SUNgas: OPPORTUNITIES AND CHALLENGES FOR SOLAR THERMOCHEMICAL FUELS

Davidson, J. H.*, Bala-Chandran, R., Chase, T. R., Hathaway, B. J., Krenzke, P. T., Sedler, S., Venstrom, L. J.
*Author for correspondence
Department of Mechanical Engineering
University of Minnesota
Minneapolis, MN 55455
USA
E-mail: jhd@umn.edu

ABSTRACT

Displacing petroleum-derived fuels with renewable solar fuels offers an opportunity to harness the earth's most abundant energy resource, to reduce anthropogenic emissions of greenhouse gases, and to meet an expanding global demand for fuel. This paper presents near-term and forward looking paths to produce solar fuels using concentrated solar energy as the source of process heat to drive thermochemical processes. Solar gasification of biomass is presented as an important stepping stone toward the goal of thermochemical metal oxide redox cycles to split water and carbon dioxide.

INTRODUCTION

Two of the most pressing challenges that face human kind are reduction of anthropogenic emissions of greenhouse gases due to combustion of fossil fuels and provision of sustainable solutions to meet an expanding global demand for energy. Solar energy offers an intelligent solution to both challenges because sunlight strikes the earth's surface at over 8000 times the world's rate of energy consumption. But to switch from a fossil fuel based economy to one based on solar energy, we must develop ways to efficiently capture, store, and convert solar energy for use when and where it is needed. If we compare solar energy to gasoline or natural gas, it is easy to see the challenge. Fossil fuels can be stored indefinitely, they are transported all over the world, and they are used in every energy sector. Imagine if we could combine the enormous potential of solar energy with the flexibility and energy density of hydrocarbon fuels.

One approach is production of solar fuels via high temperature thermochemical processes (Figure 1). Concentrated solar energy is the heat source and biomass (sustainably grown and harvested or carbonaceous waste products), brackish water and/or recycled CO_2 are the feedstock. To be carbon neutral, the CO_2 must come from the ambient air, bio-refineries or be captured at the point of use of
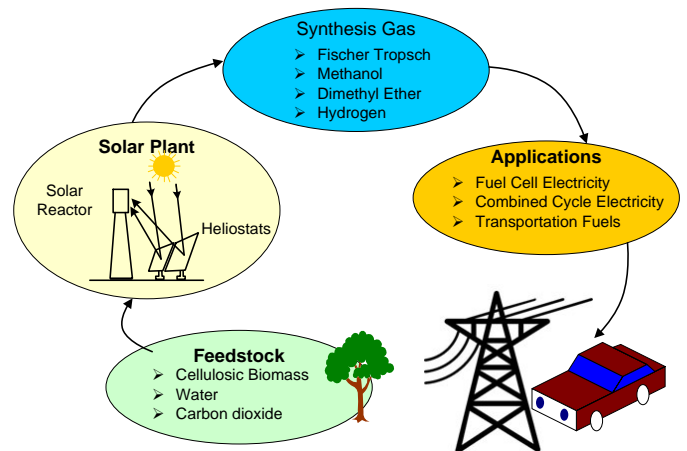
Figure 1 Solar thermochemical production of fuels

the solar fuel. The solar energy is stored in the products, either hydrogen from water splitting or synthesis gas (a mix of H_2 and CO) from water and CO_2 splitting. The *SUNgas* can be used directly in fuel cells or conventional thermal electricity production or processed to make clean liquid fuels compatible with the existing transportation infrastructure. The challenge is to convert sunlight to fuel at an efficiency that allows scale up with modest land usage and competitive cost.

The question of what efficiency is required for solar thermochemical fuel production to become commercially viable depends on numerous market and economic factors and is not easily answered. Siegel et al. [1] suggest an annual efficiency of 20% is necessary to compete with other renewable options. The annual average is defined as the ratio of the chemical energy of the produced fuel and the total solar energy input.

The present paper focuses on two routes to produce fuels using concentrated solar energy: 1) gasification of biomass and 2) water and CO_2 splitting. Water and CO_2 splitting may be the

ultimate market prize, but solar gasification of biomass or carbonaceous waste has a greater likelihood of near term implementation due to lower operating temperature, higher solar-to-fuel efficiency, and simpler reactors. Reactors developed at the University of Minnesota for solar gasification and H_2O/CO_2 splitting are presented and projections for the future discussed.
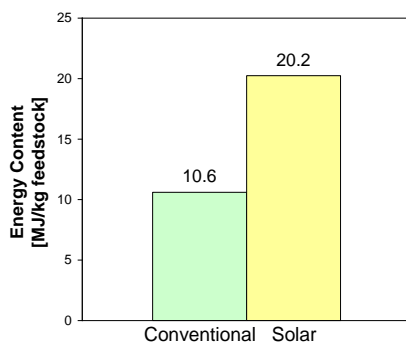
SOLAR GASIFICATION OF BIOMASS

A potentially near term route to commercial implementation of SUNgas is gasification. Solar gasification offers dramatic benefits compared to conventional gasification. With conventional gasification, air or oxygen is supplied at fuel-rich levels to combust a portion of the feedstock and in this manner generate the energy required for conversion to synthesis gas. The partial-combustion consumes up to 40% of the energetic value of the feedstock. With air combustion, the product gas is diluted by high levels of CO_2 and N_2. Using oxygen reduces the product dilution, but at the expense of adding an oxygen plant, which is a significant fraction of the overall economic and energetic cost of the gasifier plant.

