The Future of Biorefining Agricultural Biomass

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Introduction

The Biomass Research and Development Technical Advisory Committee (2002) of the U.S. Departments of Energy and Agriculture[1] defines a biorefinery as:

"A processing and conversion facility that (1) efficiently separates its biomass raw material into individual components and (2) converts these components into marketplace products, including biofuels, biopower, and conventional and new bioproducts."

Implicit in this definition is the assumption that grains will be fractionated into starch, oils, proteins, and fiber while lignocellulosic crops will be fractionated into cellulose, hemicellulose, lignin, and terpenes before these components are converted into market products. Another approach is to break plant materials into the smallest possible building blocks - carbon monoxide (CO) and hydrogen (H_2) – from which the desired chemical products are synthesized.

The successful emergence of advanced biorefineries will be influenced by many factors including the extent of biomass availability, the kinds of products that can be produced, the nature of the conversion processes employed, the ability to efficiently utilize the energy content of biomass, and the size of the plants to be built. This paper provides an overview of these issues and describes the prospects for advanced biorefineries.

Resource Availability

The amount of biomass that could be produced annually in the United States is difficult to estimate. In addition to the uncertainties in plant yields, a variety of social, political, economic, and environmental factors influence decisions about placing land into biomass production. Since these factors are not static, assessments of land available can change with time.

The U.S. Department of Agriculture performed one of the most recent biomass resource assessments for the United States.[2] This study concludes that over 1.2 billion tons of dry biomass could be produced in a sustainable manner. Equivalent to 21 billion GJ of energy, this represents 21% if U.S. energy consumption.

It is important to note that the study assumed that advances in technology will help expand the biomass supply. Specifically, small grain yields will increase by 50 percent; residue ratio for soybeans will increase to 2:1; harvest technology will allow recovery of 75% of crop residues (when sustainable removal is possible); all cropland will be managed by no-till methods; 55 million acres of cropland, idle cropland, and pasture will be dedicated to perennial bioenergy crops; and all manure in excess of allowable on-farm soil application will be used for biofuel.

Figure 1 summarizes the findings of the USDA study. Forestry resources, in the form of fuelwood, milling residues, urban wood residue, logging residues, and wood recovered from

forest thinning (for forest fire control) could yield 335 million Mg of dry wood per year or 28% of the total. Agricultural resources, in the form of crop residues, perennial crops, grains for biofuels, and processing residues and manure, could yield 907 million Mg of dry biomass per year. Crop residues and perennial crops represent 31% and 28%, respectively, of the total biomass supply. Assuming an average heating value of 18 MJ/kg, this 1.2 billion Mg supply of biomass represents 21 billion GJ of energy. This biomass supply could be used to fulfill one-third of U.S. demand for transportation fuel. Thus, biomass could be a significant contribution to the future U.S. energy supply.
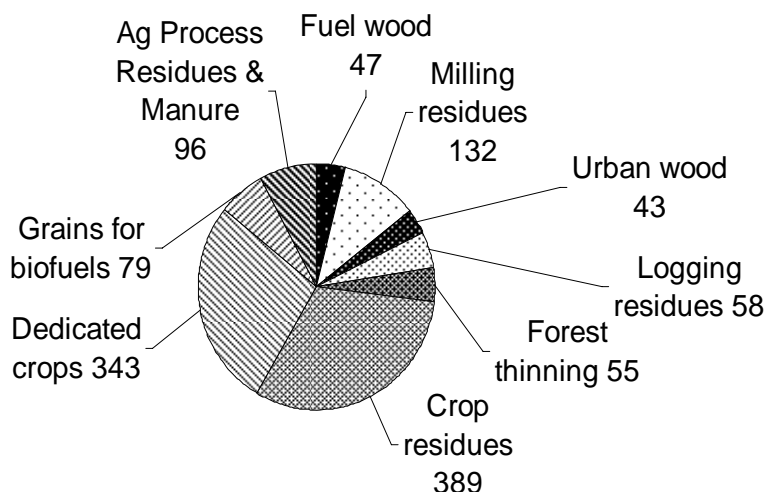

Figure 1. U.S. Biomass Potential (millions of metric tons)

Biobased Products from Advanced Biorefineries

Although transportation fuels will be the single largest biobased product from a biorefinery, commodity chemicals, natural fibers, and electricity are also products with significant economic potential. Already commercially available biobased products include adhesives, cleaning compounds, detergents, dielectric fluids, dyes, hydraulic fluids, inks, lubricants, packaging materials, paints and coatings, paper and box board, plastic fillers, polymers, solvents, and sorbents.

