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Chemical Engineers Must Focus on Practical Solutions

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Introduction

Richard Smalley compiled a list of the top 10 global challenges.[1] Topping the list were energy, water and food. These are indeed daunting issues that chemical engineers must play a role in solving.

Chemical engineers are uniquely trained to (a) close energy and mass balances, (b) understand and apply scaling laws, (c) determine and mitigate rate limiting steps, and (d) perform financial analysis. These simple concepts are ingrained in the chemical engineering curriculum yet they are sadly lacking in much of the discussion of energy, water and food challenges that must be overcome.

Chemical engineering research is as intellectually challenging and creative as any engineering science, but what distinguishes our field is its ability to turn invention into innovation. In other words, the basic application of sound engineering principles enables economical manufacturing of materials that define a society's standard of living. The distinction between invention and innovation is significant. Ask lay people who invented the light bulb, the automobile, or the telephone and you will hear, Edison, Ford and Bell. However, none of these men invented these technologies. Edison was not the first to produce light from a filament; he engineered a way to make it live long enough to be practical. Ford did not invent the automobile; he applied engineering skill to make economical automobiles. Bell was not the first to transmit sound over a wire; he turned it into a practical device. We associate these men with these technologies because they were the innovators that found a way to make inventions practical, reliable and economical. They brought these ideas to commercial production, creating innovations that people wanted to buy and could afford.

Simply put, innovation is perfecting inventions to create value that people will pay for. Invention is certainly important, but innovation is exceptionally challenging since it is society, not the scientific community, that ultimately determines the importance of a new discovery. The detection of buckyballs was amazing and earned the Nobel Prize. To think that there was an entirely new form of carbon discovered relatively recently, and, to find that it was actually present in a surprising number of places in nature[2] is astounding. It is equally astounding to realize that buckyballs are actually not very good for anything. A beautiful, highly symmetric molecular form of carbon actually has limited practical use.

The application of transport phenomena, reactor design, separations and financial discipline has produced remarkable progress in the manufacturing of materials. Polyethylene (PE) was very much a specialty material when it was discovered, with unique properties that made it a wartime secret.[3,4] Today PE is manufactured in excess of 77 million tons and sells for \$2/kg.[5] As they did with PE, chemical engineers have reduced the cost and improved the quality of the majority of products we use today. They have moved beyond invention to driving innovation. So it is puzzling why a profession founded on innovation seems to occasionally forget its heritage. Chemical engineers must do a better job explaining the difference between the subset of discoveries that offer practical solutions from the set that are simply possible. The application of sound chemical engineering principles can aid society in prioritizing resources to be deployed to solve the challenges in food, water and energy. The world has a finite GDP and we must be exceptionally efficient so we do not waste it on ideas that require simultaneous miracles or violate thermodynamic principles.

Our desire to find a simple technological solution to the related problems of energy supply and environmental impact has made these areas ripe for hype. Many new discoveries are greeted with overexcitement and the hope that each will provide the means to supply the reliable, cheap and almost limitless energy we have come to anticipate. The hydrogen economy, cellulosic ethanol, and fuel cells are examples from the list of technologies that have promised much and have, sadly, delivered little. This Perspective will use energy as a theme for applying fundamental engineering principles

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to differentiate between possible and practical. The broad lack of understanding of thermodynamics, energy density, scale, and finance likely led to erroneous beliefs that using CO_2, or biofuels are near term and practical solutions. Energy transitions are difficult to make, even when the advantages are compelling and economically driven. Misguided attempts to move failed biofuels efforts into the production of biomaterials will also be covered. The constant theme is that just because something can be done does not mean that it will or should be done. Engineers need to be on the vanguard, providing practical solutions that will address future problems. We should not be wasting our resources on solutions that, while possible, will never be practical.

Society does not Understand Thermodynamics

> *"It is 500 times thinner than the best filter on the market today and a thousand times stronger. The energy that's required and the pressure that's required to filter salt is approximately 100 times less."*[6]*

There has been much recent discussion of the water-energy nexus. Water and energy are linked in many ways, but none more starkly than where fresh water resources are in short supply. The ocean can only supply the fresh water we require with the addition of energy. Minimizing the energy required to quench the demands of growing populations is an important effort.

We have been very successful at reducing the energy requirements for desalination, both thermally and through reverse osmosis.[7–9] Our ability to further reduce that energy is constrained.[10] We face the insurmountable hurdle of the minimum work required to overcome the entropy created when salt dissolves in water. Claims that graphene[6,11] or carbon nanotubes[12] have properties that make the water move rapidly through them have incorrectly been extrapolated to conclude that this can dramatically reduce the energy required for desalination. Desalination is simply not a filtration problem, it is a thermodynamic one. The speed of transport through the membrane is not the dominating effect.

Lockheed Martin made very recent and public claims concerning the ability of a graphene membrane to reduce the energy required for desalination of sea water by reverse osmosis by a factor of 100.[13] This is regrettable because it is so clearly wrong.

Entropy increases when salt is dissolved in water and the reversible heat absorbed during dissolution must be supplied to separate the system. The minimum work required to create fresh water from seawater is approximately 0.75 kWh per cubic meter of water purified.[14] Current state of the art reverse osmosis membranes operate around 1.6 kWh/m^3 [15] at practical levels of recovery, with a state of the art complete system at about 2.2 kWh/m^3.[16] The most common configuration is a wound membrane operated at 50% recovery. In this configuration, the minimum energy requirement for the membrane is approximately 1.1 kWh/m^3 [7] for a single module system. The irreversible losses in the system, including pumping and friction, account for the additional energy required in practical application. There simply is no factor of 100 improvement to be had.

The flow of water through a reverse osmosis membrane decreases as the salinity of the brine increases as water is pumped through the module. The membrane and the system pressure are constant, but the retarding force imposed by the second law increases with brine concentration. If this were the filtration problem posed by the Lockheed scientists, the flow would depend only on the kinetics of pure water movement through the membrane channels. It would be effectively constant down the channel and not drop precipitously as the salt concentration of the brine increases with recovery. This is not an isolated incident. Fundamental engineering is often neglected, as the hype for what is possible takes precedence over practical limitations.