Supplying the required heat with concentrated solar radiation eliminates the need for partial combustion of the biomass feedstock. As a result, the product gas has an energetic value *greater* than that of the feedstock and it is not contaminated by the byproducts of combustion. Compared to water splitting, gasification can be carried out at much lower temperature, 1200K versus nearly 1800K. At 1200K, the equilibrium product is a 1:1 molar ratio of H_2 and CO, an ideal precursor for producing liquid transportation fuels. The benefit of solar gasification for production of Fischer-Tropsch fuel (after a water-gas shift reaction to obtain a 2:1 H_2 to CO ratio) is illustrated in Figure 2. The solar process doubles the yield per mass of feedstock over conventional gasification.

Solar gasification has been explored in a number of reactor designs. For this process, we define solar to chemical conversion efficiency as the difference between the heating value of the produced syngas and the feedstock delivered divided by the incident solar power,

$$\eta_{solar} = \frac{\dot{m}_{syngas} \cdot LHV_{syngas} - \dot{m}_{feed} \cdot LHV_{feed}}{\dot{Q}_{solar}} \quad (1)$$

Figure 2 Improved product yield with solar versus conventional gasification of biomass

Thermodynamic models of solar gasification predict efficiencies of 50%, or higher depending on assumed values for thermal losses etc., e.g., [2]. Achievements in practice are modest. Steam gasification of coal coke in a 3.2kW directly irradiated fluidized bed achieved solar to chemical conversion efficiencies of 5-13% [3]. A 1.5kW two-zone combined drop-tube and trickle bed reactor for steam gasification of bagasse achieved a conversion efficiency of 5% [4]. An 8kW reactor for steam gasification of carbonaceous wastes reached a conversion efficiency of 3% [5]. Petroleum coke entrained in a vortex-flow reactor underwent steam gasification with efficiencies reaching 8.6% [6].

At the University of Minnesota, we have developed a prototype solar gasification reactor that uses a molten carbonate salt to provide rapid heat transfer to the biomass, to catalyze the gasification reaction, and to provide thermal storage [7-10]. A sketch and an image of the 3kW prototype reactor undergoing testing in the University of Minnesota indoor concentrating solar simulator [11] are shown in Figure 3. The reactor is constructed of Inconel in the form of concentric cylinders. The inner cylinder serves as a cavity solar receiver and the molten salt is contained in the annulus. Feedstock is delivered into the
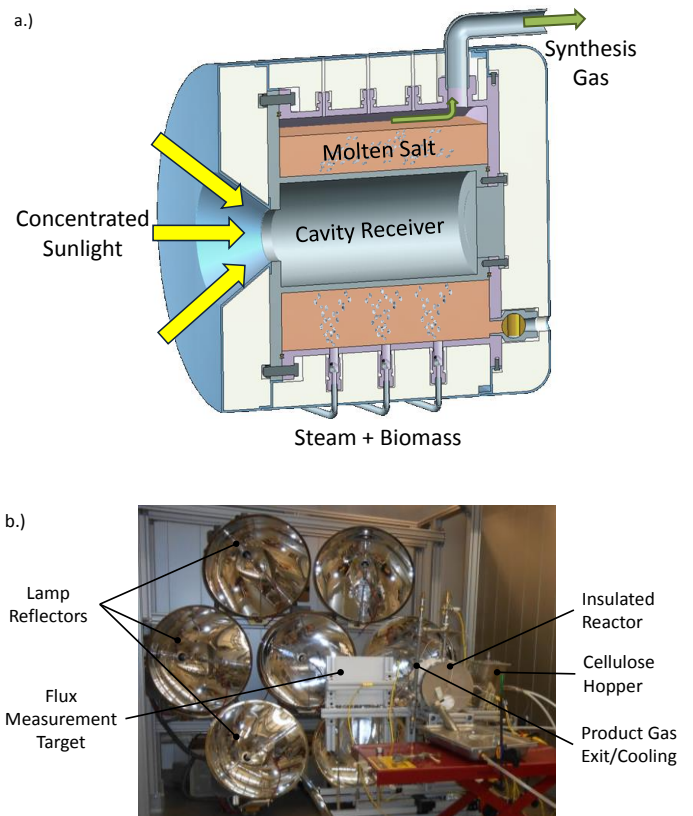
Figure 3 Solar gasifier developed at the University of Minnesota: a) conceptual sketch; b) image of the prototype reactor set up for testing in Minnesota's high flux solar simulator.

molten salt at the bottom of the reactor using a specially designed hopper and pneumatic feed system.

