Closing the Carbon Cycle:

Liquid Fuels from Air, Water and Sunshine

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Abstract

This paper outlines proposed advancements of a coherent set of technologies for a solar-powered system that uses water and CO_2 from ambient air to provide sustainable fuels to the world. These fuels would be synthetic liquid hydrocarbons that could power cars, trucks, aircraft, diesel-electric trains and generators, and heat residential and commercial buildings, without changes to current engine technology or fuel distribution infrastructure, and at costs competitive with fossil-based fuels. The explicit goal is to deliver an end-to-end solution for a complete sunlight-to-fuels system, including associated technologies for cost-efficient construction, operation and maintenance. This focus will aid cost-effectiveness and accelerate the transition to market. If desired, the system could also produce electricity, fresh water, and non-fuel hydrocarbons (e.g., plastics), thus further strengthening its economic viability. Fully developed, such a system could satisfy global demand for convenient fuel – yet would operate entirely on carbon recycled from the air, locally-available water, and sunlight.

Our approach constitutes a new engineering paradigm: We abandon the economies of scale so common in the energy industry in favor of the mass production of small units. Rather than emphasizing breakthrough advances in component technologies, we believe that the greatest cost reductions will be achieved by a systems approach that exploits economies of mass production, plug-and-play standardization of interfaces, and the fast-paced design innovations that accompany production of small units in large numbers. To see the power of this approach, consider the fact that, kilowatt for kilowatt, a car engine is about fifty times cheaper than a power plant.

The individual components of the cycle have been identified and proven feasible: solar panels to convert sunlight to electricity, water desalination, extraction of CO_2 from the atmosphere, water electrolysis, and synthesis of a variety of liquid hydrocarbon fuels from CO_2 and H_2. An integration and implementation effort will merge these subsystems into a highly modular, cyberphysical system of small, interchangeable units, and provide the substantial advances in automation technology that are necessary for successful operation, maintenance, and control. This modular approach will allow for a focus on making the overall system economically viable and sidestep the difficulties of scaling to ever larger units. Furthermore, the high degree of modularity enables the system to continuously improve by leveraging the latest innovations. Indeed, breakthrough advances in component technologies can be incorporated into the system as they are realized.

All research should ensure that the resulting technology is fully sustainable in all respects, including from a lifecycle and socioeconomic perspective. In summary, the envisioned solution will make transportation fuels both sustainable and affordable.

Table of Contents

I. Introduction

Water in the ocean and carbon dioxide in air provide nearly unlimited sources of the atoms from which high performance fuels could be made, and sunshine is a plentiful, sustainable energy source that can be used to convert the essentially zero-energy compounds, carbon dioxide and water, into high energy carbon-rich fuels and oxygen. Biomass production is a natural implementation of such a process and it is the source of most of the hydrocarbon fuels available on Earth. In this process green plants collect CO_2 from the air, water from the environment and use the energy in sunshine to convert the oxidized forms of hydrogen and carbon, i.e., H_2O and CO_2, into reduced forms, e.g. starch, that carry energy and which over geological times have been transformed into the world's fossil fuel deposits. The biofuel approach is an attempt to use this process to produce sustainable liquid hydrocarbons. However, this approach competes with agriculture and relies on photosynthesis, which seems to be limited to very low solar capture efficiency.

We propose to improve on this concept with chemical and physical rather than biological means. Carbon dioxide, water, and sunlight as the energy source can be combined to create synthetic hydrocarbon fuels without a biological system [*Graves et al.*]. By advancing a coherent set of technologies we envision a complete system that uses seawater and atmospheric carbon dioxide for material inputs and sunshine as an energy source to deliver a variety of liquid hydrocarbon fuels. These fuels can be used to support a future transportation sector or to provide an interim storage of energy in a future world that will depend on the sun as its main source of energy.

Specific implementations already exist for the five subsystems that are necessary to establish such a fuel generating infrastructure. These are photovoltaic conversion of sunlight to electricity, production of clean water from brackish or salty water, extraction of carbon dioxide from the air, electrolysis of water, and catalytic conversion of hydrogen and carbon dioxide into synthetic fuels. Some, such as air capture, are still in the laboratory stage while others, such as Fischer-Tropsch fuel synthesis, have been well established in the commercial or industrial sector. Rather than looking for the proverbial silver bullet of a technology that can combine material extraction and energy conversion into synthetic fuels via a single reactor system, we instead propose to focus on the most promising approaches that exist today for each of the five subsystems listed above and integrate them into a complete modular system.

To overcome the cost-hurdle we suggest taking advantage of the cost reductions that regularly occur when the manufacture of goods or machinery moves from the production of single units to large mass-manufacturing. Whether one is looking at consumer goods produced in China, automobiles or computer chips, mass production is a powerful tool to lower costs, quite literally by orders of magnitude. No other approach seems to have this capacity. The potential for cost reductions dwarfs those that would ensue from improving efficiencies. However, in the past the cost reductions from mass manufacturing tended to benefit industries that produce goods that are directly used by the consumer. The reason is simple; the effort in running and maintaining a unit process often does not increase much as the size of the unit increases. Hence for industrial sectors the cost of operating and maintaining a highly granular and modular system comprising many small subunits is typically prohibitive. By contrast, the consumer provides the operating input essentially for free; we drive our own automobiles and operate our own laptops. For small parallel systems to become practical in the energy sector, we need to dramatically reduce the personnel costs associated with operation and maintenance. This means we have to develop better automation and control strategies to limit the personnel cost which otherwise would go into the operation of the system.

More specifically, we suggest developing a functioning and economically viable system from modules composed of already proven technologies, by optimizing each technology to be inexpensive and to work together with the other subsystems. The basic technologies, from seawater desalination to catalytic fuel synthesis, are efficient enough to provide a solid platform on which to build a modular system of interacting process units. The challenge is to integrate the pieces into an economically viable and sustainable system. This appears to be feasible based on our analysis. The biggest challenge will come from advancing automation and control strategies to the point that these units can run largely autonomously. In other words, scaling down individual units to the point that they can be mass-produced is only possible if the attention of an individual human operator can be spread over thousands, if not tens of thousands of units. The coal industry accomplishes this by hiring individual drivers to operate fantastically large trucks. Our design is more akin to the automotive industry, in which robots are building the cars.

Figure 1 shows the envisioned, complete Sunlight-to-fuels process with a likely scenario for costs and efficiencies. The 5 subsystems, as well as the system integration and implementation effort are described below.

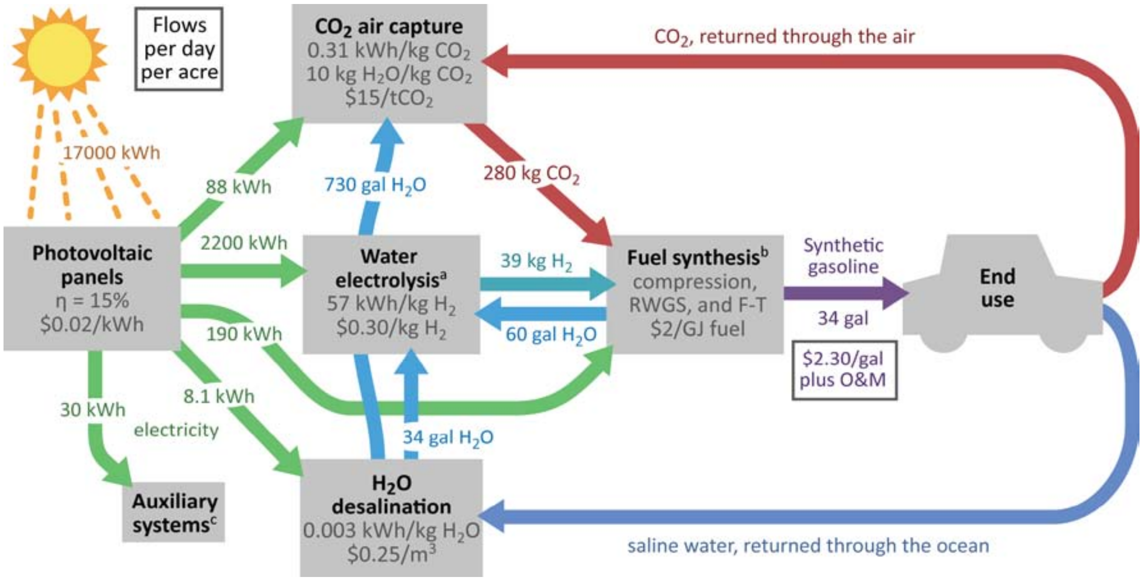

Figure 1: Sunlight-to-fuels process with envisioned scenarios for cost reductions and efficiencies (all flows per acre and day; see text for details). Costs shown represent projected fixed costs for the respective process unit (excluding electricity cost as the PV subsystem supplies electricity to all). The end-to-end energy conversion of this scenario is ~7% (based on 15% for solar-to-electricity and 50% for other systems). See text for potential alternative technologies for each modular subsystem (that may prove superior in the future and thus get exchanged in a plug-and-play fashion).
[a] low temperature alkaline cell; [b] fuel synthesis including RWGS reactor and syngas compression; [c] auxiliary power for e.g. transfer pumps and controls.

1. **Solar panels**, which generate electricity from sunshine, lend themselves to a modular implementation. In the implementation of very large systems, the use of common and naturally abundant elements is desired both from an economic and an environmental standpoint. On a scale commensurate with the replacement of global fossil carbon, mobilizing rare heavy elements with systems such as those based on CdTe and CIGS, would be hazardous for several ecosystems and

at the same time drive up costs. We therefore suggest employing silicon based PV-systems, which safely avoid these hazards. We believe that the mass production paradigm can reduce the cost of thin-film type PV technologies to viability for the system.

2. Technologies for **desalination** of seawater already exist and have matured. The most cost-efficient desalination plants are based on reverse osmosis (RO), a technology which lends itself to highly modular mass-producible implementations. One of the remaining challenges to environmentally sustainable implementation is the discharge of highly saline brines, which has proven to be a concern. With regards to necessary R&D, desalination would be a minor component of the effort, except for the crucial mass production and automated operation required to integrate desalination with its neighboring subsystems.

3. The **capture of carbon dioxide from air** is a novel technology pioneered by researchers at the Lenfest Center. They have demonstrated the utility of an anionic exchange resin as a CO_2 sorbent that can be regenerated by exposing it to moisture. So far this moisture swing absorption system has only been proven on the bench scale, but the energy balance of the process is highly favorable. Its energy cost is far smaller than the energy cost of converting H_2O and CO_2 to fuel. Air capture, too, is a technology that lends itself to modular implementation. Sustainable production of hydrocarbon-based synthetic fuels is only possible with air capture. Without the ability of removing carbon dioxide from air, the carbon dioxide produced would unavoidably accumulate in the atmosphere and contribute to the greenhouse effect.

4. **Water electrolysis systems** producing hydrogen from water are commercially available. Electrolytic cell technology inherently uses modular small units. Conversion efficiencies of 70 percent or higher are economically viable with commercially available electrolyzers. However, the capital cost will be significantly increased by only operating during the daytime on solar power. Significant capital cost reductions will be needed and we believe can be attained by similar automated production and maintenance advances. Because electrolyzers can be run at lower efficiency (using more electricity) to reduce the capital cost, it is really combined cost reductions of the PV and electrolyzer systems that are needed. It is sufficient to produce hydrogen from water, because hydrogen and carbon dioxide can be used to make synthetic fuels. For example from hydrogen and CO_2 it is possible to produce methanol, or produce carbon monoxide via the reverse water gas shift reaction. As an additional option to be explored during the integrative system design optimization, the water electrolyzers can easily be designed to run in the reverse direction (as fuel cells), generating electricity from the hydrogen that was produced earlier in the day in order to operate parts of the system when the sun is not shining.

5. The exception to a process that has not naturally scaled towards small modular units is the process of converting synthesis gas, a mixture of hydrogen and carbon monoxide, into a hydrocarbon fuel. Many of these **fuel synthesis** processes can be viewed as a variation on the Fischer-Tropsch process. Fischer-Tropsch, while well established, has typically been scaled to extremely large size to harness economies of scale. One of our goals is to establish that catalytic fuel synthesis can work on smaller scales, and there have been a number of recent efforts that suggests that such an approach is feasible [*de Deugd et al.*, 2003; *Guettel et al.*, 2008].

6. The five subsystem development efforts are held together by a sixth group focusing on **system integration and implementation**. This group is to provide intellectual leadership on the system

concepts, define the interfaces between the different subsystems, and extract automation and control issues that are common to all subsystems. This group also will develop a computational modeling capacity that will make it possible to develop different approaches to scaling and aggregating the modular units into the different subsystems.

It is instructive to consider the relative sizes of the five subsystems, which is partly laid out in Figure 1. What emerges from such an analysis is that the solar panels are by far the largest part of the system. For example, the entire membrane surface area in the RO system is a thousand times smaller than the solar panel surface, the wind-facing opening area of the CO_2 collectors amount to a fraction of a percent of the associated solar panel area. And the membrane surface area inside the alkaline electrolysis cells is about 2 percent of the solar panel area. The fuel synthesis devices are also much smaller. This observation emphasizes the need to develop cost-effective manufacturing approaches to the solar collectors.

	Electric Power	Capital Equipment	Fraction of Electric Power Consumption
CO_2 Air Capture	\$0.054	\$0.13	3.5%
Water Desalination	\$0.005	\$0.02	0.3%
Water Electrolysis	\$1.410	\$0.37	87.4%
Auxiliary Systems	\$0.019	n/a	1.2%
Fuel Synthesis	\$0.122	\$0.26	7.6%
Total	**\$1.6**	**\$0.78**	**100%**

Table 1: Subsystem contribution to the cost of a gallon of gasoline (preliminary estimates corresponding to scenario shown in Figure 1).

II. System output - Liquid hydrocarbon fuels and their advantages

II.1.1. Advantages of liquid vs. gaseous fuels

If liquid hydrocarbon fuels had not been invented yet, their invention would surely create a sensation. They have significant advantages over all other known energy carriers. For example, per unit of mass or volume they hold far more energy than batteries, flywheels or super-capacitors. In the past, scenarios have been envisioned for a technological evolution towards a hydrogen economy [*Winsche et al.*, 1973], possibly the most straightforward direct fuel from sunlight and recent advances in photoelectrochemical (PEC) cells have further spurned innovation [*Krol and Schoonman*, 2008; *Turner et al.*, 2008]. While technologies based on hydrogen or other gases have great potential, e.g. for on-site storage of intermittent renewables in homes or on micro-grids, our proposed system here rests on the fundamental view that gaseous fuels lack the tremendous advantages that liquid (hydrocarbon) fuels offer:

- Liquid hydrocarbons are far more convenient than gaseous fuels with respect to ease of storage, transportation, and safety. In essence, liquid hydrocarbons are ideal for separating, in space and in time, energy supply from demand (cars, diesel generators, etc.).

- If one accounts for the volume and weight of the tank required to confine these gases, the volume density and mass density of liquid hydrocarbon fuels stands out again.

- Convenience and energy-density combined give liquid hydrocarbons competitive advantages, especially for the small, individual amounts demanded in the transportation sector, as well as for use in more rural areas. The high energy density of liquid hydrocarbons, per weight and per volume, is a particular advantage where limited ranges of the transportation (e.g., trans-oceanic flights or long distance driving) would otherwise pose a significant restriction on society.

- Synthesized liquid hydrocarbons accommodate much of today's existing distribution and consumption infrastructure. Existing cars and trucks, diesel-powered trains and aircraft can use the proposed system's output without any modifications. The distribution of the produced fuel can to a great extent also be facilitated through existing distribution networks (gas stations etc.).

- In comparison, the additional cost for hydrogen distribution and filling station infrastructure has been estimated to be in the range of at least \$6/GJ of hydrogen fuel (about \$1 per replaced gallon of gasoline), if not several times more depending on penetration [*IEA*, 2007; *Yang and Ogden*, 2007]). These costs would come in the form of substantial capital investments which, to be economical, would require immediate, widespread adoption of hydrogen-fueled vehicles. Synthetic hydrocarbon fuels can, in comparison, smoothly substitute into the existing hydrocarbon fuel infrastructure and scale up naturally as output capacity increases.

In summary, today there is no better way for storing energy in a convenient, ready-to-use, high density form than liquid hydrocarbons, especially when a solution is needed that can operate at the scale of today's consumption and with the flexibility to serve the wide range of fossil carbon in today's economy, from industrialized hotspots to rural regions. We view synthesized liquid hydrocarbons as the only feasible candidate to rid the world of its dependence on fossil carbon (be it for limited reserves, for geopolitical or for environmental reasons).

II.1.2. Present & future demand – energy supply from the sun

A crucial premise of the proposed scheme is that there is enough energy coming to Earth from the sun to be able to replace the entire current and future demand – in the United States and worldwide – with non-fossil fuels. While in Figure 1 we give a more detailed analysis of capacity, efficiencies and cost, we feel it is important to demonstrate that sunlight is indeed plentiful and that the amount of sunlight or required land use will not be a limiting factor for the proposed solution even given the sheer amount of fuel that the system proposes to replace:

- The world currently consumes 85 million barrels of oil per day [*EIA*, 2010], the equivalent to 6 TW (assuming 5.8 million Btu per barrel).
- Sunlight offers an annual average irradiance of 175 Watts per square meter (world-wide average, on land, including day/night average, weather, etc. [*Holdren*, 1992]), with only about a factor two variation across countries and continents [*Bishop and Rossow*, 1991].
- Assuming a PV efficiency of 15 percent, we expect the full system (sunlight to liquid fuel) to operate at an overall efficiency of 7 percent. Hence we arrive at an estimated land use of a square with approximately 450 miles on each side (depending on panel geometry, i.e. flat or tilted towards the sun with shadows behind them) to produce the equivalent of 85 million barrels of oil per day (see Figure 1).

Looking forward, demand for liquid hydrocarbons may easily double by 2050, especially if we consider that fuel demand growth will outpace electricity demand growth in developing countries such as China (which currently consume less liquid fuel relative to other forms of energy [*K. S. Lackner and Sachs*, 2006]).

In summary, sunlight (and implied land use) will not pose a limiting factor for replacing all of current and future fossil fuels with non-fossil liquid hydrocarbons.

II.1.3. Products from the proposed system – and who will use them

A crucial advantage of the proposed Sunlight-to-fuels solution is that its flexible, modular design facilitates the production of more than a single type of output while keeping large parts of the system (PV, desalination, electrolysis, and reverse water gas shift) unchanged (and thus saving costs). Below, we give an overview of the products/applications and respective chemical pathways that the proposed system will provide. Because of their high desirability and current consumption, we will initially focus on replacing petroleum-derived fuels with their non-fossil equivalents. However, in essence, the proposed technology will be able to produce an alternative for all (currently fossil-originated) carbon-based products in commercial use today.

Excluded from the table are possible future designer fuels. Today's fuel choices are largely driven by the fact that petroleum distillation products are particularly easy to make. A world that uses largely synthetic fuels does not operate under this constraint. This opens the door for other fuels with different advantages and for specialized fuels particularly suitable in special circumstances. This could run the gamut from pure hydrogen to pure carbon, from methanol to dimethyl-ether. The proposed system could produce carbon-rich, coal-like products as well. However, coal is an especially low-cost fuel, and its primary use is in base-load power generation; it may not be sensible to replace coal in power plants since the newly envisioned system can generate electricity directly.

Product (from fuel-from-sunlight systems)	**Current fossil source** (that is substituted)	**Use** (with minimal changes to current infrastructure)	**Pathway**	**Substituted capacity**†††
Diesel, gasoline, jetfuel	Petroleum	Transportation: 71% Building heat & onsite electricity: 28% Utilities: 1%	From Syngas, via Fischer-Tropsch or methanol-to-gasoline	42%
Natural gas equivalent (e.g., CH_4)	Natural gas	Transportation: 3% Building heat & onsite electricity: 68% Grid electricity†: 29%	Sabatier	27%
Petrochemical feedstocks (e.g., for plastics.), other C-based chemicals	Petroleum, natural gas (non fuel-use)	Chemical industry	Various (mostly based on Syngas)	5%
			Readily substituted fossil carbon consumption:	**74%**
			Not readily substituted (coal††):	26%

Table 2: Ready-to-use end products from the proposed Sunlight-to-fuels system and potential for fossil carbon substitution. † Short term: Existing natural gas-fired turbines (e.g. peak demand) can use non-fossil CH_4. Longterm: Replace with cheap solar electricity (a by-product from the system effort) once smartgrid/storage solutions are available. †† Long-term option: Replace with cheap solar electricity (a by-product from the system effort) once smartgrid/storage solutions are available or coal-fired plants with CCS, etc. ††† In % of 2008 U.S. fossil carbon consumption [*U.S.-DOE*, 2009].