We do not Understand Energy

> *"I will have to admit to you that, not being an expert, when a Ph.D. tells me that there is a difference between energy and power, those of us who are less educated... (think) it seems rather similar."*[17]

Energy, for the most part is transported by electrons or chemical bonds. Chemical engineers are skilled at manipulating chemical bonds, so it stands to reason that chemical engineering will be essential in addressing challenges in energy. Thermodynamics is a core competency in chemical engineering and you cannot talk about energy without also talking about thermodynamics. As was exhibited in the previous water example, the popular press and society generally do not understand thermodynamics. What is worse is that we do not have the same familiarity with energy as we do with volume or mass. Everyone knows what a gallon of milk looks like, or how much mass is in a pound of hamburger. However, we do not have the same experiential feel for a kilowatt-hour. Electricity flows invisibly and effortlessly from the wall socket. It is only through indirect observation, seeing the light that is produced or feeling the heat from the bulb, that we get a sense for what energy might be. Equating the energy from the wall socket with the energy contained in gasoline or the energy we feel when we are warmed by the sun eludes us. How many miles of driving would equal the energy used by a 60 W bulb for an hour? How many watt-hours of gasoline does a typical fill-up supply, and at what rate (power)? These are difficult questions for the lay person to answer or even form a good estimate. Human eyes are not calibrated to see energy and most of the time its flow is hidden from our view. A ton of wood has less than a third of the energy content of a ton of natural gas. Because we can see the wood and feel it when we lift it, it seems like a lot of energy. Natural gas arrives invisibly. Compounding this perception issue is the fact that few people understand efficiency; know how to close an energy balance, or appreciate the difference between primary energy and ultimate work performed. This unfamiliarity with energy makes us susceptible to confusing possible hype with practical application.

The general lack of understanding around energy has been documented in a recent article by Attari and coworkers.[18] The article reports the results of a survey to test the

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[*] *John Stetson, Lockheed Martin Senior Engineer speaking about graphene desalination membranes.*

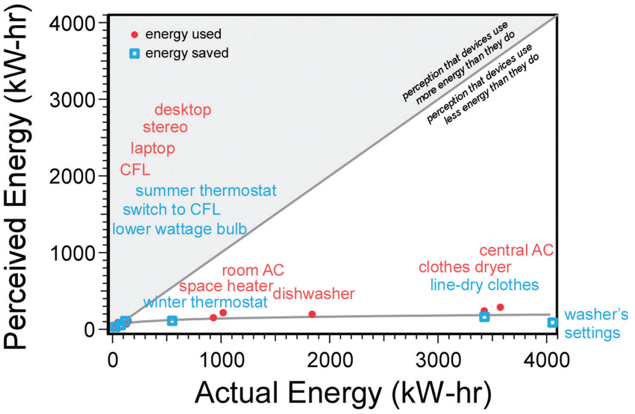

Figure 1. Results of the survey conducted by Attari and coworkers testing the perception of energy use and energy saved with a variety of technologies.

perception of the amount of energy devices consume and the perception of energy savings possible with technology changes. The devices ranged from low power compact fluorescent bulbs to big energy consumers like central air conditioning. The data from the survey are plotted in Figure 1 and show an alarming finding. The data fall not along the diagonal line indicating a correct perception of energy use, but, instead, fall on an almost horizontal line.

The almost horizontal line demonstrates society's perception that all electrical devices use about the same amount of energy. Our perception might be confused because the effort we expend in flipping a switch to turn on a light or an air conditioner feel equivalent. Our perception may be off because our eyes do not actually see the energy flow following the flip of the switch or the press of the button. Whatever the reason, we are poor judges of the energy we consume. A whole house air conditioner uses 100 times more energy than a light bulb, yet the survey clearly shows the perception is that it uses only about two times the energy. These misperceptions lead us to think we use less energy than we do and also to underestimate the difficulty in replacing our current energy sources.

As a result of our collective confusion about energy, we grossly underestimate the amount of energy that we personally use. Per capita energy consumption in the U.S. is over 250 kW-h per person per day.[19] This number accounts for the total energy in the economy. Less than half of that amount, only about 95 kW-h per day of primary energy use, is in our direct control.[20] That represents the amount that our houses and cars consume; the individual share of the residential and transportation use. Control of our thermostats, laundry settings, lighting choices and driving habits impact directly how much energy we use.

Energy Transitions

> *"The Stone Age did not end for the lack of stone, and the Oil Age will end long before the world runs out of oil"*[21]

An average American man consumes about 2,475 calories per day, and an average woman only about 1,833. Those calories can be turned into about 750 W-h of useful labor.[22] Our own ability to do work is, at best, only about 1% of the energy we consume from the modern energy infrastructure.

Our current addiction to fossil fuel is easily explained: human history has been an unrelenting march to reduce manual labor through the use of energy. Man began to use draft animals because the amount of energy a single man controls increases tenfold. [23,24] When men learned to use water power, the amount of energy an individual controlled increased 100 fold.[25] When we learned to command steam power, we increased the energy a single man could control by well over 1000 fold.[26,27] Steam power began with wood as the energy source. The transition to fossil fuels was ushered in because the forest simply could not supply the desired amounts of energy.[28,29] From that point on, we have been replacing low energy density fuels with those of ever-increasing energy density. Renewable power was replaced by fossil fuels. Horses were replaced by steam, and steam by gasoline. Boat sails were replaced by steam, steam by diesel and, in some cases, diesel by nuclear. The power, energy, convenience, and cost of these higher energy density fuels are such an advantage that moving back is as inconceivable as replacing our cars with horses. Some might argue that the cost advantage of fossil fuels is an artifact of failing to recognize the externalities such as CO_2 emissions. This is probably a valid concern, but society operates within a regulated and financial framework. Any assessment of what is practical must be performed within the current construct of regulations and cost attribution.

Figure 2 shows how biomass power has been supplanted in both relative and absolute terms as we have moved to higher and higher energy density fuels. Energy use was relatively constant as coal began to displace wood. When the American industrial revolution was really taking off, around 1900, per capita energy use also began to increase, doubling and ultimately tripling from levels supported by biomass energy. Society has moved from fuels of low energy density toward higher energy density fuels, and this is clearly shown in Figure 3. The early 1970s represents the peak per capita energy use in the U.S. Conservation drove a reduction in per capita energy consumption, although that trend has recently reversed. Currently, renewables such as wind, solar and

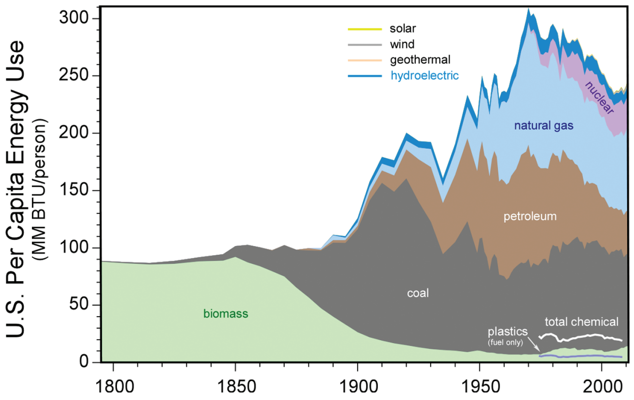

Figure 2. Energy consumption in the U.S. on a per capita basis.

Energy data from EIA annual energy review 2012 and 2009. Chemical data from DOE/EIA 2006 manufacturing energy consumption survey and ACC "updated energy slides incorporating 2008 data".