Laboratory scale experiments prove that in the presence of molten salt as opposed to in an inert gas, overall gas yields are increased by up to 22%; pyrolysis rates double, and carbon gasification rates increase by an order of magnitude. Rates of gasification measured in repeatable experiments for a variety of biomass materials are compared in Table 1 and Figure 4 [9]. The ternary blend of lithium, potassium, and sodium carbonate salts increases the total useful syngas production by up to 25%, and increases the reactivity index, defined as the inverse of twice the time needed to reach 50% carbon conversion, by as much as 600% for corn stover (Figure 5). Secondary products, in the form of condensable tar, are reduced by 77%.

The reactor has been operated in our indoor simulator to evaluate both structural and operational performance. Initial test results proved the efficacy of heat transfer. Work is on-going to extend the residence time of the biomass particles in the reactor. We anticipate the prototype reactor will achieve a steady-state solar-to-fuel efficiency of 50%

To consider scale-up, we estimated the performance of a 100 MW_{th} system to supply synthesis gas to a downstream power or fuel production process in Arizona [12]. The analysis shows the tradeoff in increasing the thermal storage capacity and hybridization. Projected annual efficiencies are 35-39%, with some reduction compared to laboratory performance due to solar transients. A moderately hybridized facility achieving a solar fraction of 50% can produce synthesis gas with low output variation using only 1 GJ/K of thermal storage resulting in a specific yield of 115 GJ per hectare. A more aggressive facility achieving 65% solar fraction would require 21 GJ/K of thermal storage, but would benefit from an increased specific yield of 128 GJ/ha and thermal efficiency of 80%.

Table 1 The increase in syngas production from gasification with molten salt

| Feedstock	Increase in syngas production with molten salt (%)
Cellulose	5.8
Perennial Blend	15.9
Corn Stover	15.9
Switch Grass	25.7

(a)

(b)

(c)

(d)
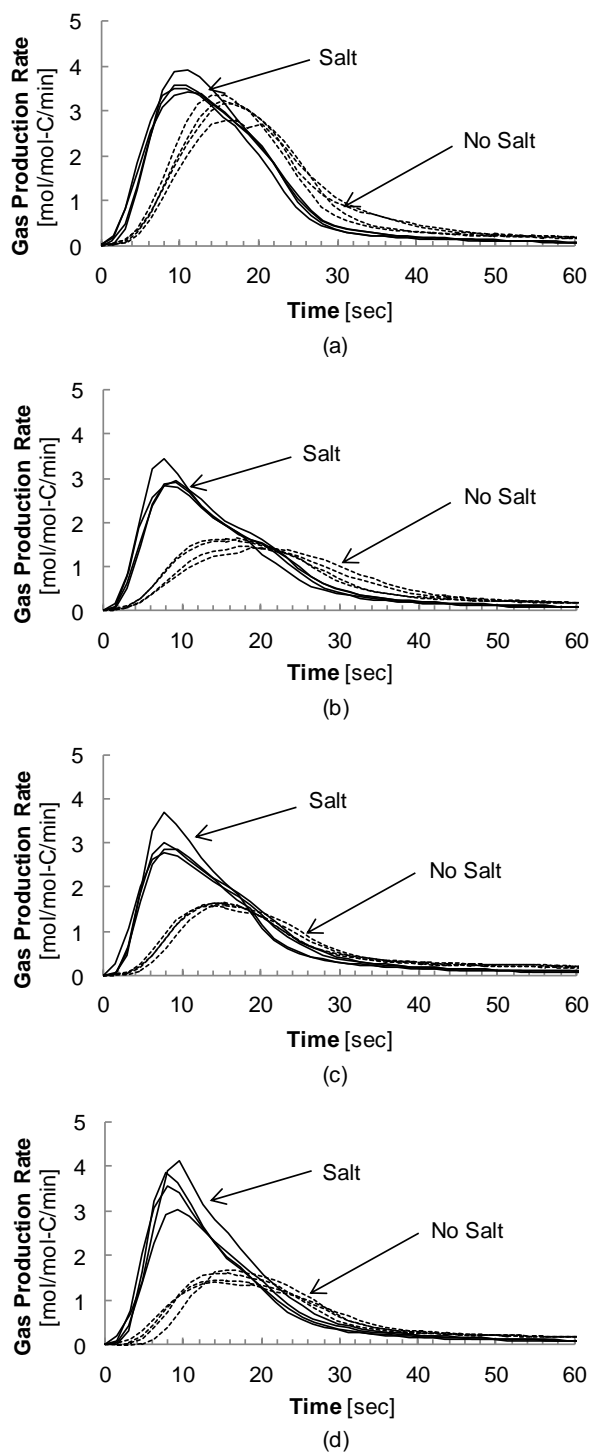
Figure 4 Molar gas production rates for the combined pyrolysis and steam gasification of (a) cellulose (b) perennial blend of grasses (c) corn stover and (d) switch grass at 1200 K with salt and in argon (no salt).
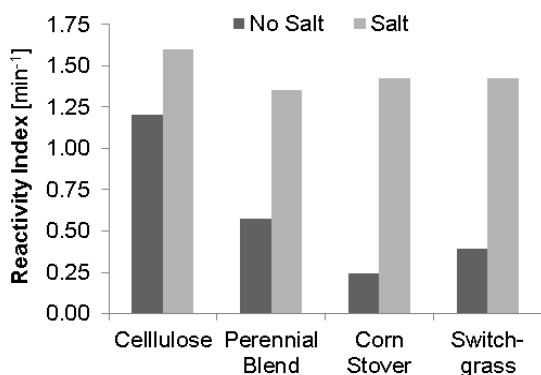
Figure 5 Reactivity index for gasification with and without salt