II.1.4. Additional applications - storage for intermittent renewables

As an additional benefit, liquid hydrocarbons could solve the problems associated with the intermittency of renewable energy. Cheap solar electricity as produced at the solar panel (primary electricity) should be distinguished from electricity the consumer demands (secondary electricity). The electricity at the solar panel is a primary energy source that flows independently from consumer demand. In order to be useful as a source of non-intermittent, secondary energy for the consumer, it will have to be stored and hence, this secondary electricity has a much higher value. Therefore it could conceivably be generated from energy stored in synthetic fuels – even if the roundtrip efficiency of first turning primary electricity energy into liquid fuel and then back into secondary electricity is quite low (say 30 percent). However, on the positive side, the storage capacity of liquid fuel is virtually unlimited and storage times could be very long without greatly affecting the price. In particular the storage cost associated with the capital cost of the storage device, makes long term storage of household electricity very unattractive. Similarly, the manpower for operating and maintaining the systems adds a cost that increases with storage time. With automated production and operation systems this cost factor could be greatly reduced.

In comparison, other approaches, such as batteries, do have somewhat higher round trip efficiencies, but typically have fairly limited storage capabilities. Large storage amounts are critical for dealing with large natural fluctuations (in particular the relatively rare events) in addition to load shifting between seasons. As another disadvantage, batteries also require expensive raw materials, contain long-term toxic components, and require much more materials per unit of stored energy as they have relatively low energy densities compared to hydrocarbon fuels.

III. The five subsystems

III.1. Solar panels

This subsystem is defined as converting solar energy into electric power, via photovoltaics (PV), concentrated PV (CPV), or concentrated solar thermal power (CSP). Per amount of fuel produced, approximately 90 percent of the electricity is used for the electrolysis (with the remainder for the other subsystems: desalination, air capture, fuel synthesis, and the systems control and automation, see Figure 1).

The generation of electric power is the most critical component of the overall system. Per amount of fuel produced, the solar panels require significantly more area (to capture the sunlight) and hence material/equipment than the other four subsystems. This is also the reason why the solar panels represent the biggest challenge (of the overall system) with regards to driving down the costs.

Analogous to the other four subsystems, the goal is to develop a solar-to-electricity solution that meets the following requirements of the complete system:

- **Capacity**: Scalable from currently 14.3 GW globally installed solar capacity (including 0.4 GW from CSP) [*DOE*, 2010] to tens of TW worldwide (rationale: today's worldwide oil consumption of 85 million barrels per day [*EIA*, 2010] represents 6 TW; account for approximately 50 percent efficiency loss of electricity-to-fuel system and expect at least doubling of demand by 2050). For comparison, in a review of 34 emissions scenarios, [*Nakicenovic and Riahi*, 2002] found a median of 22 terawatts of PV deployed in 2100 for those scenarios that include GHG stabilization. In summary, a more than three orders of magnitude increase in (solar) electricity output will be needed.

- **Cost**: 2 cents per kWh levelized cost of electricity (LCOE) – i.e., manufacturing, installation and operation/maintenance, including financing costs. Note that, as explained further below, we envision such steep cost reductions for the cost per kWh via:
    - Mass manufacturing (of the modules themselves and supporting infrastructure such as arrays and power-conditioning): 2 cents per kWh is the target for the fully matured system, i.e. once mass production is fully under way and the learning curve from cumulative installed capacity has come to full fruition)
    - Increases in efficiency (of industrially produced PV modules)
    - Initially focusing on optimal solar locations

- **Sustainability**: The solar panels will represent a large interface between the Sunlight-to-fuels system and the open environment. Here, losses of materials to environmental impacts such as storms, earthquakes are much more difficult to avoid than within manufacturing plants, where exposure to the elements can be better controlled. As a result, our major focus is to assure that the solar panels will be made from environmentally benign materials. This, together with the high abundance of silicon, is the main rationale behind our current preference for silicon based cells (see below).

- **Panel technology and design**: Suitable for low-cost mass manufacturing and highly automated operation and maintenance.

- **Unit size and deployment**: Flexible for large scale as well as small scale operations, including decentralized installations in remote areas (e.g. rough terrain).

Based on current state of the art and on past developments, we currently view silicon-based PV technology as the most appropriate choice to meet above criteria. In parallel to furthering research on silicon-based PV, one should continuously monitor progress in promising alternative technologies, such as organic or dye-sensitized PV cells, concentrated PV, 2nd and 3rd generation solar thermal, as well as catalyst-based, more direct solar-to-hydrogen systems such as photoelectrochemical (PEC) cells [*Krol and Schoonman*, 2008; *Turner et al.*, 2008].

III.1.1. Current state of the art

III.1.1.1. Cell efficiencies and industrial module efficiencies (laboratory)

Any given photovoltaic cell can only convert part of the energy it absorbs as light into electricity. This efficiency factor has theoretical limitations that cannot be surpassed. Ideal materials, manufactured into an ideal (multi-junction) photovoltaic element, will exhibit efficiencies of at most 43% [*Fan et al.*, 1982].

Currently, only (multi-junction) concentrated PV cells come close to this efficiency (see Figure 2). Most other technologies – despite enormous improvement during the past several decades – remain well below 30 percent (for an individual PV cell in a laboratory) or 20 percent (for industrially produced, larger modules).

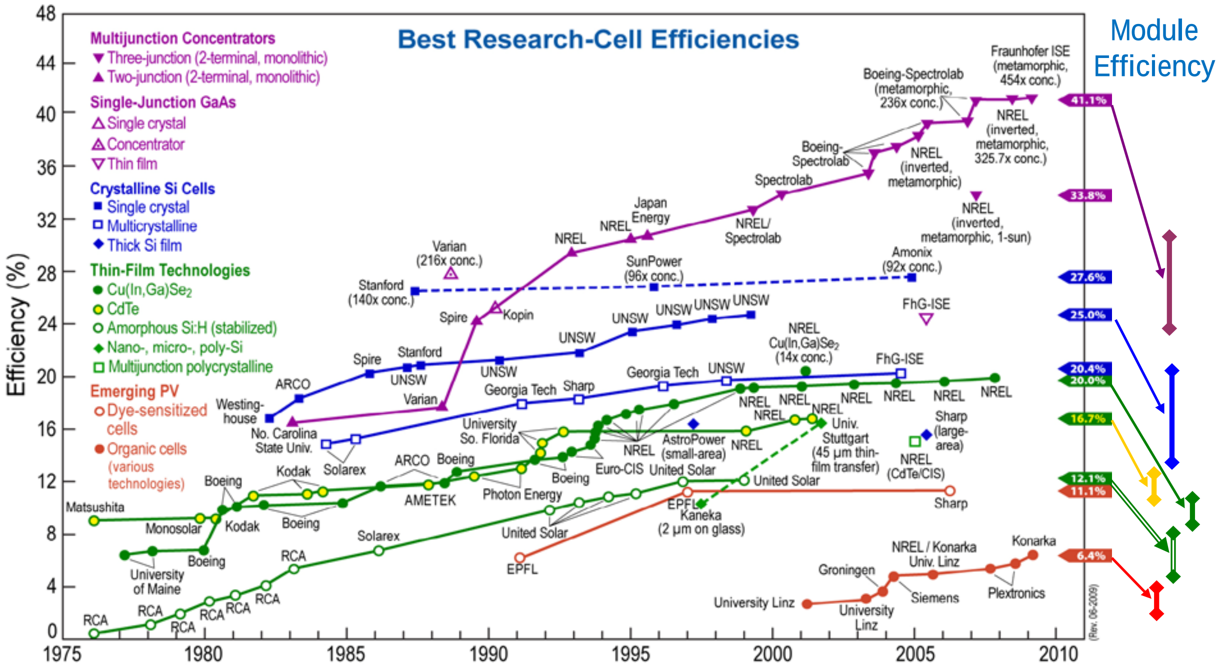

Figure 2: Past and current efficiencies (laboratory cells and industrial modules) of various PV technologies (Source: National Renewable Energy Lab, U.S. Department of Energy Solar Energy Technologies Program).

Single crystal silicon cells have shown efficiencies of 25 percent (laboratory cell), cells based on amorphous silicon and other thin film technology – often seen as the most promising in terms of cost – currently exhibit maximum efficiencies of 20% (cell). Amorphous silicon cells were first investigated in 1974 at RCA Laboratories in Princeton, NJ [*D. E. Carlson*, 1976]. Their efficiencies were about 1%. By the year 1991, stable efficiencies of 10% for an amorphous silicon based solar cell (1 cm^2 large laboratory cell) and 6% (about 1,000 cm^2 large commercial cell) had been achieved [*D. E Carlson and Wagner*, 1993]. At the same time, further improvements and a stable efficiency factor for amorphous silicon based photovoltaic cells of 18% by the year 2005 were predicted [*D. E Carlson and Wagner*, 1993]. However, today United Solar, one of the pioneers in commercial, mass-produced amorphous silicon thin film PV, has achieved efficiencies of 12% (for the cell, not a module).

Efficiency gaps between industrially produced modules and laboratory cells have also been reduced [*Stone*, 1991]. In 1993, the first larger area (28cm x 28cm) flat plate photovoltaic module repeatedly exhibited an efficiency factor of 20.5% [*Green et al.*, 1993]. The fact that individual photovoltaic modules have a large area, an aspect which has also been subject to many improvements in the past [*Sinton*, 1993], is important because it will increase the total photoactive area for a given plant size. In 1993, a group reported the development of high efficiency, low weight, 35 cm^2 silicon cells. These had efficiencies up to 21% [*Sinton*, 1993]. Another cell type, the PEARL cell, has shown efficiencies of 23%. Its area, however, has been only 4 cm^2. After further improvements this cell type has an anticipated efficiency factor of 25% [*Goldemberg et al.*, 1985]. A gallium arsenide-gallium antimonide stacked junction cell even exhibited a 35% efficiency [*Weinberg and Williams*, 1990].

III.1.1.2. Realistic operation efficiencies of industrial PV modules in the field

The above reported efficiency factors are performances achieved in laboratories under standard testing conditions. Predicting performances of photovoltaic modules in actual plant facilities requires caution. Such realistic operation efficiencies will be lower for three reasons:

- **Degradation**: By 1990, technological improvements had been made especially with respect to the adverse effects of light-induced degradation, an effect that until then had caused stable efficiency factors to be up to 50% smaller than initial values [*Ichikawa*, 1990]. Still, even modern PV modules may lose 5-10% of their out-of-the-factory efficiency over the course of their operational life[*So et al.*, 2007] .
- **Weather**: Field tests have shown that both wind and varying outside temperatures can cause efficiency factors to be 10 to 20% less than reported laboratory values [*Bücher*, 1993].
- **Spectral distribution**: Although differences in the spectral distribution of the irradiant sunlight for different locations and their effect on efficiency factors are routinely included when predicting performances for different solar cells, these spectral correction factors can be inaccurate as well. In some cases, actual outputs have been overestimated by about 3% [*Field and Emery*, 1993].

These reductions in total efficiency are often encompassed as the term “performance factor” of the cell, which typically corresponds to 70-90%.

III.1.1.3. Costs

For 2015, the U.S. DOE currently targets electricity costs from PV at 7-13 cents per kWh (levelized cost of electricity for utilities, including a 10 percent investment tax credit; DOE Solar Cost targets 2009-2030, in progress). This range represents a steep improvement over 2009 targets which were 17-29 cents per kWh (DOE, same methodology).

A cost of 7-13 cents per kWh is in line with several – albeit more theoretical – projections dating further back. To cite just one such example, [*Stolte et al.*, 1993] projected the future price per kWh electricity generated by a photovoltaic plant that is connected to the commercial grid. Using a flat plate module design of 9.9% average annual efficiency (Copper Indium Diselenide solar cell), a 50 MW plant was estimated to generate electricity at 11.8 or 10.8 cents per kWh (30 year levelized cost in 1990 U.S. dollar, for a yearly production of photovoltaic modules of 25 or 100 MW respectively). This assumed a solar module price of $1.35 per peak Watt ($W_p$),, a price achievable with some technologies today (see below). In the study, the cost of the modules themselves accounted for 58% of the total capital required. Other important cost contributors were the array structure (12%) and the power conditioning unit (5%). The overall costs (including financing) consisted of capital charges (98.5%) and operation and maintenance (1.5%).

As expected, material, manufacturing and installation costs (modules, arrays, and power conditioning) represent the vast majority of PV electricity cost, especially once the financing costs for upfront capital and discounting for later operation and maintenance are considered. How much further can module costs, and thus electricity costs, be reduced?

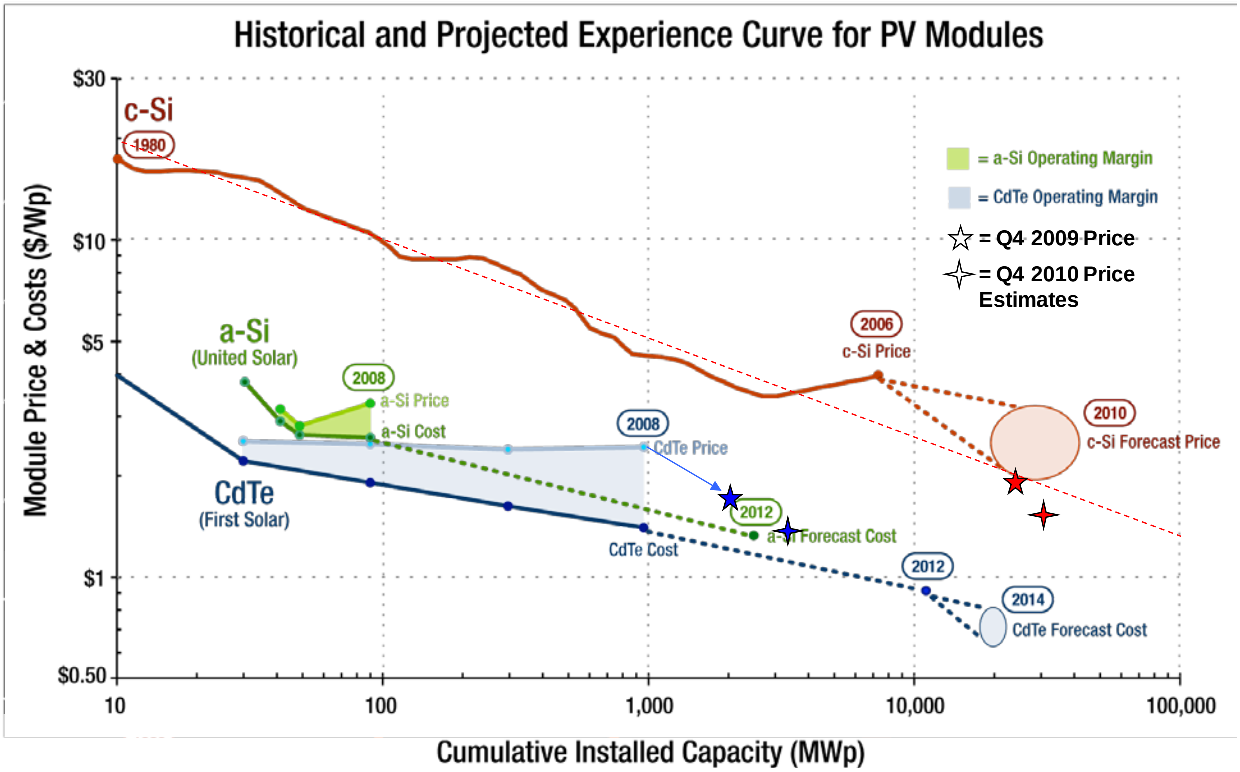

Figure 3: Average PV module prices and costs versus cumulative installed capacity. Details see text [*U.S.-DOE-SETP*, 2009].

Historically, PV module costs have seen a steep decline. Since the 1950s, the cost of PV has declined by a factor of nearly 100, more than any other energy technology in that period [*Maycock*, 2002; *McDonald and Schrattenholzer*, 2001; *Wolf*, 1974]. Even in 1994, the lowest prices for commercial photovoltaic modules were still in the range of $3.50 to $4.50 per Watt (peak) of generated electricity [*D. E. Carlson*, 1994]. As a function of cumulative installed capacity, historical data points to a 3-7 fold decrease in price for a 1000 fold increase in installed peak Watts (Figure 3).

Today, the most prevalent PV technologies are crystalline silicon, amorphous (thin film) silicon, and CdTe thin film. Benchmarks for module costs (material and manufacturing, not sales price) are ([*U.S.-DOE-SETP*, 2009], using ~20% margin where only module prices were available):

- Crystalline silicon (majority of currently installed peak Watt globally)
  1980: $13.6 per peak Watt (with 10 peak MW installed)
  2006: $3.1 per peak Watt (with 7000 peak MW installed)
  2010: $1.5 per peak Watt (with 30,000 peak MW installed) [forecasted]

- Amorphous silicon thin film (United Solar)
  2005: $3.8 per peak Watt (with 30 peak MW installed)
  2008: $2.6 per peak Watt (with 90 peak MW installed)
  2012: $1.3 per peak Watt (with 2,500 peak MW installed) [forecasted]

- CdTe thin film (First Solar)
  2005: $2.2 per peak Watt (with 30 peak MW installed)
  2008: $1.4 per peak Watt (with 960 peak MW installed)
  2012: $0.9 per peak Watt (with 11,200 peak MW installed) [forecasted]

From the above data, $1 cost per peak Watt installed appears within reach in the short term. Interestingly, $1 per peak Watt is in line with historical projections for the cost of PV modules, e.g. [*D. E Carlson and Wagner*, 1993]. This is certainly promising. Still, even a relatively cheap PV module of $1 per peak Watt (and assuming other costs such as arrays etc. have come down accordingly) will translate into a levelized cost of electricity of 5-8 cents per kWh (depending on module life time, financing structure, etc.). An outlook for further reduction towards our target of $0.02/kWh will be discussed below.

III.1.1.4. Cost and efficiency observations

How much further cost reduction can one realistically expect, and what should be the research strategy to get there? From the above historical analysis, we observe:

- The predominant driver of cost reduction is the cumulative manufactured capacity:
  - Within a broad technology class (e.g. crystalline silicon vs. amorphous silicon), a roughly factor five price drop for a 1,000 fold increase in cumulative output appears achievable (again, assuming that costs of PV modules and of array infrastructure etc. exhibit similar learning curves). These price drops were made possible by tremendous technological improvements both in the manufacturing processes as well as the specific design of the modules (e.g. single crystal vs. multi crystalline, thinner absorber materials, vertically integrated manufacturing, improved ingots and wafer designs, etc.).
  - Across broad technology classes (e.g. crystalline silicon vs. CdTe thin film), achievable price drops appear in the range of "only" factors of two. This is especially true when accounting for the fact that manufacturing expertise for later technologies such as thin film, even at yet small cumulative outputs of that particular technology, will already have benefited significantly from existing knowledge in e.g. crystalline silicon (commonly referred to as "spillover" in the learning/experience curve).

- Another important driver is improvement in efficiency, specifically in the lifetime averaged efficiencies of commercial, mass-produced PV modules. For example, First Solar has predicted a further drop in the price of their CdTe thin film modules by 2014 (to $0.70 per peak Watt) and attributes this to a marked increase in efficiency. However, we expect improvements in module efficiency factors of at most doubling. Therefore, module efficiency factor increases cannot be relied on to deliver the bulk of the targeted cost reduction, because:
    - The module efficiencies are themselves limited by the efficiencies achievable in laboratory cells. As shown in Figure 2, after the early steep advances until about 1990, the range of possible cell efficiencies is limited to 10%-30% (excl. CPV; with a theoretical limit at ~40%, see above). In other words, the range of improvement is naturally capped.
    - Also post-1990, efficiency improvements in most technologies seem to have leveled off; still, incredible cost improvements have still been possible.

