

# Solar-Thermal Production of Renewable Hydrogen

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## Introduction

One of the largest challenges facing humanity in this century is finding the energy sources to meet escalating demands that are sustainable, widely producible, and not detrimental to the global environment. World energy demand was 18 TW in 2004, and it is expected to grow to 28 TW by 2030.<sup>1</sup> Coupled with concerns over the environmental effects of long-term fossil fuel use, and the ability to increase the production of these fuels over time, this demand rise could put a crunch on the global economy that will lead to widespread decreases in standard of living. Clearly, alternative fuels are needed.

One fuel that has received a great deal of attention over the past decade is hydrogen. There have been numerous articles touting the “hydrogen economy,” in which most of the world’s energy needs will be served by this one fuel, and major governmental initiatives have sought to make this a reality.<sup>2</sup> As a fuel, hydrogen looks quite attractive, as it only produces water when burned and can be used in highly efficient fuel cells. However, no abundant supplies of hydrogen gas exist on the surface of the earth, so it must be derived from some other chemical source and is better referred to as an “energy carrier”. Such sources have typically been fossil based; indeed, most hydrogen in use today comes from steam reforming of methane.<sup>3</sup> As fossil resources are limited and generate greenhouse gases, obtaining hydrogen as a fuel in this manner subverts many of the “green” goals of the hydrogen economy. Instead, renewable sources of hydrogen (water, biomass) should be explored, and the search shifts to using renewable energy technologies for extracting hydrogen from those sources.

In this article, we explore production of hydrogen using solar thermal energy. Other reasonable methods exist to transform renewable energy into chemical energy as hydrogen, including photovoltaic (PV) or wind electrolysis and photoelectrochemical water splitting.<sup>4,5</sup> However, solar thermal

energy has some unique attributes that may give cost and efficiency advantages in regions with good solar resources.

## Solar Production of Hydrogen from Water

In order to liberate H<sub>2</sub> from water, energy must be imparted to the water molecule to coerce the hydrogen and oxygen to part ways. It doesn’t make much sense to use fossil sources of energy to perform this step, as one might as well use these fuels directly rather than transforming them to hydrogen. The task then falls to alternative sources of energy, the most abundant of which is solar energy.

Solar thermal systems consist of arrays of mirrors that can concentrate solar energy up to and beyond 2,000 times incident levels on a focal point or line. In the focal region, extremely high temperatures (potentially greater than 2,000 °C) can be achieved with relatively high efficiency, depending on the level of concentration and the design of the concentrating system.<sup>6</sup> Due to concentration limitations of troughs and cost and size limitations of dishes, power towers are the most practical for large scale thermochemical hydrogen generation.<sup>7</sup> The power tower, which consists of a central receiver surrounded by flat mirrors that track the sun and reflect it to the receiver, can achieve very high concentrations (>1,500 suns with secondary concentration), and temperatures (>1,500 °C), and are less size limited than the dish configuration.<sup>7</sup> The collected thermal energy can be used to drive a series of chemical reactions that have the net effect of splitting water. Many such reaction sets have theoretical efficiencies around 40%.<sup>8</sup> Combined with annual collection efficiencies for solar thermal systems of around 45%, the solar-to-hydrogen efficiency of this method could approach 20% with much lower installed collector costs than PV.

First, the capital cost of the tracking reflectors (heliostats) is the primary cost contributor to the final selling price of hydrogen, accounting for up to 80% of the final hydrogen selling price.<sup>9</sup> The prime factor driving required heliostat area is process efficiency, which itself is strongly related to temperature. At temperatures above 1,000 °C, radiation is the primary mode of heat transfer, and radiation losses increase as the fourth power of temperature. All things being equal, a process

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should be operated at its minimum practical temperature to maximize efficiency. Second, for highly efficient operation in a solar thermal chemical reactor, reaction kinetics must be rapid. The receiver energy balance dictates that slow kinetics lead to higher temperatures and lower efficiencies. Reactor configurations should be employed that reduce heat and mass transfer limitations and maximize kinetic rates at relatively low-temperatures. Third, any process achieving hydrogen production through water splitting should have as few chemical reaction and separation steps as possible. With each step, the degree of material and energy losses increases, decreasing overall efficiency. Finally, the nature of the process should make it amenable to the inherently intermittent quality of solar energy, a need that reinforces the emphasis on simplicity.

