented at the Department of Energy Office of Science’s Basic Energy Sciences Program (DOE-BES) Contractors Meeting on the Physical Behavior of Materials, Warrenton, Virginia, USA, March 6–9, 2011.

I. Ermanoski and G. L. Kellogg, “Low energy electron microscope studies of working oxides for the Sunshine to Petrol program: FeO on YSZ(001) and (111),” presented at the MS&T Council Review, Livermore, California, USA, February 3, 2011.

Calendar Year 2010

T. Johnson, presenter, “Process development and techno-economic analysis of a novel process for MeOH production from CO₂ using solar-thermal energy,” presented at the 2010 Annual Meeting of the American Institute of Chemical Engineers, Salt Lake City, Utah, November 7-12, 2010.

I. Ermanoski and G. L. Kellogg, “Growth and properties of iron oxides on YSZ(001),” presented at the 57th American Vacuum Society (AVS) International Symposium, Albuquerque, New Mexico, USA, October 17–22, 2010.

*J. E. Miller, “Solar recycling of carbon dioxide into hydrocarbon fuels: sunshine to petrol,” presented at Saudi Aramco: Technologies for Reducing CO₂ Emissions from Transportation Sectors and CO₂ Utilization, Houston, Texas, October 2010.

J. R. Scheffe, A. H. McDaniel, M. D. Allendorf, G. H. Evans, E. N. Coker, J. E. Miller, and A. W. Weimer, “Mechanistic investigation of the kinetics of thermochemical ferrite water splitting cycles using cobalt-iron spinel oxide,” presented at SolarPACES2010 (Solar Power and Chemical Energy Systems), Perpignan, France, September 21–24, 2010.

N. P. Siegel, T. Garino, E. N. Coker, S. Livers, A. Ambrosini, J. E. Miller, R. B. Diver, and M. Bobek, “Implementation of cerium oxide structures in solar fuel production systems,” presented at SolarPACES2010 (Solar Power and Chemical Energy Systems), Perpignan, France, September 21–24, 2010, Sandia National Laboratories document SAND2010-5493C.

I. Ermanoski and G. L. Kellogg, “LEEM, LEED, and LEEM-IV investigations of iron oxide thin films on YSZ(001),” presented at the 7th International Workshop on LEEM/PEEM, New York, New York, USA, August 8–13, 2010.

*A. Ambrosini, E. N. Coker, M. A. Rodriguez, S. Carroll, E. B. Stechel and J. E. Miller, “Sunshine to petrol: Thermochemical CO₂ splitting using concentrated solar energy and related materials issues,” presented at ETH-Zurich, Switzerland, July 2010.

*M. D. Allendorf, G. H. Evans, B. W. Jacobs, A. H. McDaniel, J. E. Miller, J. Scheffe, and A. W. Weimer “Thermodynamic and kinetic Investigations of thermochemical gas splitting,” presented at ETH-Zurich, Switzerland, July 2010.

*E.B. Stechel “Sunshine to petrol” presented at Sustainable Way for Alternative Fuels and Energy for Aviation, 2nd European Stakeholder Conference, Munich, Germany, July 2010.

*M. D. Allendorf, G. H. Evans, B. W. Jacobs, A. H. McDaniel, J. E. Miller, J. R. Scheffe, and A. W. Weimer, “Kinetics of CO₂ and H₂O splitting by mixed-metal ferrites: An experimental and computational investigation,” presented at the 1st International Conference on Materials for Energy, Karlsruhe, Germany, July 4–8, 2010 (Keynote Lecture).

A. Ambrosini, E. N. Coker, M. A. Rodriguez, S. Livers, L. Evans, J. E. Miller, and E. B. Stechel “Synthesis and characterization of metal oxide materials for thermochemical CO₂ splitting using concentrated solar energy,” presented at the 1st International Conference on Materials for Energy, Karlsruhe, Germany, July 4–8, 2010.

*N. P. Siegel, “Solar thermochemical fuel production,” presented at CIMTEC 2010, 5th Forum on New Materials, Motecatini Terme, Italy, June 2010.

N. P. Siegel, S. Livers, J. E. Miller, and R. B. Diver, “Cerium oxide materials for the solar thermochemical decomposition of carbon dioxide,” presented at the ASME 4th International Conference on Energy Sustainability ES2010, Phoenix, Arizona, May 17–22, 2010.