SOLAR WATER AND CO$_2$ SPLITTING

Spitting water to produce hydrogen using solar energy has long been touted as the ultimate achievement for solar fuels [13, 14]. Over the past decade, the international research community has paid equal attention to splitting CO$_2$, e.g. [15-18]. Hydrogen and carbon monoxide may be produced in a single step, by direct thermolysis of H$_2$O and CO$_2$, or in multiple steps as is done in metal oxide reduction/oxidation cycles. Direct thermolysis is not practical due to the extremely high temperatures required and the need to separate H$_2$ and O$_2$. To circumvent these practical challenges, two-step metal oxide cycles, most simply described by the pair of reactions (R1, R2),

(high temperature) $\quad MO \rightarrow M + \tfrac{1}{2}\,O_2$ $\qquad\qquad$ (R1)

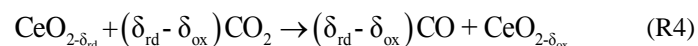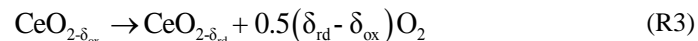(low temperature) $\quad H_2O + M \rightarrow MO + H_2$ $\qquad$ (R2)
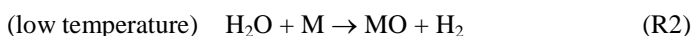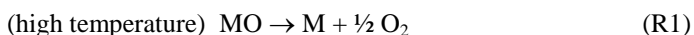
are the foci of international research efforts. The 1st step is the endothermic thermal dissociation of a metal oxide (MO) to the metal (M) or lower-valence metal oxide. This step is carried out in a receiver/reactor placed at the focal point of a solar concentrating system. The 2nd exothermic step is the hydrolysis of the reduced metal to form H$_2$ (or CO in the equivalent case of CO$_2$ splitting) and the corresponding metal oxide. A key challenge for efficient cycling is selection of the metal oxide.

Much of the early focus of work in this field was on the zinc oxide/zinc cycle, e.g. [19-22]. ZnO dissociates completely at 2325 K, the lowest temperature among metal oxide pairs. Solar thermal dissociation of ZnO with effective separation of the gaseous products has been demonstrated at the prototype scale. However, preventing recombination of Zn and O$_2$ has not been solved satisfactorily. Moreover the 2nd step has kinetic constraints; oxidation of Zn is slowed as a ZnO layer is formed at the surface, e.g. [23, 24].

Many research groups are considering non-volatile metal oxides, including iron oxides (Fe$_3$O$_4$) and cerium dioxide (CeO$_2$) [25]. Our group is currently working with cerium dioxide (ceria), which undergoes partial reduction/oxidation without a change in crystal structure. Work to date has demonstrated that ceria has the requisite reduction/oxidation properties, rapid diffusion kinetics, and morphological stability [18, 26, 27]. Efficient approaches for accomplishing the solar redox cycle remain a topic of extensive dialogue in the scientific literature [15-18, 28-33, 35]. Based on very optimistic projections, solar-to-fuel efficiency could reach 40%.