### **Direct water splitting**

The most direct method to produce hydrogen from solar thermal energy is simple thermolysis of the water molecule. The process proceeds in a single step, preventing chances for energy losses during material handling and secondary reaction process steps. Additionally, the process provides the closest match between the theoretical solar energy required and the energy released by the hydrogen when used. However, the equilibrium constant for thermolysis of water is not unity until a temperature of 4,300 K is reached.<sup>10</sup> These temperatures not only require extremely high solar concentrations ( $>38,000\times$  for 50% efficiency), but material selection for reactor construction at these temperatures proves challenging. Additionally, direct thermolysis produces a mixture of  $H_2$  and  $O_2$  that requires high-temperature separation. If allowed to cool, the gases would form an explosive mixture that would be hazardous to personnel and plant. To overcome these difficulties, researchers have looked into the use of porous ceramic membranes for reactor construction and separation, primarily those constructed of zirconia.<sup>11,12</sup> Zirconia's melting temperature is high enough to withstand very high temperatures ( $>2,000^\circ C$ ), and it does have good hydrogen permeability. At these temperatures it was found that some water splitting could be achieved (1.7% net conversion), but that sintering of the zirconia membrane severely limited lifetimes.<sup>11,13</sup> Due to efficiency and materials limitations at the high-temperatures required, direct water splitting is not expected to be economically viable in the near future.

### **Thermochemical water splitting cycles**

An alternative to direct thermolysis of the water molecule is to use a series of chemical reactions that have the same net effect. Such a process, termed a "thermochemical water splitting cycle," is characterized by a "high-temperature" ( $700^\circ C$ – $2,000^\circ C$ ) endothermic reaction step that is designed to be driven by solar energy followed by one or more low-temperature, "off-sun" exothermic reaction steps.<sup>10</sup> If the reactions are chosen carefully, the high-temperature step will have a lower required temperature than direct water splitting, reducing energy losses and capital costs and allowing the use of more conventional reactor materials. Offsetting this benefit in part will be a higher heat of reaction for the solar step, energy losses when transferring between process steps, and overall chemical process complexity. It is then important to find and develop those cycles that have relatively low operat-

ing temperatures in conjunction with few process steps, relatively simple process designs, and opportunities for energy recuperation.

The U.S. Department of Energy's Solar Thermochemical Hydrogen (STCH) program evaluated over 400 of these cycles, providing a score for each cycle based on number of criteria, including chemical reactions, suitability to various solar thermal collector architectures (e.g., troughs, dishes, power towers), use of corrosive or environmentally harmful chemicals, and projected operating efficiency.<sup>8</sup> From this large pool of cycles, nine were chosen as technically and practically feasible candidates.<sup>8</sup> The nine cycles can be broadly broken down into "high-temperature" and "low-temperature" categories, based on the operating temperature of their solar driven step. These are shown in detail in Table 1.

All of the "high temperature" cycles involve thermal reduction of a metal oxide as the solar driven step of the process. In the simplest version of the cycle, the oxide is completely reduced to a lower valence state. In a subsequent, "off-sun" reaction, the reduced oxide is contacted with steam to produce hydrogen and regenerate the original oxide. This is the pattern for cycles based on the redox pairs examined most closely in the literature,  $Zn/ZnO$  and  $FeO/Fe_3O_4$ .<sup>6,14</sup> These cycles have only two steps, leading to a low potential for energy losses between cycle steps and during separations. Second, process separations are relatively simple, involving only a solid phase and a gas phase. The hydrogen and oxygen are conveniently produced in separate reaction steps, eliminating the chance of explosive mixtures being formed. Finally, the solar step of the process is simple and easy to interface with intermittent solar energy. Solar energy is stored in the chemical bonds of solids, which are easy to store overnight. Hydrogen could be produced continuously simply by operating the hydrolysis reaction so that the solar reduced oxides are just used up over the night. With enough buffering storage, startup and shutdown of the solar portion of the plant would not severely affect the hydrolysis portion of the plant.