We conclude that focusing research on improved manufacturing and module design to drive down manufacturing costs and improve performance – within a PV material class – offers the most promise in reducing cost of PV panels. Crucially, this confirms the general strategy behind this sunlight-to-fuels system which aims to exploit dramatic improvements in both the manufacturing as well as the specific design of broad functional components to drive down the cost.

III.1.2. Remaining obstacles for integration to sunlight-to-fuels system

III.1.2.1. Costs targets

For 2015, the U.S. DOE currently targets (utility) electricity costs from PV at 7-13 cents per kWh – these would be competitive with (expected) conventional electricity (DOE Solar Cost targets 2009-2030, in progress).

Based on above analyses, electricity prices around 10 cents per kWh appear well within reach. However, a stated goal is to offer non-fossil liquid hydrocarbons that are near competitive with traditional gasoline. Therefore, we need the electricity powering the envisioned Sunlight-to-fuels system to be much cheaper than such "conventional" electricity because we expect an efficiency (electrical energy to chemical energy in final fuel) of the envisioned sunlight-to-fuels system to be significantly below 1 (e.g., ~50% in the end-to-end, all-inclusive cost scenario presented in Figure 1).

Our analyses of the end-to-end system, its efficiencies and cost structure (including capital costs), indicate that we require electricity at a price of 2 cents per kWh (in order to produce gasoline at near competitive prices). Can this be achieved? While 2 cents per kWh is certainly an aggressive target, we believe it is possible based on historical cost developments in PV: (i) cost reductions have been made possible by difficult technological advances (in manufacturing and cell design); yet, these reductions have also proven remarkably steady and consistent across several broad technologies (ii) assuming this learning curve continues, the required factor ~5 reduction on module costs appears achievable, given that cumulative peak Watt capacity will have to increase another 1,000-fold (beyond today's capacity) to reach tens of terawatt range.

III.1.2.2. Module efficiency targets

Currently, 10-15% efficiency of the industrialized module in open field conditions is within the range of today's capability, e.g. for crystalline silicon technology. We would aim for efficiencies of the commercially-produced PV modules to be increased further (towards ~20%), for example via employing nano-structured thin film. Since sunlight, even if reduced to 15% in overall efficiency (irradiance to electricity) is abundant (see above), land requirements will not be the primary constraint on the finished Sunlight-to-fuels system. This is contrary to biomass-based systems which, with usually less than 1% end-to-end efficiency, not only require much more land, but also fertile land which thus competes with food production. Because of the only moderate land requirement of PV, we will not pursue higher efficiencies unless they translate into significantly lower costs (current trends indicate the opposite relationship; see above Figure 2 and Figure 3). However, an efficiency of less than 10% (e.g., current organic PV technologies) would be a marked disadvantage – even if cost competitive – because the surface area required for PV panels would increase so much that the deployment of the overall system in populated areas would likely become infeasible (distributed generation near e.g. villages in developing countries rather than large, centralized stations in scarcely populated areas). A limitation to large plants in remote areas (because of excessive land area requirements) would be contrary to the general philosophy of the proposed approach.

III.1.2.3. Silicon PV as (current) technology of choice

We conclude that, currently, silicon-based PV cells hold the most promise to deliver sufficiently low cost and large-scale solar electricity for the sunlight-to-fuels system, for the following reasons:

- Silicon is one of the most abundant elements on the planet. This makes it an ideal candidate to supply the material required for another ~1,000 increase in installed peak Watt capacity, without risking scarcity of supply.

- Silicon is a benign material. This makes it ideally suited to comply with the stringent sustainability and LCA requirements that our envisioned Sunlight-to-fuels system is based on. Not only does the material have to be safely deployable and recoverable under normal operating conditions; rather, a destruction of an entire system by hostile weather, accidents or earth quakes, or indeed terrorist attacks should ideally not expose the environment to significant amounts of any toxic materials.

- Silicon-based technologies offer the largest, already accumulated "learning curve" that can be readily tapped and exploited further towards the envisioned (automated) mass manufacturing.

- Similarly, as a broad technology class of PV, silicon (currently) offers the most options with regards to details of the modules' design (impurity migration, light trapping, etc.), efficiencies, and material consumption, from mono-crystalline (largest efficiencies), to poly-crystalline, thick film, and amorphous thin film (smallest efficiency/lowest cost). New technologies such as Si-wire are in their experimental stage [*Kelzenberg et al.*, 2010] A variety of mount options from solid on glass to flexible film offer additional flexibility, again with mostly well understood behavior (e.g., durability, moisture sensitivity, etc.). This variety of Si-based technologies will offer advantages versus other PV technologies when optimizing manufacturing and design of the final PV module solution (e.g., efficiency versus cost trade-offs) for integration into the overall sunlight-to-fuels system.

- Silicon-based thin film, because of its ability to be deposited over large areas on flexible, even rollable substrates such as plastic or metal thin sheets, at very low temperatures, have the potential to be manufactured and installed at very low cost.

III.1.2.4. PV versus concentrating solar power and direct PEC

III.1.2.4.1. Concentrating solar power (CSP)

Compared with PV, current global capacity levels of CSP ("solar thermal") are low. At the end of 2008, worldwide (cumulative) capacity of grid-tied concentrating solar power was 430 MW, with more than 95% (419 MW) of this global capacity located in the southwestern United States. However, projected growth is high. Globally, about 13 GW of CSP was announced or proposed through 2015, based on forecasts made in mid-2009 [*DOE*, 2010].

CSP, by many, is considered more promising than PV, primarily because of lower expected electricity costs (and reduced intermittency because some of the heat can be easily stored to allow at least some continued operation after "dark"). Clearly, the jury is still out whether PV or CSP will gain the competitive edge for large plant sizes.

Still, we currently believe solar thermal has significant disadvantages as a candidate power supply for our comprehensive sunlight-to-fuels system because:

- The relative simplicity of PV (basically one well-designed PV module, many, many times over, as opposed to a large set of different kinds if equipment as for solar thermal), PV lends itself better to small-scale units produced via optimized mass-production.

- The concentration of sunlight will likely require precise installation and operation of (moving) light-redirecting parts, observing exact angles etc. This will be difficult to do well for small-scale plants in rugged terrain, and thus prevent costs from being driven down much further.

- Power electronics (conversion to DC for electrolysis cells) drive up cost via additional required equipment and reduced efficiency.

- Similarly, the mass-to-energy output ratios for CSP are higher than for PV. This puts PV at an advantage, especially as we will need to achieve much of the cost reduction via developing ever cheaper and lighter units (material consumption and transportation costs).

One likely outcome is indeed a two-track approach: a larger-scale, centralized Sunlight-to-fuels system, operating many of the air capture, electrolysis, and fuel synthesis units at the same time, in a central location, could be powered efficiently by cheap electricity from a nearby large CSP plant (because the environment may be suitable anyhow for big plants, well prepared and stable terrain, etc.). For smaller, distributed units that need to be installed quickly, flexibly, and with minimum cost and labor on the ground, the PV modules are likely the better route.

III.1.2.4.2. Hydrogen from photoelectrochemical cells (PECs)

Various attempts exist to mimic photosynthesis via catalyst-based, direct solar-to-hydrogen approaches such as those employed in PECs, e.g. [*Krol and Schoonman*, 2008; *Turner et al.*, 2008]. Such a system could replace the 2 subsystems "solar panels" and "electrolysis" with one step.

While advantageous in some respects, we believe such melding of two subsystems also have clear disadvantages vis a vis the specific strategy of our proposed approach (and even if PEC's current limitations, such as dependence on rare materials, could be overcome):

- Combining two subsystems essentially removes the ability to optimize the two systems individually – and, in particular, prevent the Sunlight-to-fuels system from quickly incorporating future technological improvements in e.g. electrolysis cells or a drastic price drop in PV electricity in a plug and play fashion.
- Electricity would be needed anyway to power the air capture step (and the automation and control of the overall system). Therefore some development into electricity generation at a suitable price would still have to be undertaken.

Still, per gallon of fuel produced, electricity requirements for air capture are significantly smaller than those to drive electrolysis cells. Therefore, if the electrolysis step did not require its own electricity, there would be significantly less pressure on the electricity having to be cheap. This introduces an interesting scenario. Suppose the price of PV electricity cannot be sufficiently driven down (e.g., only to 5 cents per kWh, but not further). In such a scenario, the catalyst-based artificial photosynthesis could offer a viable alternative – it would allow for production of non-carbon liquid hydrocarbons at a competitive price, despite the higher cost of solar electricity.

III.2. Desalination

In the proposed sunlight-to-fuels process, water serves two purposes, both as a hydrogen feedstock in the fuel synthesis step and as a necessary consumable in the air capture of carbon dioxide. With a projected process requirement of about 33 kilograms of water per kilogram of hydrocarbon fuel produced, water consumption might very well strain conventional fresh water supplies in areas best suited for operation. With the stated aim of the system to facilitate a transition away from fossil fuels on a global scale, the only viable water reservoirs on such a scale are either the oceans or underground saline aquifers. Consequently, desalination has to be considered a core technology.

III.2.1. Current state of the art

Currently employed seawater desalination technologies can broadly be categorized in thermal processes and membrane separation processes. The former category, either in a Multi Stage Flash (MSF) or a Multi Effect Distillation (MED) implementation, requires heat for evaporation of water. This relatively energy intense desalination route, as high as 50 kWh/m^3 of permeate [*Semiat*, 2008], requires cheap energy for an economically viable application, something that alone disqualifies any kind of distillation process as a possible desalination technology for the sunlight-to-fuel system. Among the membrane separation technologies electrodialysis (ED) is a proven technology that has been in use since the 1960s. However, the envisioned water reservoirs, either the oceans or saline aquifers, are too saline for ED to be competitive with processes based on osmosis [*Fritzmann et al.*, 2007].

Reverse osmosis (RO) is the seawater desalination technology that has seen the greatest growth and development in recent years. Based on energy consumption alone, RO would be the natural choice of technology since this process typically consumes less than 10% of any distillation scheme [*Semiat*, 2008]. Furthermore, RO lends itself very well to the modular, small-scale design considered here. Semi-permeable membranes, much like photovoltaic cells, are suited for modular production and implementation. Also, not relying on heat conservation, RO desalination is better suited for intermittent operation than any thermal process.

A desalination technology that seems promising but not yet mature is forward osmosis (FO) [*Cath et al.*, 2006]. One of the more promising FO implementations uses an ammonia-carbon dioxide draw solution [*McGinnis and Elimelech*, 2008], the regeneration of which could possibly be achieved by using process waste heat from the fuel-synthesis step. This would render the desalination step a no-net electricity consumer. While not being completely similar the semi-permeable membranes used in FO share enough features with those used in RO to be produced in a similar fashion.

III.2.1.1. Reverse Osmosis, background and review

At the heart of the reverse osmosis process lies the semi-permeable membrane. Separating a salt bearing solution from pure water with such a membrane, both initially at the same hydrostatic pressure, we would see a transport of water across the membrane to the saline side. This transport stops once the osmotic pressure equals the hydrostatic pressure. The idea behind reverse osmosis is, as the name implies, to reverse this water transport by applying a pressure gradient across the membrane greater than the osmotic pressure of the salty solution.

A high performance reverse osmosis membrane needs to simultaneously allow high water flux while at the same time also exhibit high salt rejection. The water flux J across a membrane is approximately proportional to the difference between applied pressure Δp and the osmotic pressure $\Delta\pi$, i.e., $J = A(\Delta p - \Delta\pi)$. A desirable feature of a membrane is to be thin enough (A, the water permeability coefficient, is indeed inversely proportional to the thickness of the membrane) and yet mechanically strong enough to withstand the applied pressure gradients and hence achieve higher flux. These competing forces have been reconciled in the industry today by using anisotropic membranes, that is, membranes consisting of a thin active surface mounted on a stronger and more porous substrate for support. Under standard operating conditions, a modern RO membrane can accommodate a flux of roughly 1 $m^3/m^2 \cdot$day of permeate. The salt flux, or rather lack thereof, is usually expressed using the salt rejection R, i.e. $R = 1 - c_p/c_f$, where c_p and c_f are the salt concentrations on the permeate side and feed side of the membrane respectively. Modern desalination membranes can typically achieve a stabilized rejection above 99% [*Lu et al.*, 2007] meaning that, for drinking purposes, one pass through the membrane is generally sufficient for a feed water salinity of 35,000 ppm.

The most common membrane assembly type used today is the so-called spiral-wound module. In these, the membranes are made as flat sheets with an enclosed permeate channel. These sheets are then curled, with a feed spacing of 0.5-1 mm, around a collector tube connected to the permeate channel, making for an easy mounting in tubular pressure vessels. Two features of this membrane assembly are subject to substantive research and development: the hydrodynamics of the feed flow, manipulated by the geometry of the feed spacers and the material in the active surface of the membrane themselves. By inducing some degree of turbulence in the feed channel, the fouling potential that the feed water has on the membrane surface can be mitigated which prolongs the lifetime of the assembly and suppresses the need for membrane cleaning. As mentioned above, the active surface determines the characteristics of the membrane. Materials resistive to degradation caused by various foulants in the feed water that also can be manufactured according to the above principles are constantly being pursued. The material first employed, making reverse osmosis desalination viable on a large scale, was cellulose acetate. While still commercially available these membranes have been more and more replaced by composite membranes with an active surface of aromatic polyamides [*Baker*, 2004; *Petersen*, 1993].

The porous support membrane, e.g. polysulfone, is dip-coated first in an aqueous amine solution followed by an organic solution of polyacyl chloride. The interfacial polymerization that occurs when the membrane is introduced to the solutions produces the thin film active surface [*Liu et al.*, 2010]. After drying and successive rinsing in di-water and methanol aqueous solution the continuous sheet of composite membrane is again rolled up and subsequent treatment depends on the desired assembly type. Assembled as the spiral-wound module mentioned above, the total production cost ranges from 20 to 30 $\$/m^2$ of active surface and, under specified operating conditions these membranes are prescribed a lifetime of up to 5 years [*Liang et al.*, 2009; *Lu et al.*, 2007]. A novel and perhaps more efficient way of applying the thin film would be to aerosolize the monomers and achieve the polymerization by spraying them onto the support membrane, possibly achieving an even thinner active surface [*Krogman et al.*, 2009].

The energy consumption in reverse osmosis desalination depends mainly on feed water salinity but also on other factors such as the geographic location of the plant, feed water quality, and temperature. Comparing energy consumption of different desalination plants should therefore be done with some care. However, for feed water salinities of 30,000 to 40,000 ppm, a specific energy consumption of 3 – 6kWh/m^3 (10 – 20 MJ/m^3) of produced water is the norm in RO desalination today [*Busch and Mickols*, 2004; *El Saliby et al.*, 2009; *Fritzmann et al.*, 2007; *Semiat*, 2008]. This energy is spent, almost exclusively, as pump work throughout the process of which the largest part, around 90%, is expended in the actual RO separation stage, where the feed water pressure is elevated to about 70 bars in order to achieve sufficient permeate flux. The remaining energy expenditures can be attributed to the extraction and transportation of raw water from the source to the plant and also in the various forms of pretreatment.

Recent demonstrations of state-of-the-art RO desalination technology have exhibited specific energy consumption of 1.6 kWh/m^3 (5.7 MJ/ m^3), corresponding to a thermodynamic efficiency of roughly 60% [*Shannon et al.*, 2008]. This demonstration was performed under ideal conditions and the energy consumption was limited to the RO separation stage alone. It therefore seems unlikely that the RO process can be made significantly more efficient while still maintaining reasonable permeate flux rates [*Semiat*, 2008].

Among the key operating parameters in RO desalination is the recovery ratio, meaning the fraction of permeate to intake flow rates. With a fixed permeate flow rate, a higher recovery ratio means less overall water being circulated. The tradeoff made when opting for a higher recovery ratio is that while less water is extracted, transported and pretreated, more energy has to be spent in the separation stage per unit permeate since the salinity, and hence also the osmotic pressure of the feed will increase accordingly. Furthermore, typical RO desalination plants are designed to operate around 50% recovery resulting in a brine stream of twice the natural salinity, something that is cause for environmental concerns when disposed back into the ocean [*Barringer*, 2009; *BBC*, 2007].

III.2.2. Remaining obstacles for integration to sunlight-to-fuels system

In the overall process, water is required both as a hydrogen feedstock for fuel synthesis and in the moisture swing of the air capture of CO_2. Using heptane (C_7H_{16}) as reference, complete combustion of a kilogram of this fuel produces about 1.4 kg of water and 3.1 kg of CO_2. In other words, in the synthesis step, hydrogen from 1.4 kg of water is incorporated into a kilogram of fuel, together with the carbon from 3.1 kg of CO_2. For the current implementation there would be substantial water consumption related to the process of capturing of carbon dioxide from the air. The moisture swing absorption developed in our group can consume 10 kg of water per kg of CO_2, or 31 kilogram of water per kilogram of gasoline [*K Lackner*, 2009]. Thus, with the air capture step possibly dominating the consumption of fresh water, slightly less than 33 kilograms of water is required per kilogram of fuel produced.

Modern RO desalination plants can produce potable water for a cost of little over US 50¢/m^3, of which typically half can be attributed to electricity costs [*Fritzmann et al.*, 2007; *Sauvet-Goichon*, 2007]. With a total water consumption of 33 kilograms per kilogram of fuel, this translates into a water cost of roughly 4 ¢ per gallon of gasoline produced. Also, when considering the overall energy economy of the entire process, desalination plays only a marginal part. Using the change in enthalpy in the electrolysis reaction, $H_2O \rightarrow H_2 + 1/2O_2$, of 286 kJ/mol (or 16 MJ/kg of water) as a figure of comparison we see that the energy consumption of desalination (7 to 15 kJ/kg) differs by three orders of magnitude. Thus, there are very few advances required in the development of reverse osmosis as a water generation approach.

The produced permeate will be used to wet the resins in the air capture process in order for these to release the carbon dioxide. Presence of dissolved salts, primarily the anions, in the water will contaminate the resins which is why the water used has to be purified. Also, presence of alien ions in the water when fed to the electrolysis cell will possibly cause competing half-reactions and hence lower the efficiency of the cell and/or cause detrimental mineral precipitation within the cell. For the air capture step, the main water consumer, we assume that typical drinking water standards are sufficient while the electrolysis will require additional purification.

With the assumptions of an overall process efficiency of about 7% and an average insolation of 175 W/m^2 this translates into a capacity of 20 grams of hydrocarbon fuels (HHV of 48MJ/kg) per square meter and day. The projected consumption of 33 kilograms of water per kilogram of fuel produced in turn translates into the need for less than 10 cm^2 of active membrane surface are per square meter of land used for the capture of solar energy assuming a permeate flux rate of 1 $m^3/m^2\cdot$day. The point of this arithmetic is to show that since nothing substantially precludes dual use of land, the otherwise common demand on high packing density of membranes in RO desalination (>1000 m^2/m^3) for civil use can here be somewhat relaxed. This opens up the possibility for developing membrane assemblies optimized for easy maintenance and replacement rather than packing density.

In summary, compared to the other four sub-processes within the system, reverse osmosis desalination has already reached sufficient levels of maturity. That is, in the event of additional substantial cost reductions in desalination, these would have only a marginal effect on the overall sunlight-to-fuels process considered here. Acknowledging both the current superiority of reverse osmosis as a desalination technology and the very low requirements on further cost reductions within this technology, the effort should be focused on streamlining production of automated, small-scale desalination capabilities.