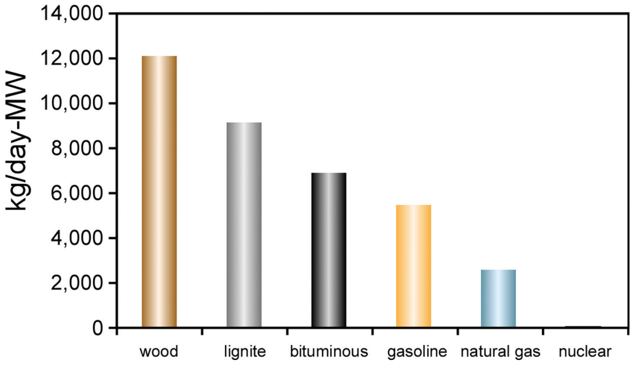

Figure 3. Plot of the mass of material required to supply a megawatt of power for a day, showing the progression from biomass to fossil and, ultimately, to nuclear power.

geothermal make up only a very small part of the U.S. energy production.

We have moved simultaneously to both higher energy density fuel sources and improved technology to take better advantage of those fuels. Figure 4 shows how the maximum efficiency of the devices we use to power our world has improved. From 1700 to today, the maximum achievable efficiency has improved from less than 6% to approximately 60%. Technologies have gotten very good at converting fuel to power, so good that we are approaching theoretical efficiency limits. We do not have another order of magnitude improvement to look forward to over the next three centuries. We are confronted with the reality that there is not an underutilized fuel that is better than what we are using today, and the devices we use to power our world are near their theoretical limits of efficiency. Understanding and explaining thermodynamic entitlement is a key area chemical engineers should champion, and are uniquely positioned to do so.

Our consumption of fossil fuels has, in large part, been responsible for the focus on sustainability. There are concerns that fossil fuels are finite and that we are rapidly exhausting them, as well as the effects on the environment that converting buried carbon to atmospheric carbon are causing. Weaning ourselves off of fossil carbon requires an alternative. Nuclear energy is far less attractive post-Fukushima. That leads us to either invent new sources of energy or to move back to less energy dense fuels, like coal and biomass. Concern over climate change pushed much of the discussion to renewable sources of energy. These include wind, solar and, of course, a return to biomass.

We have already touched on the relative inefficiencies of biological systems when compared with fossil-fueled systems. It is illustrative to put these efficiencies into economic terms. At \$1.06/L (\$4/gal), gasoline is over \$30 per GJ. Average residential electric rates equate to a cost of over \$33 per GJ.[30] Hard driven manual labor[22] produces about 90 W or an astonishing \$25,000 per GJ (\$23,600/million BTU) at the prevailing minimum wage.[31] Liquid fuels and electricity are a bargain compared with using human labor and fully explains our tendency to replace manual labor with other forms of energy.

Economics are paramount in any discussion on energy. Energy is controlled by the private sector in most of the world, but it is frequently regulated. Regulated or not, the private sector must make a profit. Energy is also a commodity. Society demands cheap and reliable energy. Shareholders demand a return on their investment. To maintain profitability, companies that supply energy have spent a century driving productivity. This has been achieved by efficiencies of scale and by utilizing high energy density fuels. Society has benefitted greatly from this efficiency. Energy expenditures as a share of gross domestic product (GDP) in the U.S. have been relatively flat since the mid-1980s, with energy consuming 6–9% of GDP.[32] Energy as a percent of inflation adjusted GDP has decreased from 19 MJ/dollar (18,000 BTU/dollar) in 1970 to less than 9.5 MJ/dollar (<9,000/dollar) in 2007.[33]

Energy transitions are slow. Figure 5 shows the percent of U.S. energy supplied by different primary energy sources over the last two centuries. In many technology substitutions the inferior technology is completely replaced by the superior one, as when diesel electric engines replaced steam locomotives. The superior technology then grows, reaching a maximum market penetration as it begins to be replaced by a better technology. This chart should push us to ask the question of "If we went away from biomass, why would we go back?" It should also be recognized that going back to a lower energy density fuel will add cost in a market built on decades of improving productivity. Investors will not give up money to a process or company that offers higher costs for the same product. Even when superior technology is developed it takes decades for adoption. This fact is well known in the chemical industry. For example, ethylene oxide was first produced commercially in 1917 in Germany, via the chlorohydrin process.[34] In 1937, Union Carbide developed silver-based catalysts that allowed the direct oxidation in air. In 1958, Shell introduced the oxygen-blown process, also using a silver catalyst. Today, the current state of the art is oxygen-fed industrial plants. In the mid 1950s, about half of the plants still employed the chlorohydrin route. The last chlorohydrin EO production in the US ended in the mid-

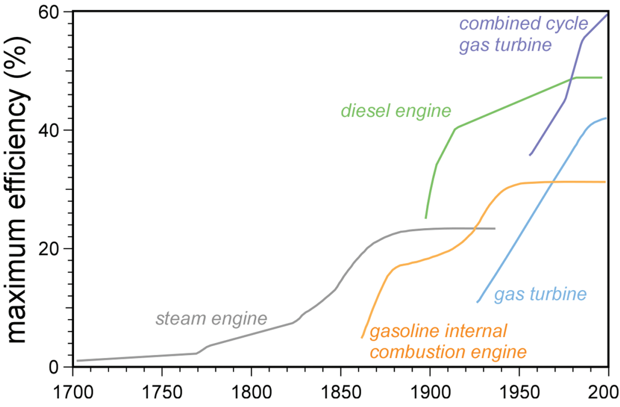

Figure 4. Maximum efficiency of prime movers from 1700–2000.

Adapted from Vaclav Smil, "Energy Transitions" (Praeger, 2010).

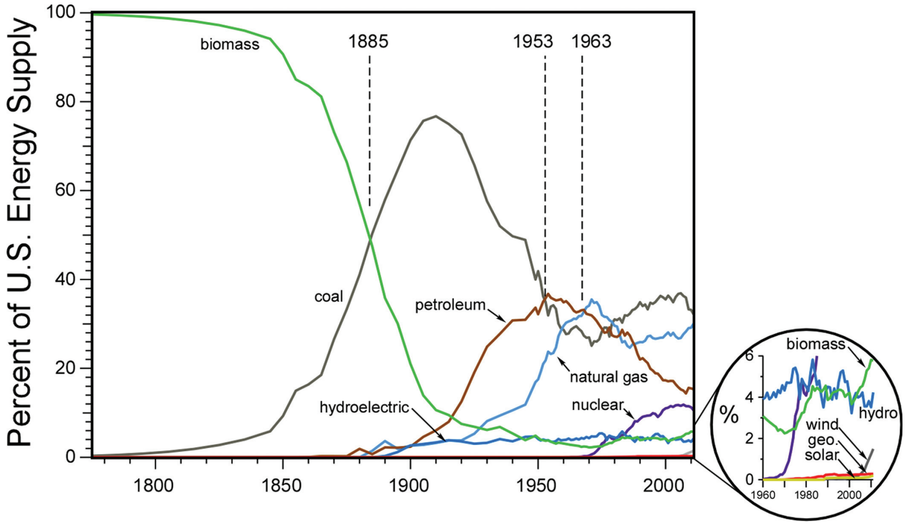

Figure 5. Percent of the U.S. primary energy use from different sources from 1785 to 2010.