Of course, the products from an advanced biorefinery will be strongly influenced by the feedstock processed by the facility. Much attention has been paid to the corn-based biorefinery, which produces predominately starch and carbohydrate derivatives from it, but also smaller amounts of oil, protein, and fiber. Commercially significant carbohydrate derivatives from starch are currently limited to ethanol, nutritive sweetener, and lactic acid (used in the production of polylactate). A number of carbohydrate derivatives are possible, of course, but a joint report by the Pacific Northwest National Laboratory and the National Renewable Energy Laboratory of the U.S. Department of Energy suggests a list of "top twelve" building block molecules from sugars, selected for their multiple functional groups.[3] These include three diacids (succinic, fumaric, and malic acids), seven carboxylic acids with additional functionality (2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, and levulinic acid), one ketone (3-hydroxybutyrolactone), and three polyols (glycerol,

sorbitol, and xylitol/arabinitol). Other groups have suggested 1, 3-propanediol as an attractive building block molecule from carbohydrate. [4, 5]

Biorefineries using fibrous (lignocellulosic) biomass as feedstock will produce C6 sugar (glucose), C5 sugars (predominately xylose and arabinose), and lignin.[6] These sugars can be fermented to produce so-called "cellulosic" ethanol although the same carbohydrate derivatives contemplated for corn-based biorefineries are also appropriate secondary products for a fiber-based biorefinery. Lignin, a phenylpropane-based polymer, is not fermentable but has potential as a urea-formaldehyde substitute or even the starting point for the production of hydrocarbon fuels.[7] First generation biorefineries, however, are expected to simply use lignin as boiler fuel. A fundamentally different approach to lignocellulosic biorefineries thermochemically breaks down plant material into a mixture of carbon monoxide (CO) and hydrogen (H_2) known as syngas. This simple gas mixture can be catalytically upgraded to a wide variety of compounds, including alcohols, carboxylic acids, and hydrocarbons.[8] It is the process proposed for the production of "green" diesel in Europe.[9]

Another kind of biorefinery is based on plant oils or animal fats and is commonly known as an oleochemical plant. For such a plant based on oilseed crops such as soybeans the primary products are oil (triglyceride) and meal, the later of which contains significant quantities of protein and fiber and some residual oil. The oil can be either hydrolyzed to fatty acids and glycerol or converted into methyl (or ethyl) esters and glycerol by the process of transesterification.[10] The fatty acids and esters are potential platform chemicals for the production of a vast array of derivative chemicals used in high value products. Much of the focus on methyl esters today has been on their use as biodiesel but there has also been limited diversification into ester-based solvents and lubricants. The industry has shown only limited interest in upgrading the glycerol byproduct although technologies are rapidly emerging for its conversion to 1, 3-propanediol,[11] a precursor in the production of plastics. Similarly, although the protein in the meal as potential to replace urea-formaldehyde in adhesives, commercialization has been slow to emerge.

Biobased transportation fuels, also known as biofuels, are currently dominated by ethanol and biodiesel. However, there are other candidate liquid biofuels including methanol, mixed alcohols, and Fisher-Tropsch liquids, as well as gaseous biofuels including hydrogen (H_2), methane (CH_4), ammonia (NH_3), and dimethyl ether (CH_3OCH_3).

Kinds of Advanced Biorefineries

Modern wet corn milling plants and pulp and paper mills can rightly claim to be biorefineries. Advanced biorefineries, however, should be able to process all components of the biomass feedstock into high-value biobased products. Corn fiber as cattle feed additive and lignin as boiler fuel from corn milling plants and pulp and paper mills, respectively, would be of relatively low economic value in a greatly expanded biofuels market. Kamm and Kamm[12] have defined three kinds of biorefineries that would meet this requirement: whole grain biorefineries that make better use of such byproducts as distillers dried grains and solubles (DDGS) and protein meal during the processing of conventional starch and oil crops; lignocellulosic biorefineries that efficiently convert cellulose, hemicellulose, and lignin to products; and so-called "green"

biorefineries that convert high moisture biomass, such as silage corn or kelp, into products via ensiling or anaerobic digestion.