K. S. Chen and R. E. Hogan, “Modeling solar thermochemical splitting of CO₂ using metal oxide and a CR5”, presented at the ASME 4th International Conference on Energy Sustainability ES2010, Phoenix, Arizona, May 17–22, 2010.

R. B. Diver, N. P. Siegel, J. E. Miller, and T. A. Moss, “Testing of a CR5 solar thermochemical heat engine prototype,” presented at the ASME 4th International Conference on Energy Sustainability ES2010, Phoenix, Arizona, May 17–22, 2010.

*R. B. Diver, “Solar driven H₂O/CO₂ splitting via thermochemical cycles,” presented at the Conference on Sustainable Fuels from CO₂, H₂O, and Carbon-free Energy, Columbia University, New York, New York, May 4, 2010.

J. R. Scheffe, A. H. McDaniel, M. D. Allendorf, B. W. Jacobs, and A. W. Weimer, “Metal oxide spinel coatings on high surface area particles for solar-thermal water splitting redox cycles,” presented at the 6th World Conference on Particle Technology (WCPT6), Nuremberg, Germany, April 26–29, 2010.

*J. E. Miller, “Sunshine to petrol: A metal oxide-based thermochemical route to solar fuels” presented at University of Texas, Austin, Texas, April 2010.

*E.B. Stechel, “Sunshine to petrol” IGERT Lecture Series, Cornell University, Ithaca, New York, April 2010.

B. Meredig, H. Hansen, and C. Wolverton, "DFT studies of two-step solar thermochemical gas-splitting cycles," presented at 2010 MRS Spring Meeting, San Francisco, California, April 5-10, 2010.

J. R. Scheffe, A. H. McDaniel, J. E. Miller, G. H. Evans, B. W. Jacobs, E. N. Coker, A. W. Weimer, and M. D. Allendorf, "Experimental and computational investigation of CO₂ and H₂O splitting by mixed-metal ferrites," presented at the 239th National Meeting of the American Chemical Society, San Francisco, California, USA, March 21–25, 2010, Sandia National Laboratories document SAND2010-1713C.

E. N. Coker, A. Ambrosini, M. A. Rodriguez, T. J. Garino, and J. E. Miller, "Production of hydrogen and carbon monoxide from water and carbon dioxide through metal oxide thermochemical cycles," presented at Materials Challenges in Alternative and Renewable Energy, Cocoa Beach, Florida, February, 2010.

*E.B. Stechel, "Sunshine to petrol" presented at the University of North Texas, Denton, Texas, February 2010.

Calendar Year 2009

C. Wolverton, "First-Principles discovery of materials for alternative energies" presented at the 2009 MRS Fall Meeting, Boston, Massachusetts, November 30-December 4.

*E. B. Stechel, "What are the challenges and opportunities of converting carbon dioxide to fuels? Sunshine to petrol" presented as a panelist at E3 2009 - The Midwest's Premier Energy, Economic & Environmental Conference, St. Paul, Minnesota, November 17, 2009.

J. R. Scheffe, A. H. McDaniel, M. D. Allendorf, and A. H. Weimer, "Solar thermal H₂O splitting via cobalt ferrite based thermochemical cycles," presented at the 2009 Annual Meeting of the American Institute of Chemical Engineers, Nashville, Tennessee, USA, November 8–13, 2009.

A. H. McDaniel, J. R. Scheffe, G. H. Evans, A. W. Weimer, and M. D. Allendorf, "Nanometer-thick cobalt-iron spinel oxide films for high temperature splitting of H₂O and CO₂," presented at the 216th Meeting of the Electrochemical Society, Vienna, Austria, October 4–9, 2009, Sandia National Laboratories document SAND2009-6650C.

*E. B. Stechel, "Sunshine to petrol" presented at Columbia University, New York, New York, October 2009.

N. P. Siegel, R. B. Diver, S. Livers, T. Garino, and J. E. Miller, "Solar fuel production through the thermochemical decomposition of carbon dioxide," presented at the SolarPACES meeting, Berlin, Germany, September 2009.

E. N. Coker, M. A. Rodriguez, A. Ambrosini and J. E. Miller, "Thermochemical cycles For H₂ and CO production: some fundamental aspects," presented at the SolarPACES meeting, Berlin, Germany, September 2009.

M. D. Allendorf, A. H. McDaniel, J. Scheffe, A. W. Weimer, "Phase equilibrium modeling of CO₂ and H₂O splitting by ferrites," presented at the SolarPACES meeting, Berlin, Germany, September 2009.