III.3. Carbon dioxide capture from air

Air capture technology is on the critical path toward a complete sunlight-to-fuels energy infrastructure. Without the ability to pull carbon dioxide back out of the air, carbon would not be an acceptable constituent of any transportation fuel. Even though a CO_2 source might be sustainable (e.g. carbonates, or fossil fuel derived CO_2), an ultimate disposition of the CO_2 in the atmosphere would make the complete process unsustainable. Removal of any emitted CO_2 from the air is necessary to fully close the carbon cycle. For carbonaceous transportation fuels closing the carbon cycle is only possible by withdrawing the carbon from the air away from the point of combustion. Capturing CO_2 on board of a vehicle and returning it to a central collection site would not be practical, as the mass of the carbon dioxide exceeds the mass of the fuel, typically by a factor of three. Thus carbon dioxide storage on board of vehicles and airplanes would strain or exceed the on-board storage capacity. In addition, such a capture system would require an extensive collection and transport system to return the carbon dioxide from the collection point, such as the fueling station for a car, back to the location where it is converted back into re-usable fuel.

The ability to remove carbon dioxide from the air is not new. Submarines and spaceships need this technology to keep the crew alive. In the preparation of air for liquefaction, CO_2 is routinely removed from the input air. This technology dates back to the 1940s [*Spector and Dodge*, 1946]. Capture of CO_2 from air, however, is different from producing CO_2 free air, resulting in rather different technologies. The general approach to extracting carbon dioxide from ambient air has been developed by us [*Elliott et al.*, 2001; *K Lackner*, 2009; *K. S. Lackner*, 2008; *Klaus S. Lackner et al.*, 1999a; *K. S. Lackner et al.*, 1999b].

The specific method for capturing carbon dioxide from air considered here is a novel technology that has been pioneered by researchers at the Lenfest Center. The capture process is based on an anionic exchange resin that readily absorbs CO_2 from the air when it is dry and releases the CO_2 again when it is exposed to moisture. Hence we refer to the process as a moisture swing absorption system. So far it has only been proven on the bench scale, but the process is conceptually very simple and its energy balance is highly favorable. The sorbent combines an energy efficient regeneration with fast kinetics in the uptake. Other alternatives either use strong sorbents like sodium hydroxide, which require a large amount of energy to regenerate the sorbent and to free the CO_2, or they use solids that are regenerated in a thermal swing. Unfortunately, the low loading one achieves in conventional, air-capture-capable, solid sorbents makes a thermal swing energetically expensive. It is difficult to recover all of the heat that went into heating the sorbent, resulting in large heat losses. Among all the possible options, the moisture swing stands out because of its low energy consumption. At 1.1 MJ/kg of CO_2 captured, the energy consumed is far smaller than the energy consumed in converting H_2O and CO_2 to fuel.

Air capture, like water desalination and photovoltaic energy collectors, is a technology that lends itself to small, modular implementations. It is therefore very well suited for a mass-manufacturing paradigm. And the approach that has been taken by GRT is to build small mass-producible capture devices that individually could produce one ton of CO_2 per day.

Successful development of a complete air capture capability is critical to the success of the overall system design concept. This research could also be leveraged by air capture efforts that aim at different applications, as the usefulness of air capture transcends sunlight-to-fuels applications. For example, air capture would be extremely useful in carbon management applications for which the captured carbon dioxide is permanently stored in an immobilized form so that it is kept out of the atmosphere. The captured carbon dioxide would then offset emissions that occurred in a different location and at a different time. Recently, air capture has also been viewed as one of the tools in geo-engineering that are designed to help stabilize the climate. Reducing the earth's atmosphere back to, for example, 350 ppm of CO_2 would be possible with a system only a few times larger than what would be required to provide ample fuel from sunshine.

Unlike the desalination of water, which is fairly routine and well developed, the extraction of carbon dioxide from the atmosphere is a novel technology that will still need substantial development to improve the current performance, before the research can transition to a focus on manufacturability. Further improvements are necessary, not only because the technology is still immature, but also because the impact of this process train on the overall system is much larger than that of the desalination effort. Thus it is necessary to reach performance goals that exceed the current state of technology, but which are well within the realm of what appears feasible.

III.3.1. Current state of the art

This section summarizes our starting point, explains the state of current knowledge, and explores which aspects of the design are based on assumptions that still need to be verified through further investigation. We already have a first implementation of the anionic exchange resin that exhibits a strong affinity for CO_2 and that readily releases CO_2 when it is exposed to moisture. We have demonstrated the moisture swing, and we have been able to custom make resins that are adapted to air capture applications [*K Lackner*, 2009].

This subsystem, like the solar panel system, is out in the open in direct contact with the environment. It therefore needs to be designed so that it can be exposed to the elements. This includes a sensitivity to life cycle concerns arising from extreme events that could end up dispersing sorbent materials in the environment.

In terms of the “black box” description for outlining the plug-and-play interfaces between the different components of the system, the subsystem is best viewed as a collector that removes CO_2 from the wind passing over its internal surfaces. The collector is sorbent based and, in the sorbent regeneration step, the system is supposed to produce a concentrated stream of CO_2 at pipeline pressure.

Collecting roughly 100 ppm of the 400 ppm in an air stream, CO_2 collectors would be more than two orders of magnitude smaller than the solar panels of the complete system. Assuming an effective air flow speed of 1 m/sec flowing through the collector, a CO_2 collection of 0.18g/m^3 (100 ppm) would result in a collection of 15 kg/m^2/day, which should be compared to a requirement of approximately 60g of CO_2 to produce the CO_2 for the daily fuel production on a square meter (about 20g).

III.3.1.1. Summary

Through work at Columbia University and GRT LLC, we have created the basis for capturing CO_2 from the air. We have recently published a detailed description of a CO_2 capture system that is based on a novel sorbent cycle [*K Lackner*, 2009]. The sorbent is anionic exchange resin. When dry the resin loads up with CO_2 in the presence of air and when wet it will release this CO_2 back to the atmosphere. We have shown that we can build the CO_2 partial pressure up to between 0.05 and 0.10 bar simply by exposing the resin to liquid water. Alternatively, we can also transfer the captured CO_2 from the resin into an aqueous solution, if the liquid that contacts the resin material is alkaline. We have shown that it is possible to produce a bicarbonate solution from a carbonate solution simply by letting it flow over a fully-loaded resin. Water in contact with the resin drives the CO_2 into the water where it reacts to form bicarbonates. Because of the role of water in the release of the CO_2, we refer to this process as moisture swing absorption.

The current technology is as follows: An anionic exchange resin with quaternary amine ions that serve as the fixed cations are attached to the polymer matrix that has approximately 1.7 mol of charge per kg and binds the CO_2 [*K Lackner*, 2009]. The resin at 400 ppm CO_2 in the air will load up in its dry state to nearly the bicarbonate form, and when wetted unload some of the CO_2 and revert, under ideal conditions, back to nearly the carbonate state. We have demonstrated this swing experimentally under various conditions, and have shown that the resin will spontaneously dry and repeat the cycle many times over. A practical swing in CO_2 content is approximately 0.25 mol/kg. By limiting the swing to the middle third of its potential range, one operates at higher uptake and release rates. We have preliminary evidence that with a carbonate wash this swing could be made larger without losing speed.

The resin material, which is commercially available, is formed into a composite material that is very robust but has a low specific surface area of 4 m^2/kg. This is the macroscopic effective specific area defined by the geometry of the composite material. The number does not capture the internal area that is accessible inside the resin particles. The reason the number is so low, is that the resins are brittle and have to be held together by some binder. Very thin strands or sheets of the material tend to disintegrate. We are currently working on improving the specific area of the composite sorbent material.

The uptake rate of the resin averages approximately 25 μmol/m^2/sec (measured against the nominal macroscopic surface area). The rate, of course, varies with the CO_2 concentration in the air, and the loading state of the resin. Unloading rates are comparable to loading rates. We have seen in experiments that the uptake rate per unit area increases, if the specific surface area is increased. Thus, we expect a substantial performance improvement as we learn how to create filter materials with higher specific surface area.

The physical properties of the resin make it possible to create a carbon capture device that is efficient, requires little energy, and can be deployed economically. The basic process involves resin material that is fashioned into a filter box designed to have natural air flow carry CO_2 over its internal surfaces. These surfaces remove CO_2 at an average rate of 25 μmol m^{-2} s^{-1}. The wet resin will release CO_2 at approximately the same rate. The resin could unload this CO_2 into an evacuated chamber, thus producing pure CO_2, or it could unload it into an air filled chamber producing CO_2 enriched air, or it could be used to produce a bicarbonate brine from a carbonate brine. Which option is best, will depend on the modules one plans to interface with. Here we will start from the assumption that a carbonate brine would provide a simple and flexible means of washing the CO_2 off the resin. We therefore will start with the carbonate wash as currently best available technology.

III.3.1.2. The resin

The anionic exchange resin, we use in air capture, is a quaternary amine. It is a very common resin that is produced in large quantities. For a quaternary amine, one can view the functional group as an NH_4^+ ion in which all four hydrogen atoms have been replaced with a carbon chain.

Because there are no hydrogen atoms left in the functional group, the amine cannot donate a proton, and it therefore always remains in the positive state. Hence the resin is referred to as a strong-base resin. According to the manufacturer, the wet resin typically contains 1.3 mole of cationic charge per kg of resin. These data appear to be taken on a resin that is wet, as they are somewhat lower than what we measured, as a fully hydrated form of the resin has more weight. Since resins are typically used in aqueous environments, this is a sensible convention, but it does not conform to our use of the material. The actual resin material we used had a measured cation concentration of 1.7 mol per kg in the dry state. We obtained this result through direct titration of the resin in its chloride form, which is a standard method for characterizing these resins.

The resins are purchased in the chloride form, and can be washed in a carbonate solution in order to transform them into the carbonate form. We established that by washing the resin in a one molar solution, the carbonate to bicarbonate ratio of ions on the resin matches the ratio in the solution within a few percent. Again we established this through titration experiments.

We have shown that the best studied resin material (Marathon A) is sensitive to the absolute humidity rather than the relative humidity in the air. If the absolute humidity level rises too high, the humidity can interfere with the ability of the material to absorb CO_2. As a result, climates that tend to extreme absolute humidity, i.e., tropical climates, are not well suited to our current devices. A better understanding of the way the resin works would help in developing better versions, as it is extremely unlikely that the materials on which the effect was first discovered are actually the best ones for the purpose. More likely, a thorough understanding of the effect would enable engineering better materials. We note that the current resin is well suited for operation in a desert climate, which is also most likely to be optimal for solar energy harvesting. It is quite possible that different climates will require different designs (which, by virtue of the modular overall system design, could be readily swapped out to customize for different regions or when altogether improved designs become available).

In the case envisioned here, we intend to accomplish the moisture swing by washing the dry and CO_2 filled resin with a carbonate solution. An aqueous carbonate solution has been shown to drive the CO_2 off the resin, but it is sufficiently alkaline to retain the CO_2 as it is immediately absorbed into the solution. As a result, the solution is transformed into a bicarbonate brine. Initially, we will also investigate a pure water wash. A water wash also drives the CO_2 off the resin, but the solubility of CO_2 in water is small and unless the water volume is very large, the CO_2 is released from the water into the surrounding gas volume. If the resin during the wash is confined to a closed space, the CO_2 partial pressure in the head space above the water will gradually approach a partial pressure of five to ten percent of an atmosphere. If the gas space has been evacuated prior to wetting the CO_2 will be essentially pure CO_2 ready for compression, with some water vapor admixture. The water will condense out under compression.

The current resin materials are very brittle and hard to form into particular shapes. Thin shapes tend to break apart. Development of more pliable materials or better composite structures that can expose more resin to the absorption swing is one avenue of investigation.

A rational engineering of the resin material requires a better understanding of the underlying mechanisms of the moisture swing. Present experimental results have characterized the overall performance of the process very well, but they leave few clues as to the molecular processes that drive the process.

III.3.1.3. Carbon dioxide uptake rates of the resin

The resin in the chloride form in which it is delivered does not take up CO_2. We have observed this in many instances. Not surprisingly, a resin after washing in sodium hydroxide will readily absorb CO_2. We have assured that we are not observing the uptake of CO_2 on residual hydroxide solution by thoroughly washing the resin in deionized water. (We have also shown that this step is not necessary for the proper functioning of the resin.) Not only does the resin work well even after washing in deionized water, the uptake rate does not diminish after multiple washings in deionized water.

Since the material is delivered in flat sheets, it is possible to compare the uptake rate of the resin to that of a surface covered in a one-molar sodium hydroxide solution. The uptake rate of the resin in its hydroxide state is significantly faster than that of the sodium hydroxide solution, by about an order of magnitude. This has been established by measuring the uptake rate of CO_2 from a closed system, in which one can directly observe the drop in CO_2 concentrations. Because the amount of CO_2 in a closed system is very limited, and the CO_2 concentration can be easily measured to within a few ppm of accuracy, this represents a very accurate way of establishing the CO_2 uptake rates and CO_2 capacity of the resin.

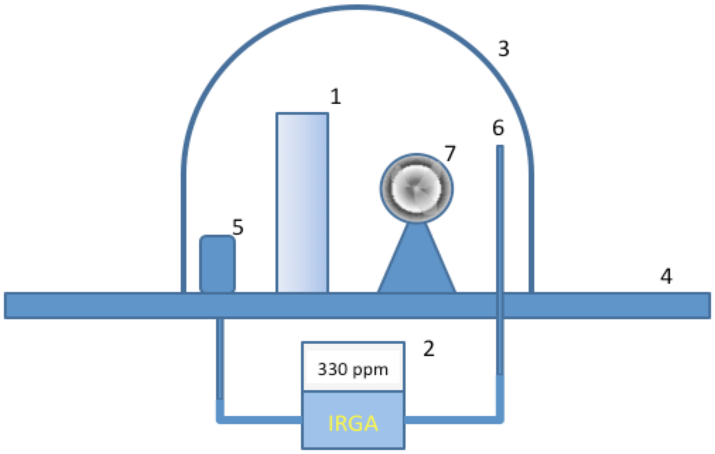

Figure 4: The closed air analyzing system used to characterize the resin performance. The numbered parts are identified as follows: 1. Resin Sample, 2. Infrared Gas Analyzer, 3. Glass Bell, 4. Bottom plate with power and gas penetrations, 5. Air pump, 6. Air return, and 7. Fan to agitate air.

The measurement system is sketched out in Figure 4. It has been used in various experiments and will be used in future experiments. In other experiments we have measured the drop of CO_2 concentration in a single pass through. More generally, we are able to perform gas analysis experiments in closed and open (single pass through) systems. We also control temperature and humidity in these experiments. In future experiments, we also will vary other components of the gas composition.

From the mass balance of the measurements in the bell as well as from direct titration we have established that the resin in its dry state approaches the bicarbonate state as it saturates. The uptake rates are slower in the carbonate state than in the hydroxide state. However, they are still comparable to that of a liquid film of one molar sodium hydroxide solutions of equal surface area. The actual operation would swing between the carbonate and the bicarbonate state.

The uptake rates are a function of the loading state of the resin, plus the temperature and humidity of the air, and thus cannot accurately be captured by a single number. However for design purposes in ambient air, a good average is 25 µmol $m^{-2}s^{-1}$. For higher CO_2 concentrations in the gas stream the uptake rate increases rapidly. This has been corroborated by preliminary measurements, but strong quantitative results are still forthcoming.

III.3.1.4. Moisture swing

It has been shown that the equilibrium partial pressure of CO_2 over a resin depends not only on its loading state, but also on the absolute humidity over the resin. A resin in its bicarbonate state, when it is exposed to water vapor in equilibrium at 45°C, drives most of the CO_2 off of the resin reverting back to the carbonate state. A resin that is exposed to liquid water will also fall back to the carbonate state, as long as the partial pressure of CO_2 is not too high. Initially it will unload against a pressure approaching 0.1 bar, but gradually the equilibrium partial pressure drops as the resin unloads. By designing a counter-stream system where the carrier gas streams over a set of resin filters each with a higher loading state then the previously encountered, is possible to maintain a CO_2 partial pressure of about 5 percent of an atmosphere of CO_2 in the return loop of the carrier gas.

We conclude from these very basic experiments that it is possible to load the resin approximately to the bicarbonate state when it is dry and release the CO_2 that has been produced into a stream that carries about five percent of CO_2.

Uptake rates for the dry resin and release rates for the wet resin have been carefully established in the context of CO_2 scrubbing from the atmosphere. At ambient conditions and averaged over an entire loading cycle, an uptake rate of 25 µmol $m^{-2}s^{-1}$ seems typical and readily achievable. Similar release rates have also been established.

III.3.1.5. Robustness of the resin

Our own experiments with outdoor resin filters have shown that the resin is very robust against the normal pollution found in outside air. The resin filters were operated at the original GRT research facility in Arizona (i.e., in a desert climate) and collected a substantial amount of dust on their surfaces. The only treatment they received to deal with these impurities was a regular washing with a sodium carbonate solution.

Samples of resin were kept on the roof of the facility a few inches above a flat tar roof. These resins were left unperturbed in the open air for seven months, exposed to high wind, strong sunlight and extreme Arizona heat and the midsummer monsoon thunderstorms. Temperatures in excess of 60°C are not unusual in the boundary layer on top of the dark roof. After seven months the resin was retrieved washed in a sodium carbonate solution and shown to be still as active as it was in the beginning.

Generally it is clear from the literature that these resins are used with strong acids and strong bases, and are remarkable resistant to chemical attack. Our experiments with the goal of showing long term survivability in air, also suggest that chemical attacks on the resin with acids and bases are not a major concern. On the other hand, we also demonstrated that the resin can be damaged with certain organic solvents, or aqueous solutions rich in organic solvents. For example, MEA solutions can damage the resin.

III.3.1.6. Temperature sensitivity of the resin

It is known that the resin in the hydroxide form is quite temperature sensitive. Temperatures above 70°C could cause damage to the resin and should be avoided. It is also known from the literature that the chloride form is substantially more heat tolerant. As a matter of fact the resin processing is performed in the chloride form because of its higher heat tolerance. We have preliminary data which show clearly that the mechanical properties of the carbonate and bicarbonate form of the resin are substantially different from those of the hydroxide. We therefore surmise that carbonates have a different heat tolerance. Outdoor experiments in Arizona during the summer, where resins where exposed to direct sunlight above a tar roof, suggest that the resin is more heat tolerant than it was expected. The same can be said about tolerance to UV light, which is not likely to play a role in these installations. However, resistance to UV light usually suggests some resistance to strong oxidants.

III.3.1.7. Cleaning of the Resin

We have developed a method for cleaning the resin after it has been exposed to anions of stronger acids than carbonic acid. This is best accomplished by washing the resin with a sodium bicarbonate brine, which is part of the standard CO_2 removal as well. This is important, because it makes it possible to use water streams that are far from fully deionized. One should compare the water quality demand for this system with that of agricultural water.

The sodium carbonate brine can be regenerated by running it through an electrodialisys station that produces an acidic waste stream separated from the sodium carbonate wash. Originally used for CO_2 separation from the sodium bicarbonate, we found this process consumes too much energy if it used for every wash cycle. However, if it is used only occasionally e.g. after 100 or 1000 cycles, in order to remove impurity cations introduced during the use of the resin, the energy cost, which is about five times larger than in the basic process, can be easily accommodated.

The system can be viewed as two separate flow systems, the alkaline fluid and the acidic fluid. The alkaline reservoir starts out as sodium bicarbonate and the electric current flow drives sodium ions from the acidic reservoir to the alkaline reservoir, converting the brine to a sodium carbonate brine. On the acidic side one enters a mixture of carbonate, bicarbonate and other anions. The electric current removes sodium ions from the acid compartment, replacing them with protons. As a result the brine becomes gradually more acidic. Eventually it will release gaseous CO_2. On the base side, the bipolar membrane provides OH^- ions that are, however, immediately neutralized against the proton donated by the bicarbonate present. Thus, on the base side one is generating a carbonate brine.

Liquid is directly injected into the acidic compartment, and with drawn from the basic department. There is no liquid outflow from the acidic compartments, and no direct inflow into the base compartment. This is possible because the membranes not only allow the passage of cations from the acid side to the base side, but they also act as osmotic membranes that let water pass from the low concentration brine to the high concentration brine (i.e., from the acid side to the base). Thus all of the major constituents enter the system on the acid side and leave on the base side. The only exception is the carbon dioxide, which leaves the acid compartment by bubbling out as a gas. This results in the dilution of the strength of this brine. The sodium ions moving to the base compartment further dilute the acidic brine, and increase the brine strength on the base side, which leads to a net flow of water from the acid compartment to the base compartment.