If one looks at the Gibbs Free Energy of the thermal reduction reaction as a function of temperature (Figure 1), the reason for the popularity of the  $Zn/ZnO$  pair becomes clear.<sup>15</sup> Of all the oxides that are capable of performing the subsequent hydrolysis,  $ZnO$  has the lowest decomposition temperature, and would be predicted to have the highest efficiency. There are other oxides that reduce at lower-temperatures ( $Mn_3O_4$ ,  $CdO$ ), but these do not have high-equilibrium coefficients for splitting water above 300 K.<sup>16</sup> The cycle based on the  $FeO/Fe_3O_4$  pair has also received large amounts of attention in the literature, but its operating temperatures are much higher than for the  $Zn/ZnO$  cycle, exacerbating efficiency and materials problems.

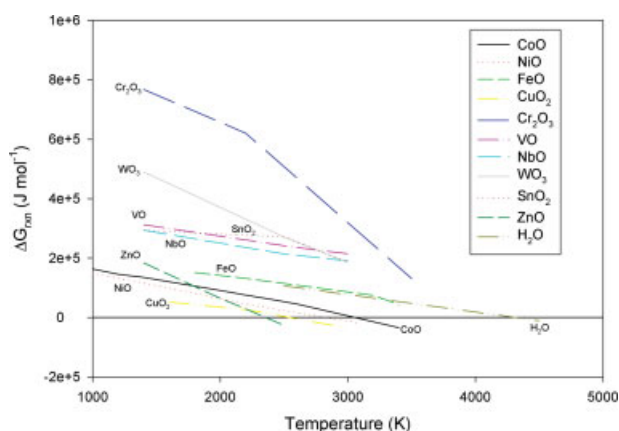
The  $ZnO$  dissociation reaction occurs at hot exposed surfaces, so that the kinetics are strongly dictated by diffusion away from the particle surface.<sup>17,18</sup> In reactor arrangements where bulk  $ZnO$  is directly irradiated, the surface area available for reaction is low. It has been shown that if small  $ZnO$  particles are instead incorporated into an inert gas as an aerosol and irradiated, dissociation will be up to three orders of magnitude faster.<sup>19</sup> As stated earlier, reaction kinetics are critical to solar efficiency. For the high-temperature cycles, receiver/reactors should be designed to maximize available area for reaction. Available surface area also plays a key role in determining kinetics and extent of reaction in the hydrolysis

