Primer

Biofuels

Chris Somerville

The global energy market provides humans with about 370 exajoules of energy per year, which is equivalent to about 170 million barrels of oil per day (Box 1) or about 11.73 terrawatts (TW) per hour [1]. Approximately 95% of this energy comes from fossil fuels. Additionally, the International Energy Agency suggests that direct combustion of plant biomass provides about one-third of the energy needs in Africa, Asia and Latin America, and as much as 80 to 90% in the poorest countries of these regions [1]. Combining estimates of the magnitude of this form of biofuels consumption with the relatively small amount for which market numbers are available suggests that biofuels currently provide about 10% of all human energy use.

There has recently been an upsurge of interest in the use of liquid biofuels for transportation in the developed world. This has been stimulated by a very rapid increase in the price of petroleum, strategic concerns about dependence on politically unstable regions of the world, and concerns about global climate change. The probable trajectory of this interest is beyond the scope of this article. But it is worth noting that there is no compelling evidence that even half of the recoverable petroleum has been used. Also, the regions that consume most of the energy are endowed with abundant coal reserves that are projected to be adequate to meet human energy needs for several hundred years. Coal can be converted into a wide variety of liquid fuels that can substitute for petroleum. Thus, it would be prudent to view the recent discontinuity in historical fossil fuel price trends as a transient imbalance rather than an indicator that fossil fuels are nearing depletion [1]. If concerns about climate change are ignored, there is not a pressing motivation to develop biofuels.

The linkage between climate change and biofuels arises from the fact that biofuels can be carbon neutral sources of energy. Energy from sunlight is collected by the photosynthetic system of plants and used to reduce and condense atmospheric CO_2 into the chemicals that comprise the body of plants. When plants are burned, the energy resulting from oxidation is released as heat and the CO_2 is recycled. If the biomass is simply burned, about 85% of inherent energy is available as heat and if that heat is used to produce steam for generators, approximately 35% of the energy can be recovered as electricity. With highly productive plants, such as *Miscanthus giganteus*, growing on good soils with adequate rainfall and favorable mean temperature, such as are found in central Illinois (Figure 1), more than 2% of annual incident solar insolation can be harvested as biomass [2].

If we use a value for average solar insolation of 120,000 TW, 2% solar conversion efficiency, and an energy recovery value of 50%, we could meet all human energy needs — 11.73 TW at the present level of consumption — by growing a plant such as *Miscanthus* on about 3.2% of the terrestrial surface area. Similar numbers can be obtained from actual yield measurements (Box 2). The calculation provides a tangible way of envisioning global bioenergy capacity. Current goals are much more modest, however; the US Secretary of Energy has established a goal for the US of obtaining 30% of transportation fuels from biomass by 2030.

Box 1

Conversions

1 exajoule = 10^{18} joules[1]
1 exajoule = 9.48 x 10^{14} BTU
1 terrajoule = 10^{12} joules
1 terrajoule ~ 0.17 barrels of oil
1 kilojoule ~ 0.2777 watt hours
1 hectare = 2.471 acres
1 bu corn ~ 56 lb[2] (25.4 kg)
1 bu soybean ~ 60 lb
1 bu canola ~ 49 lb
7.7 lbs vegetable oil ~ 1 gallon

[1] Other energy interconversions at http://www.mycomponents.co.uk/energy.htm
[2] Exact value depends on moisture content of seed

The reason for the current focus on using biomass for liquid fuels rather than for direct combustion is that coal is abundant and inexpensive, it is less expensive

Figure 1. *Miscanthus giganteus* growing at the University of Illinois.
Above-ground biomass is harvested in the fall or winter and the crop regrows from rhizomes during succeeding growing seasons. Image courtesy of Stephen P. Long and Emily Heaton, University of Illinois. Additional information at http://miscanthus.uiuc.edu/

Box 2

Biomass energy yield per acre

1 ton of dry *Miscanthus* has 17,252 GJ of heat value [2]
1 acre of *Miscanthus* at 21 dry tons/acre[1] ~ 362,292 GJ
1,021,275 acres of biomass ~ 370 EJ
Terrestrial surface of earth ~32.123 x 10^9 acres
370 exajoules could be grown on 3.2% of the surface

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[1] Stephen P. Long, University of Illinois, personal communication.

to transport (per joule) and it burns with higher energy efficiency and less ash than biomass. Because trading of carbon credits decreases the effective price of biofuel in Europe, the use of biomass for direct combustion is being encouraged. In the US and other regions, where carbon trading is not yet implemented, economic and political forces favor production of liquid transportation fuels. In the following short overview, I have attempted to outline the prospects and problems associated with moving toward greater reliance on liquid biofuels.