In an experimental test station, we were able to balance out the various flows, so that liquid only entered the acid compartment, and only left from the base compartment. As a result anions of strong acids would accumulate in the acid compartment as they have no way of escaping. This became evident as a gradual downward trend of the pH in the acid compartment.

In summary, this process can regenerate the carbonate brine that is used to wash the membranes, and it delivers an acidic waste stream that contains all the impurity anions that had been inadvertently collected on the resins. They can be further processed to be neutralized and disposed of as waste, or sold as useful industrial acids.

III.3.1.8. Energy balance considerations

The moisture swing makes it possible to raise the CO_2 partial pressure from 400 ppm in the air, to about 5% of an atmosphere. This boost of the CO_2 concentration can be achieved with very little energy expenditure [*K Lackner*, 2009; *K. S. Lackner*, 2008]. These estimates suggest that this would only require about 1% of the energy that goes into the new fuel. A larger energy expenditure is needed in compressing the resulting CO_2 to pipeline pressure. Here we estimate that the current resin will require approximately 50 kJ/mole of CO_2 in evacuation of the system, and compression energy [*K Lackner*, 2009; *K. S. Lackner*, 2008]. In delivering the CO_2 as bicarbonate after washing the resin with a carbonate solution, this energy cost can be reduced, but by how much will have to be resolved by subsequent research.

The energy demand for the moisture swing which is associated with the effective compression of CO_2 from a partial pressure of 40 Pa (400 ppm in the air) to 5,000 Pa (5%) in the off-gas (or in the formation of a bicarbonate solution) is not delivered directly but through the evaporation of water. The free energy available in the evaporation of water drives the CO_2 collection. In a thermodynamic analysis of the CO_2 absorption and desorption we realized [*K. S. Lackner*, 2008] that the system comprises four states: (1) a dry resin without CO_2 in air; (2) a dry resin loaded with CO_2; (3) a wet resin loaded with CO_2; and (4) a wet resin without CO_2. The transition from (1) to (2) is spontaneous and thus releases free energy. The transition from (2) to (3) is forced by actively wetting the resin, but it involves no significant energy (apart from the pumping effort). The transition from (3) to (4) is again spontaneous and it therefore again releases free energy. The last step is that of drying the wet resin in the presence of air. Air is rarely saturated in water vapor, thus the evaporation happens spontaneously. The process consumes liquid water and produces vapor under release of free energy. It is this release of free energy of the water evaporation that drives the entire system. As a result, we cannot entirely stop the use of water, which in effect fuels our process. However, the moisture swing offers a powerful solution for concentrating CO_2 in a dry environment with minimal expenditure of energy.

In the current implementation we need about 10 kg of water per kg of CO_2 produced. Thermodynamics suggests that in a perfect system one could do with a third of this amount of water. Even though this ratio of 10:1 may seem large, it is two orders of magnitude smaller than the consumption of water in growing corn, which represents an alternative way of capturing CO_2 from the atmosphere. Providing such an amount of water even in a desert is not difficult, particularly if one uses salt water as input. Reverse osmosis could easily produce a sufficient amount of fresh water. For seawater this requires 13 kJ/kg of water or in our case 0.13 MJ per kg of CO_2. Thus, seawater desalination would easily be the dominant energy consumption in the first step of the moisture swing, but it still would be small compared to the energy consumed in the subsequent compression of the CO_2 ~1MJ/kg. This in turn is still small compared to the energy contained in the fuel that is produced from a kg of CO_2, approximately 16MJ.

III.3.1.9. Economic Considerations

If the cost of CO_2 capture from air would come down to our target level of $30 per ton of CO_2, the contribution to the price of a gallon of gasoline would be $0.25, assuming a perfect carbon efficiency of the process. This is substantially more than the impact of water on the process design, even if the cost of water could not be reduced below its current level. However, $30 per ton of CO_2 would still represent a very tolerable contribution to the total cost of synthetic fuels. Thus, successfully achieving the cost target for air capture would remove air capture as a binding constraint on the economics of a sunlight-to-fuels infrastructure. In the following part of this section we argue that this target is indeed reasonable and achievable.

With the present technology it would require 0.31 kWh per kg of CO_2 to produce liquid CO_2 from air, (assuming a compression train producing pipeline ready CO_2, a carbonate approach would require less energy). Thus, with an internal cost of electricity of 2¢/kWh, the electricity would add approximately $6 to the cost of a metric ton of CO_2. A water generation cost of $\$0.50/m^3$ would add another $5 to the cost of a ton of CO_2. Thus the equipment cost, and the cost of operation and maintenance would have a budget allotment of approximately $20/ton of CO_2.

A major cost item in the operating equipment is the total cost of the resin. The total resin requirement scales directly with the specific surface area of the resin, and the uptake rate of the resin per unit area. Using the currently achieved values it would take roughly 5000 kg of resin for a unit that can collect one ton of CO_2 per day [*K Lackner*, 2009]. Increasing the specific surface area from 4 m^2/kg to 40 m^2/kg which implies thin hair like strands of the resin, would result in a ten times smaller resin demand and hence a ten times smaller first order cost. Commercial resin costs have been quoted as low as $2.50/kg. (Such resins are already produced in large quantities). Assuming a 15% rate on investment, and a ten year life time of the resin and 5000 kg of resin per ton per day, the cost of the resin would be $7 per ton of CO_2. This is a small fraction of the $20/ton allotted above. However, resin preparation are likely to raise the cost by factors of 2 or 3. On the other hand, increased specific surface area could lower it by factors of 10. Thus, we believe that the major cost items in the design are already close to the target values and the major challenge is to reduce the cost of the structural design of the entire air collector system, which according to internal estimates is still about a factor of ten too large.

III.3.2. Remaining obstacles for integration to sunlight-to-fuels system

Basic research is required to elucidate the molecular mechanisms that drive the moisture swing absorption of CO_2. Better insights into the mechanism of the moisture swing process will then allow improved designs of the polymer and even the implementation of novel materials to exhibit a similar swing. The sorbent materials need to be better characterized, and optimized for the task at hand. While the materials themselves are not new, and are already produced in large quantities for water purification purposes, they have never been considered for this particular application, and it is highly unlikely that these materials are anywhere close to being fully optimized for the new purpose.

In terms of practical engineering designs, the first step is to put together a small functioning system that allows us to analyze the pieces and identify those components which have the greatest need for further improvement. The construction of a first prototype will allow for a detailed analysis of the system. However, even without the benefit of the prototype, a simple analysis shows that one of the biggest improvements would come from increasing the specific surface area of the sorbent material that in its current form is far less efficient than it could be.

In our present design the time it takes for the sorbent material to saturate with CO_2 from the air takes approximately one hour. It takes another hour to release the CO_2. Even though we can match this system very well to the amount of CO_2 that is delivered by the air, it has the drawback that the amount of resin in the system is very large. The loading swing in CO_2 is a little more than 1% by weight of the resin; hence the amount of resin in the system is roughly 200 times the amount of CO_2 that is captured in a full cycle time (i.e., the sum of the loading and unloading time). Since the cost of the resin is an important component of the full cost of the system, a resin that can load and unload in a shorter time would be advantageous. A resin with higher specific surface area would therefore result in a system with the same performance characteristics but with less capital cost.

In designing the entire air capture design, developing the actual filter shape is another important issue. There is no question that improving the ability to flow air through filter systems will improve the performance of the system. Letting filter surfaces make contact with the air, while not unduly interfering with the air flow is an important design goal. Here we expect some theoretical and fluid dynamics analysis, but the majority of future research is in the interplay between better geometries for the resin filter arrangement and the structural requirements on the resin material. Better geometries are known, but better resin materials could make it possible to create structures that are more suitable for air capture designs.

In the end we expect that as the system design progresses, and small operational systems are delivering data, that we will see additional limits to the current design. We plan to address these issues as well, and will implement changes in design according to the preliminary results.

III.3.2.1. Performance Goals

In this section we set out a preliminary set of performance expectations we have for the air capture part of the overall system. As noted before, the system is supposed to remove CO_2 from natural air flows and deliver it as compressed CO_2 to the subsequent stages of the fuel synthesis stage of the process. However, more work will have to go into the justifications of the basic assumptions. For example, it needs to be investigated whether it is advantageous to produce a gaseous stream of CO_2, or whether it would be better to deliver the CO_2 in a bicarbonate solution that with the introduction of heat is transformed into CO_2, steam and a more concentrated carbonate solution that then can be diluted with additional water and recycled through the system.

The exothermic nature of most fuel synthesis units could easily provide heat for such a process. Another consideration is that the humidity swing has been developed for a system that is severely energy constrained. In this case the next step after capturing CO_2 is fuel synthesis which consumes far more energy than any air capture method uses. Hence it may turn out that optimizing the energy efficiency of air capture may prove to be a false economy.

Preliminary design constraints are that the process has to work with a photovoltaic energy input of 0.31 kWh per kg of CO_2 or less, that the process can collect at least 25% of the CO_2 from a stream of ambient air, and that its cost can be held below $30 per ton of CO_2 (Inclusive of water and electricity cost). For the resin technology this would imply a resin based sorbent with an effective surface area in excess of 40 m^2/kg, which is about 10 times better than the current version.

III.4. Water electrolysis

Attractive in its simplicity, electrolysis splits water to yield H_2 and O_2 in a single step without any need for moving parts, and the products are released separately in the anode and cathode compartments of the cell. In the proposed sunlight-to-fuels system, a photovoltaic cell could be coupled to an electrolysis cell, which would comprise a full system without moving parts. Thermolytic and thermochemical reactors, on the other hand, need a mechanical sun-tracking system to concentrate the direct incident sunlight to collect high temperature heat. Elimination of mechanical parts can reduce the need for and simplify maintenance, as mechanical systems typically experience more wear and tear and equipment failure. If the sunlight-to-fuels system is deployed in the desert, the harsh conditions may exacerbate such mechanical systems issues whereas the non-mechanical systems will be most likely less detrimentally affected. Furthermore, like photovoltaic cells, electrolysis cells are ideal for mass production and automated maintenance.

The electrolysis subsystem consumes by far the greatest amount of electricity in the sunlight-to-fuels system because it is where the solar electricity is converted into chemical energy in the form of H_2 (or possibly CO and H_2; see the section about solid oxide cells below). These compounds are then turned directly into the desired transportation fuel through exothermic reactions in the fuel synthesis step of the sunlight-to-fuels system. Therefore, the efficiency and capital cost of the solar electricity and of the electrolyzer are the major determining factors of the cost of the fuel produced and the relative size of the system (see section III.1 for a further discussion of relative importance of the different subsystem costs.). The cost of the solar power system and the electrolysis system are closely interrelated: running the electrolyzers at a higher efficiency operating point (lower cell voltage) lowers the capital cost of the solar power system (by requiring a smaller solar power system) but increases the capital cost of the electrolysis system (by operating at lower throughput per unit area of the electrolysis cells).

Economics of water electrolysis

The cost of a GJ of chemical energy in the form of hydrogen if produced by electrolysis, C_{H_2} (in \$/GJ), can be estimated as follows:

$$\begin{tikzcd} & C_{H_2} = C_{op} + C_{cap} \arrow[dl] \arrow[dr] & \\ C_{op} = \frac{C_{electricity}}{\eta_{electrolysis}} + C_{O\&M} & & C_{cap} = \frac{C_{investment}}{Q_{H_2\,prod}} \end{tikzcd}$$

$$\eta_{electrolysis} = \frac{E_{th}}{E_{op}} \cdot \eta_{current} \qquad C_{investment} = \frac{C_{stack}}{t_{stack\ life}} + \frac{C_{bal\ of\ sys}}{t_{sys\ life}}$$

$$E_{th} = \frac{\Delta H_{f,H_2O(l)}}{n \cdot F} \qquad Q_{H_2\,prod} = I \cdot f_{util} \cdot \frac{\Delta H_{f,H_2O(l)}}{n \cdot F}$$

$$I = i \cdot A_{cell} = \frac{E_{op} - E_{Nernst}}{ASR} \cdot A_{cell}$$

where C_{op} is the operating cost, C_{cap} is the capital cost, of the entire electrolysis system. These costs are in turn given by the above expressions in which, $C_{electricity}$ is the cost of electricity, $\eta_{electrolysis}$ is the electricity-to-chemical energy conversion efficiency at which the electrolyzer is operating[1], $C_{O\&M}$ is the operating and maintenance cost per unit of output, E_{th} is the thermoneutral voltage of water electrolysis, E_{op} is the actual operating voltage of the electrolysis cells, $\eta_{current}$ is the current efficiency (the fraction of the current that drives the desired reactions) which is very close to 100% for all types of state-of-the-art electrolysis cells, $\Delta H_{f,H_2O(l)}$ is the enthalpy of formation of water (or equivalently, the enthalpy of the water electrolysis reaction, or equivalently the higher heating value (HHV) of hydrogen), n is 2 (mol of electrons per mol product H_2 produced by the electrochemical reaction), F is Faraday's number (96485 C/mol), $C_{investment}$ is the investment cost of the system including financing, $Q_{H_2\,prod}$ is the average rate at which chemical energy in the form of H_2 is produced in kW, C_{stack} and $t_{stack\ life}$ are the investment cost and lifetime of a cell stack respectively, $C_{bal\ of\ sys}$ and $t_{sys\ life}$ are the investment cost and lifetime of the balance of system respectively, I is the cell operating current averaged across the cell's operating life, f_{util} is the fraction of time the cell is utilized over its life (sometimes called the capacity factor), i is the current density (e.g. A/cm^2), A_{cell} is the active area of the cell, E_{Nernst} is the equilibrium Nernst potential at the given conditions, and ASR is the internal area-specific resistance of the cell averaged across the operating life.

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[1] Since the electrolysis efficiency is defined as the thermoneutral voltage over the operating voltage and the cell can be operated at a lower voltage than the thermoneutral voltage (where the cell internal resistance does not supply enough heat), theoretically efficiencies greater than 100% are possible if external heat is available to supply the remaining energy required. However, such an external heat supply must be accounted for in the system energy balance, therefore the system will have an upper limit of 100% efficiency. The heat could be supplied by external electrical heating, giving 100% as the upper limit for the net efficiency of electricity to chemicals for the system.

This is a simplified method which assumes time-averaged parameters. In reality, many of the parameters vary with time. For example, in reality, I, t_{life} and f_{util} are encompassed together in the equation $\int_0^{t_{life}} I(t)\,dt$ which accounts for the intermittency $[1 - f_{util}]$. This includes start-stop operation and/or more smooth time-varying current operation as well as cell degradation since $I(t)$ is also a function of the time-varying internal resistance. The operating current I or $I(t)$ must be included in any economics estimation that involves variability with time, e.g. intermittency of a renewable or surplus power supply or a time-varying electricity price. Estimates in the literature that present the capital cost in terms of per watt of hydrogen produced are already optimized for a certain type of operation – usually near-constant operation (at near-100% capacity factor), e.g. including cell degradation but insignificant intermittency.

The cost is optimized between the capital cost and the operating cost. Although it is possible to operate nearly any electrolyzer at near-100% electricity-to-chemical energy efficiency, it is not always economically optimal to do so; some cells cannot attain a sufficiently high current density at the thermoneutral voltage. In that case, it would be desirable to operate a cell at lower than 100% efficiency ($E_{op} > E_{th}$, resulting in excess heat being generated in the cell) if the larger operating voltage (E_{op}) is needed in order to achieve a higher hydrogen production rate (higher current density).

In the design, manufacture and operation of an electrolysis system, 4 parameters can be controlled:

- Affecting the operating cost, C_{op}:
    1. the energy efficiency (via the operating voltage, E_{op})
- Affecting the capital cost, C_{cap}:
    2. the cost of producing the cell stack and balance of system, $C_{investment}$
    3. the operating current density, i (which is impacted by the ASR)
    4. the operating lifetimes $t_{stack\ life}$ and $t_{sys\ life}$

For the most economical hydrogen production, E_{op} and $C_{investment}$ should be as low as possible and i and t_{life} should all be as high as possible. In other words, the electrolysis cells should be cheap to produce and run efficiently at high throughputs for a long time.

III.4.1. Current state of the art

Figure 5 shows typical ranges of polarization curves for different types of state-of-the-art water electrolysis cells: Alkaline, PEM, and high temperature solid oxide electrolyzers. Advantages and disadvantages of these cells with respect to the requirements for the sunlight-to-fuels system will be explained in the following sections.

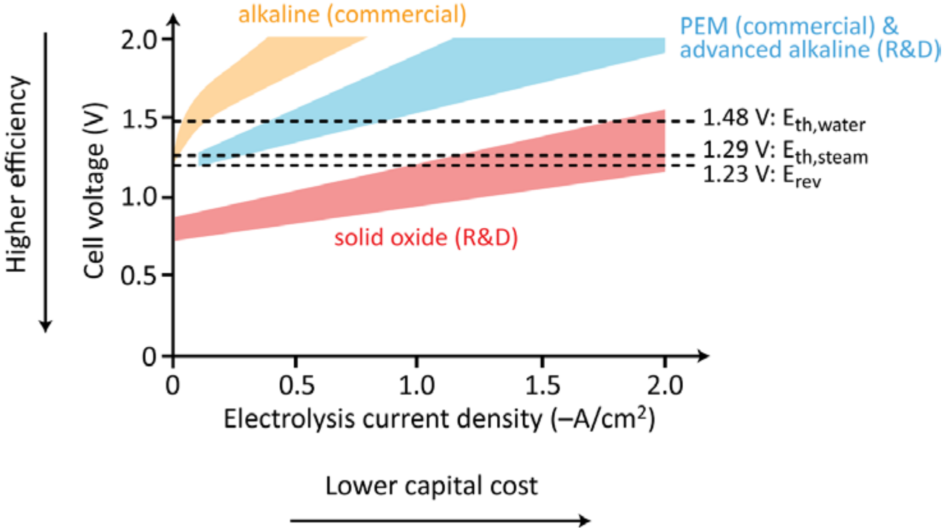


Figure 5: Typical ranges of polarization curves for different types of state-of-the-art water electrolysis cells. $E_{th,water}$ and $E_{th,steam}$ are the thermoneutral voltages for water and steam electrolysis respectively. E_{rev} is the reversible potential for water electrolysis at standard state. From [*Graves et al.*, 2010b].

III.4.1.1. Alkaline water electrolyzers

Alkaline water electrolysis cells are the dominant type of cells in commercial operation today [*Ivy*, 2004; *Jens Oluf Jensen et al.*, 2008a; *Swalla*, 2008]. The electrode reactions are:

$$\text{Cathode:} \qquad 2\ H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$$

$$\text{Anode:} \qquad 2\ OH^-(aq) \rightarrow 2e^- + ½\ O_2(g) + H_2O(l)$$

The electrolyte is typically 30 wt% KOH solution operated at 70-100 °C. The electrodes are typically porous Raney nickel electrodes which are formed by electrodeposition of a Ni-Al or Ni-Zn alloy onto a metallic (often mesh) substrate followed by leaching of the Al or Zn by a strong hydroxide solution, leaving behind a porous Ni structure. Commercial alkaline electrolyzers are typically operated at 1.8-2 V (around 70-80% efficiency based on the higher heating value of H_2) at 0.2-0.5 A/cm^2 [*Gandía et al.*, 2007; *Holladay et al.*, 2009; *Ivy*, 2004; *J. O. Jensen et al.*, 2008b]. These values are in part dependent on the cost of the electricity consumed by the cells, as well as the cost of the electrolyzer cells. For current prices, the values given above are optimal. This operating point is chosen due to the low current density attained at lower operating voltages, evident in the polarization curve (Figure 5). Some efficiency is sacrificed to attain high enough current densities to provide a low enough capital cost. This can explain why it is often cited that electrolysis can be performed with “up to 73% efficiency” [*Ivy*, 2004] – based on the materials and system cost, lifetime, capacity factor, and internal resistance of the alkaline cells being referred to, the lowest cost operation is at an operating voltage of about 2 V (= 1.48 V / 73%). This current-voltage (i-V) operating point is optimal for a near-100% capacity factor and a specific electricity price. Intermittent operation (e.g. using the solar capacity factor for the sunlight-to-fuels system) increases the capital cost of the electrolyzer and requires a different optimization of the i-V operating point. The durability of alkaline electrolyzers is sufficiently high, giving a typical operating life of 10-20 years [*Ivy*, 2004; *Jens Oluf Jensen et al.*, 2008a; *Swalla*, 2008]. For the latest commercial cells, durability was not found to suffer greatly when operating on intermittent renewable electricity (older technology suffered degradation while resting at open circuit conditions for extended periods of time).

