AIChE

Perspective

Chemical Engineering in a Solar Energy-Driven Sustainable Future

Rakesh Agrawal and Dharik S. Mallapragada
School of Chemical Engineering, Purdue University, West Lafayette, IN 47907

DOI 10.1002/aic12435

Keywords: solar energy, sustainable future, sustainability, biofuel, sustainable chemicals

Introduction

Our current lifestyle, to a large extent, has grown out of the abundant availability of fossil resources, mainly coal, natural gas, and crude petroleum. Chemical engineering as a discipline evolved primarily in the 20th century, along with the conversion and use of carbonaceous fossil matter in various forms. As the chemical transformations within fossil-based processes reached maturity, chemical engineers began to look actively for challenging problems, new directions and growth in areas such as biomolecular engineering, health-related applications and evolving technologies such as nanotechnology, etc. However, finite fossil resources, world economic growth, environmental concerns, and political forces are reshaping the technology horizon. An unavoidable transition from a fossil-resource-based state to a state where most if not all human needs will be met by sustainable resources must ultimately take place. This transition holds the promise to provide at least a similar level of opportunity and dramatic growth as was seen by chemical engineers during the early to mid-part of the last century. In order to take advantage of this promise, however, the chemical engineering profession must act now toward the goal of developing not only technologies for the future sustainable state, but also for the transition to that state.

A big challenge for implementing this goal is to envision what the sustainable future may look like. There are several options, each with its own uncertainties and challenges. In this article, we will focus on a future where the basic human needs of food, chemicals, heat, electricity and transportation will generally be met by solar energy as shown in Figure 1. We choose this future due to the singular abundance of this energy source. According to one estimate, the amount of solar energy striking the earth in 1 h is $\sim 4.3 \times 10^{20}$ J, which is comparable to the 2009 annual energy consumption of $\sim 5.1 \times 10^{20}$ J by the entire planet.[1–2] This abundant supply of primary energy ensures us that a future driven by the direct use of solar energy should be able to sustain itself for any foreseeable future.

The direct use of solar energy, however, presents many challenges. Sunlight is available during only a fraction of the 24 h day cycle. For an insolation of 1 kW m^{-2} and a yearly average availability of 20% per day, the annual solar energy incident is ~ 6307 MJ m^{-2} (1 MJ $= 10^6$ J).[3] The task at hand is to harness this intermittently available primary source of energy and convert it to not only usable forms of secondary energy such as electricity, heat and fuel, but also to chemicals and fertilizers.

A key challenge for chemical engineers in this century will be to satisfy each of the basic individual needs, within the context of the coexistence with all other basic needs, to improve the energy efficiency and cost of the entire system. For this purpose, it will be essential to explore synergy and interaction between various technologies and end usages. Figure 2 shows our attempt to depict some of the synergistic interactions between heat, electricity, storage, chemicals, fuel and biomass to efficiently utilize incident solar energy. The other major inputs in addition to solar energy in Figure 2 are water and air components. Note that the purpose here is to show only those interactions and technologies that are thought to be relevant for this perspective discussion.

Figure 2 shows technologies for each end use shown in Figure 1 that can be impacted by chemical engineering. It also shows the synthesis of fuels and chemicals from biomass and extracted CO_2 along with the impact of solar electricity and heat on such synthesis. Some of the chemicals are used as fertilizers for the growth of biomass. Similarly, the transport sector uses multiple secondary forms of energy. All of these interactions and some of the associated technologies will be discussed within the context of chemical engineering after a brief examination of the efficiencies at which solar energy is collected in various secondary forms of energy.

Collection Efficiencies for Solar Energy to Various Secondary Forms

Depending on the temperature of absorption and concentration of sunlight through the use of concentrators, sun-to-heat collection efficiencies are estimated to be as high as 50–70%.[4–5] Similarly photovoltaic (PV) modules with sun-to-electricity efficiencies in the range of 10 – 42% have been

---

Correspondence concerning this article should be addressed to R. Agrawal at agrawalr@purdue.edu.

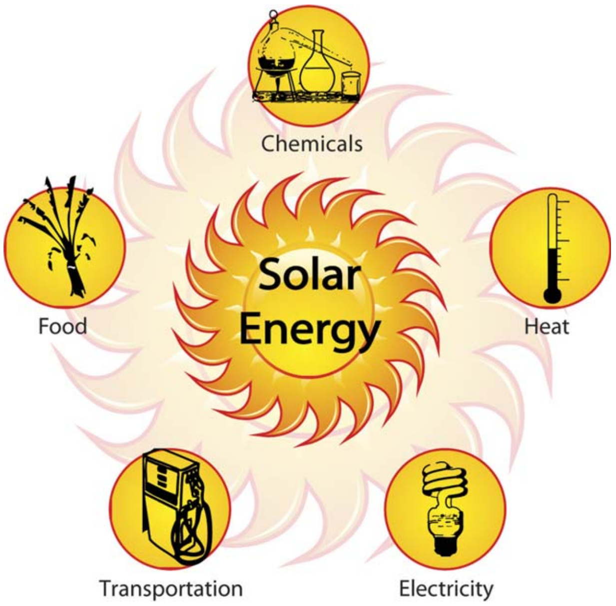

Figure 1. Basic human needs met by solar energy (adapted from Agrawal and Singh[10]).