The whole grain biorefinery, which is an outgrowth of existing grain ethanol manufacturing, is illustrated in Figure 2(a). The grain, assumed in the figure to be corn grain for illustrative purposes, is brought from the field and milled (or pressed, in the case of oil seeds) to separate economically recoverable plant components, which might include sugar, starch, oil, protein, and fiber. In Figure 2(a) an advanced dry grind operation is assumed, which recovers oil from the germ while fiber and protein remain mixed with the starch (in a wet milling operation, the oil, protein, and fiber are separately recovered, leaving nearly pure starch for further processing). One or more of these components is subjected to fermentation. In the case of corn grain, this component is either starch-rich mash from a dry grind operation or pure starch from a wet milling operation, after it has been treated with enzymes and the starch hydrolyzed to glucose. Since the fermentation products, such as ethanol and lactic acid, are usually produced in the fermentation broth at concentrations typically less than 150 g/L, distillation is required to recover these products. At this point the unfermented constituents of the mash from the dry grind operation known as distillers dried grains and solubles (DDGS) is also separated and dewatered. Although some of the DDGS from a whole grain biorefinery may be sold as animal feed, the large quantities that will be generated in a greatly expanded grain ethanol industry suggest its use in higher value applications. In Figure 2(a) it is assumed that the DDGS is gasified to CO and H_2 (syngas), which is cleaned and catalytically converted to alcohols or hydrocarbon-based fuels (Fischer Tropsch liquids).

The lignocellulosic biorefinery is illustrated in Figure 2(b). The feedstock for such a facility is fibrous biomass such as switchgrass, hybrid poplar, or cornstover. The plant material is first pretreated to increase the surface area of lignocellulose, making the polysaccharides more susceptible to hydrolysis.[13] A number of pretreatments have been developed, including dilute acid, hot water, steam explosion, and ammonia explosion. The product streams usually include cellulose, hexose and pentose from hydrolyzed hemicellulose, and lignin. The cellulose is treated with enzymes to hydrolyze it to glucose in a process known as saccharification after which the C5 and C6 sugars are separately or together fermented to ethanol or other fermentation products. Lignin, the non-carbohydrate constituent of fiber, cannot be fermented and is instead thermochemically converted to syngas followed by catalytic conversion to alcohols or other renewable transportation fuels.

Clearly, the technology to convert lignocellulose into monosaccharides could also be employed in the previously described whole *grain* biorefinery to make a whole *crop* biorefinery. For example, a whole crop biorefinery for corn would bring both corn grain and corn stover (stalks, leaves, husks, and cobs) to the facility. The starch recovered from the grain would be subjected to hydrolysis with starch enzymes as illustrated in Figure 2(a) while the cornstover and the DDGS (or corn fiber) from fractionating the grain would be subjected to pretreatment and enzymatic hydrolysis illustrated in Figure 2(b). The resulting sugar streams would be fermented into ethanol or other products while the lignin would be gasified as shown in Figure 2 (b).