Data from EIA Annual Energy Review 2011 and 2009.

1970s.[35] Despite the superior cost and environmental footprint of the oxygen-blown silver-based catalyst technology, it took 40 years to displace the original chlorohydrin process.

Biofuels and the Grand Challenge

> *"There is fuel in every bit of vegetable matter that can be fermented. There's enough alcohol in one year's yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a hundred years."*[36]

The advantages of liquid fuels make them the top choice for transportation fuels. Hydrocarbon liquids are energy dense, can provide high power, are easy to transport and store, and there exists an infrastructure that supports their use. Henry Ford is one of many to have been captivated by the thought of growing transportation fuels. It turns out that Ford was a bit off on his math and the availability of ethanol could not supply the demand he predicted. Petroleum-derived fuels filled the niche for liquid fuels and now are used to power transportation world-wide. Supply disruptions and price volatility inevitably rekindle bucolic thoughts of growing fuel. More recently, concerns about sustainability have caused renewed interest in biofuels. The U.S. Dept. of Energy has maintained a biofuels program founded on four principles:

- to reduce U.S. petroleum use
- to supply energy from indigenous sources, thereby improving energy security
- to create jobs
- to improve the environment.

These are truly grand challenges given the scale at which fossil fuels are consumed.

Fundamental engineering was neglected as we started down the biofuels path. First-generation, starch-based ethanol production ignored the energy return.[37] Energy return on investment is a key parameter when talking about fuels, but is really nothing more than an energy and mass balance, the forte of chemical engineering. Putting more energy into the creation of a fuel than you get out does not make sense. Some may argue that, as in the case of electricity, more energy goes into the boilers at the power plant than gets delivered, but in reality, the energy is upgraded in production of electricity. Coal and other fuels go in and high-value electricity comes out. In the case of biofuels, especially starch-based biofuels, high-value energy in the form of natural gas, used to make fertilizer and to provide process energy, and petroleum, used to power tractors and transportation, go in and ethanol comes out. Ethanol is a partially oxidized molecule and is an inferior fuel to the natural gas, diesel and gasoline used in its production. Energy return on investment is a key indicator in energy discussions. More energy has to come out of the energy system than is expended in the collection and conversion or the energy ROI will be poor. A system cannot be sustained if less energy comes out than is put in. Studies have shown that for a viable energy system, the energy return must exceed three, with some arguing up to eight.[39] Infrastructure for the system cannot be sustained with too low an energy ROI.

Second-generation biofuels were to be based not on plant sugars and starch, but on lignocellulosic components. Cellulosic ethanol came to the forefront as an improvement over corn-based ethanol. It would be made from waste or purpose-grown energy crops far superior to corn. It was stated to have much better energy return. Use of cellulosic ethanol was written into law in the reformulated fuel standard (RFS).

In the fall of 2012, debate about the RFS raged because cellulosic ethanol simply did not exist to meet the RFS mandates. Technology certainly existed for converting cellulosic materials to ethanol. Proponents of cellulosic fuels also ignored some very fundamental engineering principles as they held out cellulosics as the magic bullet. For any fuel to succeed, there must be sufficient feedstocks to manufacture a meaningful quantity and that feedstock has to be priced

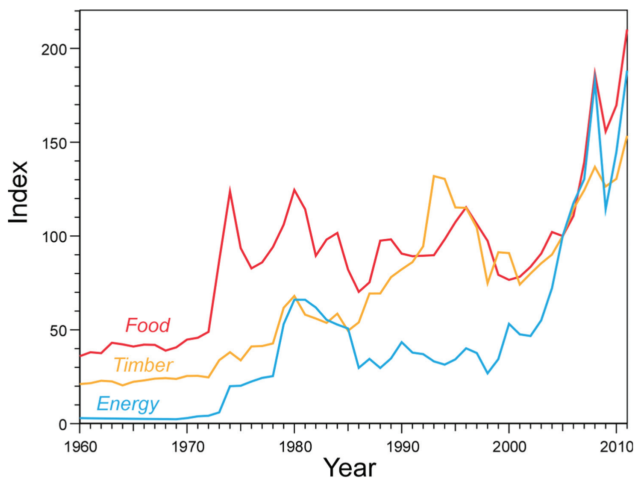

Figure 6. Plots of the World Bank indices for energy, raw timber, and food for the last 50 years showing that fossil fuel and agricultural commodities are correlated. 2005 = 100 on all plots.

reasonably compared to the value of the fuel produced. The capital efficiency of the process has to create a return on the investment, and you have to have a technology that has reasonably good operability. These tenants are the same basis for the design of a chemical plant. In fact, a liquid fuel is a mixture of chemicals. There are many technology variations that allow the conversion of lignocellulosic biomass to ethanol. This is, after all, a conversion technology that was already known in Ford's day. It is surely possible to convert lignocellulosic biomass to ethanol. It is just not practical.

The biggest reason for this impracticality is the nature of the biomass itself. Every chemical engineer knows you do not want dilute/impure feed streams, nor do you want dilute product streams. Biomass conversion has both. It tends to be low density and low energy density. Costs add-up quickly for transporting fluffy, wet, low energy density feedstocks, and the area capable of supplying cost-effective material is limited. This ultimately limits the maximum scale of any facility fed by biomass. The current energy infrastructure has no such limitation. Refineries and petrochemical complexes can continue to grow as markets grow due to the ease of transporting fossil resources. Goals of replacing significant amounts of fuel have continually been scaled back based on the feedstock availability.[38] The price of these limited supplies is also a question. Farmers ultimately are confined by the land they have and the hours in their day. They will not elect to grow crops that provide a lower return than other options.[39] This pushes the price required to pay for biomass over $100/ton for sustainable supply, well above the values quoted by cellulosic ethanol proponents. At these prices, these materials are competitive with solid fossil fuels. Chemical transformation to liquid fuels requires energy input. In the case of corn ethanol, these inputs are most commonly from fossil sources. Conversion of biomass using only a portion of the biomass resource as energy makes the feedstock cost prohibitive.