reported.[6] By using a commercially available, 20% efficient, silicon-based PV module and an electrolyzer efficiency of 60%, based on the lower heating value (LHV) of H_2, a sun-to-H_2 efficiency of 12% can be achieved. Thermochemical methods have a potential to produce H_2 at much higher efficiencies of up to 25%.[7] In a production facility, a fraction of the land area is generally not used for the collection of solar energy due to shading, access to equipment, etc. To account for this effect, the net efficiencies are calculated by assuming only 50% of the available land is effectively used for solar energy collection,[8] and the resulting numbers are shown in parenthesis in Figure 2.

Biomass generally grows at a rate of 1–3 kg m^{-2} yr^{-1}. With biomass LHV energy content of $\sim$17 MJ kg^{-1}, this growth rate corresponds to capture of 0.28% to 0.84% of the average incident solar energy of 6307 MJ m^{-2} yr^{-1}.[3] Energy-efficient sugarcane crops store only $\sim$1% of the incident solar energy. It is estimated that the maximum conversion efficiency of solar energy to biomass under today's atmospheric CO_2 concentration and at 30°C is 6% for C4 photosynthetic crops.[9] The actual annual averaged efficiencies, due to limitations on the growing season, temperatures and less than ideal conditions for biomass growth will be much less than this maximum value.

Based on the collection efficiency numbers for solar energy, for a given specific use, the pecking order to be considered is heat first, followed by electricity and H_2 with cultivation of biomass last.[10]

Fuel and Chemicals from Solar Energy

Recently the subject of solar energy to liquid fuels was reviewed in detail.[10] It is rather easy to envision the use of biomass as the renewable carbon source for the production of chemicals and fuels. However, in order to reveal some of the major constraints imposed by such use, it is helpful to consider the USA as a case study. The U.S. annual chemicals production in 2006 used fossil resources with total energy content of $\sim$4.4 trillion MJ.[11] The U.S. transportation sector uses

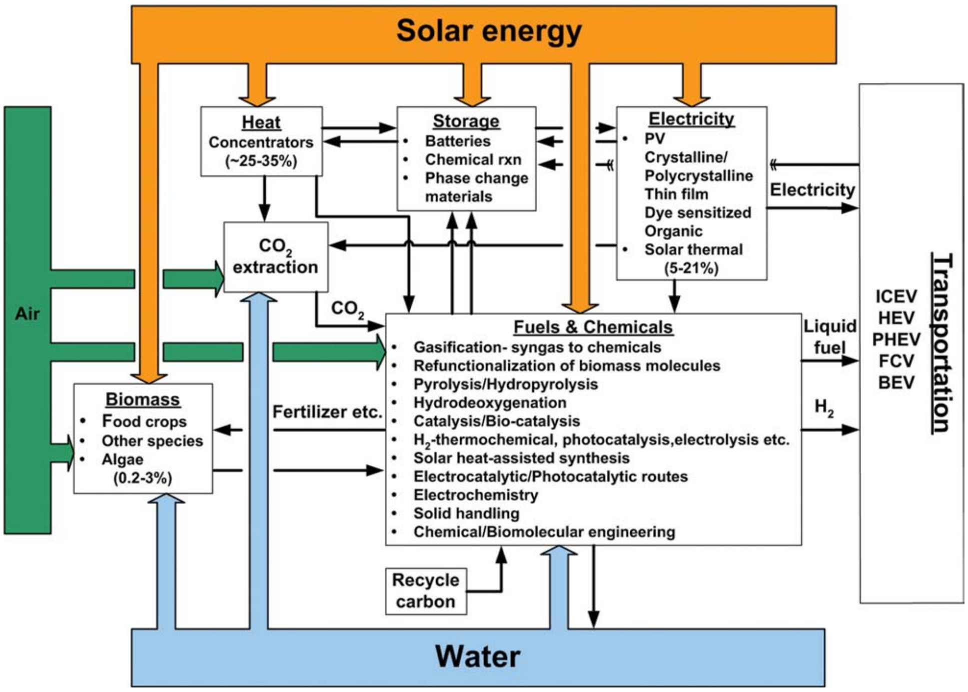

Figure 2. Process interactions to meet the demand for transportation fuels and chemicals in a solar energy driven world. ICEV = Internal Combustion Engine Vehicle, HEV = Hybrid Electric Vehicle, and BEV = Battery Electric Vehicle. The percentage numbers in parenthesis correspond to the range of solar energy conversion efficiencies for each energy form.