The lignocellulosic biorefinery illustrated in Figure 2(b) is based on hybrid biological-thermochemical processing of biomass. This concept is favored in the United States for
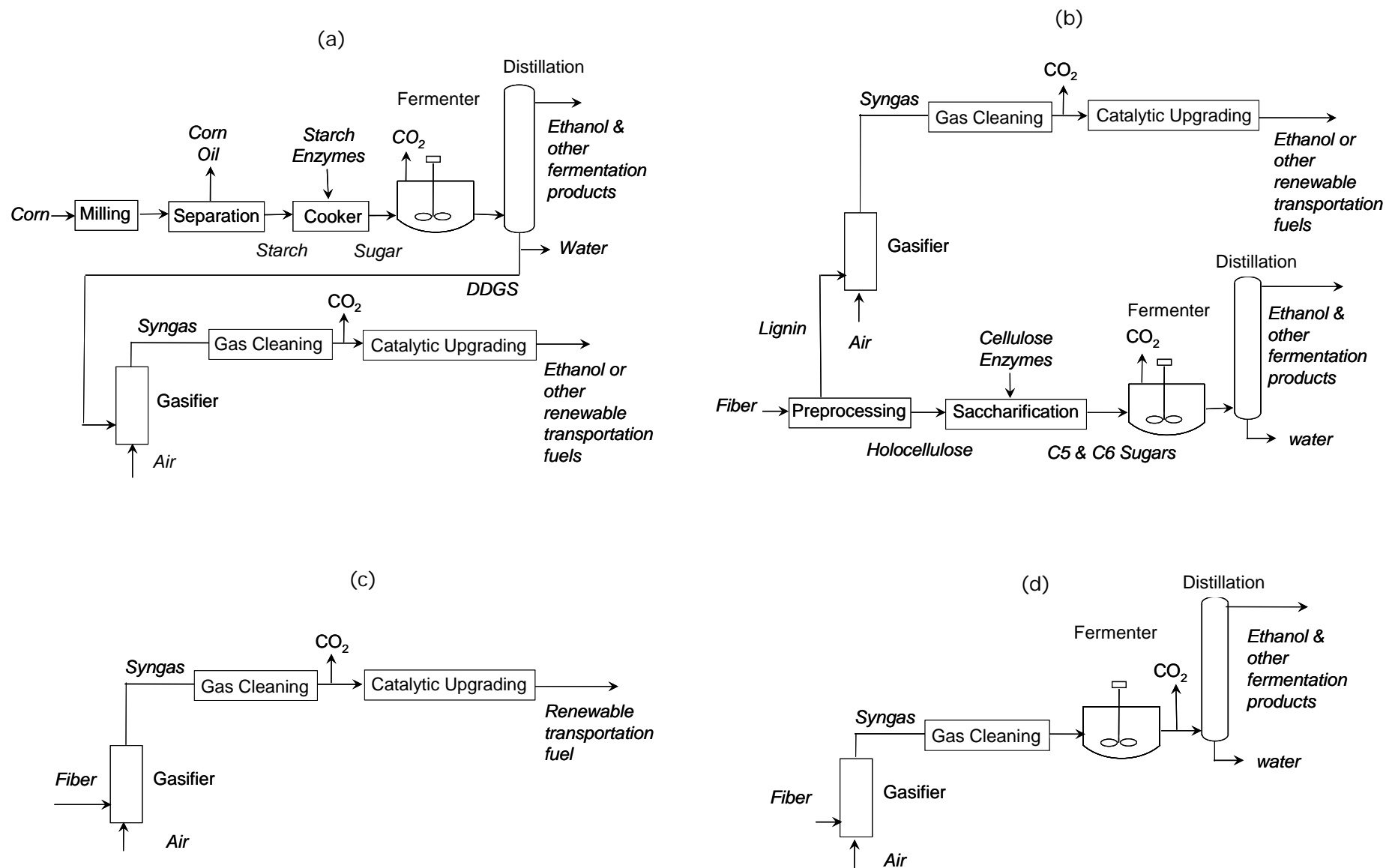
Figure 2. Types of biorefineries: (a) Whole grain biorefinery; (b) lignocellulosic biorefinery with thermochemical processing of lignin; (c) lignocellulosic biorefinery with pure thermochemical processing; (d) lignocellulosic biorefinery with syngas fermentation.

producing transportation fuels from lignocellulosic biomass since it builds upon the fermentation technology used in the present fuel ethanol industry. In Europe on the other hand, the idea of a lignocellulosic biorefinery based on pure thermochemical processing is gaining favor. This biorefinery, illustrated in Figure 2(c), is really nothing more than the lignocellulosic biorefinery illustrated in Figure 2(b) with the pretreatment, hydrolysis, and fermentation operations stripped out. Fibrous biomass is taken directly from the fields to the gasifier where it is converted to syngas and then catalytically converted into a wide selection of fuel products and commodity chemicals. This flexibility in product mix as well as the tolerance of the gasification process to a wide variation in biomass composition are among the chief attractions of the thermochemical biorefinery.

Gasification and syngas technologies were extensively developed and commercialized in Germany during World War II to convert coal into motor fuels when Germany was denied access to petroleum-rich regions of the world. Likewise South Africa, faced with an oil embargo during their era of apartheid, produced Fischer-Tropsch liquids from coal to sustain its national economy. In the United States, Eastman Kodak has used gasification to produce acetic acid from coal. Any solid carbonaceous fuel can be employed for the production of syngas as long as sulfur and chloride contaminants are removed ahead of the catalytic reactors where they can poison the metal catalysts used in the synthesis reactions. In this respect, biomass is a very suitable fuel for a refinery based on thermochemical processing although cost has historically favored coal over biomass.