**Table 1. Thermochemical Water Splitting Cycles**

Cycle	Reaction Steps
<i>High Temperature Cycles</i>	
Zn/ZnO	$\text{ZnO} \xrightarrow{1600-1800^\circ\text{C}} \text{Zn} + \frac{1}{2}\text{O}_2$ $\text{Zn} + \text{H}_2\text{O} \xrightarrow{400^\circ\text{C}} \text{ZnO} + \text{H}_2$
FeO/Fe <sub>3</sub> O <sub>4</sub>	$\text{Fe}_3\text{O}_4 \xrightarrow{2000^\circ\text{C}-2300^\circ\text{C}} 3\text{FeO} + \frac{1}{2}\text{O}_2$ $3\text{FeO} + \text{H}_2\text{O} \xrightarrow{400^\circ\text{C}} \text{Fe}_3\text{O}_4 + \text{H}_2$
Cadmium carbonate	$\text{CdO} \xrightarrow{1450-1500^\circ\text{C}} \text{Cd} + \frac{1}{2}\text{O}_2$ $\text{Cd} + \text{H}_2\text{O} + \text{CO}_2 \xrightarrow{350^\circ\text{C}} \text{CdCO}_3 + \text{H}_2$ $\text{CdCO}_3 \xrightarrow{500^\circ\text{C}} \text{CO}_2 + \text{CdO}$
Hybrid cadmium	$\text{CdO} \xrightarrow{1450-1500^\circ\text{C}} \text{Cd} + \frac{1}{2}\text{O}_2$ $\text{Cd} + 2\text{H}_2\text{O} \xrightarrow{25^\circ\text{C}, \text{electrochemical}} \text{Cd(OH)}_2 + \text{H}_2$ $\text{Cd(OH)}_2 \xrightarrow{375^\circ\text{C}} \text{CdO} + \text{H}_2\text{O}$
Sodium manganese	$\text{Mn}_2\text{O}_3 \xrightarrow{1400-1600^\circ\text{C}} 2\text{MnO} + \frac{1}{2}\text{O}_2$ $2\text{MnO} + 2\text{NaOH} \xrightarrow{627^\circ\text{C}} 2\text{NaMnO}_2 + \text{H}_2$ $2\text{NaMnO}_2 + \text{H}_2\text{O} \xrightarrow{25^\circ\text{C}} \text{Mn}_2\text{O}_3 + 2\text{NaOH}$
M-Ferrite ( <i>M</i> = Co, Ni, Zn)	$\text{Fe}_{3-x}\text{M}_x\text{O}_4 \xrightarrow{1200-1400^\circ\text{C}} \text{Fe}_{3-x}\text{M}_x\text{O}_{4-\delta} + \frac{\delta}{2}\text{O}_2$ $\text{Fe}_{3-x}\text{M}_x\text{O}_{4-\delta} + \delta\text{H}_2\text{O} \xrightarrow{1000-1200^\circ\text{C}} \text{Fe}_{3-x}\text{M}_x\text{O}_4 + \delta\text{H}_2$
<i>Low Temperature Cycles</i>	
Sulfur-Iodine	$\text{H}_2\text{SO}_4 \xrightarrow{850^\circ\text{C}} \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $\text{I}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \xrightarrow{100^\circ\text{C}} 2\text{HI} + \text{H}_2\text{SO}_4$ $2\text{HI} \xrightarrow{300^\circ\text{C}} \text{I}_2 + \text{H}_2$
Hybrid sulfur	$\text{H}_2\text{SO}_4 \xrightarrow{850^\circ\text{C}} \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ $\text{SO}_2 + 2\text{H}_2\text{O} \xrightarrow{77^\circ\text{C}, \text{electrochemical}} \text{H}_2\text{SO}_4 + \text{H}_2$
Hybrid copper chloride	$\text{Cu}_2\text{OCl}_2 \xrightarrow{550^\circ\text{C}} 2\text{CuCl} + \frac{1}{2}\text{O}_2$ $2\text{Cu} + 2\text{HCl} \xrightarrow{425^\circ\text{C}} \text{H}_2 + 2\text{CuCl}$ $4\text{CuCl} \xrightarrow{25^\circ\text{C}, \text{electrochemical}} 2\text{Cu} + 2\text{CuCl}_2$ $2\text{CuCl}_2 + \text{H}_2\text{O} \xrightarrow{325^\circ\text{C}} \text{Cu}_2\text{OCl}_2 + 2\text{HCl}$

portion of the cycle. As Zn particles react with water, a layer of ZnO forms on the outside of the particles, forming a diffusion barrier and effectively passivating the rest of the particle.<sup>20</sup> Zn particles should have very high specific surface areas to maximize conversion and cycle efficiency.