Corn and cane ethanol

Sugarcane (*Saccharum* sp.) is a highly productive tropical grass that accumulates sucrose in the stem tissues. The stalks are crushed to produce a sucrose solution that can be fermented to produce a dilute ethanol solution (Box 3). The crushed stalks or 'bagasse' are burned to produce heat that is used to distill the ethanol from the fermentation broth and to produce excess electricity. In Brazil, where land suitable for growing sugarcane is abundant, about 4.2 billion gallons of cane ethanol was produced in 2005. The ethanol is mixed with gasoline and now comprises about 40% of all liquid transportation fuel. The automobile fleet in Brazil is largely composed of 'flex-fuel' vehicles that can use widely varying ratios of ethanol and gasoline. By contrast, only about 2% of the fleet in the US are flex-fuel vehicles; the remainder of the US fleet can not burn alcohol: gasoline mixtures containing more than 10% ethanol without mechanical modifications.

Corn (*Zea mays*) is the largest US crop with ~81 million acres planted in 2005 yielding about 11.1 billion bushels of corn seed. Approximately 60% of the mass of corn seed is starch. The starch is released by grinding the seed in either a dry or wet process, cooked to gelatinize the starch, then enzymatically hydrolyzed to glucose at low cost and high efficiency and fermented. Following fermentation and separation of ethanol by distillation, the residual slurry of insoluble fiber, protein and lipid, called 'distiller dry grains with solubles' (DDGS), is used as animal food. Wet milling allows more complex separation techniques than dry milling and therefore the non-starch components may be used for higher value applications than animal food. However, wet mills are much more expensive to build and operate than dry mills, and are usually much larger in size. Thus, most of the corn processing plants in the US, which are owned and operated by farmer cooperatives, are dry mills.

At present there are ~100 corn-to-ethanol plants operating in the US which, in 2005, produced 3.9 billion gallons of ethanol from about 14% of the US corn crop. The US Department of Agriculture and the corn growers association project that production of ethanol from corn grain will increase to ~12 billion gallons per year. Indeed, ~33 new ethanol plants are currently under construction in the US and many existing plants are undergoing expansion. At present the business is very profitable because corn ethanol can be produced for approximately $1 per gallon but, in the summer of 2006, was selling for approximately $3.5 per gallon. In addition, there are some legacy subsidies that add further profit.

The technology required for cane or corn ethanol production is mature and most of the technical issues concern improvements in engineering related to the efficient use of heat and water. Unlike cane ethanol, however, which has an energy output:input ratio of about 8, for corn ethanol, calculations of the lifecycle costs of production have stirred substantial scientific debate. These calculations typically include things such as the energy costs of producing and distributing fertilizer, the cost of planting and harvesting, the costs of making the farm machinery and the factories that process the grain, in addition to the costs of converting grain to ethanol *per se*. The results have been controversial because certain assumptions about things such as heat reuse are inevitable in trying to compile all of the costs. A recent meta-analysis of all such calculations concluded that corn ethanol provides about 25% more energy than is consumed in its production [3].

Because of the low net energy ratio, corn ethanol does not offer an attractive long-term solution to meeting our energy needs in an environmentally sustainable way. But by stimulating the creation of a (profitable) industry, corn ethanol production involves a useful transition technology which will facilitate the development of more environmentally benign technologies for cellulosic ethanol production, as noted below. For instance, the availability of large quantities of corn ethanol provides a rationale to increase the production of flex fuel vehicles.

Biodiesel

In diesel engines, fuel is injected into a cylinder and then the air–fuel mixture is rapidly compressed so that it heats up to the point where combustion takes place. A wide variety of chemicals or mixtures of chemicals, including biologically produced fatty acids or lipids, will undergo combustion in conventional diesel engines. Glycerolipids, such as triacylglycerol, tend to lead to fouling of engine parts such as injectors and frequently have high melting points that are incompatible with use of lipids for fuels in temperate climates. However, the methyl or ethyl esters of biologically derived fatty acids cause less engine fouling and are miscible with petroleum-based diesel fuel. These esters can be produced from biological lipids or fatty acids by very simple reactions that can be carried out in home kitchens with commonly available reagents, for example lye, vegetable oil and alcohol. Thus, it is inexpensive and technically simple to establish a commercial biodiesel production facility. The US currently has approximately 65 such facilities, many of which include used cooking oils from restaurants as feedstocks. This is an environmentally and economically attractive use of a material that would otherwise be a waste disposal problem.