The apparent simplicity of the flow chart in Figure 2(c) is somewhat deceptive because economical operation of such a facility is thought to be strongly dependent upon integrating the many energy flows in the plant and building extremely large facilities to capture economies of scale, as subsequently described. Thus, it is uncertain whether future biorefineries will be based on biological/thermochemical processing or pure thermochemical processing.

Interestingly, a third kind of lignocellulosic biorefinery, shown in Figure 2(d), has been proposed.[14] Like the biorefinery illustrated in Figure 2(b), this lignocellulosic biorefinery is based on hybrid biological/thermochemical conversion. Instead of partitioning the plant components between biological and thermochemical processes, all of the biomass is thermochemically processed followed by biological conversion. Like the lignocellulosic biorefinery based on pure thermochemical processing, all of the biomass is gasified to syngas. However, instead of using inorganic (metallic) catalysts for the synthesis reactions, biocatalysts are employed in a process known as syngas fermentation. Whereas traditional fermentations rely on carbohydrates as the source of carbon and energy in the growth of microbial biomass and the production of commercially valuable metabolites, syngas fermentation employs microorganisms able to utilize less expensive substrates for growth and production. These include autotrophs, which use C_1 compounds as their sole source of carbon and hydrogen as their energy source, and unicarbonotrophs, which use C_1 compounds as their sole source of both carbon and energy. Among suitable C_1 compounds are CO, CO_2, and methanol (CH_3OH), all of which can be produced from thermochemical processing of biomass. Products include carboxylic acids, alcohols, and polyesters. One example is the anaerobic bacterium *Clostridium ljungdahli*, which co-metabolizes syngas to form acetic acid (CH_3COOH) and ethanol (C_2H_5OH).

Energy Balance for Biobased Motor Fuels

The energy balance for production of grain ethanol and, more recently, for any biomass-derived transportation fuel comes under periodic attack in the national press. [15, 16] Thus any prospectus for a biorefinery would not be complete without addressing this important issue. Unfortunately, it has been reduced in the minds of the public and of many policy makers to the question, "Does it take more energy to produce ethanol than you get out of it?"

The answer to this question is an unequivocal "Yes." No process exists that yields more energy than goes into it. Something as simple as a bouncing ball is a good illustration of this principle: when dropped it does not bounce back to its starting height because some energy is lost in the process. In this analogy, the rebound is equivalent to the energy efficiency of the process. Figure 3 compares the rebound of several processes for producing transportation fuels and electric power,[17] beginning with the refining of gasoline from petroleum. In some respects petroleum refining is the gold standard for production of transportation fuels: 84% of the energy entering the process appears in the gasoline product. Nevertheless, we must conclude, like the case for ethanol production, *we get less energy out of petroleum refining in the form of gasoline than we put into it.* The laws of thermodynamics do not allow otherwise. It is worth noting that in the early days of petroleum refining, only 20% energy efficiency was attained. Technological advance over the past 100 years are responsible for boosting this number to 84%.

Ethanol from corn grain has a relatively modest energy efficiency of 38%. To the public, this might appear an unacceptably low rate of return on energy investment, yet it is somewhat better than a modern electric power plant that converts coal into electricity. The reason we tolerate such "poor" efficiency in power plants is that the product is highly valued: electricity is pure work. Although the energy of grain ethanol cannot share this thermodynamic distinction, it is nevertheless a high octane fuel of great value in our transportation sector, thus we accept some energy loss upon producing it from less convenient energy sources.
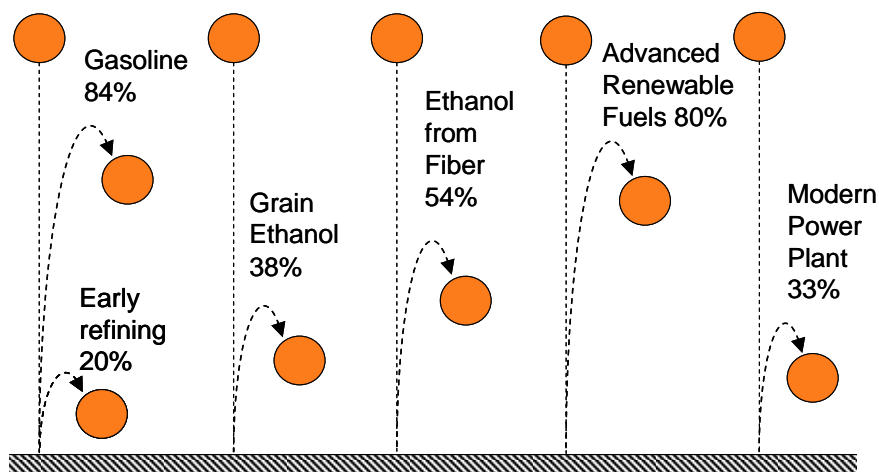
Source: RBAEF Project (Dartmouth) and R. Anex (ISU)