The ceria redox cycle for CO$_2$ splitting is represented by reactions (R3, R4).

$$CeO_{2-\delta_{ox}} \rightarrow CeO_{2-\delta_{rd}} + 0.5\left(\delta_{rd}-\delta_{ox}\right)O_2 \qquad (R3)$$

$$CeO_{2-\delta_{rd}} + \left(\delta_{rd}-\delta_{ox}\right)CO_2 \rightarrow \left(\delta_{rd}-\delta_{ox}\right)CO + CeO_{2-\delta_{ox}} \qquad (R4)$$

Water splitting is equivalent with the substitution of H$_2$O for CO$_2$. Fuel production is proportional to the change in the number of oxygen vacancies, or equivalently non-stoichiometry of ceria, between reduction and oxidation $\left(\delta_{rd}-\delta_{ox}\right)$. Chemical thermodynamics favors reduction at high temperature (1773K) and low O$_2$ partial pressure, and reoxidation at a lower temperature, typically 1000–1400K. Recuperation of the sensible heat between the thermal reduction and CO$_2$ splitting reactions is essential for achieving high efficiency.

Another option is to carry out the process isothermally or with a much smaller swing in temperature between reduction and oxidation (~100–200K). Isothermal or "near isothermal" cycling eliminates the necessity for solid-phase heat recovery and simplifies the design of reactor components. However, in comparison with the temperature swing cycle, isothermal cycling requires a lower oxygen partial pressure during reduction to produce an equivalent amount of fuel [18]. To maintain low oxygen partial pressure during reduction, a sweep gas or operation below atmospheric pressure [29, 31] is required. The work requirements for pumping, producing inert sweep gas, and extracting the fuel from the product gas mixture can be significant. For both temperature swing and isothermal cycling, the solar-to-fuel efficiency is projected to improve dramatically with effective gas phase heat recuperation [32-35].

To date, the highest cycle-average solar-to-chemical energy efficiency, defined as the energy content of the produced fuel divided by the required solar input (without full accounting of mechanical work), achieved is 1.7% for CO production in a batch process with neither solid phase nor gas phase heat recovery [36].

Research at the University of Minnesota aims to demonstrate continuous fuel production with the ceria cycle in two reactors designed for temperature swing and isothermal operation. The reactor designed for a temperature-swing cycle includes solid phase heat recovery and is shown in Figure 6. The reactor features dual zones for simultaneous reduction and oxidation with continuous cycling of ceria between the zones. The reduction reaction (R3) takes place in a directly irradiated *light* zone as a rotating hollow cylinder of porous ceria passes in front of the optical window and is exposed to a flow of inert gas. In the opposing, non-irradiated *dark* zone, the oxidation reaction (R4) takes place in a flow of oxidizing gas. A critical component is a counter-rotating cylinder of inert alumina positioned co-axially within the outer ceria cylinder. As the two cylinders rotate in opposing directions between the light and dark zones, counter-current heat recuperation occurs, primarily by thermal radiation [38].
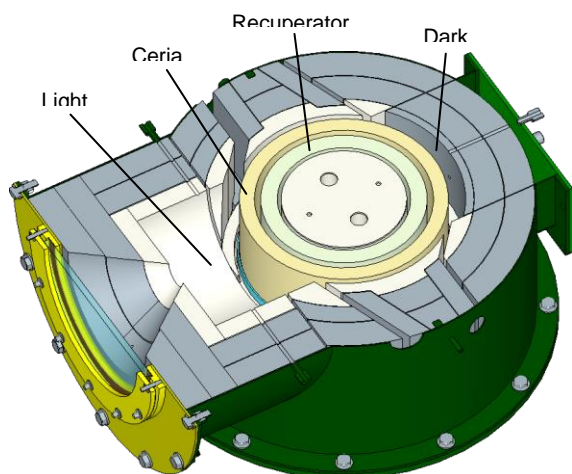
Figure 6 University of Minnesota temperature swing reactor for continuous fuel production via the ceria-based metal redox cycle. A counter-rotating cylinder of inert alumina positioned co-axially within the outer ceria cylinder provides heat recuperation of the ceria.

The isothermal reactor is shown in Figure 7 [35]. Like the temperature swing reactor, the "isothermal" reactor is operated continuously on-sun. A unique attribute is integration with a gas phase heat recovery system [34, 35, 37]. The 3 kW prototype has a cylindrical cavity lined with six tubular reactive elements that each contains a bed of ceria particles. The reactive element is constructed of concentric alumina tubes. The outer tube has a closed spherical cap at the end located near the front of the reactor cavity. The annular gap is filled with 5 mm long and 5 mm diameter cylindrical ceria particles with micro-meter sized pores, and an internal porosity of ~70%. The porous particle bed provides high surface area for chemical reaction, facilitates rapid gas diffusion and yields acceptable pressure drop through each reactive element [18]. Each tube assembly extends through the rear of the cavity to form a tube-in-tube counter-flow heat exchanger. In the insulated heat exchanger, both the tube and annulus are filled with inert alumina RPC [34, 35]. Gases enter the inner tube of the heat exchanger where they are heated, flow through the reactive element, and then return through the annulus of the heat exchanger where they are cooled. During reduction, N_2 is passed through the tubes (the sweep gas may be used in concert with a vacuum pump) to achieve low partial pressures of O_2 over the ceria particles. During oxidation, the gas flow is switched to a flow of steam and/or CO_2. In both steps of the cycle, heat is recovered from the gases leaving the reactor to preheat the gases entering the bed of ceria particles. We have demonstrated isothermal fuel production at 1773K for 100 cycles and selected gas flow rates and cycle duration to maximize efficiency [18]. Results from experimental testing of a prototype heat exchanger [34] and numerical model predictions for the integrated heat exchanger/reactor [35] indicate the potential to achieve greater than 85% effectiveness of gas-phase heat recuperation.