~13.8 million bbl day^{-1} of petroleum. This translates into an annual consumption rate for transportation of ~29 trillion MJ. In contrast, the amount of sustainably available (SA) biomass in the U.S. could potentially be ~498 million tons (MT) yr^{-1} ($1\ T = 10^3$ kg), which includes waste biomass collected via sustainable practices from the existing agricultural and forestry activities (~349 MT yr^{-1}), as well as energy crops grown on a portion of the land under the U.S. Conservation Reserve Program using little additional energy input (~149 MT yr^{-1}).[12] The energy content of the SA biomass corresponds to about ~8.5 trillion MJ. Clearly, the amount of SA biomass is far less than that needed for the combined demand for chemicals and transportation fuels. This shortage becomes even worse when one accounts for the fact that the conversion of petroleum to fuel is far more energy efficient than that of biomass to fuel. Nevertheless, the following discussion will show that chemical engineers have the potential to stretch biomass resources to cover as much as 40% of this total energy need.

Since the availability of SA biomass is constrained and additionally grown biomass captures solar energy at much lower efficiencies than for the direct production of heat, H_2 and electricity, the use of SA biomass in a solar energy driven world to produce heat, electricity or H_2 should be minimized if not totally avoided. Furthermore, in a land constrained world, it is essential that chemical engineers develop and design processes that will maximize the production of chemicals and fuels from the limited quantity of SA biomass.

Thus, the first step toward increasing the utilization of SA biomass to desired end products is to minimize its use to supply auxiliary energy such as heat and power needed by chemical processes. Also, the inherent process inefficiencies that lead to reduced yield or energy dissipation must be minimized, and any such remaining process inefficiencies must be met with more efficient forms of secondary carbon-free energy. Thus, processes will have to be developed that will directly use solar heat or electricity and avoid combusting any fraction of the biomass. For example, since electricity is produced with higher efficiencies from sunlight than atmospheric carbon as biomass, use of electrochemical processes for chemical transformations and synthesis may offer better overall process efficiencies that will need to be carefully evaluated.

An additional clue toward increasing the utilization of SA biomass comes from an examination of the energy content of biomass species based on a carbon atom basis. Switchgrass, poplar wood and sugar have energy contents of 485, 455, and 423 kJ per mol of C, respectively.[13] In comparison, the energy content of gasoline is 605 kJ per mol of C. The lower energy content of biomass species is due to the 35–40 wt % oxygen in biomass which must be removed to increase the energy content on a per carbon atom basis. These factors imply that even with a 100% energy efficient conversion process for biomass carbon to high-energy-density molecules such as those in gasoline, about one third of the biomass carbon will be released in a low-energy state as CO_2.

Given that the recovery of the carbon lost in the form of CO_2 through the cultivation of plant species is very inefficient, as shown before, it is clear that the biomass should be viewed as a source of carbon first and not as a source of energy. This presents us with a unique challenge (and opportunity) to develop augmented processes that will increase the recovery of the biomass carbon during conversion via the use of supplemental energy forms, such as H_2, heat and electricity, which are derived from sunlight at much higher efficiencies than by biomass plant growth. Figure 2 depicts this opportunity. Recently augmented processes based on biomass gasification (H_2CAR), and fast-hydropyrolysis/hydrodeoxygenation (H_2Bioil) using solar H_2 and solar heat have been suggested to increase the liquid fuel production from a given quantity of biomass by a factor of two to three when compared to the conventional stand-alone processes.[3,13–14] Another illustration of this concept involving the steam gasification of biomass using solar heat and H_2 followed by methanol synthesis, is estimated to recover ~90% of the biomass carbon as liquid fuel.[15]

Currently, fossil resources provide building blocks for 95% of all the carbon-containing chemicals that are used.[16] According to Lipinsky, the seven building blocks for these chemicals are methanol ethylene, propylene, butadiene, benzene, toluene and xylene.[17] In contrast, the available structural units of lignin, hemicellulose, cellulose, glucose, fructose, sucrose and triglycerides from biomass are quite different. This means that there is a need to find new thermal catalytic and biocatalytic processes to produce chemicals from biomass that are identical to the ones currently available from petrochemicals,[18–19] as well as to synthesize new molecules that are different in structure but could satisfy the same end functional need.[16–17] In some cases, conversion of biomass molecules to a petrochemical form will require more conversion steps. In such cases, it will be worthwhile to explore refunctionalized molecules produced from the structural units of biomass that would retain some of their original structure but meet the end use. Refunctionalization of biomass molecules will most likely involve removal of oxygen along with some molecular rearrangement. Oxygen removal in the form of H_2O rather than CO_2 is likely to be preferred because once CO_2 is formed, its recycle using H_2 to chemicals or fuels will be an energy intensive process and the potential structural benefit of starting with biomass carbon is lost.