Figure 3. Energy efficiency of various processes to produce transportation fuels or electrical power.

Nevertheless, we recognize that there is room for improvement through advanced technologies. For example, the energy efficiency for production of ethanol from fibrous crops is about 54%. This occurs because a larger fraction of the plant material goes into the final fuel product. Advanced technologies of the sort illustrated in Figure 2 are expected to eventually yield energy efficiencies approaching those of petroleum refining.

However, much of the academic debate[18, 19] is not about energy efficiency but another kind of energy balance. These two kinds of energy balance are illustrated in Figure **4** for production of ethanol from corn grain. The first energy balance, illustrated in Figure **4**(a), focuses on energy flows into and out of the processing facility – the enclosed dashed line around the facility is known as a control volume and delineates the region of interest. This energy ratio is the one of interest to plant engineers. It compares the useful energy output in the form of ethanol to the energy inputs for the facility: electricity to run machinery, natural gas for drying and distillation, and the chemical energy contained within the corn to be processed. This is the classical energy efficiency of a conversion process.
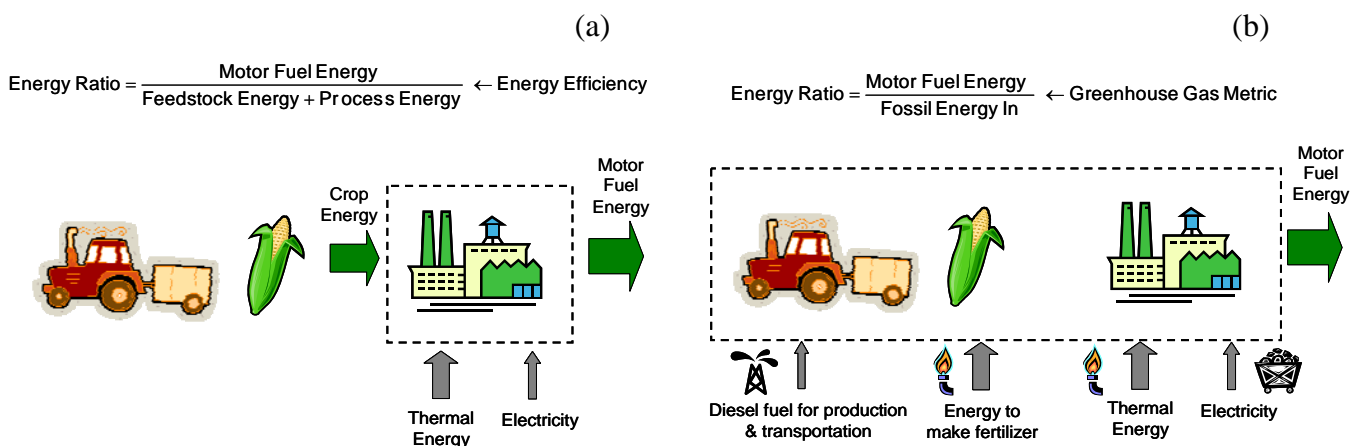

Figure 4. Two kinds of energy balance: (a) Plant engineer's energy balance (classical energy efficiency); (b) Environmentalist's energy balance (greenhouse gas metric).

The second kind of energy balance, illustrated in Figure **4**(b), expands the control volume to encompass both the processing facility and the landscape from which the crop is obtained. It considers the man-made energy flows crossing the control volume and ignores any energy flows that are fully contained within the control volume. This analysis focuses on fossil energy inputs to the system while ignoring solar energy input since this is "free" energy. From this perspective, this analysis can be thought of as an environmental energy ratio because it measures the amount of fossil fuels consumed (and the amount of greenhouse gases emitted) to produce a unit of transportation fuel. This is the energy ratio employed in the debate about ethanol production.[18, 19] Several research groups have reported values for this environmental energy ratio with values ranging from 0.44 to 2.1. Averaging over the values reported by 14 *different* study groups (to avoid replicating values of the same study groups reported in different publications) yields an energy ratio of 1.3. In comparison, and there is little disagreement on this point, the environmental energy ratio for the production of gasoline from petroleum is only 0.81.