Because of the ease of biodiesel production from raw lipids, the net energy ratio of biodiesel is better than that of corn ethanol [4]. Unfortunately, domestic biodiesel will not become more than a niche component of the liquid fuel supply because the amount of lipid produced per acre is small relative to the total amount of biomass. Thus, for instance, in 2005 the average soybean seed yield of 40.8 bu per acre yielded only about 450 pounds of oil per acre. Similarly, the average Canadian canola seed yield in 2005 of 32.6 bu per acre yielded only 650 pounds of oil per acre. This must be contrasted with the much higher yields of cellulosic biomass that could be grown on the same acres. Additionally, vegetable oils are a quantitatively important component of human diets and, therefore, relatively small disruptions in supply result in large increases in price [5]. Thus, although there is a small surplus in the edible oil market at present, once this surplus is consumed for biodiesel production, vegetable oil will become much too expensive for use as fuel.

Indeed, vegetable oil currently costs approximately twice as much to produce as a gallon of ethanol. Current government subsidies of up to $1 per gallon for biodiesel represent the triumph of politics over common sense and are likely eventually to disappear. The US Congressional Research Service recently completed a study that concluded that if every ounce of plant and animal lipid produced in the US were used for biodiesel production, the total amount would be about 4 billion gallons [5]. When compared with the roughly 140 billion gallons of liquid fuels used in the US each year, it can be seen that domestic biodiesel will not be a significant component of fuel in the US or elsewhere in the developed world.

Box 3

Ethanol production

1 bu corn (dry milled) ~ 2.65 gal ethanol
Average US corn yield 150 bu/acre[1]
Cost of production of 1 gal of corn ethanol ~$1.04[1]
Theoretical ethanol yield from sucrose 163 gal/ton
1 ton sugarcane ~ 19.5 gal ethanol[1]
Cost of production of 1 gal of sugarcane ethanol ~ $2.4[1]
1 ton sugar beets ~ 24.8 gal ethanol
1 ton of cellulosic biomass ~ 110 gal ethanol[2]
Energy density of ethanol 21.17 MJ/L
Energy density of gasoline 31.6 MJ/L

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[1] US average 2003-05. From USDA Economic Services, 2006.
[2] Approximate theoretical maximum, depending on plant species.

In contrast to annual oilseeds, several tropical plants are likely to be used to produce relatively large amounts of biodiesel for the developing world. Oil palm (*Elaeis* sp.), which grows in high rainfall zones within 15 degrees of the equator, produces clusters of oil rich fruits that are similar to small avocados. Yields of up to seven tonnes of oil per hectare per year have been recorded, although the average is lower. The plants have very long lifecycles and do not require significant energy inputs for production. In addition, mature plantations reportedly produce about ten tonnes per hectare per year of cellulosic biomass (for example, senescent fronds) that can also be used for fuel production. It thus seems likely that oil palm acreage will continue to expand, but at the expense of tropical forests. Acreage of the South American Babassu palm (*Orbignya* sp.) is also increasing. Recently, interest has been drawn to a drought tolerant bush, *Jatropha curcus*, which reportedly yields several tones of oil per hectare per year with little or no input. This plant may allow production of oil on land that is too drought-prone for food crop production. Companies have established large plantations in Africa, India and South East Asia.

Cellulosic ethanol

All higher plant cells are enclosed in cell walls composed primarily of polysaccharides and lignin which, in many plant species, comprise more than 90% of the dry body mass. The principal cell wall polysaccharide is cellulose, a fibrous material composed of hydrogen bonded chains of β-1,4-linked glucose. Cellulose is coated with a class of polysaccharides called hemicellulose. The most abundant type of hemicellulose is xylan, a polymer of β-1,4-linked xylose which may, depending on the plant species, have branches containing other sugars such as arabinose or glucuronic acid. Thus, the principal sugars in most tissues that are useful for biofuels are glucose and xylose, but many other sugars are also present in significant amounts. Cell walls from vascular tissues usually also contain lignin, a complex polymer of hydroxylated and methoxylated phenylpropanoids that is made by a free radical process (Figure 2). The polysaccharides can be converted to ethanol by fermentation in much the same way as corn starch.