It should be noted that while chemicals are generally produced with high purity and compositional consistency, petroleum-based fuels are mixtures of hundreds to thousands of compounds.[17] Furthermore, such fuels are derived from petroleum crude with relatively simple, inexpensive and energy efficient transformation steps.[16,20] These facts have two important ramifications: (1) for chemical production, starting building blocks need to be relatively pure and must be derived from complex lignocellulosic biomass. Extraction of a C_6 sugar from cellulose as a starting material is one such example. (2) For fuel production, however, processes must be developed with a few processing steps that are energy efficient in converting the entire lignocellulosic biomass to liquid fuel. Fast-hydropyrolysis/hydrodeoxygenation of biomass, consisting of only a few processing steps to produce liquid fuel containing hundreds to thousands of compounds, is one such attempt.[14] Of course, for chemicals production, one also has a choice to separate relatively pure components from such multicomponent liquid fuels for further processing.

One distinguishing feature of the biomass-based products will be the general need to remove the large amounts of oxygen present in the biomolecules. One possible method is to gasify the entire lignocellulosic biomass to syngas and then reconstruct the desired molecules. While this method has an appeal due to the fact that all biomass species are first converted to the common molecules contained in syngas, it is likely to be relatively energy inefficient when compared to the processes that make the least number of changes to the structure of the molecules from a given biomass. In particular, this inefficiency is due to the energy requirement for gasification and subsequent heat release at relatively lower-temperatures due to substantial heat of reaction during syngas conversion to liquid fuel. Therefore, a challenge will be to develop catalytic, hydrodeoxygenation processes using solar H_2 that will selectively remove different oxygen atoms that are present with different functionalities within the lignocellulosic biomass structure. Furthermore, this removal will have to be achieved while controlling the level of hydrogenation within various molecules and minimizing the formation of CO_2. For example, aromatic derivatives from the lignin component of biomass will require removal of O without ring saturation.

The desire to increase the biomass carbon recovery as chemicals or liquid fuel and the associated hydrodeoxygenation will necessitate the use of large quantities of H_2. This requirement of H_2 is distinct from that for the H_2 fuel cell vehicles in an H_2 economy.[21] The large-scale production of H_2 from solar energy provides unique process development opportunities for chemical engineers.

Some inherent drawbacks of using biomass as a feedstock are its seasonal availability and low-volumetric energy content coupled with its geographical distribution. Switchgrass bundles have an energy content of 3519 MJ m^{-3} compared to 36,000 MJ m^{-3} for crude oil.[22] Clearly, shipment of low-energy density biomass over long distances to a central processing plant will add significant cost to the final product. Petroleum refineries and petrochemical complexes, owing to the high-energy density of crude oil, have come to enjoy economies of scale by building very large-size plants. In a solar-energy-driven world, a different economy of scale with large numbers of small-size, mobile plants will be needed. Such a plant could be easily transported to a location for the duration for which biomass would be available at that location. If needed, the product from several such small plants could be shipped to one large central plant for further processing. Use of fast-hydropyrolysis/hydrodeoxygenation based processes with minimal processing steps holds the potential to provide one possible small-scale solution.[14] The small-size plants will require a lot of creativity to design and build, and should be no less efficient than their large-size cousins.[23–24] This need for innovation at small scale will generate exciting opportunities in chemical engineering.

Going back to the USA case study, we can now ask, what is the maximum potential for the production of liquid fuel from the SA biomass? One can envision augmented processes using solar energy that will lead to nearly 100% biomass carbon recovery as liquid fuel and chemicals.[3] If we assume that all the carbon in 498 MT of SA biomass is converted to carbon in diesel molecules, then the energy stored in such a product will be ~13.2 trillion MJ. While this energy content is greater than the original energy content of ~8.5 trillion MJ in the SA biomass, the number is still much short of the ~29 trillion MJ needed by the US transport sector plus ~4.4 trillion MJ needed for chemicals. Clearly even with all the process innovations and new chemical engineering developments, carbon from SA biomass alone will be unable to meet the total fuels and chemicals need of the USA. However, if necessary, the entire chemicals need could be met by SA biomass alone.