There are several reasons for the wide range of reported values for this energy ratio in the production of ethanol. First, different study groups make different assumptions about the production yield of corn grain. For example, one study group averages corn yields over all fifty states with the intention that this best represents a national average for corn yield while another averages yields over the top ten corn producing states, arguing that these are where grain ethanol plants are clustered. Second, there are major disagreements about the amount of energy needed to produce anhydrous ammonia fertilizer. Third, there is no consensus on the amount of ethanol that can be produced from a bushel of grain, probably because this number depends on the age and size of the fermentation facility. Finally, there are questions as to the amount of fossil energy consumed within the production facility. Clearly, a large amount of natural gas is consumed in drying DDGS and distilling ethanol, but it is difficult to accurately assess energy consumption in an industry that is rapidly growing and changing.   Ultimately, the disagreements among researchers likely reflect the difficulty of assigning average values for these parameters to the whole industry. Very likely there are older and smaller corn ethanol plants that are operating with energy ratios less than unity while larger, more modern facilities are operating above unity.

At any rate, there is substantial room for improvement in the grain ethanol industry. An environmental energy ratio of 1.3 means that the ethanol product contains only 30% more energy than the fossil fuel employed in the overall process of growing the grain and processing it into motor fuel. Several things could be done to reduce the use of fossil fuels in ethanol production: tractors could run on pure biodiesel; cornstover could be the energy source for fertilizer production; byproducts could be used as sources of energy for drying and distillation. Reductions in fossil fuel use would increase the environmental energy ratio: values of ten or higher could readily be achieved. Advance biorefineries are expected to contribute to these improvements.

<u>Size of Biorefineries</u>

The petroleum-based motor fuels industry is characterized by giant refineries, because plant operating costs per unit of production go down as the facilities get larger while feedstock transportation cost per unit of production remain relatively constant. The case is more complicated for biomass feedstock since it does not come from a single mine-head located a fixed distance from the plant but is dispersed over a large area surrounding the plant. Delivery cost for a unit of biofuel increases as the capacity of the plant increases because the biomass must be delivered from increasingly greater distances. Such an analysis has been explored by several researchers,[20, 21, 22] which reveals that the unit cost for motor fuel from biomass, UC, as a function of plant capacity M (measured in units of liters of biofuel per annum, for example) is given by:

$$UC = (C_{Po}/M_o^n) \, M^{n-1} + (C_{Do}/M_o^m) \, M^{m-1} + (C_{Fo}/M_o) \tag{1}$$

where C_{Po}, C_{Do}, and C_{Fo} are the plant operating cost, biomass transportation cost, and biomass feedstock cost, respectively for a baseline plant of capacity M_o. In this expression n is the exponent describing plant size scaling (usually in the range of 0.6 to 0.8) while m is the exponent describing the power law for transportation costs for widely distributed production of biomass (expected to be close to 1.5)..

From this expression it can be shown the lowest unit cost of biofuel occurs when the ratio of the cost of delivery of biomass C_D to the cost of plant operations, C_P, is given by:

$$R_{opt} = (C_D/C_P)_{opt} = (1-n)/(m-1) \qquad (2)$$

This indicates that, for a plant sized to give the minimum unit cost of motor fuel, the ratio of delivery cost to operating cost depends only on the scale factors m and n. For example, assuming n is 0.6 (the sixth-tenth rule of economies of scale) and m is 1.5, delivery costs will equal 80% of plant operating costs in an optimally sized plant for minimum unit cost of biofuel.

To illustrate the usefulness of these relationships in sizing biorefineries, two baseline cases are considered in Table 1. The first is a sugar cane-to-ethanol plant envisioned for Queensland Australia and described in Ngyuen and Prince[21] (converted to 1995 U.S. dollars). The second is for a biomass power plant described by Jenkins.[22] This table details the size of these baseline plants and their various annualized operating costs: plant operations, biomass transportation, biomass production, total operating cost, and unit cost of the product (ethanol or electricity). It also shows the ratio of plant operating cost to biomass delivery cost, R_o, for these non-optimized baseline plants.