There is the commonly stated belief that biomass cost is independent of fossil fuel cost. This is used to justify the current high costs to produce biofeedstocks by making the assumption that oil will continue to increase in price, eventually making bioderived products cost competitive. The data show that there is high correlation between energy cost and agricultural commodities. World Bank indices for average energy cost, raw timber and food,[40] are plotted in Figure 6. These show what should be relatively obvious: the dominant role that fossil energy plays in the economy means that it directly impacts the costs associated with agriculture sufficient enough to be a dominant driver of commodity costs.

British Petroleum (BP) recently announced that it is stopping development of a $300 million project that was scheduled to produce 136 million L of cellulosic ethanol.[41] The capital charge alone makes the product uneconomical. A high-capital cost with a limited raw material advantage does not make for a profitable, practical endeavor.

The Importance of Scale

> *"The business model involves packaging the biomass fractionators with a chemical procession section into modular shipping containers, each with annual capacity to produce up to 2 million gallons of fuels. The company has ambitious plans to install several mass production plants around the world and to 'provide a significant amount of the world's liquid fuel by 2020'."*[42]

It is now surprisingly common to hear arguments that biofuels and biomaterials manufacturing plants can be made at small scale and remain competitive with larger, conventional chemical and fuel production facilities. All available data suggest that industrial processing plants are moving to larger and larger scales.[43–45] Yet, the inevitability of the economies of scale is commonly disregarded when biofuels are discussed. It is well established that production costs drop as market size grows.[46,47] The underlying motivation in the biofuels and biomaterials world is that feedstock's supply is limited by simple physics. The low density of biomass limits the area that can cost-effectively supply a production facility. The maximum scale imposed by transportation led people to ask how *it might* be made to work. The solution was that mass production could lead to cost reductions and the *n*th plant was born.

Efficiencies do come from mass production, as Henry Ford and others clearly demonstrated. The logic somewhat follows that labor for the simultaneous production of three things approximately equals that for two things built sequentially. Efficiency is gained through experience. This is actually called an experience curve and it is almost the sole hope of distributed manufacturing. Applied to bio-based materials, costs will drop as more plants are made such that the *n*th plant is economical, where *n* is a relatively large number. Mass production and learning will have triumphed over scale.

There are certainly examples of objects and small machines where this has proven to be true. Photocopiers would not be in every office if it were not. The formerly ubiquitous in-store photo laboratory would also not have had its day either. It is worthwhile to remember that even in the height of the in-store photo processing machine, it was

Figure 7. A mining truck shown next to a conventional pickup truck to reinforce that scale always triumphs over mass production in the process industries.

always cheaper to send the film from the store and wait a little longer. Economies of scale still triumphed over mass production. What is missing are examples from processing industries where smaller wins. Even in biofuels, careful analysis has shown that the impact of increasing scale is the dominant reason for costs to drop.[48] Perhaps the most memorable example is shown in Figure 7, a picture of a pickup truck next to a mining truck. Millions of trucks are made in North America alone, tens of millions worldwide. When it comes to moving and containing mass in an open pit mine, mine operators do not buy a bunch of little trucks, they purchase special, very large mining trucks. The inescapable reality is that scale always wins. Making a tank or a distillation column or a truck even just infinitesimally bigger still improves the capital efficiency. Every design class teaches the 6/10th scaling law which quantifies that cost increases slower than size. Replicating many smaller plants has not been how the chemical or refinery industry has driven productivity and lower cost. These are lessons chemical engineers must share.

Algae Misses the Mark

"8,571,428 gallons of algae oil per acre."[49]

We are now moving on to third-generation biofuels. Rather than tempering expectations based on the underperformance of the first two generations, the promises being made are even more grandiose. As cellulosic fuels fade, algal biofuels are being hyped as the next big thing. There are certainly reasons that algae are attractive. Algae can grow rapidly and they directly produce algal oils. Unlike terrestrial crops that can be water limited, algae grow in water. Rapidly growing algae can be harvested for the oil they contain, or simply as a source of lignin free biomass for subsequent processing. Algae do not produce lignin, potentially making them easier to convert to fuels through either biochemical or thermochemical means.

Algae have been an area where hype runs rampant. The beginning quote in this section should immediately cause concern because it significantly exceeds the amount of energy supplied by the sun. Conservation of energy is not merely a suggestion, it is a rule. Creating more energy through photosynthesis than the sun provides is impossible.

Algae have actually been grown domestically for centuries. A recent report casts doubt on whether the promise of algae can be realized in a sustainable way.[50] The report looked only at the sustainability issues and did not directly address issues of economics. The U.S. Dept. of Energy had a large program on algae that outlined many of the economic challenges.[51] Many of the challenges outlined still await a solution.

Many options exist for exploitation of cyanobacteria, microalgae and macroalgae for the production of fuels. Most of the effort has been directed at microalgal species that store lipids when deprived of appropriate nutrients for growth. Lipids buildup in the cell, and the algae can be collected, ruptured, and the oil recovered. The algal lipids can be processed in several ways to provide fuels, either as esterified material or as drop-in hydrocarbon replacements.

Several factors loom, including availability of water, availability of flat land suitable for cultivation, ability to supplement CO_2 to the algal culture, nutrient requirements and the energy return on energy invested. The most commonly described method for production is an open raceway pond. It is widely considered that closed structures will be cost prohibitive. In the open pond configuration, the algal culture is pumped around the raceway to keep the algae suspended. This also controls nutrients and facilitates harvesting. The pond is open to the atmosphere allowing evaporation. Evaporation and photosynthesis both remove water from the system. The accumulated salts must be controlled either by freshwater addition or by purging. Either method raises concern in a world where water is becoming a scarcer commodity. While it is clearly possible to successfully manage limited cultivation, expanding this cultivation to the scale of significance to the nation is not practical with current performance. This is directly analogous to byproduct buildup in traditional chemical processes with recycle. Failure to address this issue has been the down fall of many processes.[52]

The cultivation, harvest and processing of the algae to free the oils are energy intensive. Currently reported energy returns on energy invested (EROI) are poor. Many reports show EROIs of less than one. Getting less energy out in the algal fuel than was used to power the process is clearly unsustainable. There are few absolute thermodynamic limits present in the cultivation, harvest and collection of microalgae. It is conceivable that, with the power of synthetic biology, algae can become better photosynthesizers, that they could be triggered to spontaneously flock to make separation easier, that they could be triggered to spontaneously release their lipid cargos. Any of these could make a big difference in the energy return. There is no clear indication that any are even possible, much less practical. Companies are building demonstration units today with technologies that may well work to grow algae, but will likely not be deployable in a practical way to provide meaningful amounts of fuel.