(a)

(b)
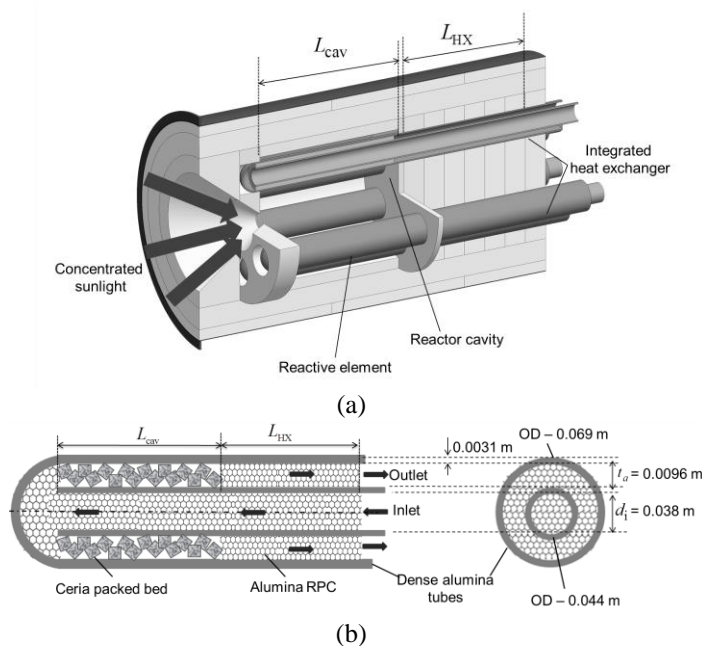
Figure 7 University of Minnesota isothermal reactor for the ceria-based metal redox cycle; (a) reactor prototype with reactive elements integrated with counter flow heat exchangers and (b) expanded view of the reactive element connected to the heat exchanger. Not to scale. [35]

The benefit of relative simplicity of the isothermal reactor is gained at the expense of efficiency compared to the temperature swing cycle. The 3 kW reactor of ceria is projected to produce fuel at an average continuous rate of 3.9×10^{-4} mol/s at an efficiency of 3.7% without consideration of parasitic energy requirements. The largest of these is production of the inert sweep gas. Production of N_2 with 1 ppm oxygen impurity at 8 bar from air by cryogenic rectification consumes 0.15 kWh $(m-N_2)^{-3}$ [37]. Assuming a 25% efficient conversion of solar heat to electrical energy, the parasitic requirement is 26.8 MJ mol-CO^{-1}. The theoretical minimum work needed to recycle the inert gas is roughly two orders of magnitude smaller. Consequently, it is plausible that the purification energy requirement may be decreased substantially through advances in gas separation technology.

CONCLUDING REMARKS

Concentrated sunlight provides a practically limitless source of high temperature process heat that can be used for the production of chemical fuels. Intelligent selection and design of the mechanisms by which this conversion of sunlight to fuels is accomplished are the topics of global research efforts. Conversion of sustainably grown and harvested biomass is potentially the most efficient and closest to commercial viability. Solar gasification is possible at modest temperatures around 1200K and based on the work to-date, it is reasonable to expect efficiencies above 50%. While promising as a first step towards displacement of some fossil fuel with solar fuel, solar gasification may never expand to a scale sufficiently large to

replace significant use of fossil fuel because of land utilization requirements, competition with food crops, and the inherently low energy conversion of photosynthesis.

In the longer term, splitting water to produce hydrogen is an even more compelling approach for a clean, carbon-free, and renewable energy supply. Splitting CO_2 along with H_2O is attractive to produce renewable hydrocarbon fuels that fit seamlessly into the existing transportation infrastructure. To close the carbon cycle, the CO_2 can be recycled from the air or captured at the point of use, or obtained from bio-refineries. The approach that appears most likely for water and CO_2 splitting is metal-oxide reduction/oxidation cycles. The highest cycle-average solar-to-chemical energy efficiency achieved to-date is 1.7% for CO production [36]. Significant advances in reactor design, operation and materials are required to approach the promise of theoretical efficiencies that based on some projections reach 40%. These topics are the subject of on-going study within the solar thermal and materials research communities.