Advanced alkaline electrolysis cells are at a pre-commercial stage. Such cells are typically operated at higher temperature and/or higher pressure [*Abe et al.*, 1984; *Divisek et al.*, 1988; *Ganley*, 2009; *Hauch et al.*, 2008; *Swalla*, 2008] which both enhances the current density at a given cell voltage and yields high pressure hydrogen, which is needed in any case for the subsequent fuel synthesis reactors in the sunlight-to-fuels system. Advanced cells also often have micro- or nano-structured electrodes made up of higher surface area nickel, alloys or composites containing nickel, or ceramic materials to improve current density [*Divisek et al.*, 1988; *Hashimoto et al.*, 2002; *Shervedani and Madram*, 2008].

Since seawater is naturally alkaline, seawater electrolysis can use modified alkaline electrolysis cells [*Hashimoto et al.*, 1999]. The cells must be modified to avoid evolution of chlorine gas. Although seawater electrolysis is in fact conventionally used to produce chlorine, the scale of electrolysis operation needed to produce the fuels needed to satisfy the world's demand for transportation fuels would exceed world demand for chlorine by many orders of magnitude. Therefore, due to the toxicity of chlorine, oxygen would be the preferred anode product from a seawater electrolysis cell. Since the anode potential for oxygen evolution is lower than that of chlorine evolution, the cell must be operated with an anode potential within a range above the oxygen evolution potential and below the chlorine potential. Therefore, new anode materials (Mo- and W-doped MnO_2) are being developed to achieve high anodic efficiency [*Hashimoto et al.*, 2002]. However, it may be unnecessary to deal with seawater in an electrolysis cell since obtaining pure water by desalination adds only a negligible cost to the fuel production process.

Related to alkaline electrolysis is the co-electrolysis of H_2O and CO_2 using aqueous carbonate or bicarbonate electrolyte. The CO_2 can be supplied by being bubbled in or dissolved in the aqueous media, or supplied from the gas phase to a gas diffusion electrode. The majority of research in aqueous co-electrolysis of CO_2 and H_2O has focused on improving current efficiency (product selectivity) at a given potential rather than maximizing energy efficiency (for lower operating cost) or current density (for lower capital cost). For example, copper electrodes were found to selectively produce CH_4 and other hydrocarbons over just H_2 and CO. However, the overpotentials needed (to either selectively produce such hydrocarbon products or to produce H_2/CO) are at present too high for a viable electrolyzer. With these types of cells, reasonable current densities have only been achieved at a very low efficiency – a current density of –100 mA/cm^2 requires application of about 3 V to produce a mixture of methane and hydrogen with small amounts of ethylene and carbon monoxide [*Gattrell et al.*, 2007] or a mixture of potassium formate and hydrogen [*Li and Oloman*, 2007].

III.4.1.2. PEM water electrolyzers

Proton exchange membrane (PEM) cells operate at a similar temperature range as alkaline cells and are also commercially available. In PEM cells, protons are selectively conducted across a polymer membrane and the following electrode reactions take place:

$$\text{Cathode:} \quad 2\,H^+(aq) + 2e^- \rightarrow H_2(g)$$

$$\text{Anode:} \quad H_2O(l) \rightarrow 2\,H^+(aq) + 2e^- + \tfrac{1}{2}\,O_2(g)$$

Because PEM cell electrodes contain expensive noble metal electrocatalysts (typically Pt particles) and expensive membranes, their capital cost is higher than that of alkaline cells. To compensate for this higher cost, they are operated at higher current density (Figure 5). With IrO_2 and Pt electrodes, Yamaguchi et al demonstrated –1 A/cm^2 current density at 1.54 V at 80 °C under atmospheric pressure [*Yamaguchi et al.*, 1998]. If three times higher current density could be achieved at a given efficiency and the production cost of the cell stack is less than three times larger, the hydrogen production price would be lower than for alkaline cells. However, the higher capital cost appears to be an obstacle to affordable PEM-based electrolysis. Less expensive materials are needed.

III.4.1.3. High temperature solid oxide electrolyzers

Performing electrolysis at high temperature has both a thermodynamic advantage and an advantage in reaction rates. With increasing temperature, a larger portion of heat and corresponding smaller portion of electricity is needed for the dissociation. This can be seen in the lower open-circuit voltage for the high temperature cells in Figure 5. This heat can be supplied from external sources, or it could be the Joule heat that is inevitably produced due to the internal electric resistance of the cell. Rather than losing this ohmic heat, it is used in the disassociation of steam and/or CO_2. The high temperature also results in fast reaction kinetics which reduces the need for expensive catalyst materials. These differences between low and high temperature electrolysis cells can be seen in the polarization curves illustrated in Figure 5. These advantages enable very efficient operation (at near the thermoneutral voltage) at very high current densities (potentially leading to low capital cost).

There are two types of high temperature electrolyzers (typically >600 °C operation), those with molten carbonate electrolytes and those with solid oxide electrolytes. Since the electrolytes of solid oxide electrolysis cells (SOECs) and molten carbonate cells conduct O^{2-} and CO_3^{2-} ions respectively, they can electrolyze CO_2 to CO in addition to H_2O to H_2. However, electrolysis using molten carbonate cells to produce H_2 or CO carries a disadvantage, in that a mol of CO_2 is effectively transported across the cell for every mol of fuel produced. This CO_2 is released at the anode along with O_2, resulting in a mixed product stream there. Additional energy must then be spent to separate the CO_2 and O_2, as the CO_2 can of course not be released to the atmosphere.and the CO_2 will be needed for the cathode reaction. No literature about molten carbonate electrolysis could be found.

Solid oxide electrolysis cells (SOECs) do not suffer from the above problem. Their electrode reactions are (depending on whether they are operating on steam or CO_2 input feed streams):

Cathode: $H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-}$ or

$CO_2(g) + 2e^- \rightarrow CO(g) + O^{2-}$

Anode: $O^{2-} \rightarrow 2e^- + \frac{1}{2} O_2(g)$

As with low-temperature electrolysis, cells designed as solid oxide fuel cells (SOFCs) can be used reversibly for electrolysis. However, due to differing conditions (the gas compositions at the electrodes and the direction of polarization across cell components and across interfaces between materials) between fuel cell and electrolysis operation, it may be desirable to make specialized cells for optimal electrolysis performance.

The most common material composition of SOECs is a porous metal-ceramic Ni-YSZ composite cathode and a porous ceramic composite anode composed of lanthanum strontium manganite and YSZ, sandwiching a dense ceramic YSZ electrolyte (YSZ = yttria-stabilized zirconia, a material with fluorite crystal structure that conducts O^{2-} ions at high temperatures). The performance, durability, and materials used in high temperature electrolysis cells have been recently reviewed [*Hauch et al.*, 2008; *Ni et al.*, 2008]. An impressive current density of –3.6 A/cm^2 was reported when operating an SOEC for steam electrolysis at 950 °C at 1.48 V [*S H Jensen et al.*, 2007]. High performance was also reported for CO_2 electrolysis as well as for co-electrolysis of CO_2 and H_2O [*Ebbesen et al.*, 2009; *Graves et al.*, 2010a; *Isenberg*, 1981; *S H Jensen et al.*, 2007; *Stoots et al.*, 2009; *Zhan et al.*, 2009]. In co-electrolysis, CO_2 may be either electrolyzed or indirectly split via the reverse water-gas shift. Co-electrolysis may be advantageous for process simplicity, eliminating the need for a separate reverse water-gas shift reactor to prepare syngas with the H_2/CO ratio needed for catalytic fuel synthesis. The durability of steam electrolysis, CO_2 electrolysis, and co-electrolysis of CO_2/H_2O mixtures has been recently studied and improved to degradation rates well below 1% per 1000 h for low current density operation [*Ebbesen et al.*, 2009; *Graves et al.*, 2010a; *Hauch et al.*, 2008].

While there have recently been significant developments in the field of solid oxide electrolysis cells, there remains some uncertainty.

- The most important is that the durability of high current density operation near the thermoneutral voltage, which will be desirable and most likely necessary for an economical process, has not yet been demonstrated.

Other potential uncertainties include:

- *The instability of the Ni-based electrode when exposed to an oxidizing atmosphere*. However, this can be managed, either by cell design (some cells with Ni-based electrodes have demonstrated only negligible performance loss through tens of such events), a fail-safe gas recirculating system that ensures the electrode is always kept in a reducing atmosphere, or the use of alternative electrode materials that do not share this problem – such materials have been discovered and demonstrated but they have not yet been integrated into commercial cells

- *Heat management issues*. Intermittent operation of electrolyzer cell stacks has not been well studied. The system may need to be designed to keep them continuously hot, even when not in operation, or sufficient stability must be built in to allow thermal cycling each day. Operation of the cells has yet to be fully optimized, e.g. at which temperature is best to operate as an optimum between throughput and durability

III.4.2. Remaining obstacles for integration to sunlight-to-fuels system

Our analysis indicates the best water electrolysis technology for the proposed sunlight-to-fuels system is, at present, alkaline water electrolysis cells. We will also keep a close eye on solid oxide electrolysis cell technology because although it is less mature, it offers potentially lower cost electrochemical energy conversion if some obstacles can be overcome and it appears that developments towards overcoming these obstacles are occurring rapidly. The advantages and obstacles of each are outlined in Table 3.

	Advantages	Obstacles
Alkaline water electrolysis cell	• Established technology in commercial operation with known high durability • Simpler operation and heat management • Cheaper materials for housing and current collection are possible due to lower temperature operation • Ability to easily replace an individual cell rather than the entire stack	• Capital cost is too high: see discussion below
Solid oxide electrolysis cell	• Potentially low capital cost because current densities at a given voltage are significantly higher • Higher electrolysis efficiency (up to 90-95% depending on heat exchanger performance) • Higher system efficiency (for fuel production) – the waste heat from exothermic fuel synthesis reactions can be utilized to rise steam which contributes directly to the electrolysis reaction (lowers the cell voltage) • Can co-electrolyze H_2O and CO_2 and produce syngas directly, eliminating the need for RWGS or other means of developing fuel synthesis from CO_2+H_2	• Capital cost – although high durability at low current density has been demonstrated, high durability at these high current densities has not yet been demonstrated. • Heat management is more complicated – it can lead to additional energy losses (e.g. keeping them hot when not in use) and to greater frequency of equipment failure; a reliable system should be demonstrated

Table 3: Advantages and obstacles of alkaline water electrolyzers and solid oxide electrolyzers.

Another potential advantage of alkaline cells that is not listed in Table 3 is the use of less exotic materials, which would lead to a potentially lower manufacturing cost and a greater ability to scale-up without running into resource constraints. However, it is not clear, because the majority of the manufacturing cost for both types of cells does not appear to be the raw materials of the electrode and electrolyte but rather the structural components, balance of system, and processing [*Saur*, 2008; *Swalla*, 2008; *J Thijssen*, 2009; *J H J S Thijssen*, 2006], and for solid oxide cells, ceramic materials, which can be cheaper than metals, are often used instead of metals as electrode materials and other components.

Focusing on just alkaline electrolyzers, manufacturing costs reductions are needed:

- Today's alkaline electrolyzers are run at 70-80% efficiency (~2 V) and around 0.3-0.5 A/cm^2 when operated at a near-100% capacity factor. This is the optimal operating point which minimizes the cost at a given electricity price and based on the manufacturing cost of the cell. The capital cost for a large-scale (~1-2 MW) alkaline electrolyzer plant has been projected at \$7.5 to \$9 per GJ of H_2 produced, assuming near-100% capacity factor operation [*Ivy*, 2004; *Swalla*, 2008]. Other studies of commercial alkaline water electrolysis plants [*Jens Oluf Jensen et al.*, 2008a] have estimated the capital cost at about half of that assuming a similar 10-20 year life, so there is some uncertainty as to how much the cost decreases with scale-up. Operating and maintenance costs for this size plant have been estimated at around \$2.5 per GJ of H_2 produced [*Ivy*, 2004; *Swalla*, 2008]. Therefore, with 1-2 cents per kWh electricity (\$3.5-8 per GJ for electrolysis efficiency of 70-80%), it is possible to produce electrolytic hydrogen for a minimum of around \$10-20/GJ (without including the additional inefficiency due to fuel synthesis and the additional costs of CO_2 air capture, fuel synthesis, etc, for hydrocarbon fuels production in the sunlight-to-fuels system). This suggests that cost reductions in electrolysis are certainly needed.

- However, cost reductions are even more necessary than evident from these estimates from the literature, because the estimates are based on an electrolysis plant that operates at near 100% capacity (near-constant power supply). Intermittent operation increases the capital cost significantly. So if one operates them at an average of 20% capacity factor (e.g., using solar electricity as in the sunlight-to-fuels system) the capital cost increases, and there is a new optimum operating point, which it is at a lower efficiency (higher voltage) and corresponding higher current density. Furthermore, this operating point may be too severe (e.g. 3 to 4 V and high current density), resulting in too rapid degradation, requiring operation at lower voltage and current density and resulting in yet more expensive fuel. Based on the capital cost and performance of current alkaline electrolyzers, our analysis shows that the sunlight-to-fuels system, which requires intermittent electrolysis operation with a capacity factor of around 20%, would need the PV electricity to cost less than 1 cent per kWh in order to produce hydrocarbon fuels at competitive prices.

- However, improvements to the electrolysis system could enable competitive fuel production using \$0.02/kWh electricity. If the capital cost can be reduced by a factor of 5, by reducing the manufacturing cost and/or decreasing the resistance of the cell (via pressurization, elevated temperature operation and/or better electrodes), the optimum operating point will return to about 2.1 V (70% efficiency) and 0.3-0.4 A/cm^2, enabling a viable system using 2 cent/kWh electricity.

First, reducing the operating and maintenance (O&M) cost via automation, so that the hydrogen cost will be significantly lower than the \$2.5/GJ estimated above will be the biggest step in reducing the cost of electrolytic hydrogen, since we already intend to build the entire sunlight-to-fuels system with a high level of automation and control to keep the operating and maintenance cost of the entire system low.

The greatest cost reductions will come from reducing the electrolyzer capital cost. Based on our analysis using a model that optimizes the i-V operating point for a given intermittency and electricity price, a factor of 5 reduction in the capital cost combined with the significantly lowered O&M mentioned above would allow \$0.02/kWh electricity and an i-V operating point similar to that described above for the non-intermittent situation. There are two routes to reducing the electrolyzer capital cost: reducing the manufacturing cost, and running at higher current density (high throughput).

<u>Potential manufacturing cost reductions:</u>

- The electrolysis cell and system lends itself well to large-scale mass production. We foresee that advanced, automated mass production can reduce the cost of the electrolysis system. It is necessary to consider:
- Which components or manufacturing processes dominate the manufacturing cost? As mentioned earlier, estimates have shown that the balance of system, not the active materials, dominate the system cost.
- Which components can be made much more cheaply? The use of less expensive alternative materials for the "inactive" components of the electrolyzer system may significantly reduce

the system cost. For example, recently a new plastic housing was developed for alkaline water electrolyzers to replace the more expensive steel housing [*Swalla*, 2008].

- What is the optimal size of an electrolysis cell stack? Commercial stacks have tended towards large units but for technology like electrochemical cells the advantage to scaling up in size is not clear. Pressurized operation, mentioned below as a means to enhance throughput, also favors smaller size electrolyzer stacks [*Jens Oluf Jensen et al.*, 2008a].

Enhancing the current density (reducing the cell internal resistance):

- Pressurized operation increases the reaction rates. This was studied for advanced alkaline electrolysis in the 1980s and again more recently, as discussed in the review presented above.
- Elevated temperature operation, which also increases the reaction rates, as discussed in the review presented above. Elevated temperature operation above the boiling point of water also can enable the entire sunlight-to-fuels system to operate at higher net efficiency, if the heat output from the fuel synthesis stage can be utilized to rise steam for the electrolyzer (see advantages of high temperature cells in the prior section)
- Improving the electrocatalytic activity of the electrodes would also enhance the current density.

For high temperature electrolyzers, enhancing the current density is not necessary because they can already achieve such high throughputs – it is their durability at the high current densities achievable that needs to be demonstrated.

III.5. Fuel synthesis

The fuel production subsystem contains the final conversion in the solar fueled chain, returning carbon to its most energetically dense form. The flexibility afforded by automation and small scale operation allows for two complementary means of exploiting the fungible nature of hydrocarbon resources: one is the Fischer-Tropsch synthesis, a chemical process by which an array of liquid hydrocarbon fuels is produced from carbonaceous synthesis gas. The other is methanol synthesis followed by methanol-to-gasoline. While both are currently viable and commercially available catalytic processes, the current paradigm exploits the minimum on a cost optimization curve at which larger is cheaper. This subsystem exploits a lower minimum on the same curve as applied to fuel synthesis, at which the loss of the economy of large singular scale is compensated by the gain in economy of smaller, more flexible, mass produced scale. Furthermore, considering that fuel synthesis as a process is highly sensitive to its reaction conditions as well as the stoichiometry of its feedstock, the synthesis will also benefit from the small-scale paradigm in which the conditions of each individual unit could be customized, optimized, and automated, perhaps even in real-time, to obtain the desired distribution of conventional or designer hydrocarbon fuel products. Regardless of the input stoichiometries of CO and CO_2, a syngas preparation step will provide optimum feedstock for the small scale reactor units, which will play off of one another as optimized by automated control.

III.5.1. Current state of the art

III.5.1.1. Production of syngas

The products of the upstream modules of the system are hydrogen in the form of H_2 and carbon in the form of CO_2. Generally, fuel can be synthesized from any carbon-based feedstock, be it coal, petroleum coke, biomass, natural gas. Typical industrial production of syngas in currently commercially significant operations is the result of coal gasification. This can also be done more efficiently using methane via catalytic steam reforming, auto-thermal reforming, partial oxidation, and heat exchange reforming. Syngas preparation, the lion's share of typical Fischer-Tropsch plants, accounts for 60-70% of the capital and operating costs [*Dry*, 2002]. This cost is incurred in no small part due to materials handling, ash removal, and purification of input fossil fuels and their concomitant sulfur, nitrogen, and soot content [*Wilhelm et al.*, 2001]. One of many advantages of synthetic fuel production subsequent to this step is that these impurities have been removed during this stage of the plant operation, improving the quality of the product. As this unit's feedstock originates in water, air, and sunlight, these impurities were never in the throughput, and so their removal is obviated here at significant financial and energetic savings. The chemical profile of this feedstock will be revisited below, but it is important to note the interchangeability of CO and CO_2 via the exothermic water-gas shift reaction (WGS, shown below) and its reciprocal, the reverse water-gas shift reaction (RWGS) which exchange an oxygen atom between hydrogen and water molecules:

$$CO + H_2O \rightarrow CO_2 + H_2 + 41.3\ \text{kJ}$$

This reaction takes place under common catalytic conditions of the synthesis step below, but its reciprocal RWGS is an important intermediary to correct the stoichiometry of the feedstock between the alkaline fuel cells and the fuel production units. The RWGS reaction, while only mildly endothermic, requires high temperatures for favorable kinetics, but recent work here at Columbia offers a highly effective means of conducting this reaction within the modular network proposed. As high temperature reactions are mass-transfer controlled, choice of substrate has a significant impact on reactor performance and size. A short contact time (SCT) approach passes a rich fuel/air mixture over catalyst at very high flow velocities (contact times on the order of milliseconds) producing very high selectivities, The extremely short channel length of these substrates is a perfect fit for a network of aggregated small units and avoids boundary layer buildup observed in conventional long channel monoliths. The heat and mass transfer coefficients also depend on the boundary layer thickness. In a long-channel monolith a fully developed boundary layer is present over a considerable length of the device. The SCT technology replaces the long channels of a monolith with a series of short channel lengths, each short enough to avoid significant boundary layer build-up. The high heat and mass transfer rates allow extremely small reactor sizes – up to 1/20th the size of conventional monoliths for equivalent conversion. The conversion per unit of geometric surface area of the SCT substrates can also be up to an order of magnitude higher than conventional monolith substrates under mass transfer limited conversion which can lead to significant cost reductions especially when using precious metal catalysts. Convective heat exchange with the gas phase is also strongly dependent on the boundary layer buildup and the excellent convective heat transfer and low thermal mass of the SCT substrate results in rapid heat exchange with the gas, allowing equilibrium conditions to be quickly achieved. In addition, reactors designed using the SCT substrates offer equivalent conversion at a fraction of the volume with similar pressure drops as conventional monolithic substrates.