Limitations imposed by fundamental chemical and physical laws ultimately constrain the yield of fuel. Mass and energy balances must be preserved. Energy coming in from

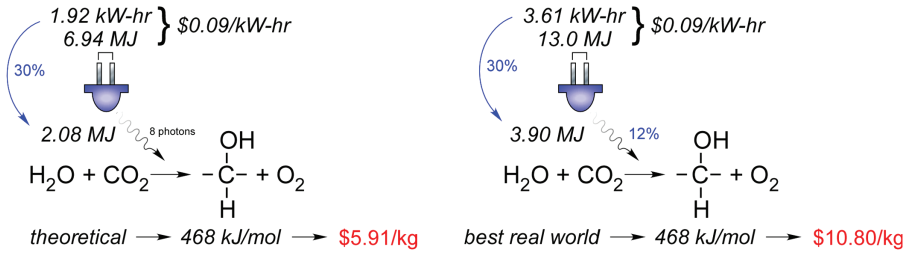

Figure 8. Comparison of best photosynthetic efficiency for production of fixed carbon, showing both theoretical for eight photons and for real world at 12% for absorption at PAR maxima.

Both show that the cost for electricity makes the cost of the end product prohibitive for most fuel and chemical uses. Input energies are per mole of fixed carbon.

the sun ultimately sets the firm upper bound on the productivity of any photosynthetic system just as the heat duty of a reboiler sets a limit on how much a distillation column can produce. The amount of light hitting the earth and the efficiency of photosynthesis are both imposed limits. Many business plans do not benefit from the insights of chemical engineers and, as a result, frequently ignore those limits. BARD Holdings is an interesting case to review and is the source of the high yield quote at the start of this section. Heralded as a top *Algaepreneur* in 2009 by the National Algae Association.[53] BARD claimed to have photobioreactor technology that would make high productivities possible. The claims of over a million gallons per acre were met with some skepticism, and rightly so. The quoted claim of 8,571,428 gallons per acre translates to over 8,000 Watts per square meter.[†] This is not only greater than the approximately 250 W/m^2 that fall on most of the continental U.S.[54] but also exceeds the solar constant[55] of approximately 1.4 kW/m^2. Units of productivity per area really only make sense for solar illumination. In response to the skeptics, reports from BARD indicated that they were not limited by sunlight, but were going to grow algae under artificial lights.[56]

Discussion of production of fuel under artificial lighting should raise concern from any engineer who is familiar with an energy balance. Fuel production requires that we be conscious of the energy return. It is certainly true that fuel upgrading can be energy intensive. As an example, gas-to-liquids (GTL) processes consume approximately 1.8 MJ of natural gas per MJ of liquid fuel created.[57,58] Taking a lower value gaseous fuel and turning it into a higher value liquid fuel might makes sense, but only when the market will compensate for the loss of enthalpy. The fact that the liquid fuel is more easily transported and has more utility could justify this if there was no less expensive alternative way to make the liquid fuel. The lack of significant GTL commercial facilities demonstrate there are few markets where there are not better alternatives.

We are in a period of rapid improvement in the efficiency of lighting. New LED technologies can produce light at power efficiencies greater than ever before. Potentially as a result of this rapid change, LED lighting for algae propagation comes up with amazing regularity. Solarix[59] continues to tout the benefits of algal cultivation for fuels production with special underwater LED lights. While it is clearly possible to grow algae illuminated by LEDs, it will never be practical for fuel. It is impractical for several reasons. On a pure energy basis, electricity is very valuable energy. Fossil fuels are converted to electricity because electricity commands price that justifies not only the conversion, but also a massive investment in capital. Electricity is far more useful, and, therefore, more valuable, than coal, natural gas, and even gasoline. Converting electricity back to fuels, even at 100% efficiency defies economics.

100% efficient energy conversions are not possible. LEDs are about 30% efficient at converting the energy supplied to light.[60] Algae are at best 12% efficient at converting PAR to biomass.[61] That still leaves an efficiency of only about 3% for electricity to algal biomass. Harvest and conversion losses only serve to further erode this value. It simply is impractical to make fuels from electricity because the energy losses during the conversion are simply too large. Figure 8 shows the approximate energy flow from electricity to fixed carbon, both theoretical and best every observed. Theoretical entitlement for just the energy cost to transform LED light to fixed carbon, ignoring growth, nutrient, separation cost, and depreciation is approximately $5.90/kg or $380/GJ ($400/MM BTU). This is approximately 100X current natural gas prices and over 10X current prices for liquid fuels[‡] just for the fixed carbon. Any claim that a high-volume chemical or fuel will be produced from electricity should be dismissed based on a simple energy balance and rudimentary financial analysis.

Photons as Reagents

> *"Someday, he'd love to see this work*[§] *used to make isobutyl alcohol, a commodity chemical and promising fuel, from just an alkene and water."*[62]

Photosynthesis is not the only light-driven reaction. Recent work[63] has shown that the light from blue LEDs can, with appropriate catalysts, drive the anti-Markovnikov addition of water to an olefin. A number of substrates are investigated in the report and none are simple olefins. This is an interesting result and gives synthetic chemists another tool to construct complicated structures.

[†] *Assumes 40 MJ/kg (17.2 BTU/lb) and 0.89 kg/L (7.4 lb/gal).*

[‡] *Assumes natural gas price at $3.79/GJ ($4/MM BTU) and gasoline at $1.06/L ($4/gal), consistent with pricing in the spring of 2013.*

[§] *Quote attributed to David A. Nicewicz, upon discovery of new catalysts for the light-driven, anti- Markovnikov addition of water to an olefin.*

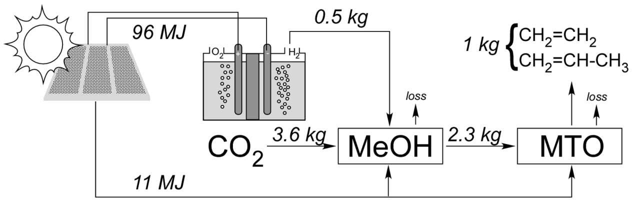

Figure 9. Hypothetical process for conversion of clean electricity and CO_2 to prime olefins.

Mass and energy are approximate values required per kilogram of olefin produced.

The comment about extension to commodity chemicals is clearly an extrapolation and one that raises hope of a practical means of manufacture of a commodity chemical using LED lights. This is not likely to be practical simply due to the cost of photons from a bulb. Isobutyl alcohol has a market value in the range of \$0.26/mol.¶ The blue photons used in this work have an energy of 266 kJ/mol. As in the previous section, LED efficiency of 30% means that for each mole of 450 nm photons, 0.25 kWh of electrical energy is required. Photons cost \$0.020/mol at a power cost of \$0.09/kWh. Forgetting for a moment about the isobutylene that is required, the electricity cost alone dictates that no more than 11 photons per molecule of product can be consumed before the electricity alone costs more than isobutyl alcohol is worth. Acridine dyes, used in this work as a photocatalyst, have been studied previously,[64] and absorption is a low-probability event, requiring thousands of photons per excitation. This is consistent with the 96 h illumination time used in these studies.