Once all the SA biomass is consumed and there is still a need for carbon containing fuel or chemical molecules, the next logical research direction is to find other efficient sources of sustainable carbon. One obvious source is the recycle of the used carbonaceous matter. For this to be feasible, society will have to adapt to recycling more of the carbon containing matter. Figure 2 depicts this need to develop reprocessing technologies for recycled carbon matter. The next source will be atmospheric CO_2. Surprisingly, the direct physical extraction of CO_2 from its low concentrations of hundreds of parts per million by volume in air, and its thermochemical conversion to liquid fuel can potentially be more efficient in utilizing solar energy incident on a given land area than growing additional biomass, including algae, and converting it to liquid fuel through augmented processes.[10] Therefore, it is plausible that in a solar energy driven future, chemical engineers may have to develop efficient and cost-effective processes to extract CO_2 from air and then convert it to liquid fuel or chemicals. However, this will be a massive undertaking due to many challenges originating from the incredibly low concentration of CO_2 in the air. The current cost estimate for CO_2 extraction using absorption based methods is estimated to be in the range of \$100 to \$200 per ton of CO_2 extracted, and will likely require a large reduction before it becomes economically attractive.[25]

So far we have focused on carbon-based chemicals. It is worth noting that of the top 15 chemicals produced in the USA in 2009, seven are noncarbon based including sulfuric acid, phosphoric acid, ammonia, chlorine, sodium hydroxide, nitric acid and ammonium nitrate.[26] Currently, for these chemicals, fossil resources provide energy for conversion and also H_2 when it is needed. In a solar-energy-driven future, the energy will come in the form of solar heat and electricity and solar H_2 will come from the splitting of water. Thus, ammonia will be synthesized using solar H_2 rather than H_2 from natural gas. Urea may be produced from the solar-energy-derived NH_3 and byproduct CO_2 derived from carbon-based liquid fuel and other chemicals production processes. Clearly new processes will be needed for some of these chemicals. Furthermore, use of solar heat and electricity for noncarbon based chemicals production would meet a sizeable portion of the ~4.4 trillion MJ of US energy demand for chemicals, leaving only the remaining portion to be met via the use of SA biomass carbon.

Systems Approach

A detailed system analysis at various levels will be needed to help in the evolution of a solar energy based sustainable future. It will be critical to perform such analyses to identify synergistic interactions at both the production as well as use levels. Figure 3 shows an example for the transportation sector. In this case the ultimate goal is to drive the entire transport sector and supply chemicals using solar energy. Therefore, electricity and H_2 may not only be used in conjunction with biomass to increase liquid fuel yield, but also be directly used in plug-in hybrid electric vehicles (PHEV), and fuel cell vehicles (FCV), respectively. An optimization of the entire system, including onboard batteries, fuel cells, onboard H_2

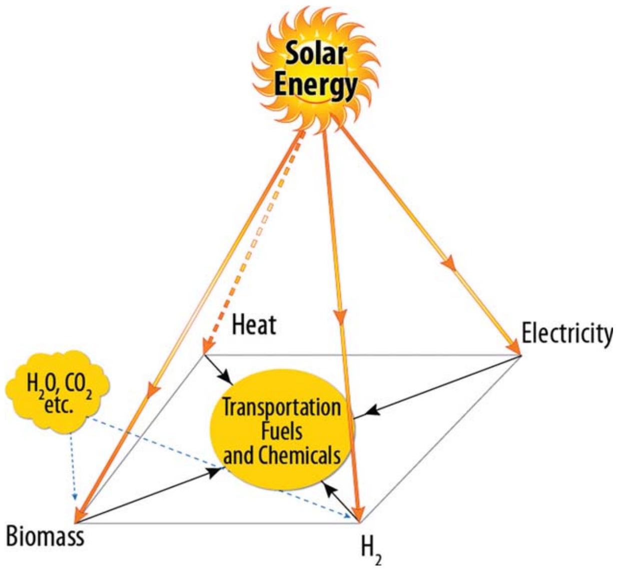

Figure 3. An example of the systems analysis approach to address the needs of the transportation sector and chemicals production.

storage, supply of electricity or H_2 to vehicles, etc., will be needed to build a cost-effective and energy efficient sustainable system. The recently reported use of a multi-paradigm modeling approach, applied to examine the impact of PHEV use on the electricity generation sector, is one example of the modeling tools being developed for such tasks.[27]

Systems analysis will also be needed to identify synergies between different technologies to maximize liquid fuel or chemicals production from a given quantity of biomass. For example, integration of biochemical processes with thermochemical processes may be explored to better utilize the unconverted lignin component of the biomass produced by the biochemical portion of the processes.[25,28–29] Synergistic process interactions to coproduce one or more chemicals along with liquid fuel can also be identified through the aid of systems analysis. At the design stage, optimal process configurations pertaining to multiple objectives may be identified by analyzing process alternatives via a superstructure, as demonstrated for the production of syngas from biomass.[30]

Transition from a fossil resource state to a solar energy driven state can be facilitated by a good systems analysis approach. For example, a systems approach has resulted in a novel integrated fast-hydropyrolysis/hydrodeoxygenation process that uses hot gases directly from a steam methane reformer or a coal gasifier.[13–14] Integrated processes using natural gas hold the promise to be synergistic, simple and to fill the gap until solar H_2 becomes economical.