*B. Meredig and C. Wolverton, "Understanding the materials thermodynamics of two-step solar thermochemical gas-splitting cycles," presented at the 2009 International Materials Research Congress, Cancún, Mexico, August 16-21, 2009.

M. D. Allendorf, J. R. Scheffe, A. H. McDaniel, G. H. Evans, and A. W. Weimer, "Kinetic mechanism development for solar CO₂ and H₂O splitting using mixed-metal ferrites," presented at the 238th National Meeting of the American Chemical Society, Washington, D.C., August 16–20, 2009.

A. Ambrosini, E. N. Coker, M. A. Rodriguez, S. Livers, L. R. Evans, J. E. Miller, "Synthesis and characterization of ferrite materials for thermochemical CO₂ splitting using concentrated solar energy," presented at the 238th National Meeting of the American Chemical Society, Washington, D.C., August 16–20, 2009.

N. Siegel, R. Diver, J. E. Miller, T. Garino, and S. Livers, "Reactive structures for two-step thermochemical cycles based on non-volatile metal oxides," presented at the ASME 3rd International Conference on Energy Sustainability ES2009, San Francisco, California, August 10-14, 2009.

K. S. Chen and R. E. Hogan, "A two-phase model for solar thermochemical water splitting with FeO/Fe₃O₄," presented at the ASME 3rd International Conference on Energy Sustainability ES2009, San Francisco, California, August 10-14, 2009.

T. Garino, N. P. Siegel, S. Livers, "Solar thermal production of H₂ using Fe₂O₃-YSZ materials," presented at the 8th Pacific Rim Conference on Ceramic and Glass Technology, Vancouver, British Columbia, June 2009.

E. N. Coker, M. A. Rodriguez, A. Ambrosini, L. R. Evans, J. E. Miller, "Thermochemical redox cycling of metal oxides for H₂ and CO production: some fundamental aspects," presented at the Western States Catalysis Club Symposium, Golden, Colorado, April 2009.

*J. E. Miller, R. B. Diver, N. P. Siegel, M. D. Allendorf, E. B. Stechel, "Sunshine to petrol: Solar thermochemical splitting of carbon dioxide and water," presented at the ACS Spring National Meeting, Salt Lake City, Utah, March 2009.

*E. B. Stechel, "Sunshine to petrol," presented at the ACS Spring National Meeting, Salt Lake City Utah, March 2009.

G. L. Kellogg, "Fundamental science challenges in the sunshine-to-petrol grand challenge LDRD," presented at the MS&T Council Review, Livermore, California, USA, January 14–15, 2009.

Calendar Year 2008

J. R. Scheffe, A. H. McDaniel, N. P. Siegel, M. D. Allendorf, and A. W. Weimer, "Kinetics of the thermochemical ferrite water splitting cycle using nano-thick cobalt-iron spinel oxide films synthesized

via atomic layer deposition,” presented at the 2008 Annual Meeting of the American Institute of Chemical Engineers, Philadelphia, Pennsylvania, USA, November 16–21, 2008.

*J.E. Miller, R.B. Diver, N.P. Siegel, M.D. Allendorf, R.E. Hogan, and E.B. Stechel, “Sunshine to petrol: Solar thermal conversion of carbon dioxide to liquid fuels” presented at the University of Arizona, Tucson, November 2008.

8.0 Publications

This section comprises a list of publications organized by category concerning the S2P project. At the time of this writing a number of publications are still in the review, editing, and composition stages. A tentative list of these documents is provided for future reference.

Journal Articles

E. N. Coker, A. Ambrosini, M. A. Rodriguez, and J. E. Miller, “Ferrite-YSZ composites for solar thermochemical production of synthetic fuels: In operando characterization of CO₂ reduction,” *Journal of Materials Chemistry* **21**, 10767–10776 (2011) [DOI: 10.1039/C1JM11053E].

J. Kim, C. A. Henao, T. A. Johnson, D. E. Dedrick, J. E. Miller, E. B. Stechel, and C. T. Maravelias, “Methanol production from CO₂ using solar-thermal energy: Process development and techno-economic analysis,” *Energy and Environmental Science* **4**, 3122 (2011) [DOI: 10.1039/C1EE01311D].

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I. Ermanoski, N. P. Siegel, et al., "Packed bed reactor for solar thermochemical fuel production" (in preparation).

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