ACKNOWLEDGEMENTS

REFERENCES

[1] Siegel N.P., Miller J.E., Ermanoski I., Diver R.B., Stechel E.B., Factors Affecting the Efficiency of Solar Driven Metal Oxide Thermochemical Cycles, *Ind. Eng. Chem. Res.*, **52**(9), 3276–3286, 2013.

[2] Melchior T., Perkins C., Lichty P., Weimer A.W., Steinfeld A., "Solar-driven biochar gasification in a particle-flow reactor", *Chemical Engineering and Processing: Process Intensification*, **48**(8) 1279-1287, 2009.

[3] Gokon N., Izawa T., Abe T., Kodama T., Steam gasification of coal cokes in an internally circulating fluidized bed of thermal storage material for solar thermochemical processes, *International Journal of Hydrogen Energy*, **39**(21) 11082-11093, 2014.

[4] Kruesi M., Jovanovic Z.R., Steinfeld A., A two-zone solar-driven gasifier concept: Reactor design and experimental evaluation with bagasse particles, *Fuel*, **117**(A), 680-687, 2014.

[5] Piatkowski N., Steinfeld A., Solar gasification of carbonaceous waste feedstocks in a packed-bed reactor – Dynamic modelling and experimental validation", *Environmental and Energy Engineering*, **57**(12) 3522-3533, 2011.

[6] Z'Graggen A., Haueter P., Trommer D., Romero M., de Jesus J.C., Steinfeld A., Hydrogen production by steam-gasification of petroleum coke using concentrated solar power – II. Reactor design, testing, and modelling, *International Journal of Hydrogen Energy*, **31**(6) 797-811, 2006.

[7] Hathaway B.J., Davidson J.H., and Kittelson D.B., Solar Gasification of Biomass: Kinetics of Pyrolysis and Steam Gasification in Molten Salt, *ASME J. of Solar Energy Engineering*, **133**(2) 021011 (9 pages), 2011.

[8] Hathaway B.J, Lipiński W., and Davidson J.H., Heat transfer in a solar cavity receiver: Design considerations, *Numerical Heat Transfer Part A*, 62(5), 445-461, 2012

[9] Hathaway B.J., Honda M., Kittelson D.B., and Davidson J.H., Steam gasification of plant biomass using molten carbonate salts, *Energy*, **49**(1), pp. 211-217, 2013.

[10] Hathaway B.J., Kittelson D.B., and Davidson J.H., Integration of Solar Gasification with Conventional Fuel Production: The Roles of Storage and Hybridization, Invited paper Special Issue: Festschrift in honor of Frank Kreith's 90th Birthday, *ASME Journal of Solar Energy Engineering*, **136**(1), 010906 (10 pages), 2014.

[11] Krueger K., Lipinski W., and Davidson J.H., "Operational Performance of the University of Minnesota 45kW$_{th}$ High Flux Solar Simulator," *ASME J. of Solar Energy Engineering*, **135**(4), 044501, 2013.

[12] Nickerson T.A, Smith, T. M, Hathaway, B.J, and Davidson, J.H., Economic assessment of solar and conventional biomass gasification technologies: financial and policy implications under feedstock and product gas price uncertainty, in review.

[13] Fletcher E.A., and Moen R.L., Hydrogen and Oxygen from Water, *Science*, **197**(4308), 1050-1056, 1977.

[14] Nakamura T., Hydrogen Production from Water Utilizing Solar Heat at High Temperatures, *Solar Energy*, **19**(5), 467-475, 1977.

[15] Chueh W. C., Falter C., Abbott M., Scipio D., Furler P., Haile S.M., Steinfeld A. High-Flux Solar-Driven Thermochemical Dissociation of CO_2 and H_2O Using Nonstoichiometric Ceria. *Science 330*, 1797–1801, 2010.

[16] Kim J., Johnson T.A., Miller J.E., Stechel E.B., Maravelias C.T., Fuel Production from CO_2 Using Solar-Thermal Energy: System Level Analysis, *Energy Environ. Sci.* **5**, 8417, 2012.

[17] Stechel, E.B. Miller J.E., Re-Energizing CO_2 to Fuels with the Sun: Issues of Efficiency, Scale, and Economics. *J. CO_2 Util.* **1**, 28–36, 2013.

[18] Venstrom L.J., De Smith R.M., Hao Y., Haile S.M., Davidson J.H. Efficient Splitting of CO_2 in an Isothermal Redox Cycle Based on Ceria. *Energy & Fuels*, **28**, 2732–2742, 2014.

[19] Fletcher E.A., 2001, "Solarthermal Processing: A Review," *Journal of Solar Energy Engineering*, **123**(2), pp. 63-74.