Electricity Generation

Unlike in the era of coal power plants, chemical engineers are likely to have a greater role in the PV and solar thermal based electricity generation. Just three years ago the cost to manufacture a silicon based PV module was ~\$3 per peak Watt.[1] A recent announcement by First Solar drops the manufacturing cost of thin film CdTe based solar modules to 76 cents per peak Watt.[31] At this module cost, the electricity produced achieves grid parity in certain parts of the world. Indeed, such lower module costs were unthinkable just a few years ago, but do reflect the strong promise of thin film solar cells in the future.

Chemical engineering is poised to impact the emergence of thin-film PV based on semiconductor nanoparticles, organic polymers and dye-sensitized cells.[32–33] These thin film technologies require lower quantities of materials and can take advantage of atmospheric pressure processing steps amenable to chemical engineering analysis, to reduce cost. Processing steps employed in the production of thin film PV, such as solution based thin film coating, are commonly practiced by chemical engineers in various forms. However, to further the role of chemical engineers in PV, synthesis and production of semiconducting materials in tandem with the understanding of the effect of these steps on the resulting film properties such as morphology, grain boundaries, charge carrier densities, defect energy levels in the band gap, minority carrier lifetime, p-n interface characteristics, origins of any low-shunt resistance, etc., leading to the final device performance is required. It is due to such relationships between the material synthesis and the device performance that it has taken a few years from the synthesis of perfect stoichiometric copper indium gallium diselenide (CIGS) nanocrystals to the production of efficient solar cell devices from the nanocrystals.[34] Chemical engineers will be in a better position to contribute to the emerging PV field if they acquire a good working knowledge of the PV device physics and the quantum laws that govern nanoscale systems. A good starting point is to draw from the similarities of the governing principles of PV device physics with the core disciplines of chemical engineering. Basic concepts such as thermodynamics, reaction kinetics, diffusion, and transport can be applied directly to light absorption, electron-hole generation and recombination, and carrier transport in a PV device.

Current reports of crystalline CIGS nanoparticle synthesis in stirred tank reactors and the resulting solar cells from these particles are an example of the chemical engineering principles being used for solar cell devices.[34–36] Inks of compound semiconductor nanoparticles made from earth abundant elements Cu, Zn, Sn, Fe and S provide further exciting opportunities.[37–40]

Energy Storage

Since, on average, solar energy is available only 20–30% of a 24 h day, systems will have to be designed to store energy for the greater portion of the day or longer. A solar farm harnessing solar energy as heat or electricity will need to have nameplate capacity that will be three to five times that of the daily average requirement. Furthermore, it is very likely that in the future there will be a proportionately greater use of electricity due to some electrification of the transportation sector. Therefore, a grand challenge where chemical engineers can play an important role is in providing efficient cost-effective workable energy storage solutions for a solar energy driven sustainable world.

There will be a need to design energy storage at all levels of use. Heat and electricity storage at tens of kWh (1 kWh = 3.6 MJ) will be needed for household and PHEVs (Figure 2).

For this level of electricity storage, cost-effective, high-volumetric energy density batteries with long life will likely be needed. At the other end of the use spectrum, extremely large-size systems to store energy equivalent to the production from a small-size refinery (~100,000 barrels per day), or a reasonable size power plant will also be needed. A small size, 125 MW coal power plant produces 3 GWh of electricity daily. An equivalent solar power plant will require daily storage of ~2.4 GWh (= 8.6 million MJ) of electricity. When one accounts for the inefficiencies in storage and subsequent use, then this number will be even greater. For reference, the highest storage densities for batteries currently are ~0.1 kWh kg^{-1} of battery.[41] The design of novel efficient storage cycles for such large quantities of energy using chemical reactions, phase change materials, etc., is of great interest to chemical engineers.[6]

Concluding Remarks

Transition from fossil resources to a solar-energy-driven future provides an unprecedented opportunity for chemical engineers. Novel technologies and solutions will be needed to satisfy all the basic needs of daily human life — food, chemicals, heat, electricity and transportation. Here, we have discussed and presented some of the possible challenges and opportunities to satisfy chemicals, fuels and electricity needs. A need for a systems approach whereby solutions are sought to maximize energy efficiency of the overall system is presented. Such an approach is capable of revealing synergistic interdependencies between different secondary forms of energy, including liquid hydrocarbon fuels, and also with the production of chemicals.