Simply stated, extrapolation of these results to the production of commodity materials is an unrealistic stretch. The cost of the electricity to create the photons required for the reaction alone is prohibitive.

Carbon Dioxide Utilization

> *"If renewable electricity becomes so efficient that it is free, can you make chemicals using CO_2 and unlimited, free electricity?"***

Concern over greenhouse gases leads many to propose that carbon dioxide utilization must be considered, and who better to consider it than a chemical company. Carbon dioxide is a product of fossil fuel combustion and the thought that it can be recycled back into fuel has captured the imagination of many. It is yet another area where what is possible is confused with what is practical, and an area sorely in need of chemical engineering scrutiny.

Chemicals can clearly be made from carbon dioxide, it simply requires energy. Ethylene and propylene form the foundation of the modern chemical industry. These materials can be made using the following scheme

$$
\begin{array}{lr}
2\,CO_2 + 6\,H_2 \rightarrow 2\,CH_3OH + 2\,H_2O & (1) \\
\underline{\quad 2\,CH_3OH \rightarrow CH_2{=}CH_2 + 2\,H_2O} & (2) \\
2\,CO_2 + 6\,H_2 \rightarrow CH_2{=}CH_2 + 4\,H_2O &
\end{array}
$$

Hydrogen can be supplied by electrolysis using carbon-free electricity. Reaction (2) is an idealized version of the methanol-to-olefin process. It makes a mixture of olefins, dominated by ethylene and propylene rather than the pure ethylene shown. With clean and unlimited electricity, it is possible to make ethylene from CO_2. While possible, it is not practical.

The process in Figure 9 is purely hypothetical, and is based on reasonable assumptions about losses in both methanol synthesis and subsequent conversion of methanol to olefins. At \$0.09/kWh, the 96 MJ of electricity required per kg of olefin is equal to \$2.41/kg (\$1.09/lb) in power cost alone. This is almost 3X current Gulf Coast production cost for ethane-only cracking.[65] Costs for raw materials alone swell to \$2.90/kg of olefin (\$1.32/lb) when other power requirements and CO_2 at \$60/metric ton are included.

Comparison to an ethane-only steam cracker shows that olefin production from electrolytic hydrogen is very energy inefficient. The ethane-only cracker produces slightly less than one ton of CO_2 per ton of ethylene produced,[66] meaning that for every four carbons that enter the cracker, slightly more than three end up in the product. Approximately 62 MJ of hydrocarbon are used in the production of a kilogram of ethylene, but the majority of that energy remains in the end product. Only about 10.6 MJ of hydrocarbon energy is supplied to make a kilogram of ethylene. Approximately nine times more energy is consumed to make the same amount of prime olefin product using clean energy. As pointed out earlier, electricity is actually the most expensive energy that most of us buy. On an energy basis, it is more expensive than natural gas, oil and gasoline.[67] Conversion of fossil energy to electricity faces thermodynamic limitations that prevent it from being 100% efficient and transmission also suffers losses. There is simply no way that electricity can be equal to, or below the cost of, the materials that are used in its production.

The capital inefficiency is also daunting. The differences in a conventional methanol plant and a hypothetical CO_2-based system can be estimated by assuming that the methanol reactor reaches equilibrium. This will be the best performance possible for the equilibrium limited reactions. The methanol synthesis reactions for both CO and CO_2 are exothermic.[68] Both reactions are favored by increasing pressure and lower temperature. The reaction of CO_2 to methanol is endoergic at room temperature.[69] Significant conversion can only occur at elevated pressure and the equilibrium conversion increases as temperature decreases. The modeling[70] done to create Figure 10 assumes equal temperature for both reactions, chosen for conventional methanol synthesis to afford a reasonable rate and to preserve catalyst activity.[71] Modeling these equilibrium-limited reactions gives directional feel for how a methanol synthesis from CO_2 would likely compare with a conventional plant. Hydrogen will be supplied from electrolysis of water assuming 4.8 kWh/Nm^3.[72] The electrical requirement for this use and for additional energy over and above what the conventional process requires can be determined. Conversion when using CO_2 rather than CO will be inescapably lower due to the equilibrium limitations. This will be manifested in a larger recycle of unreacted gases to the reactor. The magnitude of this change can similarly be estimated.

¶ *IHS Chem data for 2011 average price in the United States.*

** *Question posed by unidentified person at the 2013 American Association for the Advancement of Science Sustainable Chemical Manufacturing in a Resource-Limited World Symposium, 16 February 2013*

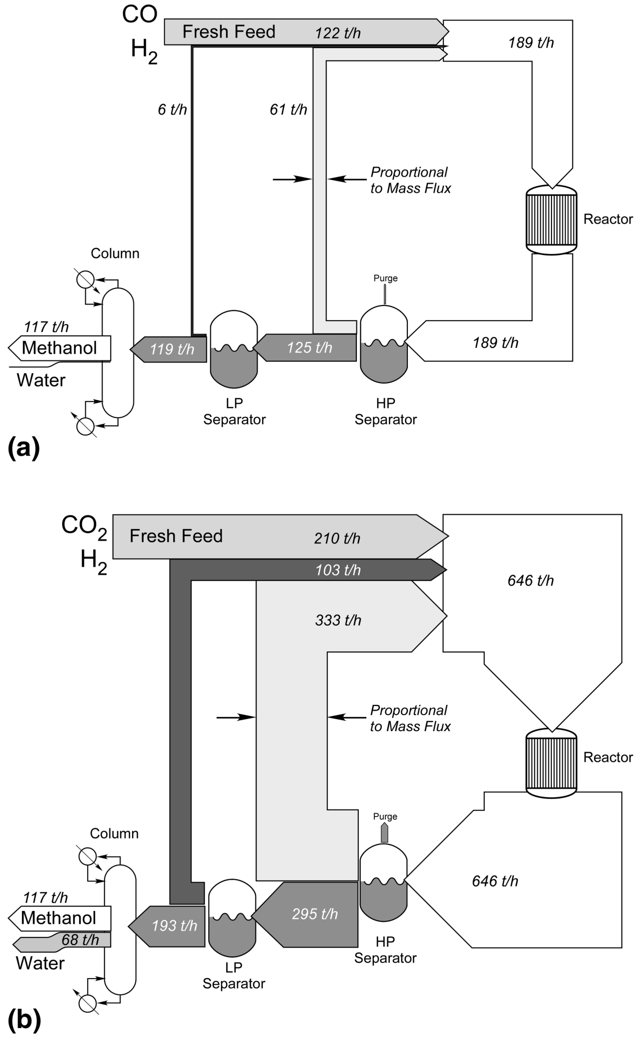

Figure 10. Simplified diagram showing the mass flows through a conventional and CO_2-based system assuming equilibrium conversion at constant reactor temperature.