[20] Palumbo R., Lédé J., Boutin O., Elorza Ricart E., Steinfeld A., Möller S., Weidenkaff A., Fletcher E.A, Bielicki J., The Production of Zn from ZnO in a Single Step High Temperature Solar Decomposition Process, *Chemical Engineering Science*, **53**(14), 2503-2518, 1998.

[21] Haueter P., Möller S., Palumbo R., Steinfeld A., The Production of Zinc by Thermal Dissociation of Zinc Oxide – Solar Chemical Reactor Design, *Solar Energy*, **67**(1-3), 161-167, 1999.

[22] Schunk L.O.; Lipiński W.; Steinfeld A. Heat Transfer Model of a Solar Receiver-Reactor for the Thermal Dissociation of ZnO—Experimental Validation at 10kW and Scale-up to 1MW. *Chem. Eng. J.*, **150**, 502–508, 2009.

[23] Ernst F.O., Tricoli A., Pratsinis S.E., Steinfeld A., Co-synthesis of H_2 and ZnO by in-situ Zn aerosol formation and hydrolysis, *AIChE J.* **52**(9), pp. 3297-3303, 2006.

[24] Nicodemus J.H., and Davidson J.H. Fluid dynamics of a transverse jet reactor for zinc aerosol hydrolysis, ASME *Journal of Solar Energy Engineering*, **134**, 041018 (9 pp.), 2012.

[25] Scheffe J.R., Steinfeld A., Oxygen Exchange Materials for Solar Thermochemical Splitting of H_2O and CO_2 – A Review, Materials Today, **17**, 341-348, 2014.

[26] Abanades S., Flamant G., Thermochemical Hydrogen Production from a Two-Step Solar-Driven Water-Splitting Cycle Based on Cerium Oxides. *Sol. Energy*, **80**, 1611–1623, 2006.

[27] Chueh W.C., Haile S.M., Thermochemical Study of Ceria: Exploiting an Old Material for New Modes of Energy Conversion of CO2 Mitigation. Phil. Trans. R. Soc. A., **368**, 3269-3294, 2010.

[28] Krenzke P.T., Davidson J.H., Thermodynamic Analysis of Syngas Production via the Solar Thermochemical Cerium Oxide Redox Cycle with Methane-Driven Reduction. *Energy & Fuels*, 4088–4095, 2014.

[29] Ermanoski I., Siegel N. P., Stechel E.B., A New Reactor Concept for Efficient Solar-Thermochemical Fuel Production. *J. Sol. Energy Eng.* **135**, 031002, 2013.

[30] Ermanoski I.; Miller J.E., Allendorf M.D. Efficiency Maximization in Solar-Thermochemical Fuel Production: Challenging the Concept of Isothermal Water Splitting. *Phys. Chem. Chem. Phys.* 2014.

[31] Ermanoski I. Cascading Pressure Thermal Reduction for Efficient Solar Fuel Production. *Int. J. Hydrogen Energy*, **39**, 13114–13117, 2014.

[32] Lapp J., Davidson J.H., Lipiński W. Efficiency of Two-Step Solar Thermochemical Non-Stoichiometric Redox Cycles with Heat Recovery. *Energy*, **37**, 591–600, 2012.

[33] Bader R., Venstrom L.J., Davidson J.H., Lipiński W. Thermodynamic Analysis of Isothermal Redox Cycling of Ceria for Solar Fuel Production. *Energy & Fuels*, 5533–5544, 2013.

[34] Banerjee A., Bala Chandran R., and Davidson J.H., Experimental investigation of a reticulated porous alumina heat exchanger for high temperature gas heat recovery," *Applied Thermal Engineering*, accepted, October 2014. 10.1016/j.applthermaleng.2014.10.033

[35] Bala Chandran R., De Smith R.M., and Davidson J.H., Model of an integrated solar thermochemical reactor/reticulated ceramic foam heat exchanger for gas-phase heat recovery, *International J. of Heat and Mass Transfer*, 404-414, 2015.

[36] Furler P., Scheffe J., Gorbar M., Moes L., Vogt U., Steinfeld, A. Solar Thermochemical CO_2 Splitting Utilizing a Reticulated Porous Ceria Redox System. *Energy Fuels,* **26**, 7051-7059, 2012.

[37] Bader R. Bala Chandran R., Venstrom L.J., Sedler S.J, Krenzke P.T., De Smith R.M, Banerjee A., Chase T.R.,

Davidson J.H., Lipiński, W., Design of a Solar Reactor to Split CO_2 Via Isothermal Redox Cycling of Ceria, *ASME J. of Solar Energy Engineering*, Accepted October 2014.

[38] Lapp J., Davidson J.H., Lipinski W., Heat Transfer Analysis of a Solid-solid Heat Recuperation System for Solar-Driven Non-Stoichiometric Redox Cycles, *ASME J. of Solar Energy Engineering*, **135**, 031004, 2013.

[39] Häring H.W. *Industrial Gases Processing*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2008.