We find that the mainstream chemical engineering curricula based on thermodynamics, transport, chemical kinetics, and reaction engineering, along with the relatively recent infusion of biomolecular engineering will have to prepare engineers for ample challenges and opportunities associated with the handling and conversion of low-energy density solid biomass to liquid fuels and carbon-based chemicals. Some of the opportunities presented to us include: design of energy-efficient and cost-effective augmented processes for the preservation of biomass carbon during the conversion process, discovery of new catalysts and processes for the refunctionalization and targeted hydrodeoxygenation of biomass derived molecules, construction of innovative small-scale mobile plants for liquid fuels and chemicals, processes for large-scale H_2 production from sunlight, and the use of solar heat and H_2 while dealing with the issue of intermittent availability of sunlight. Development of processes for noncarbon based chemicals will also provide new opportunities. Furthermore, chemical engineers ready to play in the emerging arena of electricity generation from sunlight will have to broaden their horizons by acquiring a good working knowledge of PV device physics. The solar energy future holds the promise to provide solutions for a grand challenge of our time, but poses many daunting technical problems whose solution provides important and exciting opportunities for chemical engineers.

In closing, while this perspective is written in the context of solar energy alone, most of the comments are valid even when secondary forms of energy such as heat and electricity are supplied from other sources such as nuclear, wind, geothermal, etc.

Acknowledgments

RA is thankful to Drs. Qijie Guo and Navneet R. Singh as their doctoral thesis research provided the basis for some of the thoughts expressed in this article. He is grateful to his colleagues Professors W. Nick Delgass, Hugh W. Hillhouse and Fabio H. Ribeiro for many useful discussions. Support from the Energy Center and DOE C3Bio EFRC at Purdue University is acknowledged.

Literature Cited

1. Lewis NS, Nocera DG. Powering the planet: Chemical challenges in solar energy utilization. *Proc Natl Acad Sci USA*. 2006;103(43):15729–15735.
2. EIA. *International Energy Outlook 2010*: Energy Information Adminstration, U.S. Dept of Energy Washington, DC 20585; 2010.
3. Agrawal R, Singh NR, Ribeiro FH, Delgass WN. Sustainable fuel for the transportation sector. *Proc Natl Acad Sci USA*. 2007;104(12):4828–4833.
4. Melchior T, Perkins C, Lichty P, Weimer AW, Steinfeld A. Solar-driven biochar gasification in a particle-flow reactor. *Chem Eng Process*. 2009;48(8):1279–1287.
5. Segal A, Epstein M. Comparative performances of 'tower-top' and 'tower-reflector' central solar receivers. *Sol Energy*. 1999;65(4):207–226.
6. NRC. Electricity from Renewable Resources: Status, Prospects, and Impediments. Washington, DC: National Academy Press; 2009.
7. Diver RB, Miller JE, Allendorf MD, Siegel NP, Hogan RE. Solar thermochemical water-splitting ferrite-cycle heat engines. *J Solar Energy Eng*. 2008;130(4):041001.
8. Turner JA. A realizable renewable energy future. *Science*. 1999;285(5428):687–689.
9. Zhu XG, Long SP, Ort DR. What is the maximum efficiency with which photosynthesis can convert solar energy into biomass? *Curr Opin Biotechnol*. 2008;19(2): 153–159.
10. Agrawal R, Singh NR. Solar energy to biofuels. *Ann Rev Chem Biomol Eng*. 2010;1(1):343–364.
11. EIA. *Manufacturing Energy Consumption Survey (MECS) Tables*. Energy Information Adminstration (EIA), U.S. Dept of Energy, Washington, DC. 20585; 2010.
12. NRC. Liquid Transportation Fuels from Coal and Biomass: Technological Status, Costs, and Environmental Impacts. Washington, DC: National Academies Press; 2009.
13. Singh NR, Delgass WN, Ribeiro FH, Agrawal R. Estimation of liquid fuel yields from biomass. *Environ Sci Technol*. 2010;44(13):5298–5305.
14. Agrawal R, Singh NR. Synergistic routes to liquid fuel for a petroleum deprived future *AIChE J*. 2009;55(7):1898–1905.
15. Hertwich EG, Zhang X. Concentrating-solar biomass gasification process for a 3rd generation biofuel. *Environ Sci Technol*. 2009;43(11):4207–4212.
16. Christensen CH, Rass-Hansen J, Marsden Charlotte C, Taarning E, Egeblad K. The renewable chemicals industry. *ChemSusChem*. 2008;1(4):283–289.