One of the key challenges to implementation of the Zn/ZnO process has been the propensity of Zn vapor and O<sub>2</sub> to recombine during cooling after the solar step. During the cooling process, there is a temperature regime the products must pass through in which this recombination is both thermodynamically



**Figure 1. Gibbs free energy change for the thermal reduction reaction for various single metal oxides as a function of temperature ( $P = 0.1$  MPa).**

and kinetically favored. The Zn and  $O_2$  exist in a metastable state, with recombination kinetics requiring nucleation sites to proceed. As Zn particulates form, they provide excellent sites for recombination. Palumbo, et al. have shown that by quenching the exit gas stream, high yields of Zn can be obtained.<sup>21</sup> The authors have used a water cooled copper tube to achieve rapid cooling rates ( $\sim 1,000$  K  $s^{-1}$ ) and 18% total yield of Zn, with the added benefit that the particles were of extremely small size (10 nm–30 nm).<sup>22</sup> Such particles are more reactive in the hydrolysis step of the reaction, improving overall hydrogen yields. Steinfeld, et al. have proposed an inert gas injection method to achieve this quenching while keeping products entrained.<sup>23</sup> The main disadvantage of quenching is that most of the sensible and latent heats of the product streams are lost, decreasing efficiency and increasing overall required capital investment for the solar components. Currently, though, it is the only proven method of achieving high zinc yields.

A second difficulty in execution of the ZnO dissociation reaction is finding materials that are tolerant of oxidizing environments, maintain chemical integrity at high temperatures, and are resistant to thermal shock and stress. At the temperature of operation of all of the “high-temperature” cycles, the list of materials is extremely limited.<sup>10</sup> Müller, et al.<sup>24</sup> used a rotating cavity reactor, the walls of which are made of tiles of the reactant ZnO itself. ZnO powder is distributed along the walls and held in place by centripetal force. Solar energy, incident on the ZnO through the window, brings the reactants to high-temperature and drives the reaction. The products are swept out of the reaction chamber by inert gas. The clever use of ZnO as the insulating material for the reactor eliminates the materials problem so long as the layer of particles to be reacted is thick enough that the underlying reactor material (alumina) is not subjected to rapid temperature swings. Results so far have shown good lifetime, but still show relatively low-thermal efficiencies. These efficiencies were just under 15%, and they did not account for recombination of Zn vapor with oxygen downstream of the dissociation reactor.<sup>25</sup> However, work is continuing on this reactor, and results have proven promising for the development of more efficient models.

To circumvent the problems of recombination and materials selection, some lower-temperature oxide cycles have been

proposed. Some of these are based on oxides with lower reduction temperatures than ZnO (e.g., CdO and  $Mn_2O_3$ ).<sup>26,27</sup> These oxides, when reduced, will not directly split water, so the process must be achieved through more than one additional step, as shown in Table 1. These additional steps typically operate at higher-temperatures, introduce the possibility of unwanted side reactions and complicated separations steps, and increase the overall possibility of material and energy balances. For example,  $Mn_2O_3$  has been shown to undergo thermal reduction at lower-temperature (1,400 °C) than ZnO without recombination problems.<sup>16</sup> However, the subsequent steps of the cycle form a sodium-manganese compound that requires immense amounts of water from which it is difficult to recover all of the sodium.

Another category of lower temperature oxide cycles that does not suffer from recombination problems are the “ferrite” cycles.<sup>28</sup> These processes employ a spinel ferrite that is doped with atoms other than iron (e.g., Zn, Ni, Co) in +2 oxidation states. The presence of these metals allows for partial reduction of the oxides at temperatures between 1,200 °C and 1,400 °C. These lower-temperatures make materials selection less difficult and raise the potential for improved efficiencies. These cycles are one of the few to demonstrate repeatable production of hydrogen.<sup>29,30</sup> However, theoretical hydrogen yields per unit mass of ferrite are low, requiring large amounts of sensible heat to be poured into the ferrite by the solar concentrating system. If this sensible heat is not recovered, the solar capital cost could be prohibitively high. Additionally, the hydrolysis reactions for these cycles operate at very high-temperatures ( $\sim 1,000$  °C), requiring some of the solar energy to be potentially used for that step and increasing capital cost loads.<sup>31</sup> Diver, et al. have proposed a system to recuperate the sensible heat and reduce hydrolysis heating loads.<sup>32</sup> In the concept, counter rotating rings of ferrite material are alternately exposed to solar energy and steam. Rings leaving the insulated region exchange heat with rings leaving the hydrolysis region, reducing overall sensible heat loads. The system will only be capable of producing hydrogen during daylight hours, but does have the potential to meet distributed hydrogen needs.