The RWGS approach is effective as a producer of feedstock for the Fischer-Tropsch synthesis, for which the optimal syngas consists of CO and not CO_2, due to the low conversion efficiencies with H_2-poor or CO_2-rich feedstock. However it is not necessarily the case that CO_2 as an output of the alkaline fuel cell unit needs to be converted to CO. Methanol can be synthesized from either partial or fully oxidized carbon with comparable free energies and enthalpies of reaction, and even as regards Fischer-Tropsch, recent research trends in hybrid catalyst systems point to the hydrogenation of CO_2

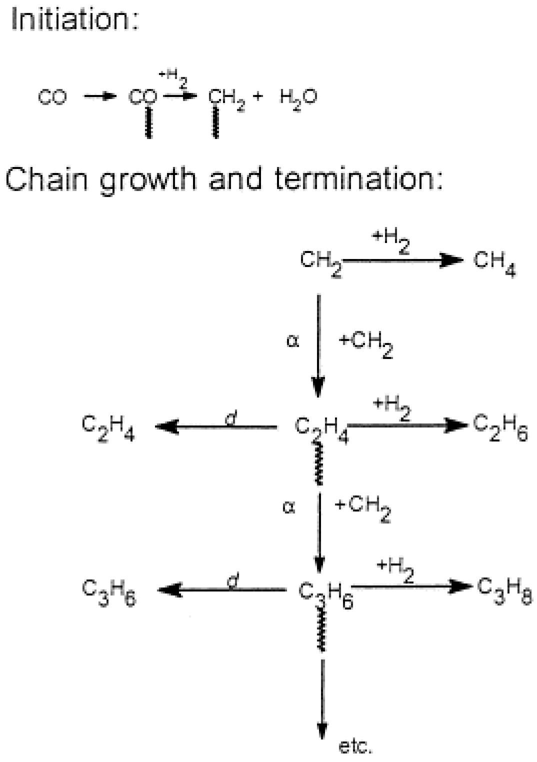
as a means of deploying that feedstock, enhancing the flexibility of the fuel synthesis step in response to its inputs [*James et al.*, 2010; *Riedel et al.*, 1999].

III.5.1.2. The synthesis step

First developed in 1923 and in ever-expanding commercial use today, the Fischer-Tropsch process consists of the hydrogenation of adsorbed CO to form CH_2 "monomers" for stepwise oligomerization on catalyst surfaces. The source of the reactants is a synthesis gas of carbon monoxide and hydrogen, which are adsorbed by the catalyst and undergo the overall exothermic reaction:

$$CO + 2H_2 \rightarrow -CH_2- + H_2O + 165\text{ kJ}$$

At each stage, the newly formed adsorbed hydrocarbon can desorb, hydrogenate, or continue chain growth with another monomer. As indicated schematically below, desorption or chain growth proceeds according to some probability parameter (here *d*, α, respectively). The result is a suite of hydrocarbon paraffin waxes and olefins of varying chain length and industrial applicability, particularly gasoline and diesel. Synthetic fuels produced by this process are sulfur-free and nitrogen-free, and are therefore chemically cleaner than those produced from crude oil.



[*Dry*, 2002]

Figure 6: Illustration of chain growth and termination.

Historically, research and development of the process assumed singular, large scale structures, embracing and discarding various reactor designs under that assumption that the ability to scale-up to larger and larger reactor units was a critical criterion for reactor choice [*Steynberg et al.*, 2004]. The exothermic nature of the reaction requires that scale-up designs have sufficient heat exchange to maintain an exothermic reaction environment; large cooling areas are required to shed this heat. The issue of pressure drop with increasing bed length is also a scale-up concern, as is observed in the long, narrow reaction chambers of multi-tubular fixed bed reactors, or in re-circulating reactors that employ multiple passes of gaseous streams to maximize the conversion of syngas to hydrocarbon product. Maintaining these process conditions is of critical importance for the Fischer-Tropsch synthesis, as increased temperature favors elective methane formation (an undesired product), deposition of catalyst-damaging carbon, and reduced chain length of products. Thus the most prolific reactor design in commercial use today is the slurry bubble column reactor, which exhibits on large scales the requisite low pressure drop, excellent heat transfer characteristics for stable reactor temperatures, no diffusion limitations, continuous online refreshment of catalyst particles, and relatively simple construction at low investment capital cost [*Wang et al.*, 2007]. As of 2007, the slurry bubble column and the multi-tubular reactor design were the only two Fischer-Tropsch models with significant market share [*van Vliet et al.*, 2009].

Methanol synthesis is another industrially significant and already well-established catalytic process by which oxidized carbon is hydrogenated by either of the following reactions [*Klier*, 1982]:

$$CO + 2H_2 \rightarrow CH_3OH$$

where $\Delta H_{600K} = -100$ kJ/mol and $\Delta G_{600K} = +45$ kJ/mol, and

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

where $\Delta H_{600K} = -62$ kJ/mol and $\Delta H_{600K} = +62$ kJ/mol. Subsequent dehydration can lead to dimethylether (DME) production via

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

where $\Delta H_{600K} = -21$ kJ/mol and $\Delta G_{600K} = -11$ kJ/mol, as methyl alcohol is thermodynamically uphill of higher alcohols and hydrocarbons (which, happily, are the ideal output of this unit). Proper choice of catalyst can either inhibit or thermodynamically lubricate this chain of hydrogenation reactions, which in industry successfully produces almost pure methanol but in this reactor network can be optimized to produce whatever hydrocarbon is desired or whatever input stream is desired for subsequent reactor units.

Like Fischer-Tropsch, the similarly highly exothermic methanol-to-gasoline attracted a great deal of attention in the 1970s when cheap oil no longer looked limitless, and conversion to synthetic fuel over zeolite catalyst is well documented [*Zaidi and Pant*, 2004]. The Motunui synthetic petroleum plant was the first of its kind, converting methanol into liquid hydrocarbons from 1987 to 1997 using the Mobil-designed MTG process over ZSM-5 zeolite catalyst with a design capacity of 2,200 tons of gasoline per day, or 1 GW. The most recent addition to the industry is a Lurgi plant converting methanol to the light olefin propene (MTP) [*Bjorgen et al.*, 2008]. Lurgi is producing propene from methanol at a rate of 474 kt/a, along with 41 kt/a of LPG and 185 kt/a of gasoline. Here, again, the intent is to assess and incorporate a process that is well-established in the literature and in industry, but instead with an eye towards modularity and scaling. An important optimization objective for the development of a sunlight-to-fuel system is working through the relative representation of MTG and Fischer-Tropsch process units comprising the catalytic fuel synthesis network.

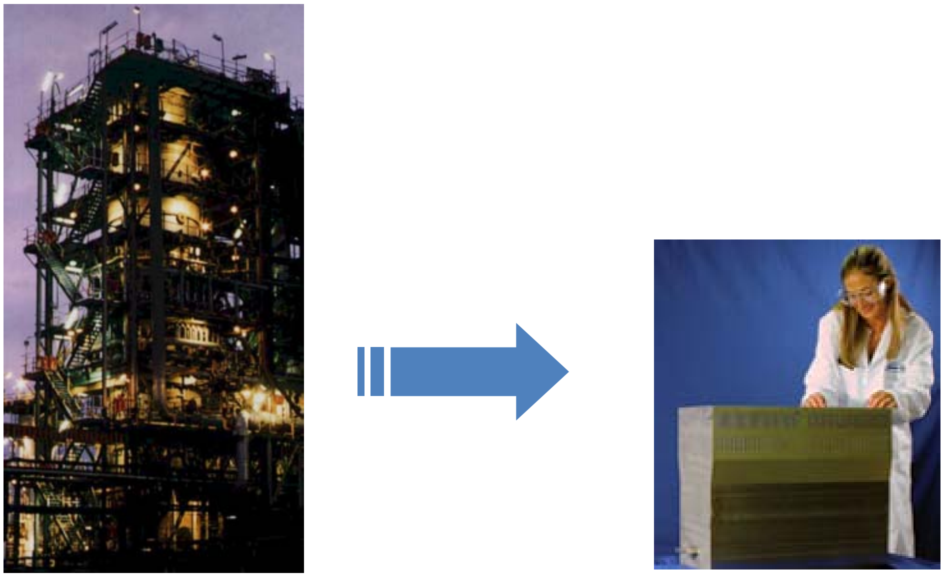
A particularly promising development in the current state of the art of MTG is the Topsoe Integrated Gasoline Synthesis (TIGAS) process, developed by Haldor Topsoe to integrate methanol synthesis and MTG into a single loop [*Spath and Dayton*, 2003]. In contrast with Mobil's MTG process in which different pressures are optimal for production of syngas, methanol synthesis, and MTG, the TIGAS process levels out these variation via catalyst alteration and in doing so invites modular deployment. Intermediate DME synthesis levels out the stoichiometry and leads to one recycle loop, but any recycle loops can be considered in our system integration to be throughput to a subsequent unit. Furthermore, demonstrated flexibility in syngas compositions in the TIGAS process is similarly compatible with an aggregated network in which a variety of throughput compositions may simultaneously flow, and demonstrated 60% per-pass conversion efficiencies can be readily compounded by an integrated system [*Rostrup-Nielsen et al.*, 2007]. Far from being speculative, the TIGAS process was first introduced in the mid-1980s, and has as recently as the past 6 months been funded by the Department of Energy to synthesize transportation fuel from wood biomass in the United States.

III.5.2. Remaining obstacles for integration to sunlight-to-fuels system

There are three primary areas of fuel synthesis investigation and implementation to be undertaken.

III.5.2.1. Demonstrating the scaling laws for fuel synthesis reactors

Research will demonstrate that the fuel synthesis at industrial output scales need not operate in monolithic units, as it can reap the benefits of technological learning incurred by the small scale approach, the cost savings of mass production, and the sharpening of selectivity offered by networking. First, the technology itself will evolve as industries learn and it will lead to the exponential growth observed in such industries.



(a) SASOL's gas-to-liquid reactor system

(b) Velocys' gas-to-liquid reactor system based on microchannel technology

Figure 7: Conventional F-T reactor system versus compact F-T reactor system based on micro-channel technology (photos adapted from SASOL [a] and Velocys [b]).

Smaller units that are mass produced, modular, and controlled in aggregate by cheap automation and control systems represent a new approach to scale in energy production and conversion infrastructure. Mass production and low unit costs would no longer require these individual reactor units to be long-lived or robust. The modularity reduces reliability requirements, and allows for frequent replacement of existing parts by newer, improved components; individual subunits of a large aggregated reactor network need not be engineered to the same high standards as monolithic plants. For example in the case of a Fischer-Tropsch process, as shown in Figure (a), the conventional design of slurry bubble column reactor s has involved a large scale reactor that must be taken entirely off-line for reactor-level maintenance, and although catalyst loading and off-loading is possible without shutting down such systems, catalyst poisoning rapidly spreads system-wide. Individual reactor units (e.g., as shown in Figure (b)) in a network can promptly and non-disruptively be taken off-line while feedstock is redirected; the cost here is, at most, the time constant to reach a new steady state in downstream affected reactors and any inefficiencies incurred during that transition. Here automation will play a particularly important role in optimizing that transition. Thus the failure of one single component out of many will not have the same catastrophic effects as the equivalent failure of a single big unit.

III.5.2.2. Customizing reactor conditions to maximize selectivity at small scales

The Fischer-Tropsch reaction as a fuel synthesis option takes these advantages of smaller units one step further, given the sensitivity of this process to temperature, pressure, input gas stoichiometric ratios of carbon and hydrogen, catalyst type, and promoters. Existing reactors separate and recycle the output streams back into their own input stream to maximize conversion, but a network of smaller scale reactors allows output streams to be refined in terms of these parameters and redirected to different small-scale units whose conditions are optimized for the products of choice. These smaller units host reactions of shorter residence time, but are operated by process automation that can make decisions in real-time redirecting the small-unit tailgas to optimal reaction conditions. Of particular importance is the study and management of the secondary reactions that occur in a Fischer-Tropsch reactor, as recycled olefins have been demonstrated to be catalytically reabsorbed for further transformation and synthesis [*van der Laan and Beenackers*, 1998]. Understanding the conditions under which this occurs and the effect of various operating conditions on selectivity of products informs a networking control strategy through which the advantages of an aggregate network might be realized; enhanced control of reactants allows more selective control of products. Research as recent as November 2007 suggests that running Fischer-Tropsch reactors may be an ever more plausible approach [*Tavasoli et al.*, 2007]. In a joint study between the University of Tehran and the Irani Research Institute of Petroleum Industry, a dual-bed reactor was studied using different cobalt catalysts. An alkali-promoted cobalt catalyst was used in the first bed of a fixed-bed reactor followed by a Ruthenium promoted cobalt catalyst in the second in order to assess the activity, product selectivity and system deactivation. Compared to a single-bed reactor, methane selectivity was 18.9 % lower, selectivity for hydrocarbons C5+ was 10.9 % higher, and accelerated deactivation 42 % lower. Catalyst recovery after regeneration was also favorable. These results hint at the possibility and promise of Fischer-Tropsch synthesis from a network of customizable reactors, reflecting optima unique to this process. The generalized advantages conferred by re-optimization of scale may further compound these gains.

III.5.2.3. Command and control to optimize modular output recycling

Integrating the modular catalytic fuel production with other units described here offers synergetic solutions to problems that each incurs on their own. Fuel synthesis deploys air-captured CO_2, for example, which would otherwise have been sequestered. The integrated process converts sunlight to liquid hydrocarbons instead of continuing to harvest fossil for that purpose. Even further process efficiency can be harnessed by marrying the tail gas to otherwise time-dependent electricity production. Large scale once-through operations have been shown to offer lower cost per unit of fuel than large-scale recycle plants [*van Vliet et al.*, 2009]. The small-scale networking approach turns the notion of "once-through" on its head, as a single run through a large network of aggregated units is in one sense a massive recycle operation, but will still not achieve 100% conversion efficiency. Unconverted tail gas contains products as light as methane and CO_2 that are expensive to reconvert into syngas but are in some cases recycled to autothermal reformers that can instead be channeled into additional electricity production during daily or seasonal downturns in incoming solar energy flux. The tail-gas therefore becomes a backstop against supply-side production instability.

As a final note, these arguments point towards an innovative and efficient production model for producing familiar liquid hydrocarbons in a renewable and carbon-neutral way. However, they also suggest the opportunity to move away from gasoline and diesel as the only transportation fuels. These convenient products of oil refining are the status quo among transportation energy carriers, but in a post-oil world the assumption that these are the most easily produced carbon chains is no longer true. The Fischer-Tropsch process itself is evidence of the fungible nature of carbon resources, and is readily able to produce whatever flavor of hydrocarbon is de rigueur. For example, it has been shown in processes that can generate 90% gasoline in the product suite that DME generation in the presence of certain catalysts is highly effective in promoting the Fischer-Tropsch synthesis reactions [*Zonetti*, 2009]. However DME could in turn become the desired product, and its production from methanol synthesis units can be either inhibited where methanol is the product of choice or encouraged via dehydration. DME has been demonstrated to be an efficient choice of turbine fuel, a competitive automotive fuel, functional as residential fuel for heating and cooking, non-toxic and non-carcinogenic [*Semelsberger et al.*, 2006]. The initial focus is on conventional fuels as their introduction does not require changes in the existing infrastructure. However, as time goes on, we expect an increasing focus on advanced designer fuels. Automated process control of process conditions and feedstock parameters over astute choices of catalyst can easily handle this transition from one fuel to another, or indeed from one catalytic process to another.

IV. System integration and implementation

IV.1. Overview and objective

In parallel to the research on each of the five subsystems, we deem it crucial to focus on aspects of the system's integration and implementation. This work – comprising theoretical and applied research – is interdisciplinary in nature, in that it ties together the in and outputs from the five subsystems, across various technologies, and enables them to be manufactured and deployed at mass scale. In addition, this effort involves assuring the integrated operation of all the different units in a highly automated fashion with little human interaction.

The research on system integration will define the framework in which the various subsystems are developed and will thus be instrumental in defining their interfaces. It will also learn from the development of automated, mass-producible subsystems defined within the different subsystems and attempt to organize the lessons learned into a higher level, and a more abstract understanding of these issues. It thus will identify general aspects of the different control strategies and assure that the different subsystems all have the benefit of these higher level insights. In short, the goal of the integration and implementation effort is to define and optimize the design characteristics of the overall system to produce synfuels from sunlight.

The integration & implementation team will meet three objectives:

- **Integration:**
  Available technologies for the five system units can be combined to produce synfuels – today. Integration will focus on advances in how the units are manufactured and how they operate together (including standardized in/output streams and interfaces) to reach commercial viability and mass scale of the system as a whole. This work should focus on leveraging existing technologies or advancing approaches to low cost, mass manufacturing and system automation (control algorithms, sensory networks and remote control with integrated self-feedback, etc.).
- **Implementation:**
  Crucially, the favored overall system design must pass socioeconomic impact and feasibility studies, including where and how the raw materials of the various system components can be harvested (e.g., life cycle impact, possibility for gradual and/or decentralized deployment, e.g. in developing countries). This effort will include dealing with the recycling/disposal of outdated units or units that have reach the end of their useful operational life.
- **(Iterative) optimization of the cyberphysical system:**
  We see the integration and implementation efforts as closely interdependent and synergetic, rather than consecutive. Examples of the interdependencies and synergies are:
  - Modeling will simulate the in/outputs, as well as automated operation of the five subprocesses to determine e.g. the reliability of the end-to-end system and expected uptimes.
  - Such simulations can identify weak links in the overall system which may in turn inform modifications to its design (e.g., Fischer-Tropsch should operate at lower temperature) or help design crucial aspects of the pilots (e.g., salinity range of water that the system should be tested for)

- Similarly, an analysis of the socioeconomic impacts of a large-scale deployment of the envisioned system in emerging markets may point to crucial advantages of having electricity and clean water as designated end products of the system (in addition to synfuels). Again, this would have ramifications for both the systems integration efforts as well as location and focus of the pilot testing.
- The interfaces between the subprocesses will need to be carefully designed and specified so that they can remain time invariant as the entire system evolves.
- We will also need to optimize managing the daily cycle (e.g., keeping the system powered when the sun is not shining) versus keeping the system operationally ready for when the sunlight returns. Alternatively, the optimal solution may be to keep some of the susbsystems actually operating, others only ready for operation, while shutting the remaining system down overnight. Different amounts of stored energy will be required depending on which option is chosen. Storage could be accomplished by a separate storage system, e.g. batteries, or by the water electrolyzers, which can be designed to easily be able to run in the reverse (as fuels cells), thus generating electricity from extra hydrogen produced during the day, to operate parts of the system at night.
- Similar considerations will be need to be applied for daytime operation to deal with fluctuating power output from the solar cells as a function of weather, time of day, and season.

IV.2. Making the system affordable and sustainable

A crucial characteristic of our proposed sunlight-to-fuels system is its focus on smaller, mass-produced units. This opens the door for several, simultaneous benefits:

- Individual components, e.g. the currently envisioned Si-based PV panels, are based on robust technology rather than elusive, magical materials or over the horizon technologies. This greatly enhances the overall reliability of the system as a whole, and also maximizes the chances of delivering a pilot-phase ready overall solution within a shorter time frame.

- Producing many smaller units (to reach the same total capacity output of synfuel) enables cost savings via mass manufacturing and automation. These cost savings will more than offset any loss in efficiency that the preference for robust technology may entail.