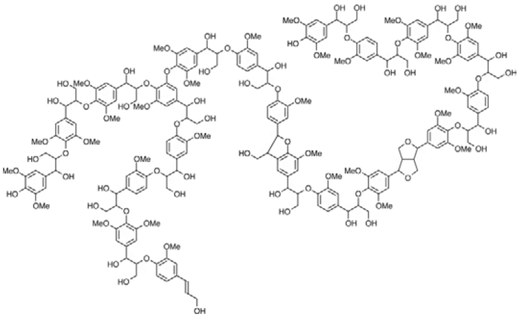

Figure 2. A fragment of lignin that illustrates some of the linkages found in poplar lignin.

The polymer does not appear to have a regular structure and is thought to arise by free radical polymerization of phenylpropanoids. Image courtesy of John Ralph, US Dairy Forage Research Center, Madison, Wisconsin. Available at http://www.dfrc.ars.usda.gov/LigninModels.html

Because the whole plant can be used, however, the yield of sugar per unit of land per year is much higher than can be obtained using only corn grain.

There are no large-scale cellulosic ethanol facilities in commercial production as yet, although several companies have announced plans to build facilities with capacities of more than 30 million gallons per year. A typical pilot-scale process for making cellulosic ethanol involves treatment of pulverized biomass with hot acid, which partially hydrolyzes hemicellulose and other polysaccharides and disrupts the association of lignin with the polysaccharides. The hydrolysate is neutralized, separated from the insolubles, and fermented to produce ethanol. The insoluble fraction is then treated with cellulase and glycosidases to release glucose which is also fermented to produce ethanol. The residual insoluble material, mostly lignin, is burned to generate energy for the overall process. The future development of plants with modified lignin that can be readily hydrolyzed, or improved enzymes or chemical catalysts for lignin hydrolysis may allow the use of lignin as a component of plastics or as a fermentation feedstock for liquid fuel production. The fermentation process produces a nutrient-rich microbial cell mass which could be inactivated and used as fertilizer so as to recycle the mineral nutrients to the land.

Many components of the cellulosic ethanol process are not yet optimized for commercial production. These are described in a recent report sponsored by the US Department of Energy [6]. For instance, the strains of yeast that are used for industrial fermentations do not normally utilize sugars other than glucose. Strains of yeast (*Saccharomyces cerevisiae*) and *Escherichia coli* have been engineered to ferment xylose to ethanol but additional work needs to be done to adapt such lines to industrial conditions, to optimize metabolic control of the pathways, and to enable fermentation of other sugars. At present the microbes do not produce sufficiently high ethanol titers and it is not yet clear whether such engineered strains offer greater long-term potential than could be realized by engineering species such as the bacterium *Xymomonas mobilis* or the yeast *Pichia stipitis* that naturally have the ability to ferment both glucose and xylose.

Another problem is that large amounts of cellulase are required to hydrolyze cellulose. Process improvements during the past decade have reduced the cost of cellulase per gallon of ethanol from about $5 to about $0.5 but that is about twenty times higher than the enzyme costs for a gallon of corn ethanol. There is widespread interest in the possibility of finding enzymes with higher turnover numbers than current cellulases by surveying the properties of enzymes from poorly explored sources such as termite guts, rumen, compost heaps, and tropical forests. Alternatively, it may be possible to improve the activity of industrial cellulases by protein engineering. It is also important to understand the structure and function of cellulosomes, extracellular enzyme complexes that catalyze hydrolysis of cellulose and other polysaccharides [7]. The holy grail of cellulosic ethanol production is to incorporate improvements on both of these fronts into a single organism that would secrete all of the necessary enzymes and utilize all of the available sugars in a process referred to as ‘integrated bioprocessing’ [8]. My impression is that we are far from realizing that goal.

There are many other problems for which multiple solutions may be envisioned, but relatively little progress has yet been made. For instance, many plant polysaccharides are acetylated. The acetic acid released during biomass hydrolysis inhibits the growth of the fermentative organisms. Similarly, furfural produced by a side-reaction during acid catalyzed polysaccharide hydrolysis inhibits microbial growth. In principle, these and related problems may be overcome by developing resistant organisms, by altering the chemical composition of the biomass, or by process improvements.