This is a value destroying proposition. The electricity is down-graded in producing methanol on a cash cost basis. Capital has not been considered in this analysis except to point out that the capital of the carbon dioxide-based plant will have to be approximately three times the cost of the methanol capital. Add to that the clean electricity capital, the electrolyzer capital and the MTO capital required to make chemicals and there is simply no way that this is a practical solution for chemical production.

Biofuels Become Biochemicals

> *"A lot of people believe that global warming is a problem, and making that choice is something they can do about it"*[††]

Chemicals have more value to society than fuels so they sell at a premium to their fuel value. Polyethylene sells for around $2/kg. On an energy basis that equates to $42/GJ, nearly twice gasoline price on an energy basis. Given the challenging economics in energy, many companies in the biofuels area have elected to pivot. Instead of being fuels companies, they are now going to be biochemical and biomaterials companies. There are several problems with this strategy. The chemical industry transitioned to fossil fuels for the same reason the energy sector did: higher energy density, cheaper, more easily transported feedstock, and lower capital cost for conversion. While chemicals do sell above their fuel value, there remains extensive competitive pressure. Chemicals can no more tolerate a higher production cost than fuels. Second, the addressable market is much smaller for chemicals. Chemical companies, while big operations, on a mass basis are generally 100 to 1000 times smaller than fuels companies.[‡‡] Per capita energy consumption in the U.S. accounts for almost 10,000 kg of coal, petroleum and natural gas. Per capita consumption of polyethylene is about 77 kg,[73] and polyester packaging is around 7.7 kg.[74] Clearly minimizing waste should be a priority, as it has always been in the process industries. A singular focus on polymers, however, simply cannot substitute for a meaningful reduction in fossil energy use.

The migration away from biofuels to biochemical and biomaterials is overdue for some scrutiny. Biofuels programs set out to reduce petroleum use, improve energy security, create jobs and improve the environment. Use of biofuels as a significant component of the global energy mix has failed to materialize. Switching focus to smaller scale markets for polymers and chemicals simply cannot address the challenges biofuels attempted to solve. The scale of the markets for polymers is so much smaller and, therefore, the scale of the impact pales by comparison to meaningfully impacting fuels and energy use. The U.S. chemical industry has returned to optimism based on shale gas, which has truly revitalized the fortunes of the U.S. chemical industry. The chemical industry in the U.S. is not a big petroleum user and it already uses indigenous, albeit largely not biological, feedstocks. The industry creates jobs in the U.S. and is a good steward of the carbon we purchase, and those carbons are from North American and are not petroleum-based. The move to lighter, natural gas liquid feeds makes our processing even more energy and carbon efficient.

Biochemicals and biomaterials certainly have their place in the market, but it is unclear that the benefit is significant relative to our other uses of fossil energy. It is certainly possible to make biochemicals and biomaterials. They are not a practical way to offset our use of fossil energy.

[††] *William Armiger, President of BioChemInsights speaking about PET soft drink bottles with bio-based content, quoted in Jagger A. SOCMA: Green technologies almost ready to go, ICIS Chemical Business, September 27, 2012.*

[‡‡] *The EPA reports that there are 13,500 chemical production facilities operating in the U.S. on www.epa.gov/sectors/sectorinfo/sectorprofiles/chemical.html, accessed on 8 June 2013. The EIA reports there are 134 operating refineries in the U.S. on from the EIA for 2012 reported on www.eia.gov/dnav/pet/pet_pnp_cap1_dcu_nus_a.htm, accessed on 8 June 2013. Total chemical production reported by the American Chemistry Council Business of Chemistry (Annual Data) from https://memberexchange.americanchemistry.com/economics/ accessed on December 10, 2012. Data for 2011, as measured by the sum of ethylene, propylene, benzene and butadiene production is 46 million metric tons per year. EIA data for 2011 in EIA. Annual Energy Review 2011. September 27, 2012, DOE/EIA-0384(2011) indicate us total petroleum use at 946 millon metric tons per year. Refineries process 20 times more material in 100 times fewer facilities, meaning that the average scale of the operations differ between by between 2 and 3 orders of magnitude.*

Chemistry and Materials Science Applied Correctly

> *"Volkswagen's 230-mpg gasoline equivalent XL1 concept car—a carbon-fiber, two-seat plug-in hybrid. Its 0.8-liter 48 hp diesel engine is hybridized with a 27 hp electric motor, and its drag coefficient is an industry-leading 0.186. The car has a top speed of 99 mph and 0–62 mph time of 11.9 s, weighs just 1,752 pounds...."*[75]

Chemistry, chemical engineering and material science are exciting fields today because they are the fields where real solutions will come from. Hyper-efficient cars are only possible due to advances made possible by chemists, material scientists and engineers. Focusing on efficiency in buildings and transportation can have a significant impact, an impact of the scale that early biofuels programs somewhat foolishly pursued. Foley discussed this in a previous Perspective.[76]

This should be a time of great anticipation for the chemical process industries. The materials that we have developed and are currently developing are critical to maximizing energy efficiency. Better batteries to aid in the electrification of transportation can significantly reduce fuel use. Lightweight composites will further improve the efficiency of transportation. LED lighting will reduce energy use in residential and commercial buildings. Better insulation continues to save energy on heating and cooling. Better packaging reduces food wastes, saving a surprising amount of energy. Improved solar photovoltaic cells and improvements in packaging that further reduce the cost of ownership can make idle rooftops power generators.

These are but a few of the examples of the way that good sound engineering can make significant reductions in the 10,000 or so kilograms of fossil fuels the average American uses. With technologies that are readily available today, 50% reduction is certainly possible. Society is incorrectly fixated on reducing the hundred or so kilograms of plastics we each use that come from fossil sources, while ignoring the much more significant energy use and the much, much larger climate change impact it can have.

Conclusion

There are probably people who disagree with the aforementioned conclusions. Unlike theology or philosophy where it might be difficult to use simple reasoning in making a choice between two opposing views, chemical engineering gives society the tools to quantitatively evaluate alternatives. Comprehensive energy balances, thermodynamics, mass balances, and financial analysis will produce one answer. There may be debate about assumptions around feedstock cost and availability, conversion efficiency, etc., but there is an abundance of data to validate assumptions. Sound application of engineering does provide answers.

We do face global challenges and solutions to those global challenges must be implemented in as environmentally sound and resource-efficient way as possible. We as scientists and engineers have to be part of the discussion and have to be part of the solution. There are troubling trends, some even presented in this journal. Work is done under the banner of sustainability showing that we can use renewable feedstocks without thought to whether practical benefits truly result. Researchers get so caught up in proving something is possible that they forget to ask whether it will be practical. When these advances are reported, society at large does not have the tools to tell the difference. Clearly, in order to be practically implemented, a technology must be possible. Only a small subset of those technologies that are possible will find practical application. As engineers, we are actually the best judges of what is practical because we evaluate both the technical and economic aspects of the technologies we develop.

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