- The modularity of the five subsystems offers flexibility with regards to future technological improvements. For example, if a new approach for the solar subsystem comes about (e.g. organic, dye-sensitized cells, see above), this can be swapped out in a plug-and-play fashion without having to otherwise overhaul the system as a whole. Furthermore, the upgrades can take place continuously, without out a major impact on overall system output.

- The previous three benefits combined also result in a more nimble system that more easily lends itself to a gradual and/or decentralized deployment; this means much smaller barriers to entry, resulting in important benefits particularly in developing countries where access to capital (or the ability to safely manage large, high-risk infrastructure projects) may be limited.

- Replacement/recycling versus repair/maintenance, especially in light of improved performance that often comes possible via mass production and the associated learning that takes place. For example, in the personal computer arena, the average lifetime of PCs is sufficiently long and performance improvements sufficiently rapid that repair/maintenance is no longer a major consideration.

- Being able to inexpensively build and fully test full-sized individual production units, either in a standalone mode or when integrated with other subsystems. This removes the difficultly of uncertain scaling effects that often cause major problems when unit sizes are increased. It also greatly reduces the cycle time required for modified versions to be realized.

However, while the above benefits demonstrate the general advantage of smaller units, some limitations to this overall concept and inherent trade-offs will need careful study, for example:

- At some point, going smaller will not offer any incremental all-in advantages; for example, because the required land-use per unit of produced synfuel will increase dis-proportionally, thus off-setting other benefits.
- A certain design in the electrolysis subunit may offer even higher reliability and lower manufacturing cost of the units, however efficiencies (H_2 over electricity input) may suffer to a degree that the system is no longer cost-viable as a whole.
- Advantages from lower manufacturing costs (e.g., via light-weighting the PV panels) have to be evaluated vis a vis potentially higher maintenance costs (e.g., frequent replacement of broken panels).

In other words, the exact design of the overall cyberphysical system offers important areas of optimization − finding the sweet spots within an interrelated set of tradeoffs − is a major task of the Integration and Implementation effort. In essence, the research in the system integration and implementation should be understood as a series of interrelated studies that produce performance metrics of the system as a function of underlying design options. The quantitative modeling will then find optimal sweet spots in the overall system design along these metrics:

- Maximum capacity and its scalability over next 5, 10, 50 years
- Cost (installing, operation & maintenance) per unit of produced synfuel
- Environmental and socioeconomic impact (raw/rare material consumption, land use (both how much and where), risks associated with disruptive technology, degree of technological dependency between developed and developing countries, etc.)
- Reliability, availability and capacity factors
- System flexibility with regards to gradual and/or decentralized deployment
- System flexibility to absorb and leverage possible technological advances in the future

The various research disciplines required for the system integration and implementation to arrive at a cost-optimized, fully sustainable sunlight-to-fuels system are explained below.

IV.2.1. Economies of mass production vs. economies of scale

IV.2.1.1. Background and mathematical foundation

The pervasiveness of economies of scale is visible across a wide spectrum of today's industries with the utility and material process sectors, such as electricity generation, petroleum refining and mining operations as prime examples. Ample data have given rise to engineering rules of thumb that show how the cost of a process unit scale favorably with increased unit size. Among the subsystems discussed here, the fuel synthesis industry, especially Fischer-Tropsch synthesis, where each new plant is built larger than the last one, is a typical example where the benefits of economies of scale are being utilized.

A diametrically opposite route to reach cost reductions, through economies of mass manufacturing, was first described and quantified by T. Wright in 1936 [*Wright*, 1936]. Constant improvements in the mass production process lead to decreasing unit cost as cumulative production grows, resulting in different rules of thumb, commonly referred to as learning curves. Learning curves, in the original literature, usually referred to cost reductions associated strictly with increased labor productivity in manufacturing plants, as workers became more efficient when they produced more of the very same units [*Alchian*, 1963; *Rapping*, 1965; *Wright*, 1936]. More recently, however, learning curves - or more widely, experience curves – have come to encompass every kind of cost reduction ensuing from a greater volume of production, including design changes to the product itself. It is these aspects which we believe are crucial to ongoing, dramatic cost reductions: fine tuning the manufacturing processes as well as the design details to produce more and more units with ever increasing utility. Consider, for example, the dramatic cost reductions achieved - over the course of just a couple of decades - in producing writable compact discs for computers.

Some industries from the outset cannot benefit for larger size unit scales. They have had to develop other means to reach cost reductions, for example through mass production. While examples of the same total output being competitively pursued both via very large unit sizes and mass-produced units of small size are hard to find, the automobile industry offers some interesting comparisons. The general function of an internal combustion car engine does not differ much from that of a fossil fired power plant. The car engine converts chemical energy to mechanical work through combustion at a fixed cost of less than $40/kW [*Tsuchiya and Kobayashi*, 2004]. A gas fired power plant performs the same job at around $850/kW and a coal fired plant at over $2,000/kW [*EIA*, 2009], with lead times in production of about two and four years respectively. Although the effective lifetime of a car engine is much shorter, this is something that the industry has been able to capitalize on since the higher turnover rates fuel learning in the process and hence benefits can be gained from economies of mass production instead of economies of scale.

Surprisingly perhaps, the cost reductions derived from the utilization of economies of mass manufacturing can be shown to be on par with the reductions stemming from economies of scale. As a result, the two ways of reducing the cost of a large production system, either by building a small number of large units or many small ones, are virtually equivalent. This in turn suggests that the factors that drove industrial processes to ever larger scale had to come from considerations other than the simple scaling laws underlying the design.

The experience with ever larger systems has led to an estimate as to how the production cost k of a process unit will scale with its capacity c. These scaling laws are derived from observations of the evolution of processes from laboratory bench-scale, to pilot plant size and finally to large-scale industrial implementations. Traditionally, this dependence is presented as a power law

$$(1) \qquad k(c) = k(c_0)\left(\frac{c}{c_0}\right)^{\alpha},$$

where $k(c_0)$ is the cost of some reference unit of capacity c_0. Numerical values for α have been estimated for a wide array of process equipment and typically range from 0.6 to 0.8 [*Euzen et al.*, 1993; *Humphreys and Katell*, 1981; *Jenkins*, 1997]. Departing significantly from the reference value c_0 will render the approximation in equation (1) invalid. Indeed, as noted in [*Jenkins*, 1997], larger nuclear and coal power plants (c >100 MW) for example, exhibit diminishing economies of scale with $\alpha \geq 0.93$.

The literature on economies of mass manufacturing, or economics of learning-by-doing was pioneered by Arrow [*Arrow*, 1962], though the progenitor of this idea seems to have been Wright [*Wright*, 1936] who proposed that the costs of manufactured goods, specifically airplanes in his case, decline with the cumulative number produced. There have since been various studies in different fields resulting in ample data on the cost reduction per unit as the cumulative production grows [*Argote and Epple*, 1990; *Ferioli and van der Zwaan*, 2009; *McDonald and Schrattenholzer*, 2001; *Tsuchiya and Kobayashi*, 2004]. This effect is usually formulated using learning curves which state that the unit cost decreases by a fraction $\varepsilon < 1$ as the cumulative production doubles. That is, the cost k_{2n} of the $(2n)^{\text{th}}$ unit is a fraction ε of the cost k_n of the n^{th} unit, or

$$(2) \qquad \frac{k_{2n}}{k_n} = \varepsilon$$

Sometimes this cost reduction is expressed by the learning rate, defined as $1-\varepsilon$. The notion of "forgetting by not doing" should be mentioned in conjunction with learning rates. This observation asserts that cost reductions attributed to learning will decrease with slower turnover rates. This may explain the relatively small cost reductions seen over time for larger, and more long lived installations that are custom made rather than mass produced [*McDonald and Schrattenholzer*, 2001].

Based on (2), a continuous approximation of k_n can be formulated as

$$(3) \qquad k_n = k_1 n^{\log_2 \varepsilon},$$

where k_1 is the cost of the first unit produced. From (3), the aggregated cost $K(N)$ of N mass-produced units following the given learning curve, can be expressed by:

$$(4) \qquad K(N) = \int_0^N k_1 n^{\log_2 \varepsilon} dn = \frac{k_1}{1+\log_2 \varepsilon} N^{\log_2 \varepsilon + 1}$$

Faced with a proposition of producing a system with a total capacity Nc_0, $N > 1$, given a reference unit of capacity c_0 with a known production cost k_0, we can now compare the two means of cost reductions. The choices are either to benefit from the economies of scale and produce a unit N times as big as our reference unit or to follow the path of economies of mass production and produce N copies of the given reference unit. The production costs of the two possible systems are:

$$k(Nc_0) = k_0\left(\frac{Nc_0}{c_0}\right)^{\alpha} = k_0 N^{\alpha} \quad \text{(Economies of scale)}$$

$$K(N) = \frac{k_0}{1+\log_2 \varepsilon} N^{\log_2 \varepsilon + 1} \quad \text{(Economies of mass production)}$$

A statistical analysis performed in [*Ferioli and van der Zwaan*, 2009], based on a sample of 22 different mass-production oriented industrial sectors, found a average learning rate of 19%, which would translate into $\log_2 \varepsilon + 1 = 0.7$. Since typical values for α ranges between 0.6 to 0.8 it is therefore reasonable to assume that $\log_2 \varepsilon + 1 \approx \alpha$ and hence, the reductions in production costs ensuing from economies of scale and economies of mass production are roughly the same.

IV.2.1.2. Implications for the sunlight-to-fuels system

We surmise that the advantages of large-scale systems can be found in costs other than those of construction of a process unit. The bigger units have a fundamental advantage of simplicity: aggregating a large number of independent units very often incurs increased complexity, and operating and maintaining a large number of small units is typically more difficult. Thus, a large number of units would, historically at least, lead to escalating personnel and maintenance (operation and repairs) costs. We believe however that this argument is becoming increasingly moot as the modern ability to automate can greatly reduce the cost associated with operating any equipment.

The computer industry offers an example where a distinct reversal in trend is noticeable and the effects are dramatic. After a few decades of development leading to larger and larger mainframe machines, the industry shifted direction toward producing the small personal computer. This paradigm shift from custom-made large machines to smaller and mass-produced units sold on mass markets resulted in rapid cost reductions, manifested by Moore's law, not to mention greatly improved capabilities. This transition would however not have been feasible if the need for labor in terms of physical operation and maintenance/repairs of the computers under the previous paradigm had remained.

Our goal is to take advantage of these potential cost savings ensuing from the mass production process and apply them to cost reductions in solar energy, in fuel-synthesis reactor design, in the development of electrolytic cells for producing hydrogen, as well as in materials extraction: water desalination and capturing carbon dioxide from the air. Furthermore, the modular and automated approach would also allow for the possibility of distributed operation.

Our analyses of mass production versus scale economics will, in part, draw on an important and well-studied analogue, namely electricity generation in large central stations versus distributed generation. For example, as may have been expected early on [*Awerbuch*, 1984], cost reduction possibilities of (ever larger) power plants were exhausted in the 1990s, and larger size no longer meant lower cost. On the contrary, U.S. utilities were facing a sharp rise in incremental cost of the central station technology, whether nuclear or coal [*Lovins*, 2002].

One of the central ideas of this proposed sunlight-to-fuels system is that improvements in mass manufacturing and automation allow for significant cost savings that, net-net, favor (distributed) small over large scale generation. Such technology may have steered U.S. electricity production away from central generation if they had been available and fully understood sooner [*Hirsch*, 1989]. Similarly, generating synfuels in smaller, distributed units rather than centrally will unlock important cost advantages, especially when the full costs of distributing the synfuels (rather than just the on-site production) are taken into account [*Awerbuch et al.*, 1996].

At the same time, consideration of external factors must always be considered, and these are in fact different for different technologies. For example, for coal plants, there are likely to be restrictions on the minimal size of the overall plant due to the cost of the rail lines needed to supply the coal. Likewise in the future, the requirement to capture and dispose of CO_2 will also mean relatively large plants. This however does not preclude the plants from being constructed using large numbers of small mass-produced units, all centrally located, and thereby still taking advantage of learning to reduce total costs.

In summary, the research effort into economies of mass production versus economies of scale will provide a set of analyses/metrics that describe the costs associated with manufacturing and operating the sunlight-to-fuels system as a function of the system's design, in particular the size (unit capacity) for each individual system. This analysis will differentiate between the following cost savings and tradeoffs (all comprised in learning curves or experience curves):

- Cost savings from modifications to the manufacturing/assembly lines that produce the units.
- Cost savings from modifications to design details of the units themselves.
  - . in other words, getting cheaper at producing the same thing over and over versus getting cheaper by producing something progressively better.
- Trade-offs between higher automation of the manufacturing process and increased flexibility and options for mass-customization resulting from more advanced manufacturing systems.

IV.2.2. Mass manufacturing, automation and robotics

This research area is essentially the practical extension and implementation of the aforementioned theoretical and empirical research into economies of mass production vs. economies of scale, as well as automation. The work on mass manufacturing, automation and robotics will determine how the above theoretical/empirical findings can be realized for the actual Sunlight-to-fuels system, its manufacturing, operation, and maintenance/repairs.

Regarding manufacturing: What should the factory/factories to produce the system and its five subsystems look like? Which additional advances in automation and robotics are required to manufacture the system at sufficiently low cost? Which solutions do already exist but may not have been employed in concert to achieve maximum benefit?

R*egarding operation and maintenance/repairs:* What further cost savings will be achieved through a largely automated operation of the system, and which novel technologies (e.g., wireless sensors and remote control) are available now to achieve this? Finally, beyond the day-to-day operation, to what extent can system repairs (e.g., replacing faulty parts) be aided by advanced robotics?

IV.2.3. Financial analysis

The financial analysis for evaluating sunlight-to-fuels systems should reflect fully loaded costs and in particular capture any indirect cost aspects that will help differentiate between large unit, central generation installments versus small units that are centrally located or deployed as distributed generation systems. Specifically, the financial analysis will break down the various drivers of the all-in cost per amount of synfuel:

- Material costs, including detailed scenarios of sourcing areas and mining of metals, and considering the extraordinary scale at which raw materials will be needed.
- System manufacturing costs, including lifetime capital costs.
- On-site construction, installment, and testing costs, including the potential cost savings associated with the essentially more rapid deployment and shorter testing time required for smaller units (i.e., reduced 'ramp-up" time).
- Operation costs (including benefits from large networks of many smaller capacity units that are fully automated via remote-sensor and control technology).
- Maintenance/repair costs, including savings available from possible robotics-based repairs. Crucially, this will capture the lower maintenance costs of the envisioned system of five subsystems, with standardized in/outputs that can be easily swapped out either with a repaired subsystem or with a new technology for a subsystem.
- Revenues from potential by-products such as desalinated water, electricity, and carbon dioxide.
- Risks (revenue risk, technology risk, etc.) and how these affect financing cost and cost of capital. Crucially, this will include the aspect that, going forward, demand for fuels will be less predictable than electricity demand growth in the 20th century. In the past, such predictable demand has favored large/long term investment into large centralized units.
- "Portfolio" effect of operating many small rather than single large units.
- Crucially, the analysis must include the costs of distributing and delivering the synfuel. This is a typical blind-spot often encountered in large industry and power generation scenarios. [*Christensen*, 2000]

IV.2.4. Lifecycle and socio-economic impact analysis

The goal of this research is to provide the integration and optimization effort with a set of analyses/metrics that quantify the lifecycle and socio-economic impacts associated with the overall Sunlight-to-fuels system as a function of the system's various design alternatives.

This will provide important information as to which specific system design to favor and thus how to allocate overall research efforts. In order to keep the impact studies efficient and on target, it will be important to observe where a simple, qualitatively based "Go" vs "No go" view is sufficient and where a more quantitative analysis is required (e.g., is the land-use requirement acceptable vis-à-vis population density in a given country or region?).

The life cycle analysis will entail a review of processes and materials that will be used in material and energy conversion devices, identification of hazards related to feedstock materials and by-products, pollution prevention and control options, assessment of pollution-control technology options, identification and characterization of routine and potential accidental releases, determination of exposures (occupational, public, and environmental) to pollutants via different pathways, assessment of toxicology of various chemicals of concern, and identification of safety and environmental issues associated with the use and decommissioning of Sunlight-to-fuels units. A comprehensive analytical framework for hazard identification, hazard characterization, and hazard management will be used. All aspects of a technology will be reviewed to examine hazards imposed by each step in material supply cycles, including extraction, processing, refining and purification of materials, and fabrication, installation, operation, decommissioning, and recycling or disposal of devices and products.

The complete life cycle and socio-economic impact analysis will consider, for each possible system design, the following aspects:

- Full life cycle impact analysis, including rare materials, toxic materials, waste during manufacturing and operation, land use, impact on water ecosystem (e.g., nature and size of desalination units), unit recycle/disposal, and decommissioning.
- Geo-political risks (e.g.. is the particular design susceptible to terror attacks,. large reactors capable of explosions, etc.)
- Is the particular design suitable for fast, large scale and/or gradual deployment? What barriers to entry (investment costs, security risks, competing technologies) will exist vis-à-vis different markets (developing versus developed)?
- What public policies (e.g., GHG emission controls; feed-in tariffs, energy independence) affect the feasibility of the envisioned Fuels-from-Sunlight system, and which particular design appears more promising vis-à-vis the inherent uncertainty of the future policy landscape? Does the viability of a particular system design depend on changes to existing policy and regulations, and if yes, what is the risk that these changes will not materialize?
- To what extent will the new Sunlight-to-fuels system negatively impact or even disrupt the markets and business practices in a given country? Which system design may do so less, and what

mitigation measures are available (either different system design or preparations in the country that could be explored during pilot tests)?

- What benefits of the system might outweigh the preceding negative impacts?

IV.2.5. Computational modeling and design optimization

The above research efforts will provide a series of interrelated studies that produce performance or suitability metrics of the system as a function of underlying design options. The quantitative modeling will then find sweet-spots in the overall system design along these metrics.

As an additional, important characteristic of the overall system, the quantitative modeling will simulate the full end-to-end process of the cyperphysical system, in order to quantify the overall reliability and "uptime" expected from any particular design option. This in turn will feed into the financial analysis, as it will be affect requirements for maintenance/repair, as well as affect the manufacturing and construction/installment costs relative to total, life-time synfuel capacity of any given system design.

By offering a consolidated view of all the above "performance" metrics, the computational modeling will reveal trade-offs in choosing the final design, for example:

- At some point, going smaller will not offer any incremental net advantages, for example, because the required land-use per unit of produced synfuel will increase disproportionally, thus off-setting other benefits.
- A certain design in the electrolysis subunit may offer even higher reliability and lower manufacturing cost, however efficiencies (hydrogen output per electricity input) may suffer to a degree that the system is no longer cost-viable as a whole.
- Advantages from lower manufacturing costs (e.g. via light-weighting the PV panels) have to be evaluated vis-à-vis potentially higher maintenance costs (e.g. frequent replacement of broken panels).

Ultimately, the integration and implementation research (and its consolidation into a quantitative model) will allow to steer the research efforts on the various subsystems more efficiently. This minimizes the risk of wasting resources employed on somewhat parallel research efforts that are either redundant or even incompatible with regards to the system as a whole. Examples for such decision support are:

- Modeling will simulate the in-/outputs, as well as automated operation of the five subsystems to determine the reliability of the end-to-end system and expected uptimes.
- Such simulations can identify hot spots/weak links in the overall system which may in turn inform modifications to its design (e.g., Fischer Tropsch should operate at lower temperature) or help design crucial aspects of pilots (e.g., salinity range of water for which the system should be tested).
- Similarly, an analysis of the socio-economic impacts of a large scale deployment of the envisioned system in emerging markets may point to crucial advantages of having electricity and clean water as designated end products of the system (in addition to synfuels); again, this would have

ramifications for both the systems integration efforts as well as location and focus of the pilot testing.

- As yet another example, suppose a new PV technology (e.g., organic, dye-sensitized cells) advances to commercial viability in a couple of years. Concerted analyses of life cycle assessment (e.g., rare material usage), cost, manufacturing and maintenance impacts of the system, and reliability will have to be carried out to determine whether a swap of one of the core technologies should be pursued (or alternatively a two-track pilot testing carried out).

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