The second broad category of thermochemical water splitting cycles are the “low-temperature” cycles, listed in Table 1. Like their higher-temperature brethren, these cycles have an endothermic temperature chemical reaction that is intended to be driven by solar thermal energy. In this case, this reaction typically has an operating temperature below 1,100 °C, potentially increasing solar efficiency. These cycles are characterized by two or more non-solar chemical reaction steps that may include complex catalytic or electrolytic reactions, corrosive or exotic chemicals, and energy intensive separation steps.<sup>33</sup> These are the costs of operating at a significantly reduced solar temperature. With complex process flow-sheets, direct interfacing with the solar heat source is difficult, as interruption of solar energy can affect many downstream unit operations. Likewise, many of the solar driven reaction products are gases, which are difficult to store overnight after excess daytime production. Instead, indirect solar absorption heating with thermal storage systems are more likely the solar interface for these processes.

As proposed by Hruby,<sup>34</sup> falling refractory particles are irradiated by a solar beam incident on the particle curtain. The



hot particles pass into a storage tank, where they are fed via gravity through a heat exchanger into a second storage tank, available to be reheated by solar energy the following day. The heat exchanger transfers the sensible heat from the particles into the reactants for the high-temperature step of the thermochemical cycle. Appropriate insulation of the hot particle storage tank and control of the rate of flow through the heat exchanger would allow continuous operation of the thermochemical cycle, even when the sun was not shining. Such a system would decouple the intermittent solar energy from the thermochemical process, eliminating many of the problems with startup and shutdown.

The low-temperature cycles themselves were originally envisioned to operate using nuclear waste heat, and much of the development of these cycles has been performed by the nuclear industry.<sup>33</sup> The cycle with the most experimental development to date is the sulfur-iodine process (SI). The process currently has an anticipated flow sheet efficiency between 36% and 50%, and progress is being made in finding materials to handle the corrosive chemicals involved, but these may be expensive (zirconium and tantalum).<sup>35</sup> Key concerns are difficulties in separating the  $\text{HI}_x$  aqueous mixture created in the process and the large holdup of iodine by the process; a plant producing 0.05% of US transportation energy demand would require 15% of the annual world production of iodine for startup.<sup>36</sup> The “hybrid” low-temperature cycles, which use an electrochemical step to reduce cycle operating temperatures, can lead to more efficient solar operation and may eliminate some of the complex steps of similar cycles. These will require the use of renewable electricity to be truly sustainable, driving up final selling cost of the hydrogen. Additionally, electrolyzer costs are still high. However, decreases in the solar capital cost may offset these increased costs and make the cycle worth further investigation.

## Solar Thermal Gasification of Biomass

Cellulosic biomass provides a very attractive hydrogen source. This biomass is composed primarily of three biopolymers (cellulose, lignin, and hemicellulose) and is typically in the form of agricultural waste (e.g., corn stover, sugarcane bagasse), forestry wastes, designed biofuel crops (e.g., switchgrass, miscanthus), or industrial wastes (e.g., distillers’ grains). The biomass itself is carbon neutral, with all of its carbon mass photosynthetically derived from atmospheric  $\text{CO}_2$ . Gasification of biomass produces synthesis gas with a 1:1 ratio of carbon monoxide to hydrogen, and the hydrogen content can be effectively doubled through the application of the water gas shift reaction