Error! Not a valid bookmark self-reference. provides the optimized sizes and corresponding operating costs for these two plants assuming m equal to 1.5 and n equal to 0.77. The optimal size for the sugar-to-ethanol plant is 242 million liters per year, processing 3 million tons per year of biomass, which is almost twice as large as the baseline plant. Nevertheless, the cost of ethanol is only 1% less than for the baseline plant ($0.80/L compared to $0.81/L). The reason for this is evident in Figure 5 (a), which plots unit cost of ethanol vs. plant capacity using Eq. 1 and parameters from Table 1. Although a minimum ethanol cost occurs for a plant of about 242 ML size, the function is relatively flat from about 150 to 450 ML capacity.

Table 1. Baseline plant sizes and operating costs for sugar cane ethanol[21] and biomass power[22]

Plant	M_o	Biomass (million tons)	C_{Po} (million)	C_{Do} (million)	C_{Fo} (million)	C_{To} (million)	$C_T/M)_o$	R_o
Ethanol	125 ML	1.55	$49.7	$14.1	$37.5	$101.3	$0.81/L	0.28
Power	25 MW	0.12	$3.29	$0.05	$3.6	$6.9	$0.042/kWh	0.015

Table 2. Optimized plant sizes for sugar cane ethanol and biomass power*

Plant	M_{opt}	Biomass (million tons)	C_{Popt} (million)	C_{Dopt} (million)	C_{Fopt} (million)	C_{Topt} (million)	$C_T/M)_{opt}$	R_{opt}
Ethanol	242 ML	3.0	$83	$38	$73	$194	0.80/L	0.46
Power	2,700 MW	13	$121	$56	$390	$567	$0.032/kWh	0.46

* Assumes n = 0.77 and m = 1.5

The optimal size for the power plant is 2,700 MW, processing 13 million tons per year of biomass, which is 100 times larger than the baseline power plant. The unit cost of electricity is $0.032/kWh, which is almost 25% cheaper than the baseline power plant. Nevertheless, as shown in Figure 5 (b) the plot of unit cost vs. power plant size is also extremely shallow, with little difference in the cost of electricity for plants in the size range of 1,500 MW and 4,000 MW.
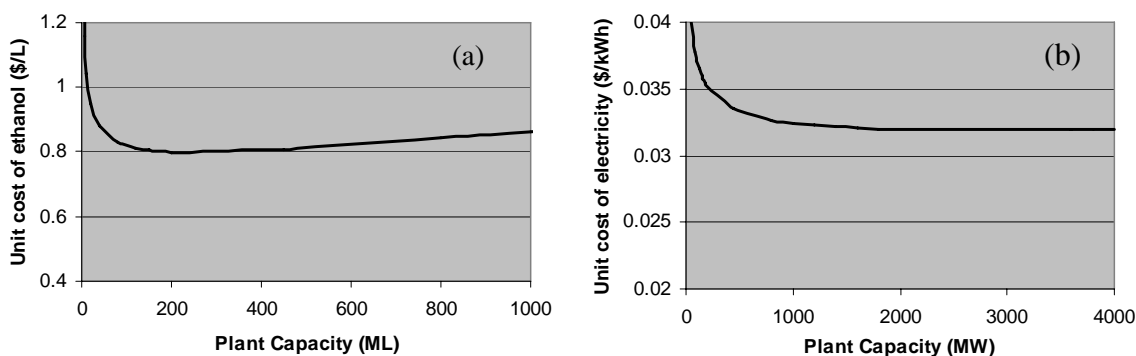

Figure 5. Unit cost of product vs. plant capacity for (a) sugar cane-to-ethanol plant; (b) biomass to power plant (both assume m=1.5 and n=0.77).

Outlook

Biorefineries offer new opportunities for the agricultural sector and rural economies. Although corn milling plants and pulp and paper mills can be a starting point for envisioning advanced biorefineries in an emerging bioeconomy, there are a number of striking differences, including the vastly larger demand of biomass, the diversity of products that would be produced, the expectations for efficient conversion processes, and the size of processing facilities to achieve the lowest cost products. As this paper has demonstrated, these differences do not represent insurmountable barriers, but they will require frequent reassessment and adoption of new technologies to assure profitable biobased companies.

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