The development of a biofuel industry is only feasible in regions where the land and water resources are available to support the growth of plant biomass that is excess to other needs. The US Departments of Energy and Agriculture conducted a study of biomass availability and concluded that approximately 1.3 billion dry tones of biomass is available each year in the US [9]. This includes unused resources such as half of the corn stover (the leaves and stalks of the corn plant), wheat straw, and using about 40 million acres of set-aside land to grow perennial grasses such as switchgrass and Miscanthus. At a conversion value of about 100 gallons per ton, this would be equivalent to about 77.4 billion gallons of gasoline (Box 1), or slightly more than half US liquid fuel consumption. Based on the proportion of transportation fuel already produced by Brazil, it seems likely that South America could meet all needs for transportation fuels with biofuels. A recent analysis of the 15 countries in the European Union concluded that Europe could produce approximately 11.7 exajoules per year of biofuels [10], almost exactly the same amount as the US goal of 30% of transportation fuels (11.6 exajoules). As noted above, Southeast Asia seems likely to develop mixed production of cellulosic ethanol and biodiesel. Thus, although biofuels will not completely meet our needs for transportation fuels anytime soon, they are expected to become a significant component worldwide. The more widespread implementation of trading in carbon credits could accelerate progress toward that goal.

Other biofuels

Ethanol is not an ideal fuel in several respects and may not be the major biofuel in 25 years. The main problem is its water miscibility, which imposes an energy cost for distillation, creates problems in transporting the fuel via pipelines, and leads to poisoning of the microorganisms that produce it. Thus, there is interest in developing biofuels that are more hydrophobic and spontaneously partition out of the aqueous phase. Although butanol is toxic at low concentrations, it is a promising biofuel in other respects. It dehydrates spontaneously at about 9% solution, has very low vapor pressure and a latent heat similar to octane so that fuel-air mixing at low temperature is not problematic. Importantly, when added to ethanol:gasoline mixtures, small amounts of butanol depress the vapor pressure, reducing the hazards of explosions during fuel handling. Several companies have recently announced plans to produce butanol by fermentation of sugars from sugarbeet in England. Additionally, because some microorganisms have been reported to secrete alkanes, it seems likely that we will see the development of additional types of biofuels with physical properties similar to those in current use. A different path to biodiesel involves thermal conversion of biomass to a gas enriched in CO and H_2. This “syngas” can be converted to high quality diesel fuel using the Fischer-Tropsch process developed in Germany in the 1920s. However, the yield of fuel is only about 40 gallons per ton of biomass. Thus, this approach makes less efficient use of biomass than fermentation to ethanol and the net energy balance is uncertain.

Biological sequestration

An alternative to reducing net CO_2 emissions with biofuels is to enhance net CO_2 sequestration by the biosphere. Since it seems likely that humans will eventually burn all available fossil carbon, sequestered carbon needs to remain out of the atmosphere longer than the probable duration of fossil energy reserves. At current rates of consumption, we have enough known deposits of oil to last 42 years, enough natural gas for 60 years and enough coal for 210 years. Thus, we should assume that sequestered carbon needs to stay out of circulation for at least 200 years. Some tree species, such as *Sequoia sempervirens*, can have lifetimes much longer than this and represent a realistic mechanism for biological sequestration.

Based on estimates of net carbon assimilation by forest plantations on productive land [11], it would take about 69 million acres of a highly productive forest species to annually sequester the amount of carbon equivalent to 30% of annual petroleum use in the US (~0.1 petagrams). Unfortunately, the requirement for both high productivity and a lifespan of more than 200 years are not present in any existing species, so the acreage would probably be substantially larger for long-lived species. By contrast, it would require about 35 million acres to produce an energetically equivalent carbon-neutral amount of cellulosic ethanol with a cellulosic biofuel crop yielding 25 tons per acre. This calculation takes into account the lower energy density of ethanol (Box 3) and assumes a five-fold energy balance for cellulosic ethanol [3]. The biofuel crop would also contribute to energy independence and would support employment for more than a million people. The key to implementing the biofuels option is the use of highly productive perennial C4 grasses, such as *Miscanthus*, which have much higher photosynthesis rates and water use efficiencies than any forest species.

Conclusions and outlook

The major opportunity to expand the use of biofuels is in improving the various components of cellulosic biofuels production. No miracles are required to develop cost effective cellulosic biofuels; a series of two-fold improvements in the efficiency of various steps will make biofuels less expensive than liquid fossil fuels. Implementing rational improvements in the overall process will be challenging, however, because there are a lot of components that need to be managed coordinately and knowledge from many scientific and engineering disciplines must be integrated.

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Carnegie Institution, Department of Plant Biology, 260 Panama Street, Stanford, California 94305, USA. E-mail: crs@stanford.edu