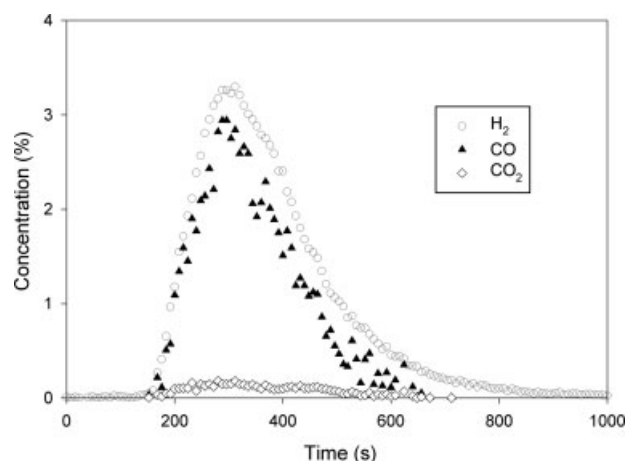


Thermochemical processing of biomass is most commonly driven by combustion of either a fossil fuel or the biomass resource itself. Application of solar thermal energy to biomass gasification has been looked at in the past, most notably by Gregg, et al.<sup>37</sup> These researchers showed solar to syngas efficiencies of greater than 45% for gasification of coal mixed with walnut shells, higher than predicted efficiencies for most thermochemical cycles. More recently, Lede has urged further

research into solar driven gasification.<sup>38</sup> Still, surprisingly little attention has been paid to this subfield, especially considering the advantages relative to both thermochemical water splitting and conventional thermochemical biomass gasification. Conventional biomass processing uses combustion to drive the gasification of the constituent biopolymers, with the fuel source typically either natural gas or the biomass material itself. As the temperature of gasification increases, the amount of fuel needed to drive the reaction becomes substantial. Temperatures are typically limited to between 600 °C and 1,000 °C, above which more than 30% of the biomass must be burned in pure oxygen to sustain the reaction.<sup>39</sup> This represents a significant loss of a valuable feedstock. At these temperatures, formation of volatile hydrocarbon tars is significant.<sup>39</sup> These tars can foul downstream catalytic surfaces and clog processing equipment, so much of the effort in traditional biomass gasification research has been directed toward mitigation of these tars.<sup>39</sup>

If solar-thermal energy is applied to the process, many of these problems may be alleviated. For solar thermal systems operating above 1,100 °C, the authors have shown that selectivity of the process to synthesis gas is high, conversion rapidly complete, and production of tars virtually eliminated. At the National Renewable Energy Laboratory’s (NREL) High Flux Solar Furnace (HFSF), pure cellulose, *Poa Pratensis* (Kentucky Bluegrass), corn stover, and sorghum have been gasified, with overall conversions to synthesis gas ranging between 70% and 95% at temperatures ranging between 1,150 °C and 1,250 °C. Production of tar was not observed at the highest temperatures, less than 5% of the syngas was methane and higher hydrocarbons, and solid products, when observed, were mixtures of carbonaceous char and ash.<sup>40</sup>

*Poa Pratensis* (“Kentucky bluegrass”) was gasified on-sun in a transport tube reactor at the HFSF at NREL at 1,160 °C, ~1 s residence time, and a 0.4:1 molar water:carbon ratio. The average spherical particle size was near 200  $\mu\text{m}$ . Grass was fed with argon gas as the carrier entrainment gas using a fluidized bed feeder. An inline mass spectrometer indicated synthesis of  $\text{H}_2$  and  $\text{CO}$  in near 1:1 molar ratios (Fig. 2). Conversion to products exceeded 99%, and selectivity to  $\text{CO}$  over



**Figure 2.** Synthesis gas composition measured via a downstream mass spectrometer for ground *Poa Pratensis* (“Kentucky Bluegrass”); 1,160 °C on-sun transport tube reactor,  $t_r \sim 1$  s, argon carrier gas.

CO<sub>2</sub> was greater than 94%. Conversion to gas products was 70%. Combustion analysis of the solid residual using a LECO carbon analyzer indicated 99% carbon by mass. No tars were detected in a downstream HEPA filter. The residual solid carbon is the result of a low water-to-carbon feed ratio for this experiment and is driven to near zero with additional steam.