17. Lipinsky ES. Chemicals from biomass: Petrochemical substitution options. *Science*. 1981;212(4502):1465–1471.
18. Serrano-Ruiz JC, West RM, Dumesic JA. Catalytic conversion of renewable biomass resources to fuels and chemicals. *Ann Rev Chem Biomol Eng*. 2010;1(1):79–100.
19. Li H, Cann AF, Liao JC. Biofuels: Biomolecular engineering fundamentals and advances. *Ann Rev Chem Biomol Eng*. 2010;1(1):19–36.
20. Katzer JR, Ramage MP, Sapre AV. Petroleum refining: poised for profound changes. *Chem Eng Progr*. 2000;96(7):41.
21. Agrawal R, Offutt M, Ramage MP. Hydrogen economy - An opportunity for chemical engineers? *AIChE J*. 2005;51(6):1582–1589.
22. Cundiff JS, Grisso RD. Containerized handling to minimize hauling cost of herbaceous biomass. *Biomass Bioenerg*. 2008;32(4):308–313.
23. Agrawal R. Separations: Perspective of a process developer/designer. *AIChE J*. 2001;47(5):967–971.
24. Briens C, Berruti F, Ferrante L. A Mobile Pyrolyzer for the Conversion of Biomass into Bio-oil. Presented at: tcbiomass 2009: The International Conference on Thermochemical Conversion Science; 16-18 September, 2009; Chicago, IL.http://media.godashboard.com//gti/TCBiomass2009_Pyrolysis_CBriens.pdf (Accessed on 8th August, 2010).
25. Zeman FS, Keith DW. Carbon neutral hydrocarbons. *Philos Transact A Math Phys Eng Sci*. 2008;366(1882):3901–3918.
26. Fact & Figures of The Chemical Industry. *Chemical & Engineering News*. ACS. 2010;88:33–67.
27. Hodge B-MS, Huang S, Shukla A, Pekny JF, Reklaitis GV. The effects of vehicle-to-grid systems on wind power integration in california. In: Pierucci S, Ferraris GB, eds. *Computer Aided Chemical Engineering*. Elsevier; 2010;28: 1039–1044.
28. Greene N, Celik FE, Dale BE, Jackson M, Jayawardhana K, Jin H, Larson ED, Laser MS, Lynd LR, MacKenzie D, Mark J, McBride J, McLaughlin S, Saccardi D. Growing Energy: How Biofuels Can Help End America's Oil Dependence. New York: Natural Resources Defense Council; December 2004.
29. Agrawal R, Singh NR, Ribeiro FH, Delgass WN, Perkis DF, Tyner WE. Synergy in the hybrid thermochemical-biological processes for liquid fuel production. *Comput Chem Eng*. 2009;33(12):2012–2017.
30. Gassner M, Maréchal F. Methodology for the optimal thermo-economic, multi-objective design of thermochemical fuel production from biomass. *Comput Chem Eng*. 2009;33(3):769–781.
31. First solar, Inc. Announces Second Quarter 2010 Financial Results. http://investor.firstsolar.com/phoenix.zhtml?c=201491&p=irol-newsArticle&ID=1454084&highlight=. Accessed on 8th August, 2010.
32. Günes S, Neugebauer H, Sariciftci NS. Conjugated polymer-based organic solar cells. *Chem Rev*. 2007;107(4):1324–1338.
33. Grätzel M. Photovoltaic and photoelectrochemical conversion of solar energy. *Philos Transact A Math Phys Eng Sci*. 2007;365(1853):993–1005.
34. Guo Q, Kim SJ, Kar M, Shafarman WN, Birkmire RW, Stach EA, Agrawal R, Hillhouse HW. Development of $CuInSe_2$ nanocrystal and nanoring inks for low-cost solar cells. *Nano Lett*. 2008;8(9):2982–2987.
35. Panthani MG, Akhavan V, Goodfellow B, Schmidtke JP, Dunn L, Dodabalapur A, Barbara PF, Korgel BA. Synthesis of $CuInS_2$, $CuInSe_2$, and $Cu(In_xGa_{1-x})Se_2$ (CIGS) nanocrystal "Inks" for printable photovoltaics. *J Am Chem Soc*. 2008;130(49):16770–16777.
36. Guo Q, Ford GM, Hillhouse HW, Agrawal R. Sulfide nanocrystal inks for dense $Cu(In_{1-x}Ga_x)(S_{1-y}Se_y)_2$ absorber films and their photovoltaic performance. *Nano Lett*. 2009;9(8):3060–3065.
37. Guo Q, Hillhouse HW, Agrawal R. Synthesis of Cu_2ZnSnS_4 nanocrystal ink and its use for solar cells. *J Am. Chem Soc*. 2009;131(33):11672–11673.
38. Steinhagen C, Panthani MG, Akhavan V, Goodfellow B, Koo B, Korgel BA. Synthesis of Cu_2ZnSnS_4 nanocrystals for use in low-cost photovoltaics. *J Am Chem Soc*. 2009;131(35):12554–12555.
39. Wadia C, Wu Y, Gul S, Volkman SK, Guo J, Alivisatos AP. Surfactant-assisted hydrothermal synthesis of single phase pyrite FeS_2 nanocrystals. *Chem Mater*. 2009;21(13):2568–2570.
40. Wu Y, Wadia C, Ma W, Sadtler B, Alivisatos AP. Synthesis and photovoltaic application of copper(I) sulfide nanocrystals. *Nano Lett*. 2008;8(8):2551–2555.
41. Eberle DU, von Helmolt DR. Sustainable transportation based on electric vehicle concepts: a brief overview. *Energy Environ Sci*. 2010;3(6):689–699.