Because the process is driven by solar thermal energy, partial oxidation of the valuable biomass resource is not required. As shown by experiment, nearly all of the carbon in the biomass can be converted to synthesis gas, stretching the ability of the biomass resource to meet energy demand and improving the overall economics of the process. Given these advantages and demonstrated experimental work, solar thermal gasification of biomass appears to be the most promising pathway to near term renewable hydrogen production from solar resources.

## Economics of Solar Thermal Hydrogen Production

If solar thermal hydrogen production is to be successfully implemented in the real world, the process chosen must be economically competitive with current fuels, preferably without support of government subsidies. Hydrogen production costs for representative thermochemical cycles, biomass gasification, and alternative hydrogen methods are estimated using the US Department of Energy's H<sub>2</sub>A analysis tool, which aims to establish uniform economic assumptions to facilitate reasonable comparison between production methods.

Both the "low-temperature" and "high-temperature" thermochemical cycles have relatively high break-even costs. The key driving factor for the ZnO cycle (and all "high-temperature" thermochemical cycles) is the solar facility capital cost, encompassing between 60% and 80% of the final selling price.<sup>9</sup> Because ZnO requires such a high solar energy input (450 kJ mole<sup>-1</sup> H<sub>2</sub>), and operates at elevated temperatures, there is little that can be done to reduce the required heliostat area. Instead, commercialization of this technology requires reductions in the cost of heliostats and central receiving towers.

For "low-temperature cycles," solar capital costs are the most significant cost as well. For hybrid cycles, capital cost is also an important component, reflecting the expense of providing significant amounts of solar electricity to the process. The cost of the low-temperature route is comparable to the high temperature Zn/ZnO process (>\$4/kg), yet still much greater than current expectations for fossil derived hydrogen (~\$1/kg).

The process that shows the greatest near-term chance of success is solar thermal biomass gasification, with selling prices of hydrogen competitive with steam methane reforming (~\$1/kg). This is largely driven by the fact that biomass already contains a great deal of chemical energy, reducing the required solar energy input to 47 kJ mol<sup>-1</sup> H<sub>2</sub>. As a result, solar capital requirements are significantly lower than those for thermochemical cycles, making the selling price much lower. The other significant piece of this selling price is biomass cost, which could be a significant concern for market-wide implementation, as good solar resources are not typically co-located with good biomass resources. However, the cost competitiveness of biomass *now* makes it a good bridge technology to move to thermochemical cycles later. Demonstration of profitable operation in the near term will attract

investment to the solar thermal field, improving collector technology and decreasing capital costs.

## The Path Forward for Solar Thermal Hydrogen Production

A number of interesting and potentially viable techniques exist for production of hydrogen from renewable resources using solar thermal energy. Direct water splitting is not likely to be feasible in the near future, but thermochemical cycles present a number of choices and opportunities. However, due to predictions of high solar capital costs, these are unlikely to be pursued until energy demand drives general prices higher and technology investment drives solar thermal capital costs lower. In the meantime, it makes sense to pursue bridge technologies that provide a profitable pathway to solar thermal hydrogen production.

The path advocated here is solar thermal biomass gasification, using rapid aerosol reactors in "power tower" configurations. Perhaps the most attractive attribute of the solar thermal gasification process, however, is the flexibility of the synthesis gas process. Synthesis gas is not limited to hydrogen production, but can be shifted to a number of useful fuel products (e.g., gasoline, diesel, methane, methanol, ethanol) through well established catalytic pathways. As a result, commercialization of a solar thermal biomass process does not depend on the emergence of a "hydrogen economy," but can produce fuels that are compatible with current infrastructure and are valuable in today's markets.

The presence of a profitable near-term market for the products of solar-thermal biomass gasification will attract investment that will develop solar thermal technology, reducing costs, working out control strategies, and improving overall efficiencies. When hydrogen distribution, storage, and application technologies mature enough for a true "hydrogen economy" to emerge, the biomass gasification process will be able to provide this fuel; as biomass becomes scarce, thermochemical water splitting can fill in demand gaps, made more affordable by advances in solar thermal technology. This pathway presents the most likely transition for using solar thermal energy to fuel the economy of the future.

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